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Zirconium Hydroxide Nanoparticles for Toxic Chemical Sequestration: Environmental Implications on Surface Reactivity, Capacity, and CWA Decomposition

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14. ABSTRACT The objective of this project was to understand how operando conditions, such as common atmospheric contaminants and environmental conditions like light and temperature, affect the adsorption and decomposition mechanisms of CWAs and CWA simulants on zirconium hydroxide, a promising sorbent and decomposition material. Decomposition of simulants and CWAs were studied primarily using ambient-compatible and “soft” characterization methods such as ATR-IR, DRIFTS, microbreakthrough, and XPS. Theoretical calculations provide experimental support and insight into most likely decomposition pathways, adsorbate stability, and potential surface poisoning resulting from decomposition products.					
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TABLE OF CONTENTS

1.	ABSTRACT	1
1.1	Project Objective and Overview	1
2.	BACKGROUND	1
2.1	Zirconium Hydroxide	1
3.	MATERIALS AND METHODS	3
3.1	Electrodeposition and Characterization of ZH	3
3.2	Thin Film Preparation	5
3.3	X-ray Diffraction (XRD)	5
3.4	X-ray Photoelectron Spectroscopy (XPS)	5
3.5	In Situ Attenuated Total Reflectance (ATR) Spectroscopy	5
3.5.1	Contaminant and Simulant Dosing	5
3.5.2	Liquid Phase ATR	6
3.5.3	Solid Phase ATR	6
3.6	CWA Degradation Studies	7
3.6.1	DRIFTS	7
3.6.2	Microbreakthrough	7
3.7	Theoretical Calculations	8
3.7.1	DFT Simulations	8
3.7.2	Electronic Structure Calculations	8
3.7.3	Ab-initio Molecular Dynamics (AIMD) Calculations	8
4.	RESULTS AND DISCUSSION - EXPERIMENTAL	10
4.1	Characterization of ZH and Thin Film Preparation	10
4.1.1	Thin Film Preparation	10
4.1.2	Scanning Electron Microscopy	12
4.1.3	Surface Characterization and Thermal Stability of Atmospheric Adsorbates	13
4.1.4	Potentiometric Titration	17
4.1.5	Gas Accessibility to ZH Reactive Sites	18
4.2	Atmospheric Contaminant Dosing on ZH	19
4.2.1	XPS of Contaminated ZH	19
4.2.2	DRIFTS of Contaminant Dosing	22
4.2.3	Ambient Contaminant Capacity Measurements	26
4.3	CWA Simulant Decomposition on ZH	26
4.3.1	Dimethyl methylphosphonate (DMMP)	26
4.3.2	2-Chloroethyl ethyl sulfide (CEES)	35
4.3.3	Dimethyl chlorophosphate (DMCP)	35
4.3.4	Malathion	36
4.3.5	Diisopropyl fluorophosphate (DIFP)	36
4.4	Live Agent Decomposition	39
4.4.1	XPS	39
4.4.2	DRIFTS	40
4.4.3	Microbreakthrough Analysis	44
5.	RESULTS AND DISCUSSION - THEORETICAL	48
5.1	Structural Calculations	48
5.1.1	Theory-Experiment Comparisons	48
5.2	Adsorbate Calculations	50
5.2.1	Partially Hydrated Surface	50

5.2.2	AIMD Simulations of Fully Hydrated ZH Models.....	51
5.2.3	Ambient Contaminants	52
5.2.4	Large cluster (nonamer) model of amorphous ZH	54
5.2.5	CO adsorption on $Zr_9(OH)_{36}$	55
5.2.6	CWA Simulants.....	58
5.2.7	Chemical Warfare Agent Calculations	60
5.2.8	Electronic Structure Calculations for ZH	64
6.	SUMMARY AND CONCLUSIONS	66
	REFERENCES	68

TABLE OF FIGURES

Figure 1. Illustration of condensation reaction of cyclic tetramers to plate-like particles. Reprinted with permission from Southon, et al., <i>Chem. Mater.</i> 2002, 14, 10, 4313–4319. Copyright (2002) American Chemical Society.[8].....	1
Figure 2. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is one of several IR analytical tools useful for monitoring changes to the ZH surface chemistry in real time under <i>operando</i> conditions.....	3
Figure 3. Overview of the electrochemical deposition of ZH and thin film preparation. Reprinted with permission from Jeon, et al., <i>ACS Appl. Nano Mater.</i> 2019, 2, 4, 2295–2307. Copyright (2019) American Chemical Society.[13].....	4
Figure 4. Schematic of environmental ATR chamber (top), photograph of actual ATR chamber (bottom left), ZH on ZnSe IRE (bottom center), and two ZnSe and one Ge IREs.	7
Figure 5. Schematic of spray coat thin film deposition.	11
Figure 6. The effect of sonication time on dispersity of the ZH nanopowder type in methanol and water. Type C has much stronger affinity for methanol; whereas, type B has much stronger affinity for water. Note all samples demonstrate increased dispersity with sonication time.	11
Figure 7. Centrifugation at 1,500 rpm of the sonicated ZH nanoparticles suspended in water greatly improves colloidal stability and reduces polydispersity as determined by particle size distribution estimated from dynamic light scattering data.	12
Figure 8. SEM images of ZH type B (left) and type C (right).	12
Figure 9. ATR-IR of ZH in both powder and thin film showing IR active surface species and adsorbates.	13
Figure 10. TGA-MS showing the loss of weight from zirconium hydroxide with temperature (red line, top). The derivative plot (dashed black line) is shown for identification of desorption onset. The bottom panel shows the normalized MS plots of water and CO ₂ desorbing from the zirconium hydroxide surface.	14
Figure 11. Powder XRD of ZH converting to monoclinic zirconia with increased temperature. ZH samples were calcined at 100, 250, 500, and 1000 C. Reference spectra provided of monoclinic (+) and tetragonal (x) zirconia.	14
Figure 12. Powder X-ray diffraction patterns of A) type B and B) type C ZH nanopowder heated in air to various temperatures for 15 min. C) For comparison, reference patterns obtained from Srinivasan et. al[25] of monoclinic and tetragonal ZrO ₂ suggest the pXRD pattern of type C ZH likely contains contributions from both monoclinic and tetragonal ZrO ₂	15
Figure 13. ATR-FTIR spectra for zirconium hydroxides.	15
Figure 14. Oxygen 1S X-ray photoelectron spectra for calcined samples (left) and O/Zr and terminal hydroxyl percentages of calcined samples (right).....	16
Figure 15. Nitrogen isotherm data for zirconium hydroxide heated to different temperatures.....	17
Figure 16. Potentiometric titration of calcined ZH powders (as-received, 100, 250, 500 and 1000 °C). pKa distribution of hydroxyl species on the ZH samples vs. temperature. According to this method, the as-received and 100 C treated ZH have the most acid and base sites.	17
Figure 17. Single beam FTIR-ATR spectra comparing integrated peak areas for ZH nanoparticles suspended in D ₂ O after 2 h sonication. About 66% OH/OD exchange was observed based on the integrated deconvoluted peak areas. Reprinted with permission from Balow, et al., <i>ACS Appl. Mater. Interfaces</i> 2017, 9, 45, 39747–39757. Copyright (2017) American Chemical Society.	18
Figure 18. (A,B) Showing formation of surface adsorbates upon dosing CO onto ZH. (C,D) N ₂ purge of CO from sample chamber demonstrating stability of CO adsorbates on ZH.....	19
Figure 19. X-ray photoelectron spectra (XPS) of the C 1s, S 2p, and N 1s photoelectron binding energy range of clean and dosed ZH showing adsorbate formation. All samples showed adventitious carbon and	

carbonate-like surface species, whereas SO ₂ - and NO ₂ -dosed ZH showed sulfite/sulfate and nitrite/nitrate adsorbates, respectively.	20
Figure 20. X-ray photoelectron spectra of the Zr 3d range for clean and CO ₂ -, SO ₂ -, and NO ₂ -contaminated ZH. CO ₂ - and SO ₂ -dosed ZH samples showed an increasing chemical shift, which is likely correlated to withdrawal of valence charge from the surface from adsorbates.....	22
Figure 21. Types of hydroxyl species on zirconium hydroxide.....	22
Figure 22. Normalized diffuse reflectance infrared Fourier transform difference spectra showing adsorbate formation during gas dosing with CO ₂ (A,D), SO ₂ (B,E), and NO ₂ (C,F) on pristine ZH over 75 min in two spectral regions.	23
Figure 23. Capacity measurement of atmospheric contaminant on ZH powders.	26
Figure 24. Comparison of a gas phase FTIR spectrum showing gas-phase reaction products from DMMP dosing on ZH-B for 24 hours (top) and reference gas phase spectra for methanol, carbon dioxide, and DMMP (below). Annotations of the “DMMP exposed to Zr(OH) ₄ -B” spectrum indicate primary chemical species contributing to spectral features. The CO ₂ peak near 2350 cm ⁻¹ is reduced by a factor of 0.15 relative to the rest of the spectrum. The inset shows the experimental configuration.	27
Figure 25. Comparison of the 24 hour DMMP / ZH-B reaction spectrum with a spectrum of air in the IR gas cell.	27
Figure 26. (a) “Dry” DMMP – ZH type B FTIR spectra. Time dependent gas phase IR spectra of DMMP mixed with ZH in N ₂ with < 6% relative humidity. (b) Hydrated DMMP – ZH-B FTIR spectra. Time dependent gas phase IR spectra of 20 μL DMMP mixed with ~37 mg ZH-B + 20 μL water in N ₂ with 36% relative humidity. The asterisk indicates loss of DMMP vibrational modes that are observed in the “dry” DMMP – ZH-B spectra. (c) Comparison of CO ₂ evolution for N ₂ dried and hydrated ZH.....	28
Figure 27. TGA of DMMP on ZH: Derivative of mass loss overlaid with MS data.	29
Figure 28. a)-d) ATR difference absorption spectra obtained while dosing a gas mixture of 0.2 sccm DMMP and 24.8 sccm N ₂ every 9.89 sec for 16 min on variously prepared EZ samples. a) and b) - plots as a function of wavenumber for the spectra finally obtained after dosing the gas for 16 min. c) and d) - plots as a function of time at specific wavenumbers during the dosage. c) The ratio of ATR difference absorption peak intensities at 2856 cm ⁻¹ to at 2818 cm ⁻¹ (inset – zoomed-in area to show the spectra for initial 50 sec). d) ATR difference absorption peak intensity at 1150 cm ⁻¹ . The spectrum intensities in a), b), and d) are scaled by the intensity at 1040 cm ⁻¹ in the lastly collected spectrum for each sample. Color codes are maintained over all panels to represent variously prepared EZ samples; as-scraped (blue) and pre-annealed at 100 °C (red), 200 °C (green), 300 °C (magenta), and 500 °C (cyan). Adapted with permission from ACS Appl. Nano Mater. 2019, 2, 2295–2307. Copyright (2019) American Chemical Society.	31
Figure 29. a) ATR difference absorption spectra obtained after purging the DMMP/EZ samples with 25 sccm N ₂ for 56 min. b) ATR difference absorption peak intensity at 1150 cm ⁻¹ as a function of time during the N ₂ purging. Color codes are maintained over all panels to represent variously prepared EZ samples; as-scraped (blue) and pre-annealed at 100 °C (red), 200 °C (green), 300 °C (magenta), and 500 °C (cyan). The dotted horizontal lines in a) represent zero difference absorption for each plot. Adapted with permission from ACS Appl. Nano Mater. 2019, 2, 2295–2307. Copyright (2019) American Chemical Society.	32
Figure 30. Impact of annealing on EZ. The O/Zr at% ratio came from the XPS elemental analysis using the O 1s and the Zr 3d peaks. The OH(terminal)/O(total) ratio was calculated from the area ratios of the fitted components in the O 1s region. The figure of merit (FOM) of DMMP decomposition activity is defined by the Δabsorption intensity ratio at 2818 cm ⁻¹ (ν(Zr-OCH ₃)) to at 2856 cm ⁻¹ (ν(P-OCH ₃)) averaged at 200–1000 seconds.	33
Figure 31. ATR difference spectra after saturating the ZH surface with CO and purging with N ₂ (see Figure 18 for details). (A,B) shows CO and DMMP co-dosed after N ₂ purge step from Figure 18. DMMP decomposition (formation of asymmetric and symmetric O-P-O stretches) is observed near 1155 and 1090 cm ⁻¹	34

Figure 32. Removal of DMMP from the CO gas stream (10,000 ppm) in the sample chamber showing continued DMMP decomposition and some formate/carbonate formation.	34
Figure 33. IR difference spectra of dry ZH Type B material exposed to CEES vapor after 0 minutes (red trace) up to 259 minutes (light blue trace).	35
Figure 34. IR difference spectra of dry ZH Type B material exposed to DMCP vapor after 0 minutes (green trace) up to 313 minutes (pink trace).	35
Figure 35. IR difference spectra of dry ZH Type B material exposed to Malathion after 0 minutes (dark blue) up to 3025 minutes (cyan).	36
Figure 36. IR difference spectra of dry ZH Type C material exposed to DIFP vapor after 2 minutes (black trace) up to 364 minutes (blue trace).	36
Figure 37. Common CWA simulant compounds.	37
Figure 38. IR difference spectra of ZH-B saturated under SO ₂ followed by DIFP exposure.	37
Figure 39. IR difference spectra of ZH under CO ₂ prior to DIFP exposure.	38
Figure 40. IR difference spectra of CO ₂ dosed on DIFP-contaminated ZH.	38
Figure 41. IR difference spectra of SO ₂ dosed on DIFP-contaminated ZH.	38
Figure 42. XPS spectra of GB dosed on clean and CO ₂ , SO, and NO ₂ pre-dosed ZH.	39
Figure 43. Time-resolved DRIFT spectra of GB dosed on clean, CO ₂ , SO ₂ , and NO ₂ pre-dosed ZH in the hydroxyl region. Note minimal loss of monodentate and bi-bridging hydroxyl species for SO ₂ pre-dosed ZH.	41
Figure 44. Normalized time resolved DRIFT spectra of GB dosed on pristine, CO ₂ , SO ₂ , and NO ₂ pre-dosed ZH. Changes to bound surface adsorbates are monitored over 75 minutes. Black arrows indicate blue-shifting vibrational modes with time. Red and black dashed vertical lines show uniquely identifiable decomposition products and adsorbed GB, respectively.	42
Figure 45. DRIFTS spectra of GB dosing on clean, CO ₂ , SO ₂ , and NO ₂ pre-dosed ZH. Red modes denote decomposition products.	43
Figure 46. Normalized diffuse reflectance infrared Fourier Transform (DRIFT) difference spectra of GB dosed onto clean and contaminated ZH over 75 min in two spectral regions. (A) Normalized KM(t) plots of the GB decomposition band (1170 cm ⁻¹ , ν _a (OPO)) over 75 min of GB dosing on clean and contaminated ZH. (B) Linear regression of the KM(t) plots using the pseudo-first order equation. Circles and lines represent data and least-square fits, respectively.	44
Figure 47. ZH capacity data for GB dosed on clean and contaminated ZH samples.	46
Figure 48. Time-resolved FTIR spectra of the effluent collected over 75 min during GB microbreakthrough testing with (A) clean ZH, (B) NO ₂ , and (C) SO ₂ pre-dosed ZH. Dashed vertical lines indicate unique vibrational modes not observed when dosing GB through clean ZH.	47
Figure 49. Ln(VX) remaining over time. Data points obtained from deconvoluted peak areas of the P ³¹ NMR spectra of VX dosed onto ZH over time.	47
Figure 50. IR difference spectra of dry ZH exposed to HD after 4 minutes (green trace) up to 273 minutes (red trace) showing substantial loss of free hydroxyls around 3700 cm ⁻¹	48
Figure 51. Calculated XRD (intensity vs. scattering angle, 2θ) for a 2-layer model equilibrated at 400 K in comparison with experimental results (Ref 4) for ZH and for crystalline tetragonal ZrO ₂ (t-ZrO ₂). The sharp structure in the "observed" XRD results from a t-ZrO ₂ impurity. All results are for Cu Kα radiation (λ = 1.5418 Å).	49
Figure 52. Zr ₄ (OH) ₁₆ · 4 H ₂ O used as a cluster model for amorphous ZH to simulate GB adsorption. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, and H atoms in white. Gray dashed lines are hydrogen bonds shorter than 1.8 Å.	51
Figure 53. A fully hydrated DMMP on ZH model. Periodic boundary conditions are shown as blue lines. DMMP and zirconium hydroxide atoms are shown as big balls colored lime and silver, respectively. Water molecules are shown as small boomerangs colored violet.	52
Figure 54. Reaction products of CO ₂ , SO ₂ , NO ₂ , HF, and GB on Zr ₄ (OH) ₁₆ (H ₂ O) ₄ . Zr atoms and non-hydrogen atoms belonging to the adsorbed molecules are labelled for emphasis. Unlabeled O atoms are	

shown in red and H atoms in white. The values in parenthesis are calculated enthalpy differences with respect to $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4$ and the gas-phase adsorbates. Dashed gray lines indicate possible hydrogen bonds (i.e., wherever an O, N, S, or F atom is within 2.3 Å of an H atom and the resulting angle is larger than 130 degrees).	53
Figure 55. $\text{Zr}_9(\text{OH})_{36} \cdot 4 \text{H}_2\text{O}$ used as a cluster model of amorphous zirconium hydroxide to simulate CO adsorption in this reporting period. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, and H atoms in white. $\text{Zr}_9(\text{OH})_{36}$ is shown as wireframes and four physisorbed waters are shown as balls-and-sticks for emphasis. Hydrogen bonds shorter than 1.8 Å are shown with gray dashed lines.....	55
Figure 56. Physisorption and chemisorption of CO on $\text{Zr}_9(\text{OH})_{36} \cdot 4 \text{H}_2\text{O}$. Shown are the lowest-enthalpy molecular complex (top left), molecular adduct (top right), bridging formate (bottom left), and monodentate formate (bottom right). Zr atoms are shown in cyan, O atoms in red, C atoms in gray, H atoms in white. Atoms belonging to molecular CO or formate anion are labeled for emphasis. Values shown in parenthesis are the computed enthalpy differences with respect to separated gas-phase CO and $\text{Zr}_9(\text{OH})_{36} \cdot 4 \text{H}_2\text{O}$	56
Figure 57. The product for SO_2 reaction with a ZH defect site. The bidentate sulfite and H_2O are circled for clarity. The green line shows an H-bond between the "free" sulfite O atom and a bridging OH group. Adapted with permission from J. Phys. Chem. C 2018, 122, 5385–5400. Copyright (2018) American Chemical Society.	58
Figure 58. Molecular structures of hydrogen-bonded complexes between DMMP and $\text{Zr}_4(\text{OH})_{16}$	59
Figure 59. Intermediates and one of the transition structures mediating $\text{Zr}_4(\text{OH})_{16}$ -assisted hydrolysis of DMMP.	59
Figure 60. Reaction diagram describing the addition-elimination mechanisms to $\text{Zr}_4(\text{OH})_{16}$ -assisted hydrolysis of DMMP.	60
Figure 61. The reaction of the iodo form of GB on ZH model under dry conditions. Iodo-GB is shown as a ball-stick model and ZH atoms are shown as big balls. Phosphorus, iodine, carbon, zirconium, oxygen, and hydrogen atoms are colored brown, purple, cyan, gray, red, and white, respectively. The length of the newly formed P-O bond is labeled in Angstroms.	61
Figure 62. Molecular adsorption of GB on $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$. Shown are the lowest-enthalpy hydrogen-bonded complex and molecular adduct. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, H atoms in white, F atoms in green, and P atoms in gold. Values shown in parenthesis are the computed enthalpy differences with respect to separated GB and $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$	62
Figure 63. Computed IR absorption spectra of GB in the gas phase and adsorbed on $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$. IR peaks discussed in the text are labeled for emphasis.	62
Figure 64. Dissociative adsorption of GB on $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$. Shown are the lowest-enthalpy structures for the chelating bidentate, monodentate, bridging bidentate configurations of HF elimination products. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, H atoms in white, F atoms in green, and P atoms in gold. Zr, P, and O atoms participating in monodentate or bidentate binding are labeled for emphasis. Dashed lines indicate hydrogen bonds. Values shown in parenthesis are the computed enthalpy differences with respect to separated GB and $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$	63
Figure 65. Computed infrared spectra of HF elimination products. IR peaks discussed in the text are labeled for emphasis.	64
Figure 66. The spin-polarized density of states (DOS) for a 3-layer ZH model with a Zr^{+3} defect in the middle layer (Defect A). The majority (minority) spin states are shown in black (red) as positive (negative) quantities. The total DOS is shown in (a), and the partial DOS for the Zr and the OH vacancy are given in (b) and (c) respectively. Note the different $N(E)$ scales in the three plots. An occupied defect level appears at 4.4 eV above the valence band maximum (VBM). The dashed green lines show the positions of the VBM and conduction band minimum. The zero of energy is at the VBM.[71].....	65

TABLE OF TABLES

Table 1. BET surface area and pore volume of zirconium hydroxides.....	16
Table 2. Identified vibrational modes for CO ₂ , SO ₂ , and NO ₂ pre-dosed ZH after overnight purge with N ₂ to remove adsorbed surface water.....	25
Table 3. Kinetic parameters from thermal desorption of DMMP and reaction by-products from ZH-C ...	30
Table 4. Data from Figure 30 in tabular form. O/Zr atomic percentage ratio and the OH(terminal) / O(total) ratio calculated using the XPS data and the figure of merit (FOM) of the DMMP decomposition activity. The result indicates that 1) EZ loses oxygen, 2) terminal OH decreases, and 3) DMMP decomposition reactivity drops with increased T _{anneal} , which is consistent with the known physicochemical properties of Zr(OH) ₄	33
Table 5. IR Bands and Assignments for ZH exposed to DIFP Simulant.....	38
Table 6. Vibrational modes of molecular GB and common decomposition products identified with DRIFTS during GB dosing on ZH.....	42
Table 7. GB breakthrough data showing total GB loading on clean and contaminated ZH samples when GB breakthrough occurred.....	45
Table 8. Calculated first order reaction kinetics determined by fitting a linear line to the ln of the remaining VX on ZH over time.	47
Table 9. Calculated adsorption enthalpies (in kJ/mol) for CO ₂ , SO ₂ , NO ₂ , HF, and GB and their reaction products on Zr ₄ (OH) ₁₆ (H ₂ O) ₄	52
Table 10. Computed frequencies of relevant modes in gas-phase, physisorbed and chemisorbed CO.	57

ABBREVIATIONS

2-CEES – 2-Chloroethyl ethyl sulfide
2DPS – Two Dimensionally Periodic Slab
AIMD – Ab-Initio Molecular Dynamics
ATR – Attenuated total reflectance
B–O – Born–Oppenheimer
CCDC-CBC – Combat Capabilities Development Command – Chemical and Biological Center
CEPS – 2-chloroethyl phenyl sulfide
cus – Coordinatively unsaturated
CWA – Chemical warfare agent
DEPPT – O,O-diethyl S-phenyl phosphorothioate
DIFP/DFP – Diisopropyl fluorophosphonate
DFT – Density functional theory
DMCP – Dimethyl chlorophosphonate
DMMP – Dimethyl methylphosphonate
DRIFTS – Diffuse reflection infrared Fourier transform spectroscopy
EXAFS - Extended X-ray Absorption Fine Structure
FOM – Figure of Merit
GB – RS-propan-2-yl methylphosphonofluoridate (Sarin)
GC-MS – Gas chromatography-mass spectrometry
GD – O-pinacolyl methylphosphonofluoridate (Soman)
GTOs – Gaussian-type orbitals
HD – Bis(2-chloroethyl) sulfide (Mustard gas)
MMs – Magnetic Moments
MP – Monkhorst–Pack
NRL – Naval Research Laboratory
PAW – Projector Augmented Wave
PL – Photo Luminescence
POM – Polyoxometalate
QE – Quantum Espresso
RH – Relative Humidity
SLAC - Stanford Linear Accelerator Center
TEM – Transmission Electron Microscopy
TGA – Thermal Gravimetric Analysis
VBM – Valence Band Maximum
VX - O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate
XAS – X-ray Absorption Spectroscopy
XRD – X-ray Diffraction
ZH – Zirconium hydroxide, $\text{Zr}(\text{OH})_4$
 Zr_{cus} – Coordinatively unsaturated zirconium site
Zr-POM – Zirconium-based Polyoxometalate

KEYWORDS

Chemical warfare agent, CWA, chemical decontamination, toxic industrial chemicals, toxic chemical destruction, chemical warfare agent simulant, toxic chemical remediation, filtration, sorption, sequestration.

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EXECUTIVE SUMMARY

This program investigated the impact of common atmospheric contaminants (CO_2 , SO_2 , and NO_2), as well as, temperature and humidity on chemical warfare agent (CWA) decomposition using a promising nanoparticle sorbent, zirconium hydroxide ($\text{Zr}(\text{OH})_4$, ZH). A suite of unique instrumentation including in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-ray photoelectron spectroscopy (XPS), and microbreakthrough were used to directly probe the surface reactions, gas sorption capacity, and decomposition performance of ZH, in real time, while dosing with environmental contaminants and the live CWA sarin.

Changes to CWA sequestration and decomposition on clean and CO_2 , SO_2 , and NO_2 contaminated ZH were identified. All gases rapidly formed adsorbates on various defect sites with the simultaneous loss of free hydroxyls, thus affecting the decomposition mechanisms of simulants and sarin. The most detrimental gases included SO_2 and NO_2 . CO_2 -based adsorbates appeared to be in equilibrium with CO_2 partial pressure and were weakly bound to the ZH surface.

The effect of temperature and humidity were also examined. Humid conditions showed improved simulant and live agent decomposition in general, likely by assisting in the hydrolysis of CWA and CWA simulants and improved desorption of surface bound byproducts. Increasing temperature accelerated simulant decomposition until approximately $200\text{ }^\circ\text{C}$, where ZH began losing free hydroxyls via a condensation mechanism. Collectively, reaction products, kinetic analysis, and decomposition mechanisms are discussed.

Additionally, a strong theoretical component comprising *ab-initio* molecular dynamics and density functional theory validated experimental work and provided most probable intermediates, decomposition products, and relative adsorbate strengths to finally address the long-standing questions surrounding the effectiveness of ZH under real-world conditions for chemical decontamination.

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Zirconium Hydroxide Nanoparticles for Toxic Chemical Sequestration: Environmental Implications on Surface Reactivity, Capacity, and CWA Decomposition

1. ABSTRACT

1.1 Project Objective and Overview

The objective of this project was to understand how *operando* conditions, such as ambient contaminants and environmental conditions like light, temperature, and humidity affect the adsorption and decomposition mechanisms of CWAs and CWA simulants on zirconium hydroxide (ZH), a promising reactive sorbent material. Addressing this objective required analytical techniques compatible with high (nominally atmospheric) pressure to ensure that the results reflect the conditions under which such materials will actually be used, rather than an unrepresentative, high-vacuum environment. These goals were achieved by combining both unique ambient-compatible analytical techniques and computational methods to provide a holistic understanding of the chemical reactions occurring between the clean and contaminated ZH surface. A strong theoretical component helped validate reaction mechanisms of clean and contaminated (H_2O , CO_2 , SO_2 , and NO_2) ZH surfaces with CWA simulants (DMMP, DIFP, and CEES) and live CWAs (VX, HD, and GB). Collectively, this work quantified the impact of ambient battlefield contaminants on the sequestration and destruction of GB.

2. BACKGROUND

2.1 Zirconium Hydroxide

Zirconium hydroxide, $\text{Zr}(\text{OH})_4$ (ZH), demonstrates exceptional decontamination and filtration properties. In fact, it is one of the fastest known solid catalysts for VX, GD and HD hydrolysis,[1] and has an extremely high removal capacity for acidic and acid-forming gases.[2-6] The ability to both readily sequester and detoxify three very different chemical warfare agents (CWAs) testifies to the unique surface reactivity and properties of ZH. Furthermore, ZH is low-cost, non-toxic, abundant, and industrially scalable.

Structurally, ZH is amorphous but has been hypothesized to comprise small zirconium tetramer units, which are connected by bridging hydroxyls.[7, 8] These tetramers condense into larger clusters by forming bridging hydroxyl linkages. The tetramers continue to condense into larger “sheet-like” aggregates that contain both highly active bridging and terminal hydroxyl species as shown in Figure 1.

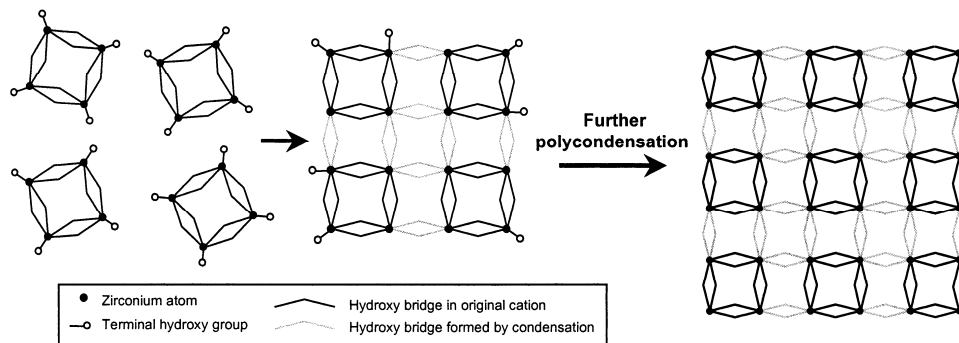


Figure 1. Illustration of condensation reaction of cyclic tetramers to plate-like particles. Reprinted with permission from Southon, et al., *Chem. Mater.* 2002, 14, 10, 4313–4319. Copyright (2002) American Chemical Society.[8]

Recently, King et al. examined amorphous ZH using X-ray pair distribution function analysis.[9] They discovered that the local ZH structure is similar to monoclinic ZrO₂, and likely contains three different surface hydroxyl sites, as well as coordinatively unsaturated Zr sites (Zr_{cus}) resulting in both Brønsted and Lewis chemistries throughout the material.[6] Although significant reactivity towards CWAs has been reported, no systematic studies of reaction rates vs common contaminants such as ambient water, carbon dioxide, sulfur dioxide, nitrogen dioxide, and volatile organic compounds, or environmental factors such as temperature exist. It is unknown if excess moisture may *increase* reaction rates due to a shift in equilibrium, or may *decrease* them in the case of HD, a water-insoluble material. Carbon dioxide may affect the surface chemistry of metal oxides even more dramatically than water, because once adsorbed, it can form carbonates, effectively blocking or passivating surface hydroxyls and reactive defects. Understanding the role contaminants and environmental factors play on reaction rates and mechanisms would enable more accurate predictions for transitioning ZH into the field.

Determining chemical mechanisms in such complex materials, e.g. whether catalytic, photocatalytic, or stoichiometric, requires knowledge of their molecular chemistry, local composition, phase, morphology, and interfacial properties. This multifaceted picture becomes even more challenging in *operando* settings, where humidity, adventitious hydrocarbons, common contaminants, and reaction byproducts can affect catalyst operation. For example, ZH-based materials are typically evaluated in pristine laboratory environments, but as discussed above, ZH reacts with common contaminants like CO₂, SO₂ and NO₂. It is unknown whether or how these contaminants degrade or modify surface adsorption or degradation of CWAs and toxic chemicals.

The ability to characterize surface species under high ambient pressure (on the order of 1 atmosphere) is necessary to elucidate realistic reaction mechanisms for chemically complex systems. Weakly-adsorbed species under practical conditions (such as high surface coverage) are observed only at high ambient pressure, because desorption is more rapid *in vacuo*.

Another consideration is the impact that analytical tools may have on the surface chemistry during analysis. Importantly, X-ray photoelectron spectroscopy (XPS) photon excitation generates secondary electrons that can damage (i.e. decompose) molecular adsorbates or alter their bonding geometry; a severe disadvantage in the proposed work. Reports describing beam-induced conversion of metal hydroxides to metal oxides are especially concerning because the two materials have drastically different surface properties and reactivity due to changes in the hydroxyl group concentration.

By contrast, damage is completely avoided using “soft” probing sources such as low energy photons common in infrared (IR) spectroscopy, which are incapable of breaking bonds. These, rather than more aggressive electron-based methods such as XPS, provide an unaltered perspective of the ZH surface chemistry while being ambient compatible. Furthermore, vibrational spectroscopy provides direct and generally unambiguous information about the chemical bonding of surface species. Using IR methods, surface-selective vibrational data can be obtained under steady-state conditions in a full atmosphere of virtually any reagent or combination of reagents. Heating ZH samples *in situ* while collecting IR spectra provided a unique perspective into the ZH surface chemistry that wasn’t achieved before. Such data was theoretically backed by both molecular dynamics (MD) and density functional theory (DFT) calculations to assist in interpretation of collected spectra, determining most likely reaction mechanisms, and guiding experimental design.

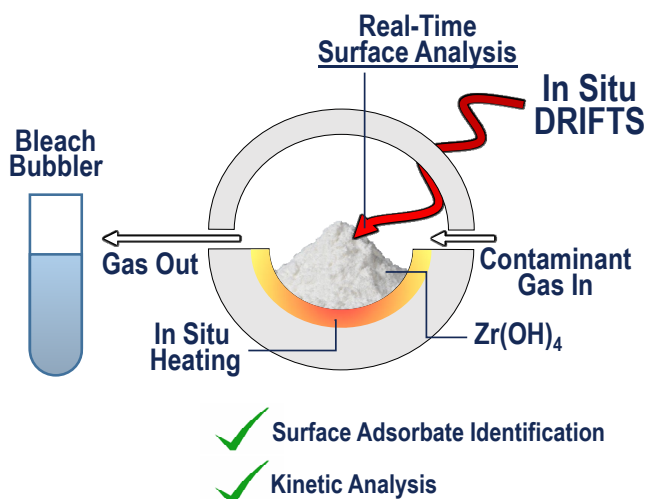


Figure 2. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is one of several IR analytical tools useful for monitoring changes to the ZH surface chemistry in real time under *operando* conditions

Collectively, these data will provide unprecedented insight into utilizing ZH in the field. The data and results produced in this program can be directly used to assist with transitioning ZH into ideal form factors and formulations to protect first responders and warfighters from CWA or toxic chemical exposure.

3. MATERIALS AND METHODS

3.1 Electrodeposition and Characterization of ZH

All reagents were used as received, and without further purification, unless otherwise noted; zirconyl chloride hydrate ($\text{ZrOCl}_2 \cdot x\text{H}_2\text{O}$, 99.9%, Alfa Aesar), zirconium (IV) chloride (ZrCl_4 , 99.5+ %, Alfa Aesar), zirconium (IV) oxide (ZrO_2 , 5 μm , 99 %, Sigma-Aldrich), and dimethyl methylphosphonate (DMMP, 97 %, Sigma-Aldrich). Deionized (DI) water was obtained from Thermo Fisher Scientific Barnstead GenPure ultrapure water system (18.2 Mohm $\cdot\text{cm}$). ZH powder was purchased from Magnesium Electron Ltd. (manufacturer's part number 1501/03). Ultrahigh purity (UHP) N_2 (99.999%) was obtained from Airgas. ZH was synthesized by cathodic electrochemical deposition using a three-electrode cell described in previous reports.[10-12] The working electrode was either a piece of $\text{SiO}_2/\text{Si}(100)$ (1 μm thermal SiO_2 on $\text{Si}(100)$, n-type, 10 $\times$ 20 mm^2) coated by electron-beam-assisted physical vapor deposition with 20 nm Au (base pressure $<3 \times 10^{-6}$ Torr, rate 2.0 $\text{\AA}/\text{s}$) or a piece of Zr foil (99.995%, 75 mm $\times$ 95 mm $\times$ 0.005 in.). For the Au/ $\text{SiO}_2/\text{Si}(100)$ electrode, the electrical contact was made through the Au film directly. While one could use virtually any metal foil that is stable at negative potential in ZrOCl_2 aqueous solution, we chose Zr to avoid potential contamination and thereby characterize the intrinsic properties of ZH. The counter electrode was Pt mesh (99.9%, wire diameter 0.1 mm, 100 $\times$ 100 mm^2) or Pt foil (99.99%, 10 $\times$ 20 mm^2). The Au film electrode was used without any treatment after Au deposition, while the Zr foil electrode was polished with 600 grit SiC sandpaper, followed by a standard ultrasonic degrease with DI water, acetone, and isopropyl alcohol. The reference electrode was Ag/AgCl (1 M KCl, CH Instruments, Inc.). The electrodes were submerged in an unstirred aqueous deposition solution containing 15.6 mM zirconium oxychloride (calculation of the concentration referred to the molecular weight of anhydrous ZrOCl_2). A stirrer was not used so as to maintain a high local hydroxyl concentration near the working electrode during electrodeposition of EZ (the hydroxyl is formed by the water reduction on the working electrode).[10-12] A potentiostat (Gamry Instruments) applied -8 V to

the working electrode. Although successful depositions have been achieved with lower cathodic potentials, -1.8 V vs Ag/AgCl, a larger voltage accelerates the deposition rate and increases the porosity and surface roughness, which is advantageous for increasing the surface reactivity.

The production of bubbles on the working electrode at around -1 V and lower is likely from H_2 gas production by water reduction, which was also observed in previous studies.[10-12] The as-deposited film was a transparent gel, and even after drying, films with thicknesses below ~ 50 nm were still transparent. Thicker films were white. The thick EZ films were easily separated from the working electrode by gently scraping with a quartz spatula. Repetition of the electrodeposition, drying, and scraping steps provided powdery particulates for characterization. Most of the residual ions (e.g., Cl^-) from the electrolyte were removed by washing the scraped ZH particulates with DI water. Ten cycles of mixing ZH with DI water, agitation, and removal of the supernatant were performed, followed by drying under N_2 . For calcination experiments, the scraped ZH particulates were calcined in an ambient oven at 100, 200, 300, and 500 $^{\circ}C$ for 6 h.

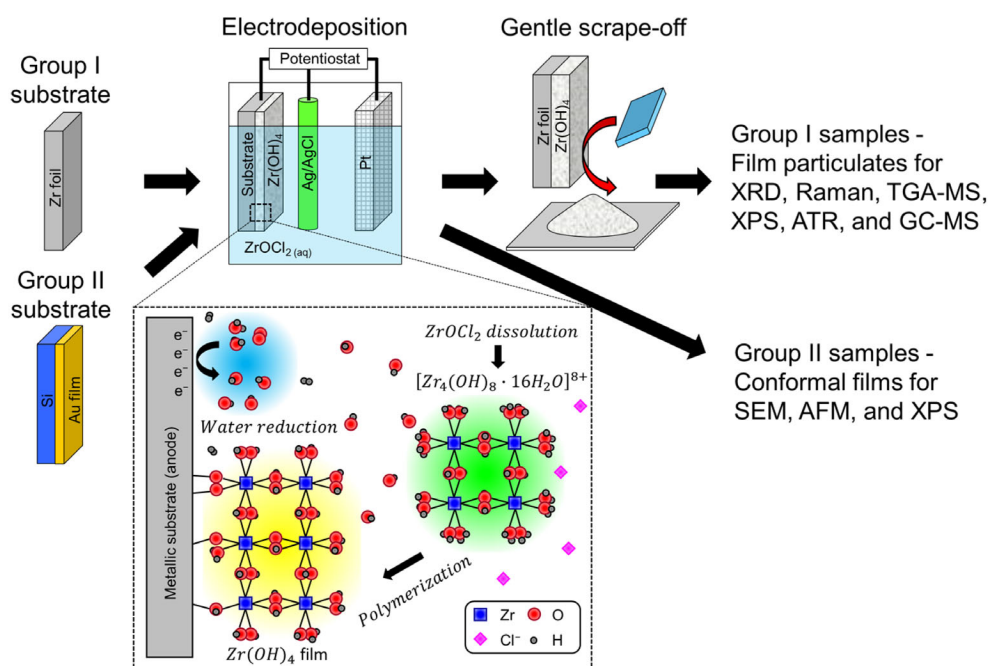


Figure 3. Overview of the electrochemical deposition of ZH and thin film preparation. Reprinted with permission from Jeon, et al., ACS Appl. Nano Mater. 2019, 2, 4, 2295–2307. Copyright (2019) American Chemical Society.[13]

As-dried films and as-scraped particulates were investigated by scanning electron microscopy (LEO, 10 $\sim$ 15 keV) and atomic force microscopy (Asylum Cypher, AC mode, with a Si cantilever (Mikromasch, HQ:NSC35/AL BS, nominal tip apex radius 5 nm). Raman spectroscopy of individual film particles ($\sim 1 \sim 10$ μm) or powder aggregates was performed with a WiTec alpha300, using a 532 nm excitation laser, and a high magnification objective lens (100X or 50X). Special care was used to exclude signal from the substrate by comparing to the substrate signal from a particle-free area. 64 scans were collected and averaged. Powder X-ray diffraction (Rigaku SmartLab diffractometer, Cu $K\alpha$ X-ray source) was performed on ZH film particulates in Bragg-Brentano geometry. X-ray photoelectron spectroscopy experiments were performed with a Thermo Scientific K-Alpha (Al $K\alpha$ X-ray source) system. ZH film

particulates were loaded in a powder sample holder. Survey, high resolution (Zr 3d, O 1s, C 1s), and valence-level scans were acquired at pass energies (step size) of 200 eV (1 eV), 20 eV (0.15 eV), and 100 eV (0.15 eV), respectively. The spectra were calibrated by aligning the binding energy of the adventitious species in the C 1s region of each sample to 284.8 eV. The Zr 3d and O 1s regions were deconvoluted into multiple components using Shirley background correction and Voigt function with a mixing parameter of 30% Lorentzian and 70% Gaussian.

3.2 Thin Film Preparation

ZH thin films were prepared by sonicating a suspension of ZH nanoparticles (5 mg/mL) in DI water for 4 h followed by three cycles of centrifugation at 1500 rpm and decantation. The supernatant was transferred to a clean centrifuge tube each time and discarding any pelleted precipitate. The ZH nanoparticle suspension (~1 mL) was then pipetted in air directly onto a multiple reflection ZnSe internal reflection element (IRE) and dried overnight under N₂. ZH suspensions with D₂O were prepared by drop casting the ZH suspension directly onto the ZnSe IRE in dry N₂.

3.3 X-ray Diffraction (XRD)

Powder X-ray diffraction (XRD) was performed using a Rigaku SmartLab diffractometer with a Cu K α X-ray source set to 40 kV and 44 mA in Bragg-Brentano geometry equipped with a D/teX Ultra 250 silicon strip detector. The obtained XRD pattern was then baseline corrected.

3.4 X-ray Photoelectron Spectroscopy (XPS)

Pristine and CO₂-, SO₂-, and NO₂-dosed ZH powders were packed into small wells of a copper XPS sample plate with a spatula and loaded into a Thermo Scientific K-Alpha (microfocused monochromated Al K α X-ray source, 30° angle of incidence, ~400 μ m spot size) XPS system equipped with a double-focusing hemispherical analyzer that is normal to the sample. The XPS sample plate and samples were evacuated in the antechamber overnight before loading into the XPS chamber. A dual-beam (electron/Ar ion) flood source with a low energy Ar⁺ ion beam and very low energy (<1 eV) electron beam was used to minimize charging. Both survey and high-resolution scans were collected for pristine, CO₂-, SO₂-, and NO₂-dosed ZH powders. High-resolution spectra were collected at a pass energy of 50 eV with 0.1 eV step size. Survey scans were collected at 200 eV pass energy at 1.0 eV step size. Nominal energy resolution (full width at half maximum) of 0.8 eV for 50 eV and 2.1 eV for 200 eV was obtained. Overlapping peaks were deconvoluted using Thermo Advantage v5.9902 software with smart background correction, Powell fitting algorithm, and Gauss-Lorentz mixed product lineshape to deconvolute the spectra into multiple components for species identification. All peaks were fit until a convergence of 1×10^{-9} was achieved. Spectra were calibrated to the adventitious C 1s carbon peak at 284.6 eV, which enabled direct comparison of the obtained XPS spectra. During typical data collection, the sample chamber base pressure was $\sim 3.5 \times 10^{-8}$ mbar. High-resolution scans were typically averaged over 16 scans. Nitrogen and sulfur spectra were averaged over at least 64 scans.

3.5 In Situ Attenuated Total Reflectance (ATR) Spectroscopy

3.5.1 Contaminant and Simulant Dosing

Gas dosing ATR experiments were performed using a Harrick Horizon accessory housed inside a Bruker Vertex 70 V. During gas dosing, the sample and instrument compartments were evacuated to <0.01 Pa to minimize infrared beam absorption from trace atmospheric gases. The sample chamber contained the ZH thin films sealed in a 316-stainless steel gas flow cell coated in SiO₂ at ambient pressure. A gas dosing manifold containing the atmospheric component gases was attached to the flow

cell via vacuum-tight bulkhead feedthrough connectors. The flow cell was purged for at least 2 h under dry UHP N₂ to remove any loosely bound surface contaminants and moisture from the ZH surface. Interferogram phase correction was conducted using the Mertz algorithm with Happ–Genzel apodization function and zero-filling factor of 2. Unless otherwise noted, all spectra reported are difference spectra, which were generated by subtracting the initial scan before the gas mixture reached the sample chamber from the obtained scans. No additional ATR corrections were performed. Deconvoluted spectra were fit using a Voigt line shape and OriginLab OriginPro 2017 software. Peak locations were determined using a second derivative approach. Baselines were fit using a B-spline curve. An iterative procedure to minimize the reduced χ^2 value to below 1×10^{-6} was used. The reduced χ^2 was obtained by dividing the residual sum of squares by the degrees of freedom. Resulting fits have an R^2 value greater than 0.99. Time-resolved difference spectra are colored from blue (initial) to red (final) to highlight spectral changes over time. Simulant vapor dosing was conducted by flowing UHP N₂ (0.2 sccm) either through a sealed vial containing simulant in N₂ using an inlet/outlet needle or through a fritted gas saturation bubbler in the case of dosing DMMP. At this flow rate, the estimated concentration of DMMP reaching the sample chamber is 7800 ppm, assuming complete saturation of the bubbler headspace with DMMP and dilution to a total flow rate of 25 sccm. The bubbler was sparged overnight to purge the headspace and minimize other dissolved atmospheric gases in the DMMP. Simulant is introduced with the atmospheric contaminant gas stream and directed over the ZH thin film. All exhaust gases were then fed into a bleach bubbler to decompose any remaining simulant. The total flow rate was maintained throughout all experiments by offsetting flow changes with dry UHP N₂ unless otherwise noted.

3.5.2 Liquid Phase ATR

Approximately 1 mL of ZH suspension in H₂O or D₂O was pipetted onto a clean ZnSe IRE in a N₂-purged sample chamber. Changes in the suspension during drying were monitored by collecting spectra at 5 min intervals with 16 scans averaged per spectrum for about 4 h.

3.5.3 Solid Phase ATR

Solid powders were placed onto a single bounce ATR internal reflection element (IRE) attached to a Thermo Fisher Scientific Nicolet iS50 FTIR spectrometer with a deuterated triglycine sulfate detector and XT KBr beam splitter. Interferogram phase correction and scan parameters were the same as described for the gas-dosed samples above, but 64 or 128 scans were averaged for each collected spectrum and background. Sample powders were placed directly onto a diamond IRE and compressed with a screw anvil to ensure good contact with the IRE.

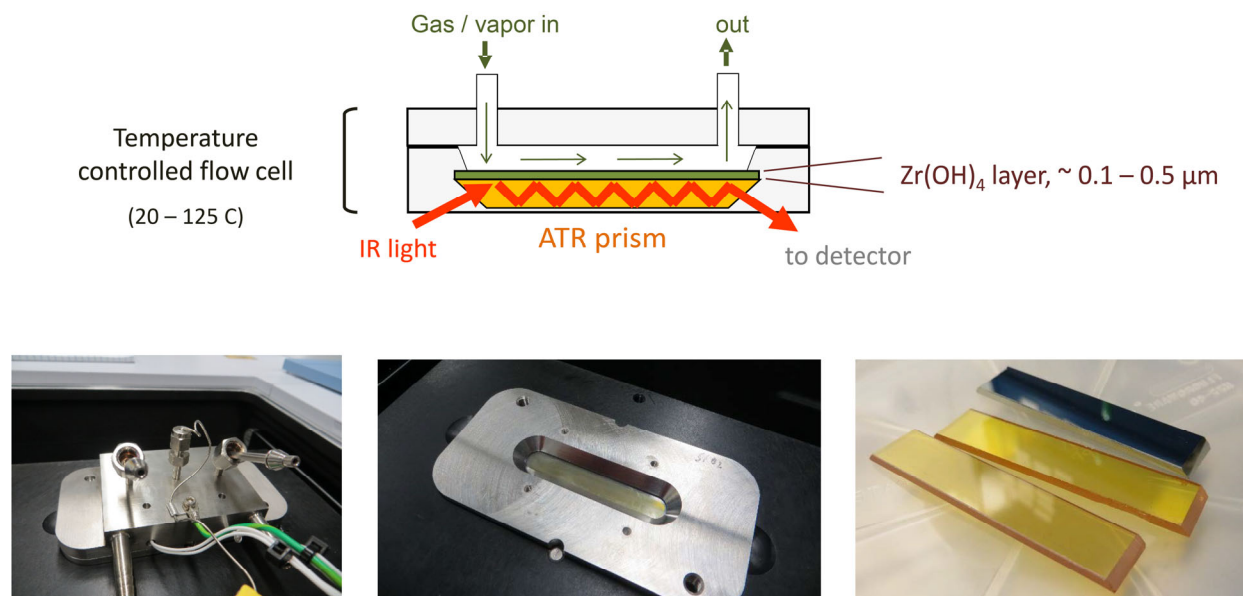


Figure 4. Schematic of environmental ATR chamber (top), photograph of actual ATR chamber (bottom left), ZH on ZnSe IRE (bottom center), and two ZnSe and one Ge IREs.

3.6 CWA Degradation Studies

3.6.1 DRIFTS

All gases were used as is unless otherwise noted. For live agent dosing, ZH powder (~14 mg) was packed into a 6 mm porous ceramic cup and placed into a sealed stainless-steel container, and purged overnight under UHP nitrogen to equilibrate the sample. The porous sample cup was then rapidly transferred to a Pike Technologies Diffuse IR environmental DRIFTS cell, which was kept under a continuous flow of filtered UHP He (to reduce moisture and hydrocarbons) at 10 cc min^{-1} . The continuous flow cell directs the gas mixtures from the bottom of the porous ceramic cup, through the sample bed, and out the top of the Pike DRIFTS cell. The sample was maintained at 25°C and typically purged overnight under UHP He to remove some adventitious hydrocarbons and bulk water from the ZH nanopowder. The sample was then immediately sealed and aligned, whereupon a DRIFTS baseline spectrum was collected to determine when the sample had equilibrated within the He stream. Once the sample had equilibrated (i.e. there were no further changes to water/hydroxyl groups of the ZH), a background scan was collected as a reference. Following sample equilibration, CWA in He was then dosed through the bed of ZH powder in the DRIFTS sample cup at 1 sccm. All toxic exhaust effluent was sequestered through an activated carbon trap in a fume hood. Infrared spectra were recorded in real-time during the exposure at 1 averaged spectrum/min (128 scan per spectrum). All DRIFTS spectra presented are Kubelka-Munk (KM) transformed difference spectra, where the reference is the background just prior to dosing. All negative bands indicate vibrational mode loss and vice versa.

Kinetics data were obtained using the obtained KM(t) plots and zero-, first- and second-order equations were fitted using the least-square method to obtain an estimated reaction rate order and apparent rate constant for CWA degradation on ZH.

3.6.2 Microbreakthrough

Caution! The nerve agent GB is extremely toxic. Experiments should be run by trained personnel using appropriate safety procedures. Breakthrough testing was conducted with GB on baseline and

contaminated ZH using a microbreakthrough apparatus that has previously been described in detail.[14] Approximately 5-10 mg ZH was loaded into a 4 mm inner diameter fritted glass test tube to a depth of approximately 4 mm. A saturator cell was used to deliver GB to a dry diluent stream at rates necessary to achieve challenge concentrations of approximately 130 ppm (750 mg/m³). A Nicolet 380 Fourier transform infrared with a DTGS detector and Axiom Inc. gas cell with a 0.5 m path length was used to monitor GB concentration in the effluent stream. After complete breakthrough, the curve was integrated and subtracted from the amount of chemical fed to the packed bed to calculate the loading. Similar procedures were used to measure the NO₂ and SO₂ capacity of ZH, with a saturator cell used to deliver NO₂ and a pressurized ballast used to deliver SO₂. The effluent concentrations were monitored using FTIR spectroscopy and a gas chromatograph equipped with a flame photometric detector for NO₂ and SO₂, respectively.

3.7 Theoretical Calculations

3.7.1 DFT Simulations

Molecular and reactive adsorption of H₂O, CO₂, SO₂, NO₂, HF, and GB on ZH was simulated using DFT and a small cluster model of the ZH surface. A square ZH tetramer [Zr₄(OH)₁₆] was previously used that mimicked the fused-tetramer ZH structure proposed by Southon, et al.[8] The geometry of the square cluster [Zr₄(OH)₁₆] was taken from our previous work.[15] Preliminary simulations with water adsorption showed that water binds strongly to the six-coordinated Zr atoms and remains bound to Zr even if other adsorbates are present. Therefore, all simulations reported in this work used the square cluster with 4 water molecules coordinated to each Zr atom [Zr₄(OH)₁₆(H₂O)₄]. Molecular complexes of H₂O, CO₂, SO₂, NO₂, HF, and GB with Zr₄(OH)₁₆(H₂O)₄ and their possible reaction products were simulated to estimate the enthalpies of molecular and reactive adsorption. For each molecular adsorbate, 100 initial structures were generated by randomly placing and orienting the adsorbate molecule near the cluster using the computational procedure described elsewhere.[15] For each reaction product, 300 initial structures were generated by randomly placing the corresponding anion near the cluster with either terminal, bridging, or both hydroxyl groups removed (100 structures for each type of hydroxyl group removed).

The generated structures were fully optimized without any constraints using the PBE[16] density functional, augmented with the D3 dispersion correction[17] def2-SVP double- ζ set[18] of Gaussian-type orbitals (GTOs), and the W06 set[19] of GTOs for charge density fitting. For each optimized structure, the absolute enthalpies were computed at the same level of theory using the ideal-gas, rigid-rotor, harmonic oscillator partition functions with the unscaled vibrational frequencies. The lowest-enthalpy structure for each molecular complex or reaction product was subsequently re-optimized using the M06 hybrid functional,[20] augmented with the D3 dispersion correction,[17] and the def2-TZVPP triple- ζ set[18] of GTOs. The enthalpies of molecular and reactive adsorption were computed as the differences between the M06-D3/def2-TZVPP enthalpies using the nominal reactions discussed below. All simulations were performed using Gaussian09.[21]

3.7.2 Electronic Structure Calculations

ZH was studied using *ab-initio* DFT with a particular focus on E_g and on impurity- or defect-induced states in the gap. These results are described fully elsewhere.[22] The calculations employed the hybrid HSE06 functional in order to avoid the well-known underestimation of E_g due to excessive delocalization that affects “pure” generalized gradient approximation functionals such as PBEsol.

3.7.3 Ab-initio Molecular Dynamics (AIMD) Calculations

All calculations were performed using density functional theory as implemented, except where noted, in the Quantum Espresso (QE) program suite (version 5.0 and higher) with the PBE functional. The projector augmented wave (PAW) method was employed with wave function and density cutoffs of 40 and 400 Rydbergs (Ry), respectively. The Zr pseudopotential was checked by computing the lattice constants and cohesive energy of bulk Zr metal. The results are $a_0 = 3.24$ and $c_0 = 5.147$ Å for the hexagonal lattice constants and 6.21 eV per atom for the cohesive energy, which are in very good agreement with the experimental lattice constants[23] of $a_0 = 3.2294$ and $c_0 = 5.1414$ Å (at $T = 4.2$ K) and the cohesive energy (6.25 eV per atom at $T = 0$ K). This work entails a study of the adsorption of SO₂, and the S and O pseudopotentials were checked by computing the properties of molecular SO₂. The results are 1.449 Å and 119.44° for the bond length and angle, which agree well with the experimental values[24] of 1.432 Å and 119.54°. As a test of convergence, the adsorption energy (ΔE_{ads}) was computed for a range of wave function and density cutoffs using DMMP as a test molecule. For nondissociative molecular adsorption, ΔE_{ads} was found to be converged to within ~2 meV at the cutoff values used here. All PAW calculations included a Grimme D2 semiempirical dispersion correction to better describe the effects of noncovalent interaction between OH groups.

Born–Oppenheimer (B–O) AIMD calculations using QE employed the Verlet algorithm with temperature controlled via velocity scaling. A typical run used a 1.0 femtosecond (fs) time step and extended for >3 picoseconds (ps), with stabilization of the total (ionic + electronic) energy occurring within the first ~0.5 ps. In some runs, H was replaced with D to increase the period of the $\nu(\text{O–H})$ stretching mode ($\tau_{\text{OH}} \approx 9.5$ fs vs $\tau_{\text{OD}} \approx 13.5$ fs), but this had no significant effect on the stabilization of the total energy. In the following, however, hydrogen (whether H or D) will be described as “H”. Proton (¹H) NMR chemical shifts were obtained using the gauge-including PAW (GIPAW) method. Here, structures obtained in AIMD were first relaxed in a static ($T = 0$) calculation with convergence criteria of 1×10^{-5} Ry and 1×10^{-4} Ry/Bohr, respectively, for the total energy and the force on any atom in any direction.

For some calculations, B–O AIMD was performed using the CP2K code, which employs a hybrid of plane waves and Gaussian basis sets. The PBE functional was used with norm-conserving pseudopotentials and a 400 Ry plane-wave cutoff. The Gaussian basis sets were of double- ζ quality, with polarization functions added, that were optimized for molecular calculations. Dispersion was included using the Grimme D3 semiempirical approach, and the AIMD trajectories were obtained using the Nosé–Hoover thermostat. To test the compatibility of the QE and CP2K results, ΔE_{ads} was computed for molecular adsorption of DMMP on a two-layer ZH model (see below) with very similar results (–0.95 and –0.99 eV, respectively, for QE and CP2K). For comparison, a cluster model[15] in which DMMP adsorbs via a single hydrogen bond (H-bond) between a bridging OH and the phosphoryl O atom gives $\Delta E_{\text{ads}} = -72$ kJ/mol = –0.75 eV. (In the present work, a negative ΔE_{ads} corresponds to an exothermic process.)

The IR spectrum was computed using the Fourier transform of the autocorrelation function of the total system dipole moment, $\langle \mu(0)\mu(t) \rangle$, obtained from the CP2K AIMD trajectory. The spectrum is given by:

$$I(\omega) = \frac{\hbar \omega^2}{2\pi k_B T} \int dt e^{-i\omega t} \langle \mu(0)\mu(t) \rangle$$

where k_B is the Boltzmann constant and $I(\omega)$ is the oscillator strength. Calculation of $I(\omega)$ was done using the visual molecular dynamics (VMD) program with the IR spectral density calculator plug-in. Here, H rather than D was used for hydrogen. Effective atomic charges were estimated using two different methods, which gave nearly identical IR intensities. One approach made use of Mulliken population analysis performed using the CPMD code. The second involved a Bader “atoms-in-molecules”

analysis of the QE wave function using the code provided by Henkelman *et al.* The charges used were -0.53 , $+0.23$, and $+1.2$ $|e|$ for O, H, and Zr, respectively. An advantage of this method is that anharmonicity is included. Hence, no semiempirical rescaling of the computed frequencies is needed, unlike in calculations based on the harmonic approximation, and the results can be compared directly with those of the experiment. A disadvantage is that the atomic displacements cannot easily be determined, which makes mode assignments difficult.

The starting model was a two dimensionally periodic slab (2DPS) constructed using a (4×4) unit cell of ZH molecules joined by bridging OH groups, as in the idealized structure. Each layer thus consisted of 16 $\text{Zr}(\text{OH})_4$ units per cell with all Zr atoms coplanar. In the starting structure, the unit cell was a perfect square; however, variable-cell optimization (at $T = 0$ K) yielded a structure with slightly different lattice constants (14.59 and 14.78 Å) but 90° corner angles. This unit cell was used in all subsequent calculations, and the 1.3% difference in lattice constants is consistent with that seen in the a and b lattice constants of monoclinic ZrO_2 . A similar variable-cell optimization for an amorphous two-layer 2DPS with mixed terminal and bridging OH groups (which results from the AIMD process described below) gave slightly smaller lattice constants, 14.34 and 14.63 Å, which is an $a - b$ difference of 1.8%.

A 2DPS typically consisted of two layers, although some results were also obtained for one- and three-layer cells. A large vacuum gap (~ 30 Å) between successive bilayers in a double-layer calculation was used to avoid spurious long-range interlayer interactions and to allow space for H_2O that desorbs during AIMD (see below) and for the diffusion of adsorbates (e.g., SO_2). Although a model with so few layers might be considered inadequate in many calculations, the system that is being simulated is in fact thought to consist typically of two or three layers without significant covalent interlayer interactions. Because of the large size of the unit cell, all calculations were for the Γ -point only; however, as a test, a calculation for a bilayer using a $(3 \times 3 \times 1)$ Monkhorst–Pack (MP) grid gave a total energy within 2 meV per unit cell of the Γ -point result. The convergence of the NMR results was also checked at higher cutoff values (60 and 600 Ry, respectively, for the wave function and the density) and a $(3 \times 3 \times 1)$ MP grid spacing.

4. RESULTS AND DISCUSSION - EXPERIMENTAL

4.1 Characterization of ZH and Thin Film Preparation

4.1.1 Thin Film Preparation

Different commercial ZH types were purchased for use in this program. Two types (“B” and “C”) have been previously identified as superior for filtration and decontamination applications, respectively. Differences between the two types are in the preparation and processing of the compounds during synthesis, which are proprietary to the manufacturer. Additionally for comparison, ZH was also synthesized electrochemically and as a sol gel to produce uniform thin films on complex surfaces for future work utilizing light-driven plasmonic decomposition to accelerate or extend the surface reaction chemistry.

Synthesis and reproducible thin film deposition is of particular importance for consistent and reliable data collection using IR-based spectroscopies, for which substrate adhesion, film thickness, smoothness, particle size reproducibility, and lack of chemical contamination are especially salient characteristics. Several deposition methods were evaluated including air brushing, electrodeposition, and drop casting. Initially, airbrushing was refined to provide superior film quality and adhesion by spraying a heated substrate (75°C) with a fine mist of ZH suspended in MeOH. Coating with DI water suspensions was very challenging as the evaporation rate for water was too slow for timely and consistent thin film formation.

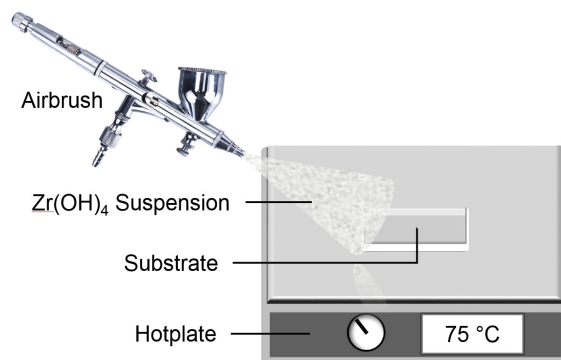


Figure 5. Schematic of spray coat thin film deposition.

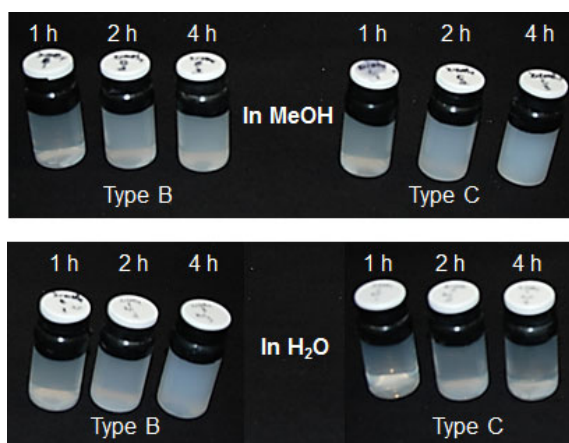


Figure 6. The effect of sonication time on dispersity of the ZH nanopowder type in methanol and water. Type C has much stronger affinity for methanol; whereas, type B has much stronger affinity for water. Note all samples demonstrate increased dispersity with sonication time.

Lack of initial colloidal stability made ZH thin film preparation challenging. ZH type B was relatively well stabilized in H_2O , whereas type C is better stabilized in methanol. Regardless, after sonication and centrifugation to reduce the aggregates and polydispersity, both types B and C were relatively stable in DI water.

Dynamic light scattering (DLS) confirmed the stability and size distributions of the suspensions over time. For reference, three samples taken approximately 5 minutes apart are shown below in the correlogram.

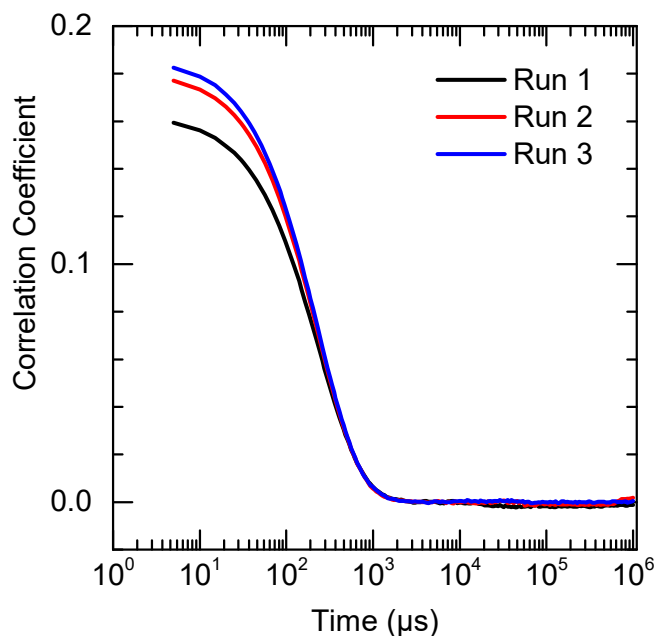
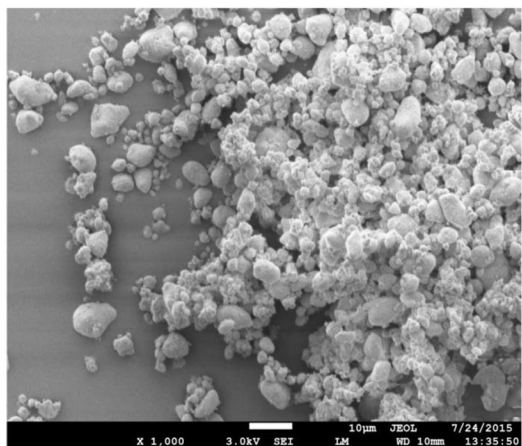


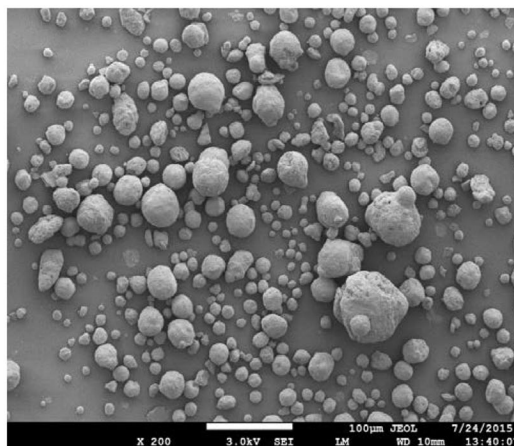
Figure 7. Centrifugation at 1,500 rpm of the sonicated ZH nanoparticles suspended in water greatly improves colloidal stability and reduces polydispersity as determined by particle size distribution estimated from dynamic light scattering data.

4.1.2 Scanning Electron Microscopy

Type B comprises of smaller, irregular particles that clump together, whereas type C appears more consistently spherical and has much better flowing properties in general. Particle sizes for type B appear to be relatively uniform and around 2-3 microns; whereas, type C appears more “bi-modal” with a typical particle size of around 10 microns (Figure 8).



Type B: Irregular particles, ~2-3 microns



Type C: Spherical particles ~10 microns

Figure 8. SEM images of ZH type B (left) and type C (right).

ATR of ZH showed a combination of free hydroxyls species near 3700 cm^{-1} and also native carbonates near 1580 and 1300 cm^{-1} (Figure 9). Additional vibrational modes indicated by * are shown for methoxy adsorbates from the methanol solvent used for spray coating. Drop casting from DI water is a much simpler and cleaner method for forming thin films and the method of choice for preparing ATR samples.

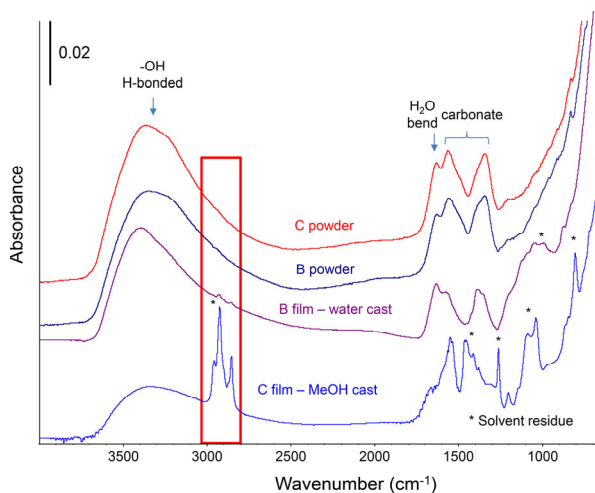


Figure 9. ATR-IR of ZH in both powder and thin film showing IR active surface species and adsorbates.

4.1.3 Surface Characterization and Thermal Stability of Atmospheric Adsorbates

Much previous work involved dosing ZH with interferents to identify potential adsorbates. Adventitious carbon in the form of various surface carbonates was identified on all ZH samples due to atmospheric carbon dioxide exposure. Thermal gravimetric analysis coupled with mass spectrometry (TGA-MS) was performed to carefully identify if this carbon contaminant can be thermally removed. ZH (~30 mg) was placed in a platinum TGA pan and heated to $700\text{ }^{\circ}\text{C}$ under argon while selectively monitoring 18 m/z and 44 m/z as well as the change in weight with respect to temperature. The data is seen below in Figure 10.

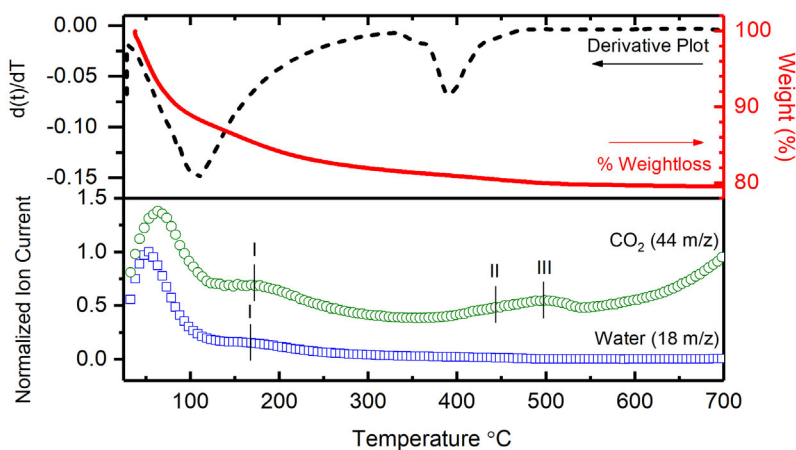


Figure 10. TGA-MS showing the loss of weight from zirconium hydroxide with temperature (red line, top). The derivative plot (dashed black line) is shown for identification of desorption onset. The bottom panel shows the normalized MS plots of water and CO₂ desorbing from the zirconium hydroxide surface.

Likely, 3 different types of carbonate desorbed from ZH at about 160, 450, and 500 °C, corresponding closely with previous attenuated total reflectance (ATR) data previously reported. The first major loss of CO₂ near 90 °C was likely the desorption of solvated carbonates. The increases in ion current for CO₂ gas at lower temperatures correlated to weaker bound carbonate species, likely bicarbonates in desorption (I). CO₂ desorption (II) and (III) were more tightly bound carbonates and likely monodentate and bidentate carbonates, respectively. Weakly bound surface water was desorbed from just before 100 °C and again near 160 °C, indicating two different types of adsorbed water such as multilayer or “multimer” water should be the weakest bound water and desorb first followed by highly-coordinated surface-bound water.

Powder X-ray diffraction data of the samples calcined at the above temperatures are shown below in Figure 11. As expected, the ZH remained amorphous until approximately 250 °C. At 500 °C, a mixture of tetragonal and monoclinic phases are present. At 1000 °C, ZH was mostly monoclinic.

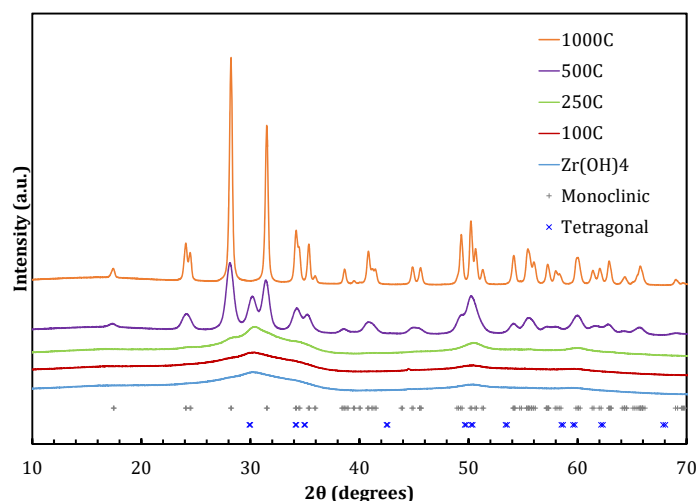


Figure 11. Powder XRD of ZH converting to monoclinic zirconia with increased temperature. ZH samples were calcined at 100, 250, 500, and 1000 C. Reference spectra provided of monoclinic (+) and tetragonal (x) zirconia.

In order to elucidate the changes occurring at lower temperatures with more granularity, a second series of glancing incidence (thin film) XRD analyses were conducted to focus on the temperature-induced crystallographic changes below 350 °C.

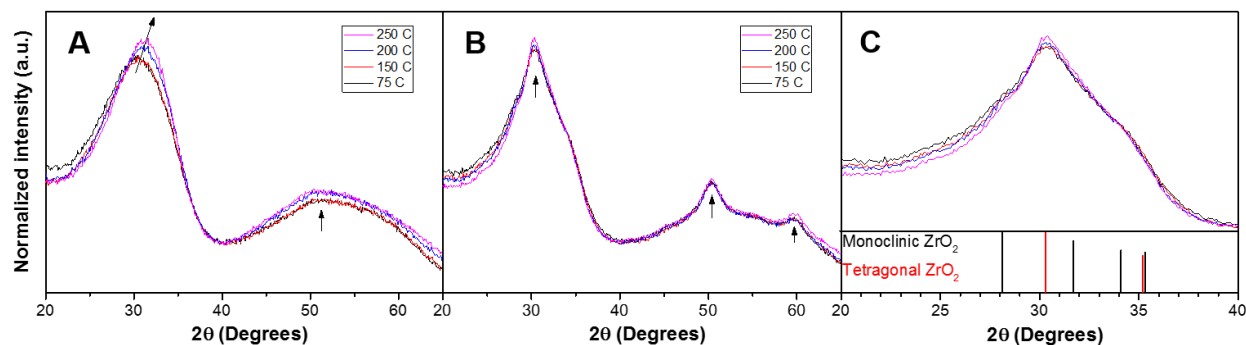


Figure 12. Powder X-ray diffraction patterns of A) type B and B) type C ZH nanopowder heated in air to various temperatures for 15 min. C) For comparison, reference patterns obtained from Srinivasan et. al[25] of monoclinic and tetragonal ZrO₂ suggest the pXRD pattern of type C ZH likely contains contributions from both monoclinic and tetragonal ZrO₂.

Powder XRD data obtained for the type B and C ZH nanopowders showed significant differences between the two types. The XRD pattern for type B exhibited only broad amorphous peaks corresponding with one or more ZrO₂ impurity phases; while type C ZH also contained more crystalline ZrO₂ impurities – likely a combination of the tetragonal and monoclinic crystal structures (Figure 12C). The morphological differences may play a role in the annealing and decomposition kinetics as these impurities can act as reactive nucleation centers to drive ZH nanopowder to less reactive ZrO₂.

Upon heating the powders in air, crystallographic changes were observed at temperatures as low as 200 °C after 15 min. The full-width at half max decreases with increasing temperature suggesting increased long-range order of the ZrO₂ impurity phases. The lack of ZH peaks confirms the highly disordered nature of the ZH, as predicted by our plane wave density function theory calculations.

ATR-IR data are shown in Figure 13. Peaks in the 1300-1700 cm⁻¹ region (likely corresponding to water and carbonate peaks) were reduced upon calcination, while peaks below 800 cm⁻¹ (likely corresponding to zirconium-oxygen bonds) increased upon calcination. Although not shown, peaks in the area of bulk water (~3500 cm⁻¹) also decrease upon calcination.

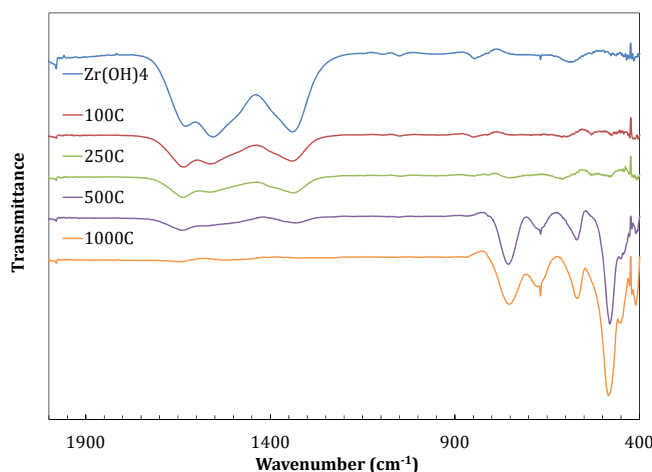


Figure 13. ATR-FTIR spectra for zirconium hydroxides.

X-ray photoelectron data are shown in Figure 14. Data in the oxygen 1s region were deconvoluted into peaks at 531.8 and 531.3 eV, representing terminal and bridging hydroxyl groups, respectively. As calcination temperature increased, both the O/Zr and terminal hydroxyl groups decreased. The physical interpretation of this observation is that ZH is condensing free hydroxyls and losing water to form O-Zr-O bonds. Indeed, as crystallization occurred, the Zr/O ratio approaches 2, consistent with ZrO_2 . These data suggest ZH loses reactive hydroxyls rapidly above about 200 °C.

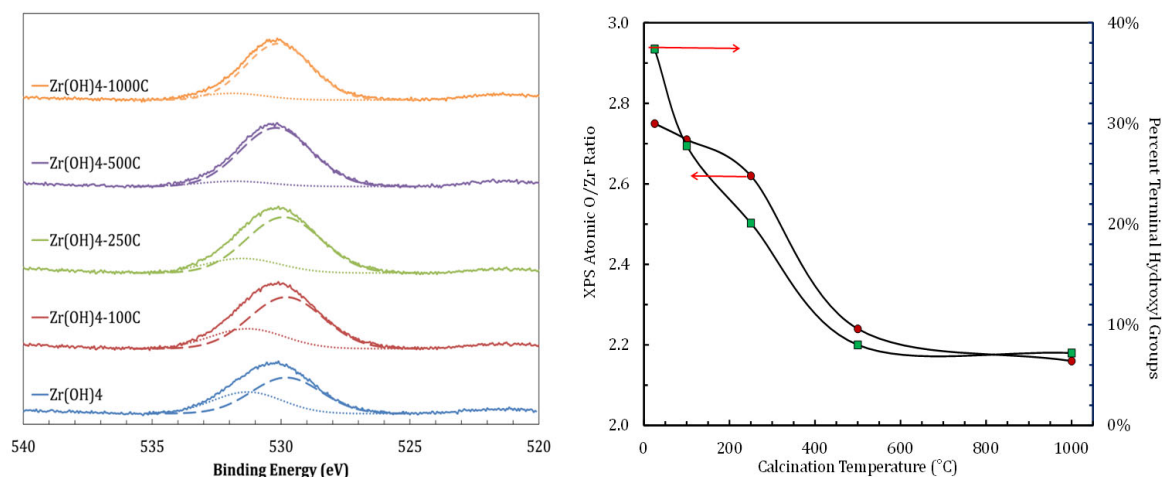


Figure 14. Oxygen 1S X-ray photoelectron spectra for calcined samples (left) and O/Zr and terminal hydroxyl percentages of calcined samples (right).

Nitrogen isotherm data are shown below (Figure 15). Data for as-received and calcined ZH at 100°C were identical within error. The surface area and pore volume numbers are found in Table 1. However, as calcination temperature increased, nitrogen uptake decreased, resulting in reduced surface areas and pore volumes. The reduction in pore volume was consistent with the reduction in surface hydroxyl content and the O/Zr ratio, as terminal groups and water may be responsible for the porosity of the structure. Likely, the small aggregates were sintering together, and losing surface area.

Table 1. BET surface area and pore volume of zirconium hydroxides.

Material	BET Surface Area (m ² /g)	Pore Volume (cc/g)
Zr(OH) ₄	406	0.81
Zr(OH) ₄ , 100°C	405	0.83
Zr(OH) ₄ , 250°C	266	0.63
Zr(OH) ₄ , 500°C	69	0.38
Zr(OH) ₄ , 1000°C	7	0.02

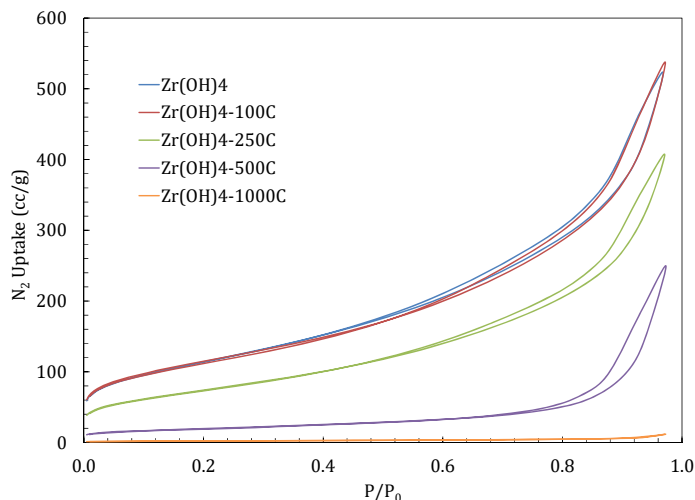


Figure 15. Nitrogen isotherm data for zirconium hydroxide heated to different temperatures.

4.1.4 Potentiometric Titration

Surface hydroxyl species, e.g. bridging and terminal hydroxyls, are of particular interest because, along with under-coordinated Zr sites, are implicated in the binding and decomposition of phosphoryl-containing CWA molecules. Collected IR and XPS spectra provide initial hydroxyl distribution data, but potentiometric titration, a corroborative electrochemical method, can also reveal the changes in the type and distribution of surface chemical species with pH change.

The ZH powders were acidified in solution and titrated to obtain a proton binding curve, from which the hydroxyl species distribution as a function of pKa can be derived. The thermal evolution of the hydroxyl distribution was revealed by comparing ZH powders heated to different temperatures (Figure 16). In this case, the more acidic groups appear to persist in greater capacity compared to basic species.

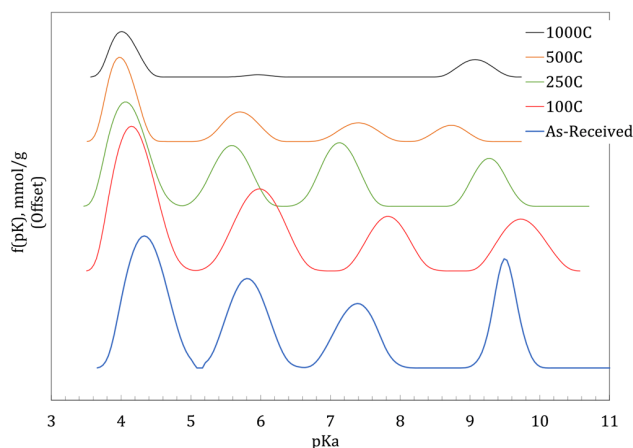


Figure 16. Potentiometric titration of calcined ZH powders (as-received, 100, 250, 500 and 1000 °C). pKa distribution of hydroxyl species on the ZH samples vs. temperature. According to this method, the as-received and 100 C treated ZH have the most acid and base sites.

4.1.5 Gas Accessibility to ZH Reactive Sites

4.1.5.1 PROBING HYDROXYLS

Unless otherwise specified, *all further experiments were performed using type C ZH*. To determine the accessibility of the available hydroxyls species, a single beam ATR spectrum was collected after dosing a ZH thin film with D₂O. D₂O readily exchanges with accessible water and hydroxyls. To facilitate rapid and complete hydroxyl exchange, ZH particles were sonicated in D₂O for 2 h. Thin films were drop casted and dried under N₂ and then quickly inserted into the FTIR for analysis under dry N₂. The integrated peak areas of the free hydroxyl regions for OH (~3700 cm⁻¹) and OD (2700 cm⁻¹) were deconvoluted and compared (Figure 17).

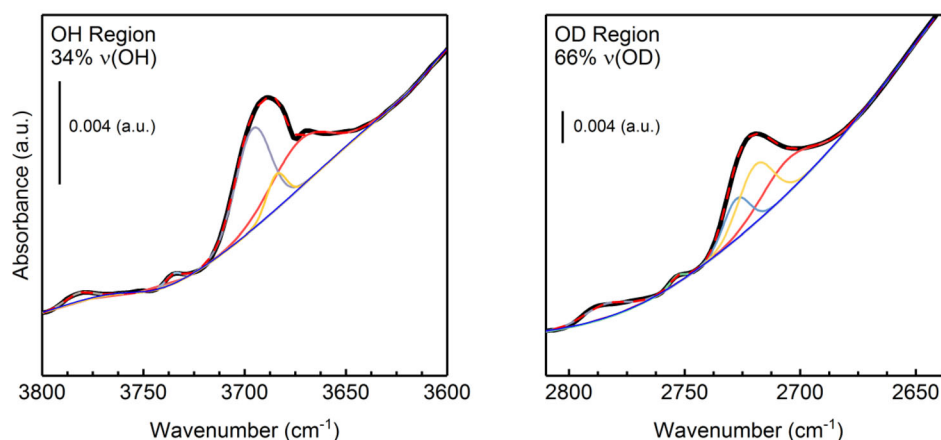


Figure 17. Single beam FTIR-ATR spectra comparing integrated peak areas for ZH nanoparticles suspended in D₂O after 2 h sonication. About 66% OH/OD exchange was observed based on the integrated deconvoluted peak areas. Reprinted with permission from Balow, et al., ACS Appl. Mater. Interfaces 2017, 9, 45, 39747–39757. Copyright (2017) American Chemical Society.

This data indicates that approximately 34% of the total free hydroxyls are inaccessible. This is important to keep in mind during simulant and live agent studies as false conclusions could be drawn if an assumption is made that all hydroxyls are accessible. The exact reason for the inaccessibility is unknown, but two likely possibilities include size of the pores of the ZH nanoparticles or perhaps interlayer trapped hydroxyl sites.

4.1.5.2 PROBING DEFECT SITES

CO is commonly used to probe and characterize acidic sites on surfaces because the C-O vibrational mode is highly sensitive to both surface interactions and the local electronic environment.[26] Depending on the interaction, the CO vibrational mode can shift to higher or lower wavenumbers.

CO (10,000 ppm) was dosed over ZH for 30 min (Figure 18A-B). The loss of free hydroxyl at 3703 cm⁻¹ with the concurrent increase in bands near 1610, 1583, 1448, 1379, and 1327 cm⁻¹ suggests CO reacted with free hydroxyls and various surface defect sites to form a variety of carbonates and formates. The Literature suggests the formation of bidentate carbonates and formates occur on O²⁻-Zr⁴⁺ acid/base sites or free hydroxyls, respectively. Furthermore, the vibrational mode of CO at 2046 cm⁻¹ is strongly redshifted from the typical frequency of 2143 cm⁻¹. This suggests a weakening of the CO triple bond,

possibly from electron back donation into antibonding orbitals (from coordinatively unsaturated O^{2-} or $O^{2-}-Zr^{4+}$ acid/base surface sites) or electron withdrawal from pi bonding orbitals on sites such as coordinatively unsaturated $Zr^{4/3+}$ sites.[27] Collectively, the formation of both formates and carbonates, along with the redshifting of the CO vibrational modes, strongly suggests a highly defective surface comprising under-coordinated O^{2-} , $O^{2-}-Zr^{4+}$, and possibly $Zr^{3/4+}$ reactive defect sites under dry N_2 at ambient pressure.

The CO was purged with dry N_2 to determine the relative stability of the carbonate/formates and CO surface adsorbates. Minor losses of the formate/carbonate species were observed, but most of the adsorbed CO at 2046 cm^{-1} desorbed, implying a weaker and less stable interaction (Figure 18C-D).

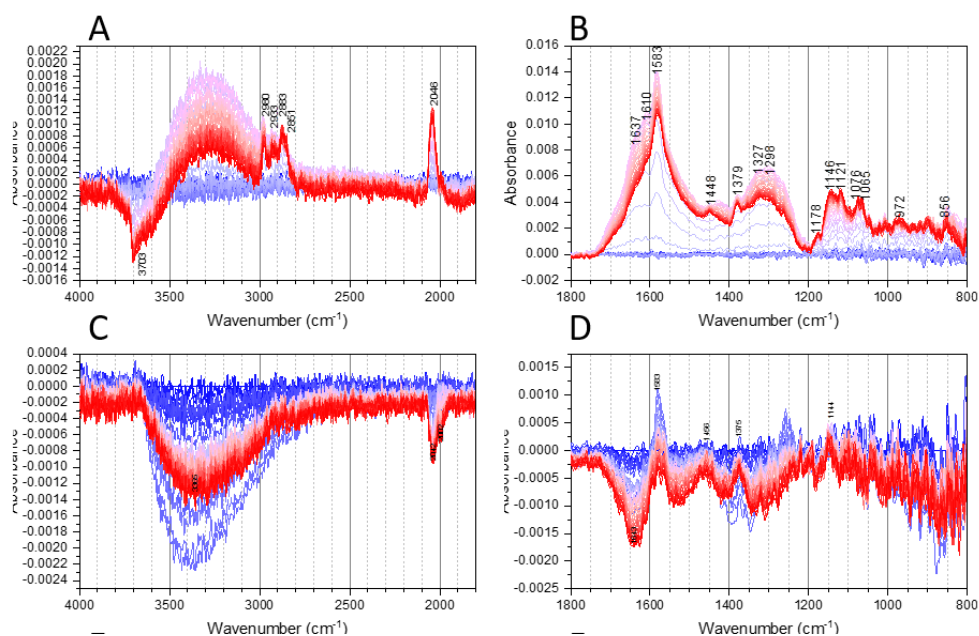


Figure 18. (A,B) Showing formation of surface adsorbates upon dosing CO onto ZH. (C,D) N_2 purge of CO from sample chamber demonstrating stability of CO adsorbates on ZH.

4.2 Atmospheric Contaminant Dosing on ZH

4.2.1 XPS of Contaminated ZH

High-resolution XPS spectroscopy was used to investigate the interaction between ZH and common environmental contaminants (CO_2 , SO_2 , and NO_2). An undosed or “clean” ZH control sample was also analyzed for comparison to contaminant-dosed ZH samples (Figure 19).

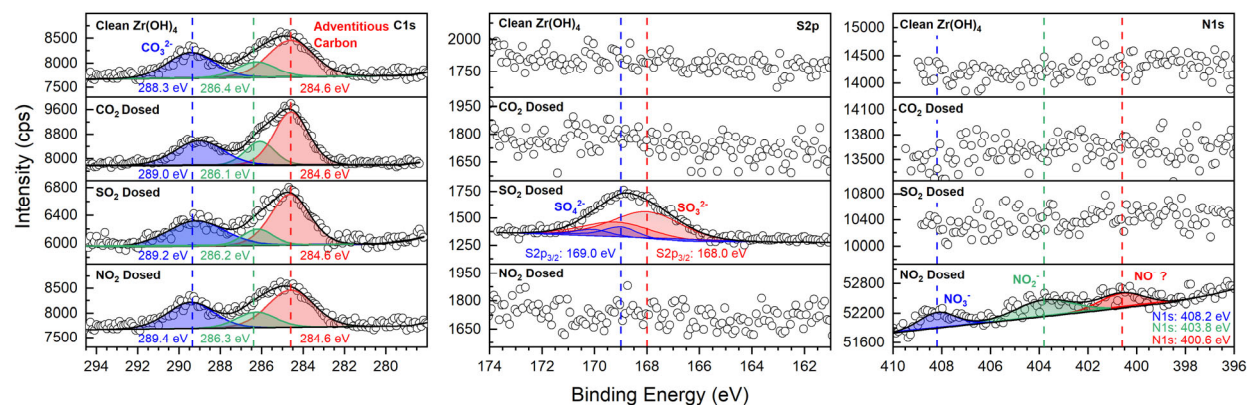


Figure 19. X-ray photoelectron spectra (XPS) of the C 1s, S 2p, and N 1s photoelectron binding energy range of clean and dosed ZH showing adsorbate formation. All samples showed adventitious carbon and carbonate-like surface species, whereas SO₂- and NO₂-dosed ZH showed sulfite/sulfate and nitrite/nitrate adsorbates, respectively.

Directly correlating dosed adsorbates to changes in reactivity requires careful disentanglement of the native (bi)carbonates, adventitious carbon, surface water, humidity, and adsorption kinetics of the contaminants. Therefore, XPS spectra interpretation is limited to providing evidence of local perturbation of the zirconium bonding environment during contaminant dosing, adsorbate identification, and relative adsorbate concentrations after contaminant dosing.

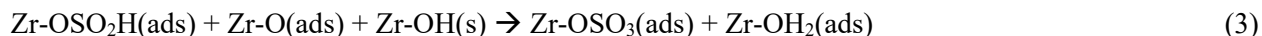
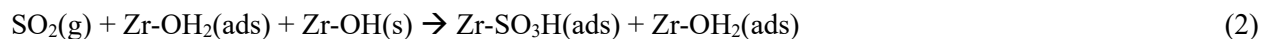
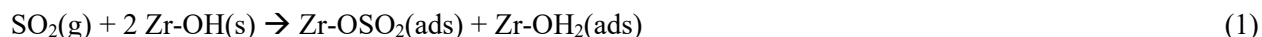
High-resolution spectra were collected in the C 1s, S 2p, N 1s, and Zr 3d energy regions. All samples contain adventitious carbon (284.6 eV, red), likely from atmospheric exposure of the samples.[28] CO₂-dosed ZH has three observable peaks corresponding to carbonyl species (286.0 eV, green), adventitious carbon (284.6 eV, red), and carbonates (289.0 eV, blue).

Various gases dosed over metal (hydr)oxides have been reported to react with cus defect sites (e.g. Zr^{3+/4+}) or free surface hydroxyls to form surface-bound adsorbates.[2, 29-33] CO₂-dosed ZH showed increased adventitious carbon at 284.6 eV compared to the clean ZH. The higher partial pressure of CO₂ in this case resulted in higher surface coverage of carbon-based adsorbates.[28] Additionally, a small carbonyl-like species was observed near 286 eV (Figure 19, green). Carbonic acid, which contains a carbonyl moiety, is known to form and remain stable under dry CO₂-containing atmospheres on mineral surfaces.[34] Such results were supported by the observation of a carbonyl vibrational mode near 1695 cm⁻¹ (Figure 22) when dosing CO₂ on ZH using DRIFTS. As such, the observed peak near 286 eV was tentatively assigned to a stabilized surface carbonic acid.

While displacement of adventitious carbon and carbonates was observed during SO₂ and NO₂ dosing DRIFTS experiments (Figure 22e-f), some (bi)carbonate and related species remain resilient on the surface in the XPS spectra. The amorphous and porous nature of ZH likely slows or blocks contaminant gas diffusion to all adsorbed carbon species and active ZH sites, making complete displacement of such adsorbates unlikely.

SO₂-dosed ZH comprises two distinct doublets in the S 2p binding energy region at 168.0 eV and 169.0 eV. Both doublets show peak splitting between 2p_{3/2} and 2p_{1/2} that are in agreement with the literature value of 1.2 eV. The first S 2p component corresponds to either SO₂ or sulfite (Figure 19, 2p_{3/2} 168.0 and 2p_{1/2} 169.0 eV, red)[35] and the second component to sulfate (Figure 19, 2p_{3/2} 169.0 and 2p_{1/2} 170.1 eV, blue).[36] Lack of significant SO₂ vibrational modes in DRIFTS imply that the peak at 168.0 eV is most likely adsorbed sulfite. A sulfite to sulfate atomic ratio of 3:2 was calculated based on integrated peak areas of both components. Recent work by McEntee et al. show similar results with sulfite

primarily forming on ZH under dry SO₂ dosing conditions (Scheme 1), but bisulfite (Scheme 2) and sulfate (Scheme 3) forming during humidified SO₂ dosing.[2]



Schemes 1-3 above suggest the formation of sulfates could occur with continued reaction of SO₂ on the ZH surface to form bisulfites and eventually sulfates. Only two components were deconvoluted in the collected XPS spectra, closely matching sulfites and sulfates. Identification of previously reported bisulfite surface species cannot be ruled out, but may be formed in trace concentrations or are less stable under these conditions compared to sulfite and sulfate adsorbates.[2, 35]

The NO₂-dosed ZH XPS spectrum was deconvoluted into 3 unique N 1s components at 408.2 (N⁵⁺),[37] 403.8 (N³⁺),[38] and 400.6 eV (N¹⁺)[39], indicating at least three different nitrogen-containing species of differing chemical states on the ZH surface. Transition metal nitrates and nitrites closely match the binding energies observed at 408.2 and 403.8 eV, respectively. Multiple nitrate and nitrite formation mechanisms on metal oxide surfaces show complex behavior of NO₂ on ambient surfaces. A pairwise nitrate and nitrite formation mechanism was proposed by Szanyi et al.,[40] which occurs via disproportionation of 2 NO₂ molecules on an aluminum oxide surface with under-coordinated aluminum and oxygen sites:



After all immediately available sites are consumed, free hydroxyls have been proposed to react with NO₂ to form additional adsorbed nitrates and water.[40] Evidence of hydroxyl loss was observed during DRIFTS contaminant dosing (CO₂, SO₂, and NO₂). NO₂-dosed TiO₂ showed similar adsorbate formation on defect sites such as Zr_{cus} metal sites and/or surface hydroxyls.[41]

The small peak at 400.6 eV is likely a reduced nitrogen species with an oxidation state between +1 and -1.[39] A previous report suggests the binding energy of NO⁻ (~401.7 eV) could be shifted to lower binding energy by bonding to a negatively charged defect site.[42] Another possibility is the in situ formation of N₂O by reduction of NO on the ZH surface; however, N₂O has 2 components separated by approximately 3.8 eV,[42] which does not match the separation of the deconvoluted components in the N 1s panel of Figure 19. Formation of zirconium nitride is also unlikely because a Zr 3d doublet near 397 eV is not observed.[43] Therefore, the 400.6 eV component in the N 1s spectrum is tentatively assigned as an NO⁻ species.

High-resolution XPS scans of the Zr 3d binding region provides information about the local bonding environment of zirconium before and after contaminant dosing. In Figure 20 below, the 3d_{3/2} and 3d_{5/2} doublets of CO₂- and SO₂-dosed ZH shift to higher binding energy, suggesting that the contaminants interact with zirconium by withdrawing electron density or displacing/modifying electron donating moieties bound to zirconium.[44]

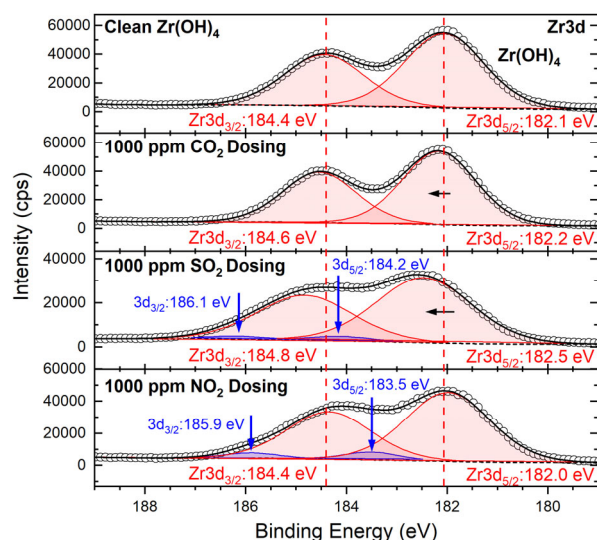


Figure 20. X-ray photoelectron spectra of the Zr 3d range for clean and CO₂-, SO₂-, and NO₂-contaminated ZH. CO₂- and SO₂-dosed ZH samples showed an increasing chemical shift, which is likely correlated to withdrawal of valence charge from the surface from adsorbates.

This observation agrees with previous reports that utilize CO₂ and SO₂ gases to probe for basic sites because of their tendency to withdraw electron density.[27] CO₂- and SO₂-dosing of ZH shifted the Zr 3d binding energy by 0.4 eV and 0.1 eV, respectively. The Zr 3d transition did not significantly shift upon NO₂-dosing. Both clean and CO₂-dosed ZH samples only had one detectable Zr 3d doublet, whereas the SO₂- and NO₂-dosed samples had an additional detectable Zr 3d_{5/2} doublet centered on 184.2 and 183.5 eV, respectively. Zr 3d_{5/2} transitions in this region are typical for a more oxidized zirconium chemical state (Figure 20, blue).

4.2.2 DRIFTS of Contaminant Dosing

Previous work by Mogilevsky et al., measured the relative amounts of bridging and terminal hydroxyl species using nuclear magnetic resonance (NMR), which include both accessible and inaccessible hydroxyl sites.[45] Bridging hydroxyls were the most abundant hydroxyl species on ZH, with a calculated bridging to terminal hydroxyl ratio of 3.4:1 determined by ¹H magic angle spinning NMR.[45] Three types of surface hydroxyls were reported for ZH with varying degrees of reactivity shown in Figure 21.[13, 31, 46, 47]

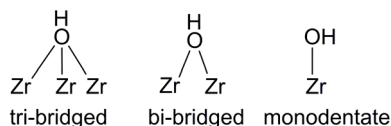


Figure 21. Types of hydroxyl species on zirconium hydroxide.

Hydroxyls can have acidic and basic behavior, depending a number of factors such as the electronegativity, oxidation state, and coordination number of the bound cation.[48] Therefore, the behavior of contaminants can vary depending on the type and accessibility of the free hydroxyls. To

determine the relative reactivity of hydroxyls species on ZH, CO₂, SO₂, and NO₂ gases were dosed over clean ZH and surface reactions were monitored using DRIFTS.

In situ time-resolved DRIFTS difference spectra were collected to identify surface adsorbates and determine the impact of contaminants on the ZH surface during GB decomposition. Representative CO₂-, SO₂-, and NO₂-dosing spectra were normalized for comparison (Figure 22). Changes to surface hydroxyls and hydrogen bonding interactions on ZH during contaminant dosing were observed in the high wavenumber region (a-c), whereas adsorbate identification and surface interaction are typically found in the lower wavenumber or “fingerprint” region (d-f). Such regions of interest are shown for clarity and ease of comparison between systems. All spectra are colored from blue to red to indicate the start and finish of spectral acquisition over 75 minutes, respectively.

CO₂ is an acidic probe molecule that can be used to measure the basicity of active sites.[30] As such, CO₂-dosing on ZH showed loss of all three hydroxyl species at 3709, 3740, and 3785 cm⁻¹, which corresponds to tri-bridged, bi-bridged, and monodentate hydroxyls, respectively. The relative loss in peak intensity across all hydroxyl species was similar, suggesting CO₂ does not significantly prefer one free hydroxyl site over another.

Several new vibrational modes form during CO₂ dosing indicating formation of surface adsorbates. Deconvolution and identification of (bi)carbonates on ZH can be due to surface hydration retention, which can alter vibrational mode position, adsorption mechanisms, and adsorbate speciation.[2, 3, 31] Depending on the degree of hydration, some surface adsorbates (e.g. carbonate) may become solvated and thus demonstrate degenerate vibrational modes, which is spectroscopically observed as a single vibrational mode comprising both the asymmetric and symmetric components.

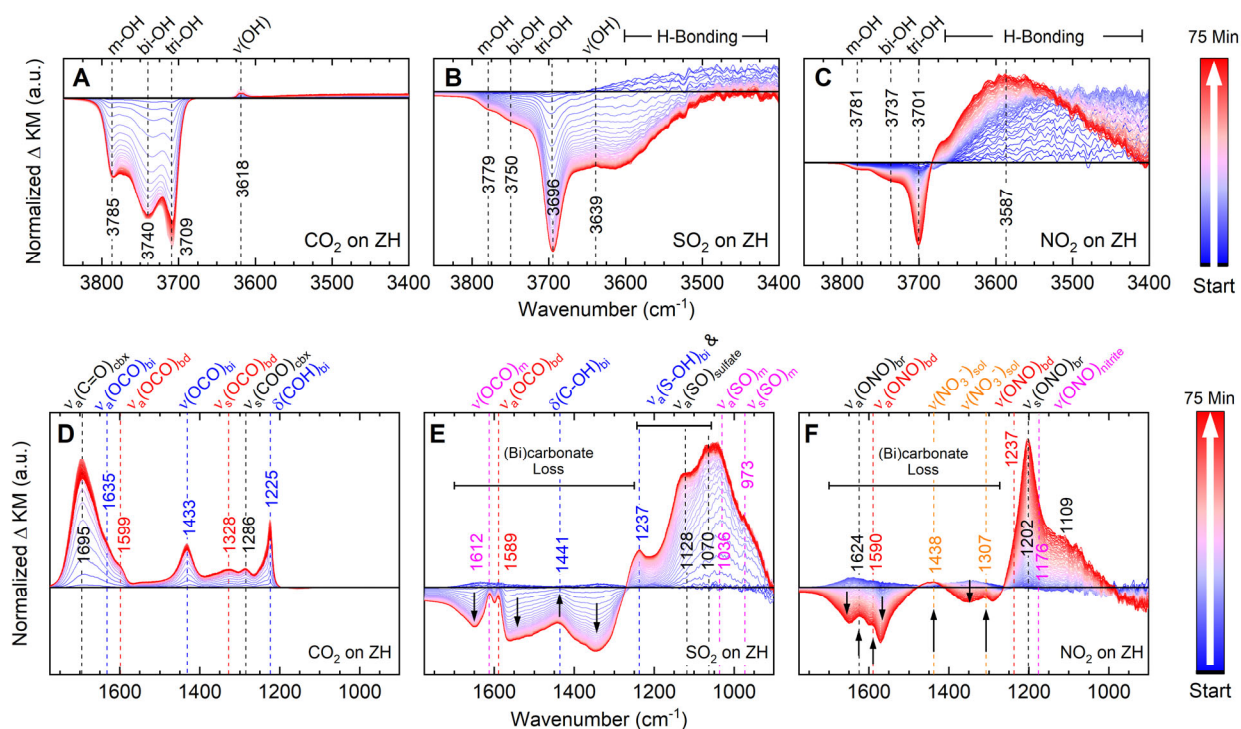


Figure 22. Normalized diffuse reflectance infrared Fourier transform difference spectra showing adsorbate formation during gas dosing with CO₂ (A,D), SO₂ (B,E), and NO₂ (C,F) on pristine ZH over 75 min in two spectral regions.

Bicarbonate, bidentate and monodentate carbonates, carboxylate, and an interfacial carbonate complex were identified on ZH during CO₂ dosing. The concomitant loss of free hydroxyls suggests free hydroxyls play a role in the formation of one or more of the adsorbates.[31] Similar adsorbates were previously observed by several groups while dosing CO₂ over metal (hydr)oxide systems, including ZH.[49, 50] Bicarbonate vibrational modes were observed at 3618, 1635, 1433, and 1225 cm⁻¹ corresponding to $\nu(\text{OH})$, $\nu_a(\text{OCO})$, $\nu_s(\text{OCO})$, and $\delta(\text{C-OH})$, respectively.[51] The characteristic OH vibrational modes at 3615 and 1225 cm⁻¹ are reliable indicators of bicarbonate formation because no other modes are active in this region.[32] The vibrational modes at 1695 and 1286 cm⁻¹ are likely $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ carboxylate modes, respectively. Finally, the remaining modes at 1599 and 1328 cm⁻¹ closely match literature values for bidentate carbonates, due to the 271 cm⁻¹ separation between the asymmetric and symmetric vibrational modes.[32] The carbonate adsorbates show relatively weak binding energies according to the calculated DFT, which matches Previous work in this program and others showing loss of surface (bi)carbonates upon reduction or removal of CO₂ partial pressure.[31]

SO₂-dosed ZH also showed decreasing vibrational modes of three hydroxyl sites at slightly shifted wavenumbers: 3779, 3750, and 3696 cm⁻¹. The loss of tri-bridging hydroxyls at 3696 cm⁻¹ appears more significant than CO₂-dosed species. However, the tri-bridging vibrational band near 3686 cm⁻¹ rapidly increased when the SO₂ was purged from the DRIFTS cell (not shown). A similar, but much smaller band near 3769 cm⁻¹ also increased during SO₂ purging, suggesting that some SO₂ was loosely bound to both tri-bridging and monodentate hydroxyl sites compared to the bi-bridged species. The large differences in peak heights between the monodentate and tri-bridging hydroxyl species is likely due to the relative abundance of accessible hydroxyl species. As previously mentioned, NMR results showed tri-bridging hydroxyl species are in excess compared to monodentate or bi-bridging hydroxyls.

During ZH SO₂ dosing, decreasing vibrational modes indicate surface water displacement (3650 – 3400 and 1650 cm⁻¹) and loss of native surface carbonates (1600 – 1275 cm⁻¹). DFT calculations discussed later show SO₂ has a high binding affinity for the ZH surface compared to CO₂. As such, preferential formation of sulfite, sulfate, and bisulfite is expected over (bi)carbonate adsorbates, which will result in displacement of (bi)carbonates.

Similar to CO₂ dosing, several sulfur containing surface adsorbates rapidly formed during SO₂ dosing on ZH. Vibrational modes at 1036 ($\nu_a(\text{SO})$) and 973 cm⁻¹ ($\nu_s(\text{SO})$) correspond to monodentate sulfite species. The vibrational modes at 1237 and 1070 cm⁻¹ have been arbitrarily assigned to the $\nu(\text{SO})$ modes of bisulfite[41] and sulfate[2] based on previous reports. Additionally, a small, but increasing vibrational mode resembling the $\nu(\text{OH})$ mode of bisulfite can be observed at 3639 cm⁻¹, where it is convoluted with a decreasing hydrogen bonding peak, providing additional support for bisulfite formation. Previous work has also reported similar sulfite and bisulfite formation on metal (hydr)oxide materials after SO₂ dosing.[41, 52] These reactions likely occur at *cus* O²⁻ defect sites and accessible surface hydroxyls as shown in Scheme 6 - 8:



Vibrational modes at 1128 cm⁻¹ can be assigned to either physisorbed SO₂ or sulfate formation.[2, 53] Physisorbed SO₂ on ZH is less stable than chemisorbed sulfate, and should be easily removed by purging the DRIFTS cell with an inert gas. However, after a 1 hour He purge, the vibrational modes near 1128 cm⁻¹ did not significantly decrease. Therefore, this vibrational mode was assigned to adsorbed sulfate. Surface sulfate formation has been reported previously via reaction of bisulfite with surface coordinatively unsaturated (*cus*) sites and hydroxyls as shown below:



NO_2 dosing on ZH rapidly formed surface adsorbates, as evidenced by increasing vibrational modes at 1202 and 1176 cm^{-1} believed to be associated with nitrate and nitrite surface species, respectively.[53] A decrease in vibrational bands near 1600, 1397, and 1350 cm^{-1} , likely from decrease and/or displacement of adsorbed native (bi)carbonates from the ZH surface during NO_2 dosing, complicates identification of individual vibrational modes.

Adsorbate formation appears to be driven by NO_2 interaction with hydroxyls, as evidenced by the concurrent loss of hydroxyls at 3781, 3737, and 3701 cm^{-1} . This surface hydroxyl interaction was consistent with both CO_2 - and SO_2 -dosing experiments. The broad vibrational band from 3675-3400 cm^{-1} provides evidence for hydrogen bonding of NO_2 molecules to the hydroxylated ZH surface. However, adsorbed water on ZH also had broad $\nu(\text{OH})$ bands around 3600 – 3100 cm^{-1} , but was accompanied by a $\delta(\text{HOH})$ mode near 1640 cm^{-1} . [31] The normalized peak heights of $\nu(\text{OH})$ (3400 cm^{-1}) and $\delta(\text{HOH})$ (1640 cm^{-1}) modes plotted over time showed similar vibrational mode behavior, and are therefore likely both water modes. Thus, the band near 3400 cm^{-1} is likely surface water formed initially during NO_2 dosing that was probably convoluted with another hydrogen bonded NO_2 species, which continuously increases over the 75 minutes of dosing. The initial increase in surface water supported the following nitrate formation mechanism, where NO_2 molecules interact with surface hydroxyls to produce a combination of NO_3^- , NO , and adsorbed surface water.[41] A small increase in the vibrational band near 1437 cm^{-1} during NO_2 -dosing may be due to nitrate solvation in surface water.



XPS data also is consistent with the formation of a highly reduced NO^- species to the ZH surface that is likely coordinated to an O^{2-} defect site.[39]

Losses in adsorbed (bi)carbonate bands were also observed during SO_2 -dosing near 1600, 1397, and 1350 cm^{-1} and also during NO_2 dosing, which suggests SO_2 - and NO_2 -based adsorbates will displace ambient or CO_2 -dosed adsorbates on ZH. Such findings agree with DFT calculations showing much higher binding energies for the SO_2 and NO_2 bound adsorbates; however, DFT results showed no reaction between the ZH cluster and NO_2 molecules directly. More discussion of the possible surface reaction between NO_2 and ZH is found in the theoretical section.

A summary of the vibrational modes observed on ZH during atmospheric gas dosing are found in Table 2 below:

Table 2. Identified vibrational modes for CO_2 , SO_2 , and NO_2 pre-dosed ZH after overnight purge with N_2 to remove adsorbed surface water.

Contaminant	Adsorbate	Vibrational Mode	This Work (cm^{-1})	TiO_2 (cm^{-1})
CO_2	Bicarbonate	$\nu(\text{OH})$	3618	n.o. ⁱ
		$\nu_a(\text{OCO})$	1635	1623 ^a
		$\nu_s(\text{OCO})$	1433	1423 ^a
		$\delta(\text{C-OH})$	1225	1222 ^a
	Bidentate carbonate	$\nu_a(\text{OCO})$	1599	1566 ^a
		$\nu_s(\text{OCO})$	1328	1355 ^a
	Carboxylate	$\nu_a(\text{COO})$	1695	1670 ^a
		$\nu_s(\text{COO})$	1286	1251 ^a

SO ₂	Sulfate	$v_a(\text{SO})$	1128	1161 ^b
		$v_s(\text{SO})$	1070	1070 ^b
	Monodentate	$v_a(\text{SO})$	1036	1033 ^b
	Sulfite	$v_s(\text{SO})$	973	971 ^b
	Adsorbed SO ₂	$v(\text{SO}_2)$	n.o. ⁱ	1139 ^b
	Hydrogen	$v(\text{OH})$	3639	3648 ^b
NO ₂	Sulfite	$v(\text{SO})$	1070	1077 ^b
	Bidentate	$v_l(\text{ONO})$	n.o. ⁱ	1286 ^c
	Nitrite	$v_a(\text{ONO})$	1176	1178 ^c
	Nitrate	$v_a(\text{ONO})_{\text{br}}$	1624	1637 ^c
		$v_a(\text{ONO})_{\text{bd}}$	1590	1584 ^c
		$v_s(\text{ONO})_{\text{bd}}$	1237	1238 ^c
		$v_s(\text{ONO})_{\text{br}}$	1202	1230 ^c
	Nitrate (solvated)	$v(\text{NO}_3^-)$	1438	1435 ^c
		$v(\text{NO}_3^-)$	1307	1303 ^c

^aRef. [54], ^bRef. [55], ^cRef. [56], ⁱNot observed.

4.2.3 Ambient Contaminant Capacity Measurements

The total capacity of contaminants was measured for NO₂ and SO₂ gases on ZH (Figure 23). Interestingly, ZH appears to have over 7 times greater capacity for NO₂ vs. SO₂, suggesting ZH would be highly effective at scrubbing NO₂ from contaminated air. Total CO₂ capacity was not measured due to complications with ambient CO₂ contamination and an inability to completely remove bound carbonaceous species.

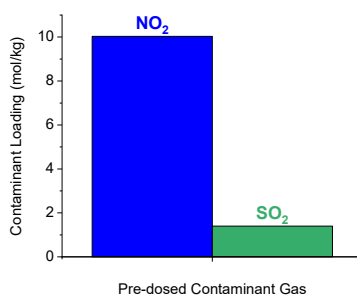


Figure 23. Capacity measurement of atmospheric contaminant on ZH powders.

4.3 CWA Simulant Decomposition on ZH

4.3.1 Dimethyl methylphosphonate (DMMP)

In addition to analyzing adsorbed reactants on ZH materials, the desorbed reaction products were analyzed as well. Such experiments were performed in both flow-through and static conditions. Static conditions enabled the collection of quantitative reaction data.

Approximately 50 mg of ZH type B powder was combined with 100 μL of DMMP and placed in a gas IR cell (KBr windows, 5 cm path length) in air under ambient conditions. The top spectrum reveals gas phase species that evolved over 24 hours. Gas phase reference spectra for methanol, carbon dioxide,

and DMMP are also available for comparison. Carbon dioxide and methanol proved to be the major decomposition products of DMMP (Figure 24).

This data provides important evidence that surface carbonates formed on ZH under ambient conditions can be liberated under CWA simulant dosing (in this case, with DMMP), and does not necessarily inhibit reactivity with ZH. Figure 25 further compares the IR spectrum from the 24 hour DMMP / ZH-B reaction to a spectrum of air in the IR gas cell, showing that a significant rise in CO_2 concentration occurred. The CO_2 absorbance from the reaction corresponds to a partial pressure of about 4.9 torr within the cell (versus ~ 0.3 torr for air). This increase in partial CO_2 pressure corresponds to decomposition of about 0.3 mg of carbonate ion.

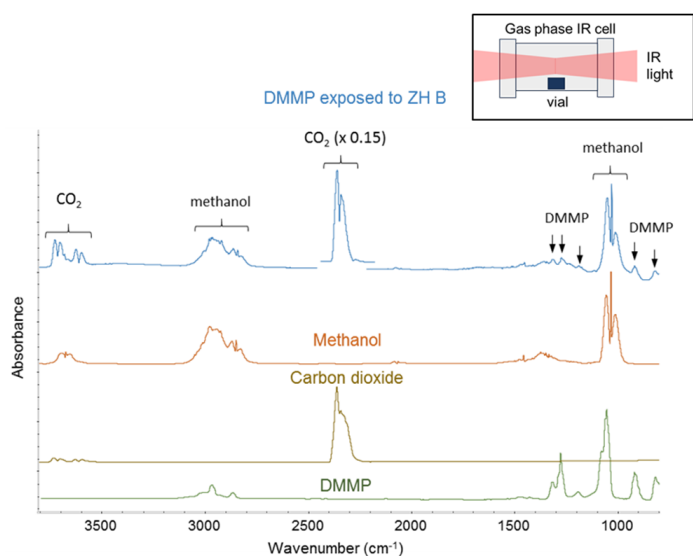


Figure 24. Comparison of a gas phase FTIR spectrum showing gas-phase reaction products from DMMP dosing on ZH-B for 24 hours (top) and reference gas phase spectra for methanol, carbon dioxide, and DMMP (below). Annotations of the “DMMP exposed to $\text{Zr}(\text{OH})_4\text{-B}$ ” spectrum indicate primary chemical species contributing to spectral features. The CO_2 peak near 2350 cm^{-1} is reduced by a factor of 0.15 relative to the rest of the spectrum. The inset shows the experimental configuration.

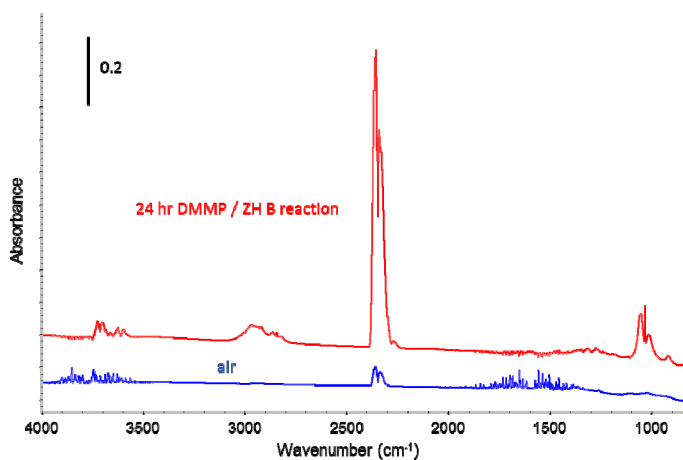


Figure 25. Comparison of the 24 hour DMMP / ZH-B reaction spectrum with a spectrum of air in the IR gas cell.

Under the “dry” conditions (6% RH in N₂, Figure 26(a)), methanol and CO₂ evolution were observed with some residual gas phase DMMP. For the hydrated conditions (50% DMMP in water under 36% RH, Figure 26 (b)) slower CO₂ and methanol formation was observed (comparison of CO₂ evolution is shown in Figure 26 (c)); however, the gas phase DMMP peaks were significantly reduced. This could indicate inhibited reactivity under the more hydrated conditions or perhaps the increased water may also increase solubility of the gas phase species. In particular, it may play a role in increased sequestration of DMMP, and/or the eventual decomposition of DMMP. Using the gas phase analysis helps to understand the reactivity of ambient exposed ZH materials under truly *operando* conditions, and gain insight into optimizing ZH materials for applied uses.

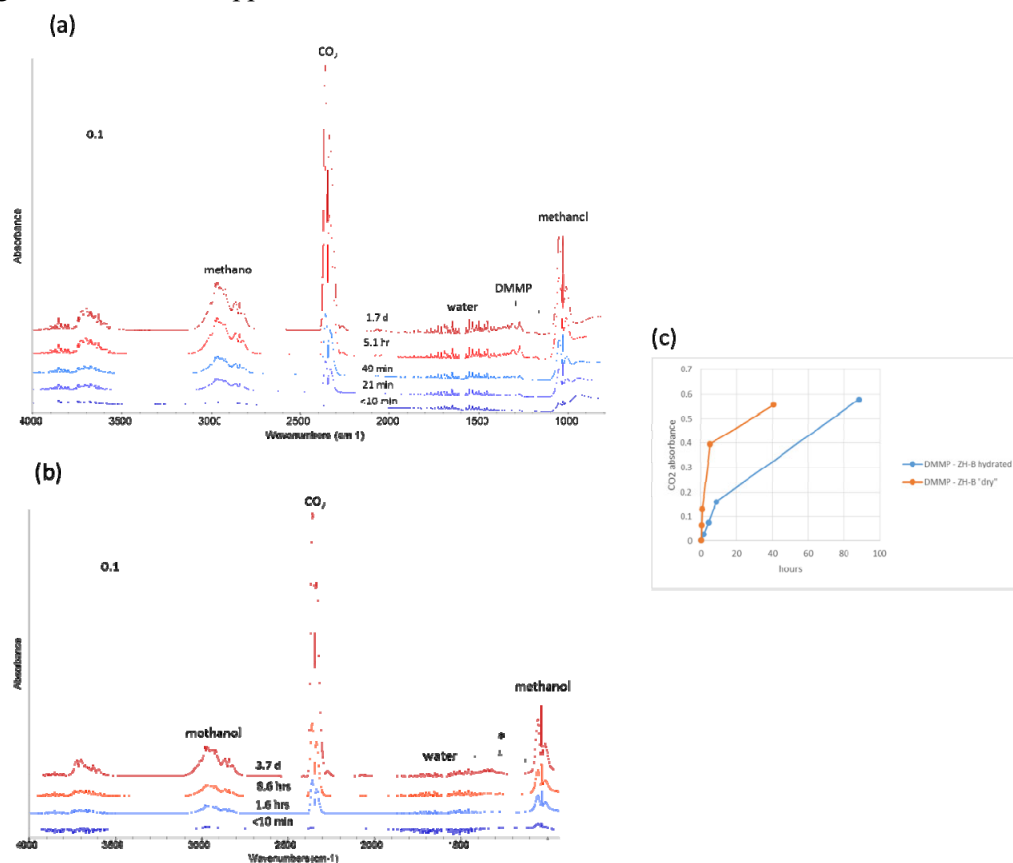


Figure 26. (a) “Dry” DMMP – ZH type B FTIR spectra. Time dependent gas phase IR spectra of DMMP mixed with ZH in N₂ with < 6% relative humidity. (b) Hydrated DMMP – ZH-B FTIR spectra. Time dependent gas phase IR spectra of 20 μ L DMMP mixed with ~37 mg ZH-B + 20 μ L water in N₂ with 36% relative humidity. The asterisk indicates loss of DMMP vibrational modes that are observed in the “dry” DMMP – ZH-B spectra. (c) Comparison of CO₂ evolution for N₂ dried and hydrated ZH.

Kinetic parameters of thermal desorption of adsorbed DMMP and its degradation products from ZH type C (ZH-C) were determined using modulated thermogravimetric analysis coupled to mass spectrometer (mTGA-MS).

Thermal desorption of DMMP from ZH-C was performed to determine the binding energy and kinetic parameters to support on-going IR studies and to aid in theoretical model development. Excess DMMP was dosed onto ZH and dried under N₂ flow for 8 h prior to mTGA-MS analysis. This process allows DMMP to fully react with ZH, form adsorbed by-products prior to analysis, and desorb any excess non-adsorbed DMMP or reaction by products. Therefore, the mass loss observed from the thermal ramp

thus represents the loss of surface adsorbed mixture of unreacted DMMP and reaction by-products. Analysis of the volatile species that evolved from ZH with increasing temperature yielded insights into the thermal decomposition mechanisms of DMMP on ZH.

Figure 27 presents the derivative of surface adsorbate mass loss from the DMMP-dosed ZH sample, as well as the most abundant ions detected. Each peak in the derivative curve corresponds to a maximum in mass loss and indicates different stages of desorption, of which 4 were identified. Analysis of the mass spectrometry (MS) data at each of these stages allowed for the identification of species that evolved in each stage. During stage I at 93 °C, peaks in MS signals corresponded to H₂O (18 & 17 amu), CO₂ (44 amu), and methanol (MeOH, 32 & 31 amu). Stage II occurred at 189 °C during which major ions comprised H₂O, MeOH, and CH₃ (15 amu). The major peak (30 amu) in Stage III at 397 °C has not been confirmed. Finally, Stage IV near 670 °C indicates that the only volatile species detected corresponded with CH₃. It should be noted that methanol is the primary degradation product from hydrolysis of DMMP. Previously, the maximum rate of evaporation of neat DMMP was found to occur at 80 °C and the most abundant ions in its MS fragmentation pattern comprised 109, 79, and 47 amu. These were all monitored in this experiment, yet surprisingly no MS fragment patterns were detected during the thermal analysis of ZH exposed to DMMP. This indicated that when DMMP resides on ZH, some DMMP either evaporates during the initial drying stage in unreacted state, reacts and/or breaks down into by-products and evolves during the thermal ramp, or irreversibly binds to the ZH surface.

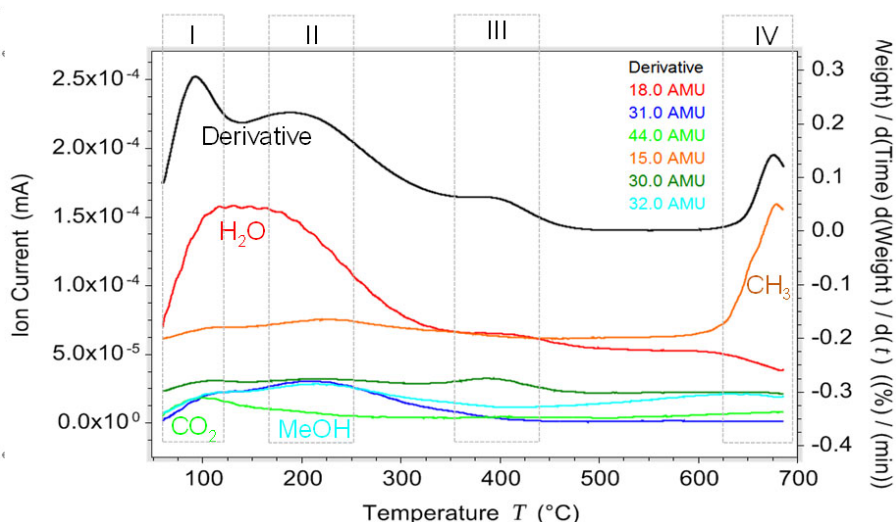


Figure 27. TGA of DMMP on ZH: Derivative of mass loss overlaid with MS data.

From these data, desorption pathways were proposed. It appears that the mass loss during Stage I represented the combined desorption of uncoordinated water, uncoordinated DMMP decomposition products of methanol and CO₂, and possibly unbound DMMP (perhaps as a component of a multilayer of DMMP on the surface).

Stage II mass loss was likely due to desorption of coordinated H₂O, as seen previously in neat ZH, and coordinated MeOH from DMMP hydrolysis. It was clear from the relative intensity of the methanol signal that a greater proportion of the observed methanol was coordinated to the ZH than uncoordinated. Of course, the experiment included an initial extended drying period, during which much of the uncoordinated methanol likely desorbed. Still, the amount of bound methoxy species remaining up

to 189 °C suggests that bound methoxy groups may hinder further hydrolysis by occupying and blocking active sites of ZH. Additional work is ongoing to confirm this hypothesis.

Stage III mass loss from DMMP-dosed ZH corresponded well with the Stage III mass loss that was previously seen in neat ZH, but at a slightly lower temperature. Previously, this transition was attributed to either hydroxyl condensation or desorption of carbonate species in the form of CO₂. Minor peaks in the H₂O signal and 30 amu were observed, while no increase in CO₂ occurred. The fact that CO₂ did not increase indicates that the carbonate species were likely replaced during the adsorption of DMMP and by-products. Therefore, it is likely that DMMP and by-products irreversibly exchanged with the carbonate species.

Finally, Stage IV desorption was entirely due to the loss of strongly adsorbed methyl (CH₃) groups at 676 °C. The methyl groups are proposed to be either the result of strongly bound methoxy species, or from DMMP. It is well known that DMMP and phosphate can strongly adhere to the ZH surface, which is supported by the high temperature at which Stage IV occurred.

Kinetic parameters were calculated from the modulated thermal ramp of ZH exposed to DMMP and are presented in Table 3.

Table 3. Kinetic parameters from thermal desorption of DMMP and reaction by-products from ZH-C

Sample	Stage	Temp. (°C)	Activation Energy (kJ mol ⁻¹)	PreExp Factor (min ⁻¹)	Max Rate (% min ⁻¹)	Major Ions (m/z)	k (min ⁻¹) ^a
ZH-C DMMP	I	92.9	110.9	13.30	2.88 x 10 ⁻¹	18, 17, 44, 31, 32	1.99 x 10 ⁻¹⁵
	II	189.4	144.1	13.64	2.21 x 10 ⁻¹	18, 15, 31, 32	7.27 x 10 ⁻¹⁶
	III	396.8	225.1	14.39	6.15 x 10 ⁻²	30, 18	4.04 x 10 ⁻¹⁷
	IV	676.1	473.7	23.27	1.42 x 10 ⁻¹	15	1.99 x 10 ⁻²⁵

^arate constant k was determined from preliminary calculation applying Arrhenius equation.

Thermal degradation of ZH and DMMP decomposition kinetic parameters were also investigated using ATR spectroscopy. Figure 28 shows the ATR spectra after DMMP adsorption and reaction on electrochemically deposited zirconium hydroxide (EZ) pre-annealed at various temperatures. This was to prepare the cleanest starting surface possible and minimize interaction with surface adsorbates. Preparation of the thin films can be found in the literature.[13]

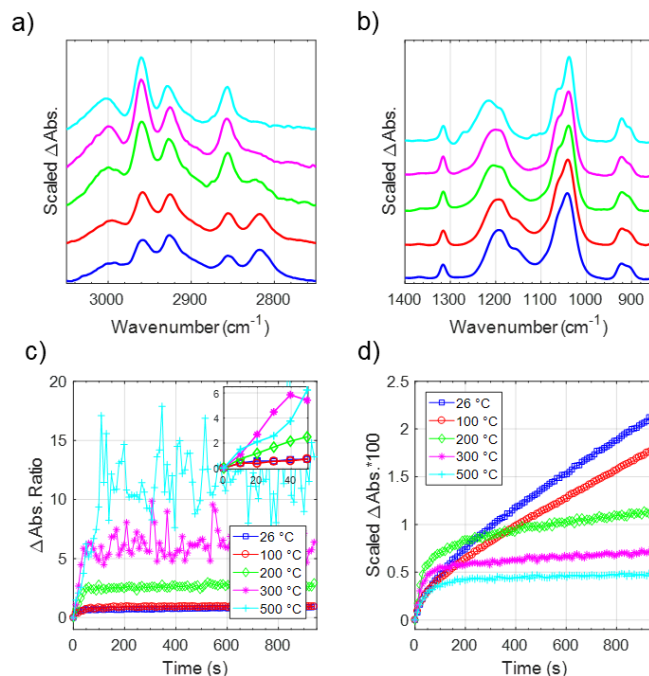


Figure 28. a)-d) ATR difference absorption spectra obtained while dosing a gas mixture of 0.2 sccm DMMP and 24.8 sccm N_2 every 9.89 sec for 16 min on variously prepared EZ samples. a) and b) - plots as a function of wavenumber for the spectra finally obtained after dosing the gas for 16 min. c) and d) - plots as a function of time at specific wavenumbers during the dosage. c) The ratio of ATR difference absorption peak intensities at 2856 cm^{-1} to at 2818 cm^{-1} (inset – zoomed-in area to show the spectra for initial 50 sec). d) ATR difference absorption peak intensity at 1150 cm^{-1} . The spectrum intensities in a), b), and d) are scaled by the intensity at 1040 cm^{-1} in the lastly collected spectrum for each sample. Color codes are maintained over all panels to represent variously prepared EZ samples; as-scraped (blue) and pre-annealed at 100 °C (red), 200 °C (green), 300 °C (magenta), and 500 °C (cyan). Adapted with permission from ACS Appl. Nano Mater. 2019, 2, 2295–2307. Copyright (2019) American Chemical Society.

In Figure 29a, the $\nu_s(\text{POCH}_2\text{-H})$ peak at 2856 cm^{-1} is attributed to molecular DMMP adsorption, while the $\nu_s(\text{Zr-OCH}_2\text{-H})$ peak at 2818 cm^{-1} is associated with methoxy adsorbates resulting from DMMP dissociation. Each plot is normalized by the intensity at 1040 cm^{-1} in the spectrum obtained after the final DMMP dosing step to minimize the effect caused by varying material quantities in the samples. The overall peak intensities at a given wavenumber cannot be compared across samples because of the high sensitivity of ATR spectra and the intersample differences during thin film formation. In addition, the backgrounds differ in the wavenumber region which overlaps with the broad hydroxyl stretch. To compensate for these effects, we subtracted a linear background between 2880 cm^{-1} and 2780 cm^{-1} and plotted the ratio of the peak intensities at 2856 cm^{-1} to 2818 cm^{-1} as a function of DMMP dosing time (Figure 29b). Samples annealed above 100 °C equilibrate in 100 sec, and the ATR intensity ratio of at 2856 cm^{-1} to 2818 cm^{-1} exceeds 1, indicating that molecular adsorption dominates compared to decomposition. By contrast, methoxy dissociation product dominates on ZH at 26 °C or annealed to 100 °C.

Dosing with DMMP generates intense peaks in the low wavenumber region (Figure 29c). The peaks at 1315, 1040, and 910 cm^{-1} resulting from, respectively, molecularly adsorbed DMMP, the decomposition product methylphosphonate (MMP), and the secondary decomposition products including methyl phosphonate (MP). The vibrational mode at 1150 cm^{-1} is a combination of $\rho(\text{Zr-OCH}_3)$ and $\nu(\text{P-O}_x)$, both of which result from DMMP decomposition.

The 1150 cm^{-1} band weakens with increased T_{anneal} . Figure 28d shows peak intensity versus time on EZ samples annealed at different temperatures. The DMMP decomposition rates for as synthesized EZ and $100\text{ }^{\circ}\text{C}$ annealed samples are similar, while the rates for the EZ samples annealed at higher temperatures are greatly reduced. The biggest change occurs between $100\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$, consistent with loss of the low binding energy O 1s in XPS (not shown). The decreased growth rate at higher T_{anneal} reflects the conversion of amorphous ZH to amorphous ZrO_2 , and eventually tetragonal ZrO_2 , which has lower DMMP decomposition reactivity than ZH.

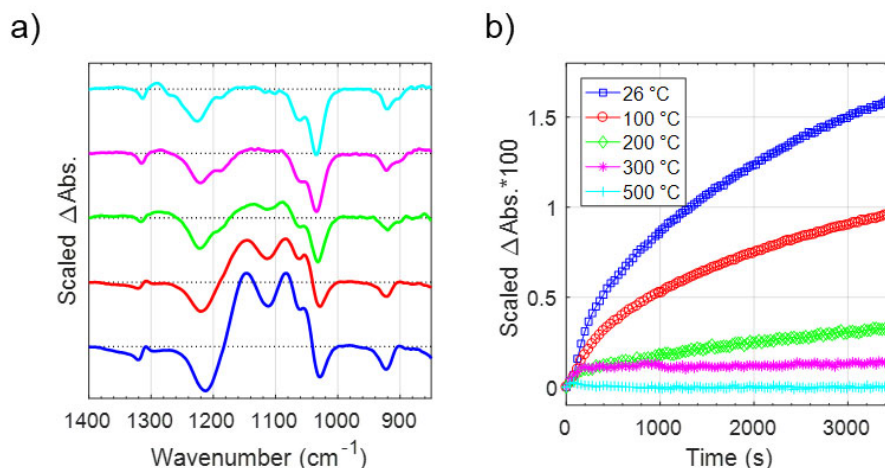


Figure 29. a) ATR difference absorption spectra obtained after purging the DMMP/EZ samples with 25 sccm N_2 for 56 min. b) ATR difference absorption peak intensity at 1150 cm^{-1} as a function of time during the N_2 purging. Color codes are maintained over all panels to represent variously prepared EZ samples; as-scraped (blue) and pre-annealed at $100\text{ }^{\circ}\text{C}$ (red), $200\text{ }^{\circ}\text{C}$ (green), $300\text{ }^{\circ}\text{C}$ (magenta), and $500\text{ }^{\circ}\text{C}$ (cyan). The dotted horizontal lines in a) represent zero difference absorption for each plot. Adapted with permission from ACS Appl. Nano Mater. 2019, 2, 2295–2307. Copyright (2019) American Chemical Society.

Figure 29 shows the ATR difference spectra collected while purging DMMP pre-dosed surfaces with N_2 . Each plot was normalized by the total adsorbed DMMP, based on the 1040 cm^{-1} peak intensity from the final DMMP dose. The difference spectra from the samples were then qualitatively compared. The $\nu(\text{CO})$ peak at $\sim 1040\text{ cm}^{-1}$ decreased because weakly bound molecular DMMP desorbed under N_2 flow. The bands from $1050\text{--}1200\text{ cm}^{-1}$ are attributed to varying amounts of DMMP decomposition products, including O-P-O, P-O_x, and Zr-OCH₃.^[31] To track the decomposition products, the 1150 cm^{-1} peak was monitored while purging with N_2 , as shown in Figure 29b. All the plots showed a decreasing decomposition rate with increased purging time. Furthermore, the decomposition reaction rate decreased as the pre-annealing temperature increased. For EZ pre-annealed at $300\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$, the absorption difference signals saturated, and stopped forming decomposition product within 200 s, consistent with the trend observed while dosing DMMP in previous work.^[1, 9, 57]

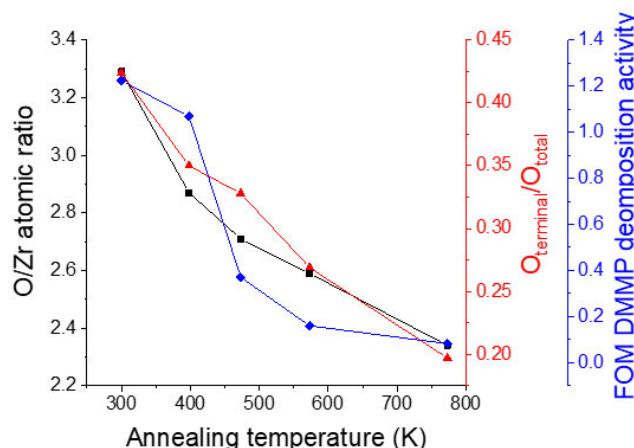


Figure 30. Impact of annealing on EZ. The O/Zr at% ratio came from the XPS elemental analysis using the O 1s and the Zr 3d peaks. The OH(terminal)/O(total) ratio was calculated from the area ratios of the fitted components in the O 1s region. The figure of merit (FOM) of DMMP decomposition activity is defined by the Δ absorption intensity ratio at 2818 cm^{-1} ($\nu(\text{Zr-OCH}_3)$) to at 2856 cm^{-1} ($\nu(\text{P-OCH}_3)$) averaged at 200~1000 seconds.

Table 4. Data from Figure 30 in tabular form. O/Zr atomic percentage ratio and the OH(terminal) / O(total) ratio calculated using the XPS data and the figure of merit (FOM) of the DMMP decomposition activity. The result indicates that 1) EZ loses oxygen, 2) terminal OH decreases, and 3) DMMP decomposition reactivity drops with increased T_{anneal} , which is consistent with the known physicochemical properties of $\text{Zr}(\text{OH})_4$.

Samples	XPS, O/Zr at% ratio	XPS, $\text{OH}_{\text{terminal}} / \text{O}_{\text{total}}$	ATR, FOM of DMMP decomposition activity
Washed EZ	3.29	0.424	1.22
Annealed EZ, 125 °C	2.87	0.350	1.06
Annealed EZ, 200 °C	2.71	0.328	0.37
Annealed EZ, 300 °C	2.59	0.269	0.15
Annealed EZ, 500 °C	2.34	0.197	0.08

4.3.1.1 IMPACT OF COORDINATIVELY UNSTAUATED DEFECT SITES

To understand the impact of Zr_{cus} sites on DMMP decomposition, ZH was dosed with CO, which is known to bind to Zr_{cus} sites.[27, 29] CO was dosed until the ZH surface was saturated with formates, carbonates, and adsorbed CO (not shown). Upon purging the ATR cell with N_2 , some minor losses of the formate/carbonate species were observed; however, most of the adsorbed CO at 2046 cm^{-1} desorbed, implying a weaker and less stable interaction compared to formates and carbonates. The ZH surface was re-saturated with CO. Once re-saturated, DMMP vapor was co-introduced. The adsorbed DMMP rapidly decomposed, producing similar decomposition adsorbates as dry N_2 purged ZH surfaces, implying minimal impact to the ZH surface from the CO dosing (Figure 31).

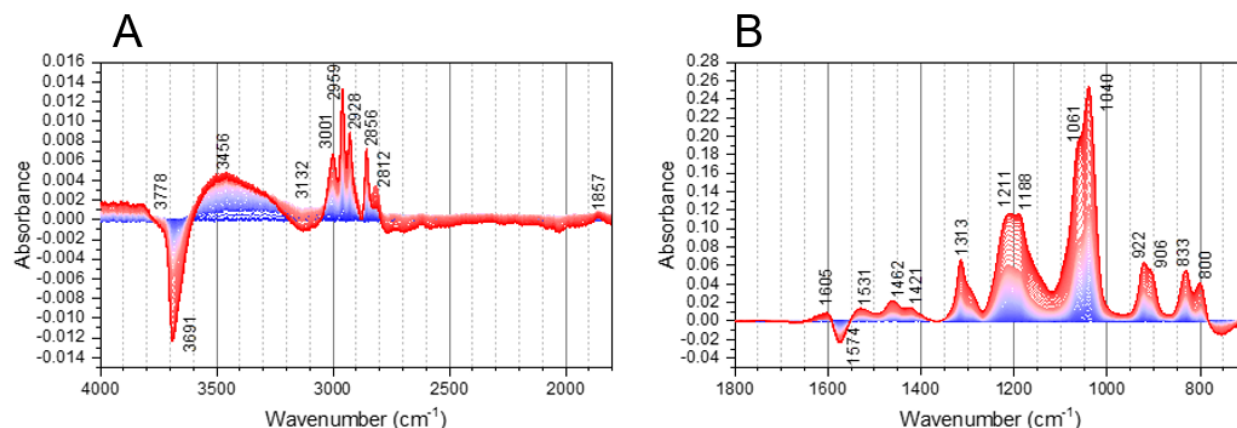


Figure 31. ATR difference spectra after saturating the ZH surface with CO and purging with N₂ (see Figure 18 for details. (A,B) shows CO and DMMP co-dosed after N₂ purge step from Figure 18. DMMP decomposition (formation of asymmetric and symmetric O-P-O stretches) is observed near 1155 and 1090 cm⁻¹.

Upon removing DMMP from the CO gas stream, DMMP continued to decompose as evidenced by the increasing vibrational bands at 1146 and 1094 (Figure 32). Loss of the adsorbed DMMP molecular bands were likely due to a combination of desorption of DMMP from the ZH surface and simultaneous decomposition. Combined with the fact that a large decrease in free hydroxyl species at was also observed at 3700 cm⁻¹ (not shown) indicated that the main reaction pathway is via hydrolysis of DMMP with free hydroxyl species, to form various P-O_x species and methanol. Furthermore, the under-coordinated defect sites on ZH play a minor role in the observed DMMP hydrolysis decomposition mechanism and likely are insignificant in the main decomposition pathway with DMMP.

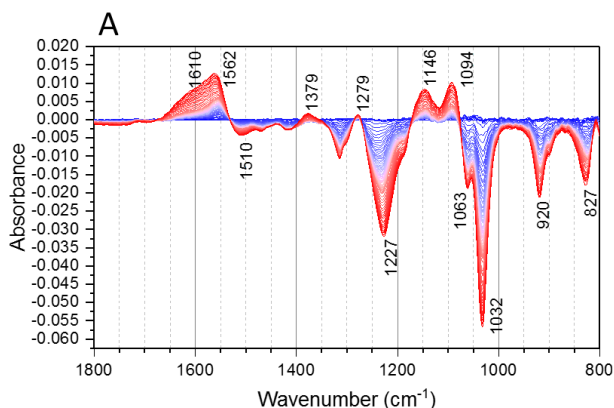


Figure 32. Removal of DMMP from the CO gas stream (10,000 ppm) in the sample chamber showing continued DMMP decomposition and some formate/carbonate formation.

In fact, as shown below, this same hydroxyl-dominated decomposition pathway was observed for several other simulants including CEES (Figure 33), DMCP (Figure 34), and Malathion (Figure 35) and DIFP (Figure 36). Note the loss of free hydroxyls species near 3700 cm⁻¹ in all spectra.

4.3.2 2-Chloroethyl ethyl sulfide (CEES)

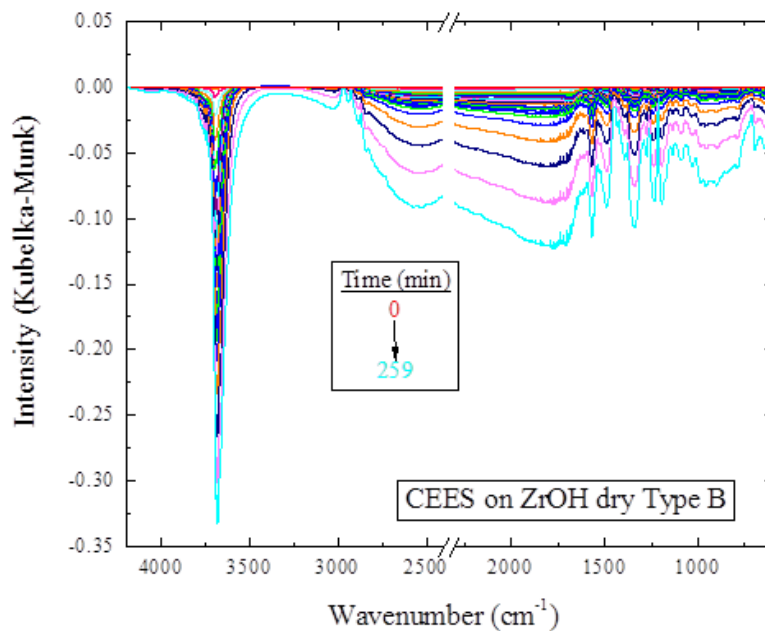


Figure 33. IR difference spectra of dry ZH Type B material exposed to CEES vapor after 0 minutes (red trace) up to 259 minutes (light blue trace).

4.3.3 Dimethyl chlorophosphate (DMCP)

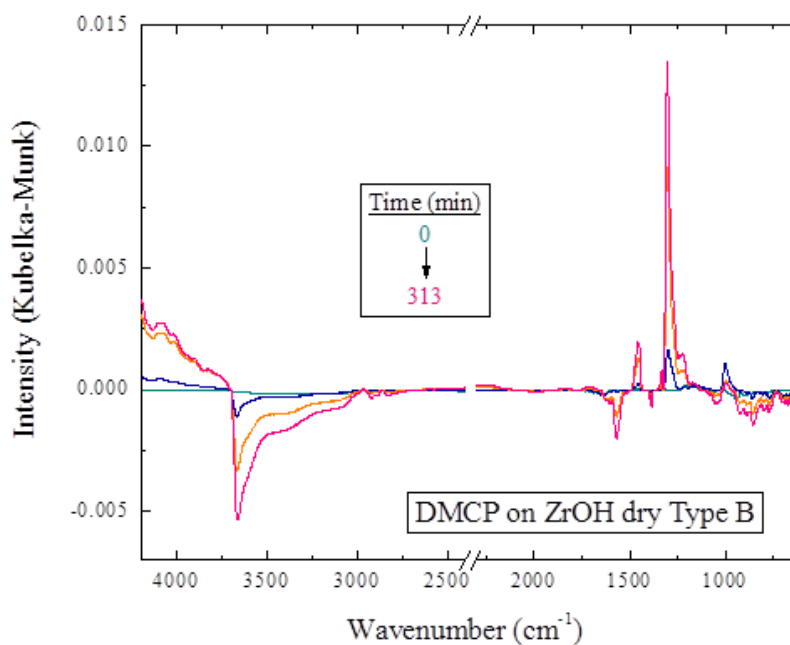


Figure 34. IR difference spectra of dry ZH Type B material exposed to DMCP vapor after 0 minutes (green trace) up to 313 minutes (pink trace).

4.3.4 Malathion

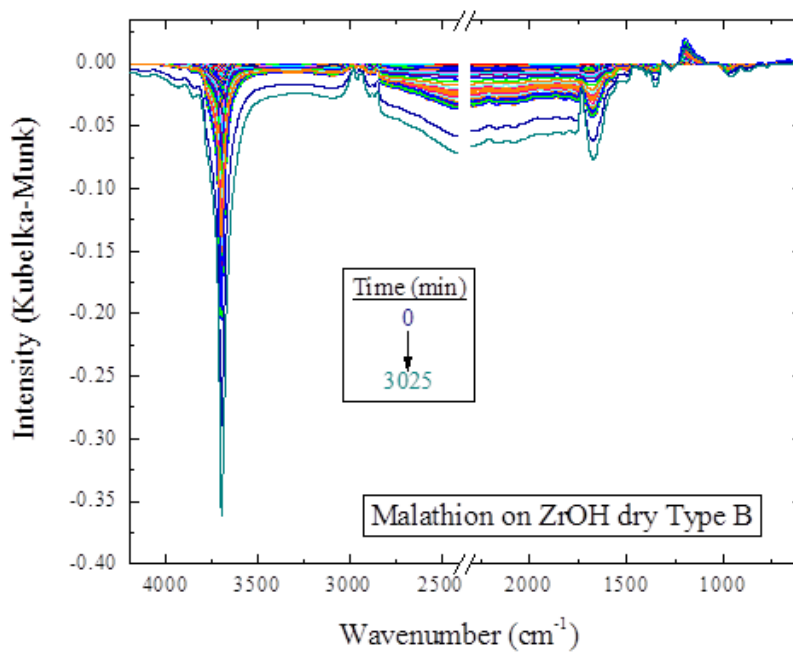


Figure 35. IR difference spectra of dry ZH Type B material exposed to Malathion after 0 minutes (dark blue) up to 3025 minutes (cyan).

4.3.5 Diisopropyl fluorophosphate (DIFP)

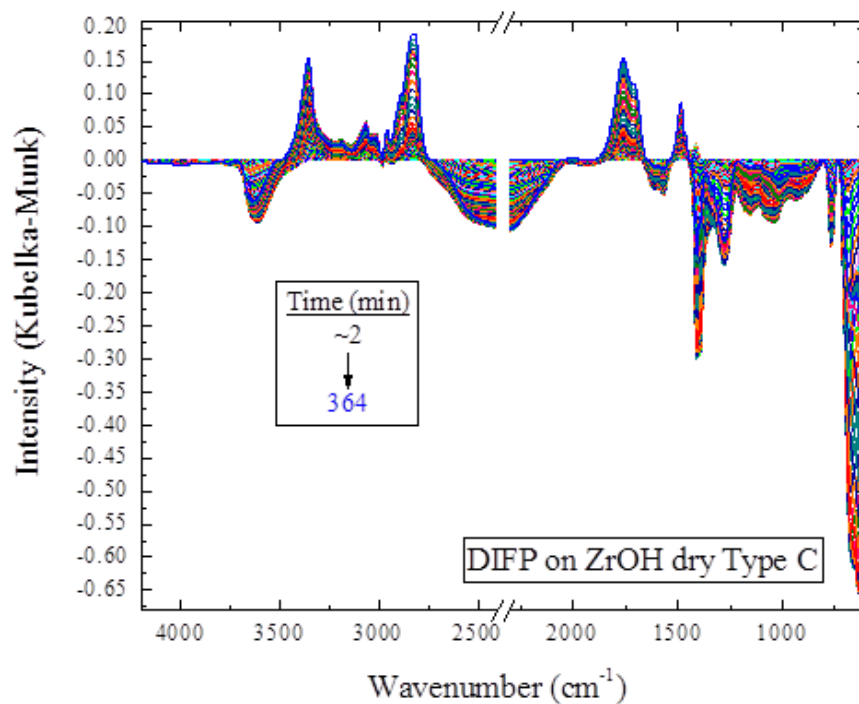


Figure 36. IR difference spectra of dry ZH Type C material exposed to DIFP vapor after 2 minutes (black trace) up to 364 minutes (blue trace).

A comparison of the chemical structures of the simulants dosed in this program are shown below (Figure 37).

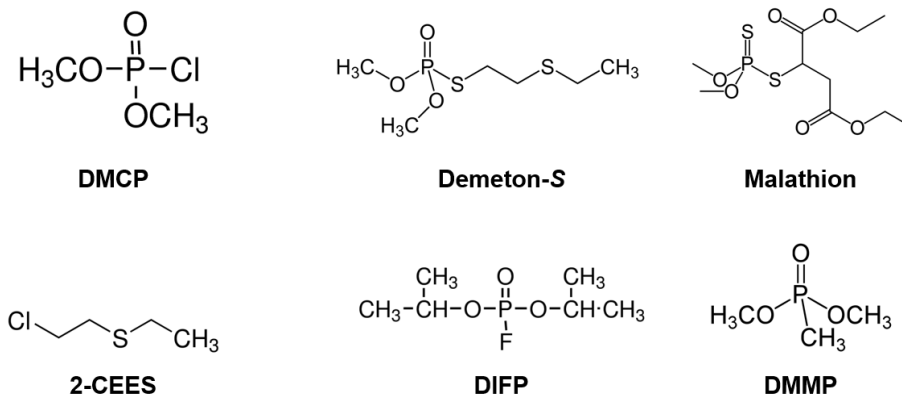


Figure 37. Common CWA simulant compounds.

Several experiments were run to determine if battlefield/atmospheric pollutants impact adsorption of DIFP and also if simulant contaminated ZH resisted ambient contaminants (CO_2 and SO_2). Experiments were performed by exposing equilibrated ZH-B/C sequentially to pollutant, followed by a purge, and then to simulant (Figure 38, Figure 39); or the same experiment in reverse order (Figure 40, Figure 41). Qualitatively, CO_2 and SO_2 do not appear to completely poison the ZH surface. In the converse case (DIFP followed by pollutant exposure), the simulant consumed active sites on ZH and dramatically impacted both the sorption of CO_2 and SO_2 contaminants. Little, if any, contaminants formed adsorbates with the simulant-dosed surface.

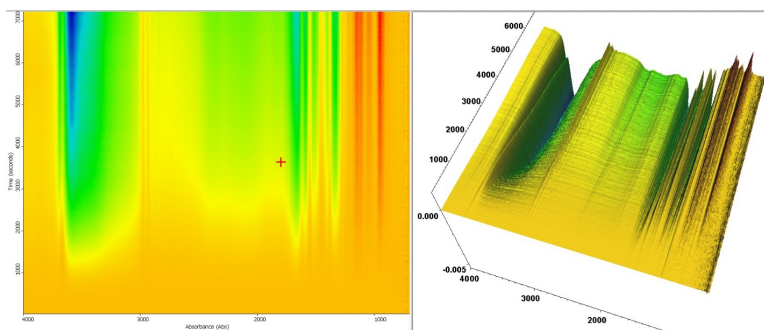


Figure 38. IR difference spectra of ZH-B saturated under SO_2 followed by DIFP exposure.

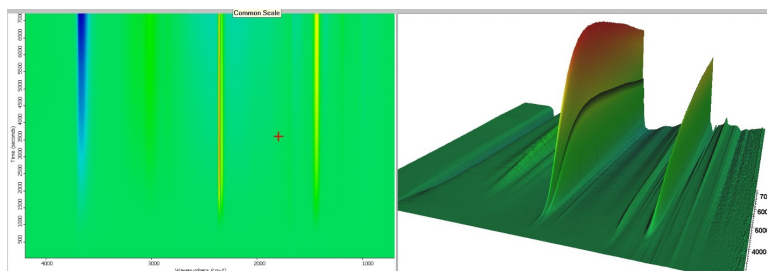


Figure 39. IR difference spectra of ZH under CO₂ prior to DIFP exposure.

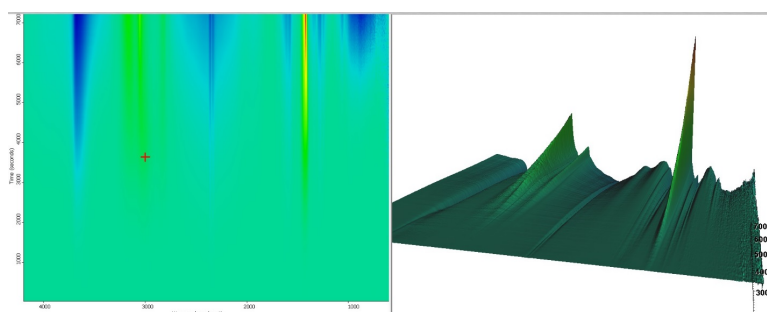


Figure 40. IR difference spectra of CO₂ dosed on DIFP-contaminated ZH.

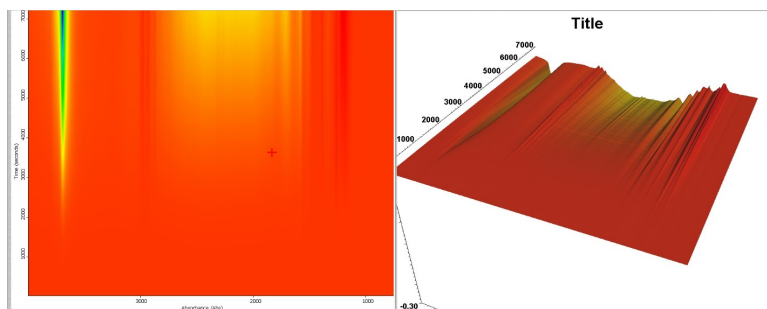


Figure 41. IR difference spectra of SO₂ dosed on DIFP-contaminated ZH.

For reference, a list of tentatively assigned peaks can be found for DIFP dosed on ZH in Table 5 below.

Table 5. IR Bands and Assignments for ZH exposed to DIFP Simulant

DIFP on ZH-B	DIFP on ZH-C	Assignments
3679 loss		$\nu(\text{OH})$ from Zr-OH
	3640 loss	$\nu(\text{OH})$ from Zr-OH and $\nu(\text{H}_2\text{O})$
3604 loss		$\nu(\text{H}_2\text{O})$
3307	3358	$\nu(\text{OH})$ from $\text{Zr}^{3+}-(\text{H}_2\text{O})$? / $\nu(\text{OH})$ from formaldehyde?
3151	3186	
3055	3066	
	3016	$\nu_a(\text{CH}_3)$ on ZrO_2 ?
2993		$\nu_a(\text{CH}_3)$

2950	2956	$\nu_s(\text{CH}_3)$
2876	2890	$\nu(\text{CH})$
2835 weak	2835-2819 sharp	$\nu(\text{CH})$ from aldehyde likely formaldehyde
1763 weak	1763 sharp	$\nu(\text{C=O})$ from aldehyde
1697 weak	1706 sharp	$\nu(\text{C=O})$ from aldehyde likely formaldehyde
	1486	$\delta(\text{CH})$ from aldehyde likely formaldehyde
	1465	$\delta(\text{CH})$ from aldehyde
1453 shoulder		$\delta_a(\text{CH}_3)$
1423 sharp		$\delta_a(\text{CH}_3)$
	1408 loss	$\nu(\text{COO}^-)$?
	1392 loss	
1388		$\delta_s(\text{CH}_3)$
1380		$\delta_s(\text{CH}_3)$
	1378 loss	
1313-1275		$\nu(\text{P=O})$
	1276 loss	$\delta(\text{OH})$ from Zr-OH
1180		$\delta(\text{CH}_3)$ wag
1147		$\nu_a(\text{C-C-C})$
1110		$\nu(\text{C-O})$
1028		$\nu(\text{P-O-C})$

4.4 Live Agent Decomposition

4.4.1 XPS

Clean and pre-dosed ZH were exposed to GB vapor and subsequently analyzed using XPS (Figure 42). High-resolution spectra were deconvoluted into components for comparison. The Zr 3d energy region of clean ZH showed one Zr 3d doublet with $3d_{5/2}$ and $3d_{3/2}$ components centered at 182.4 and 184.8 eV, respectively. Additionally, the P 2p and F 1s regions showed no measurable phosphorus or fluorine contamination after CO_2 , SO_2 , and NO_2 pre-dosing, exemplifying an initially clean ZH surface prior to GB dosing.

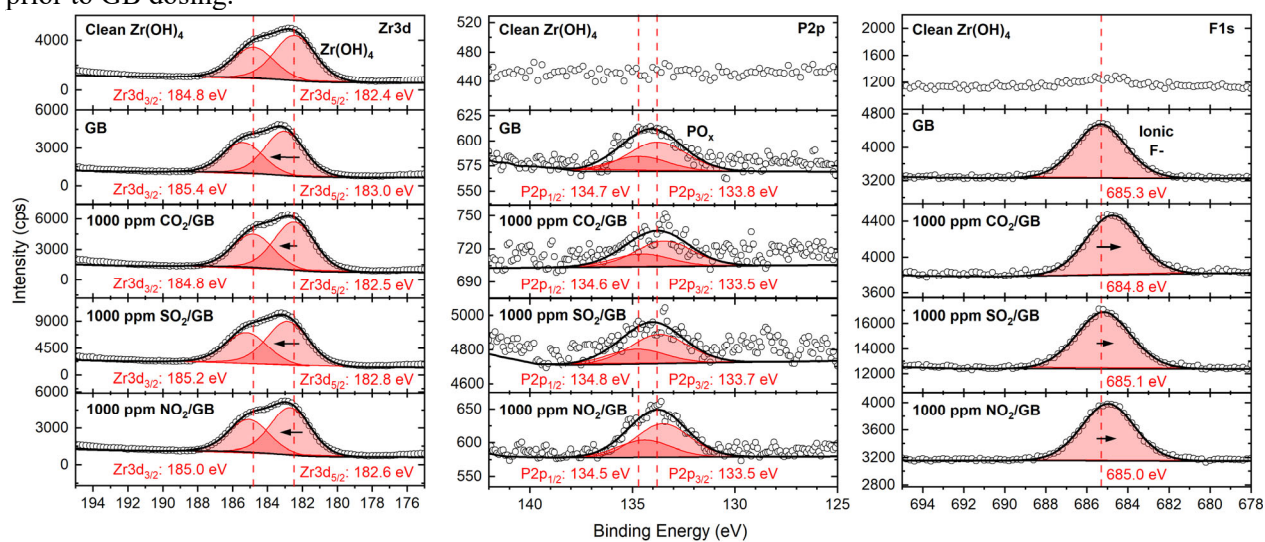


Figure 42. XPS spectra of GB dosed on clean and CO_2 , SO_2 , and NO_2 pre-dosed ZH.

Upon dosing GB, the Zr 3d peaks for all ZH samples were shifted to higher binding energy compared to pristine ZH. The largest shift (0.6 eV) occurred for GB dosed on clean ZH, followed by SO₂ pre-dosed ZH (0.4 eV). CO₂ and NO₂ pre-dosed ZH both showed minor shifts (0.1 and 0.2 eV, respectively) compared to clean ZH. Similar shifts in the Zr 3d binding energy were observed for clean ZH dosed with just the contaminants, suggesting minimal interaction of GB directly with Zr sites, possibly due to some degree of site blocking from pre-dosed adsorbates. The observed Zr 3d shift to higher binding energy is therefore attributed primarily to the contaminant interaction with available Zr sites resulting in withdrawal of Zr 3d valence charge; whereas, clean ZH samples showed the largest shift of the Zr 3d photoelectron peak after dosing GB, probably due to having unimpeded access to Zr sites and thus forming strongly electron withdrawing ionic fluoride species upon GB decomposition.[44]

P 2p photoelectron peaks were detected for all GB-dosed samples, indicating GB binds to clean and contaminated ZH. Previous work with the GB simulant, dimethyl methylphosphonate (DMMP) showed a binding energy of 134.0 eV for the P 2p_{3/2} peak of DMMP adsorbed on an unreacted graphite surface.[58] DMMP decomposition on a reactive surface formed a reduced phosphorous chemical state, identified by a shift of the 2p_{3/2} peak to 133.5 eV. With heating, this peak returned to 134.0 eV, signifying additional destruction via oxidation to PO_x species. GB decomposition on metal (hydr)oxide surfaces is also expected to occur via a similar hydrolysis mechanism, and will likely form a step-wise oxidation from adsorbed GB to isopropyl methylphosphonic acid (IMPA), methylphosphonic acid (MPA), and possibly phosphonic acid (PA) or PO_x species.[59] Thus, a similar trend of binding energy shifts of P 2p peaks during GB decomposition is also expected.

Deconvoluting the P 2p regions of GB-dosed ZH samples identified only a single phosphorous component. GB dosed on clean ZH had a 2p_{3/2} binding energy centered at 133.8 eV, which is similar to reported values for decomposed GB on reactive zirconium-based sorbents and thus indicative of GB decomposition on ZH.[44] GB dosing on CO₂ and NO₂ pre-dosed samples showed the greatest shift to lower energy by 0.3 eV, suggesting these samples interact with GB, but hydrolyze GB slower than clean ZH. SO₂ pre-dosed ZH shifted the least (0.1 eV), suggesting a potentially different reaction mechanism compared to CO₂ and NO₂ pre-dosed samples.

F 1s photoelectron peaks were best fit with a single component, indicating only one detectable fluorine species on all GB-dosed samples. Organic and inorganic fluorine compounds are easily distinguished in XPS by their differences in binding energy. Inorganic or metal-fluoride compounds such as ZrF₄ typically have lower binding energy near 685 eV,[60] whereas organic fluorine compounds often have binding energies above 686 eV.[61] More specifically, DIFP, a common simulant molecule for sarin, has an F 1s photoelectron peak at 688.5 eV, which provides excellent separation for distinguishing between adsorbed and decomposed GB chemical states. The absence of organic fluorine photoelectron peaks and the presence of a single metal fluoride peak near 685 eV provides clear evidence of sarin hydrolysis on both clean and contaminated ZH surfaces. Furthermore, GB dosed on CO₂, SO₂, and NO₂ pre-dosed ZH showed decreasing F 1s peak areas, indicative of less surface-bound fluorine for all contaminant-dosed samples compared to clean ZH. Modulated surface interactions for contaminated ZH surfaces dosed with GB are likely, as indicated by various binding energy shifts to lower energy in the F 1s region. Despite possibly having less adsorbed/decomposed GB (as indicated by the P 2p peak area in the XPS spectra), no evidence of unreacted or molecularly bound GB was observed.

4.4.2 DRIFTS

Modifications to GB decomposition on clean and contaminated ZH was clearly observed in the obtained DRIFT spectra (Figure 43). Clean, CO₂-, and NO₂-dosed samples simultaneously lost tri-bridged, bi-bridged, and monodentate hydroxyls at approximately 3698, 3754, and 3777 cm⁻¹,

respectively, in addition to the hydroxyls lost in the pre-dosing steps. SO₂-dosed ZH only showed significant loss of the tri-bridged hydroxyl at 3691 cm⁻¹ during GB dosing, confirming the vast majority of available bi-bridging and monodentate hydroxyls sites were poisoned during SO₂ pre-dosing. Thus, GB decomposition on SO₂ pre-dosed ZH likely proceeds by a modified reaction pathway due to the preferential removal of bi-bridged and monodentate hydroxyl active sites. DFT calculations herein also support these observations by showing SO₂ directly forms a strong bond with monodentate hydroxyls.

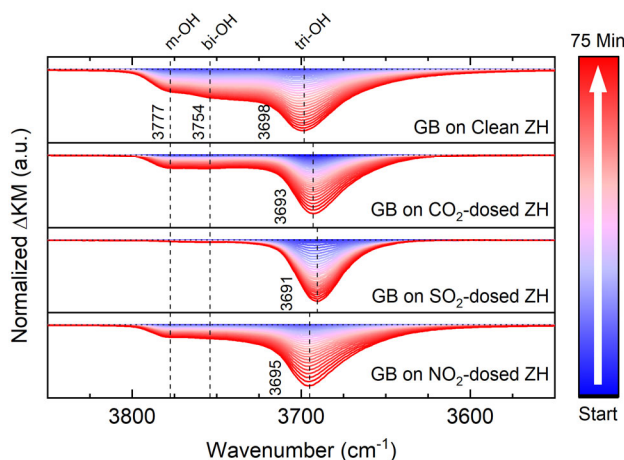


Figure 43. Time-resolved DRIFT spectra of GB dosed on clean, CO₂, SO₂, and NO₂ pre-dosed ZH in the hydroxyl region. Note minimal loss of monodentate and bi-bridging hydroxyl species for SO₂ pre-dosed ZH.

The fingerprint region in the DRIFTS spectra provides evidence for both molecular GB adsorption and decomposition on ZH depending on pre-dosing condition (Figure 44). This is contrary to the XPS data – likely because the XPS data was collected after DRIFTS, and the GB is reacted on the ZH surface longer. During GB dosing, a broad decrease near 3044 and 1636 cm⁻¹ shows disruption of ZH hydrogen bonding network possibly due to surface water displacement or possibly water consumption during GB decomposition on all ZH samples. DFT calculations (discussed later) show water has a lower binding energy than GB for the ZH surface and should not impede surface decomposition.

Intact GB vibrational modes were identified by a reference GB spectrum obtained experimentally using transmission FTIR spectroscopy from the literature.[62] Vibrational modes at 2989, 2948, and 2888 cm⁻¹ correspond to $\nu_a(\text{CH}_3\text{C})$, $\nu_s(\text{CH}_3\text{C})$, and $\nu(\text{CH})$ of GB, respectively. The bending vibrational modes of the isopropyl moiety of GB ($\delta_s(\text{CH}_3\text{C})$) were observed at 1393 and 1388 cm⁻¹. The rotational modes ($\rho(\text{CH}_3\text{-C})$) of the GB isopropyl group were detected at 1179, 1146, and 1112 cm⁻¹. [63] These modes are expected to shift upon adsorption to a surface.

The $\nu(\text{P=O})$ mode of GB is sensitive to the local environment and readily shifts with environmental changes. Shifts in $\nu(\text{P=O})$ compared to the gas phase (1303 cm⁻¹) indicate adsorption of GB on the ZH surface, likely through the $\nu(\text{P=O})$ bond. Phosphoryl vibrational modes were observed at 1246 and 1228 cm⁻¹, which correspond to two unique GB adsorption sites or configurations on ZH. The formation of these modes with the concomitant loss of monodentate (3777 cm⁻¹), bi- (3754 cm⁻¹), and tri-bridged (3698 cm⁻¹) hydroxyls suggests that GB adsorption and decomposition on ZH occurred via surface hydroxyls. Complementary adsorption and decomposition behavior has been reported by Jeon, et al. showing a loss of DMMP decomposition after removal of ZH hydroxyl species by heat treatment.[13] The vibrational mode near 1183 cm⁻¹ ($\rho(\text{CH}_3\text{-C})$) was assigned to adsorbed GB according to the collected GB reference spectrum. The vibrational mode at 1074 cm⁻¹ has been previously reported as adsorbed

GB,[64] and also exhibits similar blue-shifting behavior with time as other GB vibrational modes. As such, it is tentatively assigned to a $\rho(\text{CH}_3\text{-C})$ mode of adsorbed GB.

GB decomposition to IMPA and MPA increased with time for all ZH samples and was most apparent on clean and CO_2 pre-dosed ZH. Asymmetric ($\nu_a(\text{OPO})$) and symmetric ($\nu_s(\text{OPO})$) stretching modes of bridged IMPA and MPA decomposition products were observed near 1170 and 1079 cm^{-1} . IMPA also has three $\rho(\text{CH}_3\text{-C})$ vibrational modes at 1177, 1140, and 1085 cm^{-1} . [64] A blue-shift over time (arrows in Figure 44) indicates secondary decomposition of adsorbed IMPA to MPA. Reports of GB decomposition on similar adsorbates such as TiO_2 also show a stepwise hydrolysis from GB to IMPA, MPA, and ultimately to PA. [64]

SO_2 and NO_2 pre-dosed ZH showed the least amount of bound GB hydrolysis products as determined by DRIFTS. Decomposition products at 1170, 1142, and 1130 cm^{-1} were formed at the earliest time points and transition primarily to adsorbed intact GB at 1246, 1228, and 1183 cm^{-1} . SO_2 pre-dosed ZH samples also showed a small band near 1272 cm^{-1} that is likely “liquid-like” multilayers of GB suggesting that GB accumulates on the ZH surface with prolonged exposure. However, no evidence of adsorbed molecular GB was observed by ex situ XPS analysis, suggesting either any intact GB observed with DRIFTS desorbs from the surface under high vacuum or decomposes before XPS data can be collected. [65] These data suggest contaminated ZH surfaces potentially retain more adsorbed GB compared to clean ZH.

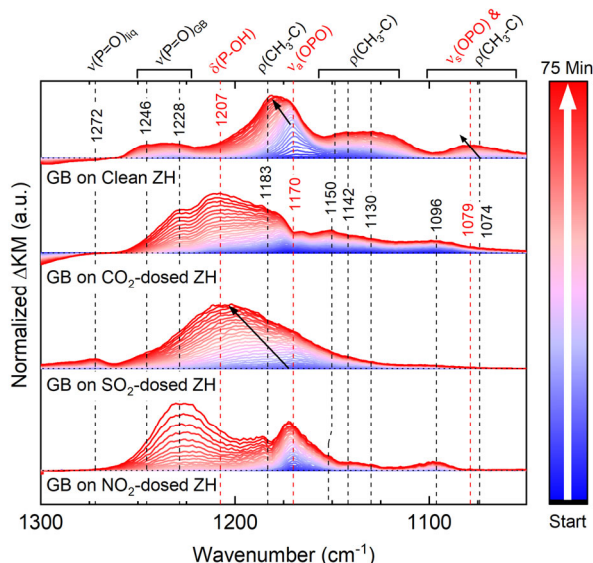


Figure 44. Normalized time resolved DRIFT spectra of GB dosed on pristine, CO_2 , SO_2 , and NO_2 pre-dosed ZH. Changes to bound surface adsorbates are monitored over 75 minutes. Black arrows indicate blue-shifting vibrational modes with time. Red and black dashed vertical lines show uniquely identifiable decomposition products and adsorbed GB, respectively.

Table 6. Vibrational modes of molecular GB and common decomposition products identified with DRIFTS during GB dosing on ZH.

Adsorbate	Vibrational Mode	This Work (cm^{-1})	TiO_2 (cm^{-1})
GB	$\delta_s(\text{P-CH}_3)$	1325	1320 ^a
	$\nu(\text{P=O})_{\text{liq}}$	1272	1277 ^a
	$\nu(\text{P=O})_{\text{ads}}$	1246/1228	1252/1210 ^a
	$\rho(\text{CH}_3\text{C})$	1183	1178 ^a
	$\rho(\text{CH}_3\text{-C})$	1142	1142 ^a

	$\rho(\text{CH}_3\text{-C})$	1074	1077 ^a
IMPA	$\delta_s(\text{P-CH}_3)$	1313	1313 ^a
	$\nu(\text{P=O})$	n.o. ⁱ	1215 ^a
	$\nu_a(\text{OPO})$	1170	n.o. ⁱ
	$\rho(\text{CH}_3\text{C})$	1170	1177 ^a
	$\rho(\text{CH}_3\text{C})$	1142	1140 ^a
	$\rho(\text{CH}_3\text{C})$ & $\nu_s(\text{OPO})$	1079	1077 ^a
MPA	$\delta_s(\text{P-CH}_3)$	1321	1316 ^a
	$\delta(\text{P-OH})$	1207	1206 ^a
	$\nu_a(\text{OPO})$	1170	n.o. ⁱ
	$\rho(\text{CH}_3)$	1130	1119 ^a
	$\nu_s(\text{OPO})$	1079	1079 ^a
PA	$\delta(\text{P-OH})$	1207	1210 ^a
	$\nu(\text{OPO})$	n.o. ⁱ	1086, 1055 ^a

^aRef [64]. ⁱNot observed.

GB dosed on clean ZH showed immediate hydrolysis of GB to IMPA indicated by the increasing $\delta_s(\text{P-CH}_3)_{\text{IMPA}}$ mode at 1313 cm^{-1} (Figure 45). No intact GB (1325 cm^{-1}) was detected on clean ZH during GB dosing. Over time, hydrolysis of IMPA to form MPA and possibly PA was identified by characteristic vibrational modes near 1207 and 1321 cm^{-1} , corresponding to the $\delta(\text{P-OH})$ and $\nu(\text{P-CH}_3)$ modes of MPA and PA, which increase with time on all samples.[64] Other GB simulants such as dimethyl chlorophosphate (DMCP) on metal (hydr)oxide surfaces report similar reactivity and mechanistic observations.

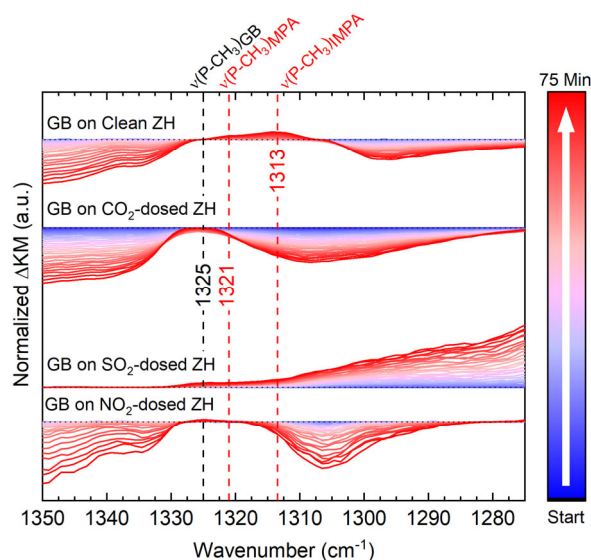


Figure 45. DRIFTS spectra of GB dosing on clean, CO_2 , SO_2 , and NO_2 pre-dosed ZH. Red modes denote decomposition products.

GB dosed on CO₂, SO₂, and NO₂ pre-dosed ZH showed a small increase in adsorbed GB for all dosing experiments near 1325 cm⁻¹, supporting a modified decomposition mechanism and/or reduced kinetics for contaminated ZH. To determine the impact of pre-dosed contaminants on GB decomposition, an elementary kinetic analysis was performed. Figure 46 shows time-resolved DRIFTS intensity of the $\nu_a(\text{OPO})$ decomposition mode (1170 cm⁻¹) over 75 minutes of GB dosing. Notably, caution should be exercised when comparing apparent rate constants obtained in this work to other systems due to the challenges with establishing similar initial ZH surface conditions, as water removal for ZH is limited under ambient pressure.

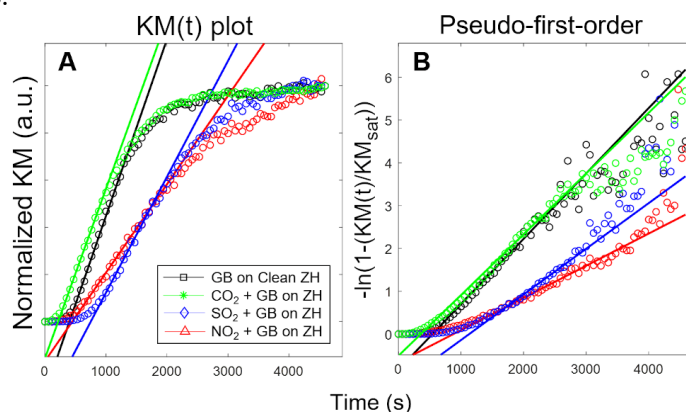


Figure 46. Normalized diffuse reflectance infrared Fourier Transform (DRIFT) difference spectra of GB dosed onto clean and contaminated ZH over 75 min in two spectral regions. (A) Normalized KM(t) plots of the GB decomposition band (1170 cm⁻¹, $\nu_a(\text{OPO})$) over 75 min of GB dosing on clean and contaminated ZH. (B) Linear regression of the KM(t) plots using the pseudo-first order equation. Circles and lines represent data and least-square fits, respectively.

Given these considerations, the obtained apparent rate constants for the hydrolysis of GB and formation of $\nu_a(\text{OPO})$ on clean, CO₂, SO₂, and NO₂ pre-dosed ZH under dry conditions are 1.5×10^{-3} , 1.4×10^{-3} , 1.1×10^{-3} , and $7.5 \times 10^{-4} \text{ s}^{-1}$, respectively. These data suggest that clean and CO₂-dosed ZH provide similar GB hydrolysis activity, whereas SO₂- and NO₂-dosed ZH both show reduced rates of GB decomposition. GB decomposition rate decreased most significantly after NO₂ dosing according to the obtained rate constants. CO₂-dosed ZH showed minimal impact to the decomposition rate of GB. These results are unsurprising given that ZH has been previously shown to effectively hydrolyzes CWAs and CWA simulants under atmospheric conditions (e.g. under 400 ppm CO₂).

The initial GB decomposition rate on NO₂-dosed ZH is comparable to reported rates for the zirconium-based metal organic frameworks MOF-808 that was dosed with a sarin simulant, DMMP.[66] Moreover, clean, CO₂, and SO₂ pre-dosed ZH decomposed sarin more rapidly than DMMP dosed on MOF-808.[66]

4.4.3 Microbreakthrough Analysis

Uptake of SO₂ and NO₂ gases dosed over ZH were determined by calculating the increase in mass after saturating a known amount ZH. Quantification of CO₂ uptake capacity on ZH was not performed due to a lack of control over the native carbonates on ZH from atmospheric CO₂. GB effluent concentration was monitored until saturation of GB was observed, after which the sample was purged with inert gas. Capacity measurements are provided in Table 7 below.

Table 7. GB breakthrough data showing total GB loading on clean and contaminated ZH samples when GB breakthrough occurred.

Clean ZH		CO ₂ -Dosed ZH		SO ₂ -Dosed ZH		NO ₂ -Dosed ZH	
	GB		GB		GB		GB
Trial	Loading (mol/kg)	Trial	Loading (mol/kg)	Trial	Loading (mol/kg)	Trial	Loading (mol/kg)
1	2.0	1	1.8	1	1.8	1	3.3 [†]
2	1.5	2	1.4	2	1.5	2	1.6
3	1.2	3	1.8	3	1.3	3	1.5
4	1.4	4	1.1	4	-	4	1.3
5	1.5	5	1.3	5	-	5	-
Average	1.5	Average	1.5	Average	1.5	Average	1.5
Standard	0.3	Standard	0.3	Standard	0.2	Standard	0.1
Deviation		Deviation		Deviation		Deviation	

[†] Not used in average and standard deviation calculation due to being a statistical outlier with 95% confidence according to a Dixon Q-Test.[67]

SO₂ sorption on ZH showed significantly reduced capacity compared to NO₂. Total gas loading for SO₂ and NO₂ at ambient pressure was 1.4 and 10.0 mol/kg ZH, respectively. This 7-fold increase in capacity was not observed in the DFT calculations and may be due to differences in the inherent behavior of the gases with the ZH surface. For example, DFT shows NO₂ does not directly interact with the ZH surface and must either dimerize or react with co-adsorbed water or hydroxyls to form HONO or HNO₃. This could explain why a binding energy shift to lower energy wasn't observed after NO₂ pre-dosing in the XPS data (less disruption to the chemical state of Zr, compared to other environmental contaminants), and may also provide an explanation for the observed capacity differences between SO₂ and NO₂ on ZH. Additionally, NO₂ can react on the surface by oxidizing adsorbates, such as nitrites to nitrates; however, this is more commonly observed in mixed oxide systems containing cerium and zirconium.[68]

Experimentally, differences in the relative loss of hydroxyl species during contaminant dosing may influence the ultimate capacity of ZH. This also has possible implications in preferred binding sites for SO₂ vs. NO₂ pre-dosed ZH.

Higher NO₂ capacity on ZH may suggest more accessible free hydroxyls or less specific hydroxyl sites for NO₂ compared to SO₂. Additionally, DFT calculations from this program and previous reports show SO₂ primarily binds to two adjacent hydroxyl sites to form a stable adsorbate on metal (hydr)oxide surfaces, whereas NO₂ can form both a monodentate and chelated adsorbates that only require a single bonding site. Furthermore, the chelated adsorbate was the lowest enthalpy binding product, further supporting this theory.

GB uptake capacity on clean and CO₂, SO₂, and NO₂ pre-dosed ZH was statistically similar across all samples tested, demonstrating that GB breakthrough was independent of CO₂, SO₂, or NO₂ adsorbates (Figure 47). However, DRIFTS data suggest mechanistic differences for GB decomposition on ZH depending on the present adsorbates. *Despite having modified surface reactivity due to adsorbates on*

the ZH powders, GB is effectively removed from a gas stream and sequestered on the ZH surface. Thus, ZH remains an effective sorbent for GB and likely other phosphonate-based CWAs with a CO_2 -, SO_2 -, or NO_2 -contaminated surface.

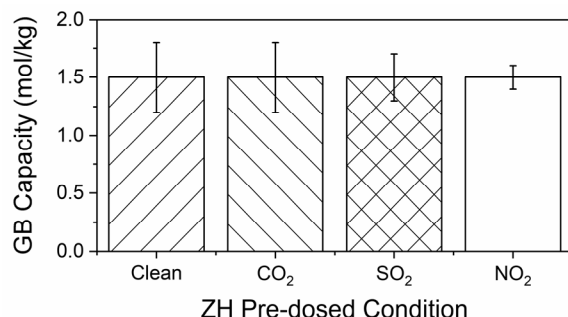


Figure 47. ZH capacity data for GB dosed on clean and contaminated ZH samples.

Transmission FTIR spectroscopy collected during GB breakthrough experiments for SO_2 and NO_2 pre-dosed ZH samples identified additional vibrational modes in the effluent gas at 1250, 1150, 1080, and 980 cm^{-1} (Figure 48). Small, volatile molecules, such as isopropanol and acetone have been reported in decomposition reactions with GB on metal oxide surfaces.[64] The vibrational mode at 1250 cm^{-1} matches well for the $\nu(\text{C}=\text{C})$ present in both isopropanol and acetone. However, the $\nu(\text{C}=\text{O})$ vibration of acetone near 1700 cm^{-1} was not observed in any of the effluent streams. Other vibrational modes typical of isopropanol overlap with GB modes and are difficult to differentiate. Alternatively, the vibrational modes near 1251, 1218, 1144, 1079, and 977 cm^{-1} closely match the $\nu(\text{P}=\text{O})_{\text{ads}}$ or possibly $\delta(\text{P}-\text{OH})$, $\nu(\text{CH}_3\text{C})$, $\nu_s(\text{OPO})$, and $\nu_a(\text{C}-\text{O}(\text{P}))$ vibrational modes of IMPA and MPA/PA decomposition species.[64] Observing potential GB decomposition products desorbing from the ZH surface presents a unique finding that indicates the possibility of modifying the ZH surface with atmospheric gases to minimize highly-stable “OPO” phosphonate decomposition products, while promoting less stable and non-toxic adsorbates that can desorb from the ZH surface. *This unprecedented strategy may enable a novel mechanism to regenerate the ZH surface*

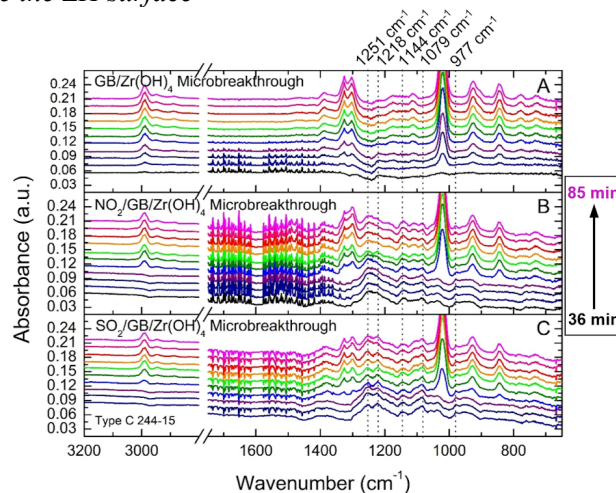


Figure 48. Time-resolved FTIR spectra of the effluent collected over 75 min during GB microbreakthrough testing with (A) clean ZH, (B) NO₂, and (C) SO₂ pre-dosed ZH. Dashed vertical lines indicate unique vibrational modes not observed when dosing GB through clean ZH.

Kinetic studies of VX decomposition on clean and CO₂-, SO₂-, and NO₂-predosed ZH was performed using P³¹ NMR under 50% RH with 4.6 kHz magic angle spinning. VX and EMPA decomposition products peak areas were integrated to determine the impact of atmospheric contaminants on VX (Figure 49).

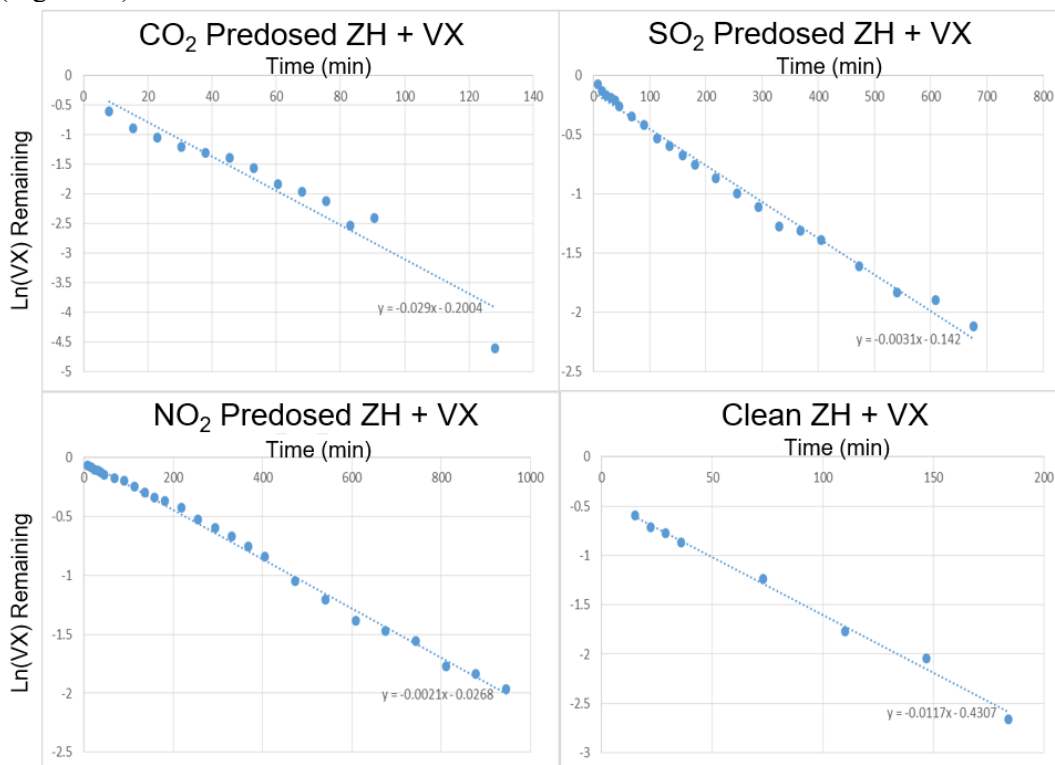


Figure 49. Ln(VX) remaining over time. Data points obtained from deconvoluted peak areas of the P³¹ NMR spectra of VX dosed onto ZH over time.

A table containing calculated pseudo first-order rate constants and half-lives determined from plotting ln(VX remaining) vs. time. The SO₂- and NO₂-predosed ZH both approximately linear through time 0, whereas the CO₂-predosed and clean ZH samples are the most nonlinear at the earliest time points (Figure 49). Please note that the 0 time point was removed from the linear fits shown in these datasets. This suggests that there are likely two decomposition reactions occurring on the clean and CO₂-predosed samples (one fast in the very beginning and the other slow thereafter).

Table 8. Calculated first order reaction kinetics determined by fitting a linear line to the ln of the remaining VX on ZH over time.

VX	ZH (mg)	VX (μL)	k (min ⁻¹)	t _{1/2} (min)	Product
Clean ZH	160	16	0.012	59	Mostly EMPA

CO ₂ -Predosed ZH	103	10	0.029	24	Mostly EMPA
SO ₂ -Predosed ZH	150	15	0.0031	224	Mostly EMPA
NO ₂ -Predosed ZH	160	16	0.0021	330	Mostly EMPA

Because SO₂ and NO₂ preferentially react with the terminal hydroxyls (as shown in the previous DRIFTS experiments), it is an obvious conclusion that the reaction rates would therefore be reduced. In fact, by NMR, the NO₂- and SO₂-predosed ZH showed a 20-fold and 30-fold reduction in rate after predosing ZH until saturation with NO₂ and SO₂ before dosing VX. This would suggest that the ZH reaction sites responsible for the fastest CWA degradation are the terminal free hydroxyls.

Finally, HD dosing on pristine ZH shows similar hydroxyl losses, as well as loss of vibrational modes that closely match surface bound carbonates also suggesting that ZH free hydroxyls species are also responsible for the decontamination of HD (Figure 50).

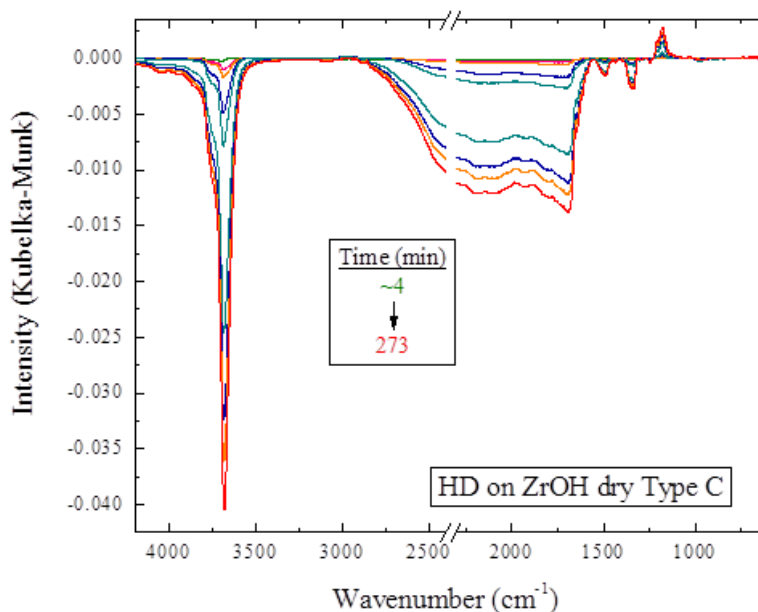


Figure 50. IR difference spectra of dry ZH exposed to HD after 4 minutes (green trace) up to 273 minutes (red trace) showing substantial loss of free hydroxyls around 3700 cm⁻¹.

5. RESULTS AND DISCUSSION - THEORETICAL

5.1 Structural Calculations

5.1.1 Theory-Experiment Comparisons

The relative concentration of bridging and terminal hydroxyls is critical in establishing the chemical properties of ZH. This stems from the fact that bridging and terminal hydroxyls are acidic and basic, respectively [45]. This was observed theoretically by calculating the energy needed to deprotonate

an H^+ away from the hydroxyl species. Bridging hydroxyls had a binding energy of 0.51 eV lower than the terminal OH.

Experimentally, the (bridging)/(terminal) concentration ratio depends on thermal history [3,4]. Annealing *in vacuo* at a low temperature (~ 75 – 100 °C) removes mostly physisorbed H_2O from atmospheric exposure. At higher temperature, up to ~ 175 – 200 °C, bridging and terminal hydroxyls are eliminated *via* condensation to form H_2O . Still-higher temperatures remove H from the remaining bridging hydroxyls, which leads to a conversion to tetragonal ZrO_2 and the loss of ZH functionality. The AIMD simulations based on the 2-layer model for amorphous ZH correctly reproduced the condensation of hydroxyl groups to yield increasing amounts of H_2O with increasing temperature. It is found that this occurred through an acid-base reaction of the form $\text{Zr-O(H)-Zr} + \text{HO-Zr} \rightarrow \text{Zr-O-Zr} + \text{H}_2\text{O-Zr}$ with most of the H_2O desorbing from the surface to leave a Zr_{cus} defect sites. Here the acidic bridging hydroxyl transfers a proton to the basic terminal hydroxyl. This was the only OH-elimination process observed in AIMD up to ~ 300 °C. The (bridging)/(terminal) ratio computed after a long (several ps) period at 75 °C is about 4.1, which is in good agreement with the experimental value [3] of about 3.3–3.7.

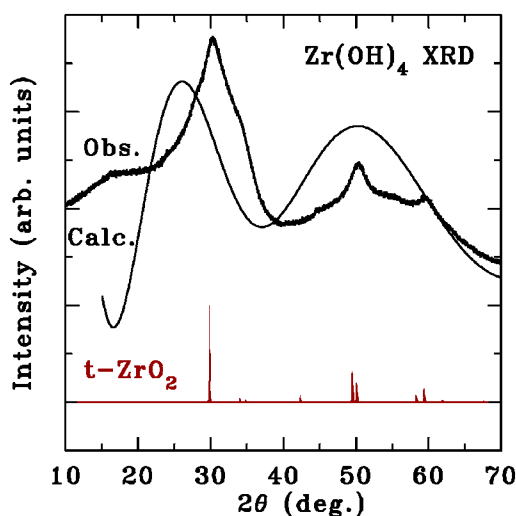


Figure 51. Calculated XRD (intensity vs. scattering angle, 2θ) for a 2-layer model equilibrated at 400 K in comparison with experimental results (Ref 4) for ZH and for crystalline tetragonal ZrO_2 (t- ZrO_2). The sharp structure in the "observed" XRD results from a t- ZrO_2 impurity. All results are for Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å).

X-ray diffraction (XRD) data [5] for amorphous ZH show two broad peaks at scattering angles of $2\theta \approx 30$ and 50° as shown in Figure 51. A 3D periodic structure comprising basically a periodic lattice of amorphous cells was built using the small unit cells from the AIMD simulations. Debye scattering theory can be applied to this model, which gives broad peaks at $2\theta \approx 25$ and 50° . The smaller 2θ corresponds to Zr-Zr spacing and the larger 2θ corresponds to the (Zr-O) nearest-neighbor pairs. There is essentially no semblance of order beyond the nearest-neighbors shells, and the model thus captures the amorphous nature of real ZH. The radial distribution function (RDF) also supports this conclusion.

An infrared (IR) spectrum has been computed for the amorphous ZH model. Comparison with experiment has been somewhat constrained by the absence of experimental data extending to low energy (<1000 cm^{-1}), where the Zr-O-Zr lattice modes occur. Data for ZH that is free of adsorbed H_2O and carbonate contamination was not found. However, the overall width of the O-H stretching region has been correctly reproduced in the calculations. This region, which extends from about 2600 – 3600 cm^{-1} , is

exceptionally wide for ZH in comparison to other amorphous oxides such as SiO_2 and $\gamma\text{-Al}_2\text{O}_3$. Here again, the disorder in the real material was reproduced in the model.

Proton nuclear magnetic resonance (NMR) frequencies are very sensitive to the chemical environment of the proton. Work by Mogilevsky, et al [45] shows that H_2O , bridging, and terminal hydroxyl resonances fall in overlapping but separable ranges of the chemical-shift parameter (δ). The width of the different resonances is a reflection of the disorder in the proton chemical environment. The resonances were spread over a total δ range of about 10 ppm (relative to the tetramethyl silane frequency standard). The calculated total spread for the amorphous ZH model is about 14 ppm. One discrepancy is that, in experiment, the average δ for bridging OH is about 1 ppm higher than for terminal OH; whereas, in the calculation, it is about 1 ppm lower. Currently, it isn't certain as to the source of this discrepancy between experimental and theoretical data.

As mentioned above, bridging hydroxyls are more acidic than terminal hydroxyls. The model was tested in this context. The calculated energy needed to remove a proton from the hydroxyl species (simulating proton donation) is 0.51 eV lower for bridging than for terminal hydroxyl. Thus, the model supports experimental observation.

5.2 Adsorbate Calculations

Density functional theory (DFT) calculations of gas-phase reactions between dimethyl methylphosphonate (DMMP) and oligomers of zirconium tetrahydroxide [$\text{Zr}_n(\text{OH})_{4n}$] have been performed for the monomer, dimer, and tetramer ($n=1, 2$, and 4). To assist in rapidly identifying pre-reaction complexes and transition structures in low-symmetry reaction environments (e.g. sites on the amorphous zirconium hydroxide), a numerical algorithm was developed to generate a user-specified number of initial structures (100-1000) by randomly placing and orienting the adsorbate near the surface. The structures are then optimized using density functional theory or a similar quantum chemistry method, which are readily available in a number of quantum chemistry codes. The thermochemical functions such as enthalpies are computed for each optimized structure and a small number (1-3) of most thermodynamically favored structures are selected for further simulations. This algorithm effectively eliminates the need to correctly guess the lowest-energy binding configurations of adsorbates on the surface and increases computation throughput substantially. More details about this specific approach are found in the literature.[15]

5.2.1 Partially Hydrated Surface

Previously reported studies of amorphous ZH and thermogravimetric analysis/mass spectroscopy (TGA-MS) measurements at NRL identified three stages in thermal dehydration of amorphous ZH: loss of bulk water at $\sim 76^\circ\text{C}$, loss of surface-coordinated water at $\sim 153^\circ\text{C}$, as well as condensation and desorption of surface hydroxyls at much higher temperatures. These measurements indicate that both bulk and surface-coordinated water is present on ZH at ambient conditions. While simulations of bulk water are not yet possible within our cluster model, calculations of surface-coordinated water can provide binding enthalpies for comparisons with other species including nerve agents and their simulants.

Previously, we used a cyclic tetramer $\text{Zr}_4(\text{OH})_{16}$ to model adsorption and reactivity of DMMP and atmospheric species (H_2O and CO_2) on Zr_{cus} . The tetramer contains four equivalent Zr atoms, which can be viewed as models for 6-fold coordinated Zr sites found at corners of ZH layers. However, there is experimental evidence of molecular water present even on nominally dry amorphous ZH. Water molecules bind strongly to vacant coordination sites of the 6-fold coordinated Zr sites, which should affect the structures and energies of CWA adsorption on those sites.

We have simulated water physisorption on the $\text{Zr}_4(\text{OH})_{16}$ by optimizing 100 initial structures with a water molecule randomly placed near one of the Zr atoms. All simulations with the tetramer model reported below were obtained using the M06 meta-hybrid density functional combined with the 6-

31+G(d,p) all-electron, double-zeta set of atom-centered Gaussian-type orbitals for elements H through P, the LANL2DZ relativistic set of effective core potentials for Zr core electrons, and the modified double-zeta basis set for Zr valence electrons, as implemented in Gaussian09. The resulting lowest-enthalpy molecular adduct has the O atom of water bound to Zr and one of the H atoms of water forms a hydrogen-bond with an adjacent bridging OH (not shown). We then repeated the optimization with two water molecules randomly placed either near one Zr atom or near two different Zr atoms. The resulting lowest-enthalpy structure has the two water molecules bound to two different Zr sites, while a structure with the two water molecules bound to the same Zr site has a much higher enthalpy. In fact, many initial structures with two water molecules bound to the same Zr site resulting in one of the water molecules desorbing from Zr during the optimization and forming hydrogen-bonds with adjacent hydroxyls. We therefore concluded that adsorption of two water molecules on the same Zr site resulting in an 8-fold coordinated Zr atom is energetically unfavorable compared to adsorption of one water molecule per each Zr sites resulting in 7-fold coordinated Zr atoms. Based on these findings, we selected $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$ as the target stoichiometry for the tetramer cluster with physisorbed water molecules and repeated the optimization with four water molecules randomly placed near different Zr atoms. The resulting model is shown in Figure 52.

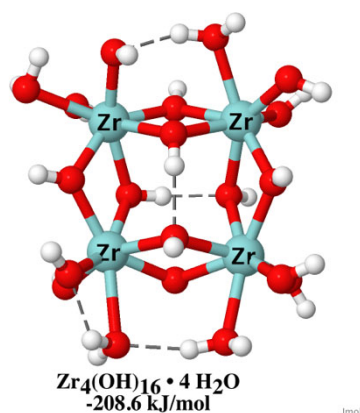


Figure 52. $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$ used as a cluster model for amorphous ZH to simulate GB adsorption. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, and H atoms in white. Gray dashed lines are hydrogen bonds shorter than 1.8 Å.

5.2.2 AIMD Simulations of Fully Hydrated ZH Models

The 4x4 double-layer ZH model was completely immersed in water to study hydration effects on different agent/simulant analytes (DMMP, DMCP, DFP, GB, and an iodo form of GB, with fluorine replaced by iodine and isopropyl replaced with methyl, to promote reactivity). Additionally, the effect of pH (acidic, neutral, and basic) was investigated via the addition of ion pairs to the fully hydrated systems. Control experiments comprising just the fully hydrated systems without a ZH surface were also performed.

Water content significantly affects reaction rates as shown by experimental NMR measurements.[1] To study this phenomenon at the molecular level, fully hydrated systems were constructed from a pre-equilibrated box of TIP3 water molecules superimposed onto equilibrated structures of previously dehydrated analyte-ZH systems. Figure 53 shows a representative water-flooded system of DMMP on ZH. The number of added water atoms is 684 (228 molecules). The number of analyte (DMMP) and surface (ZH) atoms is 304, for a total number of 988 atoms. The box dimensions (periodic boundary conditions) are 14.590 x 14.781 x 45.000 Å³.

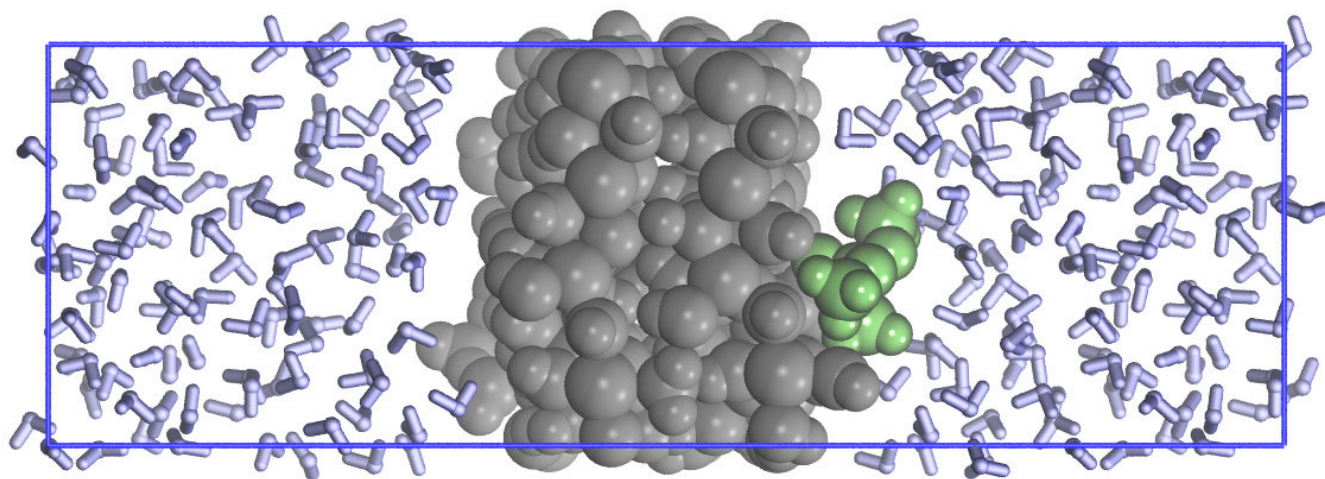


Figure 53. A fully hydrated DMMP on ZH model. Periodic boundary conditions are shown as blue lines. DMMP and zirconium hydroxide atoms are shown as big balls colored lime and silver, respectively. Water molecules are shown as small boomerangs colored violet.

5.2.3 Ambient Contaminants

The calculated enthalpies of molecular and reactive adsorption of CO_2 , SO_2 , NO_2 , HF, and GB on $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4$ are compared in Table 9. The structure optimizations of molecular complexes showed that each species can bind to several types of adsorption sites (e.g., near an edge, near a corner, and directly above the plane of the ring formed by the four Zr atoms), wherein the adsorbate forms one or more hydrogen bonds with surface hydroxyls and/or Zr-coordinated water. The length of the hydrogen bonds stabilizing these molecular adsorbates range from 1.47 Å for HF to 2.22 Å for CO_2 . The absolute binding enthalpies with respect to the gas-phase adsorbates range from -17.9 kJ/mol for $\text{NO}_2^\bullet$ to -80.7 kJ/mol for GB. Because hydrogen-bonded water is abundant on ZH, it is informative to compare the absolute binding enthalpies to that water. Unlike other adsorbates, SO_2 binds directly to a terminal hydroxyl (forming a dative S-O bond with the length of 1.92 Å, which is somewhat longer than the other two S-O bonds of 1.46 Å), in addition to two hydrogen bonds, which results in strong binding (81.1 kJ/mol). Optimizing the molecular complexes of HNO_3 and HNO_2 as possible reaction products of NO_2 hydrolysis showed instant deprotonation when placed near the cluster.

Table 9. Calculated adsorption enthalpies (in kJ/mol) for CO_2 , SO_2 , NO_2 , HF, and GB and their reaction products on $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4$.

Species	Molecular adsorption (vs. H_2O^a)	Reactive adsorption (vs. H_2O or HF)
CO_2	+30.3	-13.4 ^b
SO_2	-21.5	-107.0 ^b
$\text{NO}_2^\bullet$	+39.2	No reaction
HNO_3	n/a ^c	-79.9 ^d

HNO ₂	n/a ^c	-43.5 ^d
HF	-2.1	-65.4 ^d
GB	-21.1	-105.4 ^e

^a Values computed according to a nominal reaction: $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O} + \text{A}(\text{g}) \rightarrow \text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4 \cdot \text{A} + \text{H}_2\text{O}(\text{g})$; negative values indicates that the corresponding molecular complex is more stable than hydrogen-bonded water

^b $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4 + \text{XO}_2(\text{g}) \rightarrow \text{Zr}_4(\text{OH})_{14}(\text{XO}_3)(\text{H}_2\text{O})_4 + \text{H}_2\text{O}(\text{g})$

^c HNO₃ and HNO₂ undergo instant deprotonation reactions

^d $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4 + \text{HX}(\text{g}) \rightarrow \text{Zr}_4(\text{OH})_{15}(\text{X})(\text{H}_2\text{O})_4 + \text{H}_2\text{O}(\text{g})$

^e $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4 + \text{GB}(\text{g}) \rightarrow \text{Zr}_4(\text{OH})_{14}(\text{IMPA})(\text{H}_2\text{O})_4 + \text{HF}(\text{g})$

The calculated lowest-enthalpy reaction products of CO₂, SO₂, HNO₃, HNO₂, HF, and GB with $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4$ are shown in Figure 9. These simulations assume the corresponding reaction products (carbonates, sulfites, etc.) replace surface hydroxyls and result in formation of H₂O or HF as by-products. To simplify the simulations, by-products were excluded from the cluster models. Correspondingly, the reaction enthalpy values shown in Figure 54 and Table 9 are given with respect to gas-phase H₂O and HF.

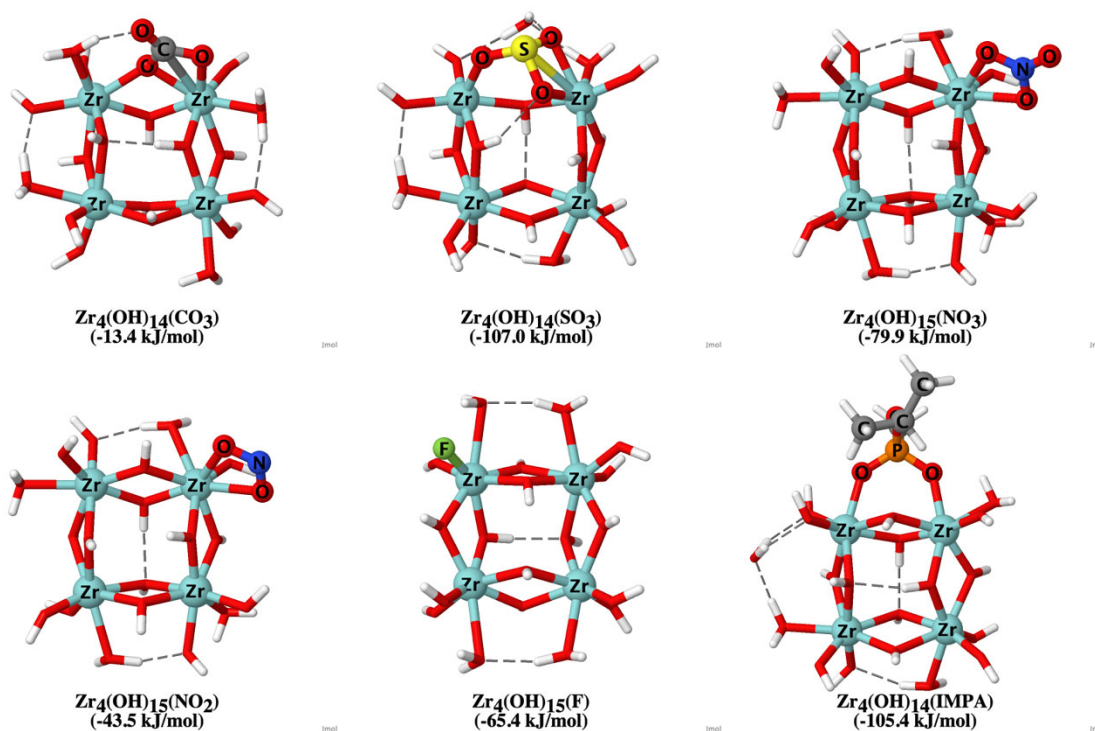


Figure 54. Reaction products of CO₂, SO₂, NO₂, HF, and GB on $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4$. Zr atoms and non-hydrogen atoms belonging to the adsorbed molecules are labelled for emphasis. Unlabeled O atoms are shown in red and H atoms in white. The values in parenthesis are calculated enthalpy differences with respect to $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4$ and the gas-phase adsorbates. Dashed gray lines indicate possible hydrogen bonds (i.e., wherever an O, N, S, or F atom is within 2.3 Å of an H atom and the resulting angle is larger than 130 degrees).

The XPS and DRIFTS results discussed above show that CO_2 and SO_2 react with ZH surfaces to form mostly carbonates and sulfite, and a smaller amount of bicarbonates/bisulfites (see also Ref. [31]). The structural optimizations with CO_3^{2-} and SO_3^{2-} replacing either two bridging hydroxyls, two terminal hydroxyls, or one bridging and one terminal hydroxyl resulted in a number of possible binding configurations with the bridging carbonate and sulfite having the lowest enthalpies. The structural optimizations with HCO_3^- and HSO_3^- replacing either a bridging or a terminal hydroxyl revealed several stable monodentate and bidentate configurations (not shown), but all bicarbonate and bisulfite structures were significantly less stable than the bridging carbonate and sulfite configuration. No zirconium sulfate structures with a negative reaction enthalpy with respect to gas-phase H_2SO_4 and $2 \text{H}_2\text{O}$ were observed when placing SO_4^{2-} near a dehydroxylated cluster. This is consistent with the periodic-slab DFT simulations reported by McEntee, et al.,[2] who reported that SO_4^{2-} in its lowest-energy bidentate configuration is significantly less stable than SO_3^{2-} (the reported difference in the adsorption energies was 1.81 eV or 174.6 kJ/mol).

Directly placing $\text{NO}_2^\bullet$ near a dehydroxylated cluster did not result in a stable reaction product. These simulations thus indicate that a direct reaction between NO_2 in its radical form and Zr-bound hydroxyls is unlikely. Nevertheless, as discussed above, ZH has a large sorption capacity towards NO_2 and the DRIFTS measurements show evidence of nitrate and nitrite species formation. A likely reaction pathway is NO_2 reacting with surface-bound water to form HNO_3 and HONO , which can further react with surface hydroxyls. Indeed, the structural optimizations with molecular HNO_3 or HONO placed near $\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_4$ resulted in instantaneous deprotonations of these species and formation of hydrogen-bonded NO_3^- and NO_2^- . Furthermore, the structural optimizations with NO_3^- and NO_2^- placed near a dehydroxylated cluster (with either terminal or bridging hydroxyl removed) formed large numbers of different stable configurations including chelating, monodentate, and bridging nitrates and nitrites, with the chelating configurations having the lowest enthalpies.

As discussed above, GB reacts with surface hydroxyls to form surface-bound IMPA and zirconium fluoride. Similar reactions were reported for Zr-based MOFs[69] and for HCl.[5] Placing the conjugate base of IMPA near a dehydroxylated cluster (with either terminal or bridging hydroxyl removed) resulted in several chelating and bridging configurations. The bridging configuration (Figure 54) was found to have the lowest enthalpy. Experimental XPS data show HF further reacts with surface hydroxyls to form zirconium fluorides. Similar reaction were reported for HCl.[5] Placing F^- near a dehydroxylated cluster (with either terminal or bridging hydroxyl removed) resulted monodentate and bridging configurations, with the monodentate configuration having the lowest enthalpy.

A large cluster model ($\text{Zr}_9(\text{OH})_{36} \cdot 4 \text{H}_2\text{O}$) of amorphous ZH was developed and used to model and calculate adsorption enthalpies and IR spectra of physisorbed and chemisorbed carbon monoxide CO . The model development and the details of CO adsorption simulations using the new model are described below. Because of a 3-fold increase in the number of atoms in the new model compared to the tetramer (93 atoms vs. 36 atoms) hybrid density functional theory (DFT) calculations were too computationally costly for an efficient exploration of different binding configurations. Instead, all results reported below were obtained using the PBE generalized-gradient functional with Grimme's D2 correction and the def2-SVP double-zeta plus polarization set of Gaussian atomic orbitals combined with Stuttgart relativistic pseudopotentials for Zr atoms. This level of theory is comparable to the periodic-slab calculations.

5.2.4 Large cluster (nonamer) model of amorphous ZH

Previously, we have used a cyclic tetramer $\text{Zr}_4(\text{OH})_{16}$ to model adsorption and reactivity of DMMP, GB and atmospheric species (H_2O , CO_2 , and SO_2) on Zr_{cus} sites. The tetramer contains four equivalent Zr atoms that can be viewed as models for 6-fold coordinated Zr sites found at corners of ZH layers. However, the tetramer does not include the 7- and 8-fold coordinated Zr atoms found on, respectively, the edges and internal sites of ZH layers. In addition, previous experimental characterization of amorphous ZH have shown the presence of strongly physisorbed water up to relatively high

temperatures. Water molecules occupy vacant coordination sites of the corner Zr atoms, which should affect the adsorption structures and energetics of other species including CO.

To include the 7- and 8-fold coordinates Zr atoms in the model, we have built a cyclic nonamer $\text{Zr}_9(\text{OH})_{36}$, which includes all three types of Zr atoms. In addition, we have simulated water physisorption on the nonamer (not discussed in detail here) and found that the energetically most favored adsorption site is at a corner Zr atom, wherein the O atom of water binds strongly to Zr and one of the H atoms of water forms a hydrogen-bond with an adjacent bridging OH. The final configuration that contains four water molecules adsorbed at four corner Zr atoms is shown in Figure 55.

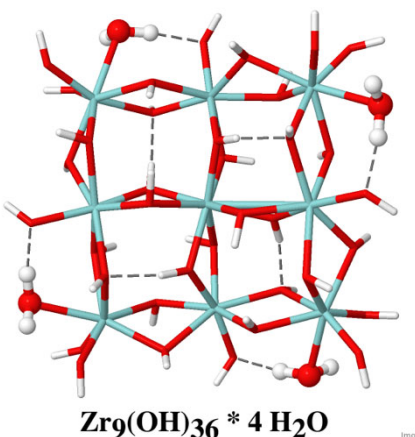


Figure 55. $\text{Zr}_9(\text{OH})_{36} \cdot 4 \text{H}_2\text{O}$ used as a cluster model of amorphous zirconium hydroxide to simulate CO adsorption in this reporting period. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, and H atoms in white. $\text{Zr}_9(\text{OH})_{36}$ is shown as wireframes and four physisorbed waters are shown as balls-and-sticks for emphasis. Hydrogen bonds shorter than 1.8 Å are shown with gray dashed lines.

5.2.5 CO adsorption on $\text{Zr}_9(\text{OH})_{36}$

Carbon monoxide (CO) is often used as a probe for defect sites in metal oxides and hydroxides because the C-O stretch frequency is sensitive to the acid-base properties of adsorption sites. Previous *operando* ATR measurements at NRL detected both red- and blue-shifted C-O stretches, as well as formation of formates on amorphous zirconium hydroxides. These measurements were completed after an initial N_2 purge, which was expected to remove bulk water from the ZH surface.

To help with the interpretation of observed experimental features, we have performed simulations of CO adsorption using the stand-alone $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$ cluster. Structure optimizations were initially performed for 100 hydrogen-bonded complexes between CO and the cluster, wherein CO was randomly placed and oriented near $\text{Zr}_4(\text{OH})_{16}$ without any restraints. The resulting lowest-enthalpy molecular cluster (top left in Figure 56) has a binding enthalpy of -24.4 kJ/mol. Hereafter, negative enthalpies correspond to exothermic reactions. This binding enthalpy is comparable to the previously computed binding enthalpy of CO_2 on unhydrated $\text{Zr}_4(\text{OH})_{16}$ (-27.6 kJ/mol). Similar optimizations were performed for 100 molecular adducts between CO and a corner Zr atom and another 100 adducts between CO and an edge Zr atom, wherein CO was randomly placed near the Zr atoms such that the C-Zr distances were less than 3 Å. Surprisingly, the resulting lowest-enthalpy molecular adduct (top right in Figure 56) has a binding enthalpy of -13.3 kJ/mol and thus is less stable than the complex. Both forms are less stable than hydrogen-bonded H_2O molecules, indicating that both of these forms are easily displaced by water and likely only serve as intermediates to surface-bound CO in its formate form.

To determine adsorption configuration of CO in its formate form (HCOO^-), initial structures were generated by first removing a bridging or terminal OH and then randomly placing the formate anion near the Zr atom (or atoms) previously bound to the removed OH. Overall, 400 such initial structures were generated with 100 structures for each type of removed OH: bridging OH connecting corner and edge Zr atoms, bridging OH connecting edge and center Zr atoms, terminal OH at a corner Zr atom, and terminal OH at an edge Zr atom. The resulting lowest-enthalpy bidentate and monodentate configurations (Figure 56) have binding enthalpies of, respectively, -172.6 and -155.0 kJ/mol. These binding enthalpies are much lower than the previously computed binding enthalpies of bidentate and monodentate configurations of CO_2 in its bicarbonate form on dehydrated $\text{Zr}_4(\text{OH})_{16}$ (respectively, -53.0 and -37.0 kJ/mol). Formates are also more stable than surface-coordinated water and thus are expected to survive thermal treatment and/or N_2 purge that would remove water and carbonates.

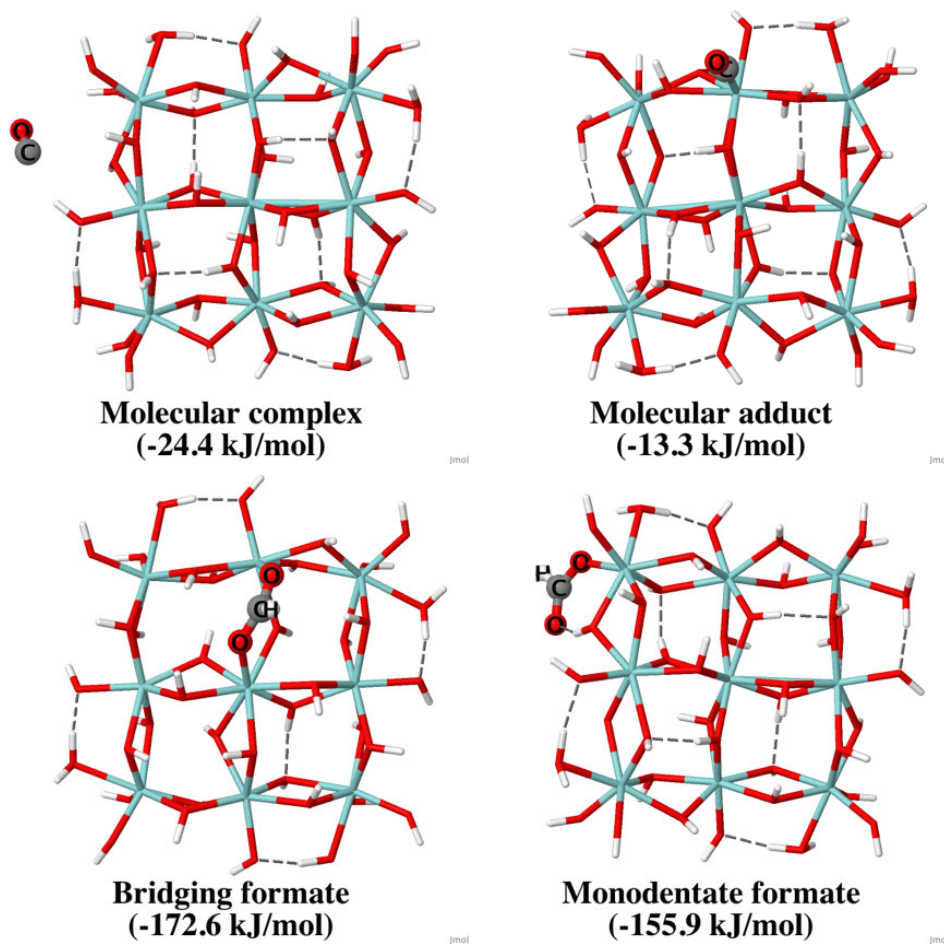


Figure 56. Physisorption and chemisorption of CO on $\text{Zr}_9(\text{OH})_{36} \cdot 4 \text{H}_2\text{O}$. Shown are the lowest-enthalpy molecular complex (top left), molecular adduct (top right), bridging formate (bottom left), and monodentate formate (bottom right). Zr atoms are shown in cyan, O atoms in red, C atoms in gray, H atoms in white. Atoms belonging to molecular CO or formate anion are labeled for emphasis. Values shown in parenthesis are the computed enthalpy differences with respect to separated gas-phase CO and $\text{Zr}_9(\text{OH})_{36} \cdot 4 \text{H}_2\text{O}$.

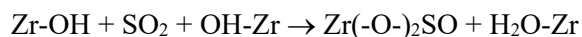
The computed frequencies of the C-O stretch fundamental bands in gas-phase and physisorbed CO as well as O-C-O asymmetric/symmetric stretches and C-H stretch in the bidentate and monodentate formats are shown in Table 10 below.

Table 10. Computed frequencies of relevant modes in gas-phase, physisorbed and chemisorbed CO.

Adsorbate	Mode	Frequency, cm ⁻¹
Gas phase	C-O stretch	2159
Molecular complex	C-O stretch	2153
Molecular adduct	C-O stretch	2147
Bidentate formate	O-C-O symm. stretch	1383
	O-C-O asym. stretch	1622
	C-H stretch	2944
Monodentate formate	O-C-O symm. stretch	1312
	O-C-O asym. stretch	1661
	C-H stretch	2872

Carbon dioxide is known from experiment [3] to adsorb mostly reversibly on amorphous ZH, which indicated the absence of any chemical reaction. However, a fraction of the CO₂ was seen to chemisorb leading to a bicarbonate, Zr-O-C(=O)(OH). This has also been successfully reproduced in AIMD calculations. When CO₂ was placed on top of a 2-layer model it rapidly desorbs with no evidence of any bond formation. However, if CO₂ is placed *between* the layers so that so it is prevented from quickly diffusing away, a reaction leading to a bicarbonate quickly occurs. This suggests that pores and microcavities in ZH are the reactive sites for irreversible adsorption of CO₂.

Sulfur dioxide (SO₂) is also known from experiment [2] to react preferentially with terminal OH groups on ZH to form a sulfite (SO₃⁻²) species, which can be monodentate, bidentate or terminal. This behavior has also been successfully reproduced in the AIMD simulations. First, a "defect" was made by removing a single ZH unit, one of the 32 such units in the model unit cell. This resulted in a localized region with a high density of terminal OHs. Such defects are expected in the real material, and the high local density of terminal OH is a reasonable representation of the edge of a nanoparticle. An SO₂ molecule placed near this defect quickly undergoes a reaction like:



as shown in Figure 57.

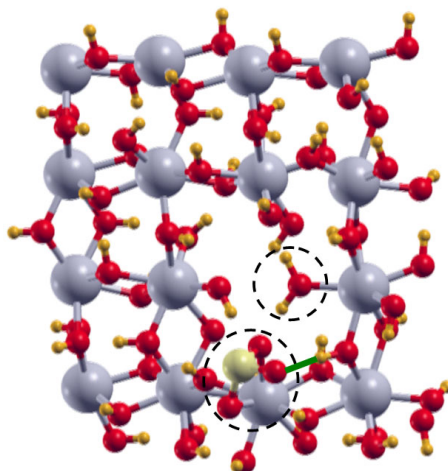


Figure 57. The product for SO_2 reaction with a ZH defect site. The bidentate sulfite and H_2O are circled for clarity. The green line shows an H-bond between the "free" sulfite O atom and a bridging OH group. Adapted with permission from J. Phys. Chem. C 2018, 122, 5385–5400. Copyright (2018) American Chemical Society.

In this case the sulfite formed is a bidentate species with two S-O-Zr bonds to the same Zr, but other types of sites form either monodentate, Zr-O-SO_2 , or bridging, Zr-O-S(O)-O-Zr , structures. The reaction is a three-center process that involves transfer of H between two terminal Zr-OH sites, which then leaves a "dangling" O atom on one Zr that bonds to the S atom. The activation energy for this process is small, <0.27 eV, and the bidentate reaction is exothermic by ~ 1.29 eV relative to bare ZH and free SO_2 . The exact reaction energy depends on the structure of the reaction site and of the type of sulfite formed.

5.2.6 CWA Simulants

5.2.6.1 DMMP

DMMP surface interaction calculations on ZH show DMMP binding to a single metal site forming a stable chelating bidentate adduct with the phosphorous in a 5-coordinated, trigonal bipyramidal configuration. The adduct readily undergoes intramolecular proton transfer and elimination of methanol. Calculations of the transition structures and intermediates mediating this addition-elimination reaction predicted that it is both thermodynamically and kinetically allowed.

The calculations showed DMMP readily formed hydrogen bonds with small ZH oligomers $[\text{Zr}_n(\text{OH})_{4n}]$, $n=1, 2$, and 4 . Using the previously mentioned algorithm, several stable structures were found with different orientations of DMMP, allowing hydrogen bonds between (1) ZH hydroxyl hydrogens and the phosphoryl, and/or methoxy oxygens of DMMP, and (2) ZH hydroxyl oxygens and the methyl hydrogens of DMMP. The resulting binding energies range from 30 to 80 kJ/mol. Figure 58 shows three such complexes. Many other similar complexes likely exist due to the conformational flexibility of DMMP and the availability of various hydroxyls.

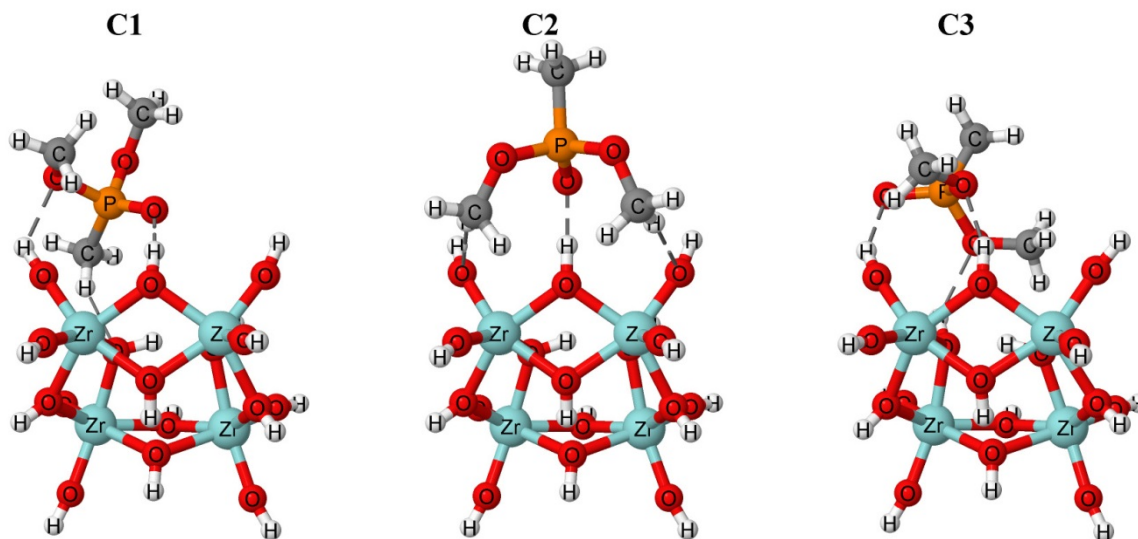


Figure 58. Molecular structures of hydrogen-bonded complexes between DMMP and $\text{Zr}_4(\text{OH})_{16}$.

One of the hydrogen-bonded complexes (labeled C2 in Figure 58) can readily isomerize into a Lewis acid-base adduct, wherein a terminal OH binds to P and the phosphoryl O of DMMP binds to the same-site Zr atom. The optimized structure of such a DMMP adduct with the tetramer is shown in Figure 59. The chelating bidentate configuration of the P5 adduct was different from the bridging bidentate adducts that have been previously reported for metal oxides. In P5, DMMP bonded to a single metal atom rather than forming a bridge between two metal atoms. However, the P atom of DMMP is 5-fold coordinated with its moieties forming a trigonal bipyramidal configuration, similar to pre-reaction adducts known to mediate addition-elimination reactions of phosphonates in solution and on metal oxide surfaces.

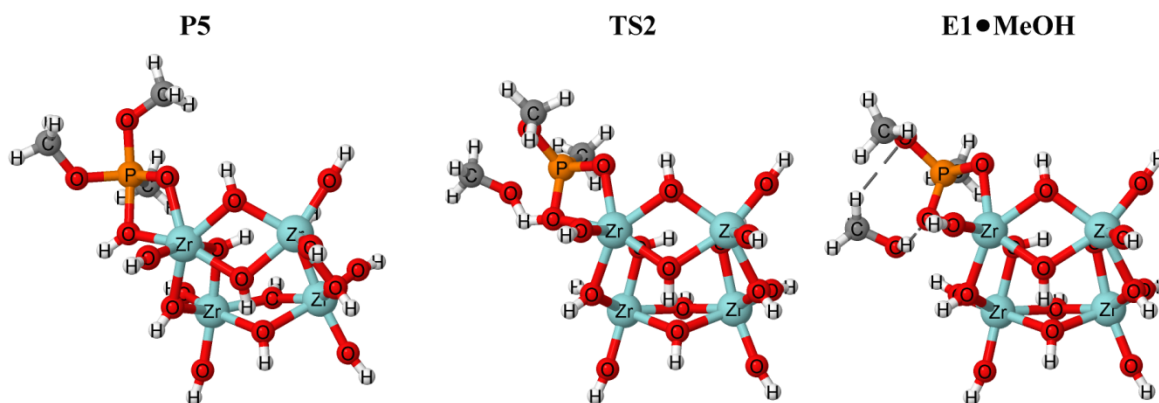


Figure 59. Intermediates and one of the transition structures mediating $\text{Zr}_4(\text{OH})_{16}$ -assisted hydrolysis of DMMP.

A transition structure (labeled TS2 in Figure 59) described the proton transfer event from the terminal hydroxyl bonded to DMMP in P5 to a methoxy group of DMMP. The subsequent IRC calculations showed that the transition structure connects P5 to a product complex (labeled E1•MeOH in

Figure 59) of methanol and a chelating bidentate adduct of deprotonated methyl methylphosphonate (MMP) and dehydroxylated ZH tetramer.

Figure 60 summarizes the detailed reaction mechanism for this reaction. First, DMMP forms a complex with the tetramer (C2). The complex can isomerize into a chelating bidentate adduct (P5), thus completing the addition part of this addition-elimination reaction. The addition step is exothermic by 95 kJ/mol and the transition structure involved (not shown) has a very low barrier (18 kJ/mol) that can be easily surmounted at room temperature. The P5 adduct can further undergo proton transfer and elimination of methanol to form a product complex (E1•MeOH). The elimination step is also exothermic by 17 kJ/mol and the corresponding transition structure has only a moderate barrier (77 kJ/mol) that should be thermally accessible. The E1•MeOH product complex can further dissociate to release methanol, yielding a chelating bidentate adduct (labeled E1 in Figure 59) of deprotonated MMP and dehydroxylated tetramer. This step is endothermic by 79 kJ/mol and involves no barrier above the product asymptote. Still, the overall hydrolysis reaction $\text{DMMP} + \text{Zr}_4(\text{OH})_{16} \rightarrow \text{E1} + \text{CH}_3\text{OH}$ is exothermic by 33 kJ/mol and should be thermally accessible.

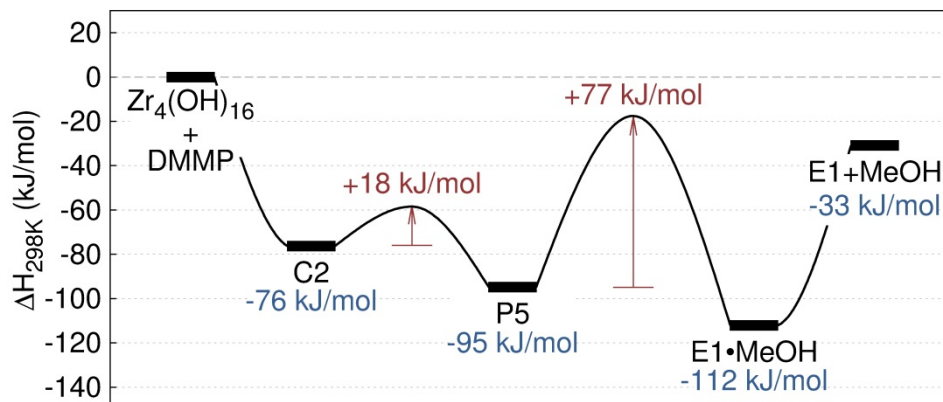


Figure 60. Reaction diagram describing the addition-elimination mechanisms to $\text{Zr}_4(\text{OH})_{16}$ -assisted hydrolysis of DMMP.

5.2.7 Chemical Warfare Agent Calculations

Sarin (GB) and its simulant dimethyl methylphosphonate (DMMP) are known from experiment to bind and react with ZH. As these chemicals are both relatively small and experimentally reactive, extensive simulations were performed with both on the ZH surface. AIMD simulations were performed at 200, 400 and 600 K, with or without water; and with two different starting orientations. The overall results of all these simulations were similar, showing that both GB and DMMP bind strongly through the surface through hydrogen bonds. Specifically, hydrogen bonds (H-bonds) form between the phosphoryl group of GB/DMMP to the surface hydroxyls, forming either one or two H-bonds. The rest of the molecule is only weakly bound through dispersive forces, and there is significant diffusion across the surface even at low temperatures. Calculated binding energies were similar for both species, with 0.7-0.8 eV for GB or DMMP singly H-bonded and 1.0 eV for both species when double H-bonded. Note that given the amorphous nature of the ZH surface, there will be significant variation in the binding energies depending on the local geometry near the binding site, which will require future work. So far, the AIMD simulations have not led to reactions with these larger molecules, most likely due to either the longer timescale of the reaction, or the need for specific surface defects.

Results from the iodo-GB molecule indicated very rapid reaction presumably due to the weak P-I bond (iodine is large, has a low electronegativity, and is known to be a good leaving group in organic chemistry, especially in its ionic form in polar solvents), which appears fairly unstable at 300 K regardless of hydration conditions. As shown in Figure 61, the iodine/iodide and a bridging surface hydroxyl attacked the phosphorus and then deprotonated to a nearby terminal hydroxyl to form surface bound water under dry conditions (no excess water). When significant water was present, a water molecule, instead of a surface hydroxyl, attacked the phosphorus in a similar manner. The difference between nucleophilic attack by a surface hydroxyl or by a water molecule, in this case, was likely due to proximity and concentration.

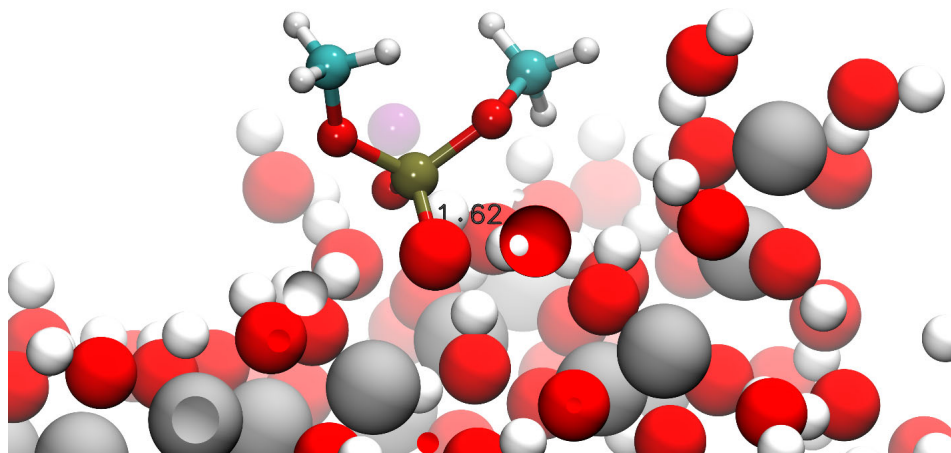


Figure 61. The reaction of the iodo form of GB on ZH model under dry conditions. Iodo-GB is shown as a ball-stick model and ZH atoms are shown as big balls. Phosphorus, iodine, carbon, zirconium, oxygen, and hydrogen atoms are colored brown, purple, cyan, gray, red, and white, respectively. The length of the newly formed P-O bond is labeled in Angstroms.

Previous experimental and theoretical studies of GB binding on pristine and hydroxylated surfaces of metal oxides have shown that GB can initially bind either (a) by forming hydrogen bonds between its phosphoryl O and surface hydroxyls or (b) by forming Lewis adducts between the phosphoryl O and *cus* metal atoms. Similarly, within the constraints of the cluster model developed within this program, GB molecularly bonded to ZH forming a strong hydrogen bond to a bridging hydroxyl or by forming an adduct between the phosphoryl O and a *cus* Zr atom. Multiple structures corresponding to these two binding configurations and the two lowest-enthalpy structures are shown in Figure 62 together with the corresponding binding enthalpies (-79.2 and -88.3 kJ/mol, respectively).

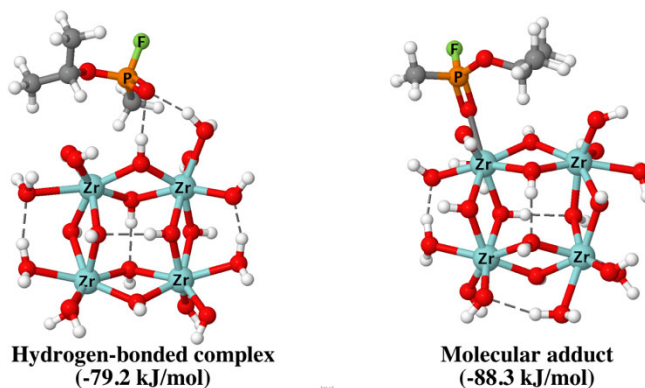


Figure 62. Molecular adsorption of GB on $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$. Shown are the lowest-enthalpy hydrogen-bonded complex and molecular adduct. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, H atoms in white, F atoms in green, and P atoms in gold. Values shown in parenthesis are the computed enthalpy differences with respect to separated GB and $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$.

The computed IR absorption spectra for the hydrogen-bonded complex and molecular adduct are shown in Figure 63 together with the gas-phase spectra of GB. Previous experimental studies used the frequency of the P=O stretch as an indicator of GB absorption and decomposition on metal oxide surfaces. Calculations for this program predict that the hydrogen bonding between the phosphoryl O and a bridging hydroxyl results in a red shift of the P=O stretch frequency by 62 cm^{-1} in the hydrogen-bonded complex when compared to gas-phase GB. The formation of the dative O-Zr bond in the molecular adduct further results in an additional red shift by 15 cm^{-1} in the molecular adduct when compared to the hydrogen-bonded complex. Furthermore, the P-O-C stretch frequency in the complex is blue shifted by 39 cm^{-1} and in the adduct by 29 cm^{-1} compared to gas-phase GB. Interestingly, the P-C stretch frequency remains unchanged in the hydrogen-bonded complex (1338 cm^{-1} in the complex and gas-phase GB), but is red-shifted by 23 cm^{-1} in the adduct (1315 cm^{-1}).

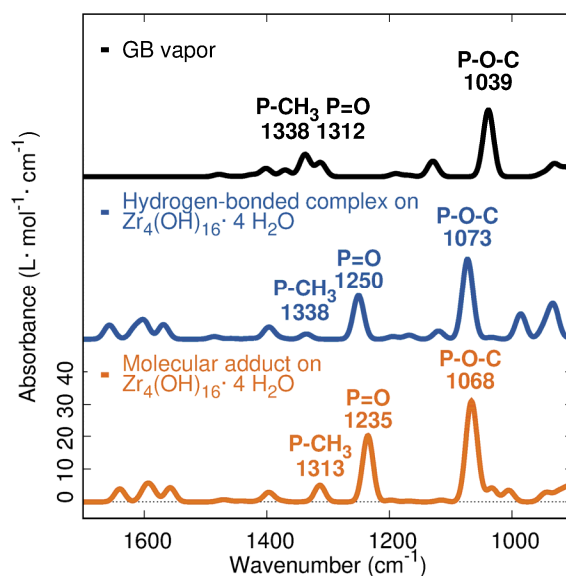


Figure 63. Computed IR absorption spectra of GB in the gas phase and adsorbed on $\text{Zr}_4(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$. IR peaks discussed in the text are labeled for emphasis.

HF elimination reactions were experimentally shown to be the dominant GB decomposition mechanism on metal oxides via loss of the P=O stretch and formation of split (symmetric/asymmetric) O-P-O stretches located at much lower frequencies. Multiple structures were found corresponding to HF elimination products bound to $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$. The bridging bidentate product (right panel, Figure 64) had a binding enthalpy of -79.9 kJ/mol, which is not the lowest-enthalpy structure. The chelating bidentate product (left panel, Figure 64) and monodentate product (center panel, Figure 64) had more stable binding enthalpy of -93.3 kJ/mol and -92.2 kJ/mol, respectively. These estimated reaction enthalpies were calculated with respect to gas-phase HF.

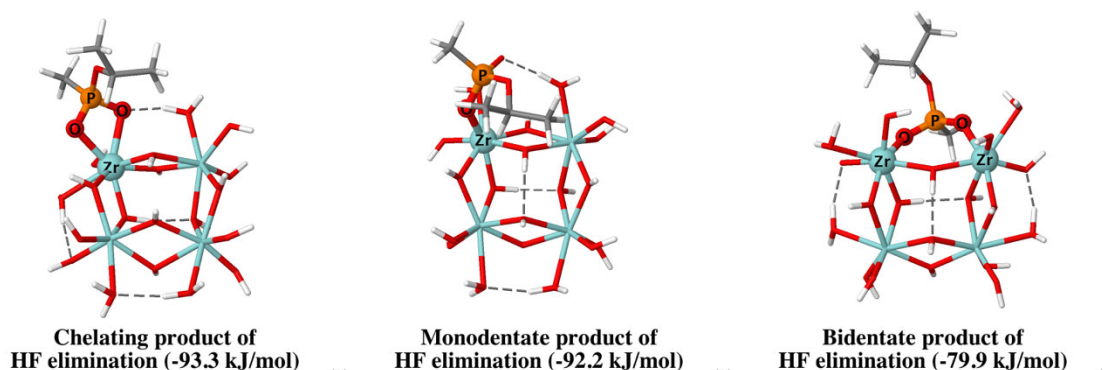


Figure 64. Dissociative adsorption of GB on $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$. Shown are the lowest-enthalpy structures for the chelating bidentate, monodentate, bridging bidentate configurations of HF elimination products. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, H atoms in white, F atoms in green, and P atoms in gold. Zr, P, and O atoms participating in monodentate or bidentate binding are labeled for emphasis. Dashed lines indicate hydrogen bonds. Values shown in parenthesis are the computed enthalpy differences with respect to separated GB and $\text{Zr}_4(\text{OH})_{16} \cdot 4 \text{H}_2\text{O}$.

The computed IR absorption spectra for the three types of HF elimination products are shown in Figure 65. Similar to experimental results, elimination of HF from GB results in reduction of the P=O bond and formation of an additional P-O bond involving a surface oxygen. As a result, elimination of HF is accompanied the appearance of three P-O stretch peaks. In the chelating bidentate product, these peaks are located at 1120, 1087, and 1037 cm^{-1} , with the 1120 and 1087 peaks involving the asymmetric and symmetric stretches of Zr-bound oxygens and the 1037 peak involving mostly the isopropyl oxygen. Visualization of the corresponding normal modes indicate that all three modes involve motions of all three oxygens, therefore the above assignment is only qualitative. In the monodentate product, the three P-O peaks are located at 1168, 1053, and 1043 cm^{-1} . In the bidentate bridging product, the three P-O peaks are located at 1174, 1073, and 1037 cm^{-1} . Interestingly, the P-C stretch frequency is slightly blue-shifted upon HF elimination, from the 1313 cm^{-1} in the molecular adduct to 1318 cm^{-1} in the chelating bidentate product.

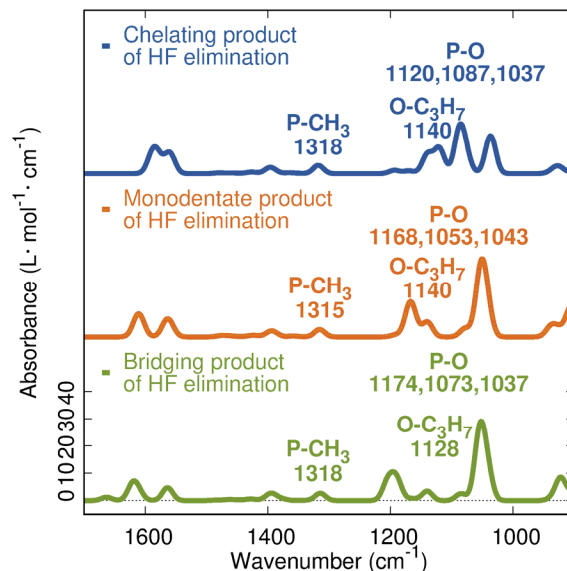


Figure 65. Computed infrared spectra of HF elimination products. IR peaks discussed in the text are labeled for emphasis.

5.2.8 Electronic Structure Calculations for ZH

A value of $E_g = 5.8$ eV has been obtained for pure ZH, which, based on test results for cubic ZrO_2 , could be as much as 0.3 eV too high vs. experiment. An estimate of about $E_g = 5.5$ -5.6 eV for ZH means that the bandgap is essentially the same as that of amorphous ZrO_2 . Various adsorbates and impurities typically found in practical ZH (H_2O , carbonate, sulfite and Cl) were evaluated as to whether they produced states in the gap. Only sulfite is found to have such an effect, giving a state at about 0.44 or 0.86 eV above the valence band maximum (VBM) depending on the adsorbate structure. The gap state is essentially a non-bonding orbital similar to the highest occupied molecular orbital of the free molecule.

One type of defect, a missing ZH unit, has little or no effect on the electronic structure. Various paramagnetic defects have also been analyzed. These include $\text{Zr}^\bullet$, $\text{Zr-O}^\bullet$ and $\text{Zr-O}^\bullet\text{-Zr}$ where $\bullet$ is an unpaired electron. The importance of such defects was suggested by the literature showing that ZH undergoes loss of H or OH during near-UV irradiation.[70] Thus ZH appears to be photochemically active, which could involve the formation of paramagnetic defects. It is, furthermore, possible that such photochemical activity would have an effect on the adsorption of agents. The $\text{Zr}^\bullet$ (or Zr^{+3}) center, which in ZH is formed by removing an $\bullet\text{OH}$ radical from a terminal Zr-OH , has been identified in electron paramagnetic resonance experiments for both ZH and ZrO_2 . The other defects are formed by removing $\bullet\text{H}$ from a terminal or a bridging OH. All three have a relatively low (endothermic) formation energy, which suggests that all should form easily. However, only $\text{Zr}^\bullet$ has been positively identified in experiment. The $\text{Zr}^\bullet$ center, which is especially interesting, results in a state at ~ 4.4 eV above the VBM, as shown in the accompanying figure. The unpaired electron partially delocalizes into the OH vacancy where it interacts with the H atom in a near-by terminal Zr-OH . This is seen in the magnetic moments (MMs) on the Zr, in the vacancy and on the H atom (0.68, 0.16, and 0.09 Bohr magnetons (μ_B) respectively). Thus the defect is largely Zr^{+3} but also involves a $\text{Zr}^{+4}(\bullet)$ component where ($\bullet$) is an electron trapped in the OH vacancy. This was clearly seen in the density of states, which shows a contribution to the gap state from both the Zr and the vacancy. The $\text{Zr-O}^\bullet$ center produces a state at 3.1 eV above the VBM with the unpaired electron localized mainly on the O atom ($\text{MM} = 0.89 \mu_B$) (Figure 66). The $\text{Zr-O}^\bullet\text{-Zr}$ center yields a state at 1.7 eV above the VBM with the unpaired electron again localized largely on the defect O atom. This demonstrates a potential pathway worth investigating for light-driven catalysis or possible surface regeneration achievable in the ultraviolet range.

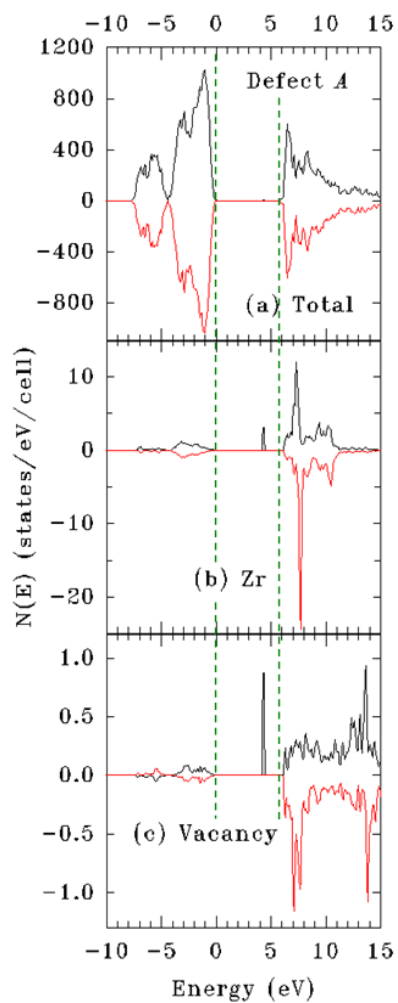


Figure 66. The spin-polarized density of states (DOS) for a 3-layer ZH model with a Zr^{+3} defect in the middle layer (Defect A). The majority (minority) spin states are shown in black (red) as positive (negative) quantities. The total DOS is shown in (a), and the partial DOS for the Zr and the OH vacancy are given in (b) and (c) respectively. Note the different $N(E)$ scales in the three plots. An occupied defect level appears at 4.4 eV above the valence band maximum (VBM). The dashed green lines show the positions of the VBM and conduction band minimum. The zero of energy is at the VBM.[71]

6. SUMMARY AND CONCLUSIONS

The Naval Research Laboratory and the U.S. Army Combat Capabilities Development Command – Chemical Biological Center investigated the impact of environmental contaminants and factors (CO_2 , SO_2 , NO_2 , H_2O , heat), on a promising sorbent for sequestration and decomposition of chemical warfare agents. Due to the complexity of the experimental protocol (ambient pressure and “real-world” contaminants), a strong theoretical component validated experimental observations and provided additional support for most likely adsorption and decomposition products and mechanisms. Briefly, ZH quickly reacted with ambient contaminants such as CO_2 , SO_2 , and NO_2 to form surface adsorbates. The strongest adsorbates being from SO_2 and NO_2 contaminants. Humidity does not appear to block active sites responsible for decomposition of CWA or CWA simulants; however, changes were observed mechanistically with both contaminant and CWA/simulant adsorption/decomposition. Surface water also solubilized some surface adsorbates. GB capacity measurements on SO_2 and NO_2 contaminated ZH showed roughly identical capacities, even though NO_2 showed over a 7-fold increase in sorption capacity compared to SO_2 adsorption. Theoretical calculations on multiple time scales and approaches also verified the experimental results and offered mechanistic insight into the most likely chemical reaction pathways. Across the program, the main active site based on both experimental and theoretical data appeared to be the free hydroxyl species of zirconium hydroxide. Collectively, these data demonstrate that zirconium hydroxide is a very versatile and robust sorbent that offers live CWA sorption capacity even on highly contaminated ZH surfaces. These data suggest ZH will likely be an excellent candidate in multiple domains personal protection against toxic chemicals for first responders and warfighter protection, toxic industrial chemical cleanup, and gas scrubbing applications for environmental remediation.

Several important experimental findings include:

1. Developed a method to electrodeposit conformal and reproducible ZH thin films and identified post-deposition procedure to remove virtually all chlorine-based contaminants and carbonates from the electrodeposited ZH surface. Such films are ideal for plasmonic or light-driven experiments on complex substrates.
2. Obtained a greater understanding of the ZH structure by EXAFS and XAS analysis of ZH performed at the SLAC beamline. As received ZH is closely related to monoclinic ZrO_2 , but heating to about 250 °C shifts to a different amorphous tetragonal-like” structure.
3. Identified that ZH reactively binds CO_2 , SO_2 , and NO_2 to form humidity dependent adsorbates primarily on free hydroxyl sites. Species observed include (bi)carbonates, (bi)sulfite, sulfate, nitrite, nitrate, and solvated forms of such species.
4. Humidity can solubilize ZH surface adsorbates, which has implications in modifying transport properties and potentially regenerate or “free” active sites as observed as increasing free hydroxyl species.
5. Spectroscopically observed coordinatively unsaturated (cus) zirconium sites using CO as a probe molecule under dry conditions. No CO adsorption was observed when dosing under 40% relative humidity (RH), suggesting water blocks these sites.
6. ZH demonstrated a 7-fold enhanced capacity for NO_2 compared to SO_2 . Theory suggests this may be due to the adsorption mechanism of NO_2 vs. SO_2 where the most likely adsorbate for NO_2 is actually HONO. Formation of nitrite and nitrates can then occur via oxidation of subsequent NO_2 /HONO molecules or via disproportionation.
7. GB and VX decomposition rate on ZH decreased for SO_2 / NO_2 contaminated ZH; whereas, clean and CO_2 pre-dosed ZH decomposed GB at similar rates.
8. Microbreakthrough analysis showed no statistical change to GB sorption capacity of contaminated vs. clean ZH samples. This exciting result suggests that CWA sequestration remains effective even on highly contaminated ZH; however, little GB decomposition occurs.
9. Identified 4 stages of thermal degradation and desorption products using TGA-MS analysis of DMMP dosed ZH (with native adsorbates). Such data suggests thermal destruction/regeneration

may not be possible for phosphonate-based agents due to the loss of reactive hydroxyls and conversion to zirconia at temperatures lower than where phosphonate-derived adsorbates decompose and desorb.

10. Humidity, in virtually all cases, improved decomposition rate of CWA simulants and likely will not hinder decontamination of live agents.

Several important computational findings include:

1. A numerical algorithm was developed for searching pre-reaction complexes and transition structures in low-symmetry reaction environments such as various reaction sites on the surface of amorphous ZH. The algorithm eliminates the need to correctly guess the lowest-energy binding configurations of adsorbates on the surface.[15]
2. Cluster DFT simulations of hydrolysis of DMMP by the cyclic tetramer of zirconium hydroxide $[\text{Zr}_4(\text{OH})_{16}]$ was performed. Hydrolysis of a $\text{P}-\text{OCH}_3$ bond of DMMP can occur either via an addition-elimination mechanism involving a same-site terminal hydroxyl or direct interchange between a terminal hydroxyl and a methoxy group of DMMP. The computed activation and reaction enthalpies showed the addition-elimination mechanism was both kinetically and thermodynamically favored over the direct interchange. [15]
3. AIMD simulations based on periodic DFT showed ZH can be maintained in an artificially ordered state either by a regular array of hydrogen bonds within layers or by interaction between layers. Infrared and proton nuclear magnetic resonance spectra were computed for the amorphous model, and chemical properties were evaluated by examining the acidity of different types of OH groups and also the reactions with NO_2 , SO_2 , and CO_2 .
4. Cluster DFT simulations of the vibrational spectra of molecularly adsorbed DMMP and its decomposition products, new interpretations of the $\rho(\text{PCH}_3)$ vibrational modes of DMMP/ZH were suggested. If both molecularly adsorbed DMMP and decomposed DMMP are present on the surface, the DFT simulations predict that the two $\rho(\text{PCH}_3)$ peaks observed in the measurements may correspond to three different modes: $\rho\parallel(\text{PCH}_3)$ in molecular DMMP, $\rho\parallel(\text{PCH}_3)$ in decomposed DMMP, and $\rho\perp(\text{PCH}_3)$ in molecular DMMP. These results established an alternative protocol for measuring the kinetics of DMMP decomposition on ZH.
5. Binding and reactivity of GB and atmospheric species (water and oxides of carbon, sulfur, and nitrogen) on amorphous ZH showed that these species can bind to several types of adsorption sites (e.g., near an edge, near a corner, and directly above the plane of the ring formed by the four Zr atoms), wherein the adsorbate forms one or more hydrogen bonds with surface hydroxyls and/or Zr-coordinated water. Furthermore, consistent with the experimental observations, GB, HF, CO_2 , NO_2 , and SO_2 , readily react with surface hydroxyls (terminal, bridging, or both) to form, respectively, IMPA, zirconium fluorides, carbonates, nitrates, and sulfites. Our simulations predicted the relative stabilities of molecular adsorbates and reaction products in the following order: $\text{CO}_2 < \text{NO}_2 < \text{HF}$, GB, SO_2 .

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