Synthesis of Complex/Multifunctional Metal (Hydr)oxide/Graphite Oxide/AuNPs or AgNPs Adsorbents and Analysis of their Interactions with Chemical Warfare Agents

Dimitrios A. Giannakoudakis

The Graduate Center, City University of New York
Synthesis of complex/multifunctional metal (hydr)oxide/graphite oxide/AuNPs or AgNPs adsorbents and analysis of their interactions with Chemical Warfare Agents

by Dimitrios A. Giannakoudakis

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York 2017
© 2017

Dimitrios A. Giannakoudakis

All Rights Reserved
Synthesis of complex/multifunctional metal (hydr)oxide/graphite oxide/AuNPs or AgNPs adsorbents and analysis of their interactions with Chemical Warfare Agents

by

Dimitrios A. Giannakoudakis

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

________________________________________
Date Teresa J. Bandosz
Chair of Examining Committee

________________________________________
Date Brian Gibney
Executive Officer

Supervisory Committee:

Charles Michael Drain

Maria Tamargo

Stephen O’Brien

THE CITY UNIVERSITY OF NEW YORK
ABSTRACT

Synthesis of complex/multifunctional metal (hydr)oxide/graphite oxide/ AuNPs or AgNPs adsorbents and analysis of their interactions with Chemical Warfare Agents

by

Dimitrios A. Giannakoudakis

Advisor: Teresa J. Bandosz

One of the most widely used chemical warfare agent (CWA) is mustard gas, which is a highly toxic blistering agent. In this study we investigated the interactions of mustard gas surrogates’ vapors on zinc and zirconium hydroxides and their composites with graphite oxide (GO) and/or Au or Ag nanoparticles. Even though a small quantity of reports about the detoxification of CWAs on metal oxides is reported in the literature, almost all of these studies are performed in the liquid phase. Both herein reported Zn(OH)$_2$ and Zr(OH)$_4$ showed a good adsorption performance, with the former being photoactive under visible light irradiation. The synthesis of the composites with graphite oxide resulted in materials with improved detoxification ability due to the synergistic effect on the structural and chemical features. The density of the hydroxyl groups per surface area showed to play the most crucial role. The further addition of nanoparticles led to an increased catalytically decomposition of mustard gas surrogate to less or non-toxic products. Based on the analysis of the volatile products and those retained on the surface of the adsorbents, the involved mechanisms are concluded.


ACKNOWLEDGEMENTS

“Chemistry is life; life is Chemistry”. Ever since I was a little boy I can still remember my late grandfather’s words. I cannot remember a time when I didn’t want to study chemistry. I am feeling blessed and lucky to have the chance to complete my education in the center of the world. Maybe New York is not my home, my birth town, but it became the place of my scientific rebirth. After my first master degree, I chose to explore alternative professional pathways, far away from chemistry. Even though I was always teaching chemistry as a tutor, there was always a hidden desire to continue in a more professional and scientific level in order to obtain a PhD. The lifetiming did not seem to work out until a simple phrase brought to light and triggered catalytically my thoughts about this desire: “Why you don’t try to come to USA for your PhD;”. This was some years before I deposited my application to CUNY. Even though I had a full life in Greece, my friends and family forced me to try. Luckily, after four and a half years of a scientific journey in the concrete jungle of New York, I can definitely say that it was absolutely worth it.

It would be impossible to start and of course to fulfill this fabulous journey without the direct or indirect help and support of countless people. But, I would like to express my supreme and sincere gratitude to the Professor, who not only helped me to improve my knowledge from a scientific standpoint, but also triggered my desire to try for this! Without guidance and mentoring from Prof. Bandosz, this journey would be aimless. She challenged me to deliver my best. This was the most important objective. Although sometimes it was hard and stressful, I don’t regret not even for a second. I will never forget my first paper. I was working continuously for days. I was feeling that both the scientific and linguistic part had to be improved. I was feeling that the level I would like the first draft to reach was far away, but I decided to send it on a Saturday afternoon, in order to
receive the guidance and help, but above all to be honest, to relax and set my mind free for a while. But this never happened. I received the draft back very early the following day, full of helpful comments and suggestions; an absolutely valuable feedback. I was deeply impressed. I asked myself “How is it possible?”. This ultra-fast reply regenerated my power and working motivation. I took a fast shower, made a double coffee and started directly afterwards to work on it on Sunday morning. Some months later, the paper was published. My first paper as a first author was a reality in less than a year in the lab. Under Prof. Bandosz’ mentorship, I learned science, traveled the world to talk about science, published many peer-reviewed articles in some of the best journals. She has provided me with the unique opportunity to strengthen my professional and communication skills via the numerous conferences and collaborations. And in the last months, she spent a lot of time in order to sharpen this dissertation. I will be always thankful! It is important for a collaboration to end after three and a half years with emotions of admiration and respect.

The first Professor I met at the Graduate Center of CUNY was Prof. Maria Tamargo as an Executive Officer of the Chemistry PhD program. The way in which she discussed with me was so kind and supportive. Her welcome attitude and friendly approach with the warm smile made me feel like I knew her for years. Her recommendations and opinions concerning what is better for my future in the program were proved ultimately correct. I was also lucky to choose to do my first rotation at Prof. Charles Michael Drain’s lab in Hunter College. His door was always open not only for scientific questions. He really cared to listen and propose what is the best to be done. During the months working in his lab, the quantity and quality of knowledge which I gain about organic chemistry helped me a lot in my later research. Especially at the lab meetings when he was starting from a small question and ended up showing many theoretical and experimental pathways of approach the problems. The nanotechnology subdiscipline contributed to my understanding of
another field of chemistry. Prof. Stephen O’Brien with a unique gentle and professional style excited my curiosity and motivated me to discover in more details this new nanoworld. He is, in my mind, as the prototype of how a young professor should be. I would like to express my extended gratitude to these three professors for serving on my Dissertation Committee. Their invaluable suggestions and comments during our meetings were totally helpful, while there were always there to respond to my questions. You helped me to grow academically, professionally, and personally. You made me feel welcome in USA.

My research would be not so productive without the fruitful discussions and help from the two Post-docs involved in the same research in detoxification of chemical warfare agents. Dr. Javier Arcibar-Orozco and Dr. Marc Florent, I thank you for making my research life more productive. Our co-authorships will always connect us as chemists, but more importantly as friends. Karifala Kante also made my everyday experiments faster. The lab was always perfectly organized and he was addressing immediately everything needed to move forward with the experiments. During every stressful personal situation, he was close to me as my eldest friend. Your voice will be always in my mind when I will listen to Sean Paul. The help from Dr. Mykola Seredych during my first steps in the lab is also deeply appreciated. Dr. Jorge Morales introduced me in the world of electron microscopy and I would like to sincerely thank him for his willingness to teach me how to obtain high quality images. I was always enjoying and gaining knowledge about optics and quantum chemistry from the sort-breaks with Dr. Jeff Secor.

My daily lab-life would not be so enjoyable without the presence of numerous colleagues, visiting scholars and students. Wanlu Li, Lilja Nelson, Nikolina Travlou, Rajiv Wallace, Mingyung Jiang, Joshua Mitchel, Oluwaniyi Mabayoje, Jimmy Escalada, Kavindra Singh, Paola Rodriguez Estupiñan, Mikolaj Koscinski, Amani Ebrahim, Yuping Hu, Carla Bastos Vidal, Barbara Herkt,
Svetlana Bashkova, Manuel Algara, Maria Concepcion Ania, Lucie Laritte, Ren Tiezhen, Anna Kleyman thank you! I will be always there for you. I would like also to express my appreciation to the colleagues during the first year in the program. But uppermost Waqar Rizvi, who was always willing to help me with various problems outside the lab. Our long term discussions opened up my mind. Rizvi you will be forever a best friend! Many thanks also to my Greek friends in NYC. Vasili Deliyanaki, Lazaros Pappas, Antony Papaioannou, Marios Georgiou, Andrea Kakolyri, Stelios Tamouridi and George Kimissi, you were responsible for limiting inside my mind the distance with Greece. Our Astoria-like nights will be unforgettable!

This journey would have been impossible without the scholarships from the Graduate Center of CUNY, Onassis Foundation, and A.G. Leventis Fountations. Moreover, the travel grants from NSF, Gerondelis Foundation, Quantachrome Instruments, Doctoral Students Research Grant number 9 and 11 from CUNY, and the program Conference Presentation Support for Ph.D. Students from the Graduate Center of CUNY offered me the opportunity to participate in many International conferences. This study was also supported by the ARO (Army Research Office) of USA.

To my parents: You gave me the opportunity, the skills and the freedom to follow my own path in life. With the mistakes and successes, failures and joys. But above all with the faith to fight for my goals without closing my eyes and trying to avoid the difficult trails. I was always feeling that during a difficult moment, both you will be there! Father, you will be always the prototype of the best academic teacher, but also of the best father. Mother, you supported me to take this chance and to go far away for the PhD, even though I knew that you would be in pain. You were always by my side to guide me in order to follow the correct life-track. Now you can relax, you did it! But more importantly, the unlimited love in which I grow up with, helped me to be full of the most
important thing in my life. Emotions. You are just the best mother! Both of you did a great job! You are the main reason I fulfilled my destiny! A thank you is not enough, but I know when I was coming back home, a hug was more than enough to feel my deepest love and respect.

I have to say that these years away from my country went smoothly, since my brother set up an environment in my mind that whatever it will happen, he would be there to solve the problem. And he did that in all cases, where his involvement was needed. You took care of everythin’k’ with a high level of responsibility! I had you in my mind as “my Young brother”, but the last years you proved in many cases that you are even bigger than me; I trust you definitely! Our favorite song “The Snow in New York” was responsible for many tears of thrill. I sang these lyrics to many times:

“There are those who fail, there are those who fall,
There are those who will never win,
Then there are those who fight for the things they believe,
And these are men like you and me.

You have always been such a good friend to me,
Through the thunder and the rain,
And when you're feeling lost in the snows of New York,
Lift your heart and think of me.”

To those who are away, my grandparents: You were always in my thoughts on this journey – you are missed. I know that you would be ultimately happy and proud for my achievement. Especially the one who I have the honor to carry his name. Thank you for teaching me how to learn. I did your dream to be a chemist, but more importantly, your dream became mine. I am lucky that my academic grandfather, Dimitris or Takis, introduced me since I was a child to the world of chemistry, but also that Antonios showed me the art to think in life with dignity. The warm hug of
my grandmothers was always a small but safe harbor for my soul, full with unconditional love. I can still feel you both!

I reserved my last sentences for the one who we lived this wonderful journey together. One is sure, that we filled our memory album with colorful pictures, which will always follow us. They are part of our life. Thank you beloved Nikolina. In few months it will be your turn to obtain the uppermost academic title. I am proud of you! Our next step will be even better!

Maybe the language in this part is not perfect, but every sentence is coming from the bottom of my heart. It is hard for a Chemist to express in a few pages everything done in four and a half years in the fastest moving town in the world. I would like to close with the lyrics that gave me power the moments of crisis:

“For what is a man, what has he got
If not himself, then he has naught
To say the things, he truly feels
And not the words of one who kneels
“This thesis” shows I took the blows
And did it my way”

Thank you for reading this, now you know better a big part of me!
This work, this part of my life is dedicated to my beloved brother,
Antonios Giannakoudakis
# TABLE OF CONTENTS

**CHAPTER 1. Introduction**

1. Chemical Warfare Agents (CWAs) ................................................................. 1

   1.1. The history of Chemical Warfare Agents .................................................... 1
   1.2. International agreements against CWAs .................................................... 2
   1.3. Classification of Chemical Warfare Agents ................................................ 4

2. World War I: Militarization of chemistry .................................................... 5

   2.1. Mustard gas: The King of CWAs .............................................................. 20
   2.2. Casualties and Fatalities from CWAs in WWI ............................................ 10
   2.3. The primarily protection attempts: pads, helmets and Gas Masks .................. 12

3. Mustard Gas: The King of CWAs ................................................................. 20

   3.1. Mustard Gas: The King of CWAs .............................................................. 20
   3.2. Mustard gas deployment post the WWI ...................................................... 22
   3.3. Possible decomposition pathways of HD and CEES .................................... 23
   3.4. Surrogates of Mustard Gas ....................................................................... 24

4. Current situation of protection against CWAs ............................................. 25

   4.1. Whetlerites: the improved military activated carbon ................................... 25
   4.2. Research on new adsorption materials ....................................................... 26

**CHAPTER 2. Objectives and research approach** ............................................ 29

1. Background ................................................................................................. 29

   1.1. Metal (hyd)oxides ..................................................................................... 29
   1.2. Zinc hydroxide ......................................................................................... 29
   1.3. Zirconium hydroxide ............................................................................... 30
   1.4. Graphite oxide ......................................................................................... 31
   1.5. Gold and Silver nanoparticles ................................................................. 32
   1.6. Degradation pathways of the mustard gas surrogate, CEES ....................... 34

2. Objectives and research approach ............................................................... 35

**CHAPTER 3. Materials and Methods** ......................................................... 39

1. Materials .................................................................................................... 39

   1.1. Zinc hydroxides ....................................................................................... 39
   1.2. Zinc oxides ............................................................................................. 39
   1.3. Zirconium hydroxide ............................................................................... 40
   1.4. Graphite Oxide (GO) .............................................................................. 40
   1.5. Gold nanoparticles (AuNPs) ..................................................................... 41
   1.6. Silver nanoparticles (AgNPs) ................................................................... 42
   1.7. Composites of zinc hydroxide and GO ..................................................... 42
   1.8. Composites of zinc hydroxide, GO and AuNPs .......................................... 43
   1.9. Composites of zinc hydroxide, GO and AgNPs ........................................... 43
   1.10. Composites of zirconium hydroxide and GO .......................................... 44
CHAPTER 4. Zinc (hydr)oxide based multi-composites ...........................................................................51

4.1. One-pot wet precipitation of zinc (hydr)oxide .............................................................................52

4.1.1. The role of the base addition rate ..............................................................................................52
4.1.2. Structural and morphological characterization .........................................................................52
4.1.3. The influence of the pH ...........................................................................................................58
4.1.4. Conclusion .................................................................................................................................59
4.2. Zn(OH)₂ vs ZnO: The key role of the hydroxyl groups .................................................................60

4.2.1. Introduction and materials ........................................................................................................60
4.2.2. Structural, chemical and optical characterizations ...................................................................60
4.2.3. Adsorption performance: the role of the visible light irradiation ............................................69
4.2.4. Role of the textural parameters .................................................................................................70
4.2.5. Role of the surface chemistry ....................................................................................................71
4.2.6. Characterization of the exhausted samples ..............................................................................72
4.2.7. Analysis of the extracts .............................................................................................................77
4.2.8. Adsorption mechanism .............................................................................................................78
4.2.9. Conclusions ...............................................................................................................................80

4.3. Effect of GO phase in Zn(OH)₂/GO composites on the extent of photocatalytic reactive adsorption 82

4.3.1. Introduction and materials ........................................................................................................82
4.3.2. Structural and morphological characterizations .......................................................................82
4.3.3. Surface chemistry analysis .......................................................................................................85
4.3.4. Adsorption performance and the optimum amount of GO.........................................................87
4.3.5. Role of the textural parameters .................................................................................................89
4.3.6. Role of the surface chemistry ....................................................................................................90
4.3.7. Study of the kinetics and the maximum detoxification performance .........................................91
4.3.8. Surface chemistry analysis of the exhausted samples ...............................................................93
4.3.9. Identification of the retained on the surface reaction products .................................................97
4.3.10. Identification of the volatile products in the headspace .........................................................100
4.3.11. Detoxification and adsorption mechanisms ............................................................................105
4.3.12. Conclusions ............................................................................................................................109

4.4. AuNPs and AgNPs embedded in nanostructured composites of zinc (hydr)oxide/GO ............111

4.4.1. Materials and Objectives ........................................................................................................111
4.4.2. Structural and morphological characterizations .....................................................................111
5.1. Effect of GO phase in Zr(OH)$_4$/GO composites on the extent of catalytic reactive adsorption.... 135
  5.1.1. Materials and Objectives .................................................................................. 135
  5.1.2. Structural and morphological characterizations .................................................. 135
  5.1.3. Surface chemistry analysis .............................................................................. 140
  5.1.4. Role of the textural parameters and surface chemistry .................................... 144
  5.1.5. Characterizations of the exhausted samples ...................................................... 145
  5.1.6. Evaluation of the detoxification performance ................................................... 152
  5.1.7. Identification of the volatile products in the headspace .................................. 154
  5.1.8. Identification of the surface reaction products retained on the surface ............ 157
  5.1.9. Detoxification mechanism .............................................................................. 158
  5.1.10. Conclusions ................................................................................................... 159

5.2. AgNPs embedded in zirconium hydroxide/GO composites ........................................ 160
  5.2.1. Materials and Objectives ................................................................................ 160
  5.2.2. Structural and morphological characterization .................................................. 161
  5.2.3. Surface chemistry analysis .............................................................................. 166
  5.2.4. Optical features – plasmon effect ..................................................................... 169
  5.2.5. Role of the textural parameters and surface chemistry on the adsorption ......... 170
  5.2.6. Analysis of the weight uptake ........................................................................ 172
  5.1.7. Identification of the volatile products in the headspace .................................. 173
  5.1.8. Identification of the reaction products retained on the surface ......................... 175
  5.1.9. Conclusions ................................................................................................... 177

CHAPTER 6. Conclusions .................................................................................................... 178

CHAPTER 7. Paths toward future research ...................................................................... 184

Appendix .......................................................................................................................... 186

Fritz Haber: The man behind the Mustard Gas ................................................................. 186

Bibliography ...................................................................................................................... 188
Sub-chapters 4.1, 4.2 and 4.3 are partially included with permission from Elsevier results reported in the follow publications (Ref. 91 and 161):

D. A. Giannakoudakis, J. A. Arcibar-Orozco and T. J. Bandosz,
Key role of terminal hydroxyl groups and visible light in the reactive adsorption/catalytic conversion of mustard gas surrogate on zinc (hydr)oxides, Applied Catalysis B, 2015, 174, 96-104

D. A. Giannakoudakis, J. A. Arcibar-Orozco, T. J. Bandosz,
Effect of GO phase in Zn(OH)₂/GO composite on the extent of photocatalytic reactive adsorption of mustard gas surrogate, Applied Catalysis B, 2016, 183, 37-46

Sub-chapter 5.1 is reproduced from Ref. 113 with permission from the Royal Society of Chemistry:

D. A. Giannakoudakis, J. K. Mitchell and T. J. Bandosz,

“I fear it will produce a tremendous scandal in the world...The higher civilization rises, the viler man becomes”, One German general wrote to his wife during WWI.
LIST OF FIGURES

(in parenthesis the page numbers)

Chapter 1.

Figure 1.2.1. Photo from a deployment of chlorine. (6)

Figure 1.2.2. Poster of Chlorpnicrin. (7)

Figure 1.2.3. Phosgene Poster used during WWI. (8)

Figure 1.2.4. Poster used during WWI. (9)

Figure 1.2.5. The predominant Chemical Warfare Agents used from the German army in World War I based on a chronological order. (10)

Figure 1.2.6. Percentages of casualties by country, out of the around 1,131,000 total recorded gas casualties (A), and the deaths per country (B) from the CWAs. (11)

Figure 1.2.7. Soldiers using Helmets during WWI. (14)

Figure 1.2.8. The chronicle of the gas masks development used until 1917. (19)

Figure 1.3.1. bis(2-chloroethyl) sulfide, known as mustard gas (molecular weight 159.07). (20)

Figure 1.3.2. Blisters caused from mustard gas. (21)

Figure 1.3.3. Detoxification pathways of HD (with asterisk the toxic compounds). (24)

Figure 1.3.4. 2-chloroethyl ethyl sulfide (CEES), known as half mustard gas (Mw: 124.63). (25)

Chapter 2.

Figure 2.1.1. Detoxification pathways of CEES reported in the literature (with asterisk the toxic compounds). (35)

Chapter 3.

Figure 3.1.1. The received graphite oxide. (41)

Figure 3.1.2. The initial tetrachloroaurieic (III) acid solution and the final colloid suspension of AuNPs. (41)
Figure 3.1.3. Details about the AgNPs, as received from NANOGAP SUB-NM-POWDER. (42)

Figure 3.2.1. A schematic representation of the used Vials-in-Vial adsorption system. (45)

Figure 3.2.2. Formation of hydroxyl terephthalate (HTA) from terephthalate (TA). (47)

Chapter 4.

Figure 4.1.1. JCPDS standard diffraction patterns for orthorhombic $\gamma$-Zn(OH)$_2$, orthorhombic $\varepsilon$-Zn(OH)$_2$ (wülfingite) and hexagonal ZnO (würtzite). (53)

Figure 4.1.2. The X-ray diffractograms of the sample obtained with a controlled addition of the base and the one prepared with a rate of 2mL/min and further thermally treated at 95 ± 5 °C for one hour. (54)

Figure 4.1.3. SEM images of the sample obtained with a controlled addition of the base. (55)

Figure 4.1.4. The X-ray diffractograms of the sample obtained with a rapid addition of the base and aged for various periods. (56)

Figure 4.1.5. SEM images of the sample obtained with a rapid addition of the base and aged for various periods of time. (57)

Figure 4.1.6. Schematic representation of the possible reaction pathways for the formation of Zn(OH)$_2$ and ZnO. (59)

Figure 4.2.1. X-ray diffraction patterns for the initial samples. (61)

Figure 4.2.2. Comparison of the porous structure parameters calculated from the nitrogen adsorption isotherms. (62)

Figure 4.2.3. The nitrogen adsorption isotherms. (63)

Figure 4.2.4. SEM images of ZnSA (A, B), ZnRA (C, D) and ZnO-C (E, F). Red (false) color the $\varepsilon$-Zn(OH)$_2$ particles and blue (false) color- the ZnO nano-flower like particles. (64)

Figure 4.2.5. FTIR spectra for the ZnSA, ZnRA and ZnO-C samples. (66)

Figure 4.2.6. pK$_a$ distributions for the samples studied. (67)

Figure 4.2.7. A) UV-Vis-NIR spectra of the samples, B) $[F(R_{\infty})hv]^2$ versus photon energy. The lines show the cut-off used to calculate the band gap energy. (68)
Figure 4.2.8. Adsorption capacities measured under the light exposure from a solar simulator and in dark. (69)

Figure 4.2.9. Dependence of the amount adsorbed on the surface area (left) and the total pore volume (right) under the light exposure and in dark. (71)

Figure 4.2.10. Dependence of the amount adsorbed on the terminal groups (left) and the bridging groups (right) under light exposure and in dark. (72)

Figure 4.2.11. DTG curves in helium for initial and exhausted under light irradiation ZnSA, ZnRA and ZnO-C. (74)

Figure 4.2.12. m/z thermal profiles (in helium) for the fragments related to CEES, EES and/or HEES (a) and EVS (b) for the exhausted ZnSA under light (L) and in dark (D) and for the ZnO-C under light (L). (76)

Figure 4.2.13. Proposed reactions scheme of CEES reactive adsorption upon the visible light exposure. (80)

Figure 4.3.1. X-ray diffraction patterns for GO and the initial samples. (83)

Figure 4.3.2. SEM images of ZnOH (A), ZnGO5 (B) and ZnGO10 (C). (84)

Figure 4.3.3. Parameters of porous structure calculated from the nitrogen adsorption isotherms. (85)

Figure 4.3.4. Amounts of terminal and bridging oxygen containing groups detected from potentiometric titration experiments. (86)

Figure 4.3.5. Capacities measured after 24 hours at various conditions exposure (ambient visible light, solar light simulator, in dark). (88)

Figure 4.3.6. Dependence of the amount adsorbed (after 24 h) on the surface area (A) and the total pore volume (B) under light exposure and in dark. (89)

Figure 4.3.7. Dependence of the amount adsorbed (after 24 h) on the number of the terminal OH groups (A) and the bridging groups (B) under light exposure and in dark. (90)
Figure 4.3.8. Weight gains measured at visible light for up to nine days. The change in the slopes of lines indicates the change in the chemistry/physics of the interface (condensation of adsorbents on the surface and saturation). (92)

Figure 4.3.9. FTIR spectra for the initial and exhausted ZnOH and composite samples after day 7 of CEES exposure (L7). (95)

Figure 4.3.10. TA and DTG curves for the initial, after 1-day (L1) and after 7 days (L7) exposure to CEES vapors in visible light for ZnOH and ZnGO10. (99)

Figure 4.3.11. Exhausted ZnGO10 L7 composite before TA analysis (A) and afterwards (B). For comparison, the exhausted ZnOH L7 before (C) and after TA analysis (D). (100)

Figure 4.3.12. Chromatograms of the headspace for ZnOH and ZnGO10 after 6 days of CEES exposure. (102)

Figure 4.3.13. Tracking of the progress of adsorption and reactions by monitoring the chromatograms of ZnGO10 for up to 9 days. (104)

Figure 4.3.14. Dependence of the area of the chromatographic peak (analysis of the headspace) for the particular compounds on the exposure time for ZnGO10. (105)

Figure 4.3.15. Schematic representation of the radical reactions. (108)

Figure 4.3.16. Schematic representation of all interactions inside the closed vessel. (108)

Figure 4.4.1. X-ray diffraction patterns for the initial samples. (112)

Figure 4.4.2. SEM images of ZnGO (A), AuZnGO (B-C) and AgZnGO (D-F). (114)

Figure 4.4.3. Proposed mechanism of AuZnGO and AgZnGO formation. (115)

Figure 4.4.4. TEM and HRTEM images for AgZnGO and AuZnGO composites. (116)

Figure 4.4.5. The nitrogen adsorption isotherm. (117)

Figure 4.4.6. Pore size distribution calculate using the BJH model. (118)

Figure 4.4.7. Parameters of porous structure calculated from the nitrogen adsorption isotherms. (119)

Figure 4.4.8. Amounts of terminal and bridging oxygen containing groups detected by potentiometric titration experiments. (120)
Figure 4.4.9. EDS elemental mapping of AuZnGO and AgZnGO. (121)

Figure 4.4.10. The analysis of the changes in the intensity of the emission at 425 nm (formation kinetics of THA) with an increase in the experimental time under ambient light irradiation. (122)

Figure 4.4.11. Mass uptakes/adsorption capacities measured at visible light for up to ten days. (123)

Figure 4.4.12. Mass uptakes/adsorption capacities measured at visible light for up to ten days of CEES exposure. (125)

Figure 4.4.13. Analysis of the chromatograms at specific retention time ranges. (126)

Figure 4.4.14. Arbitrarily classification of the detected volatile compounds in the headspace. (127)

Figure 4.4.15. Dependence of the area of the chromatographic peak (analysis of the headspace) for the particular compounds on the exposure time under light irradiation. (129)

Figure 4.4.16. The proposed reactions that take place during the CEES reactive adsorption process. (131)

Chapter 5.

Figure 5.1.1. X-ray diffraction patterns for the initial samples. (136)

Figure 5.1.2. A) nitrogen adsorption isotherms; B) comparison of the measured and hypothetical surface areas; C) micro and mesopores volumes, and C) pore size distributions. (138)

Figure 5.1.3. SEM images of the samples’ morphology. (139)

Figure 5.1.4. Amounts of bridging and terminal groups measured by potentiometric titration. (141)

Figure 5.1.5. DTG curves measured in helium for the initial samples (A), and a stereo-view of the dehydration of the hydrated zirconium hydroxide (B). (142)

Figure 5.1.6. Weight gains for all the tested materials. (144)

Figure 5.1.7. Dependence of the weight gain on the surface area (A), terminal groups (B) and the mesopore volume (C) for 24 hours of CEES exposure. (145)

Figure 5.1.8. FTIR spectra of the initial and exhausted (-E) samples. (147)

Figure 5.1.9. DTG curves in helium for the exhausted samples. (148)
Figure 5.1.10. m/z thermal profiles (in helium) of exhausted ZrOH for the fragments related to CEES, BETE, HEES and/or EES (A), EVS (B), DEDS and/or BDT (C) and to SO2 (m/z: 64), Cl m/z: (35), -OH (m/z: 17), CH3+ (m/z: 15) and C (m/z: 12). (151)

Figure 5.1.11. Weight uptakes measured up to 60 hours of CEES exposure. (152)

Figure 5.1.12. Dependence of the maximum weight gain on the surface area (A), terminal groups (B) and the mesopore volume (C) for 48 hours of CEES exposure. (153)

Figure 5.1.13. Chromatograms of the headspace for ZrOH and ZrGO5 after 48 hours of CEES exposure (A) and dependence of the area of the chromatographic peak (analysis of the headspace) of EVS (B) and BETE (C) on the exposure time. (155)

Figure 5.1.14. Dehydrohalogenation of CEES to EVS by an intermediate cyclic sulfonium cation. (156)

Figure 5.1.15. Proposed reactions scheme of CEES reactive adsorption mechanism. (159)

Figure 5.2.1. X-ray diffraction patterns for the initial samples. (161)

Figure 5.2.2. Nitrogen adsorption isotherms for all the samples. (162)

Figure 5.2.3. Pore size distribution for all samples. (163)

Figure 5.2.4. SEM images of AgZrOH and AgZrGO. (165)

Figure 5.2.5. EDX maps of AgZrGO. (166)

Figure 5.2.6. Amounts of bridging and terminal groups detected using the potentiometric titration experiments (A) and the density of the terminal groups per surface area (B). (167)

Figure 5.2.7. Differential thermal gravimetric (DTG) curves measured in helium for the initial samples. (168)

Figure 5.2.8. Photoluminescent spectra of the studied samples. (170)

Figure 5.2.9. Weight uptake of ZrOH, AgZrOH, ZrGO, and AgZrGO after 24 hours of exposure to CEES vapors. (171)

Figure 5.2.10. Dependence of the amount adsorbed on density of the terminal groups and on the mesopores volume for 24 hours of CEES exposure. (172)

Figure 5.2.11. Weight uptakes measured up to 60 hours of CEES exposure. (173)
Figure 5.2.12. Dependence of the areas of the chromatographic peaks related to EVS and BETE on the exposure time. (174)

Figure 5.2.13. DTG curves in helium for the exhausted samples. (175)

Figure 5.2.14. m/z thermal profiles (in helium) of exhausted AgZrGO for the fragments related to fragments of EES (m/z: 90), EVS (m/z: 88), Cl (m/z: 35), SO₂ (m/z: 64), C (m/z: 12), and -OH (m/z: 17). (176)

Chapter 6.

Figure 6.1. Weight uptakes after exposure to CEES at the same conditions on commercial zinc oxide nanoparticles (ZnO-C), zinc hydroxide (Zn(OH)₂), zirconium hydroxide (Zr(OH)₄), ferrihydrite (FeOOH), cerium oxide (CeO₂), magnesium oxide (MgO), activated carbon (act. carbon), and graphitic carbon nitride (g-C₃N₄). (178)

Figure 6.2. Weight uptakes of the Zn and Zn hydroxides and theirs composites with graphite oxide or graphite oxide and AgNPs. (181)

Figure 6.3. The formed products during the adsorption on AgZnGO, AuZnGO and AgZrGO. (183)
Table 1.4.1. Highlighted studies on the HD and/or CEES removal on different materials. (28)

Table 4.2.1. Details on the detected compounds on the surface. (75)

Table 4.3.1. Assignment of bands detected on FTIR spectra of ZnOH and ZnGO10 exposed to CEES. (97)

Table 4.3.2. Details on the detected compounds on the surface and in the headspace. (98)

Table 4.4.1. Details on the detected compounds in the headspace. (126)

Table 5.1.1. Details on the detected compounds on the surface and in the headspace. (149)

Table 5.2.1. Parameters of porous structure calculated from the N\textsubscript{2} isotherms. (163)

Table 5.2.2. Weight lost % at 125 °C and 450 °C. (168)
Peer-reviewed paper published during the PhD:

15. D. A. Giannakoudakis, M. Florent, R. Wallace, J. Secor, C. Karwacki, T. J. Bandosz, Surface properties of ZnO$_2$/ZnO nanoparticles and their effects on retention of mustard gas surrogate vapors, submitted


13. M. Florent, D. A. Giannakoudakis, R. Wallace, T. J. Bandosz, Mixed CuFe and ZnFe (hydr)oxides as chemical warfare agents surrogate reactive adsorbents, submitted

12. D. A. Giannakoudakis, N. A. Travlou, J. Secor, T. J. Bandosz, Oxidized g-C3N4 nanospheres as catalytically photoactive linkers in MOF/g-C3N4 composite of hierarchical pore structure, *Small, 2016*, 13, 1601758


4. J. A. Arcibar-Orozco, D. A. Giannakoudakis, T. J. Bandosz, Copper Hydroxyl Nitrate/Graphite Oxide Composite as Superoxidant for the Decomposition/Mineralization of Organophosphate-Based Chemical Warfare Agent Surrogate, *Advanced Materials Interfaces, 2015*, 2, 1-9


CHAPTER 1. Introduction

1.1. Chemical Warfare Agents (CWAs)

1.1.1. The history of Chemical Warfare Agents

The extended usage of chemicals as weapons dates since classical times, when lighting of bonfires, irritant smokes and several compositions of pitch, petroleum and sulfur (Greek fire) gave a significant advancement for mass troop eliminations. Even ancient history indicates the use of toxic chemicals to defeat enemies. Homer mentioned in his epics (the Iliad and the Odyssey), the use of poisons arrows in Trojan War (around 1200 BCE).\(^4\) Poisonous heart-toxic extracts from hellebore plants were used from Athenian forces in 600 BCE to taint the water supply during the besiege of Kirrha against Spartans.\(^4\) Around 120 years later, Peloponnesian military used sulfur fumes to cause inhabitants to evacuate the city of Plataea.\(^5\) In the middle of the 18\(^{th}\) century (1845), the French troops cornered more than 1000 people into a cave during the conquest of Algeria and executed them using smoke.

The first World War (WWI) brought out a prolonged vast scale usage of chemical warfare agents (CWAs), which can be considered as the saddest reality in a modern history. More than 50 different CWAs were deployed, while above 3000 compounds were investigated as potential weapons.\(^6\) Even though it is believed that the German Army was the first one to use poison gases, that race was in fact opened by the French army which first deployed tear-gas grenades in 1914.\(^7\) Since that time, the active involvement of chemistry in the war had begun. Many compounds were afterwards tested in the battlefields as CWAs. Most CWA related injuries and deaths during WWI were linked to three toxic compounds: chlorine, phosgene and sulfur mustard. At the beginning of
WWI, the German military established research centers to develop chemicals as weapons of mass
destruction. Many recognized scientists were involved in the synthesis of CWAs. That list includes
Nobel Prize laureates such as Max Planck (Physic, 1918), Fritz Haber (Chemistry, 1918), Wulther
Nernst (Chemistry, 1920), James Franck (Physic, 1925), Gustac Hertz (Physic, 1925), and Otto
Hahn (Chemistry, 1944). The allied Forces did not stay behind and they also started extensive
research on the development of CWAs, as well as on protection media, basically on gas masks. As
Daniel Charles pointed out in his book, “A new era had dawned in the uses of chemistry”.

1.1.2. International agreements against CWAs

1675 was a year when German and France signed in Strasbourg the first international agreement
that prohibited the use of poison bullets. In 1874, the Brussels Convention on the Law and
Customs of War banned the employment of poison or poisoned weapons, and the use of arms,
projectiles or material to cause unnecessary suffering. In 1899, during an international peace
conference in Hague, another agreement was signed, which prohibited the use of projectiles filled
with poisonous gas. These agreements proved to be pointless, since during the World War I, toxic
gases were used on a massive scale, leading to more than one million of casualties, and more than
one hundred thousand fatalities. International efforts to forbid the usage of chemical weapons
(CWs) resulted in a renewed global commitment, the 1925 Geneva Protocol.

Although the deployment of asphyxiating, poisonous or other gases, and bacteriological methods
of Warfare was banned, this commitment did not prohibit the development, production or
possession of CWAs. It is believed that the Geneva protocol played a crucial role during World
War II (WWII) during which CWAs were not used, fortunately. It happened in spite of the fact
that almost all the involved countries had stockpiled numerous toxic compounds, ready to be used. It is believed that Hitler, as a victim of the first mustard gas deployment during WWI, was against the usage of CWAs in battlefields. Nevertheless, it has to be mentioned here that German SS massacred millions in the extermination camps using the toxic pesticide, Zyklon B (silica adsorbed cyanide).

The latest agreement was signed in 1993 at the Chemical Weapons Convention (CWC). This international treaty outlaws the production, stockpiling and deployment of chemical weapons. The convention’s full title is “Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction”. An independent Organisation for the Prohibition of Chemical Weapons (OPCW), established in Hague, is responsible for the enforcement of this agreement. OPCW Mission states: “The mission of the OPCW is to implement the provisions of the Chemical Weapons Convention (CWC) in order to achieve the OPCW’s vision of a world free of chemical weapons and the threat of their use, with the cooperation of chemistry for peaceful purposes. In order this vision to be accomplished, our ultimate aim is to contribute to international security and stability, to general and complete disarmament, and to global economic development.”

Today, 192 OPCW members represent about 98 % of the global population, landmass and worldwide chemical industry. According to OPCW, 92 % of the 72,525 metric tones stockpiled CWAs have been verified to be destroyed by June 2016. In recognition of this effort to eliminate CWAs, OPCW was awarded the Nobel Peace Prize in 2013.
1.1.3. Classification of Chemical Warfare Agents.

Chemical Warfare Agents (CWAs) can be conceded the most brutal weapons among all the Weapons of Mass Destruction. According to OPCW: "The term chemical weapon may also be applied to any toxic chemical or its precursor that can cause death, injury, temporary incapacitation or sensory irritation through its chemical action. Munitions or other delivery devices designed to deliver chemical weapons, whether filled or unfilled, are also considered weapons themselves."\(^{10}\)

CWAs can be classified in various ways. From the point of a chemical structure, the main categories are organosulfur, organofluorine, organophosphorus, and arsenical compounds. They can be also categorized based on their volatility. Phosgene, hydrogen cyanide and chlorine are volatile agents, while sulfur mustard and most of the nerve agents are less volatile. The most common classification is in terms of the effects on humans.\(^{11}\) Based on that, the categories of CWAs are as follows:

- Riot-control agents (tear gases)
- Vesicants (blistering agents)
- Nerve agents
- Bloods agents (cyanogenic agents)
- Choking agents (pulmonary agents)
- Psychomimetic agents
- Toxins
1.2. World War I: Militarization of chemistry

1.2.1. The chronicle of the vast scale usage of CWAs: The road to Mustard gas

The opening act of the toxic gases deployment took place at the early months of WWI, when the French army fired tear gas grenades (filled with ethyl bromoacetate) against the Germans soldiers (August 1914). These grenades were manufactured prior to the war and first used in 1912 by French police, in order to crush a riot in Paris. Following the recommendation of Walter Nernst, the German forces filled shells with dianisidine chlorosulfonate, which was readily available due to its extensive use as an intermediate in the synthetic dye industry. Around 300 filled shells were fired against the British army from the Germans at the capture of Neuve Chapelle in France on October 27, 1914, but without any effect except of a violent fit of sneezing. In December 1914, benzyl bromides were also tried. These incidents of failure served to permanently change the course of war. A chemist, who participated in the war without any military rank, became inspired and dedicated himself to apply this novel aspect of chemistry in the battlefields. His name was Fritz Haber. He played a critical role in persuading the German generals to start the development of toxic gases for mass scale usage as a weapon and use them in the actual battles.

Three months later, the German forces fired more than 18,000 "T-shells" containing liquefied tear gas, xylyl bromide, on the Eastern Front during the battle of Bolimów (31 January 1915). All three isomers of Xylyl bromide or methyl benzyl bromide (C8H9Br) are highly toxic and irritant, and they are still used. Due to the extreme low temperature in Bolimów, the liquid failed to vaporize and the attack proved to be a complete failure. Similar unsuccessful attacks with improved tear gas mixtures were carried out against the French army in March 1915 at Nieuwpoort in Belgium.
Because of the simplicity of the xylyl bromide production, it was widely used by Germans during the war as a component of the white cross mixture (Weisskreuz) in the artillery shells. Other chemical compounds were also applied in shells and grenades as tear gases, among them chloromethylchloroformate and bromoacetone. For mass production of these shells specialized factories were built. The main drawback was that the transportation to the battlefields was difficult and time consuming. The shell shortage in many occasions revealed the necessity of an alternative practice of the chemicals.

Haber’s suggestion to use gas from pressurized tanks as CWAs, instead of using them merely in the shells was approved by Germans Generals in January 1915. His fast efforts led to around 5700 cylinders containing more than 340 tons of chlorine stocked by April 11 of that year.\textsuperscript{15} The German army was waiting for a suitable speed and orientation of the wind in order to launch the chlorine attack. On 22\textsuperscript{nd} of April 1915, the first deployment of chlorine as weaponry gas began a reality at the second battle in Ypres. The consequences of a greenish-yellow chlorine cloud were more than 1100 dead and 7000 injured soldiers. The Allied troops fled in disorder, and the German infantry easily advanced and conquered the French trenches. This act rose the moral of the German troops and Haber was promoted from a Sergeant of the reserves to a Captain.

He concluded that those toxic clouds can be more beneficial since they not only lead to asphyxiation, but to a total depletion of the enemies’ front lines. His confidence that chemistry can have an active involvement in the war as an effective weapon, changed once for good the path of...
war. The British were the first from the Allied forces that tried to respond on September 24th, 1915 with a chemical gas attack. Unfortunately, the first deployment of a mixture of smoke and chlorine gas from around 400 gas tanks, in the front line at Loos in France, led to an unexpected effect, since the wind shifted and the gases were blown to the opposite direction, resulting in more British casualties than German ones.\textsuperscript{12}

The use of pure chlorine was gradually abandoned, but it was widely used in mixtures with phosgene and chloropicrin.\textsuperscript{16} The latter, also called trichloronitromethane, $\text{CCl}_3\text{NO}_2$) was introduced as a chemical weapon by Russian forces in August 1916. The British used a mixture of chloropicrin with chlorine (30:70), called Yellow Star gas.\textsuperscript{6} Chloropicrin is an eye irritant, which had the ability to penetrate earliest gas masks, forcing the soldiers to remove the masks. The development of filters from charcoal eliminated the chloropicrin effects.

A more lethal combination of chlorine with a 5 \% choking agent, phosgene, was widely used by the German army against the Russian army of the Eastern front and against the French troops on the Western front by the end of May 1915. The same mixture was also used on June 12 and July 6, 1915 in Bolimów and in October against the French army. The casualties of the latter usage were huge, since the French soldiers were totally unprotected against phosgene. Phosgene or carbonyl dichloride (COCl\textsubscript{2}) was synthesized by John Davy in 1812 and it is considered as one of the most dangerous existing CWAs. He named it from the combination of the Greek words "phos" (meaning light) and "genesis" (meaning birth), since sunlight exposure was mandatory for the synthesis from a mixture of chlorine and carbon monoxide.\textsuperscript{17} The use of poison gas mixtures of chlorine with higher amount of phosgene (25 \%), was successfully introduced to the battlefields
by the German army, six days before Christmas of 1915. It led to 120 death and more than 1000 injured British soldiers. Even though the amount of the gases deployed at this battle was significantly greater than the one against the French in October, the casualties were lower, since the British were equipped with gas masks.

Phosgene was by far the deadliest CWAs used during WWI. It is 10 times more toxic than chlorine, volatile above 8 °C and has almost 4 times higher vapor density than air. From the estimated 100,000 recorded fatalities from poisonous gases, 85 % were attributed to it. Most of the times it was applied with chlorine in order to improve the spread of the denser phosgene. The major advantage compared to chlorine was the difficulty to be sensed by the victims since its vapors are colorless and have the smell of freshly cut grass. The first symptoms such as a burning sensation of a throat, watery eyes, and nausea appear gradually after 15 minutes. Survival rates are very low, due to the occurrence of the aggressively disruption of the blood-air barrier in the lungs. After 24 hours, the tinged liquid formed in the lungs or the low blood pressure results in death. In addition, contact with the skin leads to blisters.

Carbonyl dichloride is an important chemical for the industrial manufacturing of dyes, pigments, plastics and pesticides. It is used up today. The largest German industrial companies, such as BASF and Bayer, were producing phosgene prior to WWI, but its application as CWA is attributed to Fritz Haber, although, the first introduction of phosgene to the battlefields in a small scale was by the French army. The French Nobel laureate Victor Grignard synthesized it.
Both sides developed distinct masks in order to neutralize phosgene, a few months after its first deployment. As a response to the gas masks, the German army developed another CWA, diphosgene (DP, ClCO$_2$CCl$_3$), that is related to phosgene, with comparable toxicity and with the ability to pass through or to destroy the filters used in the first gas masks. The first documented use of diphosgene was in the artillery shells on the Western Front in May 1916.$^{15}$

The next applied CWA, Mustard gas, made its debut in a gas cloud attack on allied troops near Ypres in 12$^{th}$ of July in 1917. It was the most effective and widely used gas of WWI, since it was broadly used in huge quantities to harass and disable the defense trenches before the attacks. The consequences of nearly 6000 cylinders during the first deployment were more than 2200 casualties. Initially, Germans planned to use this gas only as a paralyzing and blister agent. However, they soon realized that in sufficient doses, it could be lethal for the enemy soldiers. The fatally exposed victims confronted extreme pain and sometimes were afflicted for up to five weeks before finally passed away. The first aid camps were fully occupied for months with mustard gas exposed soldiers and civilians. More than a million tons of HD, placed in artillery shells, were launched the following month at the battle at Ypres. Besides, mustard gas was deployed by various means, even by spraying from warplanes. This effective CWA elevated the moral of the German forces. The shells that contained mustard gas were marked yellow, compared to the green marked shells contained chlorine and phosgene. The yellow assignment came as a result of the yellow-brown color of impure gas clouds. Although not as lethal as other used CWAs, the devastating consequences of the extremely painful blisters, the internal and external bleeding of the victims, the difficulties to manufacture effective protection media and the contamination of

![Figure 1.2.4. Poster used during WWI.](image)
the soil for a long period of time shocked the world and attracted the worldwide attention. Mustard gas was established as the King of the battle gases and became the most popular CWA.

Figure 1.2.5. The predominant Chemical Warfare Agents used from the German army in World War I based on a chronological order.

1.2.2. **Casualties and Fatalities from CWAs in WWI**

There are various estimations about the number of casualties and deaths caused by CWAs and it is impossible to accurately calculate the victims. The main reason is the lack of precise records,
since not all the casualties were recorded, or they were initially recorded as “other factors”. Moreover, not all the countries released records. From the existing data, the total casualties exceeded one million, while the fatalities reached almost one hundred thousand (Figure 1.2.2). Russia suffered the highest number of casualties and deaths, since the soldiers were totally unprepared during the first gas attacks. Phosgene was responsible for the most deaths, while mustard gas contributed dramatically to the casualties’ number increase. Only 5% of those exposed to mustard gas were killed. As the war was progressed, the number of the casualties decreased because of the gas masks development.

Fritz Haber was in favor of CWAs until his death. In 1919 he stated: “Chemical warfare is certainly no more horrible than flying pieces of steel; on the other hand, the mortality from gas injuries is smaller”. And from the casualties’ point of view, he was correct. Less than 1% of the total fatalities during WWI were from poisonous gases.21

Figure 1.2.6. Percentages of casualties by country, out of the around 1,131,000 total recorded gas casualties (A), and the deaths per country (B) from the CWAs.22
1.2.3. *The primarily protection attempts: pads, helmets and Gas Masks*

The German Empire had many advantages at the beginning of WWI. Besides the foundation of special research groups on the toxic gases development, they had access to activated charcoal with an extremely high surface area, in addition to the light and porous sedimentary mineral, *Diatomit*. The combination of these two materials was used as the first filler placed in the metal drum of the gas masks, Gumminaske. *Diatomit* impregnated with potash solution was effective against chlorine, while activated charcoal against various organic compounds. This filter had the code name “26/8”, possible from the date of its establishment as the main canister. Starting in September 1915 and by the end of that year, almost all the German soldiers at the front lines were equipped with gas masks. Professor of Chemistry at the University of Berlin and Director of the Kaiser Wilhelm Institute for Chemistry, Richard Willstätter, together with the chairman of Bayer Leverkusen dyeworks, Carl Duisberg, established a procedure to produce granules of the above combination of these two materials.\(^{15}\) Richard Willstätter was called by Fritz Haber in 1915 to participate in the development of new toxic gases, but Willstätter agreed to get involved only in the development of new protection media. Willstätter was a Nobel laureate in chemistry in 1915, for his researches on plant pigments, especially chlorophyll.\(^{23}\)

The beginning of the phosgene deployment from the Allied forces raised the need of a more efficient filter for phosgene that would be based on the physical adsorption of organic gases/vapors. The upgraded metal drum version, “11/11”, had three layers. The outer layer was the same mixture used in the version 26/8. The middle layer consisted of charcoal granules for the adsorption of phosgene and other organic toxic gases, while the last layer was again *Diatomit*,
impregnated in this case with hexamine and potash. This version was applied in battlefields from April 1916. In order to further increase the efficiency and to add protection against chloropicrin used by British, an updated filter drum, with the code name 11-C-11, was introduced in June 1917. More charcoal was used in this filter. Another possible reason for the development of this filter was a potential usage of mustard gas. In the later "Lederschutzmaske" (Leather protection mask) model M1917, waterproof leather embedded in oil was used instead of rubber, with glass disc-shaped eyepieces. The M1917 model introduced in August 1917. The metal filter canister was removable, but no intake or exhaust valves were used.

The first vast scaled chlorine gas attack caught the Allies completely unprepared. Afterwards, a great effort was made to manufacture protection masks. The first home-made attempt was the usage of cotton wool mouth pads, wetted with a neutralizing solutions (urine or bicarbonate soda). The British named this respiratory Daily Mail. It was used at the chlorine attack on May 1st, 1915. Sadly, it was almost completely useless, because the wetted pads resulted to a completely airtight mass with difficulties in breathing. In the updated version, a pad of cotton waste has been used instead of cotton wool in order to avoid the breathing problems. This pad was soaked with a mixture (hyposulphite, glycerine, sodium carbonate and water), which can chemically neutralize chlorine, sulphur dioxide and nitrous fumes. This mixture was established after the analysis of a respirator obtained from a German soldier-prisoner. Gauze was used to hold the pad while the ends were plainly knotted around the head. This updated version took the name Black Veiling Respirator, because black mourning gauze was used. Although the breathing problem was solved, with the Black Veiling Respirator, it was difficult to get tied in rush, while its effectiveness lasted only for about 5 minutes. In spite of these limitations, Black Veiling Respirator saved hundreds of lives during the chlorine attack of 24 May 1915, since almost all the British troops were equipped
with one respirator by 20th of May. Moreover, it provided the option to protect the eyes from tear gases by using a part of the veiling to cover the eyes.

The next attempt was inspired by witnessing: a German soldier placing a bag over his head during a gas attack. This new mask was made by an impregnated fabric at the shape of a bag with a rectangular window to provide visibility and had no inlet or exhaust valve. It was easy to put on in rush, since the soldier had only to wear and place the bottom part of the mask into the uniform. It was known as the Hypo Helmet or the British Smoke Hood, since it was impregnated with hypo solution (sodium thiosulphate or hyposulphate and glycerin). The main disadvantage of this early model was that the rectangular window was very fragile. More than 2.5 million units of Hypo Helmet were used between May and September 1915, since it was able to efficiently protect against chlorine for three hours.

Hypo Helmet was displaced by the P Helmet, due to the need of protection against phosgene and hydrogen cyanide (HCN). The letter “P” was from the protection against phosgene. This helmet consisted of two layers of cotton flannelette, to increase the corrosion protection of the single woolen layer, while the window was replaced by two cyclic glass eyepieces. The presence of carbon dioxide from the breath had a negative effect against hydrogen cyanide, and for that reason a valve was applied for the expiration. This type of mask went through numerous stages of development until it was superseded by canister based gas masks, in 1916. P Helmet saved the life of numerous British soldiers at the time.
biggest gas attack with the mixture of chloride and 25 % phosgene on 19th of December, 1915. The helmets were later impregnated with a Phenate-Hexamine solution after a report from Russia for a higher efficiency for absorption of phosgene, hexamine or hexamethylenetetramine (C₆H₁₂N₄). This improved mask was called PH Helmet and from the end of January 1916 it started to replace the P Helmets. In spite of the severe limitations, such as inefficiency in high toxic gas concentrations, poor visibility, vulnerability to the rain and the blisters at the neck, these masks became the most precious asset for the soldiers, encouraging them to stay in the trenches and fight.

The next step in the gas mask development was the Large Box Respirator (LBR), created by the British, trying to overcome the above-mentioned disadvantages of the helmets. Moreover, there was always the fear that the Germans will use new toxic gases. The Allied forces had no knowledge on active charcoal production, which was proven to be very efficient in its application on the Germans’ canisters. First LBRs used a water flask, with three layers of neutralizing agents. The first layer consisted of lime-permanganate granules, the second of small pumice pieces impregnated with sodium sulfate solution, while the third one - charcoal. The filter-flask was connected to the mouth mask via a rubber tube. The fabric used in this mask had been soaked in hexamine-zinc solution and an exhaustion valve was installed. This complex system proved to be bulky to be used by the infantry, difficult for a massive production and very faulty. The upgraded version of LBR was the Small Box Respirator (SBR). The filter system size of the SBR was more compact and lighter, fact which rose the opportunity to be used by the infantry. The lime-permanganate granules were deposited between two layers of charcoal. From August to October 1916, all LBRs were replaced by SBRs.

The French military responded to the tear gases with a pad mask, Tampon P, together with goggles. The first model had one pad impregnated with castor oil and sodium ricinate and it could protect
also against chlorine and bromide. The anticipation of phosgene deployment led to the addition of a second pad impregnated with sodium sulphanilate. This pad was known as Tampon P1. For the protection of the soldiers from HCN that was released by French against the German army, a third pad impregnated with nickel acetate was added leading to a new mask with the code name Tampon P2. The French army used more than 4.5 million Tampon P masks between August and September 1915. These masks were not efficient for high concentrations or for long term usage, since only the part of the pad in front of the mouth was breathable and the chemical were quickly exhausted in this part. The next version of the mask had a cone shaped pad, which was covering both the nose and the mouth. The manufacturing of this Tampon T model allowed almost all the surface of the pad to come in contact with the gases and as a result the time efficiency increased. The first Tampon T masks arrived to the battlefields in the middle of November, 1915. An improved version was produced in January 1916, with a waterproof cover and a redesigned shape for faster usage, the TN model. By the end of February, around one million of T and 6.8 millions of TN models were produced. On the above-mentioned Tampon masks, goggles were a separate part.

The first attempt from the French to combine the pad inside a one-eyepiece-mask that could cover all the face, was M2. The thicker pad could protect against phosgene up to 6 hours and it was introduced to the battlefields in March 1916. The second M2 model had 2 eyepieces and three sizes. It was introduced in April 1916 and it was the main face protection medium for the French soldiers until 1918. The French army provided their soldiers with a more advanced mask with a changeable filter cartridge in the front of the face mask in February 1917. This mask had the code ARS and it was a copy of the German mask "Gummimaske".

The Italian army used the French knowledge to manufacture gas masks. The first mask was made of a thick wad of gauze impregnated with hydroxulfate and carbonate soda solution, and the
googles were worn separately. It was effective only against chlorine. Many different mask versions were developed later and because of their single purpose use they were called monovolente. These masks were abandoned after the disaster at Mount San Michele on 29th June, 1916, where the Austrian army used phosgene. The Italian casualties were more than 2000 soldiers while about 5000 were poisoned.\textsuperscript{25} The first multi-purpose (polivolente) mask was based on the French TN model. The new mask had the same pad based setup and separate goggles, but it offered protection against phosgene. The next polivolente model (Z), called the funnel type, was based on the M2 French mask. It was introduced in January 1917,\textsuperscript{26} and it covered the entire head with a rubber cloth and latter with leather. The inside gauzes presented an improved performance against phosgene, while the goggles were incorporated into the mask. In spite of all alterations, this mask had limited lifetime and inability to protect against newer toxic compounds, such as mustard gas. The polivolente mask models were abandoned and the Italian Army started to be equipped with the British SBR British masks during the battle of Caporetto in 1917 (24 October–19 November).

The Russian casualties and fatalities from the CWAs were the greatest compared to all other nations. The Russian generals assigned the task of the gas mask development to Nikolay Zelinsky, one of the founder of the theory and application of catalysis.\textsuperscript{27} He had reported that ordinary charcoal had a supreme efficiency on the adsorption of organic fumes. Zelinsky had also studied the production of activate carbons by calcination before the war. Even though Zelinsky had designed the filter system of the mask before the first gas attack by German forces, there were many difficulties on its application on a full face mask. After many trials, the engineer Kummant designed a rubber mask. The first model of the Zelinsky-Kummant mask with the code name “Petersburg”, equipped with a round filter hanging from the mask, arrived in battlefields on February 1916, saving the lives of numerous Russian soldiers. The next improved model
“Moscow” had a square shaped filtration system. More than 11 million masks were used in the fields during the WWI. It is worth to mention that most of the modern gas masks use activated carbon as the main desiccant.

The need for a more reliable respirator, which would be based on the adsorption and not on neutralization was clear. Moreover, the increased need for the development of advantageous adsorption materials, that can be applied in various protection medias, rose afterwards the deployment of mustard gas. The ability of this blister agent to penetrate the cloths as well as the skin, and to exist/last even for weeks in trenches, expanded the necessity of the protection also to uniforms, cloves and shoes.

WWI was not only taking place in battlefields, but also in the research laboratories. The militarization of academic and industrial chemistry was a reality. Chemists and engineers became one of the most valuable assets in the armies. The Allied forces were focused on the continuous improvement of gas masks, in order to counteract the Germans’ advantage in the vast scale production of various CWAs. Mustard Gas changed the path of war and revealed that gas masks as a sole protection media against toxic gases were not enough. Moreover, the contamination of the soil and HD stability brought also the necessity of the development of ground detoxification.
Figure 1.2.8. The chronicle of the gas masks development related to the CWAs used until 1917.
1.3. Mustard Gas: The King of CWAs

1.3.1. Mustard Gas: The King of CWAs

The blistering agent (or vesicant) sulfur mustard (HD), also known as mustard gas or Yperite, can be considered as the King of the Battle Gases, since it was the most effective and widely used. It caused the largest number of casualties among all CWAs during WWI. The main component of HD is bis(2-chloroethyl) sulfide (Figure 1.3.1). It was synthesized and characterized in 1860 by a British professor, Frederic Guthrie. Although there are prior reports concerning the synthesis of HD as early as 1822, Guthrie was the first one who experienced and mentioned its irritating properties after its contact with his skin. It took 57 years to realize its high toxicity and its potential for large scale production. This vesicant has a characteristic rotten odor like mustard plants or garlic, hence the name mustard gas. The initial name, before the attack at Ypres, was LOST from the first two letters of the last names of Wilhelm Lommel and Wilhelm Steinkopf, who developed the method for its large scale production for the German army in 1916. Another crucial reason for the extensive use of HD was its relatively simple synthesis from precursors that were available to the German empire at the time of WWI.

![Figure 1.3.1. bis(2-chloroethyl) sulfide, known as mustard gas (molecular weight 159.07).](image)

The name mustard is misleading, since bis(2-chloroethyl) sulfide is a colorless viscous liquid at room temperature (density= 1.2685 g/mL at 25 °C), insoluble in water, with a melting point of 14 °C, while it decomposes before boiling at 218 °C.28 Chemically, it is very stable at ambient
conditions. Interestingly, German munitions, used in the first and second World Wars that were
dug some years ago in Belgium, revealed that the agent barely degraded. The reported colored
clouds were attributed to the use of impure forms, since in almost all the cases HD was utilized as
a mixture. The fumes of HD are 5.5 times heavier than air, with a vapor pressure of 0.106 torr at
25 °C.

HD is highly toxic for humans and animals, similar to phosgene and hydrocyanic acid. The most
toxic route of exposure is inhalation, but it can also penetrate the skin. HD attacks the respiratory
tract, eyes and skin, acting at the firstly as irritant and afterwards as a poison for the body’s cells.
Its toxicity is associated with the ability to alkylate proteins and rapidly penetrate through a membrane
into a living cell, releasing HCl after hydrolysis. The effects of the exposure to HD are revealed
gradually. At the first stage, the agent attacks the skin, eyes and respiratory tract, resulting to blisters.
The most common symptoms, which are appearing even hours after the exposure, are the big blisters of the skin and the bloodshot of the eyes, accompanied by pain. At the second stage, HD attacks the cells of various organs. The victims
suffer from coughing up blood, muscle spasms, vomiting, sneezing, necrosis of the blisters’ spots
and possible blindness after days. If the victims were exposed to a high amount, the symptoms
lead to death within 3 days, caused by heard failure or lung edema. The lethal dose is around 7.5
g of liquid HD for human weight around 160 lbs. The lethality when inhaled in its gaseous form
depends on the exposure length and the concentration. On its first use at Ypres, only 5 % of the
exposed soldiers were finally killed, since the concentration of the mustard gas clouds was low when reached the allied forces.

Mustard gas became a popular CWA also for its property to contaminate enemy trenches. It remains stable in soil and under average weather conditions. The exposed fields are highly toxic for two to three days, while under very cold conditions mustard gas retain its toxicity ability even up to months. In many occasions, it can be mixed with nonvolatile solvents in order to extent the decontamination of the trenches. Another property of HD is that it can easily penetrate through clothing, such that gas masks are not enough. The mixed benefits of spread panic resulting to the breakage of the defense lines, inflicting serious sort and long term injuries, requirement of a full body protection equipment, and the decontamination of the attacked fields for days, established mustard gas as the one of the most used and dangerous CWAs.

1.3.2. *Mustard gas deployment post the WWI*

The deployment of mustard gas was not limited to WWI. Although Italy had signed the Geneva protocol upon the ban of chemical and biological weapons, in 1925, the Italian dictator Benito Mussolini, ordered bombing with mustard gas of the Emperor’s Haile Selassie army in 1935. The Italian forces used HD extensively during their colonial campaign in Abyssinia (Ethiopian Empire) from 1935 to 1936. HD was also used during the North Yemen Civil War (1962-1970) by Egyptian forces against the Yemeni monarch, in order to support a coup. The Iraqi army, under the orders of Saddam Hussein, also used mustard gas bombs against the Kurdish people, in March 1988. Mustard gas remains a standing threat, since it can be easily produced by terrorists. Even after more than 150 years of its discovery and almost 100 years after its first usage, no antidote has been
discovered., since the first step of its activity, alkylation, takes place extremely rapidly.\textsuperscript{10} Some internal injuries can be controlled by medicines. For example, the lung injuries can be treated with bronchodilatory treatment, while the eye injuries can be controlled with antibiotics. Skin injuries, that can be 2\textsuperscript{nd} and 3\textsuperscript{rd} degree chemical burns, can be controlled with soapy water and small amount of bleach (saline solution). A plastic surgery may be necessary after the skin injuries are healed.

1.3.3. \textit{Possible decomposition pathways of HD and CEES}

The most common pathways of HD decomposition are collected in Figure 1.3.2. Hydrolysis and dehydrohalogenation are the foremost desired reaction pathways reported for various neutralizing agents and adsorbents, but both result in the formation of toxic products. Hydrochloric acid forms in both pathways, while hydrolysis forms also thiodiglycol (TG). The formed chloride anion during the reactive adsorption can poison the active centers of the absorbents. The usage of the photoreactive catalyst leads to the formation of molecules with increased molecular weight, as a result of the recombination of the formed radicals. These compounds are not desirable even if they are significantly less toxic. Alternatively, selective partial oxidation leads to the sulfoxide derivatives that are considered as nontoxic, while the sulfone derivatives from the fully oxidation have vesicant properties. For that reason, the retention of the toxic products (HCl and TG) and a selective partial oxidation was, is and will be the ultimate target for developing advance materials for the detoxification of mustard gas.
1.3.4. Surrogates of Mustard Gas

Because of the extremely high toxicity of HD, several analogs-surrogates and derivatives have been used for research studies focused on the development of decontamination technologies. The most commonly used surrogate is the half mustard gas, 2-chloroethyl ethyl sulfide (CEES), which is less toxic than HD. CEES contains the same ClCH₂CH₂S- group as mustard gas does. This moiety is responsible for its toxicity. It has a boiling point of 156 °C, while its density at 25 °C is 1.07 g/mL.
1.4. Current situation of protection against CWAs

1.4.1. Whetlerites: the improved military activated carbon

Immediately after the first vast scale deployment of CWAs in battlefields, the development of protection medias for the soldiers, and predominantly gas mask, became an ultimate research target. The first trials were based on filtration means covering the mouth and nose, impregnated with various solutions that chemically neutralized the toxic compounds. The versatility in CWAs and the fear of a possible deployment of new CWAs led quickly to the development of the “ideal” respiratory system: a full face mask with a canister for the inhalation, which protects simultaneous the respiratory tracks and the eyes. The unique property of the activated carbons to physically adsorb various organic compounds led gradually to its establishment as the main filler of the canister from the Allied. Nevertheless, that development took almost a year after the first chloride attack from the German army. The latter adopted this system for the protection of all soldiers four months after the first vast scaled attack with chlorine in April 1915. Interestingly, a similar gas mask system was designed in 1850 from John Stenhouse at Glasgow, and took long time for its application in battlefields.

At the beginning, the adsorption of the toxic gases was based on physisorption by Van der Waals forces in the highly porous system of the wood charcoal. These carbons have mainly micropores.
with limited number of weakly reactive centers and as a result they did not show so high adsorption capacities for larger toxic molecules. The importance of increasing the adsorption ability of the activated carbons led to the application of impregnated carbons with active substances. In this way, these active impregnants can strongly retain the toxic molecules via chemical bonds, or catalytically decompose them to smaller molecules, which can further get physically adsorbed by the carbon phase. The main drawback is that the adsorption ability of the carbon canisters is directly proportional to the amount of the carbon and its impregnation extent. The first impregnated carbon for military use was developed by J.C. Whetzel and E.W. Fuller and based on their names it was called Whetlerite.\textsuperscript{31} There are numerous different impregnation versions, but nowadays Whetlerites commonly represent an entire family of impregnated carbons for military use. The most commonly employed type was the ASC whelterite carbon, which contains Cu, Cr and Ag. Various other non-toxic, non-carcinogenic metals were tried, mainly to replace the chromium. The ASZMT type, which contains Cu, Ag, Zn, and Mo showed the best performance with an additional impregnation with triethylene diamine.\textsuperscript{32} The combination of metals provides the ability to Whetlerites to act as catalysts and detoxify a wide range of CWAs. Whetlerites are used today as fillers in the military mask canisters.

1.4.2. Research on new adsorption materials

The challenge in the material sciences is to develop a new generation of materials, which will have improved detoxification performance per volume compared to the existing carbon-based filters, in order to be applied to smaller and more lightweight products. These materials can be used not only in the gas mask, but also in the uniforms and in industrial, medical and military applications. In
the last decades, many materials have been studied for the CWAs decontamination, and especially against mustard gas or its surrogate, CEES. The primary target is to strongly retain the toxic molecules on the surface and fast selectively catalytically decompose them to smaller and/or non-toxic compounds.

A direct comparison of the addressed in the literature materials’ performance as CEES reactive adsorbents is difficult, due to the differences in the particular experimental setups. Most of the studies investigated the adsorption performance, detoxification kinetics and decomposition pathways in solution, using various solvents like carbon tetrachloride, heptane, methanol, pentane, tetrahydrofuran, chloroform, and dichloromethane.\textsuperscript{33–41} The materials that attracted mostly the interest of the researches are predominantly metal based materials, such as single or mixed oxides/hydroxides, metal organic frameworks (MOFs) and zeolites. A summary of the performance of various tested materials, the conditions of the adsorption tests, the main findings, and the detected reaction products is presented in Table 1.4.1.
### Table 1.4.1. Highlighted studies on the HD and/or CEES removal on different materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conditions</th>
<th>Observations</th>
<th>Reaction products</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-BTC MOF</td>
<td>Solution of HD and CEES in carbon tetrachloride.</td>
<td>The porous structure plays a crucial role. The removal kinetics follows the first order reaction</td>
<td>TG, HEES</td>
<td>35</td>
</tr>
<tr>
<td>CaO nanosize</td>
<td>Direct interaction of powder with liquid HD</td>
<td>The interaction resulted 80 % elimination and 20 % hydrolysis.</td>
<td>TG, DVS, CEVS</td>
<td>34</td>
</tr>
<tr>
<td>CuO nanoparticles calcined</td>
<td>Direct interaction of powder with liquid HD</td>
<td>The calcination temperature alters the adsorption capacity, the nature of the degradation products.</td>
<td>TG, DVS, HEVS, CEVS</td>
<td>35</td>
</tr>
<tr>
<td>MgO nanoparticles</td>
<td>Solution of CEES in heptane, methanol pentane, and tetrahydrofuran</td>
<td>Crystal shape and surface area affect the decontamination performance. The highest reaction rates obtained in pentane.</td>
<td>EVS, HEES</td>
<td>36,37</td>
</tr>
<tr>
<td>VO₂ Porous nanotubes</td>
<td>Direct interaction of powder with liquid CEES and with solution in pentane.</td>
<td>The degradation is faster in the solution tests than by direct interaction with droplets.</td>
<td>HEES, sulfoxide, EVS</td>
<td>38</td>
</tr>
<tr>
<td>Zr(OH)₄</td>
<td>Direct interaction of powder with HD</td>
<td>Water-insoluble HD undergoes slow hydrolysis on hydrophilic zirconium hydroxide</td>
<td>TG and vinlylic products</td>
<td>39</td>
</tr>
<tr>
<td>ZnO nanorods and commercial ZnO</td>
<td>Solution of HD in chloroform</td>
<td>Even with almost equal surface areas, ZnO nanorods were more efficient in decomposition than the commercial bulk ZnO.</td>
<td>TG, DVS</td>
<td>40</td>
</tr>
<tr>
<td>MnO₂ nanobelts</td>
<td>Solution of HD and CEES in dichloromethane</td>
<td>Only hydrolysis took place.</td>
<td>DG, HEES</td>
<td>41</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Vapors CEES</td>
<td>26 compounds extracted from the surface after the adsorption in UV, while only 7 detected in dark.</td>
<td>26 compounds</td>
<td>42</td>
</tr>
</tbody>
</table>

*Abbreviations: thiodiglycol (TG), hydroxyethyl ethyl sulfide (HEES), divinyl sulfide (DVS), hydroxyethyl vinyl sulfide (HEVS), ethyl vinyl sulfide (EVS), chloro-ethyl vinyl sulfide (CEVS) and divinyl sulfide (DVS).*
CHAPTER 2. Objectives and research approach

2.1 Background

2.1.1. Metal (hydr)oxides

Metal (hydr)oxide based materials have been proven to be effective reactive adsorbents for the catalytic decontamination of numerous organic contaminants, especially for compounds containing sulfur or chloride. Besides their basic and acidic surface sites (Lewis and Brønsted-Lowery), and their thermal stability, they have a relatively high porosity and high density of reactive terminal groups on the surface, features that are vital for adsorption applications. Their catalytic and photocatalytic detoxification performances depend on the crystallinity, particle size, surface chemical heterogeneity, surface area and total pore volume.

2.1.2. Zinc hydroxide

Zinc (hydr)oxides are widely reported as important materials for catalysis and photocatalysis applications. The structural, morphological and chemical features of zinc oxide/hydroxide crystals formed from aqueous solutions can vary considerably. The one-pot wet precipitation from a Zn salt precursor solution with a base has been proven to be one of the quickest and most economically feasible synthetic procedure, leading to high yields. The addition rate of the base, the pH during the precipitation, the temperature and the aging time have an effect on the final crystallographic phase and structure. By controlling the above mentioned parameters the resulted precipitant could be either Zn(OH)\(_2\) or ZnO. It was reported that a rapid addition of NaOH led to the formation of ZnO, whereas a drop-wise addition yields Zn(OH)\(_2\). Nicholas and co-workers studied the precipitation of zinc salt using a NH\(_4\)OH solution (0.03 M) as base, and they found that the initially formed wülfingite transformed to würtzite ZnO after a period of aging at temperature...
less than 70 °C. \(^{51}\) By tracking the oxygen atoms via isotope labeling they reported that transformation occurs primarily through a solid state to a solid state path. Yamabi and co-workers showed that würtzite ZnO was predominantly formed at pH 9–13, while wülfingite Zn(OH)\(_2\) was mainly obtained at pH 6–9, from the precipitation of zinc sulfate with various complexing agents, such as ammonium chloride (NH\(_4\)Cl), ammonium sulfate ((NH\(_4\))\(_2\)SO\(_4\)), ammonium fluoride (NH\(_4\)F), and ammonium nitrate (NH\(_4\)NO\(_3\)). \(^{55}\)

Even though zinc oxide is established in the literature as a well-known adsorbent, due to its photocatalytic properties, \(^{43,56–58}\) limited studies are reported on the hydrated oxides and zinc hydroxides. The latter proved to be superior to zinc oxide in certain applications. For instance, Mabayoje and co-workers reported that Zn(OH)\(_2\) revealed higher removal efficiency of H\(_2\)S, \(^{59}\) SO\(_2\), \(^{47}\) and NO\(_2\), \(^{60}\) than ZnO nanoparticles. The improved performance of Zn(OH)\(_2\) was linked to the increased number of terminal hydroxyl groups, which have high reactivity and can act as a source of active radicals. \(^{59}\)

2.1.3. Zirconium hydroxide

Zirconium oxide, also called zirconia, is a well-studied ceramic. Either pure or as a composite, ZrO\(_2\) has been widely investigated for detoxification applications due to its essential features, such as high thermal stability, relatively large surface area and density of oxygen containing group on the surface. \(^{47,60–62}\) Among the reported lattices of zirconia (monoclinic, orthorhombic, and cubic), amorphous zirconium hydroxide is preferred for adsorption applications, due to its favorable structural and chemical surface features. \(^{63–65}\) This material showed a noteworthy reactive adsorption performance towards sulfur containing toxic industrial chemicals (TICs), like H\(_2\)S and SO\(_2\). \(^{47,62,66}\) Moreover, Zr(OH)\(_4\), pure or impregnated with triethylenediamine, presented elevated

removal ability of chloride containing small molecules, from air streams.\textsuperscript{48} It was recently reported that zirconium even as a dopant in TiO\textsubscript{2} or Fe-Ti mixed oxide, led to an increment of the surface area and reactivity of the composites, resulting to an improved degradation performance towards CWAs.\textsuperscript{61,67} Zirconium oxide has also been proved to play a catalytic role in the dehydration reactions of various organic molecules.\textsuperscript{68}

2.1.4. Graphite oxide

Hummers and Offeman published in 1958 the synthesis of graphitic oxide (GO) by oxidation of graphite (GR).\textsuperscript{69} The extent of GO exploration dramatically increased after 1990 in every field of science and engineering.\textsuperscript{70} In fact, this material is now used in numerous applications involving optics, electronic and sensors devices, or even for energy storage.\textsuperscript{71} Besides, it is widely used as a filler in composites with metals, metal (hydr)oxide, and other compounds.\textsuperscript{47,72–76}

GO and GR, belong to the family of carbonaceous material and they are qualified as carbon allotropes of the two dimensional monoatomic layered structure. The main difference of GO, compared to graphene, is the presence of the covalently bound oxygen containing functional groups, such as epoxide, hydroxyl and carboxyl. These groups have unique properties and they are crucial, for the synthesis of a variety of composites. The latter show supreme performance as adsorbents, sensors, or energy storage media.

It has been shown that the chemical, physicochemical, optical and textural properties of the metal (hydr)oxide change intensely upon a GO addition.\textsuperscript{76–79} The chemically active nature of GO and the recent advances in materials science have directed materials scientists to develop novel efficient and photoactive adsorbents and catalysts containing graphite oxide. The improvement in the
performance was linked to an increase in the photoactivity, porosity, and in the number and
dispersion of active centers, including terminal OH groups. These groups were found to participate
in oxidation/photo-oxidation reactions and in the formation of reactive oxygen species via a
photochemical path with the contribution of a GO phase.\textsuperscript{80} The usage of GO has been also shown
as beneficial for promoting the formation of the electron/hole pairs, generated upon light
irradiation, and for preventing their recombination.\textsuperscript{81,82}

For example, in the last decades many studies demonstrated that graphite oxide notably increases
the surface area and the number of active sites when used in composites with metal (hydr)oxides
(such as iron\textsuperscript{83} and copper\textsuperscript{84}), metal organic frameworks,\textsuperscript{85–87} or even with organic compounds
such as chitosan\textsuperscript{88,89} and porphyrinoids.\textsuperscript{90} In all the above-mentioned cases, the synergistic effects
resulting by the successful composite formation, generated unique chemical, physical and optical
properties compared to those of the individual precursors. These new properties improved the
material’s adsorption performance towards various TICs, including SO\textsubscript{2}, NH\textsubscript{3} and H\textsubscript{2}S as well as
towards chemical warfare surrogates.\textsuperscript{79,91–94} The main reported reasons were the increment of the
structural and chemical heterogeneity and the density of the active centers. Recently, the
composites of Zn or Zr (hydr)oxide with GO have been identified as efficient reactive adsorbents
of TICs such as SO\textsubscript{2} and H\textsubscript{2}S at ambient conditions.\textsuperscript{46,59,95}

\section*{2.1.5. Gold and Silver nanoparticles}

Since Au and Ag exhibit optoelectronic properties, similar to those of quantum dots,\textsuperscript{96} their
involvement in the composite-reactive adsorbents can enhance the efficiency of the surface
reactions affecting the detoxification performance. There are a few studies in which it is
demonstrated that the addition of even small amounts of noble-metal nanoparticles, such as Ag or
Au, can boost the photocatalytic performance of metal oxides, due to the introduction of a surface plasmon resonance effect.\(^{97,98}\) Awazu and co-workers reported in 2008 the supreme enhancement of the photocatalytic performance of TiO\(_2\) by the incorporation of AgNPs.\(^ {97}\) The degradation rate of methylene blue, under near-UV irradiation, increased by almost six times by the presence of Ag/SiO\(_2\) core nanoparticles. In another research, another plasmonic photocatalyst, consisted of graphite oxide enwrapped with Ag/AgCl or AgBr nanoparticles (AgXNPs), displayed distinctly enhanced photodegradation performance against methyl orange, compared to the corresponding bare counterparts.\(^ {99}\) The hybridization of GO with AgXNPs led to smaller size of AgXNPs, facilitated charge transfer phenomena, and suppressed the electron/hole pair recombination. Moreover, Martínez-Orozco and co-workers showed that the functional groups of GO acted as nucleation sites for the anchoring of AgNPs (with an average size around 10 nm), during the reduction of AgNO\(_3\) in ethanol using UV-C irradiation.\(^ {100}\) The formed nanocomposite showed enhanced adsorption performance against two dyes, Indigo Carmine and Rhodamine B. It was proposed that the photo-excited electrons of the dye chromophores were transferred via GO to the AgNPs, leading to the increment of the photoreactivity of the NPs.

Gold nanoparticles, AuNPs, have attracted enormous interest in the last decades due to their stability in various matrices (polymers, ceramic, films porous solids), biocompatibility and photocatalytic properties. Among many available synthetic routes, AuNPs can be obtained in a stable colloidal dispersion from tetrachloroaureic (III) acid (HAuCl\(_4\)), by the reduction of gold (III) with tri-sodium citrate dihydrate, with sizes between 5 to 50 nm.\(^ {101–103}\) AuNPs have the ability to absorb visible light due to the surface plasmon resonance effect (SPR), and to promote the formation of electron/hole pairs.\(^ {104–106}\) For example, Graphene/AuNPs nanocomposites showed elevated photocatalytic degradation of dyes.\(^ {107}\) Composites of metal oxides with AuNPs have been
proven as efficient photocatalysts for oxidation of various hydrocarbons and volatile organic compounds (VOCs).\textsuperscript{108–110} Hybrid nanocomposites, like TiO\textsubscript{2}/ZnO/AuNPs and Fe\textsubscript{3}O\textsubscript{4}/GO/AuNPs, revealed supreme photoactivity for the reduction of 4-nitrophenol,\textsuperscript{111,112} while ZnO/AuNPs showed an efficient photo-oxidization performance.\textsuperscript{113}

2.1.6. Degradation pathways of the mustard gas surrogate, CEES

The most common reported pathways of CEES degradation are collected in Figure 2.1.1. Hydrolysis leads to the hydroxylated sulfide (hydroxyethyl ethyl sulfide, HEES), while dehydrohalogenation leads to the vinyl sulfide (ethyl vinyl sulfide, EVS). These two pathways are the foremost reported in the literature for the interactions of metal oxides with CEES in solution. In both cases, HCl is simultaneously formed. The latter has almost equal toxicity to that of CEES. The formed chloride anion during the reactive adsorption can poison the active centers of the absorbents, leading to a decrease of the performance. The oxidation can lead to the formation of sulfoxides and sulfones. The latter are highly toxic, and for that reason only selective oxidation is desirable. Many photoreactive catalysts lead to di- or poli- sulfides with increased molecular weight compared to CEES, as a result of the cleavage of the S-C bond by the involvement of radical reaction and a further recombination to various products/combinations. Moreover, cleavage of the S-C bond of CEES and/or the formed products can lead to small fragments, such as ethanol, acetaldehyde, chloro-acetaldehyde, ethyl sulfide etc. These compounds are nontoxic and volatile, and due to their small size they can be retained inside the porous system of the filtration materials.
Figure 2.1.1. Detoxification pathways of CEES reported in the literature (with asterisk the toxic compounds).

2.2 Objectives and research approach

Based on the above-mentioned findings, our goal is to synthesize novel porous multifunctional-nanocomposites consisting of zinc or zirconium (hydr)oxides, graphite oxide and gold or silver nanoparticles. These composites will be evaluated as reactive adsorbents of the mustard gas surrogate, CEES. The key parameters enhancing the adsorption will also be identified. We hypothesize that there is a specific combination of chemical, optical and structural features resulting in an enhanced ability of these materials to catalytically and selectively decompose CEES to smaller non-or-less toxic compounds. The latter are expected to be retained on the surface, either physically or chemically. All the tests performed simulate “real-life” ambient conditions: room
temperature, pressure, and moisture content, and visible light irradiation. Since the main application of the materials are to be used as filtration media against vapors of CWAs, the adsorption tests are carried out using the surrogate in its gaseous state rather than in solution, as the most reported studies does.

The predominant phase of the nanocomposites will be the one of metal (hydr)oxide, which will be responsible for the decomposition and adsorption of the vapors. Considering this, the first target is to determine if the preferred structure is oxide or hydroxide, and then optimize the synthetic procedure in order to obtain the most beneficial porosity and amount of active oxygen containing groups. The next step is to verify if the addition of GO leads to the successful composite formation with synergistic effects on the structural and chemical features, mainly due to the enhancement in the dispersion of inorganic phase and in providing an electrical conductivity. If so, the optimum amount of the GO phase will be also defined. The last step is to examine if the addition of a limited amount of NPs will favor the adsorption and detoxification performance. The exposure to visible light is expected to result in enhanced photogenerated electrons formation. The latters should be transferred through the conductive graphite phase to the metal (hydr)oxide phase. This will trigger the reactivity of the centers that are responsible for the reactive adsorption through radicals formation, redox reactions, and ultimately selectively degradation of the toxic molecules. Up to now, to the best of our knowledge, nano-composite material consisting of Zn or Zr hydroxide-oxide, GO and Au or Ag nanoparticles have not been synthesized with the intend of their application in reactive adsorption and specifically for a vapor phase detoxification of CWAs. The targeted amount of NPs in the composites will be limited to about 1 % of the final total mass of the composites. This investigation is expected to open new possibilities for the development of
highly efficient and stable plasmonic photocatalysts that utilize visible light as an energy source for decontamination applications.

The proposed research approach to accomplish the above objectives can be summarized as follows:

- Synthesis of various metal oxides/hydroxides
- Synthesis of composites with different amounts of GO, in order to determine the optimum amount from the point of view of the structural and chemical features
- Synthesis of multi-composites consisting of metal (hydr)oxide, GO and NPs.
- All the above mentioned samples will be examined as adsorbents of CEES vapors at ambient conditions.
- The ability to retain the vapors will be evaluated by the weight uptake performance (capacity).
- The total detoxification performance will be determined combining the capacities with the remained amount of CEES in the headspace.
- The kinetic/evolution of the adsorption will be monitored following the CEES concentration in the headspace and from the capacity evolution.
- Characterization of the initial and exhausted adsorbents (structural and surface chemistry parameters) by various techniques will be performed.
- Identification of the formed products in the headspace of the closed adsorption system by GC-MS.
- Identification of the products retained on the surface after the adsorption by analyzing both the exhausted samples (FTIR, Thermal analysis coupled with MS) and the analysis of the extractions by GC-MS.
• Determination of the factors influencing the detoxification performance

• Focusing on the role of the carbonaceous phase and NPs on the feature that has the most crucial contribution for the reactive adsorption.

• Determination of the involved mechanisms in the reactive adsorption process.
CHAPTER 3. Materials and Methods

3.1 Materials

All chemicals used in this research (HAuCl₄, ZnCl₂, NaOH, tri-sodium citrate dehydrate, 3-mercapto-propionic acid, anhydrous ZrCl₄, 2- chloroethyl ethyl sulfide, and acetonitrile) were reagent grade with a purity degree higher than 98%. The solutions were prepared in deionized water. All the samples were synthesized at least twice. Silver nanoparticles dispersion was provided by NANOGAP SUB-nmPARTICLES Company (sample Ag-2103-W).

3.1.1. Zinc hydroxides

Zinc hydroxides were prepared using a one-pot wet precipitation method. 1L sodium hydroxide solution (0.05 M) was added dropwise to a 0.5 L of zinc chloride (0.05 M) solution with a specific addition rates, using a Titronic Universal (SCHOTT). The addition rates of the base were 1, 2, 10 and 20 mL per minute. The obtained materials were filtered and washed with distilled water until no chloride was detected in the washing water. The obtained gels dried at 60 °C for 48 h. This methodology is referred to as a “slow addition”. The samples that were prepared using an addition rate of 2.0 mL per minute are referred to as ZnSA.

3.1.2. Zinc oxides

Zinc oxides were prepared by a direct rapid addition of a 1.0 L sodium hydroxide solution (0.05 M) to a 0.5 L zinc chloride solution (0.05 M) and then aged under stirring for different intervals of time. The obtained materials were washed with distilled water until stable pH and no traces of chloride ions were found. The filtrated phase was dried at 60°C for 48 h. This methodology is referred to as a “rapid addition”. The ZnO received after 2 hours of aging is referred to as ZnRA.
3.1.3. Zirconium hydroxide

Zirconium hydroxide was prepared using a one-pot in situ precipitation method. In a NaOH solution (2 L, 0.05 M) was added the stoichiometric amount of ZrCl₂ (0.5 L, 0.05 M), with a rate of 0.6 mL per minute, under vigorous stirring. The obtained precipitate was filtered and then repeatable washed with deionized water, until no traces of chloride ions were found. Finally, the separated gel phase was dried at 60 °C for 48 h. This sample is referred to as ZrOH.

3.1.4. Graphite Oxide (GO)

Graphite Oxide (GO) was prepared by oxidation of a commercial graphite (Sigma-Aldrich) following Hummers method.⁶⁹,¹¹⁵ Commercial graphite powder (10 g) was stirred in concentrated sulfuric acid (240 mL, 0 °C). Potassium permanganate (30 g) was slowly added to the suspension. The rate of addition was controlled to prevent the rapid rise in the temperature of the suspension (should be less than 15 °C). The reaction mixture was then cooled to 2 °C. After removal of the ice bath, the mixture was stirred at room temperature for 30 min. Distilled water (230 mL) was slowly added to the reaction vessel, keeping the temperature less than 90 °C. The diluted suspension was stirred for an additional 15 min and further diluted with distilled water (1.4 L) and then hydrogen peroxide (100 mL, 30 wt% solution) was added. The mixture was left overnight. GO particles settled at the bottom were separated from the excess liquid by decantation. The remaining suspension was removed by decantation and fresh distilled water added. The decantation and addition of water was repeated until no BaSO₄ was detected (using BaCl₂) and the pH was around 3. Finally, the GO was separated by centrifuge and the received gel-like sample was freeze-dried. The obtained graphite oxide powder had a dark brown color (Figure 3.1.1).
Figure 3.1.1. The received graphite oxide (photo by the author).

3.1.5. Gold nanoparticles (AuNPs)

For the synthesis of AuNPs, 20 mL aqueous solution of 1 mM tetrachloroaureic (III) acid (HAuCl₄) was added in a 50 mL scratch-free flask on a stirring hot plate with reflux. The solution was heated to boil under vigorous stirring. Then, 2 mL of a 1% solution of tri-sodium citrate dihydrate, Na₃C₆H₅O₇.2H₂O and 1 % sodium 3-mercaptopropioneate (MPA-Na) were injected by syringe dropwise. The gold nanoparticles were gradually formed as the citrate reduced gold (III). The suspension was heated for 5 minutes, and the color of the colloid solution turned from yellow to red (Figure 3.1.2).¹⁰¹,¹⁰³ The 3-mercaptopropionate acid was neutralized with NaOH.

Figure 3.1.2. The initial tetrachloroaureic (III) acid solution and the final colloid suspension of AuNPs (photos by the author).
3.1.6. Silver nanoparticles (AgNPs)

The silver nanoparticles (NGAP NP Ag-2103) were obtained from the NANOGAP SUB-NM-POWDER, SA. The mixture of quasi-spherical and rod like AgNPs were dispersed in water (1.06 wt/wt % Ag). The size distribution of the nanoparticles was $47.2 \pm 15.6$ nm (Figure 3.1.3).

![Image of AgNPs size distribution](image)

Figure 3.1.3. Details about the AgNPs, as received from NANOGAP SUB-NM-POWDER, SA.

3.1.7. Composites of zinc hydroxide and GO

The composites of Zn(OH)$_2$ with GO were prepared by dispersing GO (5, 10 and 20 % wt. of the final mass of the composite) in 0.5 L of a ZnCl$_2$ solution (0.05 M). The dispersion maintained under vigorous stirring for 2 hours. Then, the stoichiometric amount of NaOH (1L, 0.05 M) was added at a rate of 2.0 mL per minute. The pH during synthesis was maintained lower than 10, in order to avoid the transformation to zinc oxide. The pH of the initial solution of zinc chloride, with or without GO, was $5.9 \pm 0.3$. During the entire precipitation, the pH of all solutions remained less than 10 ($9.3 \pm 0.2$). The obtained precipitate was filtered and washed with deionized water until
stable pH and no chloride detection. Finally, the received composites were dried at 60 °C for 48 hours. The samples are referred to as ZnGO5, ZnGO10 and ZnGO20, where 5, 10 and 20 represent the content of GO in the composites, respectively.

3.1.8. Composites of zinc hydroxide, GO and AuNPs

Composites containing gold nanoparticles were synthesized by dispersing AuNP colloid solution (37.5 mL, 10^{-3} M) in the starting ZnCl₂ solution in the presence of GO (10 wt % of the final mass of the material). After 2 hours stirring, NaOH solution (0.05 M) was added dropwise with a rate of 2.0 mL per minute. After filtrating and washing with distilled water until stable pH and no chloride detection, the composite was centrifuged for 30 minutes in 4°C at 6000 rpm. The obtained gel phase was dried at 60 °C for 48 h. The composite with zinc (hydr)oxide, graphite oxide and AuNPs is referred to as AuZnGO. The targeted final amount of AuNPs was arbitrary chosen as 1% of the total mass of the final composites, assuming that the structural and morphological features of the composite will not be altered to a great extent, compared to Zn(OH)₂/GO the composite. The 10% wt percentage of GO was chosen to compare the results with previous findings, where this amount found as the optimal one.⁵⁹

3.1.9. Composites of zinc hydroxide, GO and AgNPs

This composite was synthesized following the exact same procedure as that for the synthesis of the above-mentioned AuZnGO, with the difference that AgNPs solution (5.27 mL) was used instead of AuNPs colloid solution.
3.1.10. Composites of zirconium hydroxide and GO

The composites of zirconium (hydr)oxide/GO were prepared using the same one-pot in situ precipitation method as for zirconium hydroxide. GO powder (1, 5, 10 and 20 wt % of the final mass of the material) was dispersed in 2 L of a sodium hydroxide solution (0.05 M). The suspensions were maintained under vigorous stirring for 2 hours. Then, the stoichiometric amount of zirconium chloride (0.5 L, 0.05 M) was added with a rate of 0.6 mL/minute. The obtained precipitates were filtered and then washed with deionized water until no traces of chloride ions were found. Finally, the separated gel-like phases were dried at 60 ºC for 48 h. The composites obtained with 1, 5%, 10% and 20% of GO are referred to as ZrGO1, ZrGO5, ZrGO10 and ZrGO20.116

3.1.11. Composites of zirconium hydroxide, GO and/or AgNPs

The composites of zirconium hydroxide with AgNPs were synthesized following the same procedure as that one used for the synthesis of ZrOH and ZrGO, with the addition of AgNPs in the initial zirconium chloride solution, in order to receive 1 wt/wt % of the final composite total mass.

3.2 Methods

3.2.1. Vapor adsorption: Vials-in-Vial closed adsorption system

The adsorption of CEES was studied in batch experiments, using a homemade experimental Vials-in-Vial adsorption system. A glass vial (1 mL) containing 20 mg of the sample was introduced into a 22 mL reaction vessel. After hermetically sealing the vessel with a septum containing cap, CEES (20 µL) was injected through a septum into another 1 mL container in the reaction vessel.
A schematic representation of the homemade closed Vials-in-Vial adsorption system can be seen in Figure 3.2.1. The containers were kept in hood under ambient light, or under light irradiated from a solar light simulator (Xenon lamp, Solar light Co., INC, XPS-150™) or in dark, always at room temperature.

Figure 3.2.1. A schematic representation of the used Vials-in-Vial adsorption system.

The exposure to CEES time varied, from 12 hours up to 9 days, depending on the target experiment. Vapor phases from the headspace of the containers were sampled with a syringe and injected to GC-MS. Once the vapor sample was taken, the containers were opened and the adsorbent samples were equilibrated in air for 1 hour at atmospheric pressure and room temperature, in the absence of moisture. Finally, the containers with the adsorbents were weighed, and the mass gain as a result of the adsorption measured and expressed as capacity (mg of weight uptake per gram of absorbent). This approach will provide the opportunity to identify the volatile products that remain in the headspace, calculate the weight uptake, and analyze the products.
retained on the surface of the absorbents after the exposure. Monitoring of all the above mentioned parameters after various time intervals will provide sufficient amount of data for the kinetic/evolution and to finally propose complete mechanisms of the adsorption interactions.

3.2.2. Headspace analysis of the closed adsorption system.

The analysis of the headspace was performed by Gas Chromatography-Mass Spectrometry (GC-MS). 40 µL of the headspace were sampled using an airtight Hamilton Syringe and injected into GC/MS (Shimadzu QP5050A). A Rtx-1 column (Restek, fused silica) of 30 m length, 0.25 mm internal diameter, and 0.25 µm of a liquid film thickness was used. The injection and interface temperature were 250 °C. The instrument was operated in a split mode with the following parameters: Column inlet pressure: 101.8 KPa, column flow: 1.7 mL/min, linear velocity: 47.8 cm/sec, Split ratio: 10, total flow: 21.8 mL/min. The separation program was as follows: heating the column from initial temperature of 50 to 120 °C with a rate of 5 °C/min, and then with a rate of 40 °C/min until 250 °C. The mass spectrometer detector was used in an electron impact ionization mode.

3.2.3. Analysis of the liquid extracts by GC-MS

Liquid extracts with acetonitrile as a solvent were analyzed in GC/MS (QP5050A from Shimadzu). Separation was carried out on a Rtx-1 column. 1 µL of a liquid extract was sampled and injected into GC/MS. The injection and interface temperature were 250 °C. The instrument was operated in a split mode with the following parameters: column inlet pressure: 101.8 KPa, column flow: 1.7 mL/min, linear velocity: 47.8 cm/sec, split ratio: 20, total flow: 38.8 mL/min. The same separation program as for the analysis of the headspace was used.
3.2.4. Determination of Reactive Oxygen Species (ROSs)

Hydroxyl radicals (•OH). The formation of hydroxyl radicals was investigated based on the fluorescence of hydroxyl terephthalate (HTA) solution (Figure 3.2.2). 10 mg of material were stirred in 100 ml of a 2 mM terephthalate (TA) solution. 3 ml aliquots were regularly withdrawn at specific time intervals, filtered and their fluorescence were measured ($\lambda_{\text{excitation}} = 312$ nm). TA is non-fluorescent but it is easily hydroxylated by the presence of hydroxyl radical to form HTA, which is fluorescent. Therefore, the fluorescence intensity detected is a direct measure of the formation and the concentration of the hydroxyl radicals. The experiments were performed under ambient light irradiation and in dark.

![Figure 3.2.2. Formation of hydroxyl terephthalate (HTA) from terephthalate (TA).](image)

Superoxide radical (•O$_2^-$). The ability of the samples to form Superoxide radicals (SO$\text{r}$) was investigating using UV–visible spectroscopy and monitoring the characteristic maximum absorbance of nitro blue tetrazolium (NBT) at 259 nm of the UV-Vis spectrum. The presence of SO$\text{r}$ has as a result the conversion of NBT to mono- and diformazan. The experiments were carried out under ambient light and in dark for all the materials.
3.2.5. Sorbent surface area and porosity analysis

The surface area and porosity of the studied materials were calculated from N\textsubscript{2} adsorption isotherms measured using ASAP 2020 (Micromeritics). The BET surface areas were calculated from the isotherms. The total pore volume was obtained from the amount adsorbed at a relative pressure of 0.99 and the micropore volume was calculated from the Dubinin-Astakhov equation. The mesopore volume was calculated by the difference between the \( V_T \) and \( V_{mic} \) and the Barret-Joyner-Halenda (BJH) was used to calculate pore size distributions, PSDs. The degassing was performed under vacuum for 12 hours at 60 °C, as well as at 90 and 120 °C.

3.2.6. Structural and morphological characterizations

X-ray Diffraction (XRD). The XRD patterns were obtained on a Phillips X’Pert X-ray diffractometer with powder diffraction procedure, using a CuK\textsubscript{α} radiation (operated at 40 kV and 40 mA). The diffraction patterns were collected from a 10 to 60 2θ scan. The average crystallite size \( D \) (nm) was calculated using the Scherrer formula (eq. 1):

\[
D = \frac{K_s \cdot \lambda}{\beta \cdot \cos \theta}
\]  

(1)

where \( K_s \) is Blank’s constant (\( K_s = 0.89 \) for CuK\textsubscript{α}), \( \lambda \) is the source wavelength (\( \lambda = 0.15405 \) nm for CuK\textsubscript{α}), \( \beta \) is the peak width of the half-maximum (rad) and \( \theta \) is Bragg diffraction angle.\textsuperscript{72}

Scanning Electron Microscopy (SEM). The Scanning Electron Microscopy images were obtained with a Zeiss Supra 55 VP (accelerating voltage of 5.00 kV) or with a FEI Helios NanoLab
660instrument, equipped with a backscatter electrons detector and with 5 keV acceleration voltage. The imaging was performed in situ on the powder samples.

**Transmission Electron Microscopy (TEM).** The studies were performed on a JEOL 2100F instrument with an accelerating voltage of 200 kV. The analyses were conducted on samples previously suspended in isopropanol. For Energy Dispersive Spectroscopy (EDS) elemental mapping 15 keV was used.

3.2.7. Surface chemistry analysis

**Fourier Transform Infrared Spectroscopy (ATR-FTIR).** The analyses were carried out in a Nicolet Magna-IR 380 spectrometer, by using the Smart MIRacle accessory with a diamond crystal. The spectra were collected 64 times and corrected for background noise. Experiments were done without KBr addition.

**Raman Spectroscopy.** Raman spectra were obtained under excitation with the 488 nm laser from an argon-ion laser and dispersed by a 1200 line / mm grating using a 75 cm spectrometer with a liquid N\textsubscript{2} cooled CCD.

**Simultaneous Thermal Analysis with Mass Spectroscopy (TA-MS).** Thermogravimetric (TG), differential thermal (DTA) and derivative thermogravimetric (DTG) analyses were obtained on SDT Q600 (TA instruments) thermal analyzer. The samples were heated at a rate of 10 °C/min from room temperature up to 1000 °C. A flow of 100 mL/min of He (ultra-dry) was held during the analyses. Simultaneously, the gasified products desorbed from the surface of the adsorbents.
were analyzed by a ThermoStar Gas Mass Spectrometer (GSD; Pfeiffer Vacuum). A secondary electron multiplier was used.

**Potentiometric Titration.** Potentiometric titration measurements were performed with an automatic titrator (888 Titrando, Metrohm). In a container, 50 mg of the sample and 25 mL NaNO₃ (0.01M) were added and maintained overnight at 25 °C and continuous stirring for equilibrium. Nitrogen (N₂) was used to eliminate the influence of atmospheric CO₂ by saturating the suspension throughout the entire experiment. Starting from the initial pH of the suspended sample, volumetric standard sodium hydroxide (0.1 M) was used as the titrant up till pH 11. The experimental titration curves were transformed into proton binding curves (Q), where Q represents the total number of protonated sites. The pKₐ distributions for the species present on the surface were obtained using the SAIEUS procedure.

3.2.8. Optical properties analysis

**DRUV-Vis-NIR spectroscopy.** Diffuse reflectance spectra have been collected between 300 and 800 nm using a Cary Varian spectrophotometer equipped with a reflectance sphere. Halon was used as a reflection standard. All the measurements were made with a quartz homemade optical setup, which allowed the usage of the powder as synthesized. The band gaps (Eg) were estimated based on the Kubelka-Munk model from the extrapolation of the linear fit of Tauc plots of [F(R∞)hv]² versus the photon energy.

Factors influence the adsorption and photocatalytic performance.

In this chapter are partially included with permission from Elsevier results reported in the follow publications (Ref. 91 and 161):

_D. A. Giannakoudakis, J. A. Arcibar-Orozco and T. J. Bandosz,_
Key role of terminal hydroxyl groups and visible light in the reactive adsorption/catalytic conversion of mustard gas surrogate on zinc (hydr)oxides, *Applied Catalysis B*, 2015, 174, 96-104

_D. A. Giannakoudakis, J. A. Arcibar-Orozco, T. J. Bandosz,_
Effect of GO phase in Zn(OH)$_2$/GO composite on the extent of photocatalytic reactive adsorption of mustard gas surrogate, *Applied Catalysis B*, 2016, 183, 37-46
4.1. One-pot wet precipitation of zinc (hydr)oxide

4.1.1. The role of the base addition rate

An important task of our research was to determine the synthesis conditions leading to the formation of pure zinc hydroxide of high porosity. For this, a one-pot precipitation method was used with water as a solvent, sodium hydroxide as base (in a molar ratio 1:2 ZnCl$_2$ to NaOH) and zinc chloride as a source of the metal. It was previously reported that alteration of the solution pH, temperature and the base addition rate to the metal salt solution can result in different features of metal (hydr)oxides. Thus in this way the structural and morphological properties such as the porosity and particle size can be significantly adjusted.

The addition of the base to the zinc chloride solution was occurred following two ways. In the first approach, the base was added dropwise with a controlled rate. Even though a wide range of different addition rates were tried, the precipitations received with rates 1, 2, 10 and 20 mL/min were analyzed. After the complete addition of the base, sub-sample of the precipitation was thermally treated at 95 ± 5 °C for one hour. In the second approach the base was added rapidly addition to the salt solution. The received precipitation was afterwards aged under stirring in room temperature for 10 and 30 minutes, 2, 12, 24 and 48 hours.

4.1.2. Structural and morphological characterization

The crystallinity and purity of the synthesized samples were analyzed using the powder X-ray diffractions. The characteristics diffraction peaks of hexagonal ZnO (würtzite), orthorhombic $\varepsilon$-
Zn(OH)$_2$ (wülfingite) and orthorhombic $\gamma$-Zn(OH)$_2$, from the standard cards JCPDS 36-1451,$^{57,120}$ JCPDS 38-0385,$^{52}$ and PDF 00-020-1437,$^{121}$ respectively, are collected in Figure 4.1.1.

The XRD patterns of the samples prepared by dropwise addition of the base are collected in Figure 4.1.2. In the sample synthesized at a rate of 2 mL/min, orthorhombic $\varepsilon$-Zn(OH)$_2$ is the main crystallographic phase, since the diffraction peaks at 20.2, 20.9, 27.2, 27.7, 32.8, 39.5, 40.8, 42.1, 52.4, 57.8, 59.5 and 60.4 2$\theta$ are matching perfectly with the JCPDS Card no. 38-0385. However, the minor reflections, located at 31.7, 34.4, 36.2 and 47.6 2$\theta$, correspond to traces of würtzite structure of zinc oxide, while diffractions linked to $\gamma$-Zn(OH)$_2$ are not detected only in this sample. The rest of the samples prepared with rates 1, 10 and 20 mL/min showed, except the diffraction peaks of the $\varepsilon$-Zn(OH)$_2$, the peaks at 11.5, 28.5, 30.7 and 34.8 2$\theta$, which are related to the $\gamma$-Zn(OH)$_2$ structure. Their intensities were different. The result of the thermal treatment of the precipitation after the complete addition of the base for one hour at 95 °C revealed that the crystal structure change upon heating to well crystalized ZnO, as can be seen for the pattern of the sample prepared with rate of 2 mL/min and further thermal treatment at 95 ± 5 °C for one hour. The same pattern was found for the rest of the trials and even for lower temperatures (60 ± 5 °C). Based on
these findings it can be concluded that the one-pot in-situ wet synthesis method is very sensitive and the base addition rate plays a crucial role for the development of the final crystal structure.

Figure 4.1.2. The X-ray diffractograms of the sample obtained with a controlled addition of the base and the one prepared with a rate of 2mL/min and further thermally treated at 95 ± 5 °C for one hour.

The differences in the morphology and shape of crystal structures as a result of a different addition rate are seen in SEM images collected in Figure 4.3. In the SEM image of the sample prepared
with a rate of 1 mL/min (Figure 4.1.3.A), two different crystallographic phases are detected. The one with plate-like shape is linked to the gamma phase of zinc hydroxide, while the octahedral shaped particles correspond to the $\varepsilon$-Zn(OH)$_2$. As revealed from the XRD pattern, the sample prepared with a rate of 2 mL/min showed mainly the existence of the octahedral shaped $\varepsilon$-Zn(OH)$_2$ particles (Figure 4.3.B). Further increment of the addition rate led to the conversion of the latter particles, to the $\gamma$-Zn(OH)$_2$ phase (Figure 4.3.C-D).

![Figure 4.1.3. SEM images of the sample obtained with a controlled addition of the base.](image)

The X-ray diffractograms of the sample obtained with the rapid addition of the base, followed by various ageing periods, are collected in Figure 4.1.4. The powder X-ray diffractograms for the entire series of these samples indicate that the crystallographic phase is that of hexagonal zinc...
oxide, since the three most intense peaks at 31.7, 34.4, 36.2 and 47.6 2θ match perfectly with the JCPDS Card no. 36-1451. With the ageing periods over 2 hours, traces of wülfingite were found. They entirely disappeared for the precipitate aged for more than 48 hours. Interestingly, the diffractograms of the samples aged for more than 24 hours showed decreased intensities of the characteristic peaks of the ZnO phase. Since the peak at 34.4 2θ decreased most in its intensity, this can be linked to the partial destruction of the well-defined hexagonal structure. The broadening of the peaks is due to the decrease in the particles’ size.

Figure 4.1.4. The X-ray diffractograms of the sample obtained with a rapid addition of the base and aged for various periods.
The SEM image of sample aged for 2 hours (Figure 4.1.5.A) shows mainly flower-like nanoscaled particles linked to the ZnO phase. Defected octahedral particles of ε-Zn(OH)$_2$ are also visible. This finding agrees with the results of the X-ray diffractogram, where two distinguished crystals phases are detected. In the samples aged for 12 hours, the size of the both above mentioned phases decreases (Figure 4.1.5.B). 24 hours resulted in the conversion of the flower-like particles to rice-like particles (Figure 4.1.5.C). Further aging leads to the formation of spherical nanoparticles with significantly smaller size (Figure 4.1.5.D).

Figure 4.1.5. SEM images of the sample obtained with a rapid addition of the base and aged for various periods of time.
4.1.3. The influence of the pH

Since the main target was to obtain zinc hydroxide, for all samples the NaOH/ZnCl₂ molar ratio was 2:1, based on the targeted reaction: \( \text{ZnCl}_2 + 2 \text{NaOH} \rightarrow \text{Zn(OH)}_2 + 2 \text{NaCl} \). The precursor solution had an initial pH equal to 5.9 ± 0.2. In the case of the dropwise addition of the base, the pH of the solution never went beyond 9.8. On the other hand, the pH reached 11.4 ± 0.2, when the base was added rapidly. The addition of the base to the zinc precursor solution resulted in the formation of various intermediate aquo-complexes, such as \([\text{Zn(OH)}_4]^{2-}\), \([\text{Zn(OH)}_3]^{-1}\) and \([\text{Zn(OH)}_x(\text{H}_2\text{O})_y]^{2-x}\).\(^{51,53}\) The precipitation of stable \(\text{Zn(OH)}_2\) is favorable over that of \(\text{ZnO}\), if the pH is maintained between 6.5 to 10 at room temperature during the whole synthesis. At these conditions the intermediate aquo-complexes condensed, forming zinc hydroxide. On the contrary, the increase of the pH to more than 10.8, as in the case of the rapid addition, results initially in the simultaneous formation of \(\text{ZnO}\) and \(\text{Zn(OH)}_2\). The latter phase is unstable and can get converted to \(\text{ZnO}\) via two possible pathways.\(^{51}\) The first involves a dissolution to the zinc aquo-complexes, which then re-precipitate as the less soluble and more stable \(\text{ZnO}\) in the whole pH range.\(^{53}\) The second pathway involves a solid-state transformation caused by dehydration. It can be concluded that the formation of \(\text{ZnO}\) or \(\text{Zn(OH)}_2\) depends on the kinetics of the precipitation and can be controlled by adjusting the pH value. The proposed mechanism (Figure 4.1.6) is in agreement with studies addressing the formation of \(\text{ZnO}\) by decomposition of \(\text{Zn(OH)}_2\),\(^{51,52,54,122}\). It also further supports previous findings on the formation of different precipitates by changing the mixing time and thus the pH gradient.\(^{53,54}\)
4.1.4. Conclusion

The results presented in this chapter show that by controlling the addition rate of the precipitation agent (NaOH) to a zinc chloride solution, either zinc hydroxide or zinc oxide can be obtained. Slow rates result in the formation of orthorhombic particles of Zn(OH)$_2$, while rapid addition leads to the formation of ZnO. The main factor, which regulates the final structural form is the pH. In the case of the rapid addition, the pH rise above 10.8 after the addition of the base, while the pH during the drop-wise addition of the base remained lower than 9.8. The XRD and SEM analyses show the clear structural differences between samples.
4.2. Zn(OH)$_2$ vs ZnO: The key role of the hydroxyl groups

4.2.1. Introduction and materials

In order to compare the adsorption and photocatalytic performance, as well as to determine which factors play the most crucial role, two samples were chosen. The first one was the one prepared with a dropwise addition rate of 2 mL/min. It was chosen because it consists of zinc hydroxide phase. This sample is referred to as ZnSA. The second selected material was obtained with the rapid addition and with 2 hours aging. It predominantly consists of the zinc oxide nanoflower-like particles. This sample is referred as ZnRA. For the sake of comparison, commercial ZnO nanoparticles were used as a reference material, and it is referred to as ZnO-C.

4.2.2. Structural, chemical and optical characterizations

The diffractograms of three chosen samples are collected in Figure 4.2.1. The XRD patterns of the sample synthesized at the slow base addition rate (ZnSA) indicates zinc hydroxide as the main crystallographic phase, while the minor diffraction peaks, located at 31.7, 34.4, 36.2 and 47.6, correspond to traces of wurtzite structure of zinc oxide. The diffraction peaks of the sample prepared with a rapid addition of the base correspond to wurtzite. The presence of ε-Zn(OH)$_2$ crystals is also noticed, but in a limited quantity. The pattern of the ZnO-C matches perfectly with the one of wurtzite. The calculated crystallite sizes, using the Scherrer equations, found 48.6, 11.8 and 15.1 nm for ZnSA, ZnRA and ZnO-C, respectively.
Figure 4.2.1. X-ray diffraction patterns for the initial samples.

ZnSA and ZnRA differ markedly in their pore structure. The total pore volumes and surface areas are summarized in Figure 4.2.2. ZnSA has almost ten times higher total pore volume than that of ZnRA. The surface area of the former sample is also 350 % higher than that of ZnRA. ZnO-C has a mesoporous structure. The total pore volume is 20 % lower than that of ZnSA, but more than six times higher than that of ZnRA.
Figure 4.2.2. Comparison of the porous structure parameters calculated from the nitrogen adsorption isotherms.

The nitrogen adsorption isotherms are of Type II and clearly indicate the mesoporous nature of our materials (Figure 4.2.3). This is an important feature and might play a crucial role in the CEES reactive adsorption process. The observed limited H3 type hysteresis reveals the existence of not-complex shaped pores. The simple shape and large size of the pores is expected to allow the penetration of the CEES molecules to the reactive sites.
The well crystallized micrometric size particles of $\varepsilon$-Zn(OH)$_2$ with a rhombic octahedral shape can be seen at the SEM images of ZnSA (Figure 4.2.4 A). Moreover, the limited quantity of the ZnO phase is also revealed, with platelets-like particles of similar sizes (Figure 4.2.4 A). In the case of ZnRA, flower-like zinc oxide particles are the predominant crystallographic phase, with a size of about 0.5-1.2 $\mu$m (Figure 4.2.4 C). This is in agreement with the XRD results. Besides the oxide phase, the rhombic octahedral shape particles of $\varepsilon$-Zn(OH)$_2$ were also detected as a minor phase (Figure 4.2.4 D). The commercial zinc oxide consists of the aggregations of spherical nanoparticles with sizes in the range from 40 to 180 nm (Figure 4.2.4 E-F).
Figure 4.2.4. SEM images of ZnSA (A, B), ZnRA (C, D) and ZnO-C (E, F). Red (false) color the \( \varepsilon \)-Zn(OH)\(_2\) particles and blue (false) color- the ZnO nano-flower like particles. (A, B, C and D images are reprinted from Ref. 161, Copyright 2015, with permission from Elsevier)
The FTIR spectra of the samples studied are collected in Figure 4.2.5. The intense and sharp bands at 715 and 900 cm\(^{-1}\) in the spectrum of ZnSA are assigned to the out-of-plane bending and vibration modes of the OH groups, while the one at 830 cm\(^{-1}\) is assigned to the \(\text{–OH}\) deformation.\(^{46}\) The Zn-OH bending and twisting vibrations are seen as the bands at 1040 and 1090 cm\(^{-1}\), respectively.\(^{51,127}\) The band at 1390 cm\(^{-1}\), with a small shoulder at 1360 cm\(^{-1}\), and the band at 1500 cm\(^{-1}\) are linked to the vibrations of hydroxyl groups from the zinc hydroxide and water. The broad band between 2950 and 3350 cm\(^{-1}\) with a maximum at 3240 cm\(^{-1}\) represents the bulk OH groups of the inorganic phase, while the band at 3450 cm\(^{-1}\) is assigned to the OH groups of water molecules.\(^{51}\)

A different pattern of the FTIR spectrum was received for ZnRA. The twisting and bending vibrations of Zn(OH)\(_2\) are totally absent, while the bands related to the out-of-plane bending and vibration modes of the OH groups at 715 and 900 cm\(^{-1}\) have rather small intensities. The broad band between 2950 and 3350 cm\(^{-1}\) and the band representing water at 3450 cm\(^{-1}\) are also of a small intensity. The existence of the bands related to hydroxyl groups can be linked to the limited impurities of the zinc hydroxide phase, as detected by X-ray diffraction. This is in a perfect agreement with the reported FTIR spectra of zinc oxide synthesized by the thermal decomposition of zinc hydroxide, where the final pH of the precipitation was near to 11.\(^{51}\) In the case of ZnO-C, the nonexistence of the bands associated to the OH groups confirms it highly purity.
Potentiometric titration method was used to determine the quantity and quality of surface functional groups. The $pK_a$ distributions for our samples are collected in Figure 4.2.6. Two types of groups are identified: those with $pK_a$ from 7 to 8, and those with $pK_a$ above 10. The first ones, are associated to bridging oxygen groups, and the second ones- to terminal hydroxyl groups. The presence of the terminal hydroxyl groups of ZnSA at higher $pK_a$ than those of the other two samples indicates a stronger basic character of this sample, which is probably caused by their different chemical environment. It can be clearly seen that the amount of both types of groups...
is higher on the surface of ZnSA than on that of ZnRA. The terminal OH groups of the sample prepared with a rapid base addition represent only 29 % of the groups on ZnSA, while the later sample has 27 % more bridging groups than ZnRA. The numbers of the terminal and bridging groups of the commercial zinc oxide are 62 and 84 % smaller, respectively, in comparison to ZnSA. The higher amount of the bridging groups in the case of ZnRA compared to those on ZnO-C can be linked to the zinc hydroxide impurities.

![Figure 4.2.6. pKₐ distributions for the samples studied.](Reprinted from Ref. 161, Copyright 2015, with permission from Elsevier)

The optical properties were evaluated using UV–Vis–NIR diffuse reflectance spectroscopy. The received spectra are collected in Figure 4.2.7A. The highest photons absorption in the whole electromagnetic spectrum was obtained for ZnRA. It dramatically increases as the wavelength
approaches the UV range. The absorption spectra of the ZnSA and ZnO-C follow the same pattern, while the absorption of ZnSA is intensely lower in the UV range. The band gaps ($E_g$) were calculated from the UV-Vis-NIR spectra.\textsuperscript{125} The extrapolation of the linear fit of the plot of $[F(R:\infty)\nu]_2$ versus the photon energy ($\nu$) are provided in Figure 4.2.7B. The estimated band gaps are 3.22 eV, 3.05 eV and 2.98 eV for ZnSA, ZnRA and ZnO-C, respectively. The values of ZnO-C and ZnRA are in the range of other values reported for zinc oxide in the literature,\textsuperscript{131} while $E_g$ of ZnSA represents a typical value found for zinc (hydr)oxides.\textsuperscript{132,133} The wide band gap in the visible range is an advantage of our materials, since this characteristic is beneficial for application as photocatalyst and optical devices.\textsuperscript{134}

![Figure 4.2.7](image)

Figure 4.2.7. A) UV-Vis-NIR spectra of the samples, B) $[F(R:\infty)\nu]_2$ versus photon energy. The lines show the cut-off used to calculate the band gap energy. (Reprinted from Ref. 161, Copyright 2015, with permission from Elsevier)
4.2.3. Adsorption performance: the role of the visible light irradiation

The materials were evaluated as CEES reactive adsorbents. The weight increase after 24 h exposure to CEES vapors was recorded. The weight increases represent the capacity ($Q_{ads}$) of the samples to retain CEES and/or its surface reaction products. The values are reported as mg of weight increase per gram of material. The results obtained with irradiation from the solar simulator and in the dark (D) are shown in Figure 4.2.8.

![Figure 4.2.8. Adsorption capacities measured under the light exposure from a solar simulator and in dark.](image)

The highest adsorption capacities were recorded for ZnSA, which are 263 and 120 % higher compared to ZnSA under light and in dark, respectively. Only the former sample showed higher weight uptake of about a factor of two under light than that in dark. This is an evidence of this
sample photoactivity. Both ZnO-C and ZnRA showed the same weight uptake at light exposure and in dark. The measured capacity at light of the commercial sample is only the half than that of ZnSA, but almost double of the capacity measured on ZnRA. It is worth to mention at this point that even though the density of the light beam not measured, tests at different distances between the solar simulator and the closed adsorption system were attempted, as well as tests under ambient light. In all cases, the capacities showed equivalent values with those reported in Figure 4.2.8. This indicates that ZnSA, even at low light exposure, is photoactive.

4.2.4. Role of the textural parameters

The correlation of the capacity on the structural features (surface area and total pore volume) under light irradiation and in dark are presented in Figure 4.2.9. The dependence of the capacity on the structural features shows a linear trend for the experiments held in dark. On the contrary, the correlations are weaker for the capacities measured under light exposure. The total pore volume plays the most crucial in the extent of the adsorption in dark conditions, since the correlation coefficient is 0.99. This can be linked to the penetration of CEES molecules into the porous structure, and its further retention by weakly forces. The formed surface reaction products is possible to be retained on the surface with chemical bonds, besides the weakly physical forces.
4.2.5. Role of the surface chemistry

The dependences of the weight uptake on the number of the terminal and bridging groups are collected in Figure 4.2.10. A linear trend with $R^2=0.97$ is revealed only in the case of the terminal hydroxyl groups under light irradiation. This trend is stronger compared to the correlation between the weight uptake and the porosity in the case of the experiments held under light. It is important to point out that no liner trend between the weight uptake and the number of bridging groups was found. These results suggest a key role of the hydroxyl groups, especially for the extent of photoactivity. They also seem to be important for the retention of CEES molecules on the surface. ZnSA has the highest surface area and number of terminal hydroxyl groups and for that reason revealed the highest adsorption performance even in dark. The positive role of terminal OH groups...
during the reactive adsorption of actual vapors of CWAs on zirconium hydroxide was previously reported.\textsuperscript{39} Calcination of Zr(OH)\textsubscript{4} led to a decreased reactivity, due to the transformation to ZrO\textsubscript{2}.

![Graph](image)

Figure 4.2.10. Dependence of the amount adsorbed on the terminal groups (left) and the bridging groups (right) under light exposure and in dark.

4.2.6. Characterization of the exhausted samples

In order to evaluate the adsorption mechanism, thermal analysis was performed on the exhausted samples, with simultaneous GC analysis of outgases. The differential thermal gravimetric (DTG) curves of the initial and exhausted samples, under light for 24 hours, are collected in Figure 4.2.11. Three peaks are revealed at the DTG curve of the initial ZnSA. The first one at 140 °C is linked to the removal of the physically adsorbed water (weight loss 7.9 %), and the second one at 225 °C is be attributed to the removal of the structural water molecules (weight loss 8.9%).\textsuperscript{126} The broad and
A low intensity peak with a maximum at 450 °C can be assigned to the total dehydroxylation of Zn(OH)$_2$ to ZnO (weight loss 6.1%).$^{135}$ Combining of the last two weight losses leads to 15 %, which is in good agreement with the theoretical weight loss for the transformation of hydroxide to the oxide zinc phase (18 %). The small difference can be linked to the small content of zinc oxide, as revealed from the XRD analysis. The DTG curve of ZnRA showed similar pattern, but with considerably lower intensities of all peaks and a total weight loss only 3.9 %. Since ZnO is thermal stable up to 1000 °C, the peaks at 225 and 450 are assigned to the limited amount of the zinc hydroxide in this sample. This is in good agreement with the XRD results. Moreover, the lower intensity of the peak linked to the removal of the weakly adsorbed water molecules suggests a marked hydrophobicity. The DTG curve of ZnO-C clearly indicates the high purity of the oxide phase, since no peaks related to dehydration or dehydroxylation were observed. The total weight loss for this sample was 2.9 %.
Figure 4.2.11. DTG curves in helium for initial and exhausted under light irradiation ZnSA, ZnRA and ZnO-C. (Reprinted from Ref. 161, Copyright 2015, with permission from Elsevier)

Three new peaks are revealed on the DTG curves of the samples exposed to CEES under light irradiation, at 160 ºC, 300 ºC, and at the temperature higher than 760 ºC. The m/z thermal profiles of the exhaust gases during the thermal analysis are collected in Figure 4.2.12. Table 4.2.1 collects the names, chemical formulas, abbreviations and the characteristics mass-to-charge ratios based
on which the identifications of the surface reaction products were carried out. The MS thermal profiles of the saturated organic compounds, such as CEES, HEES or EES (m/z: 75, 63, 61, 47, 29), and the unsaturated product, such as EVS (m/z: 88, 73, 60, 59, 27) showed two peaks with a maximum at 160 and 300 °C. The decomposition of the adsorbed molecules at two different temperatures suggests two energetically diverse adsorption sites. The decomposition of the weakly adsorbed molecules takes place at lower temperature (160 °C), while the decomposition of the strongly adsorbed molecules - at 300 °C. The comparison of the intensities suggests that in the case of ZnSA, both adsorption sites are favorable. The weight loss which occurred above 750 °C can be linked to the decomposition of the formed ZnCl₂ species during the reactive adsorption, and/or to the reduction of zinc oxide to Zn⁰ (boiling point 907 °C) by the carbonaceous phase. The traces of the latter phase might be formed during the thermal analysis (charring of organic compounds). The total weight loss in the case of ZnSA was 28.3 %, and it is 5.1 % higher than the total weight loss recorded for the initial sample. This difference is in a good agreement with the amount adsorbed (Figure 4.2.8).

Table 4.2.1. Details on the detected compounds on the surface.

<table>
<thead>
<tr>
<th>Name</th>
<th>Linear formula</th>
<th>Abbreviation</th>
<th>Characteristic mass –to-charge ratio (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-chloroethyl ethyl sulfide</td>
<td>CH₃CH₂SCH₂CH₂Cl</td>
<td>CEES</td>
<td>75, 63, 61, 47, 29</td>
</tr>
<tr>
<td>2-hydroxyethyl ethyl sulfide</td>
<td>CH₃CH₂SCH₂CH₂OH</td>
<td>HEES</td>
<td>75, 63, 61, 47, 29</td>
</tr>
<tr>
<td>Ethyl vinyl sulfide</td>
<td>CH₃CH₂SCH=CH₂</td>
<td>EVS</td>
<td>88, 73, 60, 59, 45, 27</td>
</tr>
<tr>
<td>ethyl sulfide</td>
<td>CH₃CH₂SCH₂CH₃</td>
<td>EES</td>
<td>75, 63, 61, 47, 29</td>
</tr>
</tbody>
</table>
Figure 4.2.12. m/z thermal profiles (in helium) for the fragments related to CEES, EES and/or HEES (a) and EVS (b) for the exhausted ZnSA under light (L) and in dark (D) and for the ZnO-C under light (L). (Reprinted from Ref. 161, Copyright 2015, with permission from Elsevier)

Less pronounced differences exist between the DTG curves of the initial and exhausted ZnRA. The three new peaks are at the same positions as those discussed above for ZnSA. The weight loss of the exhausted sample was only 1.4 % higher compared to the weight loss of the initial sample. The small weight uptake of ZnRA limits the detections of m/z in the exhaust gases. The m/z thermal profiles of exhausted ZnO-C were recorded and the new peaks on the DTG curve match those of ZnSA. The only noticeable difference is that the saturated products are adsorbed on the
surface preferably by weak forces, since the intensity of the peaks at the m/z thermal profile is greater at low temperatures. The total weight loss on ZnO-C exposed to CEES is 2.5 % larger than that of the initial sample.

The m/z thermal profiles of the ZnSA sample exhausted in dark revealed only the decomposition of CEES molecules that were strongly adsorbed on the surface. The m/z thermal profiles of EVS did not show any peak. This suggests that the light irradiation promotes the dehydrohalogenation of CEES to EVS, due to the photoreactivity of ZnSA. The m/z thermal profiles of the exhausted in dark ZnO-C showed limited intensity of the peaks related to EVS.

4.2.7. Analysis of the extracts

The extraction of the species adsorbed on the surface of the exhausted samples was done with acetonitrile as a solvent. The extracts were analyzed by GC-MS and MS-MS. For all samples exposed to light, the main compound detected at the extracts was EVS. Only in the case of ZnSA, the hydrolysis product 2-hydroxyethyl ethyl sulfide (HEES) was also detected. This is a strong evidence that the hydroxyl groups play a key role in the reactive adsorption of CEES. It is important to mention that no oxidation products, such as sulfoxide or sulfone, were detected in the extracts, for all the tested materials. In the literature, the degradation products that resulted from the oxidative ability of various metal oxides have been reported.\textsuperscript{42,138,139} In our case, EVS detection was limited in the extracts obtained from the sample exposed to CEES in dark. This supports the results of the TA-MS analysis on the photocatalytic reactions involved during the reactive adsorption and/or on the enhanced reactivity due to an exposure to light. The lack of detection of other products demonstrates the favorable production of EVS, especially upon light irradiation.
Limited trace of CEES was found in all exhausted samples. Since the CEES presence was supported by the TA-MS analyses, its absence during the analysis of the extracts indicates even the inability of the acetonitrile to efficiently extract the CEES from the materials, due to the strong adsorption on the surface.

4.2.8. Adsorption mechanism

The calculated band gaps support the hypothesis that the materials can act as photocatalyst (Pc). The photoactivity of zinc oxide under visible light is well known.\(^{58,131,134,140,141}\) As expected, the highest porosity of ZnSA led to the best adsorption performance, due to the highest dispersion of the active centers, terminal OH groups on the surface. The acquired results indicate that the terminal OH groups play a crucial role on the extent of adsorption and the degree of CEES transformation.

The absorption of a photon leads to the excitation of the photocatalyst (Pc*):

\[
Pc + h\nu \rightarrow Pc^* \quad (1)
\]

The exited surface of the photocatalyst uses the energy for a primary photocatalytic reaction. Therefore, after being adsorbed (most likely by hydrogen bonds),\(^{142}\) CEES is transformed into ethyl ethyl sulfonium (EES) cation by means of a Photoinduced Electron Transfer (PET) reaction:\(^{41,143}\)

\[
Pc^* + \text{CEES} \rightarrow Pc^- + \text{EES}^+ \quad (2)
\]

It has been reported that once EES\(^+\) is formed, it may be converted to a cyclic cation through an intermolecular cyclization process.\(^{40,41,144–146}\) After that, a labile hydrogen from the cation transfers
to the negative charged lattice oxygen of the zinc phase, that acts like a Lewis base.\textsuperscript{147,148} This proceeds via an bimolecular elimination (E2) pathway, resulting in the formation of the dehydrohalogenation vinylic product, EVS.\textsuperscript{42,149} Simultaneously, the chloride anion reacts with a zinc atom on the surface forming ZnCl\textsubscript{2}. Zafrani and co-workers reported that the main degradation product of anhydrous HD on Al\textsubscript{2}O\textsubscript{3} was is VVS.\textsuperscript{150} In our study, EVS was detected on the ZnSA and ZnRA samples only after the CEES exposure at the light.

When hydroxyl groups and/or physisorbed water molecules are present, the CEES transformation can proceed by a substitution of the Cl\textsuperscript{−} ion by the OH group.\textsuperscript{145} The crucial role of water has been reported for CaO.\textsuperscript{34} Absorption of a photon excites the electron from the valence to the conduction band of Zn(OH)\textsubscript{2}. The formed hole reacts with water associated with the hydroxyl groups in the zinc hydroxide phase, resulting in the formation of hydroxyl radicals.\textsuperscript{151} S-CH\textsubscript{2}CH\textsubscript{2}Cl is destabilized by the electron/hole pair and gets transformed to a transient radical. The latter reacts with the hydroxyl radical that acts as nucleophile, producing the hydrolysis product, HEES.\textsuperscript{42} It remains on the surface probably by physical interactions, such as hydrogen bonding. Since water, light and thus formation of OH radicals are crucial for this process, HEES was formed and detected only on the ZnSA sample exposed to light. Other studies have also shown that the terminal groups participated in photochemical reactions via the formation of hydroxyl radicals, therefore enhancing the removal of sulfide species such as CEES [44] or H\textsubscript{2}S.\textsuperscript{151} The rate-determining step is the transformation of the cations to HEES, which is enhanced by light.\textsuperscript{144,145} The same pathways were proposed by Martyanov and co-workers on TiO\textsubscript{2},\textsuperscript{138} and Singh and co-workers on vanadium oxide,\textsuperscript{38} where large amounts of water and isolated hydroxyl groups contributed to the formation of HEES. Furthermore, Zafrani reported that on Al\textsubscript{2}O\textsubscript{3} in the presence of water HD degraded to thiodiglycol instead to divinyl sulfide.\textsuperscript{150} In our study, hydroxyl groups and associated with them
water lead to the formation of HEES on ZnSA upon the light exposure. It is worth to mention, that the two degradation products obtained on our materials are considerably less toxic than the CWA surrogate used in this study. Based on the results obtained, a schematic representation of reaction pathways on the surface of our materials is proposed (Figure 4.2.13).

![Reactions scheme](image)

Figure 4.2.13. Proposed reactions scheme of CEES reactive adsorption upon the visible light exposure. (Reprinted from Ref. 161, Copyright 2015, with permission from Elsevier)

### 4.2.9. Conclusions

The results presented in this chapter show that various addition rate of the precipitation agent (NaOH) to a zinc chloride solution, results in materials with entirely different physicochemical nature. Slow rates lead to the formation of orthorhombic particles of Zn(OH)$_2$, while rapid addition forms flower-like ZnO nanoparticles. The former sample compared to the latter showed higher:

1) Number of terminal hydroxyl groups by 249 %
2) Number of bridging oxygen groups by 27 %
3) Surface area by 347 %
4) Total pore volume 832 %
5) Wider band gap by 6 %
6) Weight uptake performance under light exposure by 263 %
7) Weight uptake performance in dark by 120 %

The almost double weight uptakes after CEES exposure measured at ambient light than compared to that in dark on ZnSA reveals photoreactivity. Even with a wider band gap, ZnSA showed significant greater photoreactivity and adsorption performance under light irradiation. The dependences of the adsorption performance on the chemical and structural features showed the terminal hydroxyl groups as the most important. These groups are involved in the hydrolysis reactions, which take place on the surface and thus enhance the detoxification ability of the samples. The surface area was also found to play a crucial role by increasing the dispersion of the active sites, and thus their contact with the organic molecules.

Ethyl vinyl sulfide was identified as the main degradation products for all materials when the adsorption tests were performed in the light. In the case of ZnSA, the detected concentration of EVS was the highest and hydroxyethyl ethyl sulfide (HEES) was also detected at the extracts. This supports the enhanced photoactivity of ZnSA. The degradation of CEES is triggered by the excitation by photons, which promote the formation of the intermediate cyclic ethyl ethyl sulfide cation and the formation of OH radicals. When the adsorption tests were performed in dark, the detected amount of EVS was dramatically lower and no HEES was detected at the extracts.
4.3. Effect of GO phase in Zn(OH)$_2$/GO composites on the extent of photocatalytic reactive adsorption

4.3.1. Introduction and materials

The objective of this study was the evaluation of effects of GO addition on the structural and chemical features of the adsorbents and on the extent of reactive adsorption. An additional objective was to identify the optimal amount of GO which could lead to an improvement in their performance as adsorbents and catalysts. Pure zinc hydroxide is referred to as ZnOH and the composites - as ZnGO1, ZnGO5, ZnG10 and ZnGO20, where the numbers represent the wt/wt % of GO to the final mass of the material. Finally, since 24 hours of exposure was arbitrarily chosen, the exposure time of the adsorption tests was extended until the maximum weight uptake was obtained for each sample. All the adsorption tests were carried out at ambient conditions.

4.3.2. Structural and morphological characterizations

In order to determine whether or not the addition of GO altered the formation of the zinc hydroxide structure, the synthesized composites were analyzed by powder XRD (Figure 4.3.1). The diffractograms of ZnOH showed zinc hydroxide as a predominant crystallographic phase. Traces of zinc oxide were also present. This result is in agreement with the X-Ray diffractograms in the previous sub-chapter, although different batches of the materials were used in this study. Interestingly, the diffractograms of the composites clearly indicate that the only crystallographic phase is ε-Zn(OH)$_2$, since no diffractions related to ZnO or impurities were detected. The diffraction peaks can be indexed as those of orthorhombic wülfingite (JCPDS 38-0385). The absence of the characteristic peak corresponding to the d$_{002}$ of GO at around 10.2 2θ suggests its exfoliation during the composite formation. The average crystallite size for all the materials was
calculated from the the (101) diffraction using the Scherrer equation. For ZnOH, the average crystallite size was estimated to be about 49.2 nm, while for the composites the values of 35, 39 and 43 nm for 5, 10 and 20 % of GO, respectively, were found.

Figure 4.3.1. X-ray diffraction patterns for GO and the initial samples.

ε-Zn(OH)$_2$ particles with bipyramid shape of micrometric size are visible on the SEM image of ZnOH (Figure 4.3.2 A). Limited amount of zinc oxide particles can be also seen with a platelets-like shape of a micron range size. The particle morphology dramatically changed upon the addition of GO, especially for the composites with the higher amount of GO. In ZnGO5, bipyramid particles of several tens of nanometers, linked to the Zn(OH)$_2$ phase (Figure 4.3.2 B), surround the graphite
oxide sheets, forming a web-like network with a high level of surface roughness.\cite{46,151} A further increase in the amount of GO results in a higher dispersion of the inorganic phases around the GO sheets, and the bipyramid particles are not detectable for both ZnGO10 and ZnGO20.

Figure 4.3.2. SEM images of ZnOH (A), ZnGO5 (B) and ZnGO10 (C).

Since it was shown previously that the porosity and the surface area are key factors for the performance of adsorbents, especially for physical adsorption, nitrogen adsorption isotherms were measured on all samples. The parameters of the porous structure calculated from these isotherms are summarized in Figure 4.3.3. The synthesis approach used led to composites with improved surface areas and total pore volumes, and marked structural heterogeneity. Compared to ZnOH,
ZnGO5 showed a slight decrease by 4 and 21 % in the surface area and total pore volume, respectively. The highest values of the porous structure parameters were obtained for ZnGO10. The surface area increased by 43 %, while the total pore volume showed an even higher increase (67 %) as compared to the corresponding structural parameters of ZnOH. Further increase in the amount of GO resulted in a decreased porosity. This can be linked to limitations in the spatial growth of the zinc hydroxide phase. It appears that 10 % of GO is the optimal amount, resulting in the most pronounced porosity.

Figure 4.3.3. Parameters of porous structure calculated from the nitrogen adsorption isotherms.

4.3.3. Surface chemistry analysis

The surface chemistry of the samples was analyzed by potentiometric titration (Figure 4.3.4). The addition of 5 % GO slightly altered the amount and the distribution of the surface oxygen containing groups. On the other hand, a higher amount of GO led to a marked increase in the
amount of the terminal hydroxyl groups, while the bridging groups showed a dramatically
decrease. ZnGO10 was found to have the highest amount of terminal groups (22 % increase
compared to ZnOH), while revealed a 79 % decrease in the amount of bridging groups. ZnGO20
showed a less pronounced increase in the amount of the terminal hydroxyl groups and almost equal
amount of bridging groups, compared to ZnGO10.

Figure 4.3.4. Amounts of terminal and bridging oxygen containing groups detected from
potentiometric titration experiments.

The ratios of the terminal to bridging groups are 0.8, 1.4, 5.0 and 5.6 for ZnOH, ZnGO5, ZnGO10
and ZnGO20, respectively. It can be seen that the addition of the carbonaceous phase led to an
increase in the dispersion and amorphicity level of zinc hydroxide, since 10 and 20 % of GO
resulted to the highest ratios of terminal to bridging groups.
4.3.4. Adsorption performance and the optimum amount of GO

The reactive adsorption was expected to be affected by the altered textural and chemical surface features. The first goal was to determine if the addition of the carbonaceous phase led to an improvement in the weight uptakes after 24 hours. The tests were carried out in ambient light (L1) and under a solar light simulator (SL1) in order to evaluate the role of the light intensity. For comparison, the tests were also performed in dark. The capacities expressed in weight uptake (mg) per gram of the adsorbents are collected in Figure 4.3.5.

Interestingly, no difference between the two different light sources were detected, suggesting that the density of the irradiation does not play a role. Further qualitative trials with different light densities from the solar simulator were held, in order to double check if the light irradiation density could change the adsorption performance. In all cases, no differences were observed. The fact that all samples the weight uptakes in dark were almost twice smaller than those measured at light, indicate that the composites are photoactive even under ambient light. Moreover, the better adsorption performance in visible light than in dark indicates the relevant role of light in improving the adsorption of CEES and/or its degradation products on the surface. This effect is found to be more pronounced for the composites than for Zn(OH)$_2$. 
Figure 4.3.5. Capacities measured after 24 hours at various conditions exposure (ambient visible light, solar light simulator, in dark).

The addition of the carbonaceous phase led to bigger weight gains after the one-day exposure for all composites compared to that on ZnOH, either at light or in dark. It is worth to mention at this point that for GO, the weight uptakes under all conditions were negligible. The weight uptake on ZnGO10 was the highest one under ambient light (81 % higher than that on ZnOH). This increase was less pronounced in dark (+ 49 %). On ZnGO5 the least effect of GO on adsorptive performance was found (27 % at light and 9 % in the dark compared to ZnOH). On the other hand, the weight uptake on ZnGO20 was significantly higher comparing to that on ZnOH, but compared to ZnGO10 the capacities were lesser by 22% under ambient light and 17 % in the dark. The results confirmed that the optimal amount of GO in the composites, that led to the maximum decontamination performance, was 10 % w/w of the final composite mass.
4.3.5. Role of the textural parameters

In order to elucidate the role of the porosity of our materials in the reactive adsorption process, the dependence between the weight uptake and the surface areas (S\textsubscript{BET}) or total pore volume was analyzed (Figure 4.3.6). The surface area found to play a role when the sample was exposed to CEES in dark, since the obtained correlation coefficients is 0.93. This suggests that in dark the CEES molecules are mainly retain on the surface via physical adsorption and the degradation is limited. On the other hand, no correlation was found in the case of the light irradiation. This suggests that the presence of light promote alternative adsorption/degradation pathways. No correlation between the capacity and the total pore volume could be established.

![Figure 4.3.6](image)

Figure 4.3.6. Dependence of the amount adsorbed (after 24 h) on the surface area (A) and the total pore volume (B) under light exposure and in dark.
4.3.6. Role of the surface chemistry

The dependence between the weight uptake and and the number of the terminal -OH groups ($S_{BET}$) or bridging groups showed a linear trend, with correlation coefficients 0.99 and 0.94, respectively. The stronger correlation in visible light designates the key role of the hydroxyl groups in the photoactivity of these samples. No correlation was found between the weight uptake and the amount of the bridging groups. ZnGO10 showed the largest surface area and the highest number of terminal hydroxyl groups. Those two factors certainly play crucial roles enhancing the CEES adsorption performance of this material, and can be considered as linked to each other since a developed surface area promotes a favorable dispersion of the reactive adsorption centers/terminal OH groups.

![Graph showing the dependence of adsorption capacity on the number of terminal and bridging groups](image)

Figure 4.3.7. Dependence of the amount adsorbed (after 24 h) on the number of the terminal OH groups (A) and the bridging groups (B) at light exposure and in dark.
4.3.7. Study of the kinetics and the maximum detoxification performance

We cannot cross out the probability that slow reactions of CEES and the products formed on the surface of the adsorbents are taking place for longer time than 24 hours, since this duration was arbitrary chosen for the adsorption/reaction process. Moreover, the materials can act as photocatalyst, degrading adsorbed CEES. For those reason, the adsorption tests were carried out for up to nine days, in order to examine the extent of the processes governed by the kinetics of the adsorption and degradation performance. The increase in the weight of the samples exposed for various periods of time (up to 9 days) was recorded. These tests were carried out at ambient light irradiation, due to the fact that the usage of the solar light simulator did not alter the adsorption uptake. The further discussion focuses on ZnOH and ZnGO10, since the latter was the best performing composite, and ZnOH was chosen for the sake of the comparison.

The recorded weight uptakes are collected in Figure 4.3.8. Interestingly, the weight gain continues until the eight day for both samples. The dependence of the capacity on the exposure time up to the sixth day shows a linear trend with correlation coefficients 0.998 for ZnGO10 and 0.991 for ZnOH. The weight gained on day 7 reached almost equal value to the initial mass of the samples (20 mg). This indicates that more than the half of the volume of the initially injected CEES transferred to the adsorbents’ surfaces. Until the sixth day, the uptake on the composite was higher than that on ZnOH. This can be due to the higher dispersion of the active sites promoting the higher degradation reactivity.
Figure 4.3.8. Weight gains measured at visible light for up to nine days. The change in the slopes of lines indicates the change in the chemistry/physics of the interface (condensation of adsorbents on the surface and saturation).

The capacities until the sixth day were fitted to the linearized-integral form of the Lagergren’s pseudo-first order kinetic model. The plot of $\ln(q_e-q_t)$ against time ($q_e$ is the maximum recorded capacity and $q_t$ is the amount adsorbed at the specific time) revealed a linearity with high correlation coefficient $R^2$ (0.981 for ZnGO10 and 0.968 for ZnOH). The pseudo-first order model indicates that the adsorption rate is constant and not affected by the amount of the material.

The weight uptake on zinc hydroxide overcame the one of the composite after seven days of interactions. A liquid film formed on the surface of the ZnOH sample, which can be linked to the
condensation of CEES or of the products of its reactive adsorption. The color of the material changed from white to yellowish. Additionally, the sample began to resemble rather a gel than a solid matter and the weight was gained at a higher rate. The latter stopped with the saturation of the sample with condensed vapors (no change in weight recorded) on the ninth day. This condensation might be responsible for a change in the reactivity since the liquid layer on the surface of the sample will change the nature of interactions. The adsorption rates indicate that the samples are acting as catalyst until they get saturated with reactants. In the case of ZnGO10, the time needed to reach the saturation is longer than that for ZnOH and the condensation of vapors starts after the eight day. That delay in the surface condensation might be related to a higher catalytic activity, the improved porosity, and/or higher number of terminal hydroxyl groups of the composite than those of ZnOH.

It is worth to mention that the maximum weight uptakes recorded on the ninth day were 1339 and 1236 mg per gram for ZnOH and ZnGO10, respectively. The amounts adsorbed on the surface of ZnOH and ZnGO10 represent 63 % and 58% of the total initial volume of initially injected CEES, respectively. If the entire injected CEES were totally evaporated, the maximum possible capacity would be 2120 mg/g (by assuming that the entire amount of the CEES retained on the surface). Since no liquid CEES remained in the vessel, the difference of the theoretical maximum capacity and the recorded suggests that unreacted CEES or its degradation products remained in the headspace.

4.3.8. Surface chemistry analysis of the exhausted samples

FTIR spectra of the initial and the exhausted samples were analyzed, in order to determine the species deposited on the surface after the exposure. A comparison of the spectra for the initial
ZnOH and ZnGO as well as for the exhausted samples exposed to CEES for 7 days in light are collected in Figure 4.3.9. In the spectrum of initial ZnOH, the bands at 715 and 900 cm\(^{-1}\) are linked to the out-of-plane bending and vibration modes of the OH groups, while the bands observed at 830, 1040 and 1090 cm\(^{-1}\) are assigned to the deformation vibration of –OH groups, Zn-OH bending and –OH twisting vibration, respectively. The bands at 1390 cm\(^{-1}\) with a shoulder at 1360 cm\(^{-1}\), and at 3450 cm\(^{-1}\) are assigned to the vibrations of OH groups coordinated to Zn(II) ions, while the bands at 1500 cm\(^{-1}\) and at 3240 cm\(^{-1}\) - to the hydroxyl groups of water. Similar bands as those for ZnOH are visible on the spectrum of ZnGO, but with a lower intensity of the out-of-planes bending and vibration modes of the hydroxyl groups. The weak bands in the region between 620 and 660 cm\(^{-1}\) are linked to the vibrations of C-C and C-H bonds of the carbonaceous phase. The bands associated to C=O and C-O bonds of the epoxy and carboxylic groups of graphite oxide (GO) were not detected.\(^{89,153}\) This supports that these oxygen functionalities were involved in the formation of the bonds with the inorganic phase.
Figure 4.3.9. FTIR spectra for the initial and exhausted ZnOH and composite samples after day 7 of CEES exposure (L7).

For the exhausted samples, groups of new bands appeared in various regions of the spectra. A summary of the formed products and the vibrational frequencies used to monitor these products...
are given in details in Table 4.3.1. For the exhausted samples, the spectral regions below 1720 cm\(^{-1}\) contain a complex overlap of stretching and deformation vibrational modes of aliphatic CH\(_x\), alone or bonded to heteroatoms (chloride or sulfur). The characteristics bands at 2976, 2886, 1453 and 1267 cm\(^{-1}\) can be assigned to -CH\(_2\)Cl, as a result of adsorbed CEES molecules on the surface.\(^{42}\) The characteristic bands from the stretching vibrations of C=C and C-H bonds of the monosubstituted alkenes (at 2976, 1613, 1550, 1593 and 900 cm\(^{-1}\)) from the vinyl group (C=CH\(_2\))\(^{154}\) indicate the presence of dehydrohalogenation vinylic products such as ethyl vinyl sulfide (EVS), vinyl vinyl sulfide (VVS) and methyl vinyl sulfide (MVS). The bands at 900 and 715 cm\(^{-1}\) show a significant intensity increase and are linked to the vibrations of the disubstituted C-H.

A dramatically increase in the intensity of the band located between 3600 and 3200 cm\(^{-1}\) for the exhausted samples is revealed. This broad band is attributed to the hydroxyl-stretching mode,\(^{72}\) and can be assigned either to the formation of 2-hydroxy ethyl ethyl sulfide (HEES), H\(_2\)O or also associated with the hydrogen-bonded molecules to the Zn-OH groups on the surface. Both chlorine and sulfur atoms can act as potential hydrogen-bond acceptor sites. Similar spectral changes, due to the hydrogen-bonded molecules, have been reported for the photocatalytic oxidation of CEES on TiO\(_2\).\(^{49}\) Moreover, the bands at 1422 and 1267 cm\(^{-1}\) can be attributed to the deformation vibrations of the -OH in the -CH\(_2\)OH group.\(^{42,155,156}\) The absence of bands related to the stretching vibration of C=O at the region of aldehydes and ketones (1780-1650 cm\(^{-1}\)) indicates that no carboxylic acids, esters or ketones were formed on the surface.\(^{42,155,156}\) The distinguishable bands related to sulfate groups were also not detected. Summarizing, the analysis of the FTIR spectra for the exhausted samples revealed that CEES, HEES and vinylic products exist on the surface.
Table 4.3.1. Assignment of bands detected on FTIR spectra of ZnOH and ZnGO10 exposed to CEES.

<table>
<thead>
<tr>
<th>Freq. (cm⁻¹)</th>
<th>Vibration mode</th>
<th>Assignment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3450</td>
<td>v(O-H)</td>
<td>(-CH₂OH)</td>
<td>142,157</td>
</tr>
<tr>
<td>2976</td>
<td>v(CH₂) as, v(CH₂Cl) as,</td>
<td>(-C₂H₃), (-CH₂ Cl)</td>
<td>42,157</td>
</tr>
<tr>
<td>2932</td>
<td>v(CH₃) as, v(CH₂S) as,</td>
<td>(-C₂H₄), (-CH₂S)</td>
<td>42,157</td>
</tr>
<tr>
<td>2886</td>
<td>v(CH₂) s, v(CH₂Cl) s, v(CH₂S) s,</td>
<td>(-CH₂S), (-CH₂Cl)</td>
<td>42,157</td>
</tr>
<tr>
<td>1613</td>
<td>v(C=C)</td>
<td>(-CH=CH₂)</td>
<td>154,158</td>
</tr>
<tr>
<td>1453</td>
<td>δ(CH₃) as bend, δ(CH₂) s</td>
<td>(-S-CH₃)</td>
<td>42,149,157</td>
</tr>
<tr>
<td>1422</td>
<td>δ(CH₂) as scissor</td>
<td>(-CH₂-S-) or (-C₂H₃)</td>
<td>42,157</td>
</tr>
<tr>
<td>1383</td>
<td>δ(CH₃) s bend</td>
<td>(-S-CH₃)</td>
<td>42,157</td>
</tr>
<tr>
<td>1267</td>
<td>δ(CH₂Cl) wag, δ(OH) b</td>
<td>(-CH₂Cl), (-CH₂OH)</td>
<td>42,157</td>
</tr>
<tr>
<td>1215</td>
<td>δ(CH₂S) wag</td>
<td>(-CH₂-S-)</td>
<td>42</td>
</tr>
<tr>
<td>970</td>
<td>δ(CH₂) wag</td>
<td>(=C-H)</td>
<td>42</td>
</tr>
</tbody>
</table>

4.3.9. Identification of the retained on the surface reaction products

Thermal analysis and MS-MS analysis of the extracts were used to further evaluate the the nature of the degradation products formed during the surface interaction reactions. At this stage is considered helpful, for the sake of discussion, to introduce the characteristic mass-to-charge ratios (m/z), based on them was held the identification of the compounds. The names of the detected compounds on the surface and in the headspace, along with their nomenclature, chemical formulas, abbreviations and the method used for their detection are listed in Table 4.3.2.
### Table 4.3.2. Details on the detected compounds on the surface and in the headspace.

<table>
<thead>
<tr>
<th>Name</th>
<th>Linear formula</th>
<th>Abbrev.</th>
<th>Identification based on</th>
<th>Characteristic mass –to-charge ratio (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-chloroethyl ethyl sulfide</td>
<td>CH$_2$CH$_2$SCH$_2$CH$_2$Cl</td>
<td>CEES</td>
<td>TA-MS, GC-MS, MS-MS</td>
<td>124, 109, 89, 75, 61, 47</td>
</tr>
<tr>
<td>Ethyl vinyl sulfide</td>
<td>CH$_3$CH$_2$SCH=CH$_2$</td>
<td>EVS</td>
<td>TA-MS, GC-MS, MS-MS</td>
<td>88, 73, 60, 59, 45</td>
</tr>
<tr>
<td>2-hydroxyethyl ethyl sulfide</td>
<td>CH$_3$CH$_2$SCH$_2$CH$_2$OH</td>
<td>HEES</td>
<td>TA-MS, MS-MS</td>
<td>106, 75, 61, 47</td>
</tr>
<tr>
<td>Vinyl vinyl sulfide</td>
<td>CH$_2$=CHSCH=CH$_2$</td>
<td>VVS</td>
<td>TA-MS, GC-MS</td>
<td>86, 85, 71, 59, 41, 40</td>
</tr>
<tr>
<td>Methyl vinyl sulfide</td>
<td>CH$_3$=CHSCH$_3$</td>
<td>MVS</td>
<td>TA-MS, GC-MS</td>
<td>74, 59, 47, 44, 40</td>
</tr>
</tbody>
</table>

Thermal gravimetric (TA) and differential thermal gravimetric (DTG) curves measured in helium atmosphere are collected in Figure 4.3.10. For initial ZnOH, the DTG curve was analyzed in the previous sub-chapter. For ZnGO, the intense peak on the DTG curve between 130-170 °C can be assigned to the removal of the physically adsorbed or structural water molecules, while the peak assigned to the dehydration of Zn(OH)$_2$ phase centered at 215 °C is overlapped from the intense peak of the GO decomposition. The shoulder at about 450 °C can be attributed to the totally dehydroxylation of Zn(OH)$_2$. The additional wide peak over 800 °C is assigned to the reduction of formed zinc oxide to Zn (boiling point 907 °C) by the carbonaceous phase.
Figure 4.3.10. TA and DTG curves for the initial, after 1-day (L1) and after 7 days (L7) exposure to CEES vapors in visible light for ZnOH and ZnGO10.

For both exhausted samples after 7 days CEES vapor exposure, the enlarged weight loss up to 170 \(^\circ\)C is related to the removal of water molecules and to the large amount of the degradation products of lower boiling points than that of CEES, such as MVS (b.p. 86 \(^\circ\)C), VVS (b.p. 78-92 \(^\circ\)C) and EVS (b.p. 92-97 \(^\circ\)C).\(^{137}\) Physically adsorbed CEES and HEES with boiling points of 156 \(^\circ\)C and 184 \(^\circ\)C,\(^{137}\) respectively, were removed from the pores at the temperature range around 210 \(^\circ\)C. Moreover, the new peak that appears for both samples at 460 \(^\circ\)C can be assigned to the decomposition of the new surface products such as ZnCl\(_2\), ZnS, and ZnSO\(_4\).\(^{59}\) The existence of
new sulfur containing products can be supported by the color change of the samples after the thermal analysis. The exhausted ZnGO sample after 7 days exposure was grey before the TA analysis, but it turned to yellow afterwards (Figure 4.3.11). ZnOH L7 was bright white before the thermal analysis and it turned to yellowish. In the case of the latter sample, it can be observed the dramatically mass loss after the thermal analysis (Figure 4.3.11 C-D).

Figure 4.3.11. Exhausted ZnGO10 L7 composite before TA analysis (A) and afterwards (B). For comparison, the exhausted ZnOH L7 before (C) and after TA analysis (D).

To further analyze the compounds formed as a result of the interactions/decomposition during the exposure to CEES and retained on the surface, the extracts from the exhausted samples were tested by MS-MS. The compounds detected on both samples were EVS, HEES and CEES. No traces of VVS, MVS or any oxidation product (diethyl sulfoxide, diethyl sulfone or diethyl sulfone) were found. This does not exclude the presence of the latters in the headspace in a non-adsorbed form.

**4.3.10. Identification of the volatile products in the headspace**

Although the weight uptakes and the detailed analysis of the exhausted samples are important for assist the evaluation the adsorption performance in solitary they cannot deliver enough
information to totally understanding of the photocatalytic activities. The results presented above suggest that the adsorption process includes photodegradation of CEES vapors simultaneous with chemical and/or physical adsorption of various formed compounds and no degraded CEES. It is possible that the many products formed during the adsorption process do not remain on the surface, especially if they are of high volatility.

Consequently, the analysis of the headspace provides additional information, which helps to determine the reactive adsorption pathways. The qualitative and semi-quantitative identification of the volatile compounds in the headspace was carried out using GC-MS.

The analysis of the chromatograms indicated that the amount of CEES in the headspace of the closed reaction vessel gradually decreased with the exposure time. Except CEES, the compounds detected, were EVS, VVS and MVS. Interestingly, the latter two compounds were not detected at the acetonitrile extracts from the surface. The comparison of the chromatograms of ZnGO10 and ZnOH after 6 days of exposure are showed in Figure 4.311. Only the chromatograms after 6 days of adsorption are presented, since, as it was aforementioned, after 7 days vapors started to condense on the surface of ZnOH. For the composite, the intensity of the peaks related to the photo-degradation of CEES were higher, while the peak of unreacted CEES had lower intensity (retention time 5.1 min). Similar trend was found for the samples exposed to CEES for all time periods. The revealed enhanced photocatalytic performance of the composite can be attributed to the alteration in the surface and chemical heterogeneity as a result of the GO addition. The developed porosity as well as the increased amount and the higher dispersion of the hydroxyl groups play a key role.
Figure 4.3.12. Chromatograms of the headspace for ZnOH and ZnGO10 after 6 days of CEES exposure.

The analysis of the chromatograms suggests that the degradation of CEES undergoes mainly through the dehydrohalogenation, since the most intense peak is the one of EVS. This is in good agreement with the results obtained from the analysis of the extracts by MS-MS. The absence of HEES in the headspace could be due its high boiling point (180-184 °C) and/or the possibility to form hydrogen bonds with surface sites. This might result in its strong retention on the surface.

The adsorption progress in the case of ZnGO10 was monitored analyzing the evolution of the chromatograms features and the peak areas of every detected compound in the headspace for up to nine days, Figures 4.3.12 and 4.3.13, respectively. After a day, only the peak related to CEES was visible. The absence of other peaks indicates that the formed products remained adsorbed on
the surface and/or in the pores of the absorbents. In facts EVS and HEES were detected in the extracts of after 1-day exhausted sample. The continuous photocatalytic transformations of CEES until the sixth day can be clearly observed from the gradually decreasing intensity of the CEES’ signal and the increase of the EVS, VVS and MVS signals. After the sixth day, the decreasing trend of the intensity of the peaks linked to the formed degradation products can be due to the vapor condensation on the surface of the sample. This supports further the conclusion that the sample is acting as a photocatalyst, until its surface get saturated with CEES and/or with the formed compounds.

It is important to mention that after eight days, the liquid CEES totally evaporated from the container in the reaction vessel of ZnGO10, while after nine days of exposure, no CEES was detected in the headspace. These two facts indicate that the entire initially injected amount of CEES either retained on the surface of the samples or degraded.

Taking into account the weight uptake of the exhausted ZnGO10 (1230 mg/g) and the density of CEES ($d_{CEES} = 1.06 \text{ g/mL}$), the amount of the surrogate that retained or decomposed on the surface after 9 days was 58 wt %. Thus the remaining 42 % was totally degraded. Remarkably, our composite has the ability for detoxification of the amount of CEES that exceeds twice of its mass. On the other hand, ZnOH did not detoxify the entire CEES, since at the headspace after 9 days of exposure, CEES was still detected, while the liquid CEES did not totally evaporated. Even though the weight increase of ZnOH was higher than that on ZnGO10, its performance for vapor detoxification was less pronounced. It is possible that the major factor affecting this performance is the condensation of CEES on the surface, limiting the interactions of the surface active sites with the vapors. The adsorption test was carried out also on the pure GO under light or in the dark for up to nine days. The analysis of the headspace and the extracts from the exhausted materials
did not reveal any formation of the degradation products.

Figure 4.3.13. Tracking of the progress of adsorption and reactions by monitoring the chromatograms of ZnGO10 for up to 9 days.
Figure 4.3.14. Dependence of the area of the chromatographic peak (analysis of the headspace) for the particular compounds on the exposure time for ZnGO10.

4.3.11. Detoxification and adsorption mechanisms

The degradation pathways of CEES to the less toxic EVS and HEES on Zn(OH)$_2$ and ZnO for 24 hours of exposure have been thoroughly reviewed and analyzed in the previous sub-chapter. Briefly, the detoxification to the dehydrohalogenation vinylic product, EVS, takes place via a bimolecular elimination (E2) pathway. Adsorbed CEES is transformed to ethyl ethyl sulfonium cation. Then through an intermolecular cyclization process it is converted to a transient intermediate cyclic cation. A negative charged lattice oxygen of the zinc hydroxide phase acts like a Lewis base and accepts a labile hydrogen from the cation. Simultaneously, a Zn atom reacts
with the produced Cl\(^-\) to form zinc chloride. This pathway is promoted by photo-excitation of the material. By the absorption of a photon, an electron is excited from the valence to the conduction band of the zinc hydroxide phase, resulting to the formation of an electron-hole pair. The formed electron/hole pair leads to the formation of hydroxyl radicals\(^{138}\) and the simultaneously formation of a transient radical from the destabilization of CEES. This transient radical can react with a hydroxyl radical, forming HEES or it can get involved in the cleavage of a C-S and/or a C-C bond. Transient radicals can be also formed from the destabilization of the formed EVS.

The distinctive finding at the reactive adsorption of CEES on our composites, except the total detoxification of the CEES vapors in a closed system, is the detection of MVS and VVS in the headspace. The formation of these compounds is promoted by the high photo-reactivity of the surface, which promotes additional radicals’ reaction of the produced EVS. The surface of the composite exhibits a high efficiency for the photo-decomposition of CEES and GO seems to increase the efficiency of electrons transfer owing to its electrical conductivity.

The contribution of the radical reactions to the catalytic formation of VVS, MVS, EVS and HEES deserves more attention. The photogenerated holes in the valence band and the photogenerated electrons at the conduction band and the hydroxyl radicals play a crucial role in the photochemical destruction of CEES, by attacking the formed EVS, following the reactions schematically shown in Figure 4.3.14 (1, 2 and 3). The presence of water during the adsorption is a constant source of hydroxyl anions that are transformed to hydroxyl radicals when reacting with the formed holes (Figure 4.3.14, reaction 8). It is also possible that H\(_2\)O condense on the surface, forming an ultra thin layer with an increased radical population. This can be explained by the observed gel-like state of the absorbents after eight days of exposure in the case of ZnGO10 and after seven days for ZnOH. Moreover, the water formation on the surface can be confirmed by the intense bands on
the FTIR spectra of the exhausted materials (Figure 4.3.9), as well as by the marked weight loss observed at the temperature less than 100 °C during the thermal analysis of the exhausted samples (Figure 4.3.10).

The thiol radical (EVS') can undergo further elimination to form VVS by the creation of a vinylic bond (Figure 4.3.14, reaction 4) or to form MVS through the cleavage of the C-C bond (Figure 4.3.14, reaction 5). The “fishhook” half arrows indicate the transfer of a single electron. The formation of EVS can also happen through an intermolecular radical pathway of the produced ethyl ethyl sulfide radical from the adsorption of a photo-exited electron (Figure 4.3.14, reaction 6). It was previously reported that sulfides may undergo the cleavage of S-C bonds (two in CEES molecule), resulting in various radicals. These radicals can recombine forming disulfides, which are toxic, but less than is HD. This pathway was reported in the case of the photocatalytic oxidation of CEES on TiO₂. Disulfides were not detected on the surface or at the headspace of our samples by any of the analytical techniques.

Based on the obtained results, a collective schematic representation of all the reaction pathways is proposed in Figure 4.3.16. Since in our Vials-in-Vial adsorption system the surrogate does not directly interact as a liquid with a solid, the first step is its evaporation (Figure 4.3.16, I). CEES vapors in an adsorbed state interact then on the surface of our absorbents (Figure 4.3.16, II). How fast the equilibrium is reached in Step I and Step II plays a crucial role in the reactive adsorption process. It is proposed that the adsorbed CEES undergoes the abovementioned photocatalytic reactions pathways, which lead four degradation products (EVS, HEES, MVS and VVS), which are less toxic compared to CEES or non-toxic.
Figure 4.3.15. Schematic representation of the radical reactions.

Figure 4.3.16. Schematic representation of all interactions inside the closed adsorption vessel.
4.3.12. Conclusions

The successful formation of the composite of zinc hydroxide and graphite oxide resulted in an improved detoxification performance compared to pristine zinc hydroxide, since both adsorption and photocatalytic degradation ability of the materials remarkably increased. The synergistic effect of the formation of a composite led to a development of the most important features governing the detoxification performance, such as surface area, total pore volume and number of terminal hydroxyl groups. The extent of surface features alterations, as well as the adsorption performances strongly depend on the amount of the carbonaceous phase in the composite. The addition of GO has a positive effect on:

1) surface structural and chemical heterogeneity
2) dispersion of the inorganic phase
3) number of terminal -OH groups
4) surface area and the total pore volume
5) efficiency of electron transfer/sep rating holes from electrons
6) adsorption capacity
7) degradation-detoxification yield

The optimal amount of GO was found to be 10 %. The significantly higher weight uptakes in visible light compared to those measured in dark confirm the existence of the photocatalytic reactivity. The comparison of the composite, which consists of 10 percent of GO to the pure zinc hydroxide showed the following numerical increases, compared to Zn(OH)$_2$:

1) Number of terminal hydroxyl groups by 22 %
2) Surface area by 43 %

3) Total pore volume by 67%

4) Weight uptake performance after 24 hours of exposure under light irradiation by 81 %

5) Weight uptake performance after 24 hours of exposure in dark by 49 %

The increased density of the hydroxyl groups and chemical heterogeneity (presence of the carbon based phase) in the composite promoted the dispersive interactions of the organic molecules with the active sites of the adsorbents. Moreover, the active radicals on the composite with 10 % of graphite oxide are formed with greater efficiency than on Zn(OH)$_2$. The sample retained and/or decomposed the entire amount of CEES introduced to the system, which exceeds more than twice the mass of the composite, after nine days of exposure. This improved photocatalytic detoxification ability is a desirable property. Finally, the formed products are less toxic or non-toxic, which is an important feature of an effective decontamination process.
4.4. AuNPs and AgNPs embedded in nanostructured composites of zinc (hydr)oxide/GO

4.4.1. Materials and Objectives

The next goal was to evaluate if an addition of gold or silver nanoparticles can further promote the adsorption and photocatalytic degradation of CEES, under visible light irradiation. For that reason, the composites with zinc hydroxide, graphite oxide and NPs were synthesized, following the same synthetic procedure of the zinc hydroxide/GO composite. The arbitrarily chosen amount of NPs were 1 wt/wt % of the final total mass, and 10 % of graphite oxide, since this amount of GO was found previously to be the optimal. The composite of zinc (hydr)oxide, GO and AuNPs are referred to as AuZnGO, while the sample with AgNPs is referred to as AgZnGO. ZnGO was used in the analysis of the data for the sake of comparison.

4.4.2. Structural and morphological characterizations

The X-ray diffraction patterns of ZnGO, AuZnGO, and AgZnGO samples showed entirely different crystal morphologies (Figure 4.4.1). In the case of ZnGO, the diffraction peaks are matching perfectly with those of orthorhombic \( \varepsilon \)-Zn(OH)\(_2\) (JCPDS 38-0385).\(^{52}\) The addition of the silver nanoparticles led to the formation of two crystallographic phases. The diffraction peaks at 20.2°, 20.8°, 27.3°, 27.8°, 32.8°, 39.4°, 40.7°, 42.2°, 52.3°, 57.9°, 59.5°, and 60.4° can be indexed as those of orthorhombic \( \varepsilon \)-Zn(OH)\(_2\), while the diffraction peaks at 31.7°, 34.4°, 36.2°, and 47.6° can be linked to a well-crystallized hexagonal wurtzite structure of ZnO (JCPDS 36-1451).\(^{159}\) Low temperature and basicity, during the precipitation without any additive (GO or NPs), facilitate the nucleation and growth of Zn(OH)\(_2\) rather than of ZnO.\(^{160}\) The initial precipitation rate of Zn(OH)\(_2\) is faster than that of ZnO, due to the solubility differences.\(^{51}\) No change to the pH values was
observed by the addition of GO and AgNPs, so the resulted formation of the zinc oxide phase can be linked to a different crystallization pathway. The addition of AuNPs led to an entirely altered crystallization process and nucleation mechanism. The XRD diffraction pattern of AuZnGO indicates a high level of amorphicity. The absence of well defined diffraction peaks can be also attributed to an ultra small size of the crystals.111

![X-ray diffraction patterns for the initial samples.](image)

Figure 4.4.1. X-ray diffraction patterns for the initial samples.

The SEM images of the samples are collected in Figure 4.4.2. The texture of ZnGO (Figure 4.4.2 A) resembles those previously reported.82,151 The carboxylic groups at the edges of GO layers are likely “seeds” for the creation of a web-like network, with the inorganic phase connected to GO particles.59,82,151 The orthorhombic shaped Zn(OH)$_2$ particles are well crystalized around the organic phase. The composites revealed entirely different structural and morphological features.
For the composites consisted of AuNPs (Figure 4.4.2 B-C), spherical-like particles with sizes between 40 and 80 nm are well dispersed around the graphitic layers, resulting in a highly heterogeneous and amorphous material. The nanoscale crystal size might be responsible for the absence of diffractions peaks at the X-Ray diffractograms. For the composites consisted of AgNPs (Figure 4.4.2 D-F), both Zn(OH)\(_2\) and ZnO phase can be clearly seen around the GO phase. The zinc hydroxide phase can be detected as orthorhombic shaped particles, while the zinc oxide as a cobweb-like network. The pore in the shape of cages and tunnels are seen in Figure 4.4.2 F with sizes from 20 to 500 nm. These pores can promote the diffusion of vapors into the mesopores, which as showed in the previous sub-chapter play the uppermost role on the adsorption performance.

Apparently, an addition of NPs during the composite altered the chemistry of composite formation. The XRD and SEM results showed that in the case of AuZnGO, amorphous nano-crystallites are formed and they homogeneously surround the GO sheets.\(^{46}\) It has also been previously reported that the presence of metal NPs altered the ZnO growth.\(^{161}\) It is possible that AuNPs increase the number of nucleation centers for ZnO instead those for Zn(OH)\(_2\). This leads a to a drop in the size of the particles, which was also reported for alumina.\(^{54}\) The above mentioned details of the composites formation with embedded NPs are illustrated in Figure 4.4.3.
Figure 4.4.2. SEM images of ZnGO (A), AuZnGO (B-C) and AgZnGO (D-F).
The sizes of the Ag or Au nanoparticles were estimated by TEM (Figure 4.4.4). For the AgZnGO, the spherical shape of AgNPs retained with sizes in the range from 30 to 90 nm. These sizes are in good agreement with the size distribution of the initial AgNPs (see chapter 3). The AuNPs had even smaller sizes, starting from 10 nm up to 40 nm. For both AuZnGO and AgZnGO, the NPs were predominantly aggregated on the outer phase of the composites. The high resolution TEM images of both samples revealed areas with various overlapped lattices. The areas with darker contrast represent Au$^0$ and Ag$^0$ nanoparticles, respectively, due to the stronger scattering factor for electrons of these heavier atoms. The predominant gray areas are linked to the iron zinc hydroxide phase, while the even lighter gray areas to the GO phase.
Figure 4.4. TEM and HRTEM images for AgZnGO and AuZnGO composites.
The N₂ adsorption (Figure 4.4.5) are of Type II(b) for all composites (according to the extended IUPAC classification) with capillary condensation in inter-particle slits within the aggregates. The absence of a curvature at low p/p₀ indicate the lack of micropores. A very small Type H₃ hysteresis loop, between the adsorption and desorption isotherms indicates that the pores do not have a complex structure. The hysteresis loop increases for AuZnGO, suggesting a more complex porous structure.

![Figure 4.4.5. The nitrogen adsorption isotherm.](image)

The pore size distribution (Figure 4.4.6), obtained using BJH method, shows the heterogeneity of pore sizes, with no volume of micropores (< 2 nm) and a wide distribution of large mesopores, with a predominant size of about 15 to 35 nm. The addition of AuNPs resulted in a slight decrease in the pore sizes, and in the formation of small volume of pores with sizes less than 10 nm. On the
contrary, the addition of AgNPs led to an increment in the pore sizes, with a decrease in the volume of the mesopores.

Figure 4.4.6. Pore size distribution calculated using the BJH model.

The parameters of the porous structure calculated from the isotherms are summarized in Figure 4.4.7. The surface area of AuZnGO increased by 13.4 %, and the total pore volume of about 4 %, compared to those parameters for ZnGO. For AgZnGO, both surface area and total pore volume decreased, by 10 and 7 %, respectively, compared to ZnGO. That results suggest that the addition of AuNPs leads to a higher dispersion of the inorganic phase around the GO. The formation of nano-sized zinc (hydr)oxide particles can be another reason why AuZnGO exhibited the highest values of surface area and porosity.
4.4.3. Surface chemistry analysis

The amount of the terminal and bridging oxygen containing groups calculated from the results of potentiometric titration are collected in Figure 4.4.8. Comparing to ZnGO, the addition of NPs resulted in an increase in the number of the bridging oxygen groups by 96 and 81 % for AuZnGO and AgZnGO, respectively. This increase can be linked to the formation of zinc oxide phase, due to the altered nucleation. The addition of AuNPs did not alter the amount of terminal hydroxyl groups. On the contrary, the addition of AgNPs resulted in a decrease of terminal groups by 22 % as compared to ZnGO. The ratios of the terminal to bridging OH groups are 5.1, 2.7 and 2.3 for ZnGO, AuZnGO, and AgZnGO, respectively. This supports the finding that the addition of the nanoparticles led to an increase in the ZnO phase. The total amount of the oxygen containing groups detected using potentiometric titration was the highest for AuZnGO, as a results of the enhanced dispersion of the zinc (hydr)oxide phase and the nano-scaled particles.
Figure 4.4.8. Amounts of terminal and bridging oxygen containing groups detected by potentiometric titration experiments.

The element maps for the composites (Figure 4.4.9) further supports the high dispersion of NPs on the surface. For both composites, the absence of chloride (< 0.2 %) indicates that the NPs did not react with chloride from the initial ZnCl$_2$ solution. The comparison of the Au and Ag amounts on the surface showed than in the case of AgZnGO the AgNPs are mostly dispersed on the outer surface of the composites.
In order to acquire additional perceptions into the reactive oxygen species (ROS) that can be involved into the detoxification/decomposition reactions on our catalysts, the ability of the samples to generate hydroxyl radicals (•OH) and superoxide radicals was evaluated at ambient light and in dark. Terephthalate (TA) can be converted to HTA at the presence of hydroxyl radicals, and the later has a characteristic emission at 425 nm. The ability to promote the formation of •OH was evaluated by analyzing the fluorescence intensity of hydroxyl terephthalate (HTA) after various intervals of time (10, 30, 60, 120, 180 and 240 minutes) for all samples. The changes in the fluorescence spectra of the TA solution mixed with AuZnGO and AgZnGO are presented in Figure 4.4.10. It can be clearly concluded that the fluorescence intensity at 425 nm increased only for
AgZnGO. ZnGO and AuZnGO show the same behavior. No sample was able to form hydroxyl radical in dark.

Figure 4.4.10. The analysis of the changes in the intensity of the emission at 425 nm (formation kinetics of THA) with an increase in the experimental time under ambient light irradiation.

The ability of the samples to form superoxide species had been investigated by monitoring the nitro blue tetrazolium (NBT) degradation by UV-Vis spectroscopy. No material was found to promote the degradation of NBT either under light or in dark conditions, since the emission of the solution remained unchanged even after 4 hours.
4.4.5. Study of the kinetics and the maximum detoxification performance

The main goal of the addition of the NPs were to enhance further the photocatalytic performance of the ZnGO composite, which showed a supreme detoxification performance, especially after 8 days of exposure. For that reason, the detoxification tests were held under ambient light irradiation. In order to achieve the maximum evaporation of the injected liquid CEES, to examine the kinetics of the weight uptakes, and to monitor the evolution of the formed products, the adsorption tests were carried out for up to ten days. The weight uptakes were recorded and are collected in Figure 4.4.11.

![Figure 4.4.11. Mass uptakes/adsorption capacities measured at visible light for up to ten days.](image-url)
The mass uptakes increase almost linearly for all samples until the eighth day. Interestingly, the maximum weight uptake was found after 9 days for AgZnGO that have the smallest surface area, total pore volume and amount of terminal hydroxyl groups. AuZnGO also showed higher maximum weight uptake than did ZnGO. These facts elucidate that the addition of the nanoparticles into the composites play a beneficial role on the degradation ability, which apparently does not depend on the porosity and the number of surface functional groups.

4.4.6. Monitoring the evolution of the volatile products in the headspace

Since the weight uptakes suggested that the reactions that occur during the adsorption play a crucial role in governing the adsorption capability, the formation of the volatile products was monitored and their amounts were compared semi-quantitatively. The chromatograms of AgZnGO and AuZnGO are presented in Figure 4.4.12. Comparison of the intensities of the peaks related to CEES (at retention time slightly higher than 5 minutes) suggests that AgZnGO interact faster with the vapors of the surrogate than does AuZnGO since for all the time intervals the intensity of this peak was lower than the one for the latter sample. After 9 days, no CEES was detected in the headspace of AgZnGO. On the contrary, for AuZnGO the peaks related to CEES showed higher intensities after the same exposure time. The main two detected peaks at the retention time of about 2 minutes are from ethyl vinyl sulfide (EVS) and divinyl sulfide (DVS). In the case of AuZnGO, these peaks totally disappeared after 9 days of interactions, suggesting than even the formed products degraded further or retained on the surface.
A further comprehensive analysis of the chromatograms suggested that more compounds can be identified based on the chromatograms (Figure 4.4.13). All the identified species in the headspace along with their characteristic mass-to-charge ratios (m/z), names, chemical formulas, abbreviations, and boiling points are collected in Table 4.4.1. It is important to mention that all seven volatile compounds detected are non-toxic or significantly less toxic when compared to CEES.
Figure 4.4.13. Analysis of the chromatograms at specific retention time ranges.

Table 4.4.1. Details on the detected compounds in the headspace.

<table>
<thead>
<tr>
<th>Name</th>
<th>Linear formula</th>
<th>Abbrev.</th>
<th>b. p. (°C)</th>
<th>Characteristic mass-to-charge ratio (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-chloroethyl ethyl sulfide</td>
<td>CH₃CH₂SCH₂CH₂Cl</td>
<td>CEES</td>
<td>156</td>
<td>124, 109, 89, 75, 61, 47</td>
</tr>
<tr>
<td>Ethyl vinyl sulfide</td>
<td>CH₃CH₂SCH=CH₂</td>
<td>EVS</td>
<td>98</td>
<td>88, 73, 60, 59, 45</td>
</tr>
<tr>
<td>divinyl sulfide</td>
<td>CH₂=CHSCH=CH₂</td>
<td>DVS</td>
<td>84</td>
<td>86, 85, 71, 59, 41, 40</td>
</tr>
<tr>
<td>Diethyl disulfide</td>
<td>CH₃CH₂SSCH₂CH₃</td>
<td>DEDS</td>
<td>110</td>
<td>122, 94, 66, 60, 47, 45</td>
</tr>
<tr>
<td>1,2-bis(ethylthio) ethane</td>
<td>CH₃CH₂SCH₂CH₂SCH₂CH₃</td>
<td>BETE</td>
<td>218</td>
<td>150, 122, 90, 75, 61, 47</td>
</tr>
<tr>
<td>Methyl vinyl sulfide</td>
<td>CH₂=CHSCH₃</td>
<td>MVS</td>
<td>69</td>
<td>74, 59, 47, 44, 40</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>CH₃CHO</td>
<td>MeCHO</td>
<td>20</td>
<td>44, 43, 42</td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH₃CH₂OH</td>
<td>EtOH</td>
<td>78</td>
<td>46, 45, 43, 42</td>
</tr>
</tbody>
</table>
The detected products are arbitrarily classified into three categories (Figure 4.4.14) based on their molecular weight (Mw). The first group includes the vinylic compounds EVS and DVS, which have similar Mw. They are formed in the dehydrohalogenation reactions. The second group contains the species with smaller Mw than CEES (MVS, EtOH and MeCHO). For the formation of these species, cleavage of C-C or S-C bond has to take place.

Oxidation was also acquired for the formation of ethanol and acetaldehyde. The third group includes molecules with notably higher Mw than that of CEES (DEDS and BETE). For the formation of these compounds, S-C cleavage is expected to take place and to be followed by a dimerization.

Figure 4.4.14. Arbitrarily classification of the detected volatile compounds in the headspace.
The trends in the concentration of the six detected compounds in the headspace (peak areas) with the progress of adsorption are presented in Figure 4.4.15. The results indicate that various interactions/reactions between CEES and the surface of the samples were taking place simultaneously, although EVS is the predominant degradation product. The composites with the nanoparticles showed significantly higher reactivity as can be observed from the peak areas of EVS and DVS. In the case of single ZnGO composites, MVS was also detected in a limited quantity. This compound was not detected for AuZnGO and AgZnGO, suggesting that it get degraded fast. The comparison of the peak areas between the two multi-composites showed that AgZnGO showed higher formation rate for the vinylic products, EVS and DVS.

The areas of the peaks representing products from the dimerization showed similar trends. Interestingly, only on AuNPs he formation of MeCHO and EtOH is promoted, as a result of photo-oxidation, since the latter compounds was not detected when the tests were performed in dark. The enhanced photocatalytic performance by NPs addition was reported also for other metal oxides, since NPs can introduce a surface plasmon resonance effect. 97,98,163
4.4.7. Detoxification and adsorption mechanisms

The proposed reactions pathways that take place during the CEES reactive adsorption process are collected in Figure 4.4.16. The formation of the predominant vinylic product, EVS, can occur though two pathways. In the first one (pathway 1), the Zn(II) centers act as Lewis acids and promote the cleavage of the C-Cl bond.\(^{83,94}\) The formed diethyl sulfonium cation (DES\(^+\)) get converted to an unstable intermediate cyclic cation, through an intermolecular cyclization process. Afterwards, the cyclic alkyl sulfide cation is re-arranged via a bimolecular elimination (E2) pathway, which leads to the formation of EVS, with the simultaneous elimination of a labile
hydrogen atom by a hydroxyl group. The formation of water was also afore mentioned in the previous sub-chapter, as well as in the case of the adsorption of CEES on Fe(OH)$_3$,$^{83,164}$ and can explain the gel-like form of the exhausted samples after 7 days of exposure. The second pathway (pathway 2) involves the formation of a diethyl sulfide radical, which undergoes a further intermolecular electrons rearrangement to form EVS. This pathway can be the reason of the higher amount of EVS detected in the headspace for the NPs containing composites than that of ZnGO, as a result of higher photoreactivity by the addition of the NPs.

The formation of DEDS, BETE, ethanol and acetaldehyde can be attributed to the third pathway included in Figure 4.4.16 (pathway 3). The $\alpha$-carbon radical thioether can be protonated to $\alpha$-carbon radical thioether cation. The reaction of the latter with an activated hydroxyl groups can lead to ethyl sulfide radical and ethanol. The sulfide radical can react with another sulfide radical or a diethyl sulfide radical, resulting in the formation of the products with two sulfide atoms and higher Mw than CEES (DEDS and BETE). The limited detected amount of ethanol in the headspace for AgZnGO can be due to its strong retention on the surface by hydrogen bonds without additional oxidation to aldehyde. Further photo-oxidation of the EtOH to acetaldehyde was found only on AuZnGO. AuNPs in the structure of the multi-composite altered the chemical environment and activated the oxygen containing groups of the inorganic phase, which can photo-oxidize ethanol. It is paramount important to mention that no other oxidation products, such as sulfoxide or sulfone, were detected.
DVS can be formed in two pathways (pathway 4 and 5). In the first one, CEES is transformed to a radical by a photo-excited electron or a formed hole, and through an intermolecular electron rearrangement it gets further transformed to chloroethyl vinyl sulfide. The latter is converted to DVS, following the same pathway as described for the first formation pathway of EVS. The hydroxyl radicals can convert EVS to DVS via an intermediate diethyl sulfide radical (pathway 5). The high amount of DVS in the headspace of AgZnGO can be linked to this pathway, since only this composite revealed the ability to form hydroxyl radicals. Finally, these radicals can react with
diethyl sulfide radicals, forming hydroxyl ethyl ethyl sulfide (HEES). Indeed, the analysis of the extracts showed a significantly higher amount of HEES for AgZnGO, compared to other two samples.

4.4.8. Conclusions

The simultaneous incorporation of AgNPs or AuNPs during the synthesis of zinc hydroxide/GO composite resulted in the formation of composites with improved adsorption/detoxification performance against the surrogate of mustard gas, CEES, under visible light irradiation. The nanoparticles altered also the nucleation pathway. The composite consisted of AgNPs revealed two distinguished crystallographic phases, orthorhombic zinc hydroxide and zinc oxide nanorods that created a cobweb-like network. In the case of AuNPs addition, the resulted amorphous crystallographic phase consisted of zinc (hydr)oxide nanoparticles, which surrounded the GO phase. The detectable on the outer surface NPs maintained their spherical shape. It is plausible to assume that the existence of NPs on the outer phase promoted the photoreactivity, altered the chemical environment, and activated the oxygen species. Addition of NPs caused increases in:

1) chemical and structural surface heterogeneity
2) amount of highly reactive terminal groups
3) activity of the oxygen containing surface groups
4) separation of electron/holes pair, preventing their recombination
5) photocatalytic detoxification performance

The addition of AgNPs resulted in the highest weight uptake and photo-degradation yield, even though this this composite showed the lowest porosity. AgNPs incorporation promoted also the
ability of the hydroxyl radicals’ formation. On the other hand, the addition of AuNPs showed lower weight uptake performance compared to AgNPs addition, but introduced a selective photo-oxidation ability. Only ethanol oxidized to acetaldehyde and no sulfoxides or highly toxic sulfones were formed. This can be explained by the introduction of a surface plasmon effect. Since AuNPs and AgNPs have a relatively high cost, other non noble metal NPs probably would be able to replace their function in the composites.
Sub-chapter 5.1 is reproduced from Ref. 113 with permission from the Royal Society of Chemistry:

*D. A. Giannakoudakis, J. K. Mitchell and T. J. Bandosz,*

5.1. Effect of GO phase in Zr(OH)$_4$/GO composites on the extent of catalytic reactive adsorption

5.1.1. Materials and Objectives

The main goal of this study was to prepare Zirconium (hydr)oxide and its composites with various amounts of graphite oxide (GO), using a controlled rate precipitation method, and to evaluate their ability for the removal of CEES vapors at ambient conditions. Additional objectives were to identify the optimal amount of the carbonaceous phase, which could lead to the greatest enhancement in the performance as adsorbents and catalysts, and to determine how the structural and chemical properties which affect the detoxification ability and the reactive adsorption mechanism.

5.1.2. Structural and morphological characterizations

X-ray diffraction patterns of all samples are presented in Figure 5.1.1. Regardless the presence and amount of GO, all samples are amorphous. Moreover, the characteristic diffraction peak of graphite oxide at 11.6$^\circ$ 2$\Theta$ is not seen, indicating an exfoliation of GO within the amorphous structure of zirconium hydroxide.
Figure 5.1.1. X-ray diffraction patterns for the initial samples.

The structural parameters calculated from measured nitrogen adsorption isotherms are presented in Figure 5.1.2. If the final products were a physical mixture, an increase in the GO content would lead to a decreased porosity of the synthesized materials, since the surface area of GO is only 4 m$^2$/g and its total pore volume is 0.002 cm$^3$/g. The hypothetical surface areas and total pore volumes were calculated assuming a physical mixture of both components and their percentage contribution to the values analyzed. The comparison of the parameters of the porous structure is presented in Figures 5.1.2 B and C. The synergistic effect of the composite formation on the porosity development is clearly seen from the comparison of the measured and hypothetical values. The most visible differences are those for ZrGO5 (+36%) and ZrGO20 (+42%). The measured surface area of the former is 29% higher than that of ZrOH. The increases for ZrGO1, ZrGO10 and ZrGO20 were 4, 18 and 16%, respectively.
The addition of GO led also to a significant alteration in the total pore volumes and especially in the volume of mesopores. It is worth mentioning that all materials are both a micro and mesoporous as seen in Figure 5.1.2 D. The ratio of the micropore to mesopore volumes decreased with the addition of GO (Figure 5.1.2 C). While the addition of 1 % GO to ZrOH affected only slightly the volume of the pores, the increase in the pore volume of ZrGO5 was the most pronounced. Its pore volumes are 17, 83 and 52 % higher than $V_{\text{mic}}$, $V_{\text{mes}}$ and $V_{\text{Total}}$ for ZrOH, respectively. For the composites with 10 and 20 % of GO, the increase in the pore volume is less pronounced than that for ZrGO5. The results indicate that 5 % GO is the critical/optimal amount for the development of the high porosity.
Figure 5.1.2. A) nitrogen adsorption isotherms; B) comparison of the measured and hypothetical surface areas; C) micro and mesopores volumes, and C) pore size distributions.

The SEM images (Figure 5.1.3) show the heterogeneous features of the ZrOH surface. The addition of 1 % GO leads to smaller zirconium hydroxide particles than those in ZrOH. They surround the GO flakes. Further increase in the GO content enhances the dispersion of the inorganic phase around GO, and encapsulates more GO in the formed particles.
Figure 5.1.3. SEM images of the samples’ morphology.
5.1.3. Surface chemistry analysis

The amount of surface functional groups was determined by the potentiometric titration method. For ZrOH, they can be grouped into two categories: those with pK\textsubscript{a} between 7 and 9, and those with pK\textsubscript{a} higher than 9. The first ones are linked to oxygen bridging groups and coordinated water, and the second ones- to hydroxyl terminal groups.\textsuperscript{5,9} It was reported that the terminal hydroxyl groups played a key role in the adsorption of CEES vapors on zinc and iron (hydr)oxide.\textsuperscript{125,164} They were also found crucial for the removal of VX nerve agent on Zr(OH)$_4$,\textsuperscript{39} and of H$_2$S on metal (hydr)oxides.\textsuperscript{46,166,167} The results of potentiometric titration (Figure 5.1.4) clearly revealed that the addition of GO increased the total number of functional groups, and especially of the terminal hydroxyl groups. The most pronounced increase was found for ZrGO5, which has the highest number of surface acidic species. Compared to ZrOH, the number of terminal hydroxyl groups increased by 141 % and the number of bridging groups by 56 %. Interestingly, the composite with 1 % GO showed almost the same number of groups as did ZrGO5. A further addition of the carbonaceous phase led to a decrease in the number of surface groups, however the amount of total groups was always higher than that on ZrOH. It is worth to mention that the synergistic effect of the composite formation on the amount of functional groups on the surface is also seen from the comparison of their measured and hypothetical values calculated assuming the physical mixture. Since the total number of functional groups of GO in the pK\textsubscript{a} range 7 to 11 is 2.009 mmol/g, the measured amounts of functional groups are higher than the hypothetical values by 95, 91, 36 and 1 % for ZrGO1, ZrGO5, ZrGO10 and ZrGO20, respectively.
The above mentioned results indicate that 5 % GO is the optimum amount resulting in the composite with both highest porosity and richest surface chemistry. Thus the addition of GO plays an important role in increasing the dispersion and amorphicity of the inorganic phase.

The differential thermal gravimetric (DTG) curves for the initial samples are presented in Figure 5.1.5 A. For all samples, a gradual weight loss from a low temperature up to 400 °C is visible. Until 125 °C, it can be linked to the removal of the water, coordinated as ligands or physically adsorbed. Above this temperature, the dehydroxylation of the complex hydroxide structure of zirconium hydroxide to the bridged structure takes place (Figure 5.1.5 B). The decomposition of the epoxy groups of GO is visible between 190 and 210 °C for the samples with more than 10 % of GO, while this decomposition is barely detected for ZrGO5. The sharp peaks between
450 °C and 650 °C, with a limited intensity, can be assigned to the formation of metastable tetragonal or monoclinic zirconium oxide.\textsuperscript{47,168}

Figure 5.1.5. DTG curves measured in helium for the initial samples (A), and a stereo-view of the dehydration of the hydrated zirconium hydroxide (B).
Clearfield et al. first pointed out that the addition of a base to ZrOCl$_2$*8H$_2$O leads to the formation of a polymeric oxohydroxide with the general formula [ZrO$_{6b}$(OH)$_{4-2b}$ • xH$_2$O].$^{63,169}$ This structure (Figure 5.1.5 B) consists of four types of oxygen groups. On the outer phase of the structure there are terminal –OH groups and coordinated water molecules. In the interior part of the matrix, the Zr atoms are connected via bridging OH or oxygen groups. The existence of both types of hydroxyl groups was also reported by Chitrakar et al. in the case of ZrO(OH)$_2$•(NaO)$_{0.005}$•1.5H$_2$O and by Huang et al. for Zr(OH)$_4$.$^{63,168}$ Zirconium hydroxide reported in the literature revealed a broad weight loss up to 400 °C, which was linked to the dehydration. Assuming the existence of pure Zr(OH)$_4$, its thermal transformation to ZrO$_2$ should lead to a 22.6 % weight loss. In our case, the weight loss of unmodified ZrOH was 16.7 % up to 450 °C. This indicates that our materials have the random amorphous structure of hydrate zirconium (hydr)oxide instead of zirconium oxide. The terminal –OH groups are proved to be more active for adsorption/degradation of the organic molecules. Owing to their position in the lattice, they may interact faster with CEES, while the bridging groups are less active and will interact slower, since the diffusion into the lattice requires a longer time.$^{63}$

5.1.4. Adsorption performance and the optimum amount of GO

All studied samples were evaluated as adsorbents of 2-chloroethyl ethyl sulfide vapors. The measured weight gains are collected in Figure 5.1.6. Owing to the negligible adsorption capacity of GO (7 mg/g), the hypothetical weight gains, assuming the formation of a physical mixture instead of a composite, for the adsorption capacity were expected to decrease with the increasing GO content. On the contrary, all composites revealed greater weight gains than that for ZrOH,
showing a significant synergetic effect of the composite formation. The largest weight gain was found for ZrGO5, and it is 67 % higher than that of ZrOH and 75 % higher than that calculated for the hypothetical physical mixture of the composite components. The amounts adsorbed on ZrGO1, ZrGO10 and ZrGO20 were higher than that on ZrOH by 9, 39 and 28 %, respectively. The adsorption tests were held also in dark and the measured weight uptakes showed the same values with those measured under light irradiation.

Figure 5.1.6. Weight gains for all the tested materials.

5.1.5. Role of the textural parameters and surface chemistry

The dependences of the weight gain upon exposure to CEES for 24 hours on the surface area, on the number of terminal hydroxyl groups and on mesopore volume are presented in Figure 5.1.7.
Linear correlations suggest that these factors play important roles in the reactive adsorption process. No correlation of the capacity on micropore volume and bridging groups was found.

![Graph showing linear correlations between weight gain and surface area, terminal groups, and mesopore volume](image)

Figure 5.1.7. Dependence of the weight gain on the surface area (A), terminal groups (B) and the mesopore volume (C) for 24 hours of CEES exposure.

5.1.6. Characterizations of the exhausted samples

The changes in surface chemistry after the exposure to CEES were evaluated from the FTIR spectra (Figure 5.1.8). The characteristic vibrations for zirconium hydroxide appear at 1590, 1390 and 854 cm\(^{-1}\). The broad band with a maximum at 1590 cm\(^{-1}\) can be assigned to the hydroxyl groups of water molecules and at 1390 cm\(^{-1}\) to O-H vibration from Zr-OH.\(^{47,62}\) The small band at 854 cm\(^{-1}\) is attributed to the lattice vibration of a Zr-O bond. For graphite oxide, the stretching
vibration of C-O bonds from carboxylic groups, bending vibration of O-H from hydroxyl/phenol groups, and O-H vibration of water appear at 1050, 1390 and 1630 cm\(^{-1}\), respectively. The band at 990 cm\(^{-1}\) corresponds to epoxy/peroxide groups, while the band at 1730 cm\(^{-1}\) is characteristic of a C=O stretching vibration in carboxylic acids. The band at 1228 cm\(^{-1}\) might be related to C-O vibrations in epoxides. The vibrations of oxygen groups from graphite oxide are not visible for the composites with the low GO content (1, 5 and 10\%) owing to the involvement of these groups in the formation of the composites. For the sample with 20 \% GO, only one broad peak at 1000 cm\(^{-1}\) appeared that corresponds to the vibration of epoxy/peroxide groups. The characteristics bands of zirconium hydroxide are visible for all samples. The exhausted samples are referred to with letter E added to their names. After the CEES vapor adsorption, the intensities of the bands at 850, 1390, and 1590 decrease, indicating that the –OH groups and the water molecules participate in the reactive adsorption.
Figure 5.1.8. FTIR spectra of the initial and exhausted (-E) samples.

The differential thermal gravimetric (DTG) curves for the exhausted samples are presented in Figure 5.1.9. The formation of new compounds after the reactive adsorption is evident since four new peaks which appear at 110, 170, 270, and 300 °C with various intensities for all exhausted samples. We refer to them as Peak 1, 2, 3 and 4, respectively. Mass spectrometry of the exhaust gases/vapors was carried out simultaneously with the TA analysis in order to determine the origin of these new peaks. The assignment discussed below is based on the detected m/z fragments. The
MS thermal profiles for ZrOH are collected in Figure 5.1.10. Nomenclature, abbreviations and details on the detected compounds are collected in Table 5.1.1.

Figure 5.1.9. DTG curves in helium for the exhausted samples.
Table 5.1.1. Details on the detected compounds on the surface and in the headspace.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Abbreviation</th>
<th>Characteristic mass –to-charge ratio (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-chloroethyl ethyl sulfide</td>
<td>CH$_3$CH$_2$SCH$_2$CH$_2$Cl</td>
<td>CEES</td>
<td>124, 109, 90, 75, 61, 47</td>
</tr>
<tr>
<td>2-hydroxyethyl ethyl sulfide</td>
<td>CH$_3$CH$_2$SCH$_2$CH$_2$OH</td>
<td>HEES</td>
<td>106, 90, 75, 61, 47</td>
</tr>
<tr>
<td>1,2-bis(ethylthio) ethane</td>
<td>CH$_3$CH$_2$SCH$_2$CH$_2$SCH$_2$CH$_3$</td>
<td>BETE</td>
<td>150, 122, 90, 75, 61, 47</td>
</tr>
<tr>
<td>Ethyl ethyl sulfide</td>
<td>CH$_3$CH$_2$SCH$_2$CH$_3$</td>
<td>EES</td>
<td>90, 75, 61, 47</td>
</tr>
<tr>
<td>Ethyl vinyl sulfide</td>
<td>CH$_3$CH$_2$SCH=CH$_2$</td>
<td>EVS</td>
<td>88, 73, 59, 45</td>
</tr>
<tr>
<td>Diethyl disulfide</td>
<td>CH$_3$CH$_2$SSCH$_2$CH$_3$</td>
<td>DEDS</td>
<td>122, 94, 66, 60, 47</td>
</tr>
<tr>
<td>1,4-butanedithiol</td>
<td>SHCH$_2$CH$_2$CH$_2$SH</td>
<td>BDT</td>
<td>122, 88, 73, 60, 55, 47</td>
</tr>
</tbody>
</table>

Based on the m/z thermal profiles, the Peak 1 at the DTG curve with a maximum at 110 °C, is assigned to CEES (m/z: 90, 75, 61, 47) and to the compounds with identical series of main-intense m/z signals. The latter species include BETE, HEES and/or saturated sulfides such as EES. Moreover, it can be also assigned to EVS (m/z: 88, 73, 59, 45) and DEDS (m/z: 66, 60, 47). Peak 2 with a maximum at 170 °C is related to the dehydroxylation, since only the profile of OH (m/z: 17) gives signal at this temperature. The lower intensity of this peak and the higher temperature of the decomposition, compared to those for the initial sample, suggest that the hydroxide groups are involved in the adsorption/degradation of CWA and they are stabilized by interactions, such as polar or hydrogen bonds, with the organic molecules. Moreover, for the composites with the higher amounts of GO (ZrGO10 and ZrGO20), the decomposition of GO in the same temperature range contributes to an increase in the intensity of Peak 2. Peak 3 (maximum at 270 °C) likely represents
DEDS and BDT, since m/z 55 which is characteristic for the later compounds appears only at this temperature. Peak 4 at 300 °C can be linked to CEES, HEES, BETE, EES and EVS. The existence of two decomposition temperatures for the same compound is linked to the adsorption at two energetically different sites.\textsuperscript{41} The first one, at a lower temperature, represents weakly adsorbed molecules, likely via polar forces on the external surface and/or in the mesopores and the second one - the removal of strongly adsorbed molecules in the micropores or those hydrogen-bonded to the -OH groups. The same trends for the removal of CEES and EVS were found for the adsorption of CEES on iron and zinc (hydr)oxides.\textsuperscript{83,164}

For ZrOH, the evolution of the m/z signals corresponding to Cl (m/z: 35) supports the removal of CEES at two different temperatures seen by two maxima at 100 and 300 °C. Moreover, a small maximum at temperature lower than 60 °C is linked to the formation of small molecules containing chloride and a stable signal above 600 °C can be assigned to the decomposition of the Zr-Cl bonds. Finally, the evolution of the m/z signals of SO\textsubscript{2} (m/z: 64), CH\textsubscript{3} (m/z:15) and carbon (m/z: 12) further supports the decomposition of a variety of compounds at the aforementioned temperatures. The acquired m/z thermal profiles for the composites show the same origin of the new peaks. Since many compounds can be formed upon heating during the TA analysis, this method does not provide enough evidence for the mechanism and the progress of the reactive adsorption process.
Figure 5.1.10. m/z thermal profiles (in helium) of exhausted ZrOH for the fragments related to CEES, BETE, HEES and/or EES (A), EVS (B), DEDS and/or BDT (C) and to SO$_2$ (m/z: 64), Cl m/z: (35), -OH (m/z: 17), CH$_3^+$ (m/z: 15) and C (m/z: 12).
5.1.7. Evaluation of the detoxification performance

In order to determine the maximum weight uptake and to analyze the progress of reactive adsorption, different CEES exposure times were studied (Figure 5.1.11). Since ZrGO5 showed the best performance for CEES adsorption after 24 and 48 hours among all others composites tested, this sample along with ZrOH were chosen to study the extent of the adsorption in more details. ZrOH reached the maximum weight uptake after 36 hours \( (105 \pm 6.2 \text{ mg/g}) \). For ZrGO5, the maximum weight uptake was revealed after 48h with almost twice more weight increase \( (204 \pm 8.3 \text{ mg/g}) \) than that of ZrOH. For the other composites the weight increases after 24 and 48 hour of CEES exposure are also included in Figure 5.1.11. The results show that the graphene phase enhanced the amount of CEES adsorbed and/or the amount of the degradation products adsorbed on the surface.

Figure 5.1.11. Weight uptakes measured up to 60 hours of CEES exposure.
The correlations of the maximum uptakes (at 48 hours) with the surface area, mesopore volume and number of the numbers terminal groups showed linear trends, with $R^2$ values 0.97, 0.98 and 0.96, respectively (Figure 5.1.12). The results indicate that both the chemical and physical features of the materials play a key role in the adsorption performance, suggesting that both chemical and physical interactions are involved in the reactive adsorption process. The increased porosity and the amount of the surface groups of ZrGO5 lead to a fast weight gain. It has to be mentioned here that long adsorption times are only apparent, since a low vapor pressure of CEES causes that a considerable length of time is required for its evaporation. Prasad et al. reported that to reach the maximum weight uptake of mustard gas on activated carbon (with surface area 1250 m$^2$/g) 576 hours (24 days) were needed.\(^3\)\(^8\)

![Graph showing the dependence of weight uptake on surface area, terminal groups, and mesopore volume](image)

**Figure 5.1.12.** Dependence of the maximum weight gain on the surface area (A), terminal groups (B) and the mesopore volume (C) for 48 hours of CEES exposure.
5.1.8. Identification of the volatile products in the headspace

An increase in the exposure time to 48 hours increased the amount of CEES and/or of its decomposition products adsorbed. It is likely due to slow transformations, which take place on the surface of the materials, or due to the time needed for the evaporation of CEES. Even though the adsorption performance can be evaluated by the measured weight increase, the latter cannot provide a sufficient sole evidence about the activities and the mechanism of the interactions. Therefore, to study in detail the interactions and to throw light on the products of surface reactions, the headspace of the closed adsorption system and the extracts from the surface of the exhausted materials were analyzed by GC-MS. As mentioned above, the analysis focused on of ZrGO5 and ZrOH. For both ZrOH and ZrGO5, CEES in the headspace was detected at the elusion time of 3.3 min, EVS at 1.8 min, and BETE at 4.8 min. The chromatograms after 48 hours are presented in Figure 5.1.13 A. The intense peak at 3.3 min indicates that the marked amount of CEES vapors is still present in the reaction vessel even after 48 hours. The low intensities of the peaks representing EVS and BETE are due to the saturation of the headspace with CEES or due to their adsorption on the surface of the materials.
Figure 5.1.13. Chromatograms of the headspace for ZrOH and ZrGO5 after 48 hours of CEES exposure (A) and dependence of the area of the chromatographic peak (analysis of the headspace) of EVS (B) and BETE (C) on the exposure time.

The trends in the concentration of EVS and BETE in the headspace (represented by peak areas) with the progress of adsorption are presented in Figure 5.1.13 B and C. The results suggest that various interactions/reactions between CEES and the surface of the samples take place simultaneously. The continuous increase in the amount of EVS detected in the headspace is in agreement the TA-MS results. This indicates that the degradation of CEES leads mainly to the dehydrohalogenation products (Figure 5.1.14). Briefly, CEES can be transformed to a transient
cyclic sulfonium cation by an intermolecular cyclization process. Sulfur atom acts as a nucleophile and attacks the electrophilic carbon to which the chloride is bonded. Afterwards, via a bimolecular elimination (E2) reaction, a labile hydrogen from the cyclic cation transfers to a negatively charged lattice oxygen of the zirconium phase, which acts as a Lewis base. The cleavage of the C-Cl bond in the first step of this elimination pathway is promoted by the Lewis acidic Zr(IV) centers. The analogous degradation pathway was reported for the adsorption of CEES or HD on aluminum oxide, zinc hydroxide, and iron oxyhydroxide.\textsuperscript{17,31,42} The thermal profile of m/z 35 shows a strong signal at the temperature of ZrCl\textsubscript{4} decomposition (330 °C) owing to the bonds between the chlorine atoms and the inorganic matrix as a result of the intermolecular cyclization process.

![Figure 5.1.14. Dehydrohalogenation of CEES to EVS by an intermediate cyclic sulfonium cation.](image)

The trend in the BETE concentration was opposite compared to that for EVS. A decrease of its concentration in the headspace can be linked to both its limited formation and a simultaneous strong retention on the surface. The mechanism of the BETE formation includes the cleavage of S-C bond and the formation of a new S-C bond between two distinct molecules. Alkoxy species on the surface react with sulfonium cations, resulting to the formation of BETE and –OCH\textsubscript{2}CH\textsubscript{3}.
groups. The involvement of the oxygen containing groups in the formation of the alkoxy species is supported by the FTIR spectra, in which a decrease in the intensity of the bands assigned to the –OH was found. Verma et al. reported the formation of EVS and alkoxy species after the interaction of CEES with the isolated hydroxyl groups on ZrO$_2$ or WO$_3$ nanoparticles.$^{43,44}$

The aforementioned pathways require the adsorption of CEES on the surface as a first step. As it was suggested from the TA analysis, there are two diverse adsorption centers with different energies for both CEES and EVS adsorption. The lower energetically adsorption process likely includes the polar interaction of S$^{δ-}$ with the Zr$^{δ+}$. Stronger adsorption can be due to the formation of hydrogen bonds between the OH groups of the materials and both S and Cl moieties of the organic molecules. Panayotov and Yates studied in details the adsorption of CEES on a high surface area TiO$_2$-SiO$_2$ mixed oxide and they found that hydrogen bonding of this molecule to Si-OH groups occurs through both Cl and S moieties.$^{46}$ The removal of the adsorbed molecules at low temperature (110 °C) in the TA-MS analysis is linked to the weak interactions and at higher temperature (300 °C) - to the hydrogen bonding interactions.

5.1.9. Identification of the surface reaction products retained on the surface

The analysis of the surface extracts by GC-MS revealed the existence of both CEES and BETE. It is worth to mention that the signal related to BETE has higher intensity in the chromatograms of the extracts than those of the headspace. The areas corresponding to BETE consist of 16-20 % of the total areas of all detected compounds, while these values were in the range of 1 to 3 % from the analysis of the headspace. HEES, disulfides like DEDS and BDT, or any oxidation products such as sulfoxides and sulfones were not detected either in the headspace or in the extracts. The possible detection some of them (such as BDT, DEDS) from the TA-MS analysis can be due to
the thermal transformation during the analysis and the involvement of the released oxygen in their formation. Finally, the higher concentrations of BETE in the extracts of the composites, than in that of ZrOH, further supports our finding that the addition of GO leads to a significant increase in the extent of reactive adsorption and in the selective catalytic transformation of CEES to EVS and BETE. It is due to the alterations of the active surface sites and chemical heterogeneity of the composites. The increased dispersion of the hydroxyl groups and the developed porosity play the key roles in the detoxification process.

5.1.10. Detoxification mechanism

All the above-mentioned interactions of CEES and of its degradation byproducts with the samples’ surfaces are presented in Figure 5.1.15. The amorphous zirconium hydroxide phase acts as a reactive adsorbent, since it physically adsorbs the organic molecules and catalytically transforms CEES to the dehydrohalogenation product, EVS, and to the polymerization product, BETE.
Figure 5.1.15. Proposed reactions scheme of CEES reactive adsorption mechanism.

5.1.11. Conclusions

The results presented in this chapter showed for the first time that zirconium (hydr)oxide and its composites with graphite oxide can be used as reactive adsorbents of the mustard gas surrogate vapors. The aqueous synthetic route leads to the materials with amorphous nature, various levels of complexity, a relatively high surface area and a high density of active hydroxyl group. The addition of GO resulted in an increased degree of the structural and chemical heterogeneity. The most pronounced increases in the surface area (+141%) and in the number of terminal hydroxyl
groups (+ 67 %) compared to the pure zirconium hydroxide were found for the composite with 5 % GO (ZrGO5).

Notably, the unmodified zirconium (hydr)oxide showed the highest weight uptake in comparison to those reported in the literature for hydrous ferric oxide and zinc hydroxide (at the same conditions for 24 hours). ZrGO5 showed the best adsorption performance (155 mg/g after 24 hours and 205 mg/g after 48 hours). The results indicate the paramount role of surface chemistry and porosity in the reactive adsorption process of CEES.

Based on the collected results, two steps removal of CEES were proposed. The first one involves the retention of the organic molecules by physical forces and the second includes the catalytic and selective transformation of CEES to ethyl vinyl sulfide by dehydrohalogenation and to 1,2-bis(ethylthio) ethane by degradation/dimerization. The conversion rates on the composites with carbonaceous phase were also higher than that on the unmodified sample.

5.2. AgNPs embedded in zirconium hydroxide/GO composites

5.2.1. Materials and Objectives

The objective of this particular study was to investigate whether or not the addition of AgNPs further enhances the catalytic detoxification performance, as a result of a plasmon effect or of the structural and chemical features alteration. For that reason, the composites of zirconium hydroxide with AgNPs and with or without GO were synthesized. 5 % of GO was chosen, since this amount of carbonaceous phase showed the best performance, while the amount of AgNPs was 1 wt % of the final mass. The composites of Zr(OH)₄ and AgNPs are referred to as AgZrOH and AgZrGO,
with the absence or presence of GO, respectively. For the sake of comparison, the results for pure zirconium hydroxide (ZrOH) and the composite with 5 % GO (ZrGO) addressed above are included to the discussion.

5.2.2. Structural and morphological characterization

The XRD powder diffraction patterns are collected in Figure 5.2.1. All samples show a high level of amorphicity. The absence of the characteristic diffraction peaks of GO indicates an exfoliation of GO within the amorphous structure of the inorganic phase. More interestingly, no diffractions of metallic Ag, Ag₂O or AgCl suggest that the nanoparticles did not aggregate to bigger silver crystals, got oxidized or reacted with the chlorine atoms of the initial ZrCl₄ solution during the precipitation.

![Figure 5.2.1. X-ray diffraction patterns for the initial samples.](image-url)
The nitrogen adsorption isotherms (Figure 5.2.2), the pore size distributions (Figure 5.2.3) and the parameters of porous structure calculated from the isotherms (Table 5.2.1) showed that all samples have both micro- and meso- porous structure. ZrOH has the highest ratio of the micropores volume to the total pore volume, while AgZrGO- the lowest. For all composites, the surface area and total pore volume increased compared to ZrOH. The highest values of the porous structure parameters were found for ZrGO. The addition of only AgNPs increased the surface area and pore volume by 13 % and 12 %, respectively. The comparison of ZrGO and AgZrGO showed that AgNPs addition in this case led to a 8 % lower surface area, but almost to no change in the pore volume (- 2 %). The addition of AgNPs led to a broadening of the hysteresis loop (Type H2(b)) between the adsorption and desorption isotherms for AgZrOH and AgZrGO, compared to ZrOH and ZrGO. This suggests a more complex pore structure.\textsuperscript{124}

![Nitrogen adsorption isotherms for all the samples.](image-url)
Table 5.2.1. Parameters of porous structure calculated from the N\textsubscript{2} isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>(V_{\text{Total}}) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>(V_{\text{mic}}) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>(V_{\text{meso}}) (cm\textsuperscript{3} g\textsuperscript{-1})</th>
<th>(V_{\text{meso}}/V_{\text{T}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrOH</td>
<td>208</td>
<td>0.124</td>
<td>0.058</td>
<td>0.066</td>
<td>0.53</td>
</tr>
<tr>
<td>AgZrOH</td>
<td>235</td>
<td>0.139</td>
<td>0.061</td>
<td>0.078</td>
<td>0.56</td>
</tr>
<tr>
<td>ZrGO</td>
<td>269</td>
<td>0.162</td>
<td>0.068</td>
<td>0.094</td>
<td>0.58</td>
</tr>
<tr>
<td>AgZrGO</td>
<td>247</td>
<td>0.156</td>
<td>0.061</td>
<td>0.095</td>
<td>0.61</td>
</tr>
</tbody>
</table>

As discussed in the previous sub-chapter (5.1.2.), the SEM images of ZrOH and ZrGO revealed heterogeneous and amorphous surface morphology. The addition of 5 % GO led to an enhanced dispersion of the inorganic phase around GO. No structural or morphological differences between
the particles were seen at the SEM images of the composites with AgNPs (Figure 5.2.4). Although, aggregates of NPs were observed. These aggregates are dispersed on the outer surface of the particles. They have sizes between 100 to 300 nm and consist of bundles of nanorods.

To identify the chemical nature of these nanoparticles, the dispersion of elements on the surface was analyzed in EDX maps (Figure 5.2.5). The results indicated that the NPs consist of exclusively Ag, since the oxygen intensity is dramatically lower at the spots where Ag detected compared to the spots where no Ag detected, and chloride was not detected.
Figure 5.2.4. SEM images of AgZrOH and AgZrGO.
Since in the previously sub-chapter (5.1.5) was revealed that the amount of terminal hydroxyl groups plays a crucial role in the adsorption performance, the amounts of surface functional groups for AgZrOH and AgZrGO were determined using the potentiometric titration method. The results collected in Figure 5.2.6 A revealed that the addition of GO led to an increase in the total number of acidic groups, especially the terminal hydroxyl groups. That number for AgZrOH increases by 41 % compared to that ZrOH. On the contrary, AgZrGO has a slightly lower amount of terminal hydroxyl groups compared to those of ZrGO (-3 %). The addition of AgNPs led to a significant increase in the number of bridging groups, and thus in the total number of surface functional groups.

Since the weight gain showed a strong dependence on the amount of terminal groups and on the surface area, the densities of the terminal groups per surface area (d_{gsa}) were calculated and
presented in Figure 5.2.6 B. Even though both AgNPs and GO addition caused an increase in $d_{gsa}$, as a result of the composite formation synergistic effect, the effect was greater for GO. AgZrGO showed the highest $d_{gsa}$ among all the studied materials. The calculated $d_{gsa}$ are 1.91, 2.39, 3.57, and 3.77 mol m$^2$, for ZrOH, AgZrOH, ZrGO and AgZrGO, respectively.

Figure 5.2.6. Amounts of bridging and terminal groups detected using the potentiometric titration experiments (A) and the density of the terminal groups per surface area (B).

The differential thermal gravimetric (DTG) curves for the initial samples are presented in Figure 5.2.7. For all samples, a gradual weight loss from a low temperature up to 350 °C is observed. The weight loss until 125 °C is assigned to the removal of water (coordinated as ligand or physically adsorbed). Above this temperature, the dehydroxylation of zirconium hydroxide to zirconium oxide takes place. The decomposition of the epoxy groups of GO is barely observable between 190 and 210 °C for the samples with GO.$^{46,62,72}$
Figure 5.2.7. Differential thermal gravimetric (DTG) curves measured in helium for the initial samples.

The thermal transformation of Zr(OH)$_4$ to ZrO$_2$ should lead to a 22.6 % weight loss. In our case, the weight loss for all samples was between 13.5 to 16.6 % up to 450 °C (Table 5.2.2). Based on this, we can assume that our materials have an amorphous structure of hydrate zirconium (hydr)oxide.

Table 5.2.2. Weight lost % at 125 °C and 450 °C.

<table>
<thead>
<tr>
<th>sample</th>
<th>Weight loss until</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>125 °C</td>
</tr>
<tr>
<td>ZrOH</td>
<td>2.3</td>
</tr>
<tr>
<td>AgZrOH</td>
<td>3.4</td>
</tr>
<tr>
<td>ZrGO</td>
<td>6.6</td>
</tr>
<tr>
<td>AgZrGO</td>
<td>6.1</td>
</tr>
</tbody>
</table>
5.2.4. Optical features – plasmon effect

Zirconium hydroxide is photoluminescent under ultraviolet irradiation, emitting blue light. It was reported that its photoluminescence spectrum (PL) can be quenched in different chemical environments, as for example, a red shift was reported by the replacement of hydroxyl groups. In order to determine if the presence of AgNPs in the structure of the composites chemically alters the hydroxyl groups as a result of the plasmon effect, the normalized PL spectra of the materials were analyzed (Figure 5.2.8).

Pure ZrOH showed a maximum at 510 nm (2.43 eV). This cyan-green emission peak is in a good agreement with the measured band gap for zirconium hydroxide as reported by Whitten and co-workers. They related this emission to the valence-to-conduction band excitation. The addition of the AgNPs led to a broadening of the PL spectrum and to a strong shift to longer wavelengths. For AgZrOH, the maximum of the PL spectrum red-shifted to 555 nm (2.23 eV). This shift was more pronounced for AgZrGO, which showed a maximum at 570 nm (2.17 eV). These changes can be linked to the possible excitation of electrons from the valence band to the hydroxyl $^3\Pi$ excited state. In the case of the composites with AgNPs, this decreases of eV indicates alterations in the chemical environment of the hydroxyl groups.
Figure 5.2.8. Photoluminescent spectra of the studied samples.

5.2.5. Role of the textural parameters and surface chemistry on the adsorption

All studied samples were evaluated as adsorbents of 2-chloroethyl ethyl sulfide vapors. The measured weight gains after 24 hours of exposure are collected in Figure 5.2.9. The addition of the AgNPs resulted in an increased weight uptake. AgZrOH showed a 31 % higher weight uptake (122 mg g⁻¹), compared to that on ZrOH (93 mg g⁻¹). The weight uptake on AgZrGO increased 83 % compared to that of ZrOH and 10 % compared to that of ZrGO (155 mg g⁻¹).
Figure 5.2.9. Weight uptake of ZrOH, AgZrOH, ZrGO, and AgZrGO after 24 hours of exposure to CEES vapors.

The dependence of the weight gains after 24 hours of CEES exposure on the surface area, and on the number of terminal hydroxyl groups was analyzed and rather low correlation was found, with $R^2 0.72$ and $0.92$, respectively. No correlation of the weight gain on the amount of the bridging groups or on the micropore volume was detected. On the contrary, the dependence of the weight gain on the density of the terminal groups per surface area and the mesoporous volume showed linear trends with $R^2 0.99$ and $0.97$, respectively. (Figure 5.2.10). These correlations suggest that these features play a crucial role in the reactive adsorption process, since the interactions take place in the mesopores.
Figure 5.2.10. Dependence of the amount adsorbed on density of the terminal groups and on the mesopores volume for 24 hours of CEES exposure.

5.2.6. Analysis of the weight uptake

The progress of the reactive adsorption was studied after various CEES exposure times (Figure 5.2.11). ZrOH reached the maximum weight uptake after 36 hours (105 mg g\(^{-1}\)), while the composites after 48 hours of exposure. AgZrOH revealed a 73 % higher maximum weight gain (161 mg g\(^{-1}\)) than did ZrOH, but 21 % smaller than did ZrGO (204 mg g\(^{-1}\)). The highest weight gain was recorded for AgZrGO (237 mg g\(^{-1}\)), which was 125 and 16 % higher than those for ZrOH and ZrGO, respectively. The correlations of the maximum weight gain on the density of the terminal groups and the mesopore volume showed linear trends, with R\(^2\) value 0.95 in both cases.
Figure 5.2.11. Weight uptakes measured up to 60 hours of CEES exposure.

5.1.7. Identification of the volatile products in the headspace

It has been previously shown that the extent of detoxification on the materials can be sufficiently evaluated using two factors: the ability to retain CEES and its degradation products (measured weight increase) and the catalytic degradation extent (monitoring the chromatographs of the headspace). In the case of ZrOH and ZrGO, the two detected volatile products in the headspace were ethyl vinyl sulfide (EVS) and 1,2-bis(ethythio) ethane (BETE). The trends in the areas of the peaks representing BETE and EVS in the headspace, measured by GC-MS, with the progress of adsorption are presented in Figure 5.2.12. A continuous increase in the amount of EVS was revealed for all samples. Although, the presence of the AgNPs significantly increased the concentration of BETE, as a result of a higher reactivity through the activation of the hydroxyl
groups, as discussed based on the PL spectra. AgZrGO showed almost a twice larger peak area related to BETE compared to that for ZrOH. The highest concentration of BETE among all the tested materials was revealed also for AgZrGO. Since only EVS and BETE were detected in the headspace, the composites reactively adsorb CEES vapors and convert them to nontoxic products. The addition of AgNPs notably improved the degradation performance.

Figure 5.2.12. Dependence of the areas of the chromatographic peaks related to EVS and BETE on the exposure time.
5.1.8. Identification of the reaction products retained on the surface

The analysis of the reaction products retained on the surface was accomplished by thermal analysis of the exhausted samples and GC-MS analysis of the extracts. Only EVS, BETE and CEES were detected in the extracts from all samples, even for the samples exposed to CEES for 48 hours. For the sake of the comparison with the results described in the previous sub-chapter (5.1), the samples exposed for 24 hours were analyzed by TA-MS. The differential thermal gravimetric (DTG) curves for the exhausted samples are presented in Figure 5.2.13, while the m/z thermal profiles are collected in Figure 5.2.14. The evolution of the m/z signals corresponding to Cl (m/z: 35) and to the saturated diethyl sulfide (m/z: 90) supports the adsorption of CEES. The m/z signal of 88 can be assigned to the unsaturated ethyl vinyl sulfide (m/z: 88, CH₂=CH₂SCH₂CH₃), while the m/z 64, 12 and 16 to SO₂, C and O, respectively.

Figure 5.2.13. DTG curves in helium for the exhausted samples.
Compared to the initial samples, the DTG curves for all the exhausted samples revealed four new decomposition features. The first one, at temperature up to 70 °C, is assigned to the weakly adsorbed CEES and EVS, since the m/z profiles of 35, 88 and 90 showed intense signals in this region. The second one, at 110 °C, can be linked to the removal of EVS, since only m/z of 88 showed peak in this temperature. The third new peak, at 260 °C, can be related to the decomposition of both EVS and CEES, which are strongly retained on the surface by hydrogen bonds. Finally, the last peak at 300 °C can be linked to a further desorption of CEES. The two energetically different sites of the strong adsorption of CEES suggest that the hydrogen bonds between the hydroxyl groups of the inorganic phase and CEES are formed with S or Cl atoms.

Figure 5.2.14. m/z thermal profiles (in helium) of exhausted AgZrGO for the fragments related to fragments of EES (m/z: 90), EVS (m/z: 88), Cl (m/z: 35), SO₂ (m/z: 64), C (m/z: 12), and -OH (m/z: 17).
5.1.9. Conclusions

Amorphous composites of zirconium hydroxide/graphite oxide/silver nanoparticles were successfully synthesized. The addition of AgNPs either to pure zirconium hydroxide or to the composite with GO led to a significant increase of the mesoporosity and the density of the terminal hydroxyl groups. These two factors were found to play the most crucial role in the reactive adsorption process. Interestingly, the existence of AgNPs in the structure resulted in alterations of the chemical environment of the hydroxyl groups, due to the introduced plasmon effect. Consequently, the composites with silver nanoparticles showed an improved catalytic degradation. The composite with both GO and AgNPs showed the largest weight uptake and most advanced catalytic degradation yield of CEES to EVS and BETE.
CHAPTER 6. Conclusions

This dissertation provides a summary of our research regarding the reactive adsorption of the mustard gas surrogate’s vapors, CEES, at ambient conditions on zinc or zirconium (hydr)oxides and their composites with graphite oxide (GO) and/or gold or silver nanoparticles. All the syntheses were accomplished by an one-pot wet precipitation method with water as a solvent. Various materials were studied in the literature as potential adsorbents of mustard gas surrogates, but in solutions. The chemical warfare agents were deployed in the most of the cases in their gaseous phase. For that reason, a throughout research on the heterogeneous interactions is required. This work elucidates in details the structural and chemical features that play crucial role on the catalytic detoxification performance. The closed Vials-in-vial adsorption system provides us the ability to identify the formed products of the surface reactions, which remained in the headspace of the closed system and/or on the surface of the powder, and as a result to ascertain the involved mechanisms.

The weight uptake tests are efficient in order to evaluate the ability of the material to adsorb vapors of the CWA and its decomposition products. The weight uptake results after 24 hours of CEES exposure of the herein studied commercial zinc oxide nanoparticles (ZnO-C), zinc hydroxide (Zn(OH)\textsubscript{2}) and zirconium hydroxide (Zr(OH)\textsubscript{4}) are collected in Figure 6.1. For the sake of comparison are included in the same Figure the weight uptakes reported for CEES adsorption for 24 hours of exposure at the same conditions on ferrihydrite (FeOOH),\textsuperscript{125} cerium oxide (CeO\textsubscript{2}),\textsuperscript{171} magnesium oxide (MgO),\textsuperscript{1} activated carbon with surface area 1250 m\textsuperscript{2} g\textsuperscript{-1} (act. carbon),\textsuperscript{2} and graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}).\textsuperscript{3} Remarkably, Zr(OH)\textsubscript{4} performs best among all materials addressed so far as adsorbents of CEES vapors, while it showed the same adsorption performance also in dark. Zinc hydroxide showed also higher weight uptake that those of cerium, magnesium
and zinc oxides, but slightly lower than those of zirconium hydroxide and ferrihydrite. On the contrary, zinc hydroxide presented higher photocatalytic degradation performance among all the afore mentioned materials. It is worth to mention that the maximum weight uptake in the case of activated carbon was reached after 576 hours (24 days).  

Figure 6.1. Weight uptakes after exposure to CEES at the same conditions on commercial zinc oxide nanoparticles (ZnO-C), zinc hydroxide (Zn(OH)$_2$), zirconium hydroxide (Zr(OH)$_4$), ferrihydrite (FeOOH),$^{125}$ cerium oxide (CeO$_2$),$^{171}$ magnesium oxide (MgO),$^1$ activated carbon (act. carbon),$^2$ and graphitic carbon nitride (g-C$_3$N$_4$).$^3$

The composites of both zinc and zirconium hydroxides with GO showed an improved weight uptake performance against the surrogate of mustard gas. The optimum amount of GO was 10 % in the case of zinc hydroxide based composites and 5 % for the zirconium hydroxides composites. The addition of GO showed a positive effect on:

1) surface structural and chemical heterogeneity
2) dispersion of the inorganic phase
3) number of terminal -OH groups
4) surface area and the total pore volume
5) efficiency of electron transfer/separate holes from electrons
6) adsorption capacity
7) degradation-detoxification yield

The simultaneous incorporation of AgNPs, during the synthesis of the composites, resulted in the formation of materials which showed even better performance, compared to the composites without the NPs (Figure 6.2). After 24 hours of exposure, the composite of zinc hydroxide with graphite oxide and AgNPs (AgZnGO) showed 137% increase in the weight uptake compared to pure zinc hydroxide. For the composite consisting of zirconium hydroxide, GO and AgNPs (AgZrGO), the weight uptake was almost two folds higher than that of pure zirconium hydroxide. AgZrGO showed higher weight uptake than AgZnGO. On the contrary, the opposite trend was found for the maximum weight uptakes, since the latter composites showed dramatically higher maximum weight uptake. The recorded 1.63 gram per gram weight uptake is the greatest value reported in the literature and revealed that this material adsorbed almost twice its mass.
Figure 6.2. Weight uptakes of the Zn and Zn hydroxides and theirs composites with graphite oxide or graphite oxide and AgNPs.

The identification of the formed volatile products, as well as of those retained in the porous system of the absorbents, by various methods led us to propose the mechanisms that governs the heterogeneous adsorption. The obtained results clearly indicate that the detoxification process undergoes mainly through two pathways. The first one is the retention of CEES and its degradation products on the surface by physical forces (physisorption). The second one is by a catalytic decomposition/degradation to nontoxic products (reactive adsorption). The latter pathway found to be more crucial, since the dependence of the weight uptakes on the porosity did not show a linear correlation, while it showed a linear dependence on the number of surface hydroxyl groups.

For the zinc based absorbents, the main decomposition pathway is the dehydrohalogenation of CEES, via the formation of the intermediate cyclic sulfonium cation that through an intermolecular
rearrangement transforms to ethyl vinyl sulfide (EVS). More interestingly, the photocatalytic activity of these materials promotes the formation of radicals, which participate in the decomposition of CEES. Cleavage of the S–C bond lead to smaller compounds, whose recombination resulted in molecules with two sulfur atoms. On the other hand, the zirconium based composites with GO degrade CEES in most selective way, which is not affected by the light irradiation.

The addition of silver nanoparticles to the matrix of both abovementioned composites led to a marked advancement in the reactive adsorption. The altered nucleation during the precipitation led to an improvement of the features that play the paramount role on the adsorption, and to an altered chemical environment of the hydroxyl groups by the introduced plasmon effect. More precisely, addition of NPs caused increases in:

1) chemical and structural surface heterogeneity
2) surface area and total pore volume
3) amount of highly reactive terminal groups
4) activity of the oxygen containing surface groups

Furthermore, for the zinc based composites which are photoactive under visible light irradiation, the addition of the nanoparticles led to an increased photocatalytic detoxification efficiency, since NPs enhance the separation of electron/holes pair due to the introduced plasmon effect, preventing simultaneously their recombination. The addition of gold nanoparticles in the case of zinc hydroxide/graphite oxide composite introduced a selective photo-oxidation capability. The density of the hydroxyl groups found again to play a key role. The main detoxification pathways for
Nanocomposites are summarized in Figure 6.3. It is worth to point out that all the formed products are less or non-toxic.

Figure 6.3. The formed products during the adsorption on AgZnGO, AuZnGO and AgZrGO.

The first conclusion arises from the comparison of the composites of Zn(OH)$_2$ and Zr(OH)$_4$. Zirconium based materials interact faster with the vapor than the Zinc based ones. On the other hand, the latter ones, even though the detoxification is slower on them, bring the photoactivity enhancing the extent of CEES transformations. Ultimately, it is of paramount importance to define the requirements of the specific application, and then to define which material can fulfill better the necessities. But in all cases, the addition of GO and NPs will lead to a supreme enhancement of the detoxification performance.
CHAPTER 7. Paths toward future research

In this chapter some ideas on future research directions related to the detoxification of CWAs vapors are proposed:

• The materials that showed a good detoxification performance on the laboratory-scale should be tested for real applications. The possibility of their deposition on different materials, such as cloths, textiles or fibers, should be also studied.

• The viable regeneration of the spent materials without changing the structural and chemical properties should be explored. If this would not be possible, due to the strong/reactive adsorption, recycling of the materials and their further reuse for other application could be studied.

• So far, the studies in the literature focus on the adsorption of only one CWA each time. It would be interesting to extend the adsorption tests using mixtures of various surrogates of different chemical warfare agents. This would provide the additional option of studying the selectivity of the materials investigated as potential adsorbents.

• Graphitic carbon nitride (g-C₃N₄) has a layered structure similar to graphite and consists of triazine and tri-s-triazine units. It is an n-type semiconductor with a band gap in the visible range (2.7 eV), but it suffers from a fast electron-hole (e⁻/h⁺) recombination. g-C₃N₄ has recently attracted the interest of the scientific community in various solar-driven applications. In attempt to address the drawback of the fast e⁻/h⁺ recombination, several modification methods have been developed. The oxidation using the Hummers method resulted in the incorporation of oxygen functional groups at the edges of the g-C₃N₄ layers, leading to the formation of spherical nanoparticles (5 to 50 nm) as a result of the folding of the layers. These materials can be used as alternatives to GO for the synthesis of the
composites. The introduced photoactivity may result in an enhancement on the detoxification performance.

- Alternative metal or carbon based nanoparticles can be used instead of silver or gold nanoparticles. Even though the surface chemistry of the final material would be different than that of the nanocomposites tested here, it is possible that the new composites will present a different degradation selectivity, or an even more improved detoxification performance.
Appendix

Fritz Haber: The man behind the Mustard Gas

The German chemist (9 December 1868 - 29 January 1934) was a unique figure in the earliest 1990s, since he placed his stamp to various fields, which he touched, from science to industry. He was established in the science community as Nobel laureate in 1918, for the invention of the Haber-Bosch method, for the synthesis of ammonia from hydrogen and nitrogen gases. He also established the Born-Haber cycle for rationalizing the formation of ionic salts. His ability to marry scientific knowledge with the practical application, gave him a huge recognition, especially during the World War I. He completed his Ph.D. in 1891, and three years later gained an assistantship in Karlsruhe, where he accomplished the ammonia synthesis. Afterwards, he was invited by the emperor of Prussia in 1910, as a scientific initiative and Director of “Kaiser Wilhelm Society” at the hundredth anniversary of Berlin’s University.

One of the greatest problems that German’s war industry confronted even from the first months of WWI, was the blockage by the British warships ships from Chile with nitrate supplies. Nitrate was needed for the production of nitric acid, a crucial compound for the ammunitions. His first remarkable achievement was its faith and contribution to the development of the method for the transformation of ammonia to nitrate in a large scale. His method for synthesis of ammonia saved the Germany war machine from the nitrate crisis. From the beginning of 1915, BASF’s factories were producing tons of nitrate each day, replacing the Chile’s mines.

Dianididine chlorosulfonate and benzyl bromides were the first toxic gases used as weapons from the German forces in October and December of 1914, respectively. Their absolute failure inspired Haber to make this novel application of chemistry to work in the battlefields. His institute started
directly after this failure to test new toxic chemicals. His suggestion, to deploy from pressurized tanks clouds of chlorine gas in order to asphyxiate the enemy soldiers, was approved on January 1915. On April 22, the first usage of chlorine as gas weaponry became a successfully reality, and Haber gained the military rank as Captain.

As a personality, he was not a fanatical nationalist or hungry for blood, but he was ambitious for power and fame. The Nobel Prize laureate in Physics (1925) James Franck, who was working as a young researcher under Haber’s supervision commented: “The only deplorable thing about Haber was that he was a bit power-hungry…He knew his own intelligence and wanted power. He knew what was capable of, and his fingers were itching to do it”. Haber’s Jewish heritage was intolerable to Hitler, although Haber had converted as Christian. He lived the last years of his life in exile, and he died in France in 1934. The Institute for Physical and Electrochemistry at Berlin-Dahlem was renamed as Fritz Haber Institute after his death.
Bibliography


(8) Charles, D. Master Mind: The Rise and Fall of Fritz Haber, the Nobel Laureate Who Launched the Age of Chemical Warfare; 2005.


(19) Gunther, M. chemistryworld.com


(21) 100 years of chemical weapons http://chemicalweapons.cenmag.org (accessed Mar 11, 2016).


(25) Itineraries of WWI-Travelling in history


(29) Esfandiary, D. The Five Most Deadly Chemical Weapons of War


(99) Zhu, M.; Chen, P.; Liu, M. Graphene Oxide Enwrapped Ag/AgX Efficient Visible-Light


(108) Fu, Q.; Salrsburg, H.; Flytzani-Stephanopoulos, M. Active Nonmetallic Au and Pt Species on Ceria-Based Water-Gas Shift Catalysts. *Science (80-. ).* 2003, 301 (5635), 935–938.


1976, 80 (4), 567–583.


Chem. 1967, 45, 579.


(168) Huang, C.; Tang, Z.; Zhang, Z. Differences between Zirconium Hydroxide (Zr (OH) 4· nH2O) and Hydrous Zirconia (ZrO2· nH2O). *J. Am. Ceram.* ... **2001**, *38*, 1637–1638.


