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| 14. ABSTRACT<br>Surface chemistry combined with specific pore sizes was found as the most important factor for retention of small molecule toxic gases at ambient conditions. To design efficient adsorbents for TICs the materials should have small pores and specific chemistry promoting oxidation, reductions, complexation, and acid-base reactions. Those reactions lead either to incorporation of species to the adsorbents' matrix or they convert the toxic agents into nontoxic compounds. Water contributes significantly to surface reactions.                                                                                                                                                                                                                                                                                                                                                                      |                   |                                |                                  |                                                         |                                                   |
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## Report Title

### SORBENTS AND MECHANISMS OF REMOVAL

#### ABSTRACT

Surface chemistry combined with specific pore sizes was found as the most important factor for retention of small molecule toxic gases at ambient conditions. To design efficient adsorbents for TICs the materials should have small pores and specific chemistry promoting oxidation, reductions, complexation, and acid-base reactions. Those reactions lead either to incorporation of species to the adsorbents' matrix or they convert the toxic agents into nontoxic compounds. Water contributes significantly to surface reactions.

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**List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:**

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

1. The role of water and surface acidity on the reactive adsorption of ammonia on modified activated carbons  
L-M Le Leuch, T.J. Bandosz,  
Carbon, 45, 568-578 (2007).
2. Removal of ammonia by graphite oxide via its intercalation and reactive adsorption  
Mykola Seredych and Teresa J. Bandosz  
Carbon, 45 2130-2132 (2007).
3. Interactions of ammonia with the surface of microporous carbon impregnated with transition metal chlorides  
Camille Petit, Christopher Karwacki, Greg Peterson, Teresa J. Bandosz  
J Phys. Chem. 111, 12705-12714 (2007).
4. Role of graphite oxide and polyaniline in NO<sub>2</sub> reduction on GO-PANI composites  
Mykola Seredych, Robert Pietrzak and Teresa J. Bandosz  
Ind. Chem. Eng. Res., 46, 6925-6936 (2007).
5. Role of aluminium oxycations in retention of ammonia on modified activated carbons  
Camille Pettit and Teresa J. Bandosz.  
J. Phys. Chem. 111, 16445-16452 (2007)
6. Reactive adsorption of NO<sub>2</sub> at dry conditions on sewage sludge derived materials  
Robert Pietrzak, Teresa J. Bandosz  
Environ. Sci. Technol., 41, 7516-7522 (2007)
7. The mechanism of ammonia retention on graphite oxides: role of surface chemistry and structure  
Mykola Seredych and Teresa J. Bandosz  
J.Phys.Chem.. 111, 15596-15604 (2007)
8. Activated Carbons Modified with Sewage Sludge Derived Phase and their Application in the Process of NO<sub>2</sub> Removal  
R. Pietrzak and T. J. Bandosz  
Carbon, 45, 2537-2546 (2007)
9. Activated Carbon Modified with Aluminum-Zirconium Polycations as Adsorbents of Ammonia  
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Micro Meso. Mat, 114 (2008) 137-147.
10. Interactions of NO<sub>2</sub> with Sewage Sludge Based Composite Adsorbents  
Robert Pietrzak and T.J. Bandosz  
J. Haz.Mat., 154 (2008) 946-953.
11. Removal of Ammonia From Air on Molybdenum and Tungsten Oxide Modified Activated Carbons  
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Environ. Sci. Technol. 42 (2008) 3033-3039.
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Mykola Seredych and T. J. Bandosz  
J. Colloid Interface Sci., 324 (2008) 25-35
13. Surface Features of Exfoliated Graphite/Smectite Composites and their Importance for Ammonia Adsorption  
Mykola Seredych, Albert V. Tamashauskyy, and Teresa J. Bandosz  
Carbon, 46 (2008) 1241-1252
14. Complexity of Ammonia Interactions on Activated carbons Modified with V<sub>2</sub>O<sub>5</sub>  
Camille Pettit and Teresa J. Bandosz  
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Micro Meso Mat. 118 (2009) 61-67.
16. Adsorption of NO<sub>2</sub> on activated carbons modified with cerium, Lanthanum and sodium chlorides.  
Karifala kante, Eleni Deliyanni, Teresa J. Bandoz,  
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17. Role of Graphite Precursor in The Performance of Graphite Oxides as Ammonia Adsorbents  
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18. The Effects of Urea Modification and Heat Treatment on the Process of NO<sub>2</sub> Removal by Wood-based Activated Carbon  
S. Bashkova, and T. J. Bandoz  
J. Colloid Interface Sci. 333 (2009), 97-103.
19. Graphite Oxide/polyoxometalate Nanocomposites as Adsorbents of Ammonia  
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J. Phys. Chem., 113 (2009) 3800–3809
20. Effects of surface chemistry on the reactive adsorption of hydrogen cyanide on activated carbons.  
Mykola Seredych, Martin van der Merwe and Teresa J. Bandoz  
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21. Graphite oxide/AlZr polycation composites: surface characterization and performance as adsorbents of ammonia  
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22. On the Reactive Adsorption of Ammonia on Activated Carbons modified by Impregnation with Inorganic Compounds  
T.J. Bandoz, C. Petit  
J. Coll. Interface Science, feature article, 338(2009) 329-345..
23. MOF-Graphite Oxide Composites: Combining the Uniqueness of Graphene Layers and Framework of MOF  
C. Petit Ad T. J. Bandoz  
Advanced Materials. 21 (46) 2009, 4753-4757.
24. MOF-Graphite Oxide Nanocomposites: Surface Characterization and Evaluation as Adsorbents of Ammonia  
C. Petit And T. J. Bandoz  
J. Mater. Chem. , 19 (2009) 6521-6528.
25. Enhanced adsorption of Ammonia on Metal-Organic Framework / Graphite Oxide Composites: Analysis of Surface Interactions  
C. Petit And T. J. Bandoz  
Adv Funct. Mater., 19 (2009) 1-8
26. The Adsorption/Reduction of NO<sub>2</sub> On Graphite Oxide/Iron Composites  
S. Bashkova, T.J. Bandoz  
Ind. Chem. Eng. Res. 2009, 48 (24), pp 10884–10891
27. Adsorption of ammonia on graphite oxide/Al<sub>13</sub> composites  
M.Seredych and T. J. Bandoz  
Colloids and Surfaces A.,353 (1) 2010, 30-36.
28. Revisiting the chemistry of graphite oxides and its effect on ammonia adsorption.  
C. Petit, M. Seredych, and T.J. Bandoz  
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29. The role of sulfur-containing groups in ammonia retention on activated carbons  
Camille Petit, Karifala Kante, and Teresa J. Bandosz  
Carbon, 48, 2010, 654-667.
  
30. Combined Role of water and surface chemistry in reactive adsorption of ammonia on graphite oxides  
M. Seredych and T.J. Bandosz  
Langmuir, 26 (2010) 5491-5498
  
31. Reactive adsorption of arsine on sulfur-containing carbons: role of surface chemistry in the oxidation process at ambient conditions  
Camille Petit , Gregory W. Peterson, John Mahle, and Teresa J. Bandosz  
Carbon, 48, 2010, 1779-1787
  
32. Interactions of arsine with microporous carbons role of heteroatoms in the oxidation process at ambient conditions  
Mykola Seredych, Gregory W. Peterson, John Mahle, and Teresa J. Bandosz  
J. Phys. Chem. C114 (2010) 6527-6533.
  
33. Graphite Oxides Obtained from Porous Graphite: Role of Surface Chemistry and Texture in Ammonia Retention at Ambient Conditions  
Mykola Seredych, Albert V. Tamashauskyy, and Teresa J. Bandosz  
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34. Adsorption of Dibenzothiophenes on Nanoporous Carbons: Identification of Interactions of NO<sub>2</sub> and NO with Carbonaceous Adsorbents Containing Silver Nanoparticles  
M. Seredych, S. Bashkova, R. Pietrzak, T.J. Bandosz  
Langmuir, 26 (2010) 9457-9464
  
35. Graphite Oxide /Zr(OH)<sub>4</sub> Composites: Evaluation of the Effects of Surface Features on Adsorption of SO<sub>2</sub>  
M. Seredych, , T.J. Bandosz, J. Phys. Chem. In press.

Number of Papers published in peer-reviewed journals: 35.00

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

Number of Papers published in non peer-reviewed journals: 0.00

**(c) Presentations**

1. Removal of Ammonia on Modified Activated Carbons: Role of Surface Features  
L.M. leLeuch and T.J. Bandosz  
Carbon 2006, Aberdeen, Scotland, July 16-21, 2006
2. The Role of Water and Surface Acidity on the Reactive Adsorption of Ammonia on Modified Activated Carbons  
Camille Petit and Teresa J. Bandosz  
Fundamentals of Adsorption 9 Conference, Gardine Naxos, Italy, May 25-31, 2007
3. Reactive Adsorption of Ammonia on Modified Activated Carbons  
Camille Petit and T.J. Bandosz  
Carbon 2007 Conference, Seattle, July 15-20, 2007
4. Removal of NO<sub>2</sub> on Modified Carbonaceous Adsorbents  
Robert Pietrzak and T.J. Bandosz  
Carbon 2007 Conference, Seattle, July 15-20, 2007
5. Removal of Small Molecule Toxic Gases on Graphite Oxide Based Adsorbents  
Adsorbent Workshop  
Camille Petit, Roberts Pietrzak and T.J. Bandosz  
Seattle, WA, July 12-14, 2007.
6. Removal of small molecule gases on modified activated carbons.  
Camille Petit and Teresa J. Bandosz  
Carbons for Energy Storage and Environmental Protection Conference ( CESEP 2), Krakow, Poland, Sept. 2-6, 2007.
7. Removal of Small Molecule Toxic Gases on Graphite Oxide Based Adsorbents  
Camille Petit, Roberts Pietrzak and T.J. Bandosz  
Individual Protection Equipment 2007 Conference  
Melbourne, Australia, Oct. 16-19, 2007
8. Activated Carbon/Inorganic Oxide Composites as Adsorbents of Ammonia  
Teresa J. Bandosz, Camille Petit  
AR OIC workshop. Boston , March 17-19 2008
9. Removal of Ammonia on Graphite Oxides  
Mykola Seredych, Teresa J. Bandosz,  
IEP2008, Kyoto, Japan, June 1-5, 2008
10. Removal of ammonia from air on molybdenum and tungsten oxide modified activated carbons  
Camille Petit, Teresa J. Bandosz  
Carbon 2008, Nagasaki Japan, July 14-20, 2008.
11. Understanding Reactive Adsorption of Small Molecule Toxic Gases on Carbonaceous Materials: Experiments And Simulation  
Teresa J. Bandosz  
Chemical Biological Filtration group meeting, Arlington, Sept. 9-12, 2008
12. Understanding Reactive Adsorption of Small Molecule Toxic Gases On Carbonaceous Materials: Experiments and Simulation  
Instituto Nacional Del Carbon, Oviedo Spain,  
Sept. 17, 2008
13. Understanding Reactive Adsorption of Small Molecule Toxic Gases On Carbonaceous Materials: Experiments and Simulation  
Teresa J. Bandosz  
University of Thessalonica  
Thessalonica, Greece, Sept. 30, 2008
14. Role of Graphite Precursor in the Performance of Graphite Oxides as Ammonia Adsorbents

Mykola Seredych, Camille Petit, Albert V. Tamashauskyy, and Teresa J. Bandosz  
Chemical and Biological Defence Science and Technology Conference, New Orleans, Nov 17-21, 2008

15. MOF-Graphite Oxide Nanocomposites: Surface Characterization and Evaluation as Adsorbents of Ammonia  
Camille Petit and Teresa J. Bandosz  
ARO Workshop, Savannah, GA, June 22-25, 2009

16. The Effects of Urea Modification and Heat Treatment on the Process of NO<sub>2</sub> Removal by Wood-based Activated Carbon  
S. Bashkova, and T. J. Bandosz  
Porous Materials Workshop 2009, Ne Brunswick, June 23-26, 2009

17. MOF-Graphite Oxide Nanocomposites: Properties And Application For Gas Separation  
Camille Petit and Teresa J. Bandosz  
Porous Materials Workshop 2009, Ne Brunswick, June 23-26, 2009

18. MOF-Graphite Oxide Nanocomposites: Surface Characterization and Evaluation as Adsorbents of Ammonia  
Camille Petit and Teresa J. Bandosz  
ICCM-17, International Conference on Composite Materials, Honolulu HI, July 26-August 1, 2009.

19. Understanding Reactive Adsorption  
T.J Bandosz  
Blucher Corporation, Dusseldorf, November 2009

20. GO-MOF composites; An insight into New Materials  
T.J Bandosz  
CNRS-SMRS, Orleans France , November 2009

21. Removal of Toxic species on Activated Carbons  
T.J. Bandosz  
Nova University of Lisboa, Portugal, December 2009

22. MOF / Graphite oxide composites: Exploring the New Concept of Adsorbents and Catalysts  
C. Petit and T.J Bandosz  
Fundamentals of Adsorption 10, Awaji Island, May 22-26, 2010.

23. MOF-Graphene Composites: An insight into the texture and adsorption properties of new materials  
C. Petit and T.J Bandosz  
Carbon 2010. July 11-16, 2010. Clemson, SC.

24. Reactive Adsorption of Arsine on Sulfur-Containing Carbons: Role of Surface Chemistry in the Oxidation Process at Ambient Conditions  
C. Petit, G. Peterson, J. Mahler, and T.J Bandosz  
Carbon 2010. July 11-16, 2010. Clemson, SC.

**Number of Presentations:** 24.00

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

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):** 0

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

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):** 0

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#### **(d) Manuscripts**

1. MOF / Graphite oxide hybrid materials: Exploring the New Concept of Adsorbents and Catalysts  
C. Petit and T. J. Bandosz  
Adsorption, in press.

Number of Manuscripts: 1.00

Patents Submitted

MOF/GO composites as adsorbents on acidic gases

T.J. Bandoz, C. Petit

Patents Awarded

Graduate Students

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| Camille Petit          | 0.10                     |
| <b>FTE Equivalent:</b> | <b>0.10</b>              |
| <b>Total Number:</b>   | <b>1</b>                 |

Names of Post Doctorates

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| L.M. le Leuch          | 1.00                     |
| Robert Pietrzak        | 1.00                     |
| Svetlana Bashkova      | 1.00                     |
| <b>FTE Equivalent:</b> | <b>3.00</b>              |
| <b>Total Number:</b>   | <b>3</b>                 |

Names of Faculty Supported

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> | National Academy Member |
|------------------------|--------------------------|-------------------------|
| Teresa J. Bandoz       | 0.10                     | No                      |
| <b>FTE Equivalent:</b> | <b>0.10</b>              |                         |
| <b>Total Number:</b>   | <b>1</b>                 |                         |

Names of Under Graduate students supported

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| Karifala Kante         | 0.00                     |
| <b>FTE Equivalent:</b> | <b>0.00</b>              |
| <b>Total Number:</b>   | <b>1</b>                 |



### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... 0.00

### Names of Personnel receiving masters degrees

NAME

**Total Number:**

### Names of personnel receiving PHDs

NAME

**Total Number:**

### Names of other research staff

NAME

PERCENT SUPPORTED

Mykola Seredych 0.00 No

Eleni Deliyanni 0.00 No

**FTE Equivalent:** 0.00

**Total Number:** 2

### Sub Contractors (DD882)

### Inventions (DD882)



## **SUMMARY OF THE FINDINGS FOR ARO AGREEMENT #W911NF-05-1-0537**

### **1. ADSORPTION OF AMMONIA ON CARBONS**

Ammonia adsorption was studied under dynamic conditions, at room temperature, on activated carbons of different origins (coal-based, wood-based and coconut shell-based carbons) before and after their impregnation with various inorganic compounds including metal chlorides, metal oxides and polycations. The role of humidity was evaluated by running tests in both dry and moist conditions. Adsorbents were analyzed before and after exposure to ammonia by thermal analyses, sorption of nitrogen, potentiometric titration, X-ray diffraction and FTIR spectroscopy. Results of breakthrough tests show significant differences in terms of adsorption capacity depending on the parent carbon, the impregnates and the experimental conditions. It is found that surface chemistry governs ammonia adsorption on the impregnated carbons. More precisely, it was demonstrated that a proper combination of the surface pH, the strength, type and amount of functional groups present on the adsorbents' surface is a key point in ammonia uptake. Water can have either positive or negative effects on the performance of adsorbents. It can enhance  $\text{NH}_3$  adsorption capacity since it favors ammonia dissolution and thus enables reaction between ammonium ions and carboxylic groups from the carbons' surface. On the other hand, water reduces the performance from the strength of adsorption standpoint. It promotes dissolution of ammonia and that ammonia is first removed from the system when the adsorbent bed is purged with air. Ammonia, besides adsorption by van der Waals forces and dissolution in water, is also retained on the surface via reactive mechanisms such as acid-base reactions (Brønsted and Lewis) or complexation. Depending on the materials used and the experimental conditions, 6 to 47% ammonia adsorbed is strongly retained on the surface even when the bed is purged with air.

Two carbons with different contents of sulfur were prepared and oxidized either by heating in air or by chemical treatment. The materials were then tested as adsorbents of ammonia in dynamic conditions, at room temperature. Their chemical and structural features were analyzed by energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray fluorescence spectroscopy, scanning electron microscopy, thermogravimetric analyses, potentiometric titration and sorption of nitrogen. It was found that not only oxygen-containing groups but also sulfur-containing groups enhance ammonia adsorption. In particular, sulfonic groups play a predominant role. In the presence of superoxide anions, they are converted into sulfates that react with ammonia to form ammonium sulfates. These salts are strongly retained in the micropores of the adsorbents.

### **2. ADSORPTION OF AMMONIA ON GO**

Graphite oxide was synthesized from three commercial graphites. The samples were used as adsorbents of ammonia at dry and wet conditions. Exceptionally high capacities reaching 10 wt% were measured. The initial and exhausted materials were characterized using adsorption of nitrogen, XRD, FTIR, TA, and potentiometric titration. The results showed differences in the texture and chemistry of adsorbents depending on the type of graphite precursor whose features determine the mechanism of ammonia adsorption. The strongly adsorbed species are either interacting with carboxylic groups to form salts, or with epoxy groups to form amines. A small amount of ammonia is weakly adsorbed via dispersive interactions or dissolved in the film of adsorbed water. As the concentration of amorphous carbon in the initial graphite increases, the ammonia removal capacity on the derived graphite oxide is improved.

Graphite oxide (GO) was synthesized using two different methods: one with sulfuric acid as part of the oxidizing mixture (Hummers-Offeman method), and another one without the sulfur-containing compound involved in the oxidation process (Brodie method). They were both tested for ammonia adsorption in dynamic conditions, at ambient temperature, and characterized before and after exposure to ammonia by X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, potentiometric titration, energy-dispersive X-ray (EDX) spectroscopy, X-ray photoelectron spectroscopy (XPS) and elemental analysis. Analyses of the initial materials showed that besides epoxy, hydroxyl and carboxylic groups, a significant amount of sulfur is incorporated as sulfonic group for GO prepared by the Hummers-Offeman method. The process of ammonia adsorption seems to be strongly related to the type of GO. For GO prepared by the Brodie method, ammonia is mainly retained via intercalation in the interlayer space of GO and by reaction with the carboxylic groups present at the edges of the graphene layers. On the contrary, when GO prepared by the Hummers method is used, ways of retention are different: not only does the intercalation of ammonia is observed but also its reaction with the epoxy, carboxylic and sulfonic groups present. In particular, during the ammonia adsorption process, sulfonic groups are converted to sulfates in presence of superoxide anions  $O_2^{\cdot-}$ . These sulfates can then react with ammonia to form ammonium sulfates. For both GOs, an incorporation of a significant part of the ammonia adsorbed as amines in their structure is observed as a result of reactive adsorption.

Graphite oxide synthesized using Brodie method was tested for ammonia adsorption after two different levels of drying in dynamic conditions at the ambient temperature. Surface characterization before and after an exposure to ammonia was done using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy and potentiometric titration. On the surface of the initial materials, besides epoxy, hydroxyl and carboxylic groups, various amounts of water within the interlayer space are present. The results showed that ammonia is intercalated within the interlayer space of graphite oxides. Water enhances the amount of ammonia adsorbed via the dissolution and promotes the dissociation of surface functional groups. This enhances formation of ammonium ions. On the other hand, water screens the accessibility of epoxy and  $-COOH$  groups for reactions with ammonia and thus limits the amount adsorbed. The retention of ammonia on a partially dried graphite oxide is enhanced not only owing to those reactions but also

due to the formation of new adsorption centers as a result of an incorporation of ammonia to the graphene layers.

Graphite oxides (GO) synthesized using Brodie and Hummers methods were tested for ammonia adsorption at ambient conditions with different contents of water in the system. Surface characterization before and after exposure to ammonia was performed using X-ray diffraction, Fourier-transform infrared spectroscopy, potentiometric titration, thermal analysis, adsorption of nitrogen and X-ray photoelectron spectroscopy. Oxidation of the same porous graphite using two methods results in the materials with different textural and chemical features. On GO obtained using the Brodie method mainly epoxy and carboxylic groups are present whereas on the GO obtained using Hummers method chemisorbed oxygen is also found. The contribution of the carboxylic groups in latter material is greater. It also contains sulfur either in sulfones or as residual sulfuric acid. Ammonia is adsorbed either via reaction with surface groups or dissolution in water. The former is responsible for strong adsorption. The evidence of the catalytic effect of the carbon surface on activation of oxygen leading to surface oxidation was also observed.

### 3. ADSORPTION OF AMMONIA ON GO COMPOSITES

Adsorbents for ammonia were prepared by modifications of graphite oxide with two different Keggin polycations:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ . The high acidity of those polyoxometalates combined with the functionalities and acidity of graphite oxide are expected to initiate strong interactions with  $\text{NH}_3$ . The materials were characterized before and after exposure to ammonia by X-ray diffraction, transmission electron microscopy, sorption of nitrogen, potentiometric titration, thermal analyses and Fourier transform infrared spectroscopy. Even though, the nanocomposites prepared have a disordered structure, an improvement in ammonia retention compared to the parent graphite oxide was observed owing to the formation of complexes between ammonium and polycations. It was found that under specific conditions, interactions between the polycations and the carboxylic groups located at the edges of graphite oxide limit the accessibility of the interlayer space and thus decrease the amount of ammonia adsorbed.

Graphite oxide/aluminium-zirconium polycation composites were prepared using graphite oxide and commercial solution of Rezal®. To improve the dispersion of graphene-like layers two different surfactant concentrations were used. The resulting materials were used as adsorbents of ammonia either in as received form or prehumidified for two hours before the breakthrough test. The challenge gas was either dry or with 70% humidity. Although the highest amount adsorbed was measured on adsorbents after prehumidification, the strongest adsorption takes place at dry conditions. Water on the surface increases the amount adsorbed via acid-base reactions, whereas water in the challenge gas decreases the removal of ammonia owing to the competition with  $\text{NH}_3$  for adsorption centers. The amount of

surfactant used for dispersion affects the final performance. More surfactant likely leads to a higher degree of dispersion of graphene like layers and thus relatively less undisturbed interlayer space where intercalation of ammonia can occur. Higher dispersion of graphene layers lead also to higher dispersion of polycations and thus greater adsorption on their Brønsted acidic centers.

Graphite oxide/ $\text{Al}_{13}$  composites were prepared using graphite oxide and commercial solution of Chlorhydrol®. Although surfactant was used to disperse of graphene-like layers, they were restacked together upon addition of  $\text{Al}_{13}$  Keggin polycations. The crust of inorganic phase was deposited on the outer surface of GO platelets. The resulting materials were used as adsorbents of ammonia in dry or wet conditions either in an as received form or prehumidified for two hours before the breakthrough test. It was shown that water in the system decreases the amount adsorbed, likely as a result of the competition with ammonia for adsorption centers. The highest and strongest adsorption was found in the dry conditions where interlayer space was partially available and the acidic centers of an inorganic phase played an enhancing role in the retention of ammonia.

Graphite oxide (GO) / metal-organic framework (MOF-5) nanocomposites are synthesized with various ratios of the two components. In developing the concept of these new adsorbents, it was expected that distorted graphene sheets would contribute to the enhancement in the dispersive interactions, whereas MOF-5 component would contribute to the expansion of the pore space where adsorbates could be stored. Moreover, taking into account the variety of transition and noble metals, which can be used to form the MOF structure, those materials have a potential to provide active sites for reactive adsorption or heterogeneous catalysis. The composites have a unique layered sandwich-like structure where GO units divide the MOF-5 units. A possible scenario for the formation of such structures is the involvement of linkages between epoxy groups of distorted graphene layers of GO and zinc oxide building units of MOF-5. An increase in the content of GO leads to a greater distortion of the MOF-5 cubic structure and visible changes in the texture of nanocomposites. The materials are predominantly microporous with sizes of pores defined by the cavities of MOF-5 units. Moreover, specific combination and synergy between GO and MOF-5 units also result in the formation of a unique porosity characteristic of the nanocomposites.

Metal-organic framework (MOF-5)/graphite oxide (GO) composite was synthesized using solvothermal synthesis route. The parent materials (MOF-5 and GO) and the nanocomposite were characterized using X-ray diffraction, SEM, TEM, FTIR and adsorption of nitrogen. They were also tested as adsorbents of ammonia in dynamic conditions. The composite material obtained had a unique layered texture with a

preserved structure of MOF-5 and GO. When tested as ammonia adsorbent, the composite showed some synergy enhancing the adsorption capacity in comparison with the hypothetical physical mixture of the components. Although the removal capacity was high in the presence of moisture, water had a detrimental effect on the chemistry of materials and destroyed their porous framework. This caused that ammonia retained on the surface was progressively desorbed from the materials when the samples were purged with air.

Composites of metal-organic framework (MOF-5) and graphite oxide (GO) with different ratios of the two components were prepared and tested in ammonia removal under dry conditions. The parent and composites materials were characterized before and after exposure to ammonia by sorption of  $N_2$ , X-ray diffraction, thermal analyses and FT-IR spectroscopy. The results showed a synergetic effect resulting in an increase in the ammonia uptake compared to the parent materials. It is linked to enhanced dispersive forces in the pore space of the composites. Besides, ammonia interacts with zinc oxide tetrahedra via hydrogen bonding and is intercalated between the layers of graphite oxide. Retention of a large quantity of ammonia eventually leads to a collapse of the structure of MOF-5 in the composites. The effect resembles that observed when MOF-5 is exposed to water. Taking into account the similarity of ammonia and water molecules, it is hypothesized that ammonia causes a destruction of the MOF-5 and composite structure as a result of its hydrogen bonding with the zinc oxide clusters.

#### 4. ADSORPTION OF $NO_2$ ON CARBONS

The removal of  $NO_2$  on urea-modified and heat-treated wood-based activated carbon was studied. From the obtained results it was found that urea modification and heat treatment of carbon, especially at  $950^\circ C$ , has a positive effect on  $NO_2$  adsorption and on the retention of NO (the product of  $NO_2$  reduction by carbon). The presence of moisture in the system enhances the removal of  $NO_2$  likely by the formation of  $HNO_2/HNO_3$  acid intermediates inside the carbon pores and the subsequent gradual oxidation of the carbon surface by these acids. On the other hand, the presence of moisture negatively affects the retention of NO. An increase in the adsorption of  $NO_2$  and in the retention of NO was also found on high-temperature-treated carbon without urea modification. It is possible that the formation of supermicropores and active centers on the carbon surface during high temperature treatment plays a significant role in these removal processes. The products found on the carbon surface after  $NO_2$  adsorption/reduction/oxidation were physisorbed and chemisorbed  $NO_2$ , bidentate and/or bridging nitrato compounds ( $-ONO_2$ ),  $NO_2^-$ , and  $HNO_3$ . The latter one was found only in moist conditions.

Interactions of  $NO_2$  and NO (the product of  $NO_2$  reduction by carbon) with the biomass-based carbonaceous materials with silver nanoparticles deposited on the surface were studied. The surface of the materials was characterized using adsorption of nitrogen, XRD, SEM, FTIR and TA. The results showed that the amount

of NO<sub>2</sub> adsorbed, its conversion to NO, and the amount of NO released from the carbon surface depend on the carbon's content of silver. More silver results in a better performance of the adsorbent. The products of NO<sub>2</sub> interaction with silver include surface chelates such as Ag<sub>2</sub>-O-NO or Ag-O<sub>2</sub>-NO. Another element, active in the surface reactions with NO<sub>2</sub>, is phosphorus. Both silver and phosphorus species are oxidized by NO<sub>2</sub>. The product of NO<sub>2</sub> reduction, NO, is either retained on the carbon surface by its interactions with metallic silver or it is further reduced to N<sub>2</sub>O or N<sub>2</sub>.

## 5. ADSORPTION OF NO<sub>2</sub> ON GO COMPOSITES

Adsorption of NO<sub>2</sub> and the retention of NO (the product of NO<sub>2</sub> reduction by carbon) on the materials prepared from iron acetate complex and its mixture with graphite oxide were studied. The surface of the materials was characterized using adsorption of nitrogen, XRD, SEM, FTIR and TA. The results showed that the development of texture and porosity along with formation of some active surface species on the graphite oxide/iron composite materials leads to an increase in NO<sub>2</sub> adsorption. An immediate reduction of NO<sub>2</sub> to NO by carbon was noticed for all samples except for the one that contained a smallest amount of carbon in a mostly oxidized form. The retention of NO on the surface of the materials does not depend on their structural characteristics. Better performance is found for the materials that contain active iron species, such as  $\gamma$ -FeOOH and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which likely react with NO molecules forming surface nitrates.

## 6. ADSORPTION OF ARSINE ON CARBONS

Two carbons with different contents of sulfur were prepared and oxidized either by heating in air or by chemical treatment. The samples were then tested as adsorbents of arsine in dynamic conditions at room temperature, in dry conditions and in the presence of moisture. Chemical and structural features of the initial and arsine-exposed materials were analyzed by energy dispersive X-ray spectroscopy, X-Ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analyses, sorption of nitrogen and sorption of water. It was found that oxygen and sulfur containing groups participate in arsine oxidation to arsenic tri- and pentoxide and/or in the formation of arsenic sulfides. This occurred either via activation of oxygen or a direct involvement of these groups in reactions with arsine. A very hydrophilic surface of sulfur-containing carbons, which causes the presence of adsorbed water, even at dry conditions, enhances arsine removal. On the other hand, in moist conditions water totally occupies the pore system blocking the catalytic action of the surface toward oxidation, which leads to a very limited or nil capacity.

Two carbons obtained from polymers containing no ash and commercial wood based carbons, as received and modified with nitrogen, were tested as adsorbents of arsine in



dynamic conditions at room temperature. The chemical and structural features of the initial and exhausted carbons were analyzed by energy dispersive X-ray spectroscopy, X-ray fluorescence spectroscopy, X-Ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analyses, sorption of nitrogen and sorption of water. It was found that heteroatoms present on the surface of the carbons studied, namely oxygen, nitrogen and sulfur catalyze arsine oxidation mainly to arsenic tri- and pentoxide and/or in the formation of arsenic sulfides. When the surface has a high degree of hydrophilicity and water is present in the system it blocks these active centers resulting in the negligible arsine removal capacity. On the other hand, on a relatively hydrophobic surface with active nitrogen species arsine is adsorbed and oxidized to arsenic oxide. A small quantity of adsorbed water converts arsenic oxide to arsenic acid, which migrates to small pores releasing the centers for further adsorption and surface reactions. The process proceeds until all pores are filled/blocked, disallowing for further adsorption/reaction of arsine molecules.

## 7. ADSORPTION OF HCN ON CARBONS

Two activated carbons of different origins were modified by heating at 950 °C either with or without previous urea impregnation. The treatment causes changes in surface chemistry and porosity. The materials obtained were used as adsorbents for hydrogen cyanide in dry air at ambient conditions. The samples before and after adsorption were characterized using nitrogen adsorption, potentiometric titration, elemental analysis and thermal analysis. On selected samples extraction was carried out to identify surface reaction products soluble in alcohols. The results indicated differences in the amount adsorbed and the products of surface reactions on specific surface features. The presence of nitrogen incorporated in the carbon matrix leads to an enhanced performance owing to the basic environment and the ability of the surface to activate oxygen. These lead to complex surface reactions in which the derivatives of hydrogen cyanide form oxamide, and are incorporated in the carbon matrix, or are deposited as the bulky insoluble polymers of paracyanogen on the surface. The reactions mainly occur in pores with sizes between 10-20 Å where the functional groups can be present and HCN, or its derivatives, and water can take part in the reactions

## 8. ADSORPTION OF SO<sub>2</sub> ON ZIRCONIUM HYDROXIDE/GO COMPOSITES

Zirconium hydroxide/graphene composites were synthesized from zirconium chloride and graphite oxide with the content of graphene component between 5 and 50 %. They were used as adsorbents of sulfur dioxide at ambient conditions. The initial and exhausted materials were characterized using adsorption of nitrogen, infrared spectroscopy, potentiometric titration, scanning electron microscopy and thermal analysis. The results indicated enhanced adsorption of SO<sub>2</sub> on the composites, which is linked to the formation of new basic sites and porosity as a result of interactions between zirconium hydroxide units and the oxygen groups attached to the graphene layers. Both physical adsorption and reactive adsorption of

SO<sub>2</sub> via formation of sulfites play a role in the retention process. The graphene component catalyses oxidation of SO<sub>2</sub> and leads to the formation of sulfates.