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Report Title

The study and development of metal oxide reactive adsorbents for the destruction of toxic organic compounds

ABSTRACT

The achievements realized during the course of this project provide an important alternative method for mitigating the effects of the exposure of personnel and systems to chemical warfare agents and other toxic organic compounds. The research program that was developed built upon earlier results achieved in the room temperature oxidative decomposition of a chemical warfare agent simulant, dimethyl methylphosphonate (DMMP), on solid reactive adsorbents and examined ways of improving those results by modifying the nature of the reactive adsorbent itself and by adding an energetic co-reactant.

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)

Mark B. Mitchell, Viktor N. Sheinker, Woodrow W. Cox, Jr*, "The Room Temperature Reaction of Ozone and Dimethyl Methylphosphonate (DMMP) on Alumina-Supported Iron Oxide," J. Phys. Chem. C, 2007, 111, 9417-9426.

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Mark B. Mitchell, V. N. Sheinker, and W. W. Cox, Jr.* "The Room Temperature Reaction of Ozone and Dimethyl Methylphosphonate on Alumina-Supported Oxides," poster presentation at the 2006 Denver DECON Science and Technology Conference, Denver, CO, October 31-November 2, 2006.

Mark B. Mitchell, V. N. Sheinker, W. W. Cox, Jr.* "Gas-phase co-reactants for the ambient temperature decomposition of organophosphonates on metal oxides," oral presentation at the ACS National Meeting in Atlanta, GA, March 26-30, 2006.

Woodrow W. Cox, Jr.*, V. N. Sheinker, M. B. Mitchell "The development of a colorimetric detector for the decomposition of dimethyl methylphosphonate on metal oxides," poster presentation at the ACS National Meeting in Atlanta, GA, March 26-30, 2006.

INVITED: Mark B. Mitchell "The Study of Surface Chemical Reactions with FT-IR and FT-Raman," Thermo Electron 2006 Research Symposia Series on Vibrational Spectroscopy, Princeton, NJ (February 28, 2006).

INVITED: Mark B. Mitchell "The Study of Surface Chemical Reactions with FT-IR and FT-Raman," Thermo Electron 2006 Research Symposia Series on Vibrational Spectroscopy, San Diego, CA (February 6, 2006).

Woodrow W. Cox, Jr.*, Viktor N. Sheinker, and Mark B. Mitchell, "The Adsorption and Decomposition of Dimethyl Methylphosphonate (DMMP) on Titania-Supported Cerium Oxide Adsorbents," Water CAMPWS Annual Symposium, April 13-15, 2005, Atlanta, GA.

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Mark B. Mitchell, Viktor N. Sheinker, and Woodrow W. Cox, Jr., "Sustained Room Temperature Decomposition of Dimethyl Methylphosphonate (DMMP) by O3 on Alumina-Supported MnOx," Platform Presentation, 2007 Scientific Conference on Chemical and Biological Defense Reserach, November 13-15, 2007, Timonium, MD.

Mark B. Mitchell, Viktor N. Sheinker, and Woodrow W. Cox, Jr., "Decomposition of Dimethyl Methylphosphonate (DMMP) on Supported Oxide with Gas-Phase Co-Reactants," Platform Presentation, 2005 Scientific Conference on Chemical and Biological Defense Research, November 14-16, 2005, Timonium, MD.

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Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Woodrow W. Cox, Jr.	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Viktor N. Sheinker	1.00
FTE Equivalent:	1.00
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Mark B. Mitchell	0.25	No
FTE Equivalent:	0.25	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
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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: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

NAME

Total Number:

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NAME

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Sub Contractors (DD882)

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**The study and development of metal oxide reactive adsorbents for the
destruction of toxic organic compounds**

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SUMMARY

The achievements realized during the course of this project provide an important alternative method for mitigating the effects of the exposure of personnel and systems to chemical warfare agents and other toxic organic compounds. The research program that was developed built upon earlier results achieved in the room temperature oxidative decomposition of a chemical warfare agent simulant, dimethyl methylphosphonate (DMMP), on solid reactive adsorbents and examined ways of improving those results by modifying the nature of the reactive adsorbent itself and by adding an energetic co-reactant.

The results obtained by modification of the nature of the reactive adsorbent, in our studies an alumina-supported cerium oxide, achieved only limited success. In earlier studies, we had developed a solid reactive adsorbent that was active in dry air at room temperature. Although the solid was several times more reactive, on a total decomposition capacity basis, than other adsorbents, the solid was still ultimately limited by the number of total reactive sites on the surface. Initial experiments in this program were developed to examine whether or not increasing the surface dispersion of cerium oxide on the alumina support by adding zirconium oxide to the surface would increase the decomposition capacity of the solid. Atomic Force Microscopy (AFM) results indicated that an increased dispersion of the cerium oxide had been achieved, but our microreactor studies showed a slight loss in product flow from the reactor, indicating a loss of decomposition capacity for the reactive solid.

A different support for the cerium oxide was investigated, as well. We examined titania-supported cerium oxide for its decomposition capacity, using a commercially available, nano-sized titanium oxide material as the support. Unfortunately, the relatively low surface of the support resulted in only limited decomposition capacity for the reactive adsorbent, even though fairly high dispersions of the cerium oxide on the titanium dioxide were obtained.

Good success was achieved using ozone as a co-reactant, added to the flow of DMMP prior to exposure to the reactive solid. Ozone is a promising co-reactant because it is easily generated with only dry air and electricity, and can be easily destroyed at room temperature with an inexpensive oxide catalyst. While the results obtained using the alumina-supported cerium oxide were not particularly impressive, no significant additional decomposition capacity was observed when the ozone co-reactant was added, when alumina-supported iron oxide was used as

the reactive solid, significant gains in decomposition capacity were observed. This reaction system was carefully characterized in terms of the important reaction variables. It was found that the reaction mechanism was most likely a Langmuir-Hinshelwood mechanism involving a reaction between two adsorbed species. The reaction between DMMP and O_3 on the supported iron oxide was shown to decompose about 3x as much DMMP as the reaction in the absence of ozone. However, the decomposition reaction was still limited by stoichiometry. It was decided to examine the reaction of manganese oxide as the reactive adsorbent in the presence of ozone with DMMP given the work of others with ozone and manganese oxide.

The DMMP surface decomposition reaction with ozone on the alumina-supported manganese adsorbent generated five times as much gas-phase carbon, in the form of CO_2 and CO , as did the same reaction on alumina-supported iron oxide. The reaction on the MnO_x/Al_2O_3 surface showed a long period (approximately nine hours) of relatively-constant, sustained product formation. The length of this period appeared to depend on the amount of available manganese on the surface. The amount of gas-phase carbon produced was observed to increase with increasing manganese on the surface, but not linearly, and was found to be consistent with a model involving the efficient reaction of DMMP with exposed manganese species, and a less efficient decomposition reaction involving manganese species that are relatively less exposed. Carbon dioxide was the primary reaction product observed. However, most of the experiments yielded nearly as much carbon monoxide as carbon dioxide in the product stream; the $CO_2:CO$ branching ratio is found to be 1:1 over a broad range of operating conditions. Additionally, small amounts of methanol were formed from the reaction even in the presence of a two-fold stoichiometric excess of ozone. The combined yield of CO_2 and CO increased rapidly with manganese content up to a loading of approximately 10 wt%, followed by a slower rise in yield with manganese content after this loading. The surface oxidation reaction appeared to follow the Langmuir-Hinshelwood mechanism as was found in earlier work for the DMMP plus ozone reaction on alumina-supported iron oxide. Surface infrared diffuse reflectance spectra of the reactive adsorbent obtained during various phases of the adsorption and reaction process suggested that the reaction of the carbon functional groups of DMMP is not selective at room temperature, with both the $O-CH_3$ the $P-CH_3$ methyl groups being removed by the reaction with ozone at room temperature.

Introduction

The time that elapsed between the last interim progress report, dated August 31, 2007, and the end of the project, October 31, 2007, was very short. In addition, the principal investigator was transitioning to a position at a new institution, Kennesaw State University, beginning July 1, 2007. As a result, no new data was obtained in the period between the date of the last interim report and the end of the project. The principal investigator continued to work on writing up the data and preparing a manuscript for publication, and there is significant new insight gained into the reaction stoichiometry between DMMP and O₃ on the solid surface generated from the data analysis of the final experiments performed. As a result, this final report contains some new data and analysis at the end of the report, along with a project summary and a comparison of the results obtained for different reaction systems and reported in the earlier interim progress reports.

Our studies were targeted toward the development of a powder that could be deployed in a number of different forms for the detoxification and decomposition of chemical warfare agents and other toxic organic compounds. We have had good success developing improved reactive adsorbents, and our initial steps in this project were to build on those earlier studies to find even more efficient and reactive adsorbents. The first investigations took two approaches. The first was to examine ways to increase the dispersion of cerium oxide on an alumina-supported cerium oxide reactive adsorbent after having had good indications that this parameter should have a strong impact on the amount of DMMP that these materials could decompose. The second approach was to try to develop an efficient screening method that could be used in a combinatorial fashion to speed up the development of improved reactive adsorbents.

Neither of these initial investigations were progressing well, so a second line of investigation was initiated examining the use of an added co-reactant to increase the reactivity of reactive adsorbents at room temperature. This approach, using ozone as the co-reactant, quickly showed progress, and ultimately yielded a reaction system that could be incorporated into a number of different processes for mitigating the effects of the exposure of personnel and equipment to chemical warfare agents and other toxic organic compounds.

Discussion of Program Results

Increasing the Cerium Oxide Dispersion

This investigation used two different strategies to develop the increased dispersion. The first strategy was to take advantage of the known ability of zirconium oxide to cause an increase in the dispersion of cerium oxide on alumina surfaces.^{1,2} Results from atomic force microscopy (AFM) surface topography plots comparing the surfaces of two representative solid materials are shown below. The CeO/ZrO/alumina (ZrO first) sample was prepared by impregnating a η - Al_2O_3 substrate with zirconium oxide using precipitation deposition, followed by calcining, followed by impregnation with cerium oxide, and finally calcining again. The CeO/alumina sample was prepared by impregnating the same alumina with cerium oxide using precipitation deposition, followed by calcining. Both materials contain 20 wt% cerium, while the material containing zirconium has a Ce:Zr mole ratio of 5:3. The topographies of the two samples are significantly different as can be seen most clearly by comparing the vertical scales of the two plots, Figure 1. The “tallest” vertical features observed on the CeO/ZrO/alumina material show a height of just under 4 nm, while a similar plot for cerium oxide alone on the same substrate shows features with heights of almost 20 nm. This seems to indicate that we did, in fact, achieve the goal of higher cerium oxide dispersions on the solid supports. However, the abilities of the solids to decompose DMMP were very similar, with the material containing cerium alone showing a slightly higher decomposition yield than the solid containing zirconium. It is suspected that the Lewis acid/base interaction that takes place between the aluminum oxide substrate and DMMP is masked by increasing the cerium oxide dispersion, resulting in no net increase in the decomposition yield. Yao et al. observed a reduced interaction between supported ceria and the alumina substrate when zirconia was present.¹

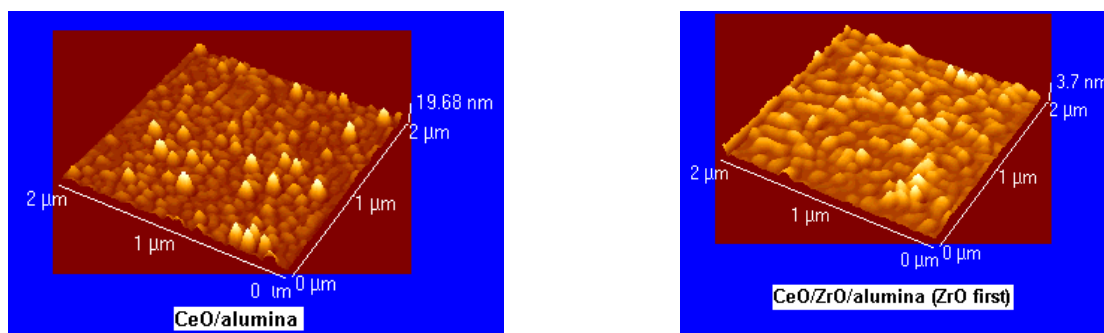


Figure 1. AFM images of ceria on alumina with and without added zirconia.

The second strategy that we examined to increase the cerium oxide dispersion was to use a different substrate. Cerium oxide has been shown to disperse readily on titanium oxide, so titanium oxide (Degussa P-25) was used as a substrate for cerium oxide. Previous investigators have shown that cerium oxide on titania forms a monolayer with loadings corresponding to 10 wt% cerium.³ Solids that were prepared using this weight loading were found to very effectively decompose DMMP to form methanol, showing virtually quantitative decomposition for the first doses of DMMP. (The decomposition measurements were carried out as explained in earlier publications.⁴) However, the observed decomposition activity is relatively short-lived due to the low surface area of the titania substrate (50 m²/g) compared to that of the alumina substrate (~400 m²/g). Also, although there is a generally increasing trend in the amount of methanol produced with amount of supported cerium, the increase is not particularly dramatic, and the increase in decomposition yield observed is not really sufficient to justify the extra costs that would be associated with the synthesis of these materials.

Development of a Screening Method

We attempted to build on a colorimetric analytical method for the detection of methanol that could be used in a combinatorial method for simultaneously screening different solids for their decomposition activity. The method used methanol as the primary indicator of decomposition activity, and a sequence of reactions that ultimately resulted in the formation of a blue or purple color in an indicator. The enzyme alcohol oxidase was used to convert methanol to formaldehyde, and the formaldehyde was then detected by the reagent Purpald[®], which turns purple in response to formaldehyde.⁵ The initial apparatus for testing was a simple glass tube that contained the reactive adsorbent in series with a small amount of the enzyme on glass wool. DMMP (1000 ppm) in a mixture of O₂/He (20% O₂ flows into the glass tube and exits into a vial that contains the Purpald[®]. In the photographs below, Figure 2, the vial on the left shows what happens when the DMMP mixture flows directly into the detection system without contacting an adsorbent, the vial in the center shows what happens when the mixture contacts mesoporous silica (MCM-41) which shows no decomposition activity, and the vial on the right shows the results when the DMMP/O₂ mixture contacts the cerium oxide on alumina adsorbent, the most active reactive adsorbent we have synthesized. As can be seen, the reactive adsorbent generated

a result that was easy to differentiate from the inactive silica sample or when no reactive adsorbent was present. The goal was to develop an analytical technique that could be rapidly scanned to determine the relative decomposition capacities of different reactive adsorbents. Unfortunately, a number of problems developed that were difficult to trace and which prevented us from ever realizing quantitative or even semi-quantitative accuracy in the determination. Although the technique showed considerable promise, we were unable to track down the origin of fluctuations in the response of the technique. Ultimately, we began to using ozone as a co-reactant, which made the methanol determination superfluous, since ozone is not compatible with the enzyme or purpald, and methanol is not the primary product in the reaction with ozone.



Figure 2. Color change observed after two hours. The vial on the left was exposed to the flowing reaction mixture but no oxidation catalyst was used. The middle vial was exposed to the reaction mixture after it had passed through a sample of MCM-41 (mesoporous silica, unreactive). The vial on the right shows the color changed observed after the reaction mixture had passed through a sample of mesoporous cerium oxide, one of our more effective decomposition materials.

Use of Ozone as a Co-Reactant

Supported Iron Oxide

Since new successes in the development of higher capacity solid reactive adsorbents were increasingly difficult to achieve, we decided to examine the use of a more reactive co-reactant than oxygen. Ozone came to the forefront as a possibility given its higher chemical energy as well as its ease of preparation and ease of destruction. A commercially-available ozone generator and ozone monitor were purchased and added to the DMMP flow system in such a way that the DMMP and added ozone were mixed just prior to the inlet to the u-tube reactor containing the reactive adsorbent. A diagram of the experimental set-up is shown in Figure 3. The original set-up has been described in detail earlier.⁴

Experiments with the ozone co-reactant initially used the alumina-supported cerium oxide as the reactive adsorbent, but no significant improvements in decomposition capacity were

observed. It was then decided to examine alumina-supported iron oxide as the reactive adsorbent, based on other studies that examined iron oxide in combination with an active oxygen species, typically hydrogen peroxide, to oxidize organic compounds via Fenton-like chemistry. The combination of ozone and the supported iron oxide did show a significant increase in decomposition capacity over that found for the iron oxide reactive adsorbent alone (see Table 1).

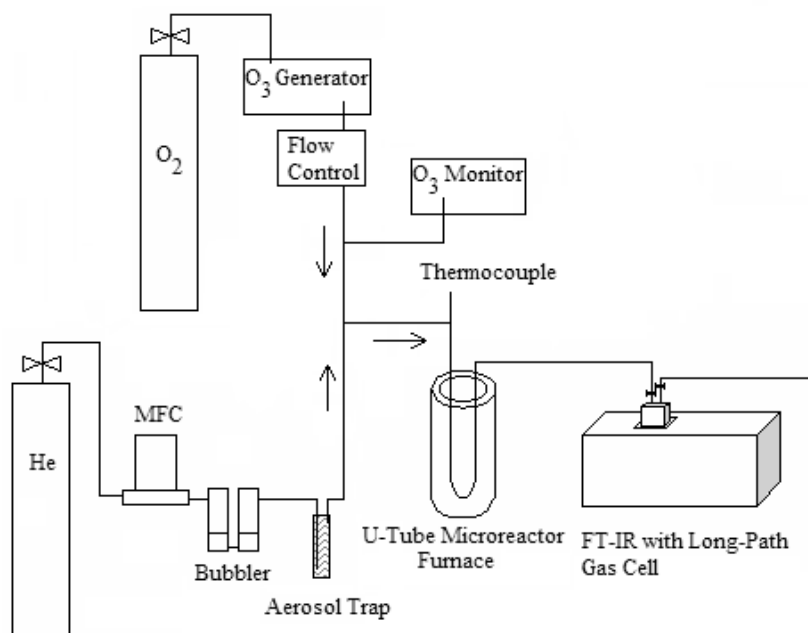


Figure 3. Experimental set-up for determining the decomposition of DMMP on oxides in the presence of O₃. This is a modification of an earlier setup for examining the decomposition of DMMP on oxides alone (see References **Error! Bookmark not defined.** and 6).

The detailed analysis of the reaction between DMMP and O₃ on alumina-supported iron oxide indicated that the reaction occurred between *adsorbed* DMMP and *adsorbed* O₃ via the Langmuir-Hinshelwood mechanism. The production of CO₂ from the decomposition, measured as fractional conversion (the fraction of DMMP decomposed relative to the amount entering the reactor) was shown to plateau as the ozone concentration was increased in different experiments. This type of result is typical for the reaction between two adsorbed species, and occurs when the surface adsorption sites are fully occupied and no additional reactant can be adsorbed. A variety of other experiments were carried out to elucidate the kind of interaction that was occurring between DMMP and ozone on the surface, and all were consistent with the Langmuir-Hinshelwood mechanism.

Table 1. Products formed from DMMP decomposition on 10 wt% Fe₂O₃/Al₂O₃ After Exposure to 650 μ mol DMMP

O ₃ Concentration (ppm)	CO ₂ Produced (μ mol)	CO Produced (μ mol)	CH ₃ OH Produced (μ mol)
0	0	0	14.1
50	16.7	0	4.5
100	35.6	0	2.5
200	44.4	0	0
300	49.1	0	0
400	50.0	2.1	0
500	50.6	3.4	0
1000	61.3	5.2	0
1500	69.7	7.9	0

The reaction of DMMP with ozone on alumina-supported iron oxide showed a much higher decomposition capacity, indicated by the formation of 77.6 μ mol of CO₂ and CO (total), than did the DMMP reaction on the same reactive solid in the absence of O₃, which formed 14.1 μ mol of gas-phase methanol, (see Table 1). However, the alumina-supported cerium oxide generated nearly 45 μ mol of gas-phase methanol and dimethyl ether without any added ozone. So, while we felt that the reaction mechanism for the case of added ozone was well-understood for this new method of decomposing DMMP, the real increase in room temperature decomposition capacity that we were able to achieve by adding ozone was less than a factor of two, independent of the reactive solid used, and was less than we had hoped to achieve.

Supported Manganese Oxide

Oyama et al. had shown that manganese oxide was an efficient catalyst for the destruction of ozone, and also for the destruction of acetone by ozone.^{6,7,8} On this basis, it was decided to try manganese oxide for these studies for the decomposition of DMMP. Those experiments yielded significantly greater amounts of DMMP decomposition products than had the experiments ozone and supported iron oxide or the supported cerium oxide. Figure 4 shows a comparison of the gas-phase flow from two experiments in which the only difference was the solid reactant. In both experiments, the weight loading of the metal on the alumina support was

10 wt%, the inlet DMMP concentration was approximately 750 ppm (1.41 $\mu\text{mol}/\text{min}$ flow rate) and the gas-phase concentration of ozone at the inlet was 1000 ppm. The total yield of gas-phase products from the decomposition of DMMP on the manganese oxide material is a factor of five greater than that formed from the decomposition on the iron oxide material.

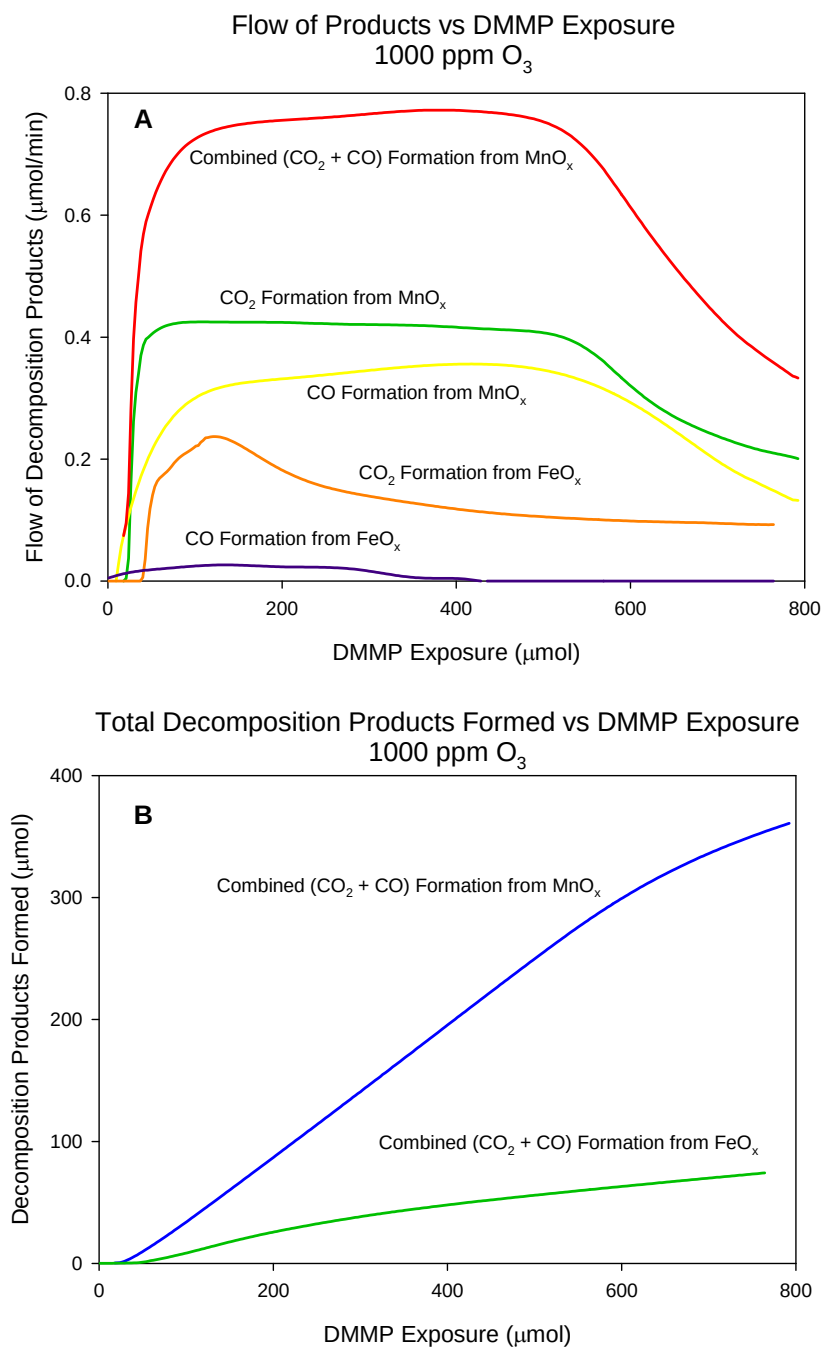


Figure 4. Comparison of the flow of products ($\mu\text{mol}/\text{min}$), (A), and the total integrated product formation (μmol), (B), from the DMMP + O_3 decomposition reaction over alumina-supported manganese oxide and alumina-supported iron oxide.

There are significant differences in the product distribution from the reactions of the two solids, which indicate differences in the decomposition chemistry. One of the critical assumptions used when comparing different reactive adsorbents is the decomposition stoichiometry. For reactions that take place in oxygen at room temperature on oxide reactive adsorbents, it is typically assumed that for every DMMP molecule that decomposes on the surface, one methanol molecule is released, so that there is a direct correlation between the amount of methanol, and sometimes dimethyl ether, measured and the amount of DMMP decomposed. This relationship seemed to hold for the reactions with ozone over iron oxide, as it seemed that the methanol product was converted to CO₂, with additional decomposition activity observed from the increased energy of the ozone molecule as the ozone concentration was increased.⁹ CO₂ was the only significant decomposition product observed, with CO making up about 10% of the product yield at high ozone concentrations, and no methanol being observed for ozone concentrations above 100 ppm. However, the product distribution observed for the manganese oxide reactions was significantly different. The CO₂:CO branching ratio observed was nearly unity and changed only slightly with ozone concentration. Additionally, methanol continued to be observed, although the amount was not large compared to the CO₂ or CO produced (see Figure 5), and persisted even when the ozone concentration was a factor of 2 greater than that of DMMP.

Additional observations from the experiments with manganese oxide indicate the following (these conclusions were discussed in detail in the August 2007 interim progress report):

- All results from this reaction system are consistent with the reaction following the Langmuir-Hinshelwood mechanism, involving a reaction between two adsorbed species.
- The rate of product formation has not reached a plateau as a function of ozone concentration even at 1500 ppm O₃.
- The rate of product formation reaches a plateau as a function of manganese content at 5 - 10 wt% Mn.
- The total product formation has not reached a plateau as a function of manganese content even at 20 wt% Mn, although the slope is decreasing at this content.

- There is some indication that the Mn precursor used may lead to different CO₂:CO branching ratios.
- The difference in breakthrough points for DMMP and O₃ suggests that the ozone decomposition process, which likely yields the active oxygen species, occurs readily on this surface and the active sites for this process are only slowly poisoned by DMMP fragments or molecular DMMP.

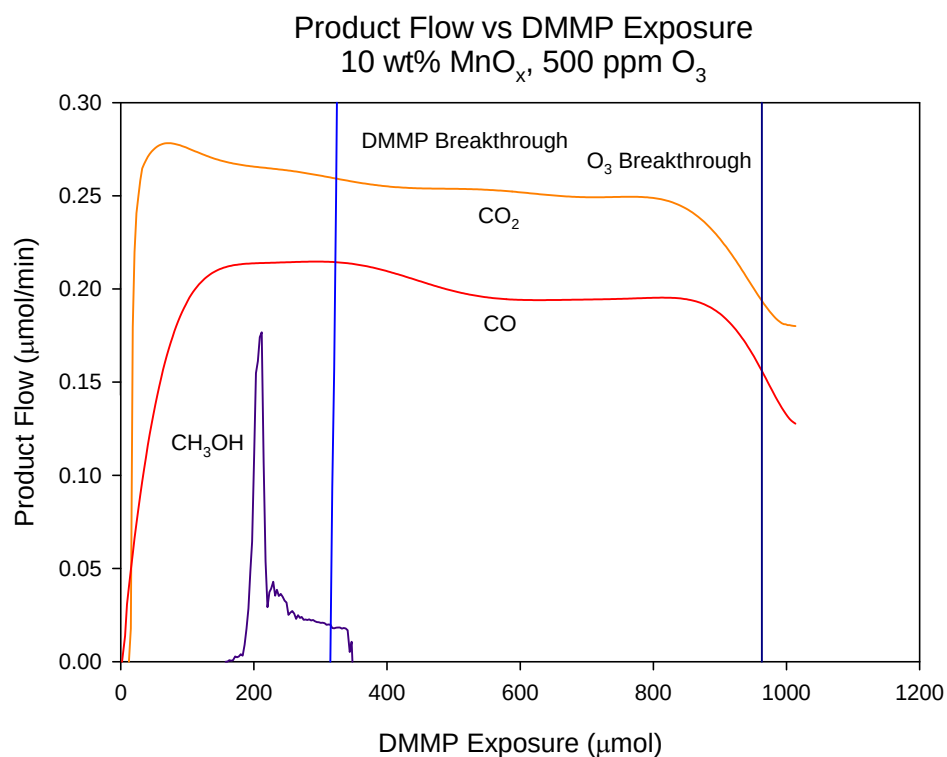


Figure 5. Typical results from DMMP decomposition experiment in the presence of 500 ppm O₃ on 10 wt% MnO_x (with Mn(NO₃)₂ as the manganese oxide precursor and using precipitation impregnation).

New Results and Conclusions from Supported Manganese Oxide

An experiment was designed to examine the nature of the decomposition products that remained on the reactive adsorbent after the decomposition reaction was complete. A 10 wt% MnO_x on alumina sample was placed in the microreactor and the experiment set up to dose the solid with 50 μmol of DMMP. After the DMMP dose, the gas flow was switched to pure helium and allowed to run for several hours. After this, the solid was removed and placed in a sealed vial for later examination by infrared spectroscopy. A second sample of the same solid was placed in the microreactor as before and treated in the same fashion, except that after the DMMP dose, the DMMP flow was replaced with pure helium and a flow of O₃ was initiated (500 ppm O₃ in He) with the same flow used in earlier experiments. The flow of ozone was continued for 24 hours, after which time the solid was collected and placed in a sealed vial for later examination by infrared.

During the preparation of these samples, the gas flow from the solid was collected and analyzed as usual. The adsorption capacity of the solid for DMMP is significantly greater than 50 μmol and all of the DMMP was expected to be adsorbed. This was verified during the experiment by the lack of DMMP breakthrough observed. The flows of CO₂ and CO that evolved from the reactor during the O₃ exposure were measured for the solid and are shown in Figure 6. The total CO₂ produced was found to be 24 μmol and the total CO produced was found to be 70 μmol. Most of the decomposition had occurred by approximately 5 hours of O₃ flow, and no DMMP was observed in the flow from the reactor suggesting that all of the DMMP, (50 μmol) was adsorbed and/or decomposed. However, 94 μmol of gas-phase carbon was produced as products. This clearly argues against the normal assumption of 1 molecule of gas-phase carbon for each DMMP molecule decomposed. The relative amounts of CO₂ and CO produced and their relative flow rates are significantly different for this experiment compared to the results from Figure 5. The difference is no doubt due to the continuing flow of DMMP in the experiment of Figure 5 compared to the single dose experiment in Figure 6. Clearly the system is complicated and the results must be interpreted with care.

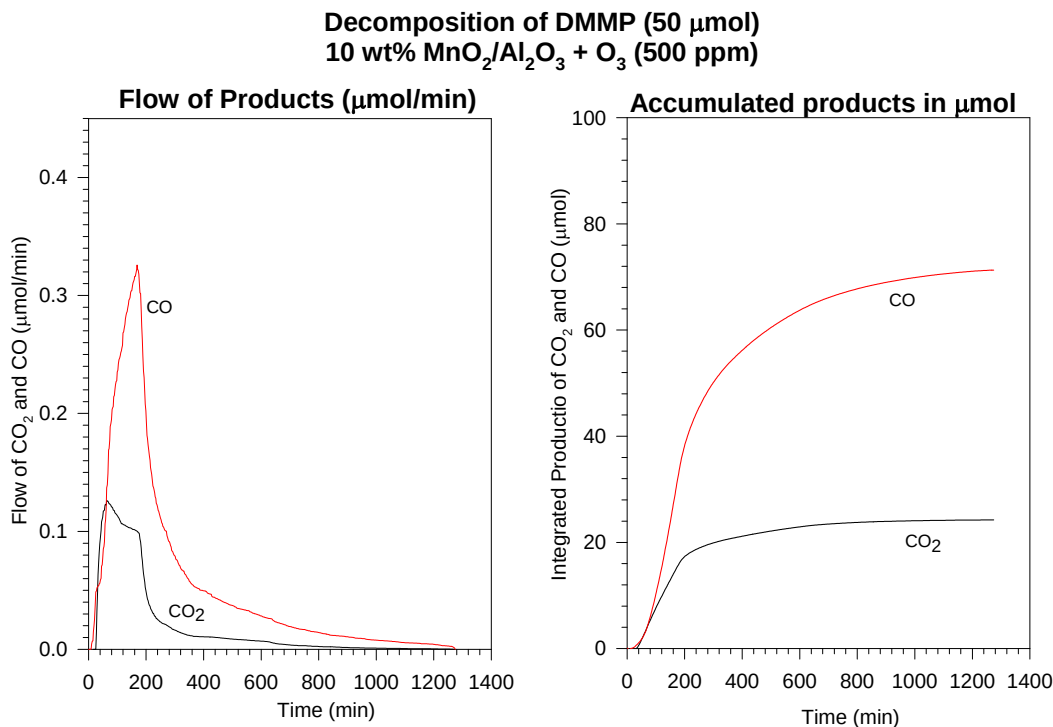


Figure 6. Flow of products from the decomposition of 50 μmol of DMMP adsorbed on 10 wt% Mn on Al_2O_3 . The red curve corresponds to CO and the black curve to CO_2 .

Figure 7 shows the infrared diffuse reflectance spectra of the solid with adsorbed DMMP, but without exposure to ozone, and the solid with DMMP after exposure to ozone. The spectrum shown on top in Figure 7A and 7B is characteristic for DMMP adsorbed on oxides and shows C-H stretch absorptions for the two methoxy group (2854 and 2958 cm^{-1}) and for the methyl group bound to the phosphorous atom (2930 and 2995 cm^{-1}). The hypothesis behind this particular experiment was that selective decomposition, oxidation of one of the $\text{O}-\text{CH}_3$ groups rather than the $\text{P}-\text{CH}_3$ group or vice versa, would show a decrease in the relative intensities of one pair of bands, corresponding to one type of CH_3 functional group, compared to the other pair. This is exactly what was observed in the thermal decomposition of DMMP on oxides in our earlier work.¹⁰ However, the infrared spectra in Figure 7 do not show this trend, even after 24 hr exposure to ozone. The bands are only slightly shifted and show very similar relative intensities, except for the 2998 cm^{-1} absorption which has a higher intensity compared to the other absorptions. This indicates that the oxidation reaction leading to gas-phase products is not selective, at least in terms of reactivity. There is a possibility that the CO_2 and CO originate from different methyl groups, but this cannot be determined from the current set of experiments.

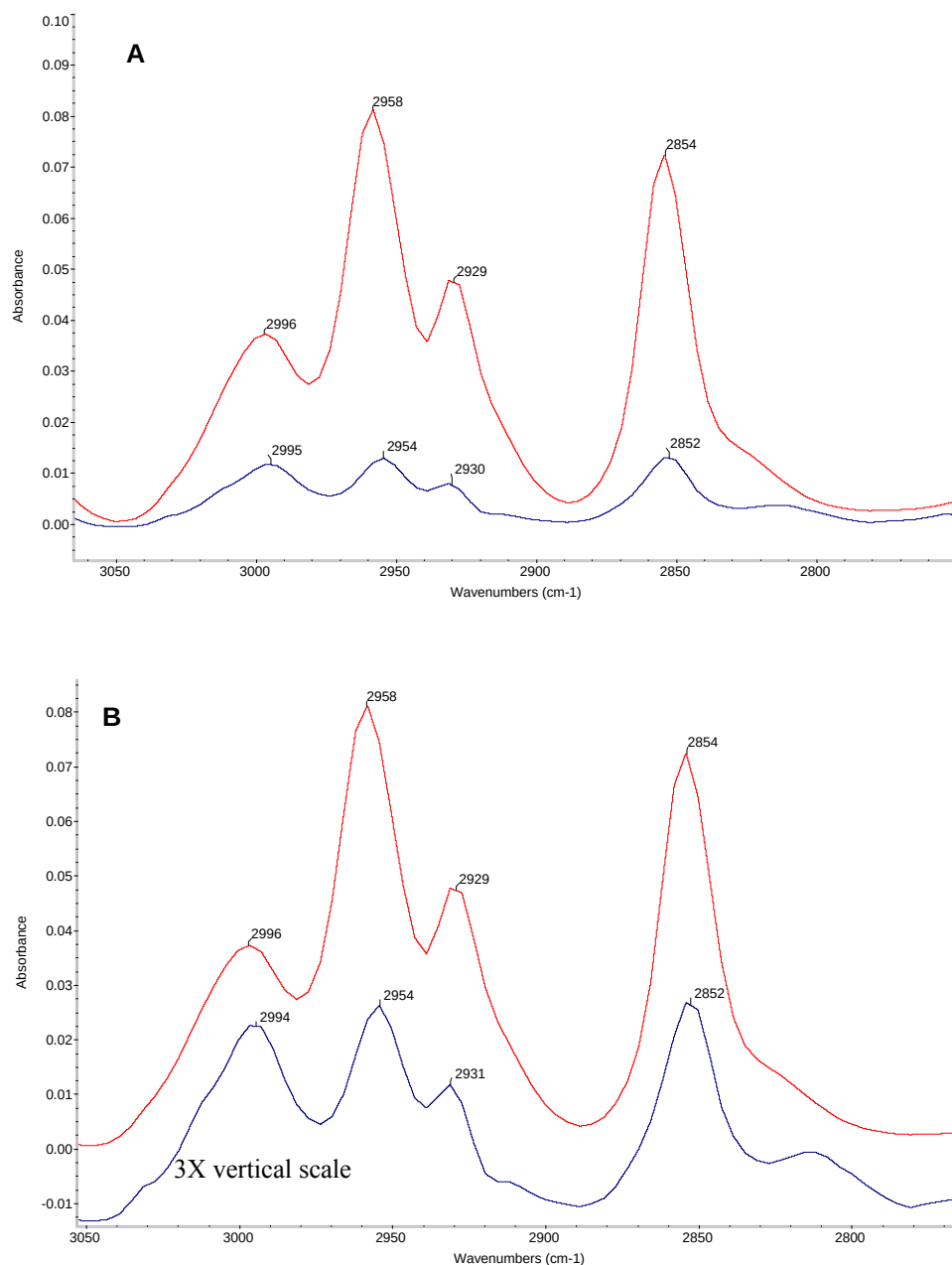


Figure 7. Infrared diffuse reflectance spectra showing the C-H stretch region for 50 μmol of DMMP adsorbed on the reactive adsorbent before exposure to ozone (top spectrum) and after exposure to ozone (bottom spectrum). Figure 6A shows the spectra on the same vertical scale, while Figure 6B shows the bottom spectrum with an expanded vertical scale (3X) relative to the top spectrum.

The apparent lack of selectivity of the ozone decomposition reaction for either the O-CH_3 group or the P-CH_3 group suggests that there is not a 1:1 correlation between the amount of gas-phase carbon measured and the amount of DMMP decomposed (which agrees with the results from Figure 6). Instead, the fact that the infrared spectra (in the C-H stretch region) of the species remaining on the surface after oxidation are very similar to the initially-adsorbed DMMP

suggests that there are some sites at which the DMMP is mineralized completely by the reaction with ozone, and contribute nothing to the CH_3 absorption bands, and some at which very little decomposition occurs.

Based on the results shown in Figures 6 and 7, it is clearly indicated that in the case of DMMP decomposition by ozone on the alumina-supported manganese oxide species, there is no apparent selectivity in the type of DMMP methyl group that reacts with ozone. The selectivity appears to be based on sites; that is, those DMMP species that adsorb at an active site are mineralized, while those adsorbed away from active sites are, for the most part, adsorbed molecularly. This argument could be followed to suggest, based on the relative amounts of CO and CO_2 observed, that the CO that evolves from the reactor is due to reaction with the $-\text{O}-\text{CH}_3$ groups while the CO_2 is from the $\text{P}-\text{CH}_3$ groups. Without further evidence and careful study, however, it is premature to suggest such a direct correlation.

Conclusions

It appears from our studies that most of the improvement in the activity of room temperature reactive adsorbents will come from the use of a co-reactant such as ozone. There remains the potential of increasing the decomposition capacity of the reactive adsorbents by using other supported nanodimensional oxides, for example, and increasing the active surface area still further. Our work with supported nanodimensional cerium oxide, however, indicates that even the most active materials will still be limited by poisoning of the surface sites by the phosphate residues. It is possible that novel synthetic methods or materials may provide a way of increasing the decomposition capacity by as much as a factor of ten per gram of reactive solid.

There are still significant amounts of work to be done on the reaction with ozone to understand the surface chemistry and how it might be optimized, but the reactive solids that we have examined are extremely promising and show decomposition activity that is significantly greater than any other material we have examined at room temperature, when used with the co-reactant. Future studies will involve a detailed study of the surface chemistry using infrared diffuse reflectance. Other mixed metal oxide materials or materials with higher surface areas may provide a way of improving the overall decomposition capacity and decomposition efficiencies of these materials, as well.

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