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Decontamination of Chemical Warfare Agents with Resin-based Catalysts and POMs

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Decontamination of Chemical Warfare Agents with Resin-based Catalysts and POMs

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Bachelor of Science, Nanjing University, 2013

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An abstract of
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Abstract

Decontamination of Chemical Warfare Agents with Resin-based Catalysts and POMs

By Juncheng Yang

Chemical warfare agents pose a great danger to the whole world, therefore in this thesis, I worked on two aspects of chemical warfare agent (CWA) decontamination. The first focus was to develop a heterogeneous catalyst for the oxidation of sulfur mustard. Compared to homogeneous catalysts, heterogeneous catalysts are more amenable to real-life applications such as self-decontaminating fabrics. In this part, I focused on the development of a new series of heterogeneous catalysts (AM series) derived from NO_3^- and Br^- with an ion-exchange resin (AG-MP1), which then was used for the selective oxidation of sulfur mustard. Subsequently I found this heterogeneous catalyst is destroyed when used in solution by chloride exchange (displacement) of NO_3^- and Br^- from the original polymeric catalyst during turnover. Following this, I focused on the decontamination of sulfur mustard vapor using the same polymeric-NO_3^-+Br^- catalysts. It was determined that this AM series catalysts did not work in gas phase either. The second focus of the thesis was to develop a bi-functional catalyst, one capable of simultaneously decontaminating sulfur mustard by selective oxidation and hydrolysis of nerve agents using a combination of NO_3^-/Br^- and two POMs, a polyniobate (henceforth "Nb-POM") and a mixed cesium-proton salt (henceforth "$Cs_{2.5}$-POM"). The Nb-POM was not compatible with NO_3^-/Br^-, while the Cs2.5-POM was partly compatible, but we needed to find a suitable solvent for the system. In conclusion, this thesis concentrates on the development of new systems for decontaminating two kinds of chemical warfare agents using only air and water.

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Acknowledgment

Chemistry is an interesting subject, and chemical experiments are just like magic enabling one to transform one compound into another. I was deeply attracted by this magical power so I decided to devote myself to chemical research at the end of my high school. That was now five years ago. However, as for nearly all research efforts, chemical research is usually hindered by different kinds of failure, and I want to acknowledge the help of several others in these times of trial.

I would first like to thank Dr. Hill, who has given me plenty of guidance in research. Besides this, he is so easy-going and he always inspired me during my graduate work. Although most of my results in this thesis are negative, he still supported me and my work. There are a lot of things I want to thank him for, among them, the most important is his support for me to pursue my other interests and new life after departing the Emory University Chemistry Ph.D. program. Besides Dr. Hill, I also want to thank my two other committee members, Dr. Lian and Dr. Scarborough.

I wish to thank many others who were instrumental in my graduate research efforts. My parents have supported my decisions and me all my life, both psychologically and financially. I also want to thank my girlfriend who helped me when I was depressed about my experiments. In addition, many others in the lab also helped me and without them, I would not have what I have today.

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Part II:

I. Introduction

The use of chemical warfare agents (CWAs) has a long history dating back to 1770 BCE (before the Common Era)[1] and this 'tradition' continues till today. For example, in the past several hundred years, especially during the two world wars, chemical warfare agents were widely used for mass destructions[2]. Although nowadays there are restrictions on the use of CWAs, some countries still possess weaponized chemical warfare agents[1]. Worse yet, there are new stories about terrorists developing CWAs[1]. In order to reduce the potential danger posed by these highly toxic agents, it is urgent to develop some materials that can readily break down CWAs.

Among all the chemical warfare agents, vesicant agents like sulfur mustard and nerve agents like VX and sarin are notorious; they have been widely used in terrorist attacks and in the two World Wars[2].

Bis(2-chloroethyl) sulfide, also known as sulfur mustard, just "mustard" or "HD", is a structurally simple compound (Fig. 1) that is very easy to synthesize. Simply mixing thiodiglycol and thionyl chloride affords mustard in reasonable yield. The triviality of this synthesis contributes to the danger of this CWA. In the following two parts of this thesis, I focus on developing a new heterogeneous catalyst for the decontamination of sulfur mustard. We use 2-chloroethyl ethyl sulfide (CEES; Fig. 2) as it is recognized as the best overall simulant for mustard. CEES has a similar structure to mustard; indeed, the only difference between them is one chlorine atom.

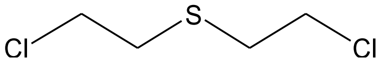


Figure 1. Structure of Mustard (HD)

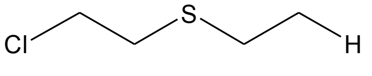


Figure 2. Structure of CEES

In order to develop an efficient catalyst for the decontamination of mustard, it is essential to understand the mechanism behind mustard working as a chemical warfare agent. As a member of the mustard family, sulfur mustard shares similar chemical activities and thus a similar mechanism for toxicity with nitrogen mustard[1,3]. In short, the divalent sulfur is a good nucleophile and can attack either of the two proximal intramolecular chlorines via a S_{N2} mechanism (Fig. 3). The resulting 3-membered ring is very active and returns back to chain structure upon attack by an amino group. Many amino groups in the human body come from biomolecules like DNA and proteins. This means that once mustard enters the human body, it forms biomolecular-linked units, which can react further with other terminal chlorides of a second mustard molecule. In other words, mustard functions to cross link two biomolecular segments. This is the primary reason why mustard is toxic. Clearly the sulfur and chlorine atoms are key to mustard activity, thus if somehow these centers can be destroyed, the toxicity of the molecule will be greatly decreased. This points to the two chemical methods that are currently available for the decontamination of mustard. The first involves hydrolysis[4-7], which results in replacement of the chlorine atom with a hydroxide group. The second approach involves the oxidation of sulfur atom[8-10], to the corresponding sulfoxide. This reduces the nucleophilicity of the sulfur center and stops the formation of three-member rings. For oxidative decontamination, the catalytic selectivity is very important because the sulfoxide product is far less toxic than the more highly-oxidized sulfone product.

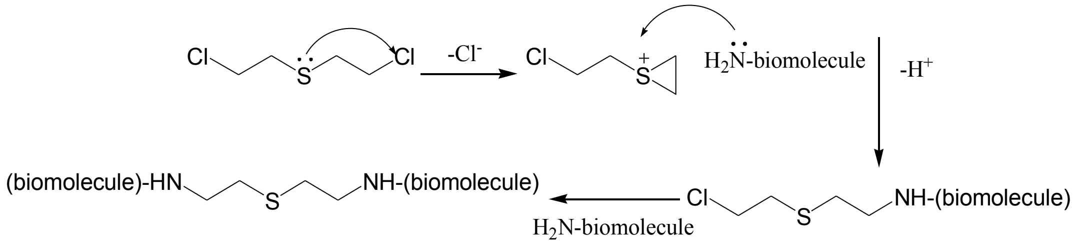


Figure 3. Mechanism of sulfur mustard's toxicity

In addition to these two well-documented chemical methods for mustard removal, one can also use physical methods like mustard physisorption[11-13]. However, the initial products usually need further treatment to realize full decontamination. For example, in Stout's report[14], after adsorption, mustard or its simulant still needs to be oxidized for decontamination of toxic substrate and for reuse of the adsorbent. Therefore, chemical methods are more reliable. Hydrolytic decontamination requires a small amount of water be present, and this may not always be convenient on the battlefield. Besides, hydrolysis of phosphonate esters is a reversible reaction controlled by thermodynamics, which means, that in order to fully hydrolyze it, one of the products must be removed or consumed. For example, in order to fully hydrolyze mustard, one needs to neutralize the HCl by-product. Moreover, the hydrolyzed product of mustard is not safe; it remains fairly toxic. Thus the best catalytic decontamination for mustard is selective oxidation, which I address in the next section.

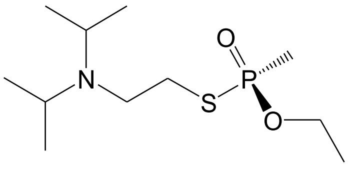
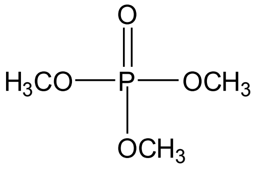


Figure 4. The structure of VX



$$H_3CO-\overset{\overset{\displaystyle O}{\|}}{P}-OCH_3$$
$$\quad\; |\; OCH_3$$

Figure 5. The structure of DMMP

Nerve agents, mainly organophosphate (OP) compounds, are colorless and relatively odorless, but highly toxic because they can bind to the active sites of the cholinesterase family of enzymes, resulting in effective inhibition[1]. Five OP compounds are by far the most well-known and studied: Tabun (*O*-ethyl *N,N*-dimethyl phosphoramidocyanidate, GA), Sarin (isopropyl methyl phosphonofluoridate; GB), Soman (pinacolyl methyl phosphonofluoridate, GD), Cyclosarin (cyclohexyl methylphosphonofluoridate, GF), and VX (*O*-ethyl S-2-*N,N*-diisopropylaminoethyl methyl phosphonofluoridate, Fig. 4)[1]. One way to decontaminate nerve agents is to hydrolyze the P-O/P-S/P-N single bond. In academic laboratories, dimethyl methylphosphonate (DMMP) is used as a simulant OP hydrolysis experiments because it is quite low in toxicity[15]. As we can see (Fig. 5), the main difference between VX and DMMP is that in hydrolysis reaction, we break P-S single bond for VX, while P-O single bond for DMMP. From basic organic chemistry, we can know that the P-S bond is much easier to break than the P-O single bond, which means if we can successfully develop an efficient catalyst for the hydrolysis of DMMP, it is highly likely that the catalyst will exhibit a higher turnover frequency (TOF) for the hydrolysis of VX and other similar nerve agents. Therefore, we focus on this in the last part of the thesis.

II. Decontamination of Sulfur Mustard in Solution

Background

As we have discussed in the previous chapter, the oxidation of mustard has several advantages over other modes of decontamination. It can destroy sulfur mustard completely and the reactant for this reaction, O_2/air, is ubiquitous and free. To date, however, there are few reports on heterogeneous oxidation catalysts that are effective under ambient conditions. Indeed, nearly all the heterogeneous oxidation catalysts require the use more expensive and frequently dangerous oxidants such as hydrogen peroxide[16-18] or do not have an acceptable activity[19]. In contrast, homogeneous catalysts are easy to modify, usually more active under mild conditions[20,21] and can use oxygen as oxidant[20,21]. Therefore, it would be really interesting, if one could immobilize homogeneous catalysts onto attractive (robust, nontoxic, inexpensive) supports while maintaining their catalytic activity. Such oxidation catalysts should have the use and robustness advantages of heterogeneous catalysts with the reactivity (using ambient air as oxidant) advantages of homogeneous catalysts. In addition, key reactivity properties of the soluble catalyst can be obtained prior to immobilization. An impetus for this research is the keen interest on the part of governments and industries alike to be able to incorporate catalytic decontamination and/or deodorization activity into fabrics for use in upholstery, carpeting and protective apparel.

Therefore, in this chapter, I target the development of a heterogeneous oxidation catalyst for mustard elimination. One homogeneous oxidation catalyst potentially amenable to immobilization that attracts our attention is the mixture of two simple anions, NO_3^- and Br^- in part because of this catalyst is simple structurally, effective in organosulfide (thioether) oxidation and inexpensive[22]. Critically, this catalyst can use the oxygen in the air as oxidant, which is far more attractive than other oxidants, including the also "green" hydrogen peroxide that require solvents and additional safety considerations[9,23-25]. According to the report[22], oxidations by this catalyst proceed primarily by the mechanism in Scheme 1. In the first step, $NO_{x(ox)}$ oxidizes Br^- to Br_2, then Br_2 reacts with Br^- to produce Br_3^- which serves as a Br_2 reservoir. Br_2 oxidizes sulfide, R_1R_2S, to the sulfonium salt, $R_1R_2S^+$-Br, which reacts with any water present to produce the sulfoxide $R_1R_2S{=}O$. $NO_{x-1(red)}$ is re-oxidized back to $NO_{x(ox)}$ at the end of the catalytic cycle, by oxygen in the air. The net reaction is sulfide + air/O_2 forming sulfoxide catalyzed by NO_3^- and Br^-.

$$NO_{x(ox)} + 2Br^- + 2H^+ \rightarrow NO_{x-1(red)} + Br_2 + H_2O$$

$$Br_2 + R_1R_2S \rightarrow Br^- + R_1R_2S^+\text{-Br}$$

$$R_1R_2S^+\text{-Br} + H_2O \rightarrow R_1R_2S{=}O + 2H^+$$

$$NO_{x-1(red)} + 1/2\ O_2 \rightarrow NO_{x(ox)}$$

$$Br_3^- \rightleftharpoons Br_2 + Br^-$$

Scheme 1. Mechanism of O_2-based sulfide oxidation catalyzed by NO_3^- + Br^-

In order to fix NO_3^- and Br^- on the support, I invoked two principles. The first was that NO_3^- and Br^- should be loosely bonded to the support, otherwise, the bi-component catalyst may not be active. The second principle was that the NO_3^- and

Br^- should not be soluble in the solvent and remain effectively 100% immobilized on the support before, during and after catalytic turnover. Otherwise we would simply have homogeneous catalysis by NO_3^- and Br^- in solution, which would be useless in context with formulation of catalytically self-decontaminating materials. With these two principles in mind, we chose to use an ion exchange resin as the support, which can, in principle, satisfy both principles. I chose to use the AG-MP1 (short for AM) from Bio-Rad. AM is one kind of styrene divinylbenzene copolymer with quaternary ammonium side chains (Fig. 6). It has a macroporous structure with a relatively large surface area (23 m^2/g). Moreover, AM has almost 1:1 selective ratio for NO_3^- and Br^-, which is very helpful when preparing catalysts with different NO_3^--to-Br^- loading ratios.

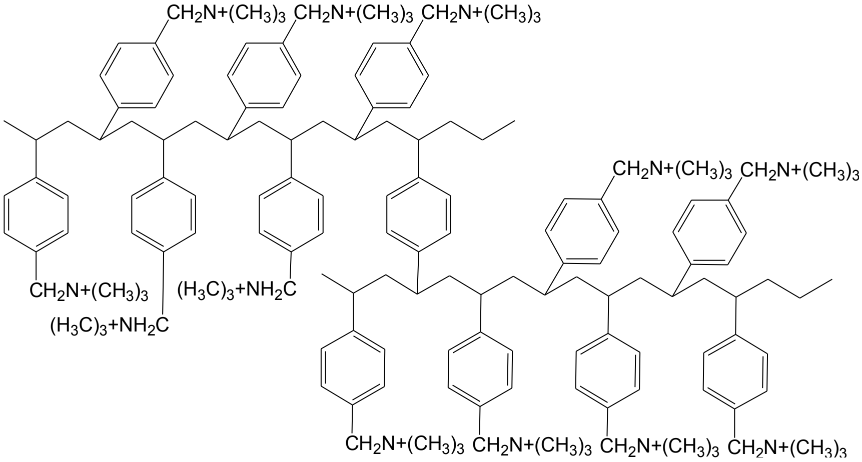


Figure 6. Structure of the ion exchange resin, AG-MP1 (AM)

Experimental Section

Preparation of catalysts

Our heterogeneous catalysts were prepared by exchanging the chloride counterions in the initial AM with NO_3^- or/and Br^- and continuing the ion exchange process until the effluent contains no Cl^- (detected by adding several drops of 1M $AgNO_3$ solution to the supernatant). The exchanged solid was then rinsed thoroughly with water and dried.

Table 1. Sample names and their preparation conditions

Solution	None	KNO_3	KBr	KNO_3+KBr solution with concentration ratio x:y
Sample	AM	AM-NO_3	AM-Br	AMxy (for example: AM11, AM12)

For example: AM11 means AM exchanged with a 1:1 KNO_3 and KBr mixed solution (the resin also has a ~1:1 NO_3^- : Br^- ratio because AM has around 1:1 ratio selectivity towards NO_3^- and Br^-; AM13 means AM exchanged with a 1:3 KNO_3 and KBr mixed solution (and a 1:3 NO_3^- : Br^- ratio is found in the resin); AM31 means AM exchanged with 3:1 KNO_3 and KBr mixed solution (and a 3:1 NO_3^- : Br^- is found in the resin).

Characterizations of the catalysts

Elemental analysis

Elemental analysis was carried out by Atlantic Microlabs. All the samples were dried during preparation, but no additional drying was conducted before submitting the samples for elemental analysis.

Fourier transform infrared spectroscopy (FTIR)

FTIR of all samples were obtained in Nicolet 510 FT-IR spectrometer using KBr pellets.

Catalytic reactions

Preparation of 2-chloroethyl ethyl sulfide (CEES) stock solution: 2.00 mL of CEES and 2.00 mL of 1,3-dichlorobenzene (DCB, internal standard for GC analysis) were added to 200 mL of acetonitrile.

Weigh 0.100 g of catalyst into a 5 mL sealable vial with rubber septum, then add 2.040 mL of the CEES stock solution to the same vial and seal it. Stir this solution overnight to achieve the balance of adsorption (the adsorption of CEES on catalyst).

After overnight adsorption, a sample is withdrawn for GC analysis (this sample is referred as blank or 0 minute), then inserted a needle into the septum in the cap to avoid the depletion of oxygen. Subsequently, 0.100 mL of water is added and the vial placed into a water bath maintained at a temperature between 55°C and 58°C. Samples are withdrawn every hour and the CEES concentration quantified by GC.

Control experiments with different amounts of CEES

A certain amount of CEES (10 μl, 20 μl, 40 μl, 60 μl, and 100 μl that are given the labels CEES0.5, CEES1, CEES2, CEES3, CEES5, respectively) and the same volume of DCB (as CEES) are dissolved in acetonitrile to make the total solution volume equal to 2 mL. Then 0.100 g of the catalyst (AM11) is added and the reaction stirred overnight. The rest procedure is the same as described in the process above.

Detection of NO_3^- *and* Br^-

After the first use:

After the catalytic reaction, the reaction system is filtered and the supernatant passed through a syringe filter to obtain a clear solution. Several drops of 1 M $AgNO_3$ is added to this solution.

After the second use:

The supernatant is centrifuged several times to obtain the supernatant without catalyst. Several drops of 1 M $AgNO_3$ are then added to the supernatant.

Results and Discussion

In order to confirm that NO_3^- and Br^- were successfully bound to AM via ion exchange, I characterized the resin with FTIR using KBr pellets (Fig. 7, Fig. 8, Fig. S1, Fig. S2). Fig 7 shows all three have similar characteristic peaks at around 3400 cm^{-1}, 3000 cm^{-1}, 2900 cm^{-1}, 1600 cm^{-1}, 1500 cm^{-1} which correspond to N-H stretching, aromatic C-H stretching, aliphatic C-H stretching, aromatic C=C stretching, deformation and skeletal vibration of C-H, respectively[26,27]. The peak at *ca.* 2300cm^{-1}

can be assigned to C=O stretching in CO_2 and some O-H stretching. In addition, both Figs. 7 and 8 display a peak around 1380 cm^{-1} that can be attributed to the N-O stretch in the nitrate ligand for AM-NO_3 [28,29]. Consistent with this assignment, Figs S1 and S2 show that the relative intensity of the peak at around 1380 cm^{-1} increases with the increasing content of NO_3^-.

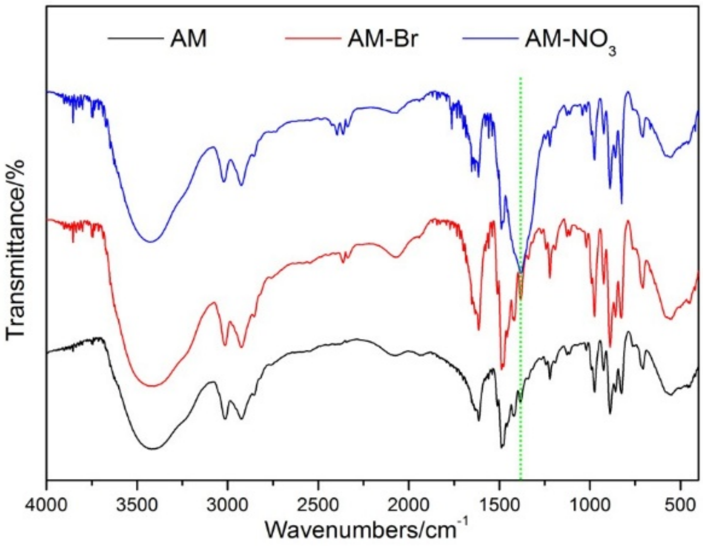


Figure 7. FTIR spectra of AM (black), AM-Br (red), AM-NO_3 (blue)

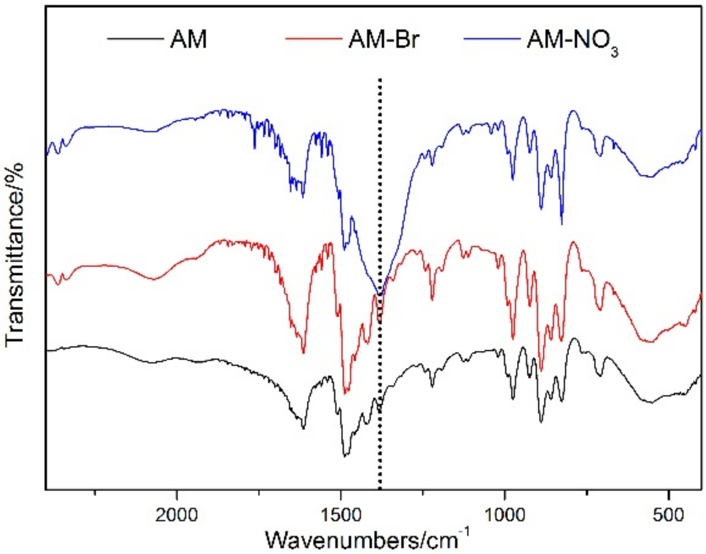


Figure 8. Local FTIR spectra (2400cm^{-1} - 400cm^{-1}) of AM (black), AM-Br (red) and AM-NO_3 (blue)

From the Bio-Rad specification sheet, we know that AM has an approximately 1:1 selectivity ratio towards NO_3^- and Br^-, which means the ratio of NO_3^- and Br^- in the resin should be consistent with the ratio of NO_3^- and Br^- in the solution during and after exchange processes. In order to verify this, elemental analysis results are shown in Fig. 9. It is clear that from AM-Br to AM-NO_3, the content of nitrogen increases, corresponding to the increasing NO_3, while the content of bromine decreases as there should be less bromide in these catalysts. These results confirm that the amounts of NO_3^- and Br^- are consistent with the attainment of full ion exchange equilibrium and the intrinsic 1:1 selectivity of this particular ion exchange resin.

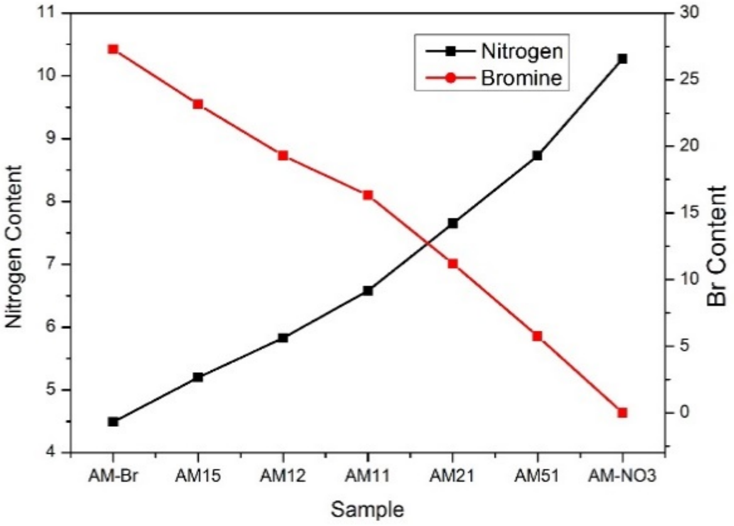


Figure 9. Elemental analysis of nitrogen and bromine content in the AM series of catalysts

After confirming the successful ion exchange and the predicted NO_3^- and Br^- content, I assessed the activity of AM11 with AM, AM-NO_3 and AM-Br as controls (Fig. 10). From the figure, we can see that AM11 shows strong activity towards the oxidation of CEES, while the three controls, AM, AM-NO_3 and AM-Br show no catalytic activity. The decrease in CEES concentration at the beginning comes from the change in adsorption of CEES on the resin, which was confirmed in Fig. S3. In this figure, we conducted a control reaction, which did not add water. As we can see from the mechanism in Scheme 1, water is a key component in this catalytic system, so no water means there would be no catalytic reaction. This is seen in Fig. S3: there is no drop in the concentration of CEES after the second data point. In addition to this, we can also see at the beginning of the reaction, there is a drop in CEES concentration from the first point to the second point. Since there was no catalysis going on, this drop was not from catalytic reaction but from the change in adsorption due to the change in temperature. (The only difference between the first data point and the second data point is the change of temperature.) To conclude, the drop in CEES concentration between the first and second point, partially (for AM11) or completely (for AM, AM-NO_3, AM-Br), comes from the increased adsorption on the resin resulting from a temperature change.

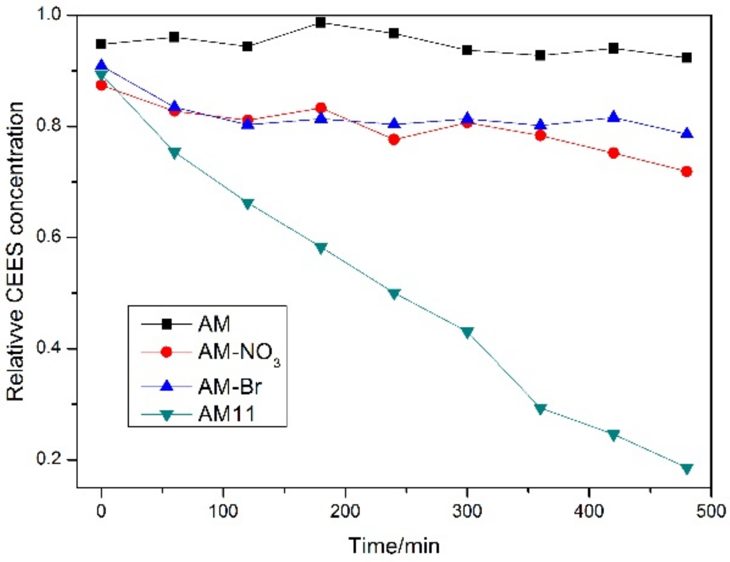
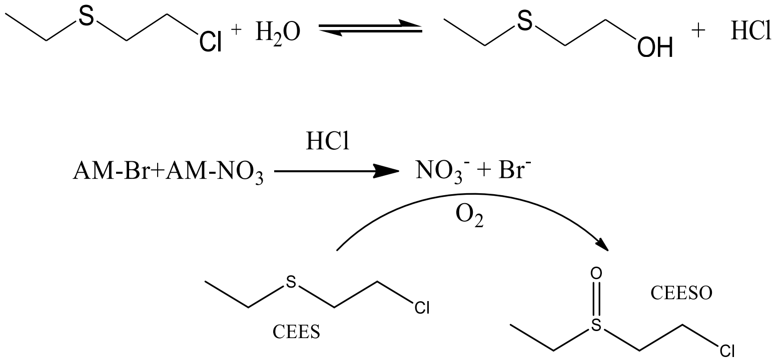


Figure 10. Oxidation of CEES catalyzed by AM, AM-NO_3, AM-Br, AM11 (Conditions are given in the Experimental section).

As mentioned above, it is very important that NO_3^- and Br^- do not dissociate from the catalyst. Otherwise, the immobilization is a failure. Therefore, after catalytic reaction, I used syringe filter to separate the catalyst and supernatant, then I added several drops of $AgNO_3$ solution to the supernatant. As one can see (Fig. S4), there was no precipitate, which means there was no Br^- in the solution which in turn indicates that no NO_3^- and Br^- dissociate from the catalyst. However, after a lengthy set of experiments, I obtained several strange and unexplainable results, so I did this test again. This time, however, I separated the precipitates by centrifugation instead of syringe filtration. These experiments indicated that during the previous test, the syringe filter was adsorbing the trace amounts of freely diffusing NO_3^- and Br^-, which led to erroneous interpretation of the results.



Scheme 2. Mechanism of AM series catalyst in solution

In fact, NO_3^- and Br^- were shown to dissociate from the catalyst and re-enter the solution. To probe this further, I carried out several experiments, which lead to a new proposed dominant mechanism (Scheme 2). In the system, CEES can react with the small amount of water present, producing the corresponding CEES-alcohol and HCl.

With HCl in the system, the free Cl^- can exchange with the NO_3^- and Br^- electrostatically associated with the catalyst. This exchange produces freely diffusing NO_3^- and Br^- in the solution after reaction. To prove this, firstly I measured the pH value of the mixture of CEES and water with pH paper; it was acidic (ca. 3~4) consistent with 10^{-3} M protons and thus same amount of anions (including NO_3^-, Br^- and Cl^-) in the solution.

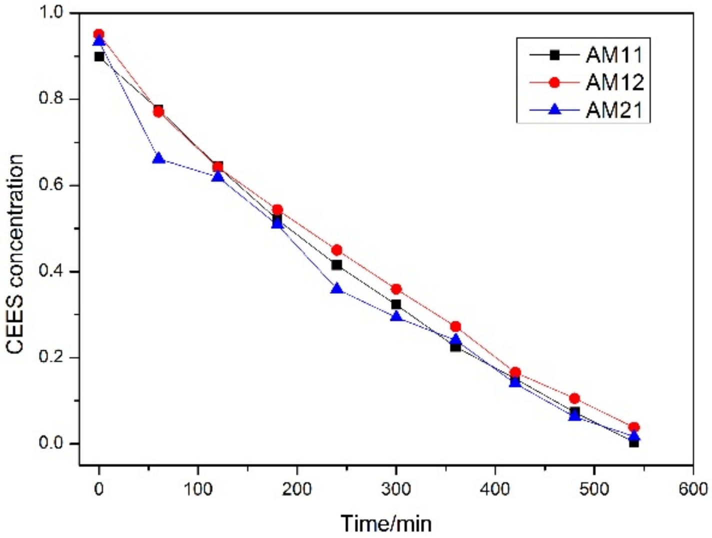


Figure 11. Activity of AM11, AM12, AM21 in selective oxidation of CEES

To further prove this mechanism, I carried out several control experiments to explore the activity of AM series catalysts (Fig. 11). It is obvious that AM11, AM12 and AM21 have almost the same activity. Moreover, we also carried out the same reaction using all the other catalysts (AM11, AM12, AM13 and AM15 in Fig. S5, AM11, AM21, AM31 and AM51 in Fig. S6), and all the samples displayed similar oxidation rates. Whatever the loading ratio of NO_3^- and Br^- in the resin is, they all showed similar activities. This result is readily explained. Because the amount of

CEES and water used in each control experiment was the same, the amount or the concentration of Cl^- produced in each control was also the same, which means under same conditions, we would have same amount of NO_3^- and Br^- in the system. Thus the same amount of NO_3^- and Br^- were present and all the samples showed similar activity.

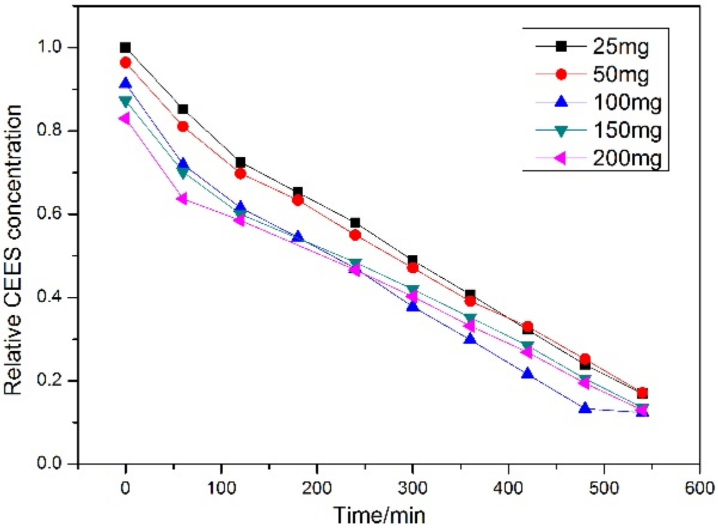


Figure 12. CEES oxidation activity using different amounts of catalyst

Further establishing the NO_3^- and Br^- displacement hypothesis, we measured the activity of different quantities of AM11 catalyst (Fig. 12). Clearly, varying the weight of catalyst from 25 mg to 200 mg did not change the activity. This is consistent with the concentration of Cl^- and thus the amount of NO_3^- and Br^- being constant resulting in similar activities with different amounts of catalyst. However, this assumes there is excess NO_3^- and Br^- for exchange. In other words, if there was not enough NO_3^- and Br^- for exchange, the catalysts would not show similar activities. This was verified by further reducing the amount of catalyst used in the reaction. Upon consideration of the accuracy limit of the balance used and the limited accuracy of the experiments in general, we chose to use 25 mg of catalyst. But we changed the catalyst from AM11 to AM13 and AM31, in which the amount of NO_3^- (AM13) or Br^- (AM31) is less than that in AM11. The results are shown in Fig. 13. As expected, there was a difference between these three controls, and AM11 had the best activity. These experiments indicate that only in some ranges is the activity of AM series catalysts independent of the amount of catalyst used and the ratio of NO_3^- and Br^- in the resin. Outside this range, the activity still depends on the amount of catalyst and the ratio of NO_3^- and Br^-. According to the mechanism, this range is determined by the amount of Cl^- produced in the first step, which is determined by the amount of CEES and water in the reaction. Increasing the amount of CEES increases the concentration of Cl^-, which increases the amount of NO_3^- and Br^- in the solution. On the other hand, increasing the amount of water has several effects. First, increasing water produces more Cl^-, but the concentration of anions in the water (solution phase) can either increase or decrease. Second, increasing the amount of water also affect the catalytic process, as too much water will inhibit the reaction.

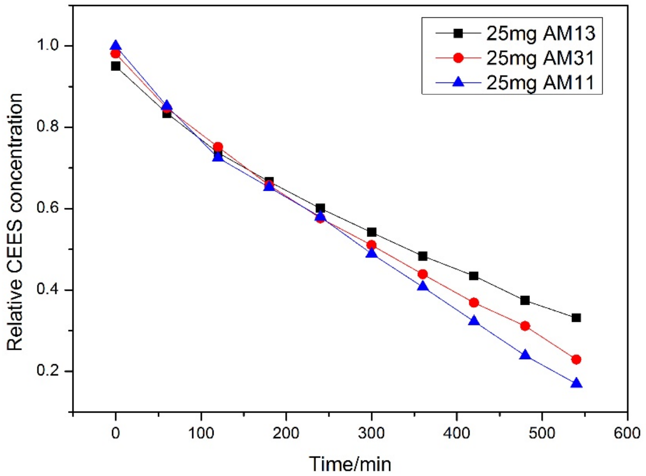


Figure 13. Oxidation activity of AM11, AM13 and AM31 (25 mg)

In the course of these experiments, I also discovered that the mixture of AM-NO_3 and AM-Br also catalyzes the O_2-based oxidation of CEES. Further, the activity of 1:1, 1:2, 2:1 ratio of AM-NO_3 and AM-Br mixture (named AM1+1, AM1+2, AM2+1 respectively, Fig. 14) have similar activity to AM11 (AM with 1:1 loading ratio of NO_3^- and Br^-). This further confirms the chloride-displacing NO_3^- and Br^- mechanism because according to this mechanism, AM11 or a mixture of AM-NO_3 and AM-Br should only function as a source of NO_3^- and Br^-. In addition, I prepared another resin IRN-400 with NO_3^- or Br^- as the counterion (noted as "IRN-NO_3" and "IRN-Br" respectively). A 1:1 mixture of IRN-NO_3 and IRN-Br also showed similar activity to AM11, indicating that this second type of resin also serves primarily as a reservoir for NO_3^- and Br^-.

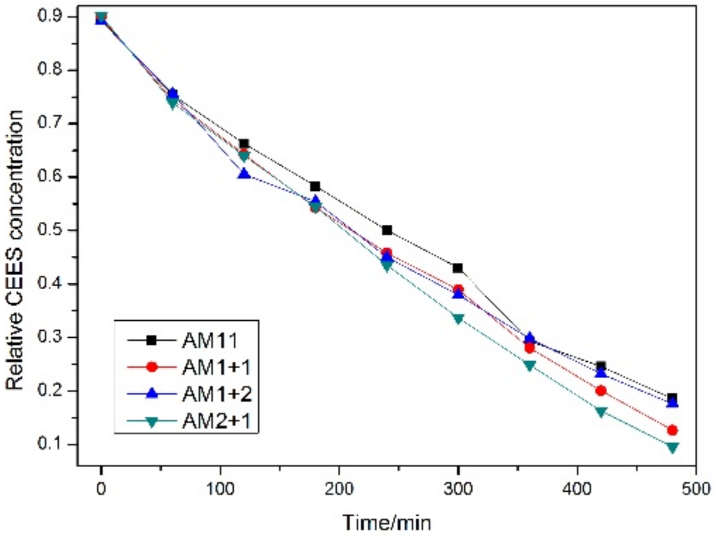


Figure 14. Activities of air-based CEES oxidation by AM11, AM1+1, AM1+1, AM2+1 (AM1+1, AM1+1, AM2+1 indicate 1:1, 1:2, 2:1 mixture of AM-NO_3 and AM-Br respectively)

In a further experiment, I also varied the amount of CEES used in the reaction (Fig. 15). (CEES1 means the same amount of CEES used in previous experiments, which is 20 μL, while CEES0.5 means half of the amount of CEES above (10 μL); CEES2 means double the original amount (40 μL) and CEES5 means five times the original amount (100 μL). From this figure, we can see that as the CEES concentration increases, the rate of the catalyzed reaction (the absolute value of the slope) also increases. However, this slope is not linear, which is explained by the proposed ion exchange mechanism. As noted above, the reaction of CEES and water is a reversible, thus when we add more CEES, we produce more HCl, and consequently more NO_3^- and Br^-, resulting in an increased reaction rate.

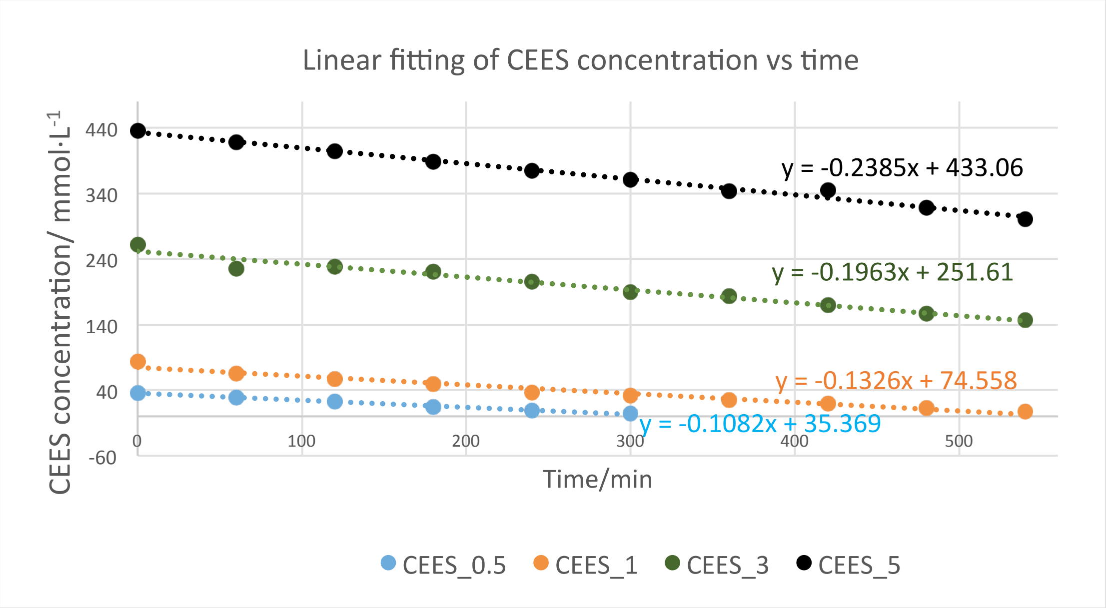


Figure 15. Control experiments with different amounts of CEES

It is now established that Cl^- generated *in situ*, results in electrostatic displacement of NO_3^- and Br^- and that these ions in solution function as the aerobic oxidation catalyst. However, we were uncertain as to whether the solid may also be working as a catalyst simultaneously with the ions in solution. In other words, we would like to know if CEES is oxidized solely by the NO_3^- and Br^- in solution or by both NO_3^-/Br^- in solution and also by immobilized forms of these anions. One key experiment is to obtain the supernatant after reaction and then use it to catalyze the oxidation of more CEES. This experiment was conducted and the supernatant had similar activity as in the previous reaction, strongly suggesting that the active catalyst was not the heterogeneous solid, but only the dissolved NO_3^- and Br^-.

Conclusions

To conclude, I prepared a series of heterogeneous materials with NO_3^- and Br^-, electrostatically immobilized on ion exchange resins. These were characterized by elemental analysis and FTIR. The suspension of these materials in acetonitrile solutions containing CEES resulted in effective air (O_2)-based oxidation of the CEES to the corresponding sulfoxide, CEESO. However, a series of control experiments established that in this solvent and under these reaction conditions, chloride ion generated *in situ* from CEES hydrolysis with a small quantity of water present results in displacement of NO_3^- and Br^-, and that these ions in acetonitrile solution account for effectively all the CEES oxidation.

Appendix

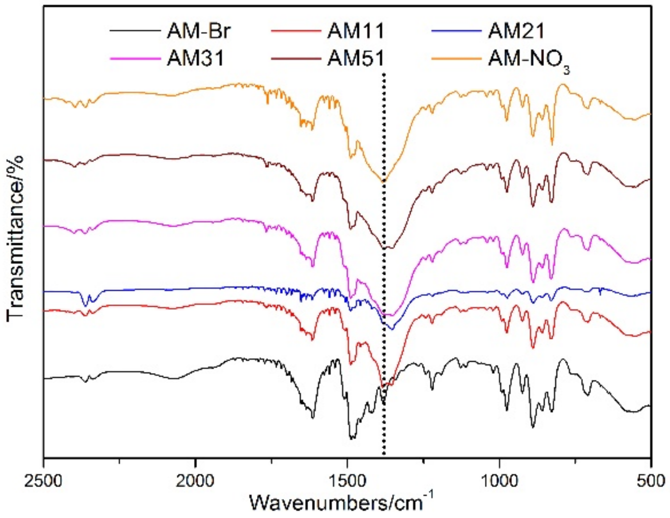


Figure S1. Local FTIR spectra of AM-Br, AM11, AM21, AM31, AM51, AM-NO$_3$ (bottom to top)

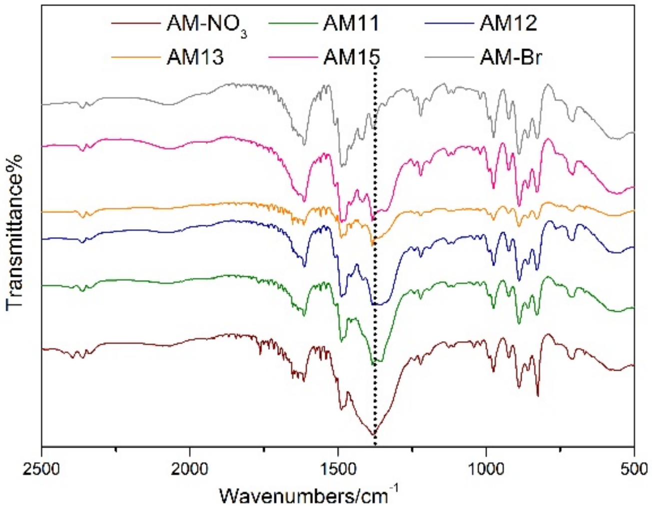


Figure S2. Local FTIR spectra of AM-NO$_3$, AM11, AM12, AM13, AM15, AM-Br (bottom to top)

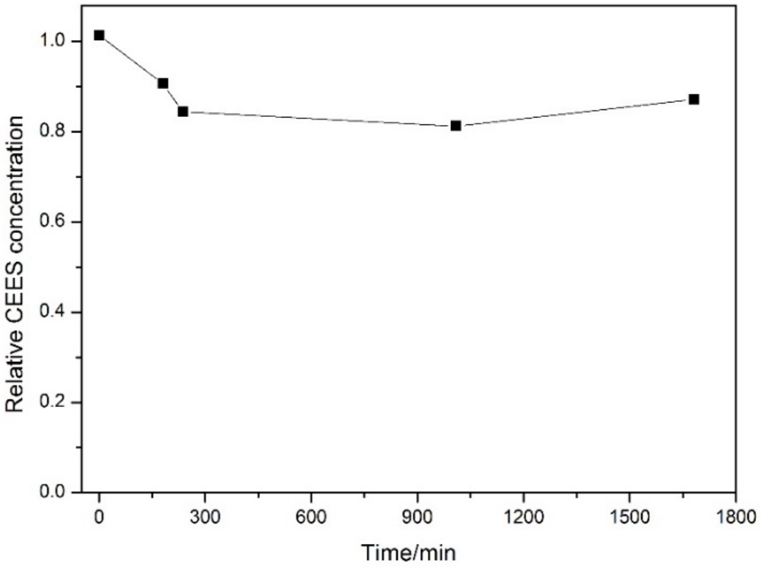


Figure S3. Control catalytic reaction without water

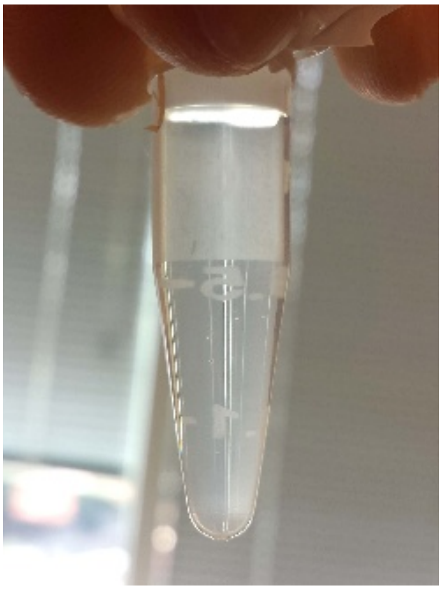


Figure S4. Mixing supernatant of the reaction system and 1 M $AgNO_3$

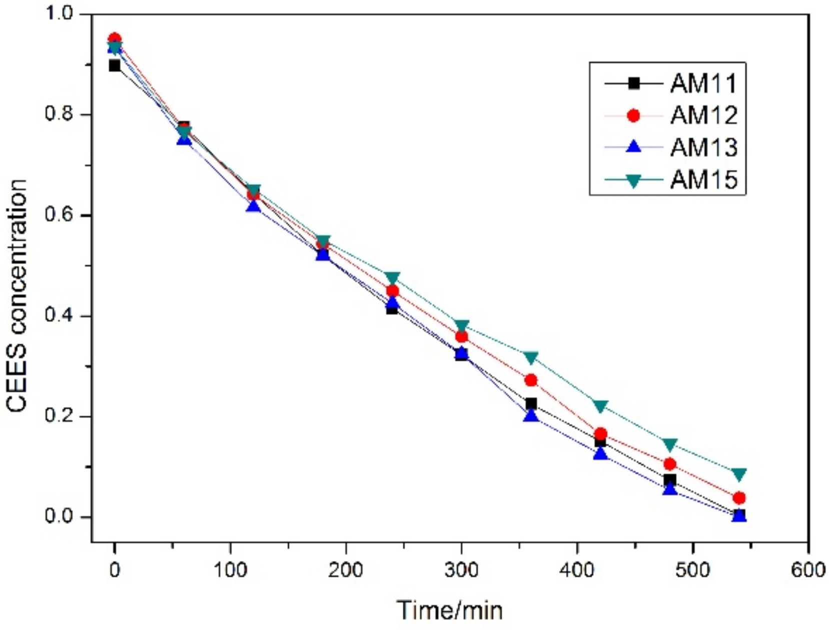


Figure S5. Activity of AM11, AM12, AM13, AM15

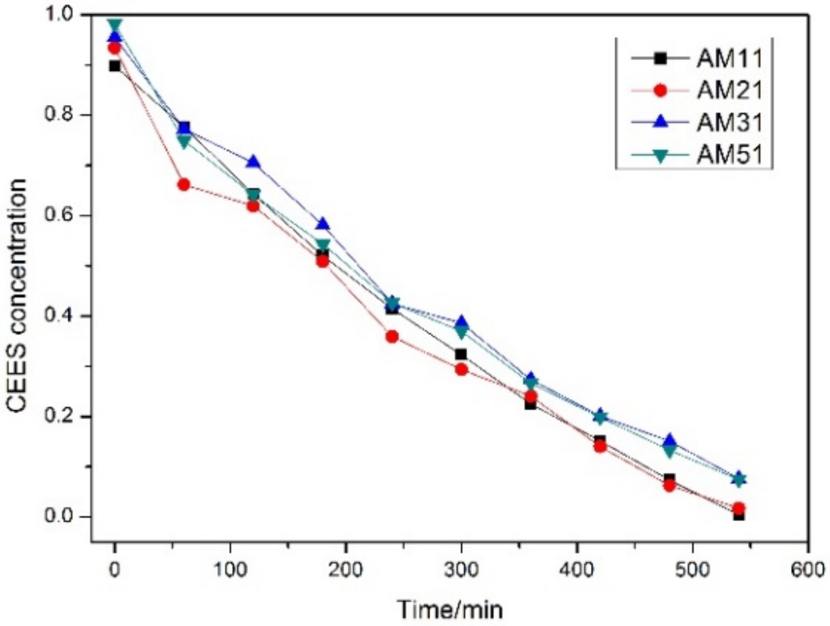


Figure S6. Activity of AM11, AM21, AM31, AM51

III. Decontamination of Mustard Vapor

Background

Given that effective and catalytic decontamination of mustard in vapor form would also be of great value, an obvious idea is whether we can just get rid of water and aqueous solution and use the catalyst in an air flow only. The greatest challenge in doing this is formulating a device and method to quickly and quantitatively evaluate the catalytic activity. Thus this part of the thesis focuses on developing a new device for assessing catalytic activity for air-based decontamination of mustard vapor.

Experimental Part

Device set-up

To develop an effective and efficient method for the purpose, we designed a device like the one shown below (Fig. 16). On the right, CEES vapor is produced by flowing air through a mixture of CEES and water; when the air emerges, it contains a certain amount of CEES and water. This mixed CEES/water vapor is then flowed through the reactor. Fig. 17, is a close-up of the right part of the device in Fig. 1, for generating the CEES/water vapor. The left part of Fig. 16 shows the reactor and its accessories, including a big round flask wrapped in aluminum foil that is heated in a sand bath maintained at a given temperature. The air/CEES/water vapor is heated in the big flask, which can potentially accelerate the oxidation reaction. Fig. 18 is a close-up of the reactor, which consists of two parts, which can be separated; when they are separated, the catalyst can be stored in the resulting small space. The hope was that when the hot air/CEES/water mixture goes through the reactor, these molecules on contact with the catalyst would produce the decontamination product, CEESO.

Figure 16. Device for assessing catalytic activity for air-based oxidation of CEES

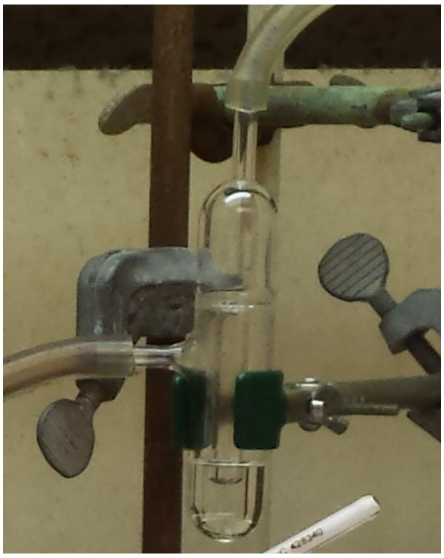


Figure 17. Close-up of vapor generator

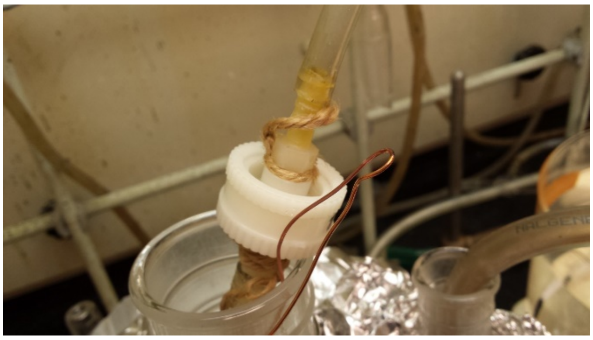


Figure 18. Close-up of the reactor

Assessing catalytic activity for air-based oxidation of CEES vapor

The test of catalytic activity was carried out by loading 0.100 g of AM11 in the reactor, turning on the air facilitating a flow of the air/CEES/water vapor into the reactor. Gas aliquots were then withdrawn from the reactor from time to time and analyzed by GC. The CEES consumption kinetics displayed bi-phasic behavior. The phase is an induction period resulting from adsorption of CEES on the reactor and catalyst surfaces. The CEES content then increased until it reached a plateau, indicating a balance between CEES flowing into the reactor and flowing out of the reactor. If there is no catalyst, the CEES flowing into the reactor and the CEES flowing out of the reactor should be equal; otherwise, CEES flowing out of the reactor should be less than CEES flowing into the reactor. Given these points, we can obtain the CEES content at the plateau and compare this kinetics data with that from various control experiments with and without catalyst. If the CEES content at the plateau is less for control experiments with catalyst, then the catalyst is indeed working; otherwise, it means the catalyst is not working under these conditions.

Cu-POM catalytic activity test

The preparation of AM-POM was carried out by doing ion-exchange on AM using an aqueous $CuPW_{11}O_{40}^{7-}$ solution.

The catalytic activity of AM-POM in gas phase was assessed under the same condition (60 ℃) as reaction above. The only difference was that for the catalyst, we used the three-component catalyst, which consists of 1:1:1 AM-NO_3, AM-Br, AM-POM (usually 0.330 g for each).

The catalytic activity of AM-POM in solution was carried out under exactly the same conditions as the reactions in the previous section of the thesis using the same three-component catalyst.

Results and Discussion

First, we determined the activity of 1:1 AM-NO_3 : AM-Br for the gas phase oxidation of CEES at room temperature. The CEES content in the air flow was the same indicating that the catalyst was not working. Then we raised the temperature to around 60 ℃, however, the result was still negative. There may be two possible reasons for this, the first is that the activity of the catalyst is too low and the decrease in CEES concentration was not sufficiently large to be seen by GC analysis. The second reason is that the catalyst does not work for a gas phase reaction.

To rule out the first possibility, we needed to further enhance the activity of the catalyst. Dr. Zhen Luo in our group indicated that the presence of Cu-POM ($CuPW_{11}O_{40}^{7-}$) increases the catalytic activity of NO_3^- and Br^-. So I tried to prepare AM-$CuPW_{11}O_{40}$ (AM-POM) by doing ion exchange and added this AM-POM to the previous catalyst making a 3-component catalyst for aerobic CEES oxidation.

Fig. 19 shows the FTIR spectra of AM, Cu-POM and AM-POM. AM-POM has the characteristic peaks of both AM and POM, which indicates POM was successfully exchanged into AM. However, when I used this 3-component catalyst for the gas phase oxidation of CEES, I still could not see a clear decrease in the quantity of CEES in the air flow. Thus this catalyst was inactive.

To find out whether the AM-POM was working or not, I used this 3-component catalyst in a solution reaction (Fig. 20). The 3-component catalyst (AM-NO_3 + AM-Br + AM-POM) was less active than the 2-component catalyst (AM-NO_3 + AM-Br). The 3-component catalyst has only 66% of activity of the 2-component catalyst (AM-NO_3+AM-Br). We thought the reason why Cu-POM enhances the activity of NO_3^- and Br^- while AM-POM does not enhance the activity of the 2-component catalyst was that Cu-POM has high negative charge and high charge density. Thus when it was exchanges into the AM, it binds to the cationic polymer very firmly, so it no longer can act like a freely diffusing POM molecule.

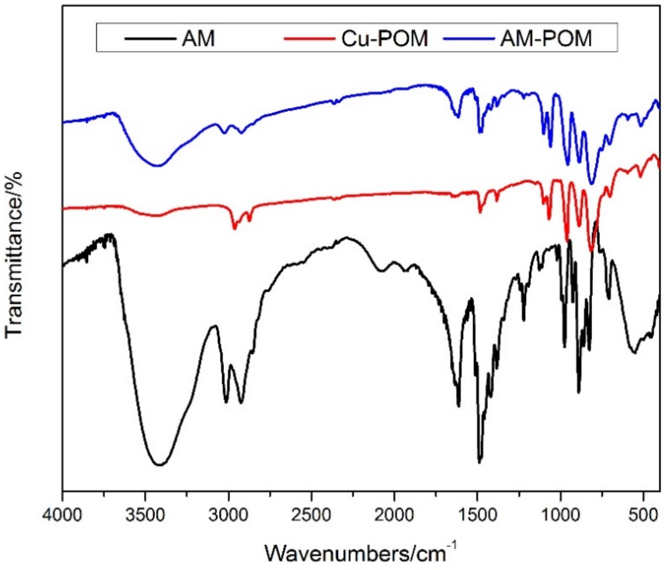


Figure 19. FTIR spectra of AM, Cu-POM and AM-POM

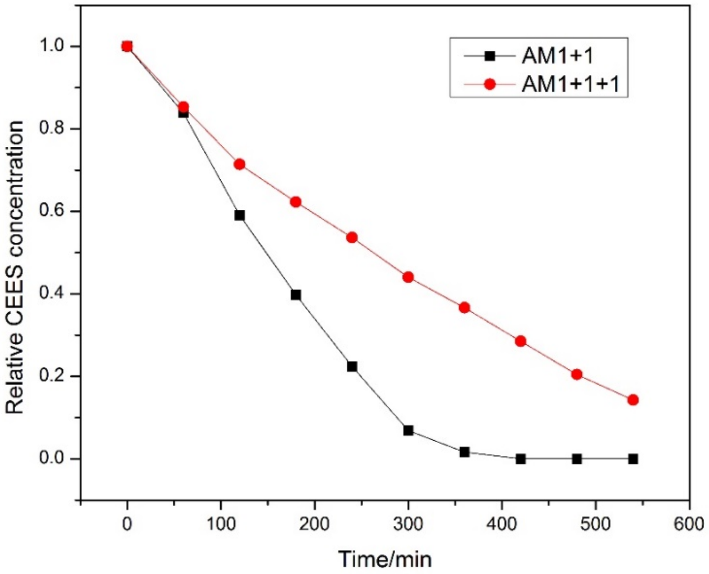


Figure 20. Activity of 2-component catalyst (AM1+1) and 3-component catalyst (AM1+1+1)

Conclusion

We have designed a device and tried to use the AM series of catalysts with this device to oxidize CEES vapor. However, the results show that it does not work at room temperature or up to 60 ℃. We then attempted to use AM-POM to enhance the activity of AM-NO_3/AM-Br. Unfortunately, due to charge neutralization, AM-POM does not enhance the activity of AM-NO_3/AM-Br for aerobic CEES oxidation unlike the presence of Cu-POM in solution.

IV. Simultaneous Decontamination of Sulfur Mustard and Nerve Agents

Background

As we previous discussed, nerve agents are a class of organophosphonate esters and one way to decontaminate them is by hydrolysis, i.e. breaking the P-X (X=N, S, O) bond. Some of the nerve agents exhibit autocatalytic hydrolysis, while others do not. But for even those that hydrolyze fairly readily, the reaction rates are unacceptably slow. Therefore, it is necessary to develop catalysts for the hydrolysis. Many organophosphonate ester hydrolysis catalysts have been reported, including peroxide. It should be noted that in this context, peroxide is not working as an oxidant, but as the highly nucleophile peroxy anion (HOO^-). This reactive species attacks the phosphorus atom leading to a peroxyphosphonate intermediate, which then reacts with peroxide to from O_2 and hydrolyzed product[30].

There are several other ways to decontaminate organophosphonate esters in addition to hydrolysis. One approach is to oxidize it using hypochlorite-based reagents, Indeed bleach formulations were the first studied and deployed chemical decontamination methods for nerve agents[31]. The dominant mechanism for hypochlorite-based hydrolysis of these OP esters is actually hydrolysis as well. However in the case of nerve agents with a P-S bond (VX being the most significant), hypochlorite can also oxidize the sulfur center, a processes that can also accelerate the hydrolytic reaction[31]. In addition to hydrolysis and oxidation of OP esters by low molecular weight species, there are also biochemical methods[32-36] that have been much studied recently.

However, among all these methods, basic hydrolysis of nerve agents remains very effective and efficient, and thus popular[37-40]. In this context, one report by May Nyman, an expert in polyniobate chemistry, in 2014 attracted our attention[41]. They reported that hexaniobate ($Nb_6O_{19}^{8-}$) is a strong candidate for base hydrolysis of nerve agents. $Nb_6O_{19}^{8-}$ (Nb-POM) is a small and discrete molecule that can dissolve in many of solvents. It is also amenable to functionalization. So in this third part of the thesis, I first focus on the immobilization of Nb-POM and then on the development of bi-component catalyst/bi-catalyst for the simultaneous decontamination of sulfur mustard (CEES) and nerve agents (DMMP) using NO_3^-/Br^- catalyst combined with Nb-POM and other POMs.

Experimental Part

Detection of DMMP and hydrolyzed products

Dimethyl methylphosphonate (DMMP) and its corresponding hydrolysis products were analyzed using GC. When Cs-POM was used as a decontamination (hydrolysis) catalyst, DMMP and corresponding hydrolyzed products were identified using ^{31}P-NMR.

Preparation of AM-Nb-POM

First, 1 g of $Cs_8Nb_6O_{19}$ was dissolved in 6 mL of water, then for every 0.2 g of AM resin, 3 mL of the Nb-POM solution was added, the product mixture stirred for *ca.* 1 hour, the POM solution removed, then an additional 3 mL of Nb-POM solution was added. This procedure was repeated three times, then the product washed with water and dried in vacuum.

Catalytic test of Nb-POM

First, 25 μl of DMMP was added into 3 mL of 0.1 M $Cs_8Nb_6O_{19}$ solution. The mixed solution was stirred under 60 ℃. Then liquid aliquots were withdrawn from the solution every certain time.

Catalytic test of AM-Nb-POM

0.100 g of AM-Nb-POM was added into 3 mL of water (1:2 water : acetonitrile in other controls), then 25 μL of DMMP added. Thereafter the solution stirred under 60 ℃ and for every certain time, samples were withdrawn for analyzing.

Catalytic test of Nb-POM and NO_3^-, Br^-

Two sets of experiments were conducted in this part, both under 60 ℃.

In the first set, 10 drops of 1 M $TBANO_3$ (tetrabutylammonium nitrate) and 10 drops of 1 M TBABr (tetrabutylammonium bromide) was added to 3 mL of 0.1 M $Cs_8Nb_6O_{19}$ solution, then 25 μL of DMMP, 25 μL CEES and 25 μL dichlorobenzene were added.

In the second set of experiment, acetonitrile was used as solvent, in 2 ml of acetonitrile, 10 drops of 1 M $TBANO_3$ and 10 drops of 1 M TBABr were added, then 1 mL of 0.1 M $Cs_8Nb_6O_{19}$ solution, 25 μL CEES, 25 μL dichlorobenzene, 25 μL DMMP were added.

Synthesis of $Cs_{2.5}$-POM

The synthesis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$-POM) followed Toshio Okuhara's paper[42]. In a typical synthesis, Cs_2CO_3 was added into $H_3PW_{12}O_{40}$ aqueous solution under vigorously stir (molar ratio 1.25:1). White solid precipitated during the process of adding Cs_2CO_3 was allowed to stand overnight. Then, water was evaporated at around 45 ℃. The obtained white solid from evaporation was then transferred into a muffle oven to calcinate at 250 ℃ for 3 hours.

Catalytic test of $Cs_{2.5}$-POM

The catalytic test of $Cs_{2.5}$-POM was carried out under 60℃ in water. Firstly 20 μL of DMMP and 1 g of $Cs_{2.5}$-POM were added into 2 mL of water, then the system was sealed, put into water bath and kept running for 2 days. After that, the solution was separated from the catalyst for NMR analysis.

Catalytic test of $Cs_{2.5}$-POM and NO_3^-, Br^-

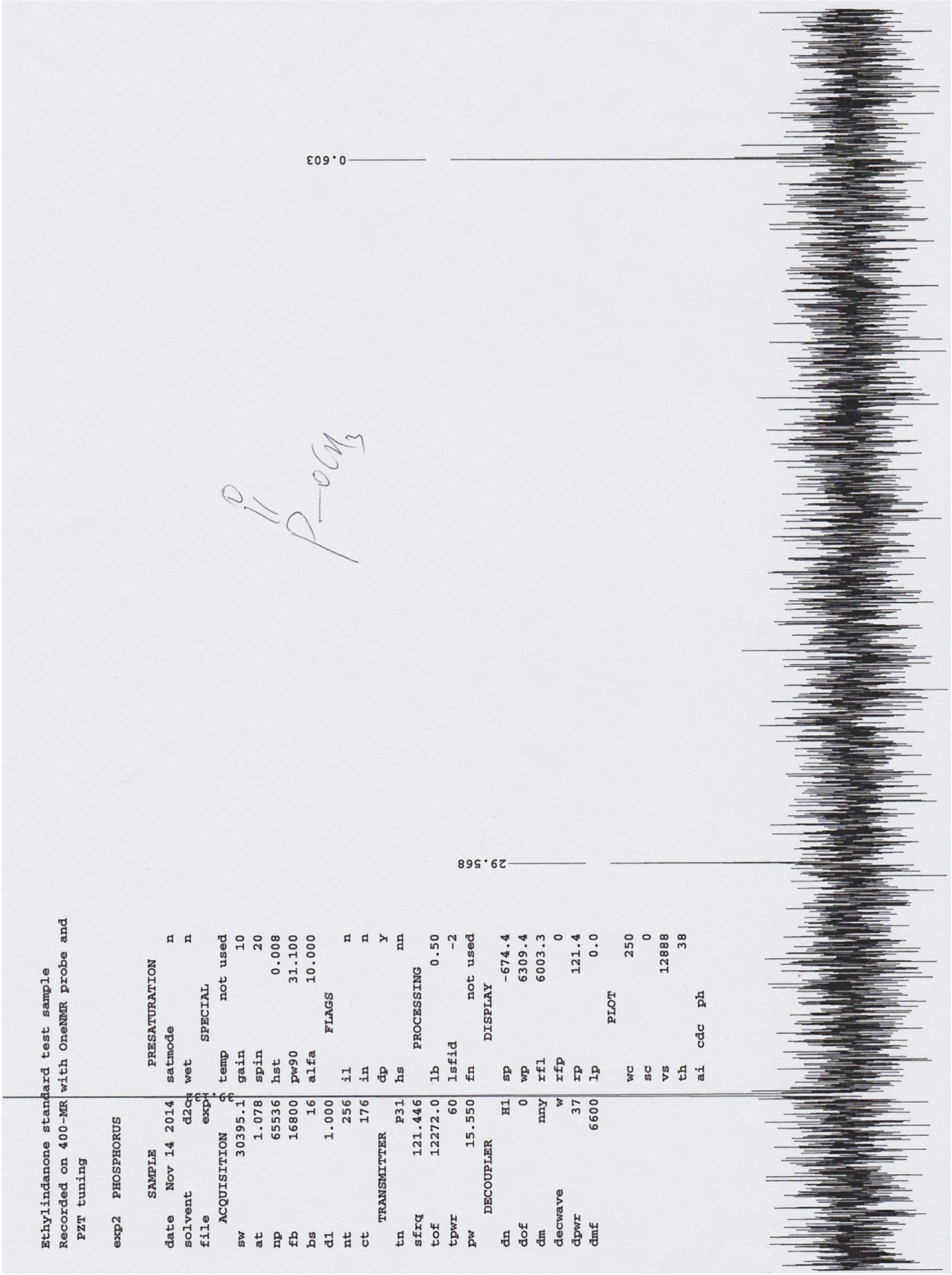
The catalytic test of $Cs_{2.5}$-POM and NO_3^-, Br^- was carried out under exactly the same condition as the one for Nb-POM and NO_3^-, Br^-, the only difference for both two sets of experiments was replacing 0.1 M Nb-POM solution by 1 g of $Cs_{2.5}$-POM.

Results and Discussion

Initially, we tested the activity of Nb-POM in a different way than the May Nyman group did[41], and we found that Nb-POM has strong catalytic activity towards the decontamination of DMMP. Since Nb-POM is soluble in water, we tried to incorporate it into AM in order to have a more useful heterogeneous catalyst, but we found that AM-Nb-POM does not catalyze hydrolysis of DMMP. We attribute this result to neutralization of the high charge density in Nb-POM by the polycationic AM resin. Without high negative charge density, Nb-POM loses its catalytic activity.

We then gave up the idea of making Nb-POM heterogeneous and chose to focus on the development of a bi-catalyst for the simultaneous decontamination of both CEES and DMMP by combining this catalyst with the existing NO_3^-/Br^- aerobic catalyst (second part of this thesis). However, once again the catalyst proved to be inactive. We determined that Nb-POM only works in water and in no other solvent. In most organic solvents (including organic/water mixtures) it precipitates and loses its activity. Therefore, in acetonitrile-water mixed solvents, DMMP does not hydrolyze. Thus using pure water as the solvent, neither base hydrolysis by Nb-POM nor aerobic oxidation by NO_3^-/Br^- happens. The reason why CEES oxidation does not proceed is that O_2-based oxidations catalyzed by NO_3^-/Br^- are inhibited by water and 100% aqueous media results in also complete inhibition. DMMP is not be hydrolyzed because, as explained in the second part of the thesis, CEES reacts with water and the resulting HCl neutralizes Nb-POM (protonated the Nb-POM oxygens). These set of experiments establish a key point: that the NO_3^-/Br^- catalyst and Nb-POM are not compatible because NO_3^-/Br^- only works in neutral or acidic environments, while Nb-POM cannot work in acidic solutions.

In order to utilize the highly efficient NO_3^-/Br^- catalyst, we turned our attention to other possible catalysts that are compatible with acidic condition. We found several reports by Toshio Okuhara[42,43] on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}$-POM). According to him, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is different from both $Cs_2HPW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$, however, it is composed of a combination of $Cs_2HPW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$. As he noted, $Cs_{2.5}$-POM has the ability to catalyze acidic hydrolysis, and in his report, he reported the hydrolysis of esters. In addition, $Cs_{2.5}$-POM has a relatively large surface area (~180 m^2/g), which makes it a good candidate for hydrolyzing DMMP. Therefore, I synthesized $Cs_{2.5}$-POM and tested its activity. Indeed $Cs_{2.5}$-POM is capable of catalyzing the hydrolysis of DMMP as we can see in Fig. 21. In this figure, there are three peaks: the left one at *ca.* 40 ppm corresponds to unreacted DMMP, the peak in the middle corresponds to the mono-methyl decontamination product, and the peak on the most right corresponds to the completely hydrolyzed product, methylphosphonic acid. I also evaluated the activity of $H_3PW_{12}O_{40}$, which may have better potential as it has more protons. Significantly, I found that $H_3PW_{12}O_{40}$ is not able to catalyze hydrolysis of DMMP, so there was something special about $Cs_{2.5}$-POM with regard to its ability to catalyze acid-sensitive reactions. This special ability may derive from the structure that forms during calcination, and DMMP may adsorb on the surface of this material, which facilitates catalysis.



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Ethylindanone standard test sample
Recorded on 400-MR with OneNMR probe and
 PZT tuning

exp2  PHOSPHORUS

      SAMPLE              PRESATURATION
date   Nov 14 2014  satmode            n
solvent         d2o  wet                n
file            exp       SPECIAL
   ACQUISITION       temp       not used
sw          30395.1  gain             10
at            1.078  spin             20
np            65536  hst           0.008
fb            16800  pw90         31.100
bs               16  alfa         10.000
d1            1.000        FLAGS
nt              256  il                n
ct              176  in                n
   TRANSMITTER       dp                y
tn              P31  hs               nn
sfrq        121.446       PROCESSING
tof         12272.0  lb             0.50
tpwr             60  lsfid            -2
pw           15.550  fn         not used
    DECOUPLER             DISPLAY
dn               H1  sp           -674.4
dof               0  wp           6309.4
dm              nny  rfl          6003.3
decwave           w  rfp               0
dpwr             37  rp            121.4
dmf            6600  lp              0.0
                           PLOT
                     wc              250
                     sc                0
                     vs            12888
                     th               38
                     ai   cdc   ph
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Figure 21. ^{31}P NMR spectrum of the mixture after reaction catalyzed by $Cs_{2.5}$-POM

Since $Cs_{2.5}$-POM is a heterogeneous catalyst, its activity is not high compared to Nb-POM, however, the activity of $Cs_{2.5}$-POM is much higher than a similar heterogeneous catalyst recently reported by Zhongmin Su and co-workers[15].

I tried combining $Cs_{2.5}$-POM, which is already a heterogeneous catalyst, with NO_3^-/Br^- catalyst and I discovered that in pure water, $Cs_{2.5}$-POM works, i.e. catalyzes hydrolysis of DMMP. However, CEES oxidation is inhibited. In acetonitrile and water mixture, CEES oxidation takes place, but DMMP hydrolysis does not. However, $Cs_{2.5}$-POM as an acidic catalyst and thus likely compatible with the NO_3^-/Br^- catalyst, so the main challenge left is to find a suitable solvent to realize both decontamination reactions, aerobic oxidation and acid-hydrolysis, simultaneously.

Conclusions

We tried to prepare a bi-catalyst that can catalyze both CEES oxidation and DMMP hydrolysis. We evaluated the combination of Nb-POM and $Cs_{2.5}$-POM with NO_3^-/Br^- but found that Nb-POM was not pH compatible with NO_3^-/Br^-. $Cs_{2.5}$-POM was partly compatible with NO_3^-/Br^-, but we still need to find a suitable solvent for this reaction and to try to make them work in gas phase reactions.

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