ROUTING AND ACTION

MEMORANDUM

ROUTING

TO:(1) Chemical Sciences Division (Poree, Dawanne)

Report is available for review

(2) Proposal Files Report No.: Proposal Number: 61754-CH.35

DESCRIPTION OF MATERIAL

CONTRACT OR GRANT NUMBER: W911NF-12-1-0136

INSTITUTION: Emory University

PRINCIPAL INVESTIGATOR: Craig Hill

TYPE REPORT: Final Report

DATE RECEIVED: 3/13/17 12:31AM

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TITLE: Final Report: New multi-functional structures for sensing and decontamination

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ACTION TAKEN BY DIVISION

(x) Report has been reviewed for technical sufficiency and IS [x] IS NOT [ ] satisfactory.

(x) Material has been given an OPSEC review and it has been determined to be non sensitive and, except for manuscripts and progress reports, suitable for public release.

(x) Perfomance of the research effort was accomplished in a satisfactory manner and all other technical requirements have been fulfilled.

(x) Based upon my knowledge of the research project, I agree with the patent information disclosed.

Approved by SSL\DAWANNE.POREE on 3/5/18 2:14PM

ARO FORM 36-E

REPORT DOCUMENTATION PAGE

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

This grant has seen development of gelating catalytic nanoarray polymers (GNA polymers) and studied their mechanism of color-change detection and catalytic decontamination. Ion exchange chemistry has led to many new types of GNAs including Li+ salts and Zr4+ and Ce4+ salts that catalyze effective nerve agent decontamination while retaining a catalytic oxidative decontamination ability. A patent was filed on these systems in December, 2015. POM-based catalysts (vanadium-tungsten polyanions) for air-based catalytic removal of formaldehyde, a common toxin and carcinogen, were developed. These POM-catalyzed oxidations are not greatly inhibited by

15. SUBJECT TERMS

multifunctional polymers, hydrolytic and oxidative catalytic decontamination, polymeric polyniobates (PONbs)

16. SECURITY CLASSIFICATION OF:

a. REPORT	b. ABSTRACT	c. THIS PAGE
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PI: Craig L. Hill ARO grant: **W911NF-12-1-0136**

Forward

The last years of this ARO grant lead to the development of several new types of reactive, tunable materials, including polymeric polyniobates (P-PONbs), gelating catalytic nanoarray (GNA) polymers, and hybrid POM-pyrene conjugates, as well as study of their structural, spectroscopic, and catalytic properties. The grant also enabled multi-dimensional NMR and other studies of polyoxometalate (POM) counterions including their movement around the polyanion as a function of experimental conditions. This grant also funded other important fundamental studies of these systems. New broad-spectrum activity by GNA polymers led to fining of a patent on this new class of reactive materials.

Table of Contents

The PI and his co-workers have worked in the following linked areas and accomplished the following in the last time period:

1. Gelating catalytic nanoarray polymers (GNA polymers).

The abstract of a paper on this topic is below; it outlines the reason for this research and several of the unique findings. The paper, uploaded as a manuscript in submission, should be accepted shortly.

Abstract: Materials with the ability to react instantaneously to external stimuli while exhibiting catalytic functions are highly sought. Here, we report a new class of organic/inorganic hybrid polymers composed of organic linkers and anionic polyoxometalate clusters which form gels upon contact with a range of organic liquids. The solvent-induced gelation occurs rapidly (within seconds) at room temperature and is reversible, allowing for a large volume of liquid to be immobilized within the gel network. This capability can be used to form gels immediately upon exposure of the solid to polar aprotic molecules, including nerve agent simulants (e.g. dimethyl methylphosphonate). Simultaneously, these materials catalyze the degradation of a range of toxic compounds under mild conditions, including hydrolysis of nerve agent simulants and oxidative removal of undesirable organic compounds. The oxidation reactions result in a color change in the polymer arising from reduction of the polyoxometalate centers, providing a built-in colorimetric detection capability. The tetrabutylammonium counter cations in the as-synthesized material can be readily exchanged to modulate the physical properties or catalytic capabilities of the polymer. Exchange for lithium results in enhanced gelation properties, whereas exchange for tetrameric zirconium hydroxide increases the rates of catalytic hydrolysis. This work opens avenues of research into highly modular catalytically active polymers capable of instantaneous and reversible gel formation under ambient conditions.

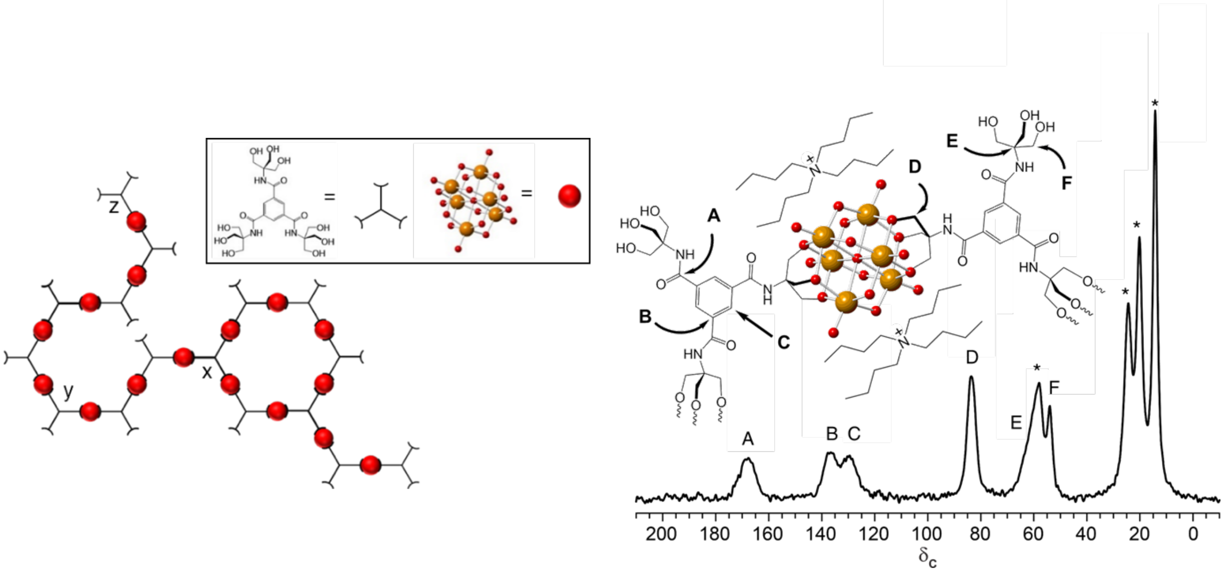

Figure 1. TBA-polyV_6 polymer molecular structure. (a) Representation of the cross-linked TBA polyV_6 polymer that results in fiber formation, indicating triply-bound (x) doubly-bound (y) and singly-bound (z) linkers. Inset: Orange and red spheres represent V(V) and O^{2-}, respectively. (b) CP-MAS ^{13}C (150.9 MHz) NMR of TBA-polyV_6. A representative structural unit is shown. Orange and red spheres represent V(V) and O^{2-}, respectively, with two TBA^+ cations required to balance the charge of the V_6 core. TBA^+ (*) peaks are indicated.

The most important recent achievements in this work are clarification of the mechanism of solvent (and nerve-agent-simulant) swelling (gelation). This process is complex; it involves the rapid formation of many hydrogen bonds of different types as well as cation-polyanion interactions. Some of these cation-polyanion interactions were addressed in very recent (in press) research described in Section 5 below.

We achieved the most rapid gelation we are aware of in the field of protective (barrier-forming) materials. A patent has been recent filed on these materials.

2. Further elucidation of the mechanism of color change detection of mustard analogues

We have found that mustard simulants (primarily, chloroethyl ethyl sulfide = CEES) form complexes with the counter cations of POMs and these complexes exhibit electron donor-acceptor interactions that have electronic transitions in the visible region. However, the main part of the color change involves transfer of an electron from the CEES sulfur atom to polyvanadate units. The electron goes into a lowest unoccupied molecular orbital; this LUMO is delocalized over the six V(V) centers.

3. Exchanged GNA counterions for a very wide variety of other cations. Tunable POM-based multiple functional materials.

The manuscript noted above (abstract given above) and other recent work establishes that the counter cations of GNAs (usually tetrabutyl ammonium = TBA which is used in the synthesis) can be exchanged for many others. The Li^+ and Zr_4^+ exchanged forms have been studied extensively. The Li-GNA has enhanced gelation (protective barrier formation) properties related to the original (TBA salt) GNA, while the Zr-GNA is a remarkably active hydrolysis catalyst while retaining other properties attractive in context with decontamination and detection. A patent was filed on these systems in December, 2015.

4. Catalysis of reduced polyoxometalate (POM) reoxidation by air/O_2

The Hill group with funding for ARO has developed several POM-based systems for catalytic oxidation of organic molecules, including some chemical warfare agents (CWAs). The mechanism involves two general steps: (1) oxidation of the target molecule, such as mustard (or CEES) or one of many oxidizable toxic industrial chemicals (TICs) by the oxidized POM, and (2) the resulting reduced POM being re-oxidized by O_2 (and in many cases, by ambient air). The latter is usually the slow step. In some cases, this slow reduced-POM reoxidation by O_2/air is too slow to make these catalysts useful on short time scales. In the last 2 years, our group achieved a solution to this problem.

One of the papers published in the last 2-3 years in this area reported catalysis of this air-based reoxidation step by simple aqueous Cu(II). Some of the dramatic data are shown in Figure 2. In the Figure 2, $\mathbf{1}_{\mathbf{red}}$ (top) and $\mathbf{2}_{\mathbf{red}}$ (bottom) are the two common and readily prepared POMs, α-$X^{n+}W_{12}O_{40}^{(8-n)-}$ in their 1e-reduced forms (POM_{red}, where X = Al^{3+}, Si^{4+} respectively).

In addition, based on our considerable data and literature studies, we proposed eqs 1−7 as the mechanism for the copper-catalyzed reaction of POM_{red} with O_2. The reaction rates for all of these processes were worked out and are given below ($\mathbf{3}_{\mathbf{red}}$ is the reduced form of α-$PW_{12}O_{40}^{3-}$, namely the one-electron intensely-blue-colored POM, α-$PW_{12}O_{40}^{4-}$).

More recently broad spectrum evaluation found that a combination of both Cu^{2+} and Fe^{3+} catalyze the re-oxidation of reduced POMs even more effectively. A paper on the latter system, an extremely complicated one mechanistically, is about to be submitted.

We have achieved successful immobilization of such POMs and catalytic counterions. This materials research is not yet published but will hopefully be developed by our group in collaboration with researchers at the Natick Soldier Center (Natalie Pomerantz) and ECBC (Chris Karwacky).

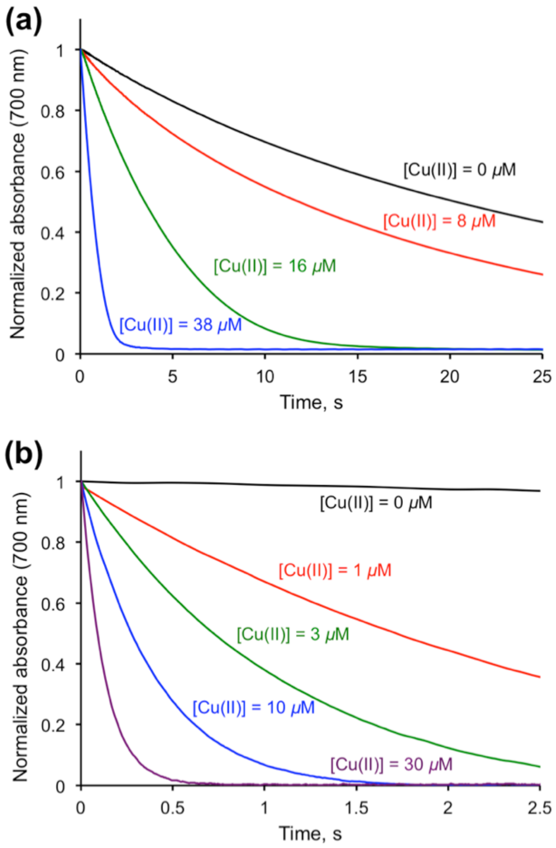

Figure 2. Effect of Cu(II) concentrations on kinetics of (a) $\mathbf{1}_{\mathbf{red}}$ and (b) $\mathbf{2}_{\mathbf{red}}$ oxidation by O_2 followed by the decrease of absorbance at 700 nm (the initial absorbance is normalized to 1.0). (a) $[\mathbf{1}_{\mathbf{red}}]_o \sim 0.55$ mM, $[O_2]_o = 0.58$ mM, pH 7.2, 50 mM phosphate buffer, 100 mM $NaClO_4$, 25 °C. (b) $[\mathbf{2}_{\mathbf{red}}]_o \sim 0.11$ mM, $[O_2]_o = 0.12$ mM, pH 2.0, 50 mM sulfate buffer, 100 mM $NaClO_4$, 25 °C.

$$\mathrm{POM_{red}} + \mathrm{O_2} + \mathrm{H^+} \rightarrow \mathrm{POM_{ox}} + \mathrm{HO_2^{\bullet}} \qquad k_5 = 8.5\ (\mathbf{2}_{\mathbf{red}}) \text{ and } 1.4\ \mathrm{M^{-1}s^{-1}}\ (\mathbf{3}_{\mathbf{red}}) \tag{1}$$

$$\mathrm{POM_{red}} + \mathrm{HO_2^{\bullet}} + \mathrm{H^+} \rightarrow \mathrm{POM_{ox}} + \mathrm{H_2O_2} \qquad k_6 = 2 \times 10^8\ \mathrm{M^{-1}s^{-1}} \tag{2}$$

$$\mathrm{POM_{red}} + \mathrm{Cu(II)} \rightleftarrows \mathrm{POM_{ox}} + \mathrm{Cu(I)} \qquad K_7 = k_7/k_{-7} \tag{3}$$

$$\mathrm{Cu(I)} + \mathrm{O_2} + \mathrm{H^+} \rightleftarrows \mathrm{Cu(II)} + \mathrm{HO_2^{\bullet}} \qquad k_8 = 4.6 \times 10^5\ \mathrm{M^{-1}s^{-1}}$$

$$k_{-8} = 5 \times 10^7\ \mathrm{M^{-1}s^{-1}} \tag{4}$$

$$\mathrm{Cu(I)} + \mathrm{H_2O_2} \rightarrow \mathrm{Cu(II)} + \mathrm{HO^{\bullet}} + \mathrm{HO^-} \qquad k_9 = 5 \times 10^3\ \mathrm{M^{-1}s^{-1}} \tag{5}$$

$$\mathrm{HO^{\bullet}} + \mathrm{Cu(I)} + \mathrm{H^+} \rightarrow \mathrm{H_2O} + \mathrm{Cu(II)} \qquad \text{Fast, } > 10^9\ \mathrm{M^{-1}s^{-1}} \tag{6}$$

$$\mathrm{HO^{\bullet}} + \mathrm{POM_{red}} + \mathrm{H^+} \rightarrow \mathrm{H_2O} + \mathrm{POM_{ox}} \qquad \text{Fast, } > 10^9\ \mathrm{M^{-1}s^{-1}} \tag{7}$$

5. The roles of counter cations and pH on POM chemistry.

The counterions of POMs impact POM reduction potentials, aggregation phenomena, and most other physicochemical properties of this huge and growing class of charged inorganic clusters.

They also impact the structural and catalytic properties of POM-containing polymers like the tri-functional ones described above. Despite the importance of POM-counterion interactions, there have been few studies of such interactions beyond simple structural effects obtained from scores of X-ray crystal structures.

In a joint study with Tianbo Liu and his co-workers (*Angew. Chem. Int. Ed.*; early view: DOI: 10.1002/anie.201612008), we prepared and characterized a series of POM-organic hybrid anionic clusters and revealed the positions and motions of the counterions of these POM derivatives by regular and multi-dimensional NMR spectroscopy, including Diffusion-Ordered Spectroscopy (*DOSY*), and by all-atom molecular dynamics calculations. DOSY NMR separates the NMR signals of different species according to their diffusion coefficient. Some of the POM hydrids containing fluorescent pyrene groups could also facilitate probing of the POM-counterion interactions using other techniques. With this ensemble of approaches, we were able not only to pin-point the location of the counter cations in solution but also to characterize their movement around the polyanion surface as a function of the experimental conditions. For these initial studies, we demonstrated that electrostatic interactions dominate over cation-π interactions (cation-pyrene interactions) in determining the locations of the counterions in the current system. It is clear that this combination of methods will enable the locations and importance of POM counterions in other POM chemistry to be elucidated. This includes the POM oxidation and hydrolysis decontamination catalysts.

6. Catalysts (vanadium-tungsten polyanions) for air-based removal of formaldehyde, a common toxin and carcinogen.

POM-based catalysts (vanadium-tungsten polyanions) for air-based catalytic removal of formaldehyde, a common toxin and carcinogen, were developed and the catalysis studied. The abstract from this 2014 paper below gives some of the main points.

Abstract: Three tetra-*n*-butylammonium (TBA) salts of polyvanadotungstates, $[n\text{-Bu}_4\text{N}]_6[\text{PW}_9\text{V}_3\text{O}_{40}]$ (**$\mathbf{PW_9V_3}$**), $[n\text{-Bu}_4\text{N}]_5\text{H}_2\text{PW}_8\text{V}_4\text{O}_{40}$ (**$\mathbf{PW_8V_4}$**), $[n\text{-Bu}_4\text{N}]_4\text{H}_5\text{PW}_6\text{V}_6\text{O}_{40}\cdot 20\text{H}_2\text{O}$ (**$\mathbf{PW_6V_6}$**), have been synthesized and shown to be effective catalysts for the aerobic oxidation of formaldehyde to formic acid under ambient conditions. These complexes, characterized by elemental analysis, fourier transform infrared (FT-IR), UV-vis spectroscopy and thermogravimetric analysis (TGA), exhibit a higher catalytic activity for this reaction than other polyoxometalates (POMs). Importantly, they are more effective in the presence of water than the metal-oxide-supported Pt and/or Au nanoparticles traditionally used as catalysts for aerobic formaldehyde oxidation. The polyvanadotungstate-catalyzed oxidation reactions are first order in formaldehyde, parabolic order (slow, fast, slow again) in catalyst and zero order in O_2. Under optimized conditions, a turnover number (TON) of *ca.* 57 has been obtained. These catalysts can be recycled and reused without significant loss of catalytic activity.

Figure 3 summarizes some of the data. Immobilization of such catalysts on MOFs and other high-surface-area supports is underway**.**

7. Polyniobates (PONbs): catalytically decontaminating inorganic nanothreads

All-inorganic polymers based on polyniobates (PONbs) were realized that catalyze hydrolysis of many target compounds including live nerve agents and live mustard in both the liquid phase and gas phase (the latter experiments in collaboration with ECBC). The following abstract of this

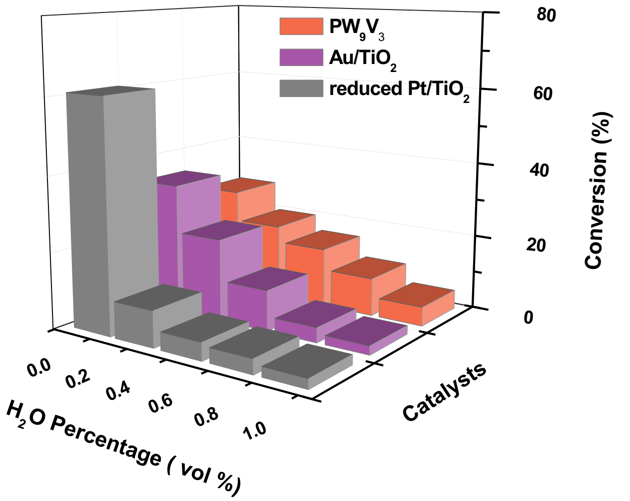

Figure 3. Oxidative removal of formaldehyde catalyzed by **PW_9V_3**, reduced Pt/TiO_2 and Au/TiO_2 in the presence of water. Concentration of formaldehyde, $[CH_2O]$ = 0.52 M, [catalyst] = 3.8 mM, 1 atm of air, 2 mL of solvent, 40 °C, 144 h.

Angew. Chem. Int. Ed. publication (DOI: 10.1002/anie.201601620) addresses some but not all the new chemistry seen with such systems:

Abstract: A wide range of chemical warfare agents and their simulants are catalytically decontaminated by a new one-dimensional polymeric polyniobate (P-PONb), $K_{12}[Ti_2O_2][GeNb_{12}O_{40}]\cdot 19H_2O$ (**KGeNb**) under mild conditions and in the dark. Uniquely, **KGeNb** facilitates hydrolysis of nerve agents Sarin (GB) and Soman (GD) (and their less reactive simulants, dimethyl methylphosphonate (DMMP)) as well as mustard (HD) in both liquid and gas phases at ambient temperature and in the absence of neutralizing bases or illumination. Three lines of evidence establish that **KGeNb** removes DMMP, and thus likely GB/GD, by general base catalysis: a) the $k(H_2O)/k(D_2O)$ solvent isotope effect is 1.4; b) the rate law (hydrolysis at the same pH depends on the amount of P-PONb present); and c) hydroxide is far less active against the above simulants at the same pH than the P-PONbs themselves, a critical control experiment.

Figure 4 gives the structures of these new P-PONb nanothreads including placement of the counter cations neutralizing the high negative chargers on the inorganic polymer. Work on the structural and dynamic properties of these systems using synchrotron radiation in collaboration with Anatoly Frenkel and co-workers at Brookhaven National Laboratory is underway as are gas adsorption studies in collaboration with John Morris at Virginia Tech. The latter work is funded by a DTRA grant, not this ARO grant which facilitated this new materials and catalysis chemistry.

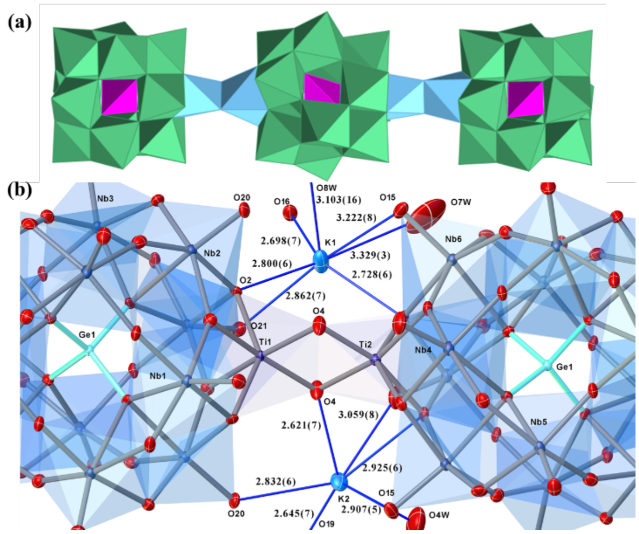

Figure 4. (a) Polyhedral representation of the one-dimensional polyanion chain of **KGeNb**. Color code: green: NbO_6; blue: TiO_6; pink: GeO_4. (b) Precise structural environments of two potassium counter cations interacting with the polymeric polyanion unit (bond lengths in Å) are shown.

8. Nontoxic immobilization of mustard oxidation catalysts on cloth samples without loss of catalytic activity (collaboration with Natick and 3 companies; work completed in 2016)

POM catalysts for air-based oxidation of mustard, developed in recent years with sole funding by this ARO grant, were successfully placed on fabrics using supercritical CO_2. The main fabric in the initial study was carbon cloth. It was quite exciting when we found that these carbon cloth-POM composites retained this catalytic air-based mustard simulant (CEES) oxidative decontamination activity. This work was in collaboration with Natick and 3 companies. Heidi Schreuder-Gibson initially approached us about a substantial effort involving the above entities for development of nontoxic, inexpensive methods to immobilize decontamination catalysts on fabrics. This large Natick-based effort had already been initiated before they contacted me. Thus, we helped by supplying the catalysts and different kinds of know-how, but we did not have funding for this work. This ARO grant funded the development of these catalysts and some of their immobilization chemistry.

Summary of most important results:

- Developed and studied polymeric polyniobates (P-PONbs), a new class of broad-spectrum decontamination catalysts
- Developed and studied gelating catalytic nanoarray (GNA) polymers whose gelating (barrier formation) and catalytic properties can be tuned. Filed patent.
- Elucidated the location and movement of POM counterions around their partner polyoxoanions by multi-dimensional NMR and other methods (in collaboration with Tinabo Liu, U. Akron)
- Elucidated the mechanism of color-change detection of the HD simulant CEES by polyvanadate systems
- Developed catalysts (vanadium-containing POMs) to catalyze oxidative removal of formaldehyde, the common carcinogenic air pollutant, using air (O2).