

Polyoxometalate-based gels and nanostructured materials for decontamination under ambient conditions

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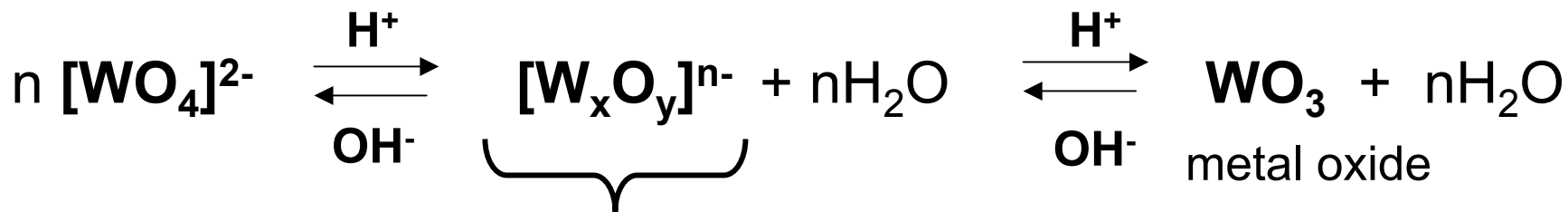
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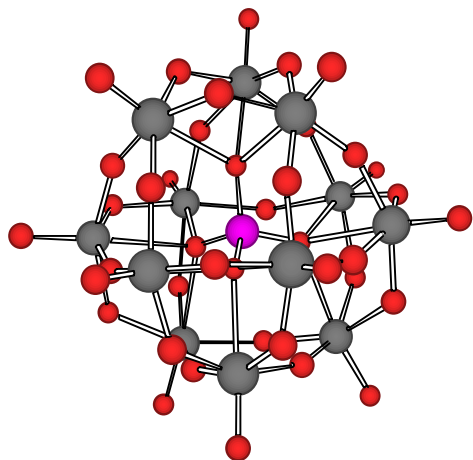
Abstract

Four new types of materials that all catalyze the desired oxidative decontamination (selective sulfoxidation) of CEES, the best mustard (HD) simulant, using simply air as the oxidant under extremely mild conditions will be described. The high reactivity for this challenging yet attractive decontamination/protection chemistry derives in all cases from the incorporation of particular catalytically active polyoxometalates (POMs) into the materials. First, a gel comprised of esterified hexavanadate (V_6) POM units will be described. This concept material exhibits 3 target properties: It swells with and physically traps CEES, changes color by CEES reduction of the V_6 units, and catalyzes the O_2 /air oxidation of CEES. The second material comprises negatively-charged POMs electrostatically bound to cationic cellulose. This “catalytic cotton” constitutes one attempt to render BDUs and other protective apparel catalytically self-decontaminating and thus more effective. The third material entails POMs electrostatically bound to cationic metal oxide nanoparticles. The fourth is a nanoporous material that forms by self assembly of silver cations and the heteropolyanion $PV_2Mo_{10}O_{40}^{5-}$. The preparation, characterization and catalytic properties of the materials will be summarized, and their common catalytic features will be addressed. This work was and is supported by Army Research Office.

Transition-metal oxygen anion clusters (polyoxometalates or “POMs”)



polyoxometalates



$[\text{AlW}_{11}\text{O}_{40}]^{6-}$ (Keggin)

Al, purple; W, gray, O, red

readily alter:

- stable (O_2 , H_2O)
- accessible
- scalable
- nontoxic
- inexpensive
- elemental compositions
- potentials
- acidities
- solubilities
- shape, size, charge
- others
- counterions

extremely versatile

An interplay and interdependence of characterization methods for soluble, insoluble and nanostructured materials

Techniques for soluble species

- (1) NMR (all nuclei in POMs)
- (2) FTIR, Raman
- (3) UV-visible
- (4) Electrochemical methods
- (5) mass spec (LC-MS/MS)

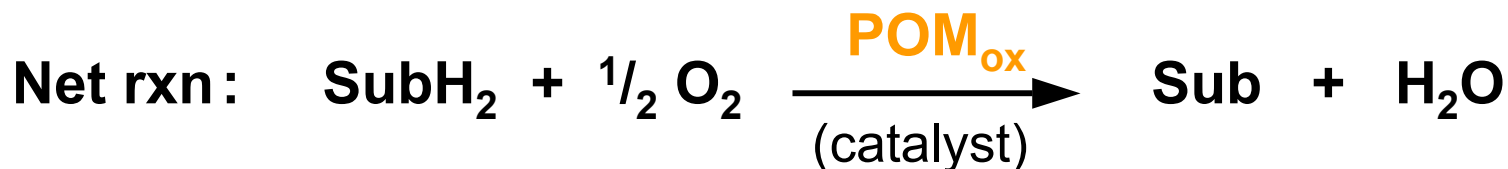
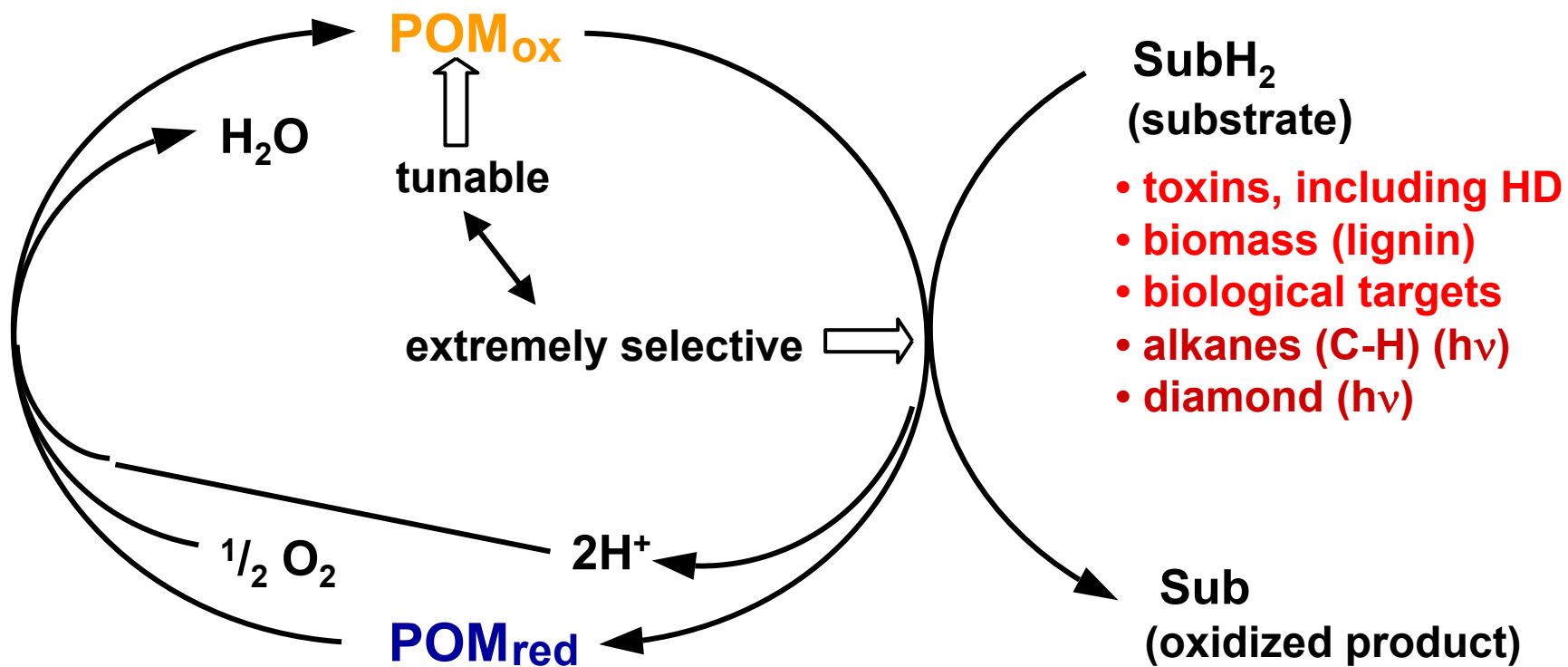
Techniques for solids

- (1) X-ray
- (2) CP/MAS NMR
- (3) SEM (SEM/EDS)
- (4) TEM
- (5) TGA & DSC

Techniques for nanostructure

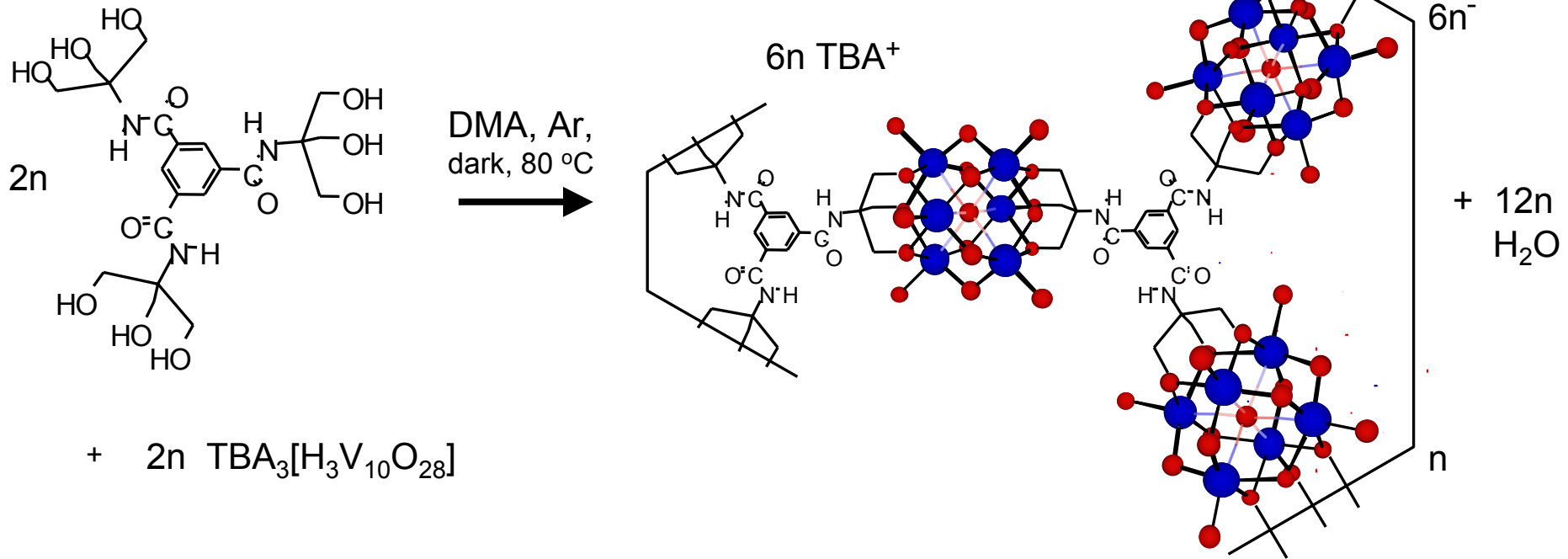
- (1) STM
- (2) AFM
- (3) SAXS

General catalytic cycle for selective O₂-based oxidation



Covalent multi-functional, nanostructured material

- One-pot self-assembly synthesis

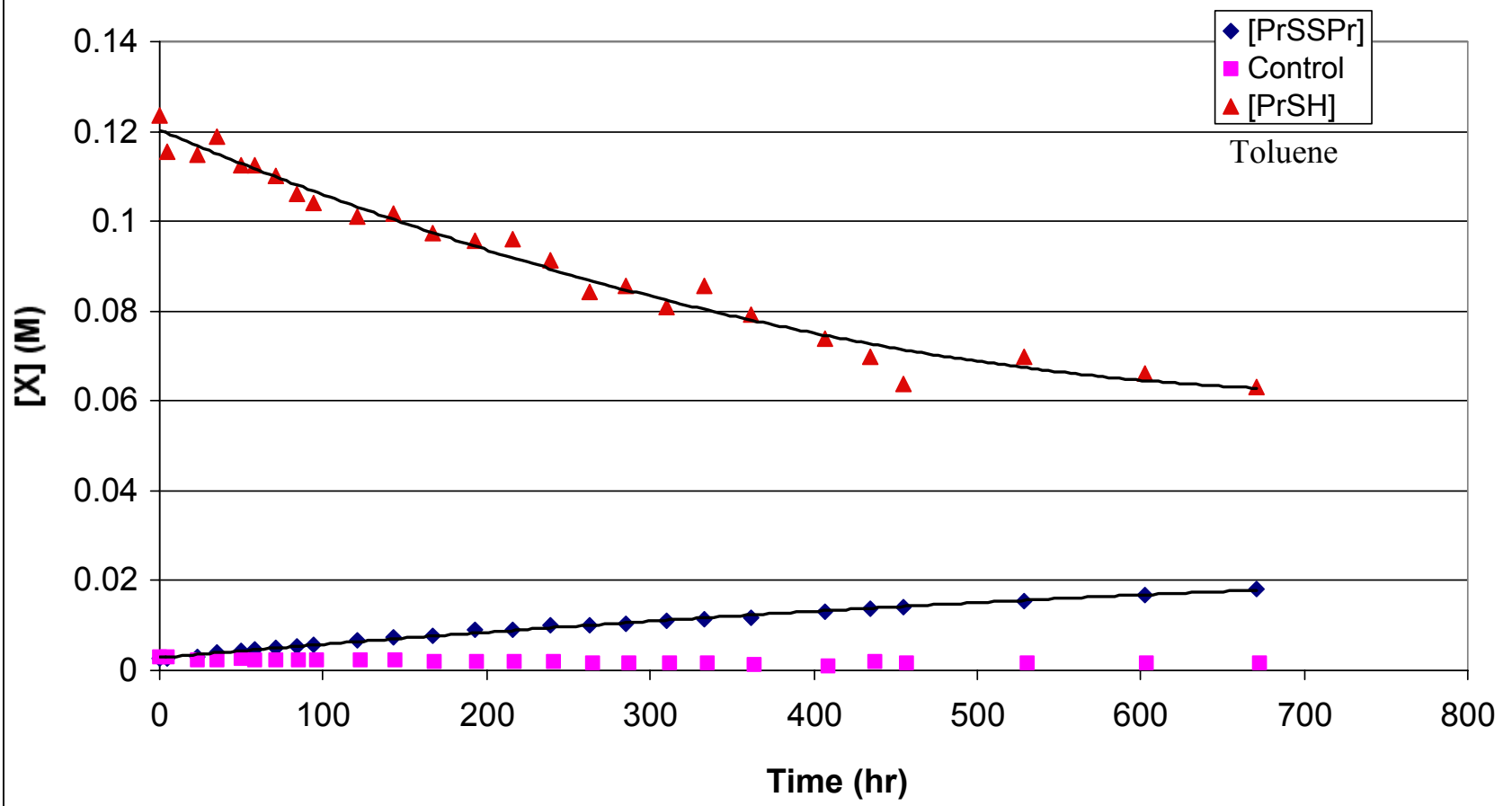


- Recognizes, bind target (swells)
- Detects target (color change)
- Catalytically transforms target (air oxidation)

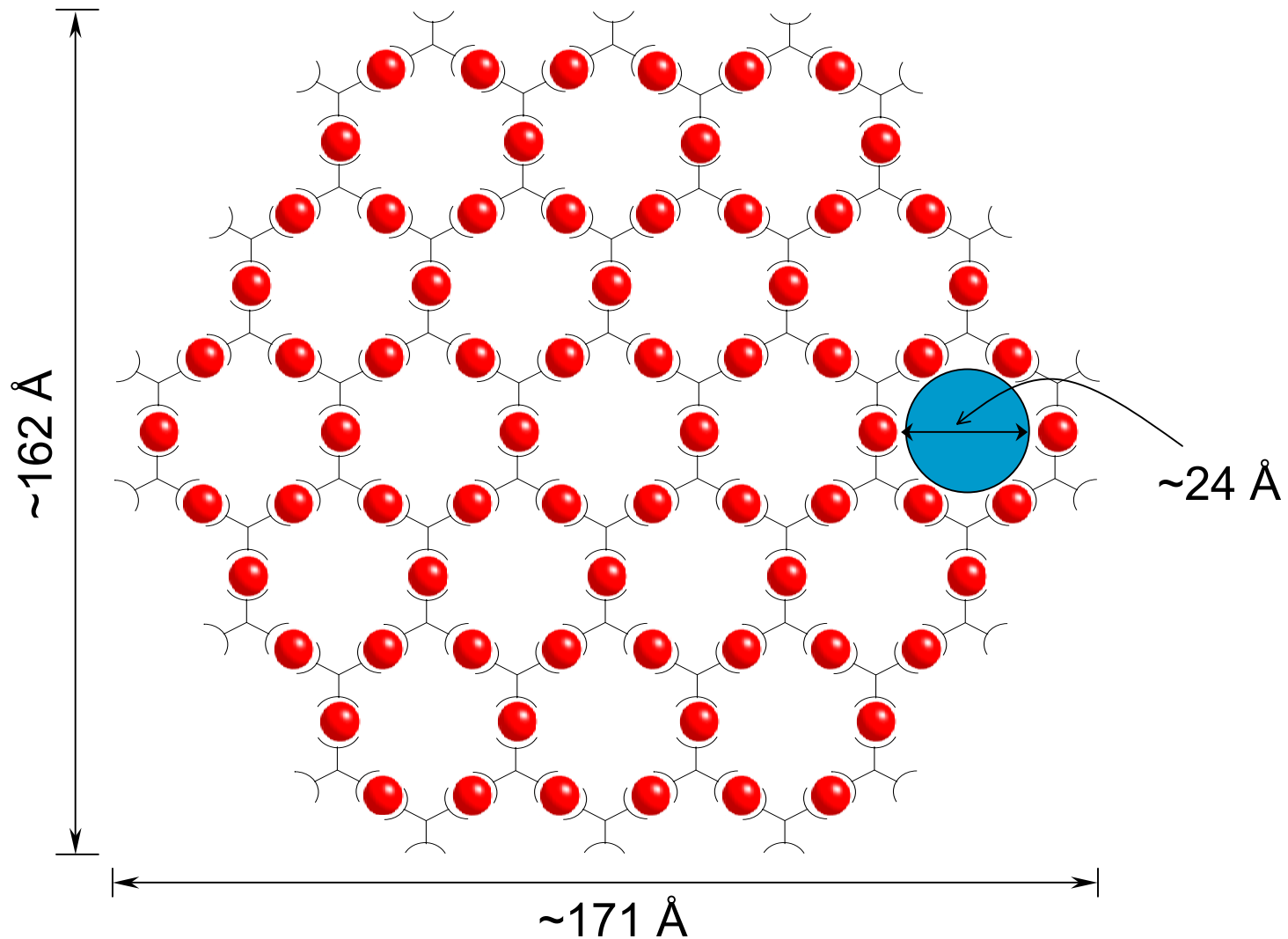
Systematically alter:

- cluster composition, linkage sizing, counterions, Controls pore size, pore polarity, swellability, etc.

Catalysis by gel (air, 25 °C)

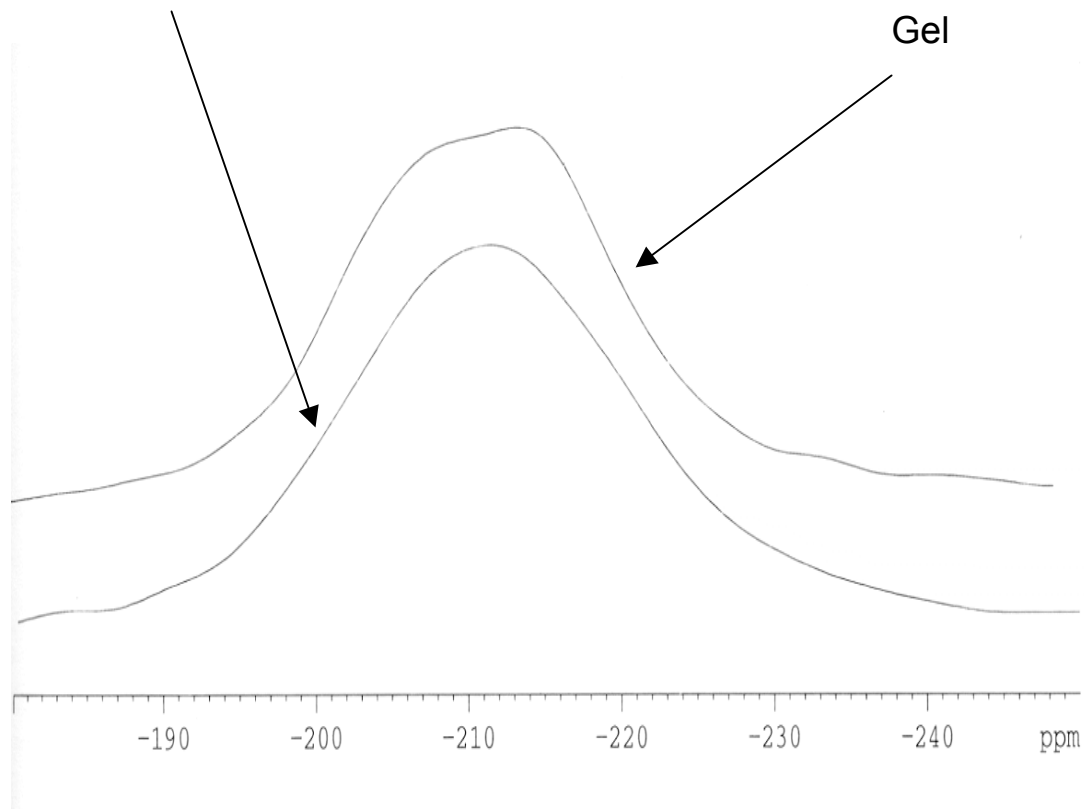
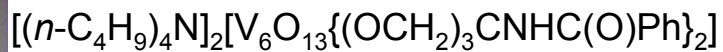
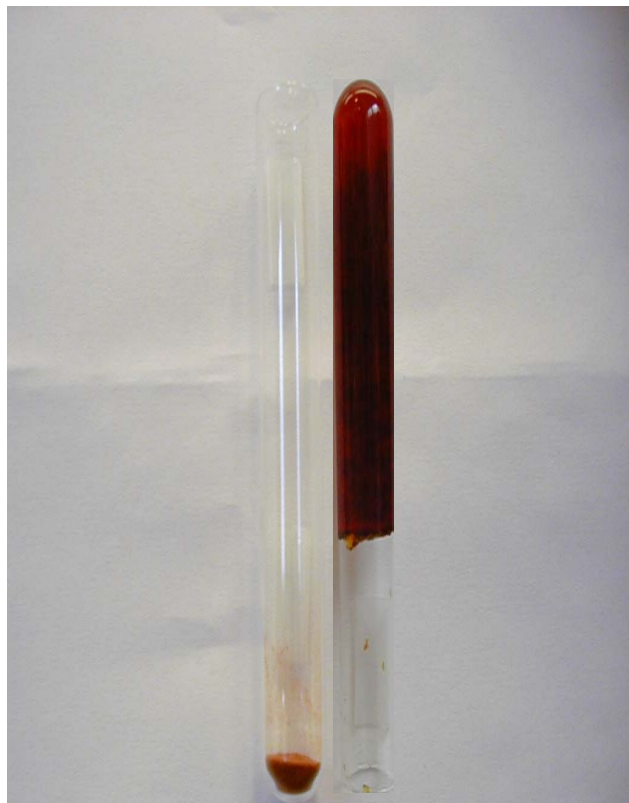


Small Angle X-ray Scattering (SAXS) gives Nanostructural Information Confirmed by X-ray Analysis of a Monomeric Model and Atomic Force Microscopy (AFM)



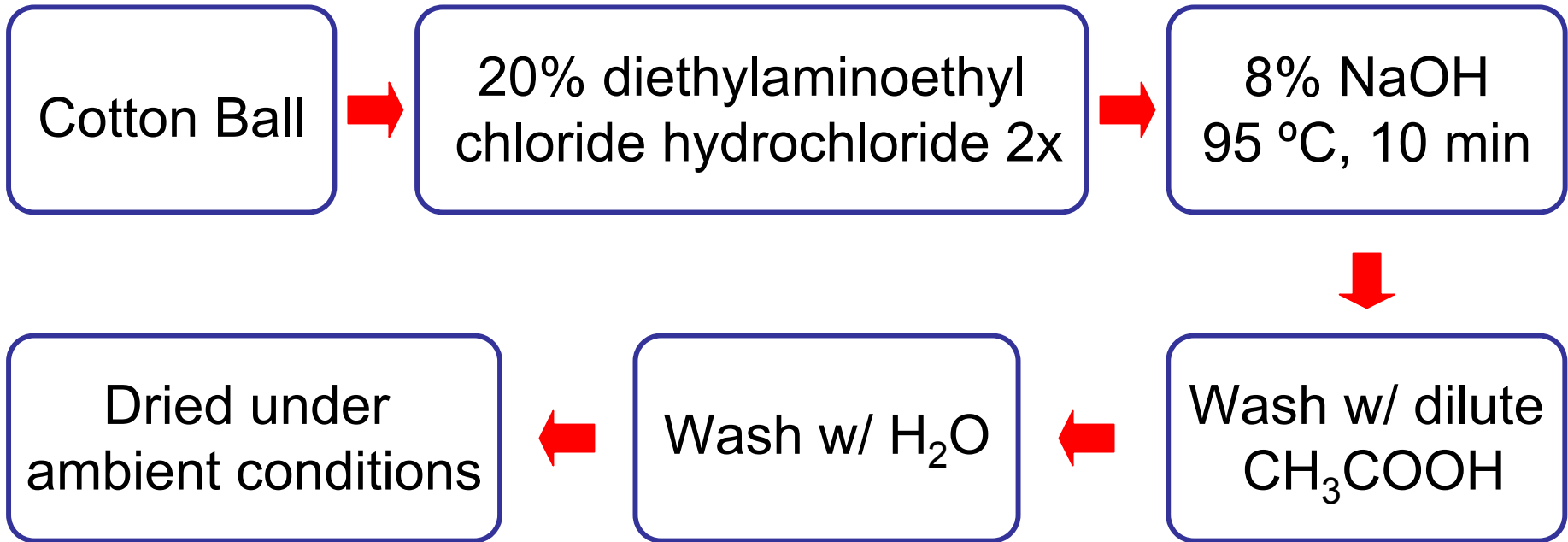
array is a gel

^{51}V Solid-State NMR of Gel and Monomer

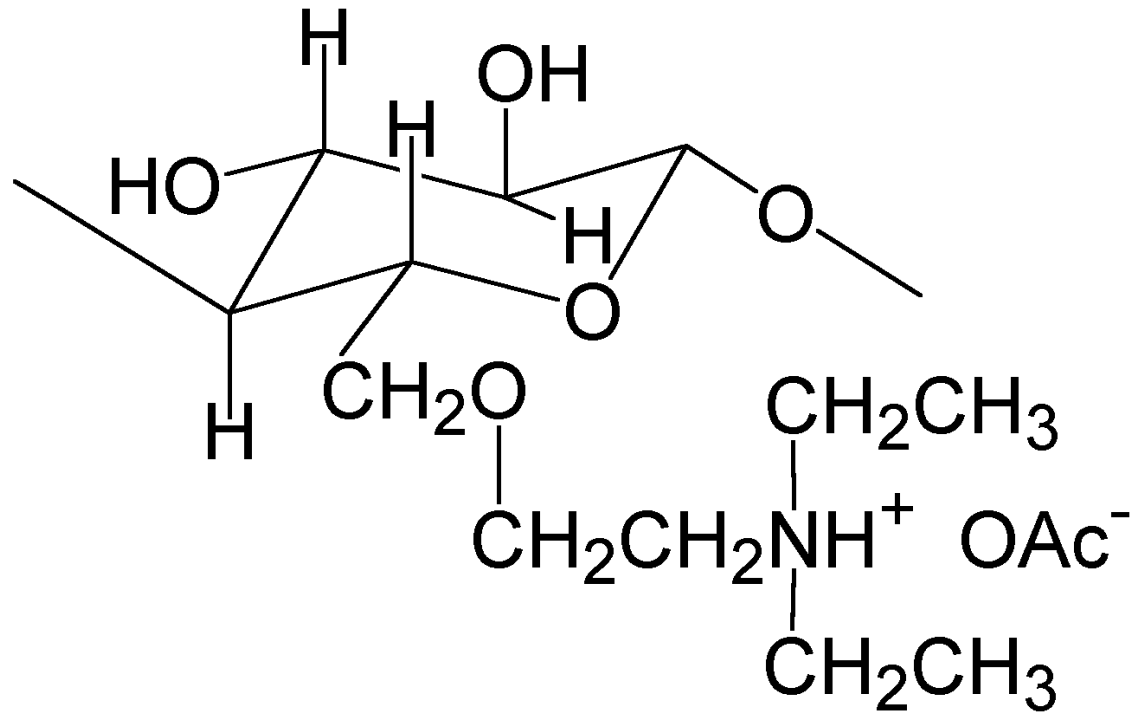


↑ ↑
before & after DMF
(same sample)

Synthesis of “Catalytic-Cotton”

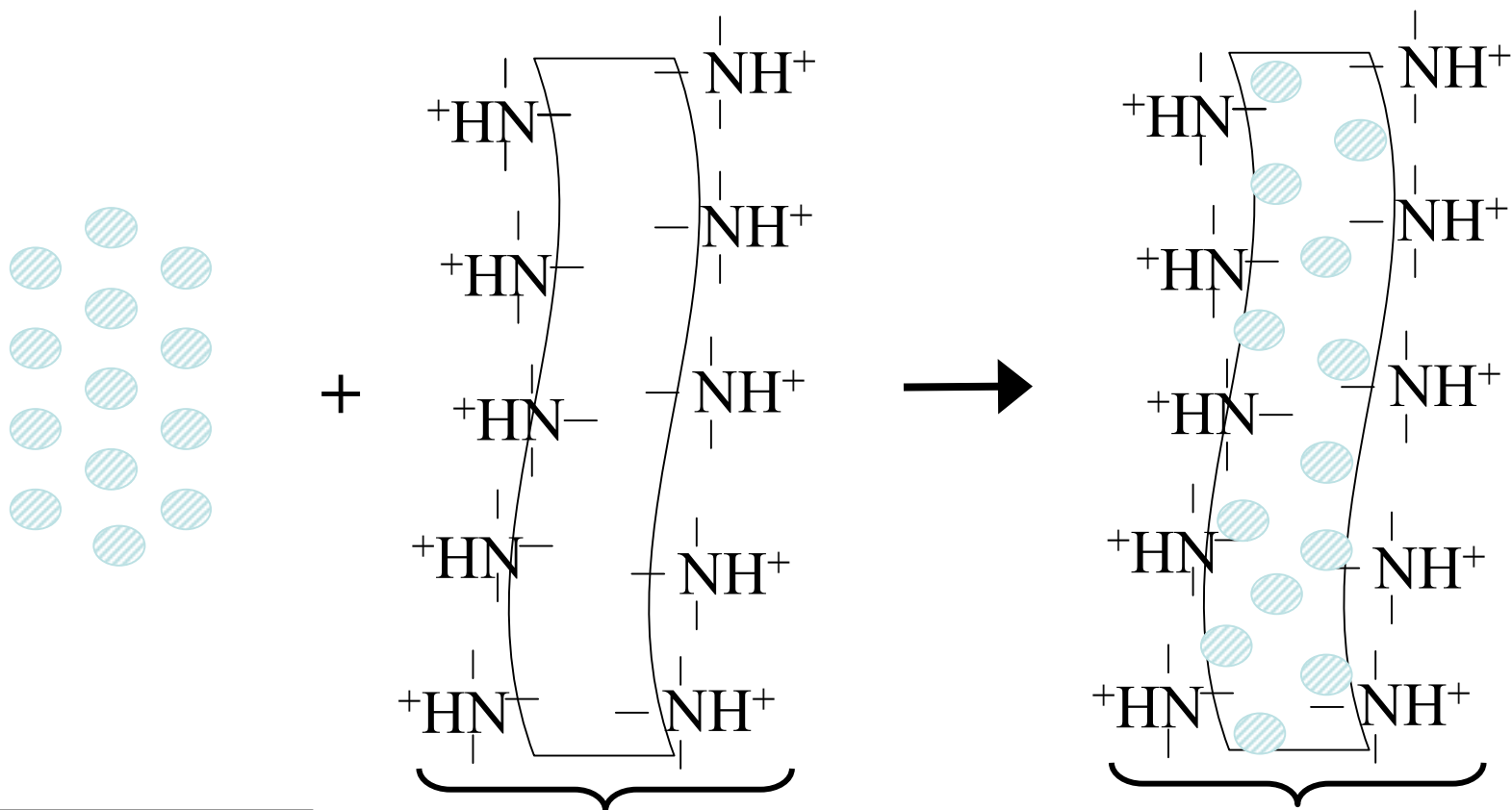


Example of DEAE-Functionalized Subunit



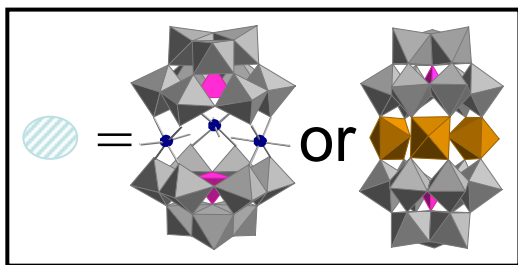
- After 2 treatments ~25% of subunits functionalized with DEAE groups

Synthesis of $\text{POM}^{n-} + \text{HDEAE-Cottons}$

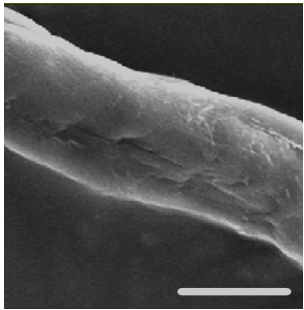


$\text{OAc}^- + \text{HDEAE-cotton}$

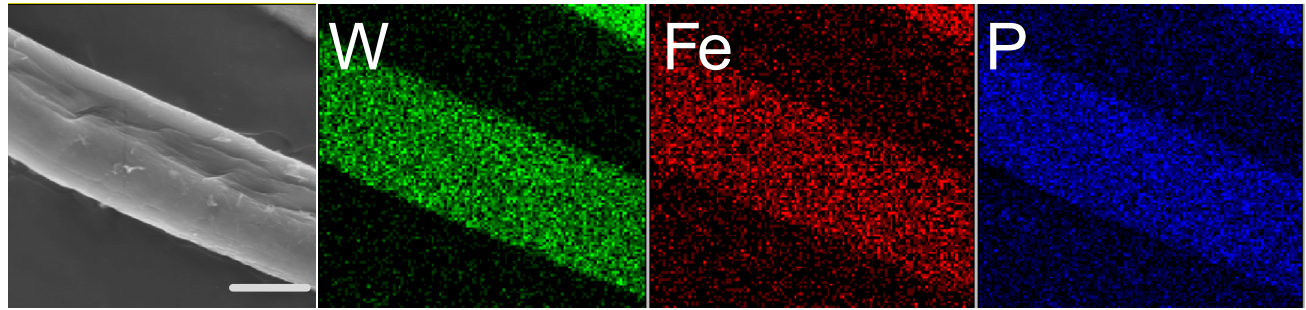
$\text{POM}^{n-} + \text{HDEAE-cotton}$



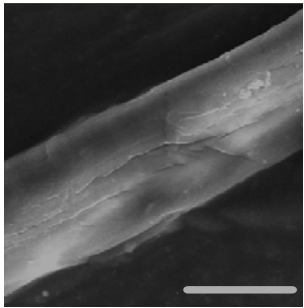
SEM-EDS



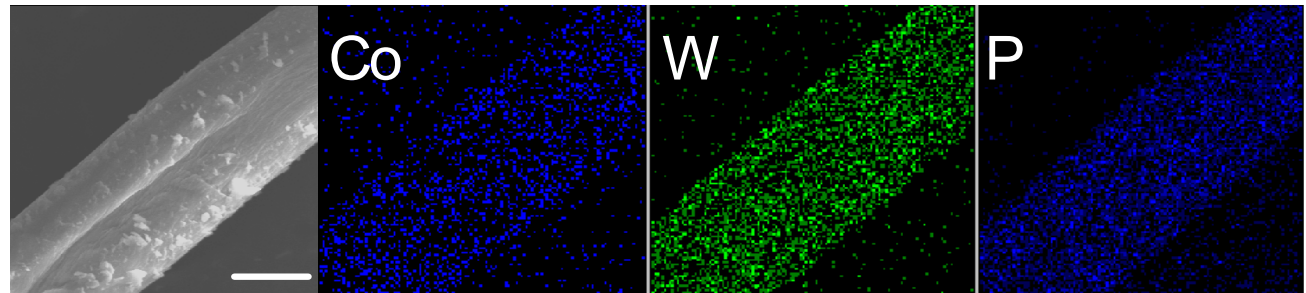
Untreated cotton



$[(\text{Fe}(\text{OH}_2)_2)_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]^{9-}$ + HDEAE-cotton



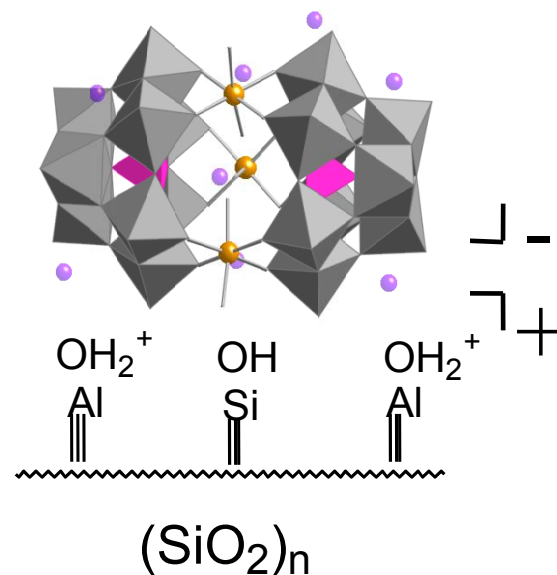
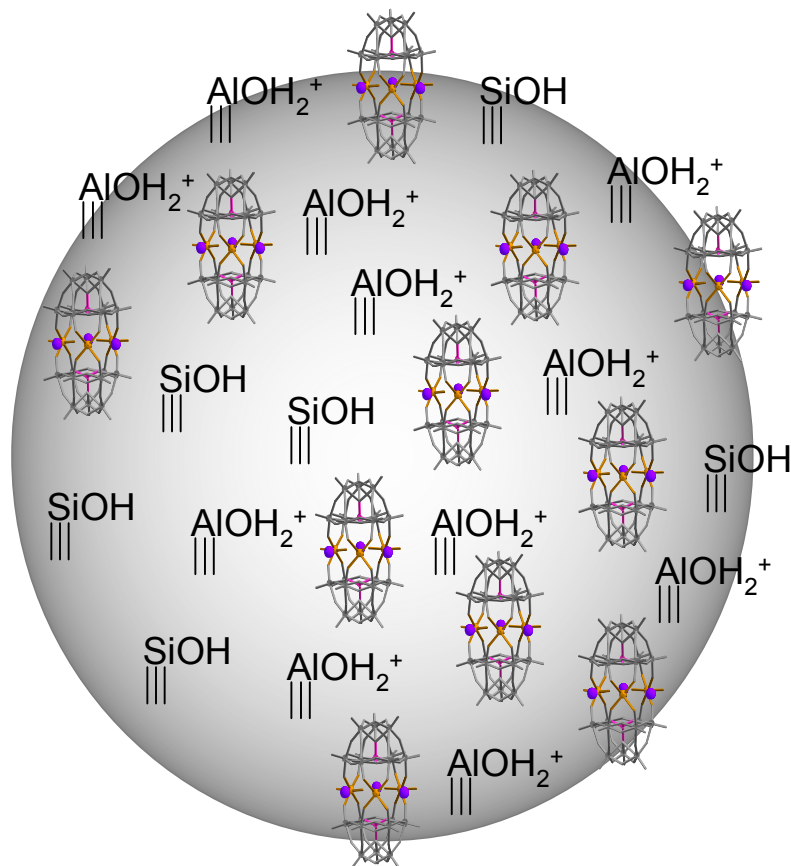
DEAE-cotton



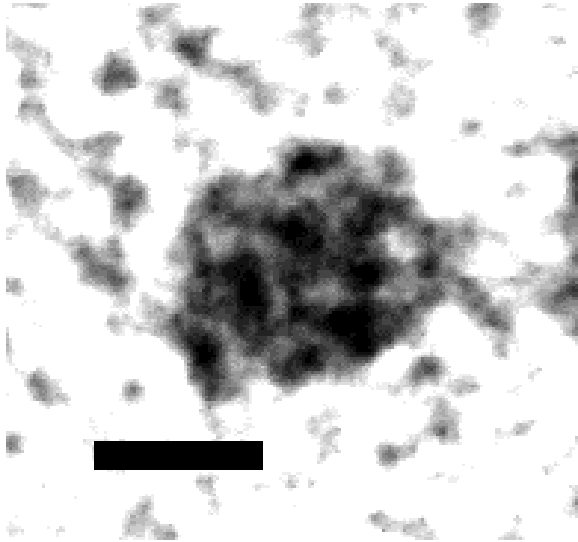
$[(\text{Co}(\text{OH}_2)_2)_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]^{12-}$ + HDEAE-cotton

Bar = 10 μm

Illustration of the electrostatic association of $\{\text{K}_8[\text{Fe}_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]\}^-$ monoanions with the cationic surfaces of the $(\text{Si}/\text{AlO}_2)^{n+}$ nanoparticles

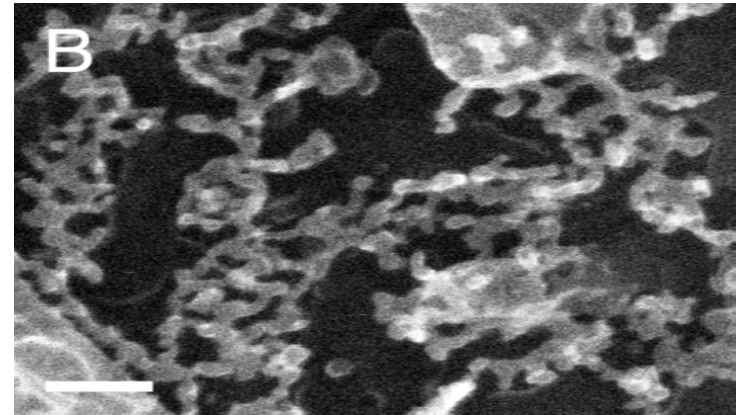
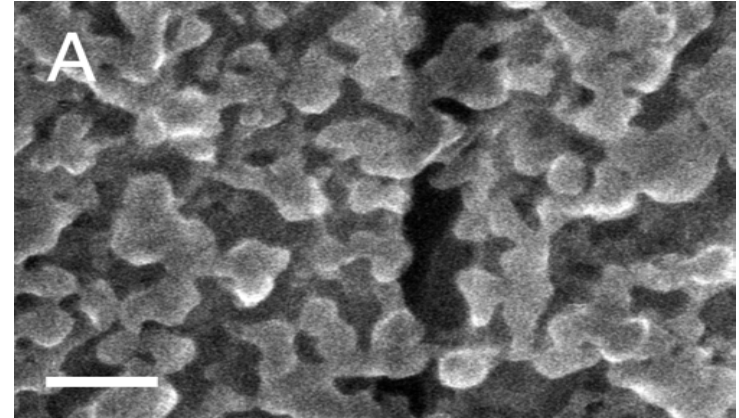


TEM and cryo-HRSEM



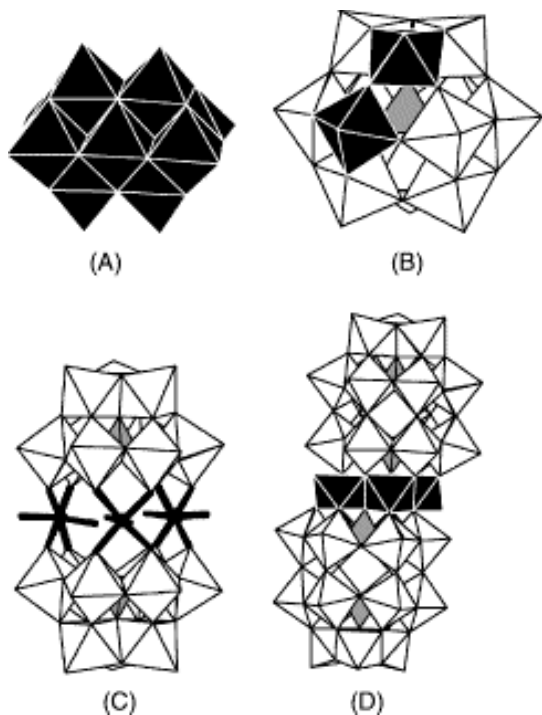
TEM image of an average-sized (~17 nm) particle of POM after catalysis. The sizing bar is 10 nm in length.

The dark spots of POM are more visible on the lighter background of the larger Si/AlO₂ nanoparticles.



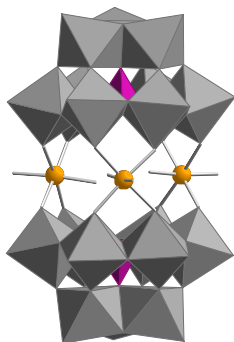
Cryo-HRSEM of cationic silica ((Si/AlO₂)Cl) and POM-nanoparticles. Both samples were aged 4 months prior to imaging.

Binary Cupric Nitrate/Triflate Systems

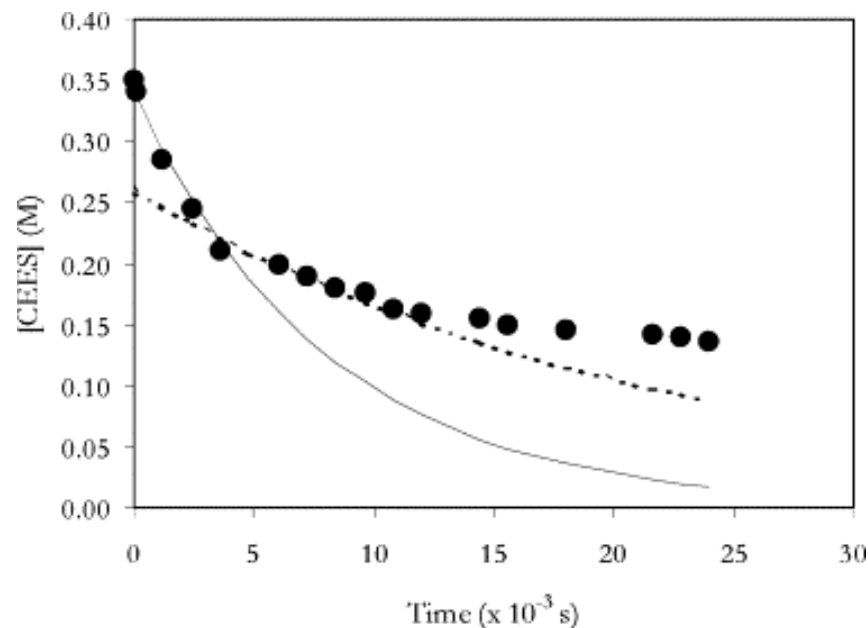
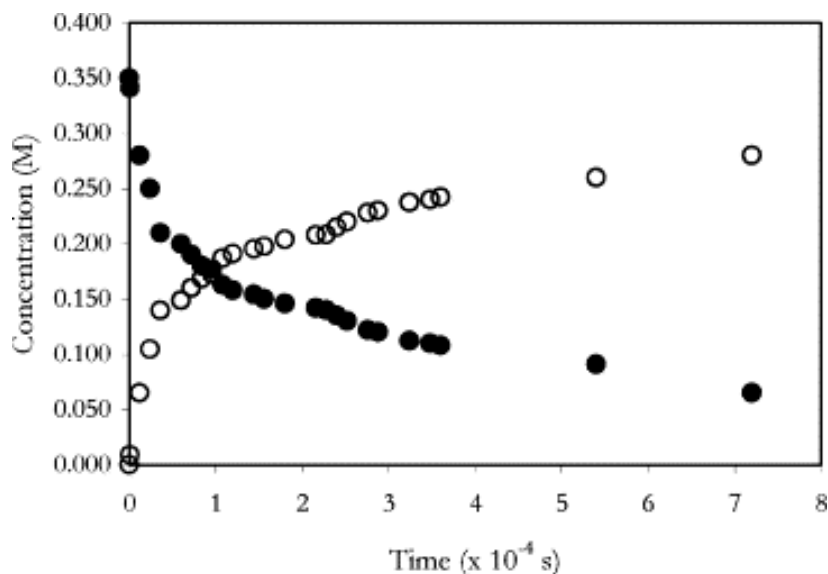


1. POMs alone (solution or solid) are ineffective.
2. Binary cupric nitrate/triflate gives ~56% conversion in 24 h.
3. Binary cupric system + POMS still only gives 56% conversion.
4. Binary cupric system + POMs on cationic silica is highly effective with up to 94% conversion in 24 h.

Binary Cupric Nitrate/Triflate Systems



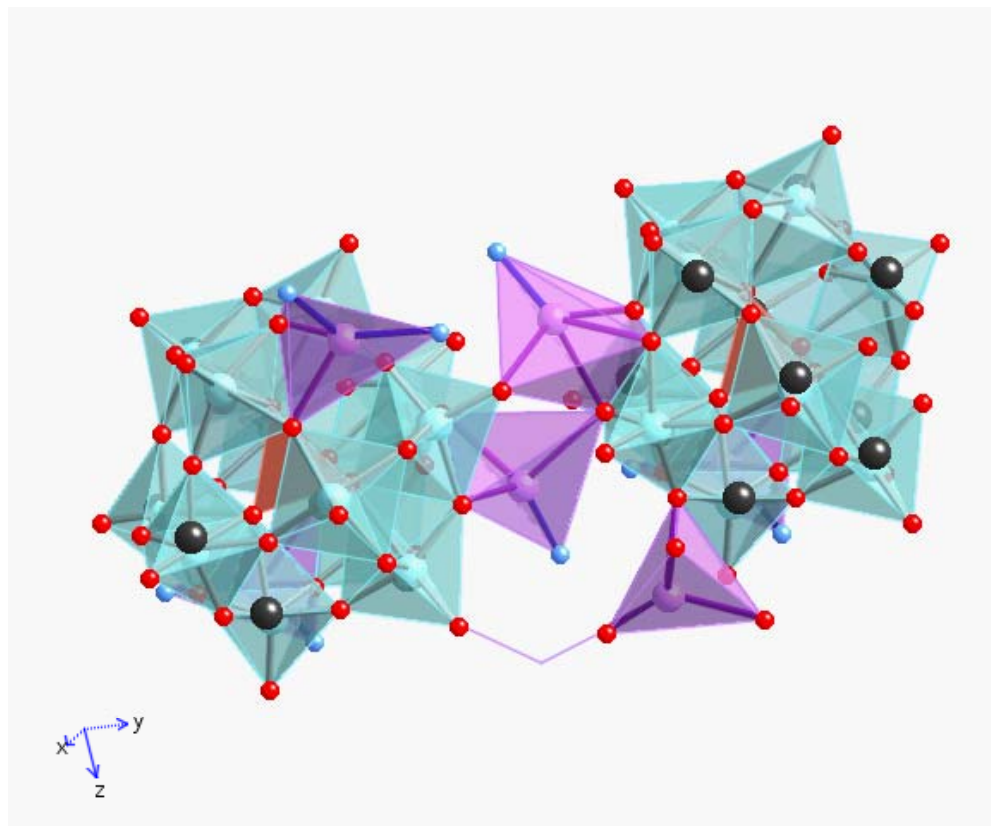
The best catalyst was the A-type Fe(III) sandwich on cationic silica plus the binary cupric nitrate/triflate co-catalyst.



$\text{Ag}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$

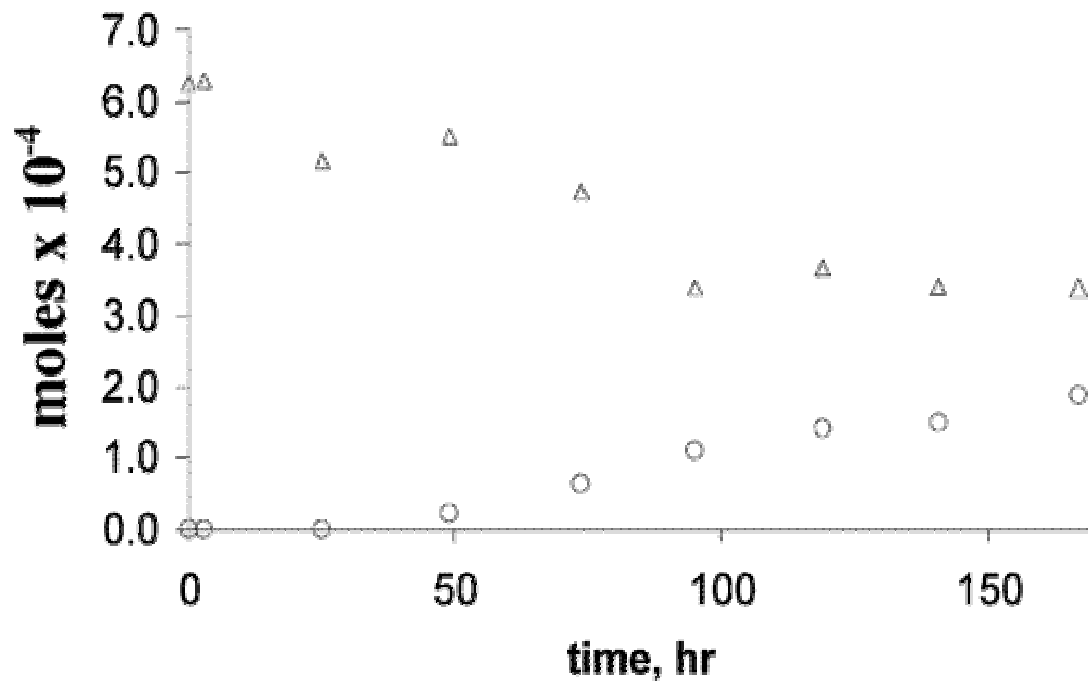
X-ray: Ag^+ bound to
POM oxygens
forming network.

Catalyzes air
oxidation of S
compounds at *R.T.*
and as a solid (3
lines of evidence)



J.T. Rhule, W.A. Neiwert, K.I. Hardcastle, B.T. Do, C.L. Hill, *J. Am. Chem. Soc.* **2001**, 123, 12101.

Oxidation of CEES to CEESO by Ag₅[PV₂Mo₁₀O₄₀] in 2,2,2-trifluoroethanol at ambient conditions (1 atm air, RT)



[CEES]₀ = 0.275 M

Support

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TDA Research

NanoScale Technologies

ONR (MDI)