

Catalytic Decontamination of Surfaces: Fundamental Considerations and Test Methods

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Outline of Presentation

- **Fundamental considerations and approach**
 - Define the goals
- **Catalyst characterization, sample preparation and test procedures**
 - Define methods to measure progress toward the goals
- **Recent results at TDA**

Fundamental Considerations and Approach

Self-Decontaminating Materials

- **Goal: powders and coatings that will self-decontaminate through catalytic reaction at ambient temperature**
- **Effective against VX, G-agents, and HD**
 - Activity against BW agents not considered here
- **Objective is non-hazardous products, not complete mineralization**
 - TDA's effort does not consider photochemical processes
- **Plan to use both hydrolysis and oxidation reactions to detoxify agents**

Applications of Self-Decontaminating Materials

- **Sorbents to extend the life of filters**
- **Use in sacrificial coatings**
 - Coating absorbs CW agent, removed to decontaminate. Here a slow reaction (e.g., >1 day to 100% decon) may still offer value: no hazmat to recover and dispose of
- **Potential use in surface decon, like the M100 kit**
- **Use in textiles for protective clothing and tentage**

Application: Military Ground Vehicles

Aircraft, Other Sensitive and High-value Assets

- **Currently use chemical agent resistant coating (CARC)**
 - Absorbs minimal amount of CW agents
 - Epoxy primer for corrosion protection
 - Polyurethane topcoat; light-stable, camouflage (visible and NIR)
 - Any modifications must maintain current features of CARC coating system



HMMWV could benefit from catalytic coating

Quantify the Challenge

Example with Agent HD

- **Assume the CW agent would be dispersed as an aerosol**
- **Heavy loading (10 g/m²) is a common assumption**
 - 0.0629 moles HD/m²
- **Light loading (1 g/m² or less)**
 - Assuming agent spread as aerosol, need to consider 1 droplet of HD; sphere 5 μm diameter; model as hemisphere on surface, 31.2 μm² area, 5.2 x 10⁻¹³ moles of agent, 0.017 mole HD/m²
 - Even in light exposure, the concentration of aerosol-dispersed agent in the covered area is fairly high

Catalyst Coverage

- **Assume catalyst particle is 1 nm diameter**
 - A monolayer of catalyst would have $\sim 2 \times 10^{-6}$ mol catalyst/m²
 - Agent/catalyst mole ratio:
 - With heavy loading: 30,000
 - Under aerosol droplet: 8,100
- **With a (theoretical) monolayer of catalyst, thousands of turnovers would be required for complete decontamination**

Structured Surface

An Approach to Increasing Effective Catalyst Surface Area

- **Potential advantage of a catalytic coating with a porous surface**
 - Consider a typical heterogeneous catalyst support, 500 m²/g specific surface area, as a surface layer on the CARC paint
 - Assume the weight of the catalyst support is 7.5 g per square meter (ca. 5% of the weight of the paint)
 - Surface area on the support is 3,750 m² per square meter of coated surface (dimensionless multiplier)
 - Now assuming the same size for one catalyst particle as before, and that 2% of the support surface area is catalyst, we have 1.6×10^{-4} moles catalyst per square meter

Structured Surface (2)

- **With an appropriate support, mole ratio of HD to catalyst:**
 - Heavy coverage: 400
 - Light coverage: 100
- **Weight of catalyst: 160 mg per square meter**
 - Assuming MW = 1,000
- **This approach could increase the number of accessible catalyst sites per nominal surface area by a factor of 80 or more**
 - Corresponding decrease in turnover number required for complete decontamination
- **Structured catalyst consistent with signature management**
 - CARC uses particulate materials (flattening agents) to lower gloss

Catalyst Characterization, Sample Preparation and Test Procedures

Characterization of Structured Catalysts

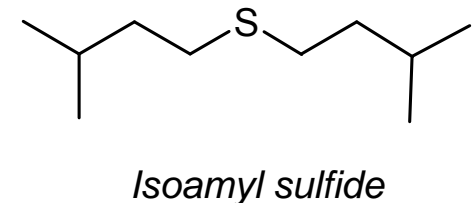
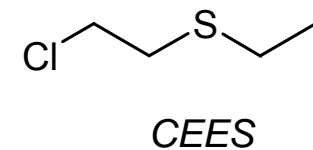
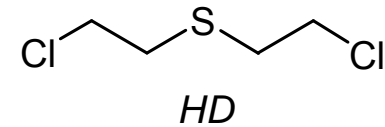
- **Can use standard methods developed for industrial catalyst**
 - Elemental analysis
 - TGA
 - Surface area (BET)
- **The best probe would be the catalytic activity itself**

Implications for Catalyst Development and Testing

- **Tests must be able to distinguish between developmental catalysts that have only a fraction of the required activity per time**
- **Test with surrogates (e.g., thioether for HD)**
 - Later work must validate with live agents
- **Use of structured catalyst increases surface area available for reaction, can simplify experimental challenge of evaluation**

HD Surrogates

- **Vapor pressures at 20 to 25 C**
 - HD: 0.00095 to 0.00145 atm
 - CEES: 0.01039 atm at 22 C
 - Isoamyl sulfide: 0.00116 to 0.00139 atm
- **CEES: similar structure, more volatile**
 - Difficult to recover in heterogeneous experiments; need closed system
 - Higher VP may lead to significant mass transport via gaseous diffusion, not representative of HD behavior
 - May react with some nucleophilic materials, as can HD
- **Isoamyl sulfide: VP similar to HD**
 - Easier to recover and quantify
 - Will only undergo oxidation
 - Greater steric requirement may affect reactivity



Screening with HD Surrogates

- **Identify reaction products**
 - Sulfide should be oxidized to sulfoxide, not sulfone (the sulfone of HD, although less toxic, is still a vesicant)
 - Confirm that product inhibition does not limit turnover
- **To achieve mass balance, try to quantify both unreacted substrate and reaction products as a function of time and other conditions**
 - Experimental difficulties in quantifying oxidation products
 - All tests at ambient temperature
 - Vary atmosphere: in cases where oxidation is expected, changes in reaction rate or product distribution under N₂, air and O₂ will help to confirm aerobic oxidation
 - Vary humidity

Tests with CEES, Closed Reactor in Air

Choice of conditions to maintain sufficient O₂, minimize amount of CEES in vapor phase. Columns: (1) CEES loading in 300 mL reactor (2) CEES in vapor phase (3) Equivalents of O₂. A useful experiment has 100 mg CEES (5.3 equivalents O₂).

CEES Loading (mg)	% CEES Evaporated	Mole ratio O ₂ :CEES
10	100	53
20	80	27
30	53	18
40	40	13
50	32	11
100	16	5.3
150	11	3.5
200	8	2.7
400	4	1.3

Sampling Methods

- **Thermal desorption is undesirable: heating may promote reaction**
- **If the substrate or reaction products are extracted with a solvent for analysis, important to assure that the reaction is not occurring in the extraction solvent**
 - Use appropriate controls
- **Desirable to recover and quantify reaction products, e.g., sulfoxide or sulfone**
 - Low volatility complicates analysis
- **Desirable to follow course of the reaction, but difficult in sealed vessel**

Measurement of Gas Uptake

- **Changes in volume or pressure could be used to follow the reaction**
 - In oxidation reactions, O_2 is converted to a non-volatile product, so the pO_2 and total pressure will change
 - In hydrolysis reactions, $H_2O_{(g)}$ is similarly converted to a less-volatile product
 - Experimentally challenging to measure small changes in partial pressure of water

Development Plan

- **Move toward goal in small steps, verifying activity at each step**
 - Homogeneous solution
 - Dispersion
 - Use of fluorocarbon solvent
 - Thin liquid film
 - Solvent-free catalyst powder
 - Catalyst on surface

Tests in Homogeneous Solutions

- **Both catalyst and substrate soluble**
- **Relatively easily monitored by sampling and analysis**
- **Dramatic differences in mass transport in stirred solution vs. reaction on dry surface**
- **If the reaction product (e.g., sulfoxide) is soluble in the solvent, there is a mechanism to minimize product inhibition that is not available on a dry surface**

Tests in Dispersions

- **One change from the homogeneous solution experiment: change the solvent so that the substrate is still soluble, but the catalyst is insoluble**
 - Verify activity before proceeding
 - Assumption: if the catalyst is not active with a solvent to transport substrate to the catalyst site and remove product, it will not be active in a coating.
- **Test a stirred, fluid mixture**

Use of Fluorocarbon Solvents

- **Allows one small change from the dispersion experiment: possible to select systems where the catalyst is insoluble and the substrate insoluble or only sparingly soluble**
- **Particularly useful for oxidative catalysts**
 - Expect high O₂ solubility in fluorocarbons
- **Test a stirred, fluid mixture**

Tests in Thin Liquid Film

- **One change from dispersion: test a static (not stirred) system**
- **To enhance mass transport, prepare a thin film**
 - Spin coating may be useful
- **Model for catalyst activity within a permeable polymer matrix**
- **May require new experimental configuration**

Tests in Solvent-Free System

- **Use catalyst in powder form, neat simulant or agent**
 - Difficult to disperse simulant evenly within catalyst powder; may use mechanical agitation
- **One step from dispersion: no solvent**
- **Challenging to follow course of reaction**
 - May need to prepare and test multiple samples
- **If the substrate or reaction products are extracted with a solvent for analysis, important to assure that the reaction is not occurring in the extraction solvent**

Catalyst on Surface: Sample Preparation

- **Design decision: is the test polymer matrix permeable or impermeable to substrate and O₂/H₂O?**
- **Agents and reactants have some solubility in polyurethane coatings**
 - Diffusion may be slow, tests difficult
- **Use impermeable test coating, deposit catalyst on surface**
 - Catalyst within coating will be inactive; need to maximize fraction of catalyst on surface

Characterization of Sample Test Surfaces and Their Reactivity

- **Spectroscopic analysis of reactants or products *in situ***
- **For structured surfaces, could measure active surface area (BET)**
- **Test reactivity with surrogate or agent**
 - Gas uptake
 - Extraction for analysis

Application of the Substrate to Sample Test Surfaces

- **Neat liquid – difficult to disperse evenly**
- **Deposit substrate as aerosol**
 - Consistent with CW agent dispersion as aerosol
- **Droplet size is a significant component of the test protocol**

Materials Compatibility

- **Current chemical agent resistant coating (CARC) has epoxy primer and polyurethane topcoat**
- **Catalyst incorporated into/onto topcoat**
- **Catalytic coating must be durable, not alter critical properties of coating: corrosion protection, low observable, etc.**
- **Catalyst must maintain service life of coating**

Recent Results at TDA Research

Measurement of Catalyst Activity, Supported Catalyst Dispersion

- **Stirred heterogeneous mixture**
- **CEES as simulant**
- **Monitored reaction by GC analysis of aliquots**
- **Observed 55% removal in 2 hours, 100% removal (~23 catalyst turnovers) in 3 days.**
- **CEES sulfoxide detected after reaction**

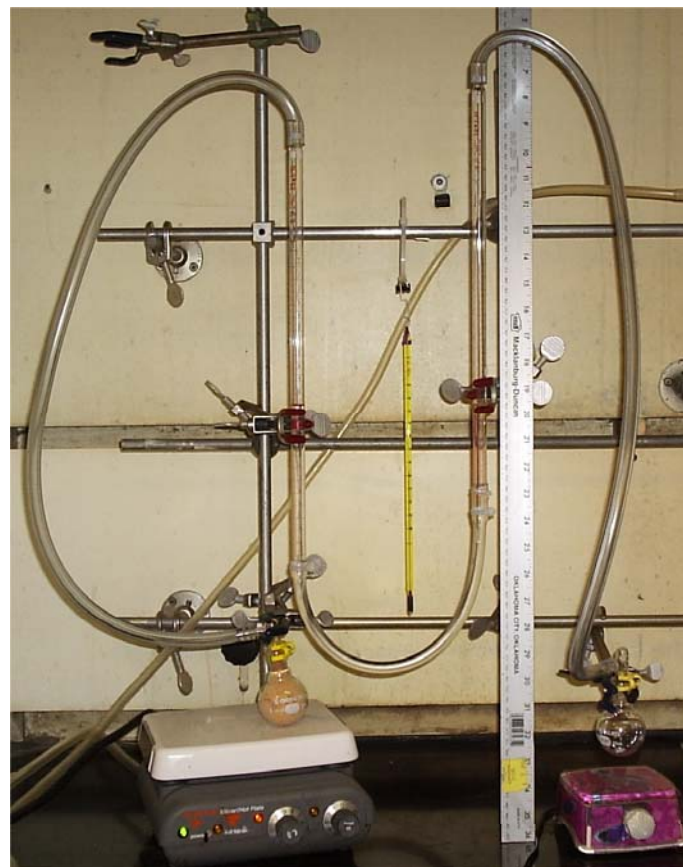
Oxidation of CEES in a Static Container

- Container must have sufficient volume of air to provide oxygen for reaction
- At 5:1 mole ratio O_2 :CEES, 13% of CEES is in vapor phase
- It should be possible to follow the oxidation reaction by measuring oxygen consumption using either a gas burette or a pressure transducer



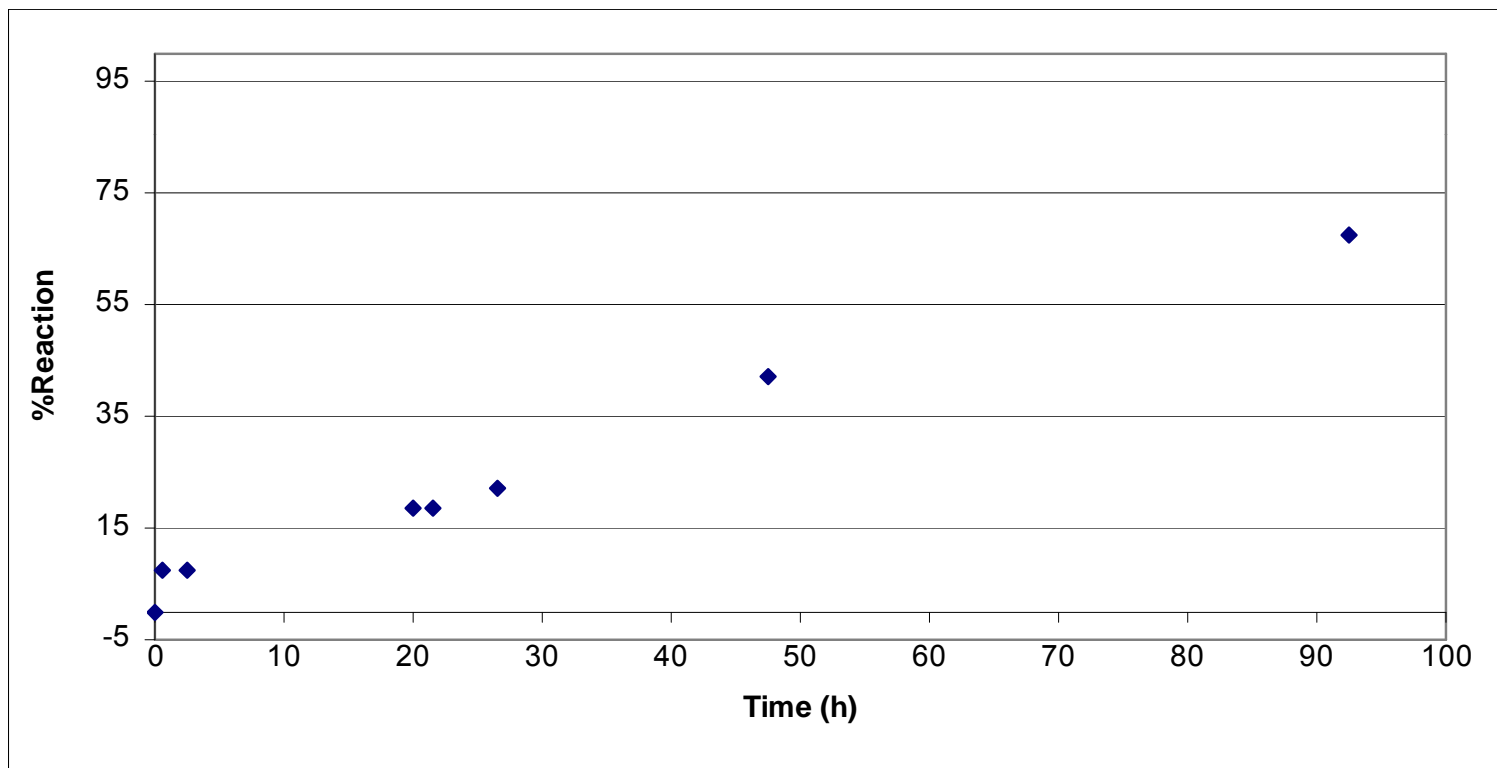
Oxygen Uptake Apparatus

- Dual gas burettes partially filled with oil
- One flask holds the stirred catalyst/substrate and the other is a reference flask
- Both flasks sealed at same time with identical initial volume, temperature and pressure
- Uptake measured by change in volume at constant pressure



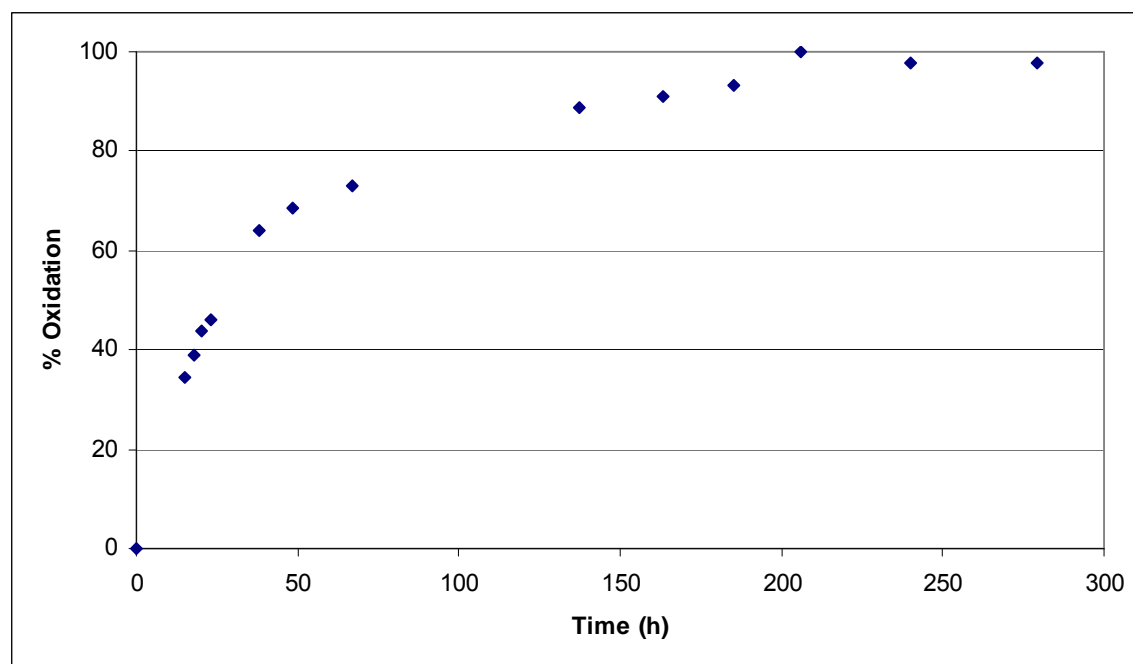
Measurement of Oxygen Uptake, Supported Catalyst and CEES in Fluorocarbon Slurry

- After 139 hours, 80% of CEES oxidized, 25 catalyst turnovers

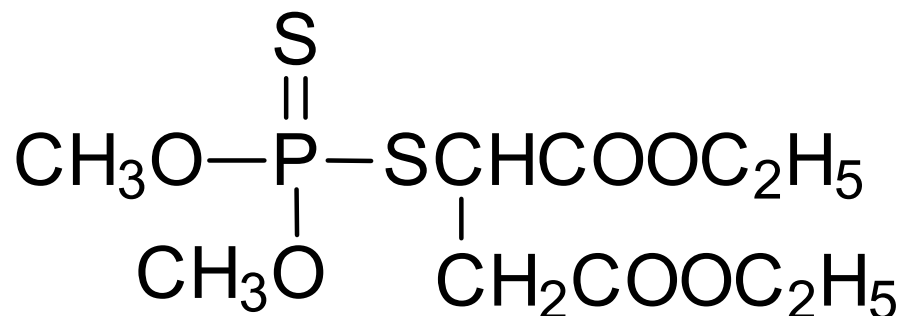


Measurement of Oxygen Uptake, Supported Catalyst and CEES in Solvent-Free System

- Supported catalyst as powder, neat CEES; mechanical agitation
- Catalytic oxidation of CEES; ~20 turnovers
- Oxidation stops after conversion of sulfide to sulfoxide
- Reaction significantly faster than in fluorocarbon system
 - Rate in fluorocarbon may be limited by diffusion of CEES to catalyst



Results with Malathion



- Initial tests show 40% of Malathion (6 turnovers) consumed after 2 days over a dry catalyst
- Tests in toluene solution show 40% oxidation after 2 d (12 turnovers)
- O₂-uptake measurements show more O₂ consumed than expected- there may be further oxidation of the leaving group

Preparation of Coated Panels

- **Use epoxy primer, highly crosslinked**
 - From CARC qualification test, known to be impermeable to HD
- **Adjust viscosity and cure kinetics**
 - Apply, wait specified interval; coating is partially cured but still tacky. Apply supported catalyst as powder, remove material that does not adhere; repeat as necessary. Allow coating to cure completely
- **Resulting coating has significant fraction of catalyst particles on surface**
 - Analogous to methods to prepare non-skid coatings

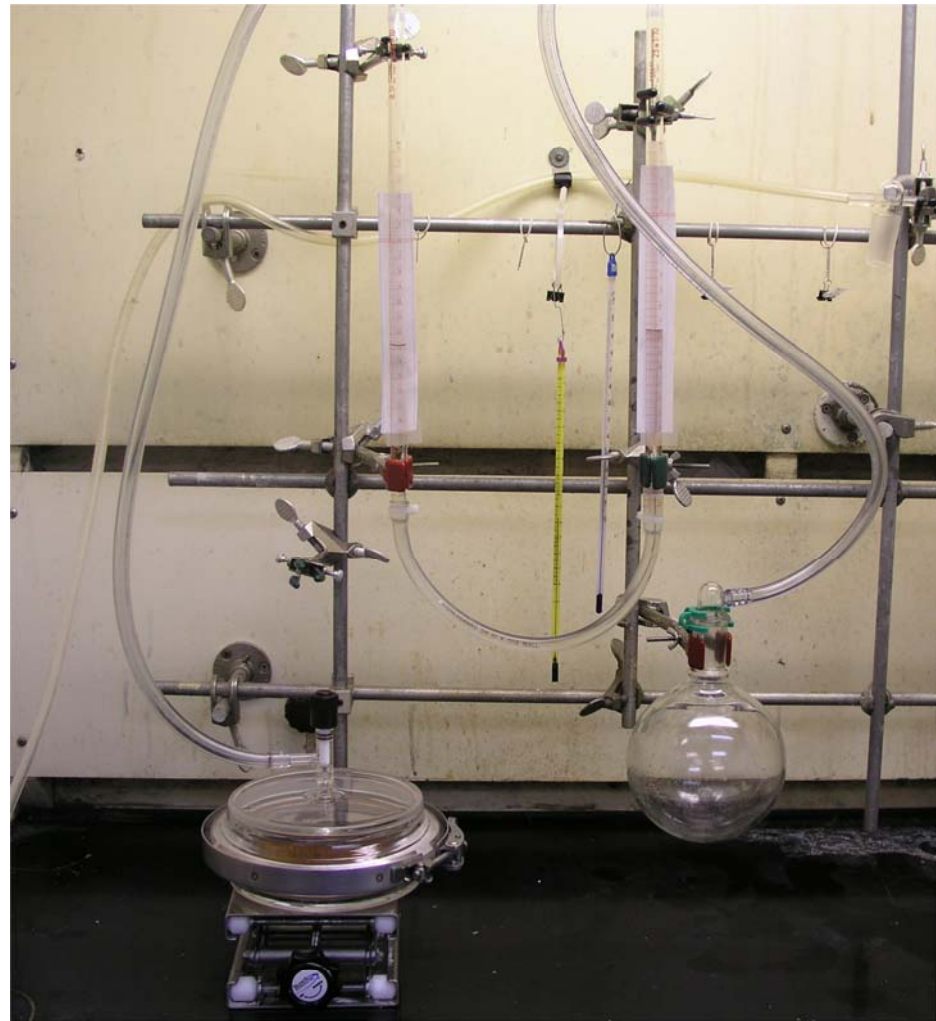
Catalyst on Coated Panels

Steel coupons that were used to test the activity of the supported catalyst for CEEs oxidation. Left: epoxy coating only. Right: supported catalyst on epoxy coating.



Tests of Coated Panels

Catalytic oxidation of CEEs on a coated surface. The apparatus on the left holds a metal disc that has been treated with an epoxy primer coating, then catalyst. The apparatus is connected to a dual gas burette. A 1 L flask (right) is used as a reference so that the oxygen uptake measured is not complicated by changes in the ambient temperature and pressure.



Tests with HD

- **At CUBRC (Buffalo)**
- **Supported catalyst as powder, neat HD; mechanical agitation**
- **Ambient temperature, sealed vessel under air, 28-hour test**
- **Only partial recovery (~40%) of HD in control (support only); much lower recovery in presence of supported catalyst (~5%)**

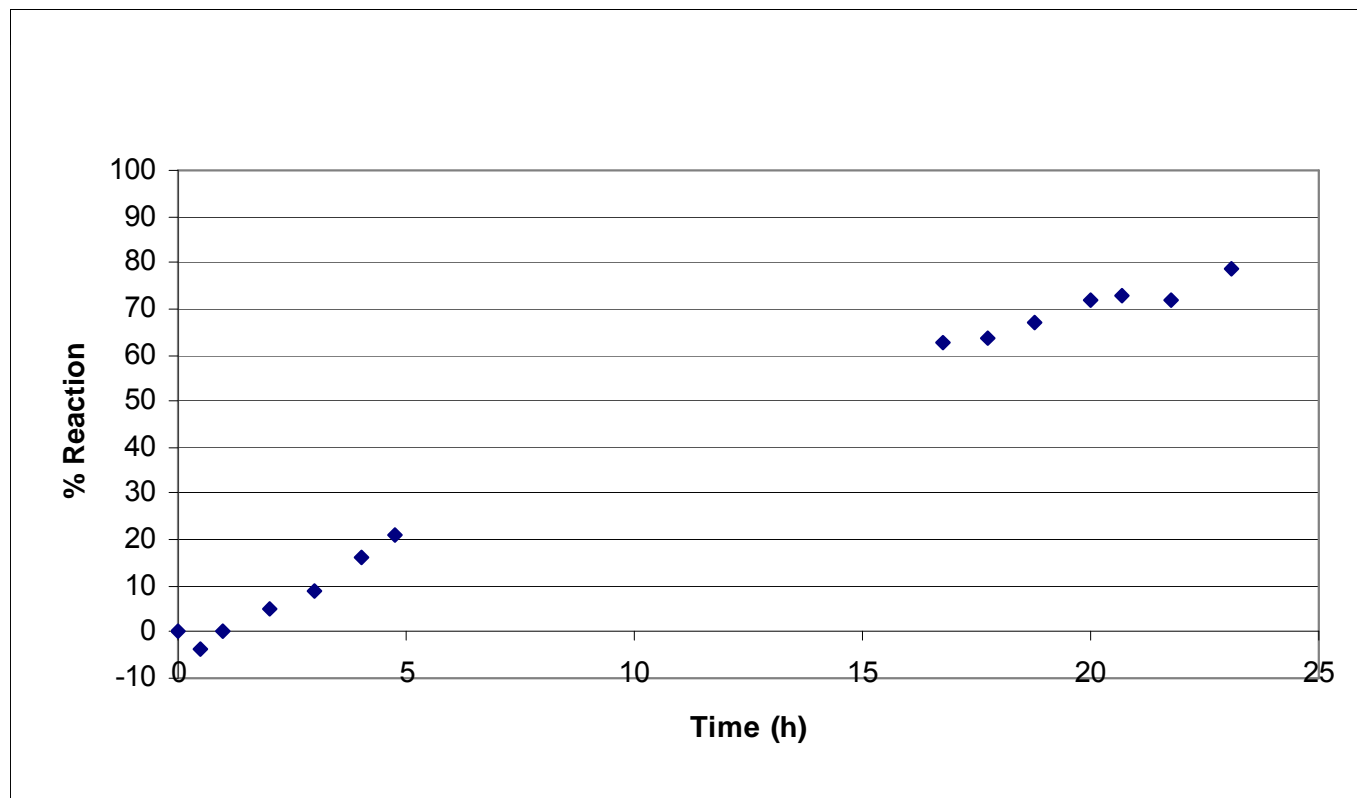
Tests with HD



Assembly of two dual gas burettes for HD tests at CUBRC. The dual burette on the left was connected to a flask with the catalyst and HD (and to an empty flask as a pressure reference). The dual burette was connected to a flask that held untreated catalyst support and HD.

Measurement of Oxygen Uptake, Supported Catalyst and HD in Solvent-Free System

- Supported catalyst as powder, neat HD; mechanical agitation
- Based on difference between HD recovery with catalyst and control, 6 to 7 turnovers
- After extraction, HD-sulfoxide found in supported catalyst sample, not in control
- Faster rate than earlier test with CEES; modified catalyst



Summary

- **Structured surfaces could improve catalyst loading and performance in reactive coatings**
- **Stepwise approach to catalyst development**
- **Use of O₂ uptake measurement to follow course of oxidation reactions**
 - TDA tested catalysts in dispersion, fluorocarbon slurry and dry powder, with CEES and HD
 - Test with HD showed oxygen uptake and sulfoxide formation consistent with aerobic oxidation
- **Demonstrated activity with Malathion**
- **Measuring reactivity on surfaces**

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