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Catalytic Neutralization of Organophosphate Simulant Over Undercoordinated Fe, Cu, Co, and Zn on SiO2

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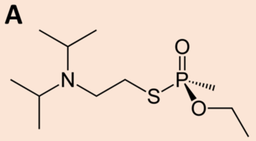
Background

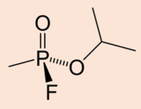
- Organophosphates (OP) inhibit normal breakdown of neurotransmitters

A



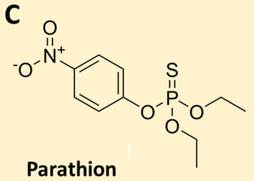
VX
Chemical Warfare
$LD_{50,rat}$ = 0.007 mg/kg
Imperial Chemical Ind.
England (1952)

B



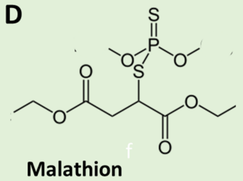
Sarin
Chemical Warfare
$LD_{50,rat}$ = 0.55 mg/kg
IG Farben
Germany (1938)

C



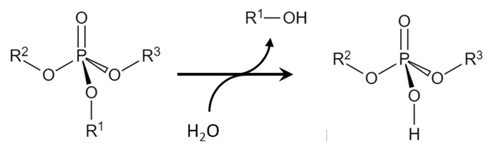
Parathion
Pesticide
$LD_{50,rat}$ = 2 mg/kg
IG Farben
Germany (1947)

D



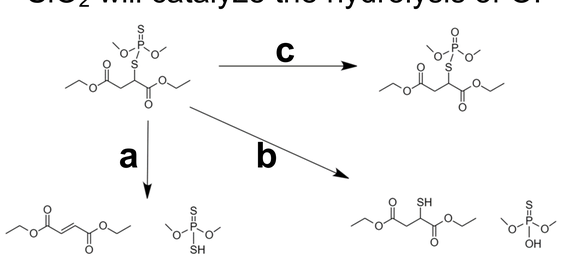
Malathion
Insecticide
$LD_{50,rat}$ = 290 mg/kg
American Cyanamid Co.
USA (1956)

- Zn dimers, Zr clusters neutralize OP by hydrolyzing its best leaving group



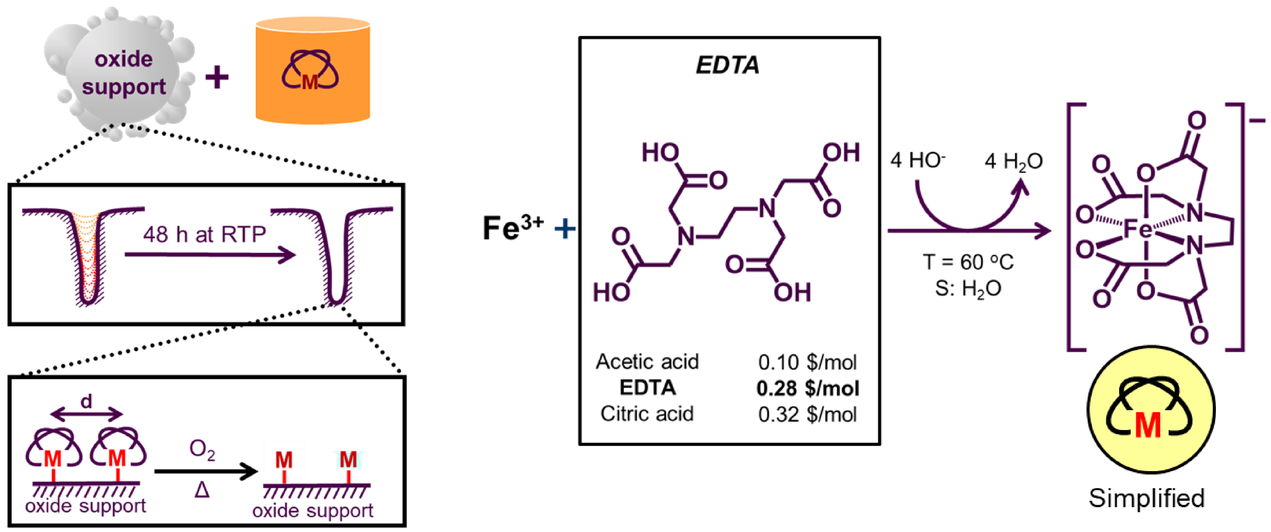
Hypothesis

Low-coordination transition metals on SiO_2 will catalyze the hydrolysis of OP



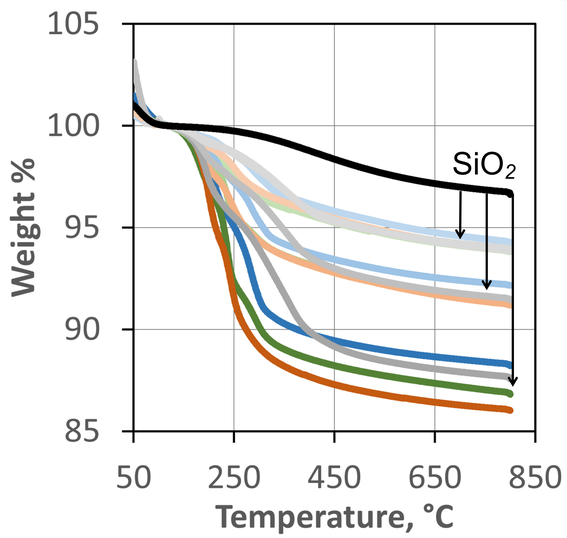
- 3 potential reactions; a & b preferred

Simple, versatile, and scalable preparation of catalysts and precursors



Acetic acid	0.10 $/mol
EDTA	**0.28 $/mol**
Citric acid	0.32 $/mol

EDTA mass loss correlates to loading

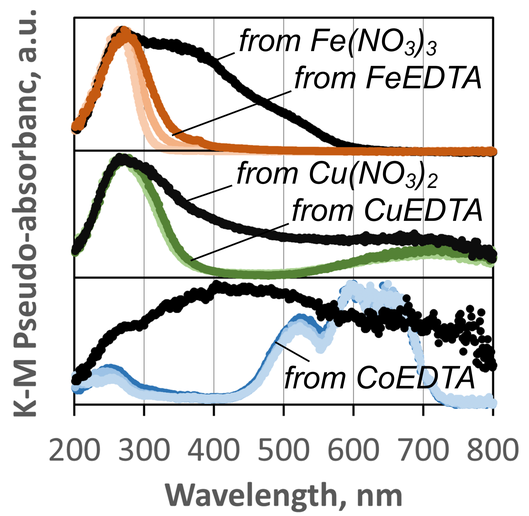


- Ligand mass loss as metal loading proxy
- Metal loadings of 0.6–2.4 wt%
- Surface density of 0.16–0.64 nm^{-2}

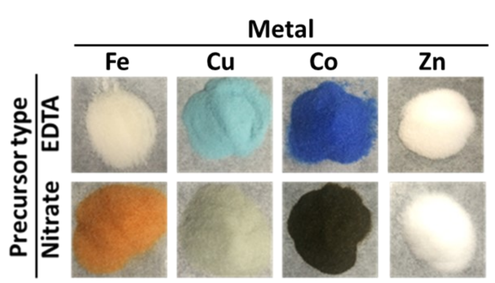
Instruments

- TA Instruments TA500
- Agilent Cary60 + Pike Tech DiffusIR

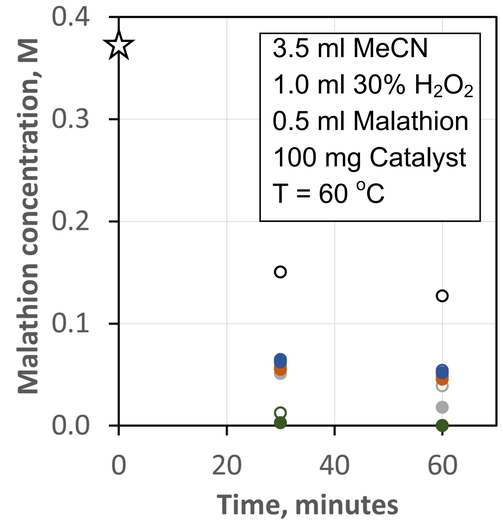
EDTA promotes metal dispersion



- Higher dispersion relative to M-nitrates



Catalytic OP neutralization w/ H_2O_2



- No reaction without H_2O_2
- No activity-precursor relations
- No selectivity-precursor relations
- ~ 1-to-1 reaction a to reaction b
- Activity increases Co = Fe < Zn < Cu

Homogeneous reaction of OP with •OH

Instrument Shimadzu GC2030-FID/NPD

References

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