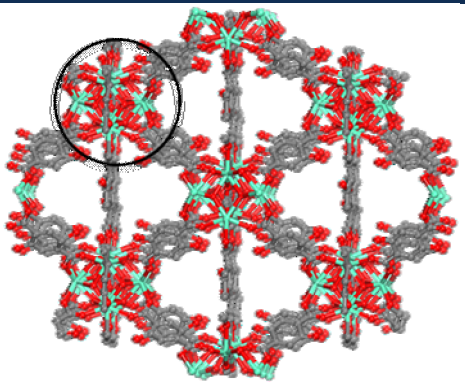
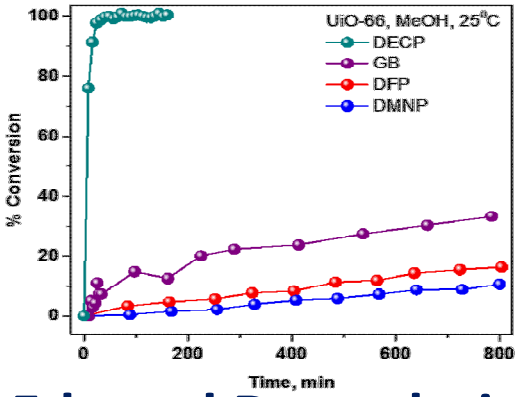
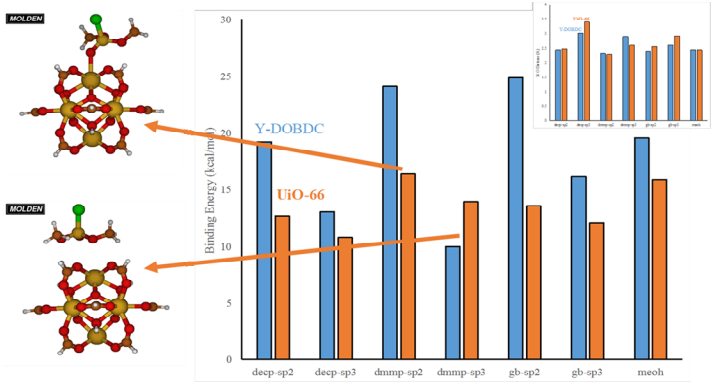
SAND2017-8912C







Insights into the MOF-based Degradation of Organophosphates in Non-Aqueous Media: a Combined Experimental-Modeling Study

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Jared DeCoste, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD

2017 ACS Fall Meeting, Washington DC

Fundamental Aspects of Metal Organic Framework Catalysis

August 20, 2017

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Goal: investigate chemistries to degrade organophosphates in water free environments

Sandia National Laboratories

Sandia has worked in the area of chemical and biological decontamination since the mid 1990s

Fundamental understanding of materials chemistry → **Engineering delivery options** → **Enabling technologies**

Sandia DF-200: Broad Spectrum Decontaminant

More than a decade of testing has proven EasyDECON DF200 to be effective against:

Biohazards (Bacteria, Spores and Viruses)

- Aspergillis Niger
- Avian Flu H5N8
- Avian Flu H5N1
- Bacillus Anthracis (Anthrax)
- Bovind Coronavirus
- Candida Bombicola
- Cholera
- Citrus Canker
- Clostridium Botulinum
- Clostridium Difficile (C.diff)
- Staphyloccus Ssp.
- Erwinia Herbicola
- Escherichia Coli (E.coli)
- Feline Calicivirus
- Foot & Mouth (FMD)
- Hepatitis A (HAV)
- HIV Type 1
- Influenza A
- Listeria Monocytogenes
- Mycobacterium Bovis
- Norovirus
- Penicillium Digitatum
- Tuleremia
- Plague – Y. Pestis
- Pseudomonas A.
- Pseudomonas F.
- Rhinovirus – Mult. strains
- Ricin Toxin
- Salmonella Enterica
- Salmonella Choleraesuis
- SEB (Staph Toxin)
- Staph A (MRSA)
- Smallpox
- Stachybolys chartarum
- Yellow Fever Virus

https://intelagard.com/portfolio/easydecon-df200/

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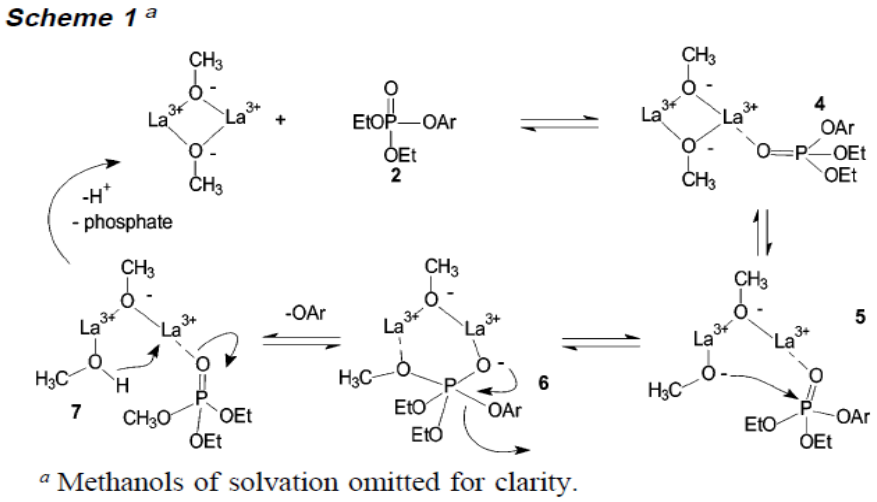
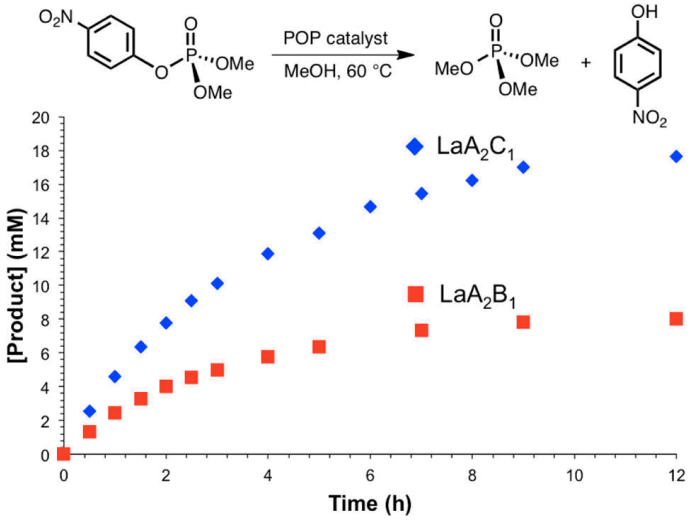
Limited literature on the solvolysis organophosphates

Methanolysis of organophosphates is accelerated by La-based catalysts

Billion-fold Acceleration of the Methanolysis of Paraoxon Promoted by La^{3+} complexes



La $^{3+}$ catechol-functionalized POPs show accelerated activity towards methanolysis



J. Am. Chem. Soc. **2003**, *125*, 7602-7607.

ACS Catal. **2013**, *3*, 1454−1459.

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Rare earth-based MOFs are not prevalent

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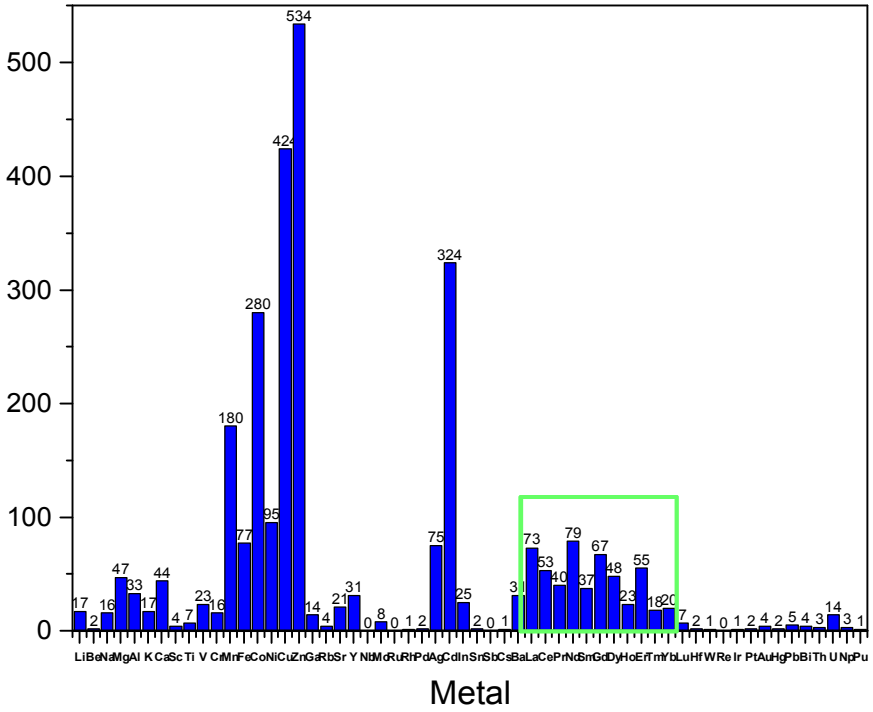
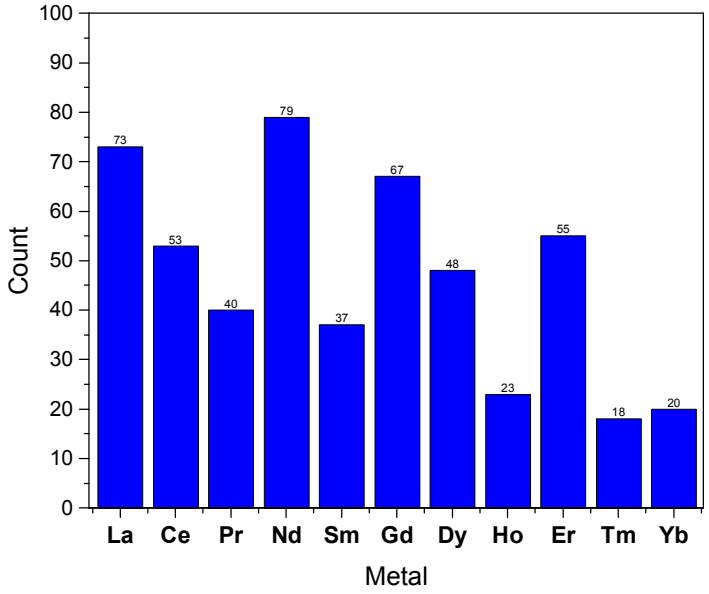
MOF structures by metal type





Unique features of RE metals in the context of MOFs:

- High coordination numbers to generate metal clusters with ***catalytically active*** unsaturated metal centers
- Similar coordination chemistry to aid systematic studies on isostructural MOF series

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RE-DOBDC platform based on a building block akin to prototypical Zr-hexanuclear cluster

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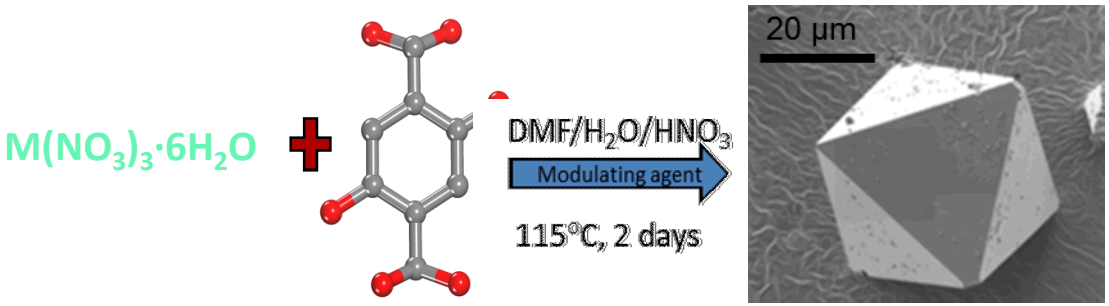
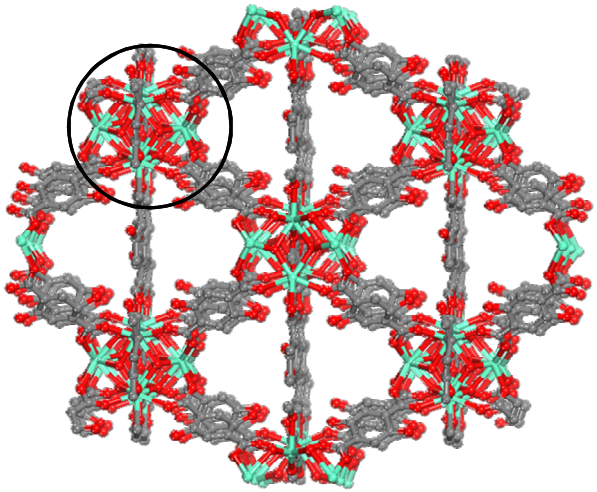
Proof-of-concept prototype structure

Single-crystal X-ray diffraction

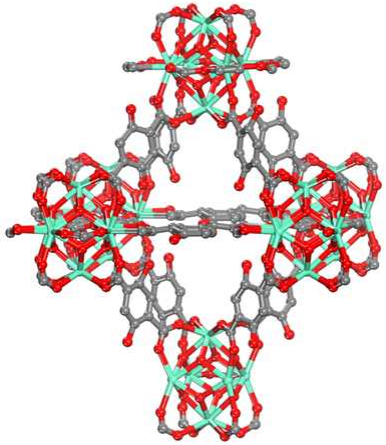
Tetragonal, 3D framework
P4NC
a= b= 15.5567 Å
c= 21.334 Å
α=β=γ= 90° = V= 5163.06 Å^3





$M_6(\mu_3\text{-}OH)_8(C_8H_4O_6)_5(C_2H_6O_6)_1(H_2O)_6{\cdot}24\ H_2O$

M= Eu, Nd, Yb, Y, Tb

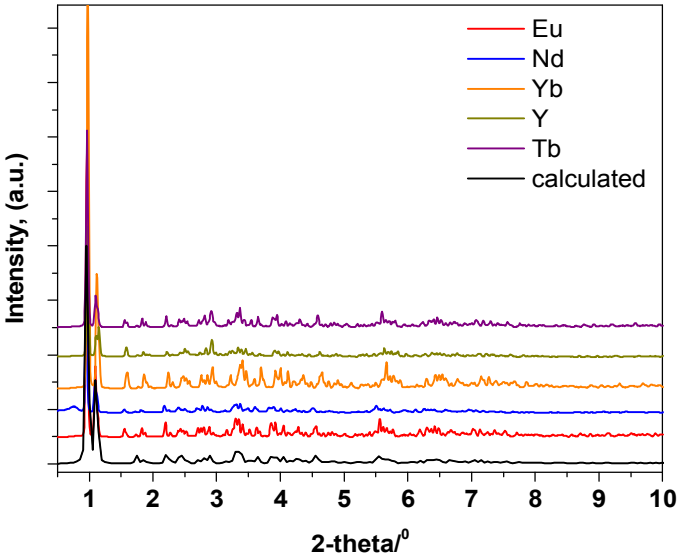


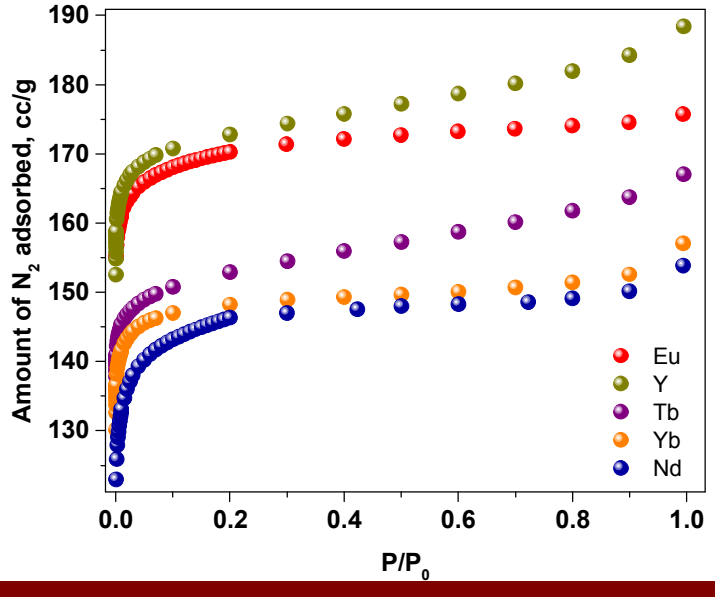
Octahedral cages of ~ 14 Å diameter, accessible via triangular windows of ~ 5.5 Å

M
C
O

Sava Gallis et al., *ACS Appl.Mater.Inter.* **2017**, *9*, 22268–22277. US Patent Application #62522006 *dfsava@sandia.gov*

All analogs are isostructural and possess permanent porosity





Gradual expansion of the unit cell volume with the increase in the RE ionic radius : Nd>Eu>Tb>Y>Yb

Compound	a (Å)	c (Å)	Volume (Å^3)
EuDOBDC, 1	15.36(1)	21.76(2)	5133(19)
EuDOBDC, 1 (single crystal)	15.56	21.33	5163
NdDOBDC, 2	15.50(1)	21.89(1)	5258(7)
YbDOBDC, 3	15.07(1)	21.29(1)	4834(7)
YDOBDC, 4	15.143(7)	21.385(7)	4904(6)
TbDOBDC, 5	15.23(2)	21.51(1)	4993(19)

Compound	BET SA	Langmuir SA
EuDOBDC, 1	700 m^2/g	730 m^2/g
NdDOBDC, **2**	587 m^2/g	620 m^2/g
YbDOBDC, **3**	613 m^2/g	630 m^2/g
YDOBDC, **4**	710 m^2/g	730 m^2/g
TbDOBDC, **5**	630 m^2/g	650 m^2/g

Sava Gallis et al., *ACS Appl.Mater.Inter.* **2017**, *9*, 22268–22277.

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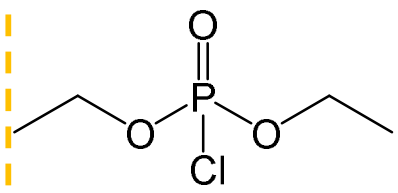
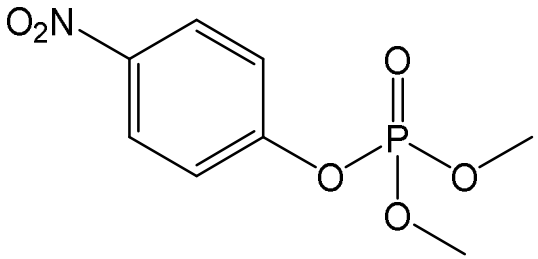
Simulants vs. CWAs: striking the balance between toxicity and reactivity

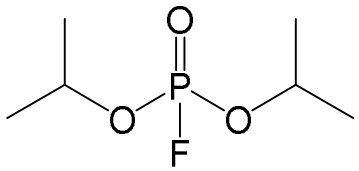
Increase in Toxicity
Increase in Correlation to Live Agent?



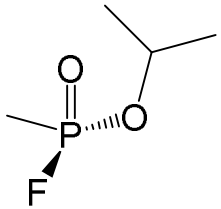
Diethyl Chlorophosphate (DECP)



Dimethyl Nitrophenylphosphate (DMNP)



Diisopropyl Fluorophosphate (DFP)



Sarin (GB)

Simulants

Live Agent

- The molecular structure/reactivity of simulants vs. Chemical Warfare Agents (CWAs) is different
- Tests performed on CWAs are not trivial and conducted only at authorized facilities
- Simulants allow screening of materials

This study aims to *identify the most appropriate simulants* that correlate best with the solvolysis of GB

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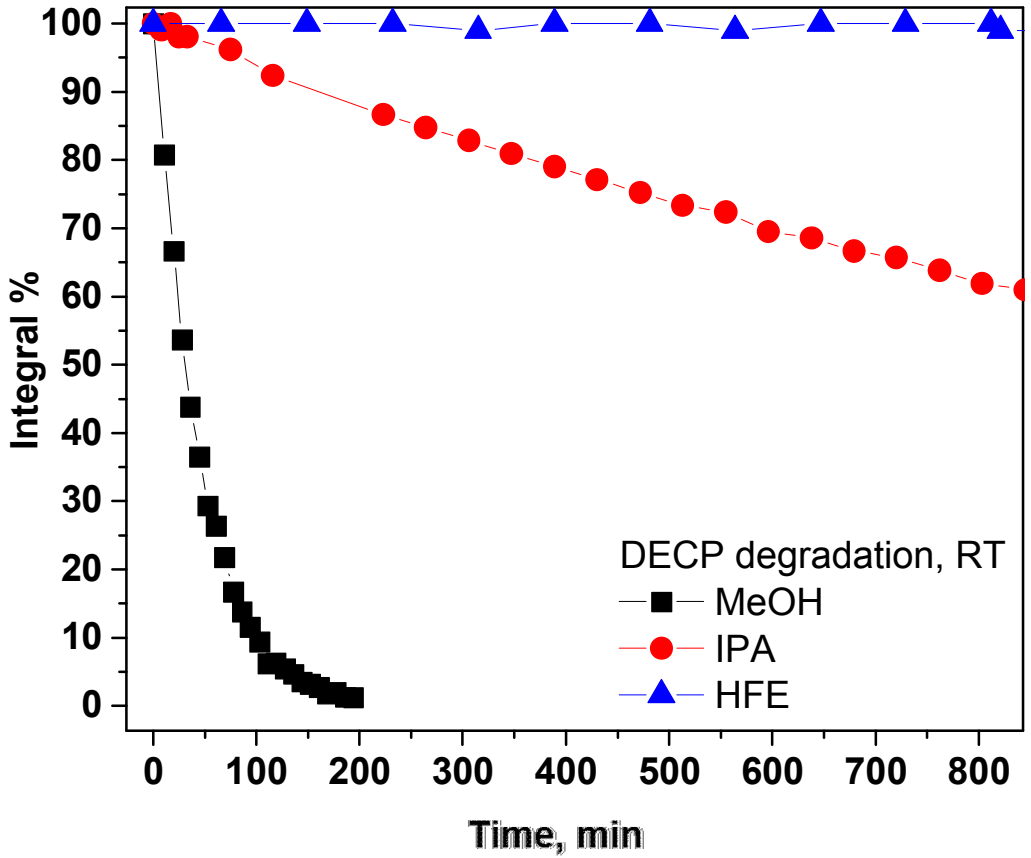
DECP degradation at RT in various relevant solvents measured by ^{31}P NMR



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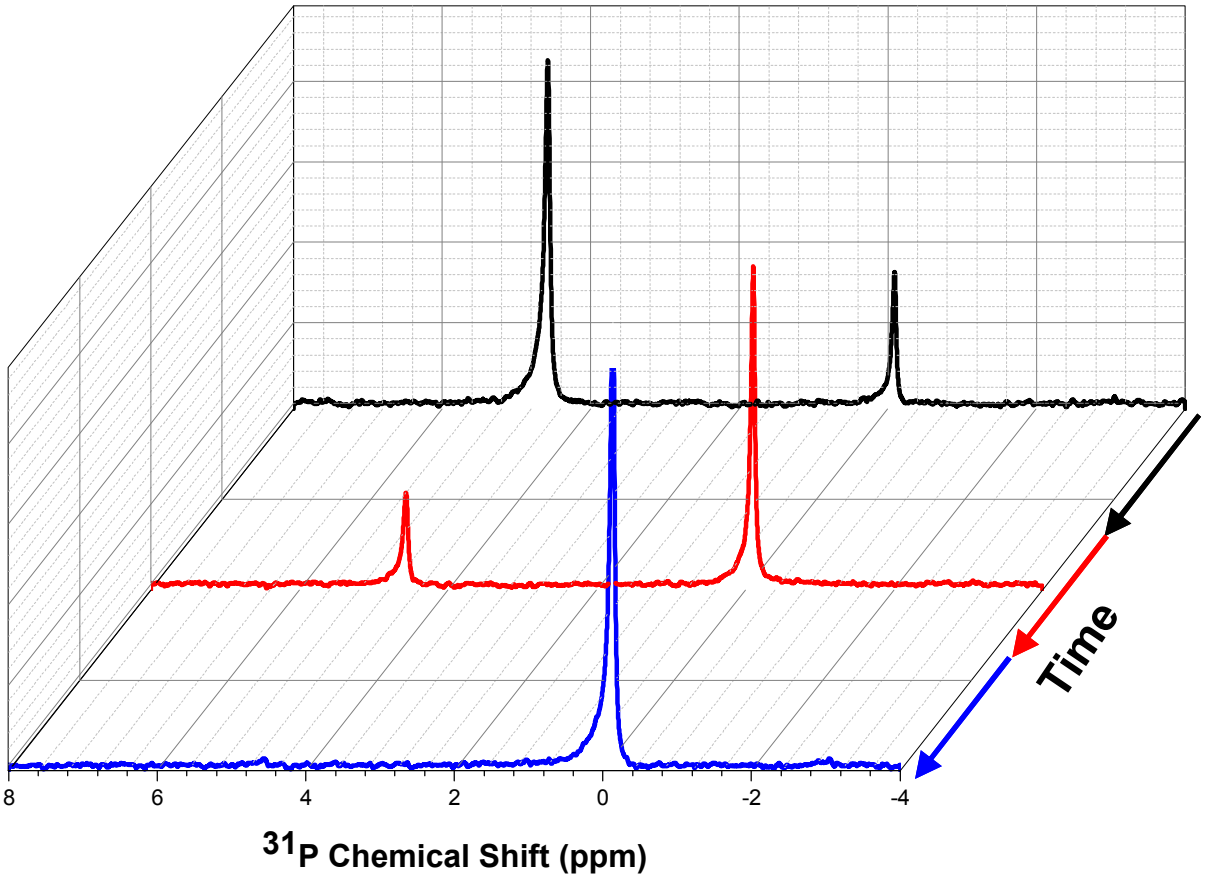
Representative ^{31}P NMR plot for DECP degradation in MeOH



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Materials downselection to probe the effect of metal site and linker functional groups

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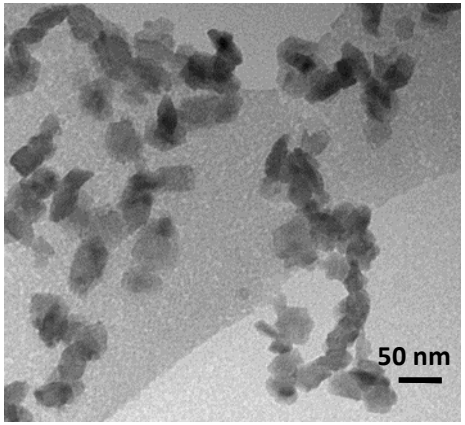
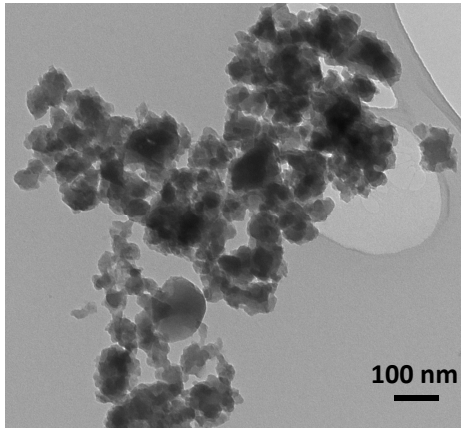
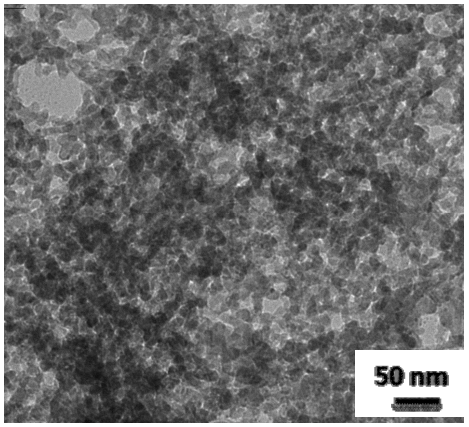
EuDOBDC



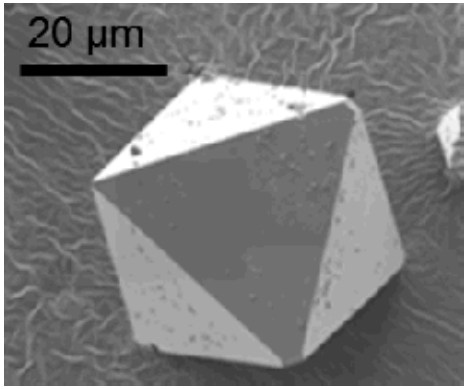
UiO-66



UiO-66-DOBDC



YDOBDC



Sample	Surface area, m^2/g
EuDOBDC UiO-66	508
UiO-66-DOBDC	550
YDOBDC	710
UiO-66	1667

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Computational Methods

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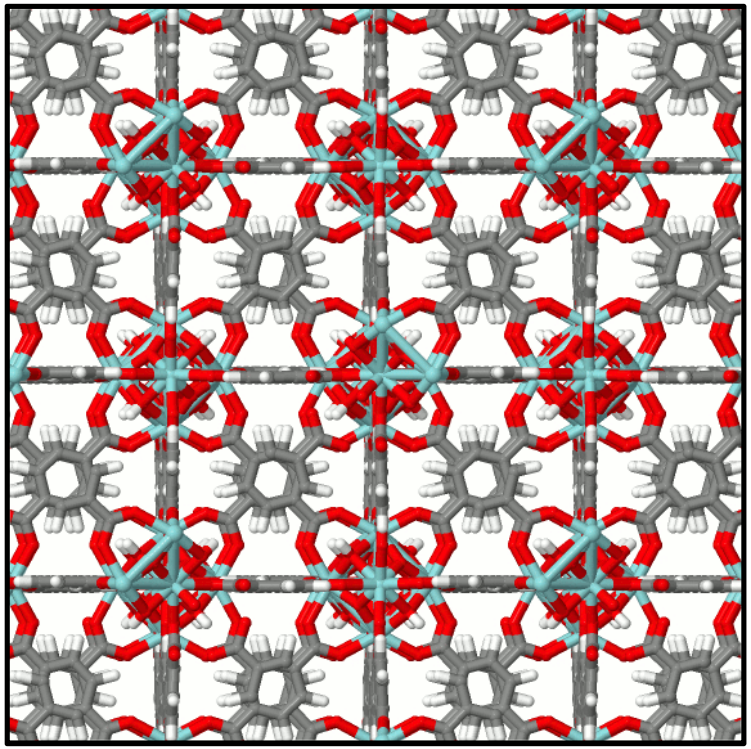
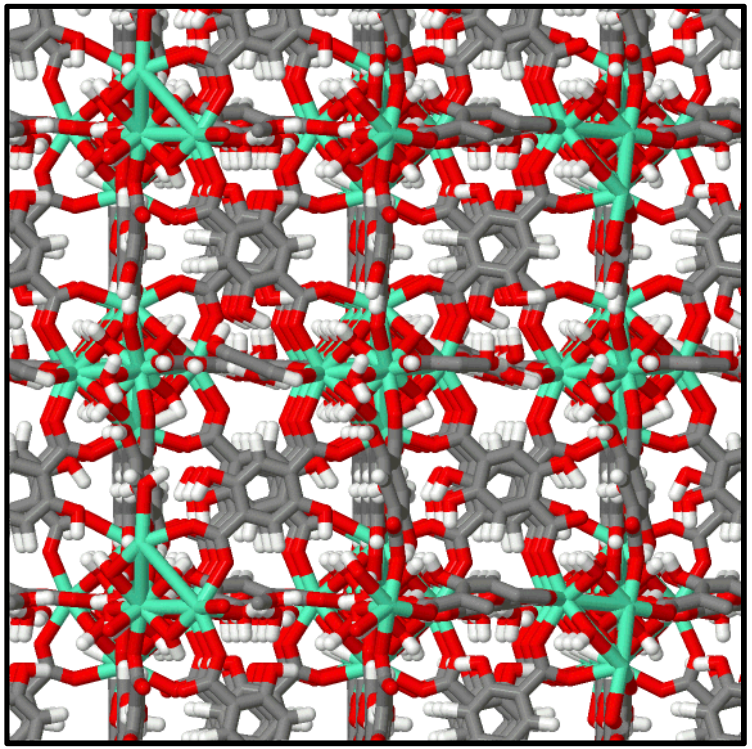
Periodic DFT:

- Optimize crystal structure with VASP
- PAW approach with PBESol functional
- VDW interactions via DFT-D3 method

UiO-66



EuDOBDC



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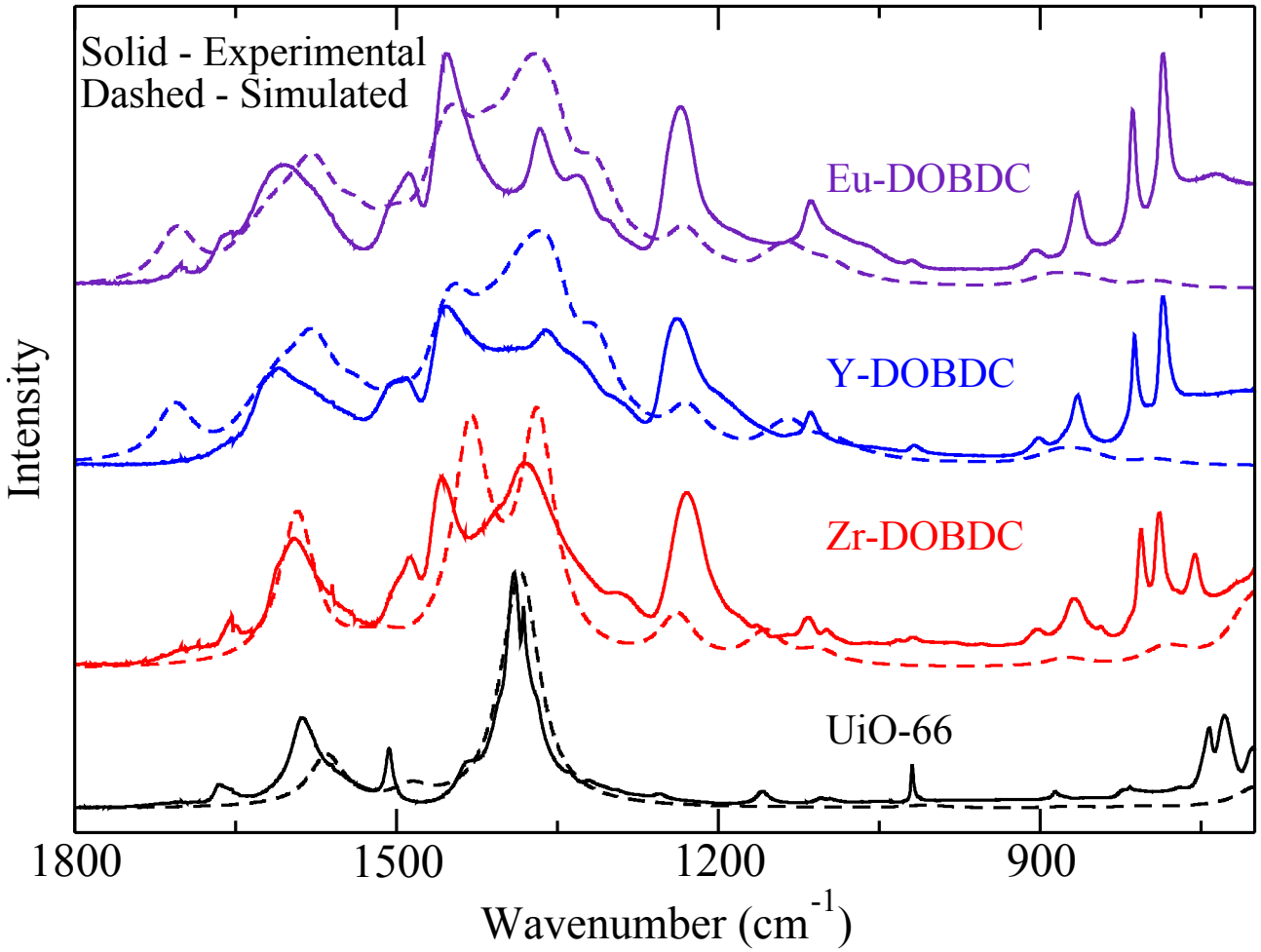
Simulated IR spectra are in very good agreement with experimental results



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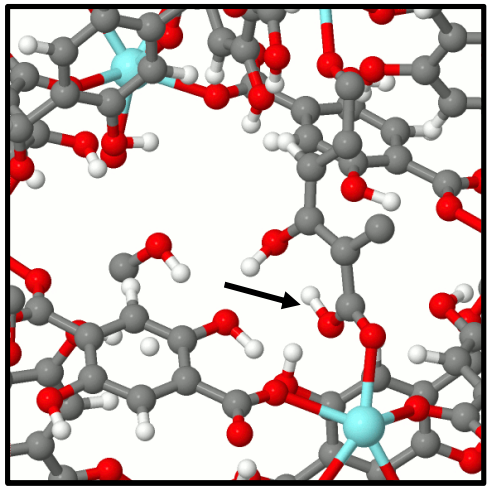
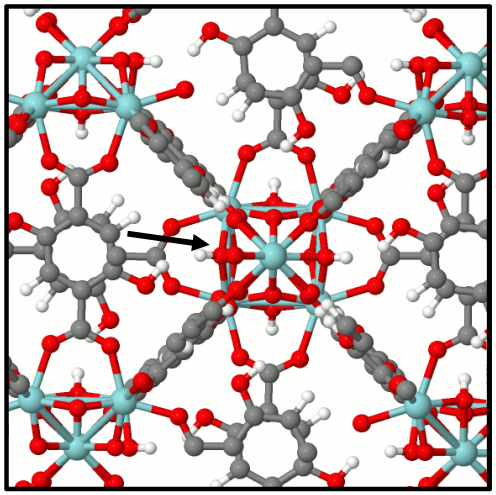
Effect of metal

1315 cm^{-1}
C-O-H
at metal bend

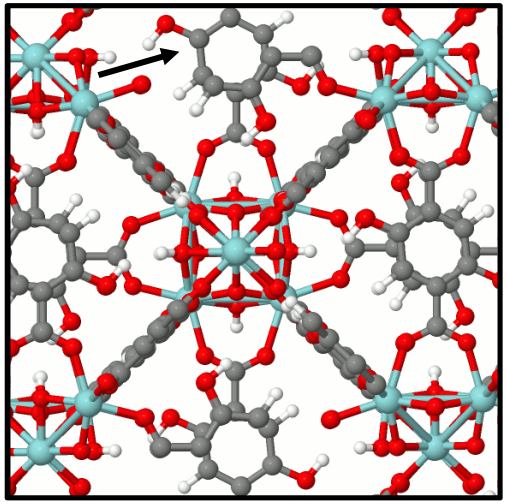


M-O-H bends

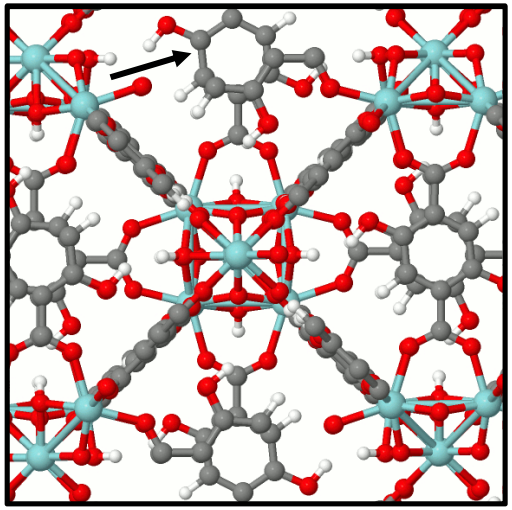


Effect of ligand

1430 cm^{-1}
C-O-H bend + C=C
stretch



1237 cm^{-1}
H-C=C-O-H bend



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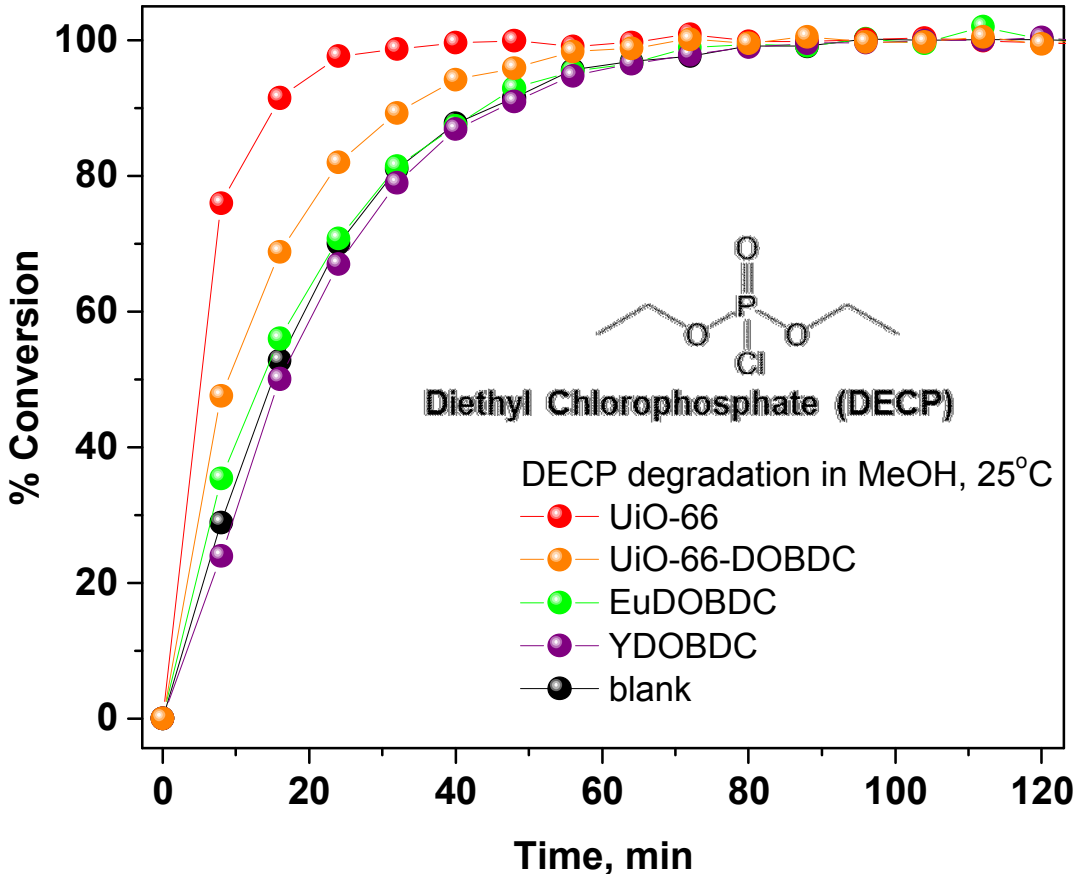
Room temperature DECP methanolysis: the highest activity is primarily dependent on the metal identity



Sample	$t_{1/2}$, min
UiO-66	7.58
UiO-66-DOBDC	8.2
EuDOBDC	11.65
YDOBDC	12.3
MeOH	12.3

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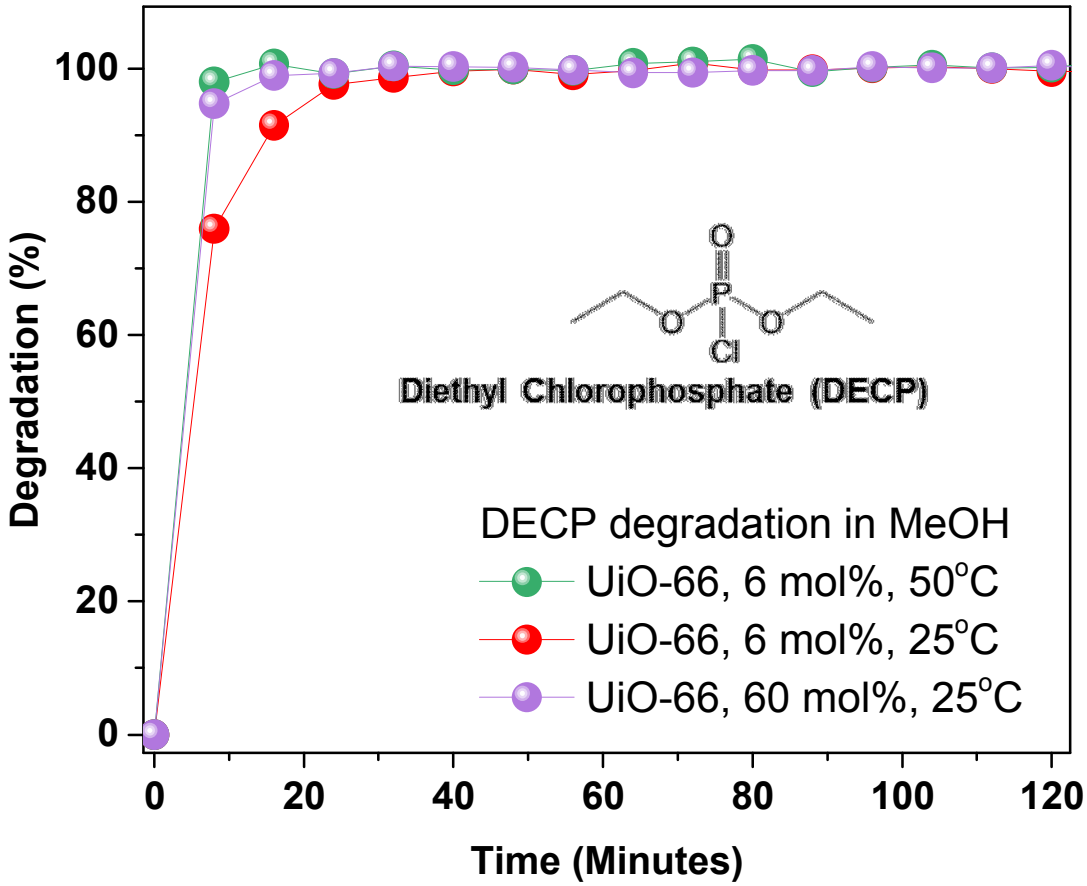
DECP reaction kinetics in MeOH are improved with temperature and amount of catalyst



Sample	$t_{1/2}$, min
UiO-66, 6 mol%, 50°C	1.41
UiO-66, 60 mol%, 25°C	3.35
UiO-66, 6 mol%, 25°C	7.58

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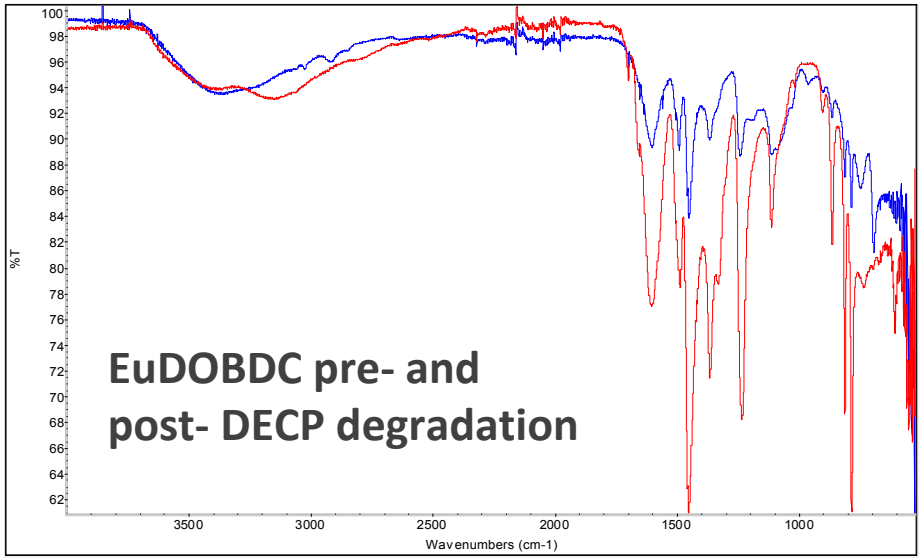
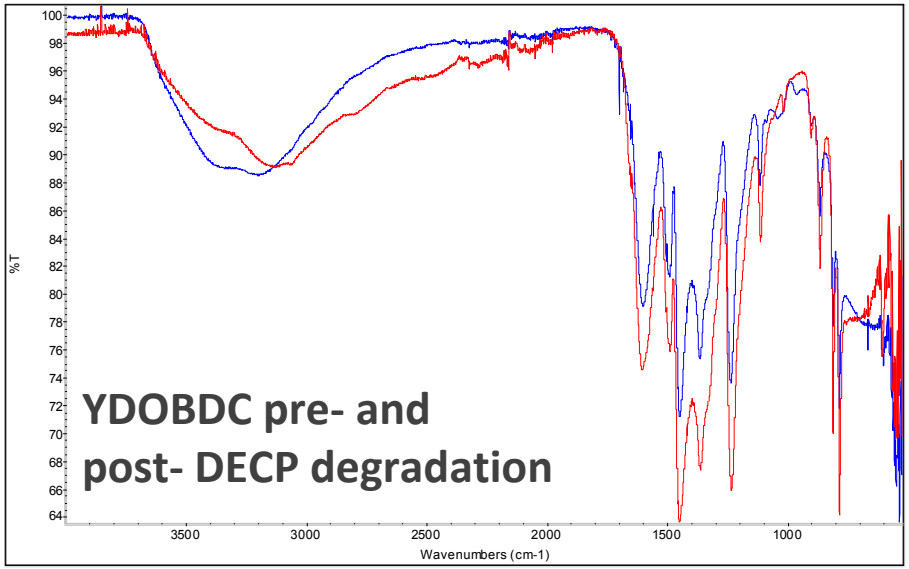
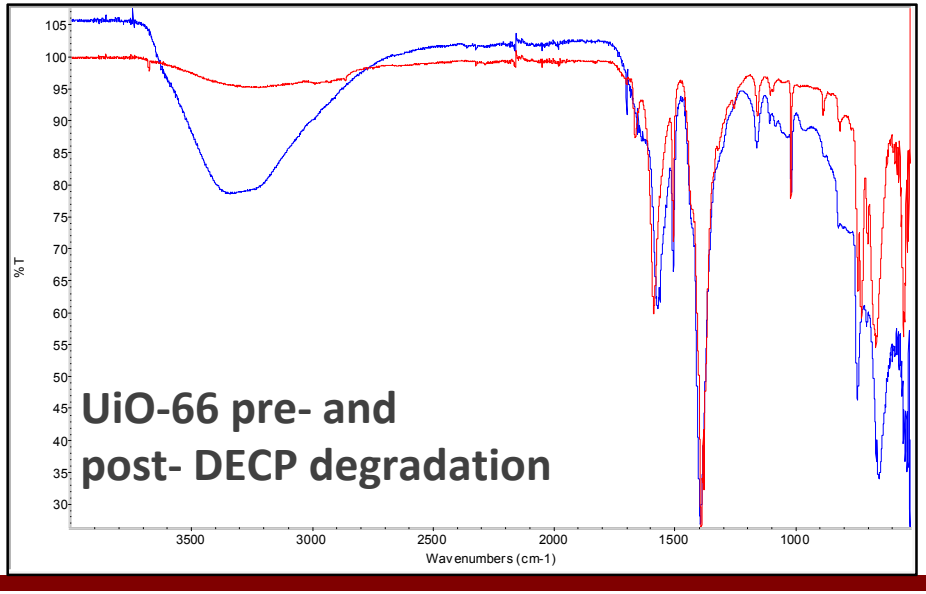
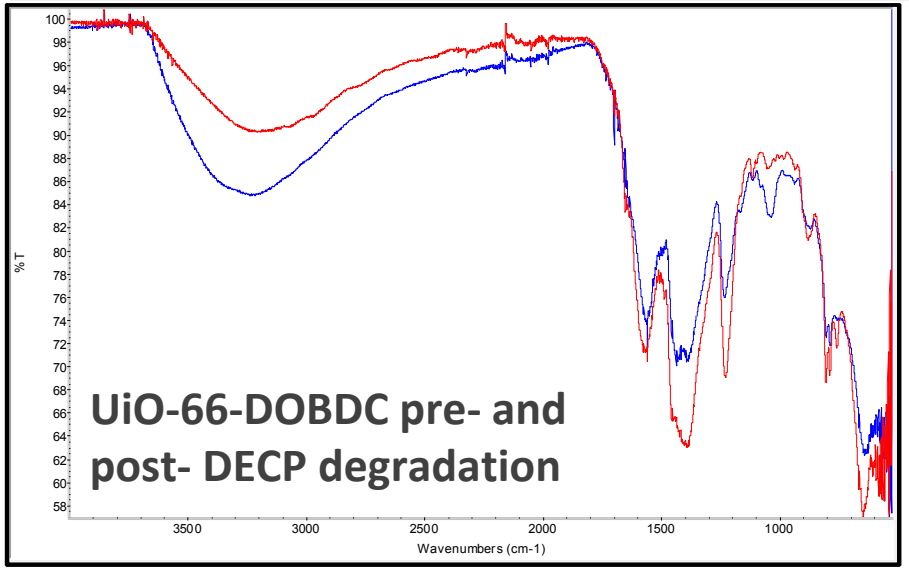
IR confirms no DECP adsorption and no structural changes post catalytic activity









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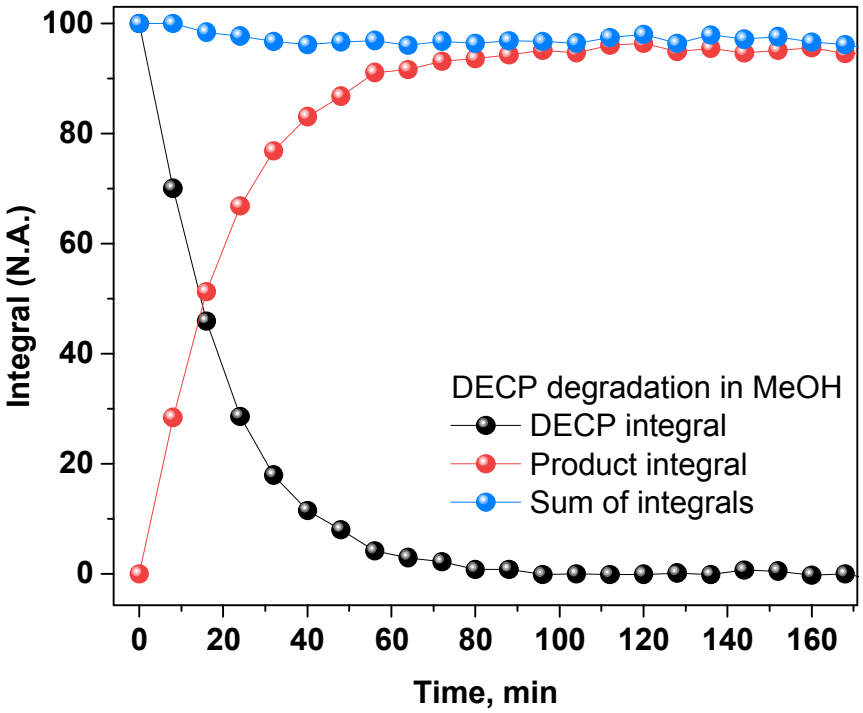
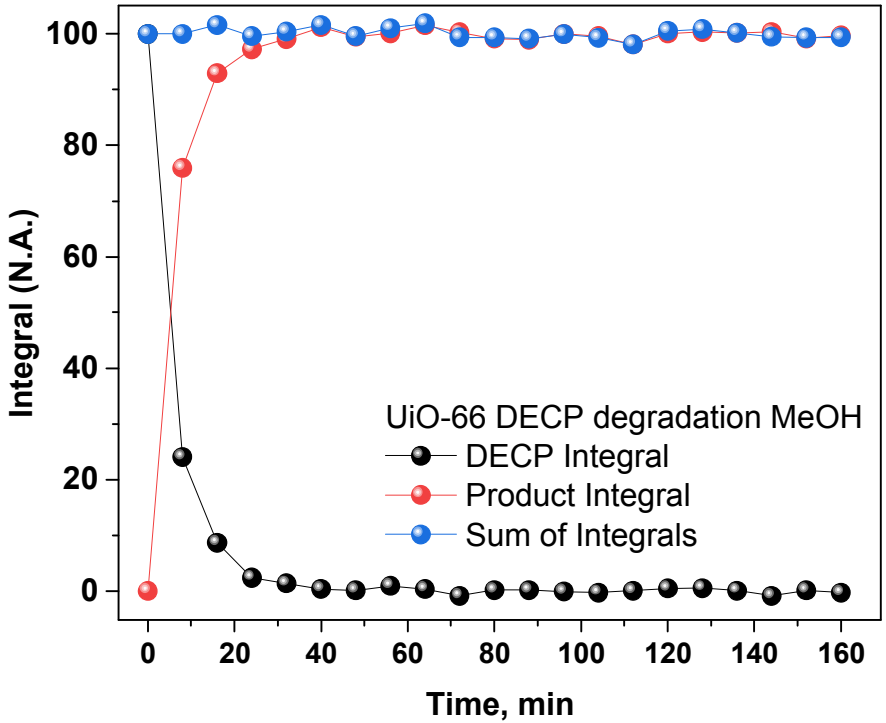
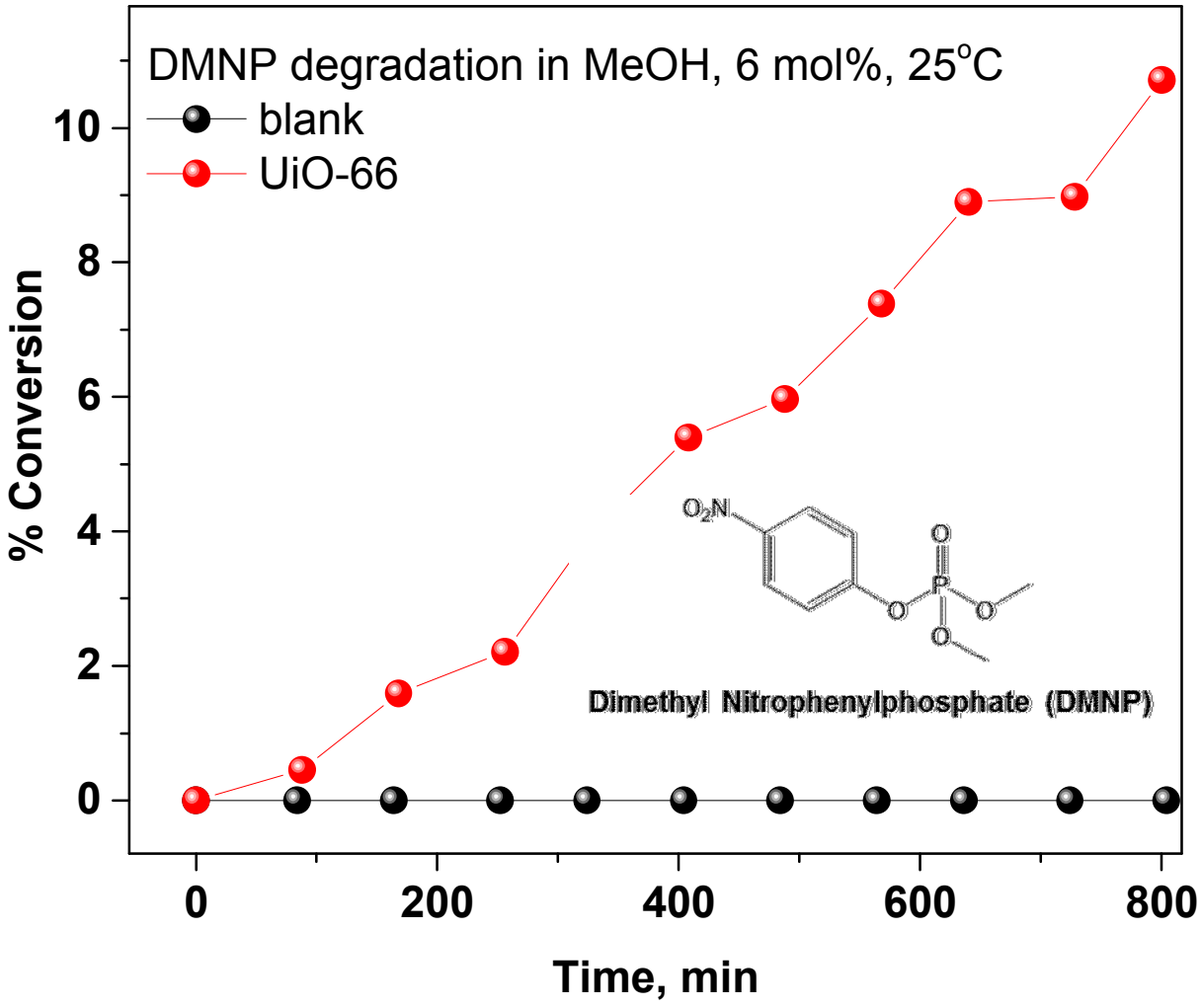
DECP methanolysis occurs via a catalytic process





The activity is strictly catalytic (NO physical adsorption), as shown by the sum of product and reactant peak integrals

Room temperature DMNP methanolysis: significantly slower reaction kinetics as compared to DECP



Sample	$t_{1/2}$, min
MeOH	N/A
UiO-66	3143.27

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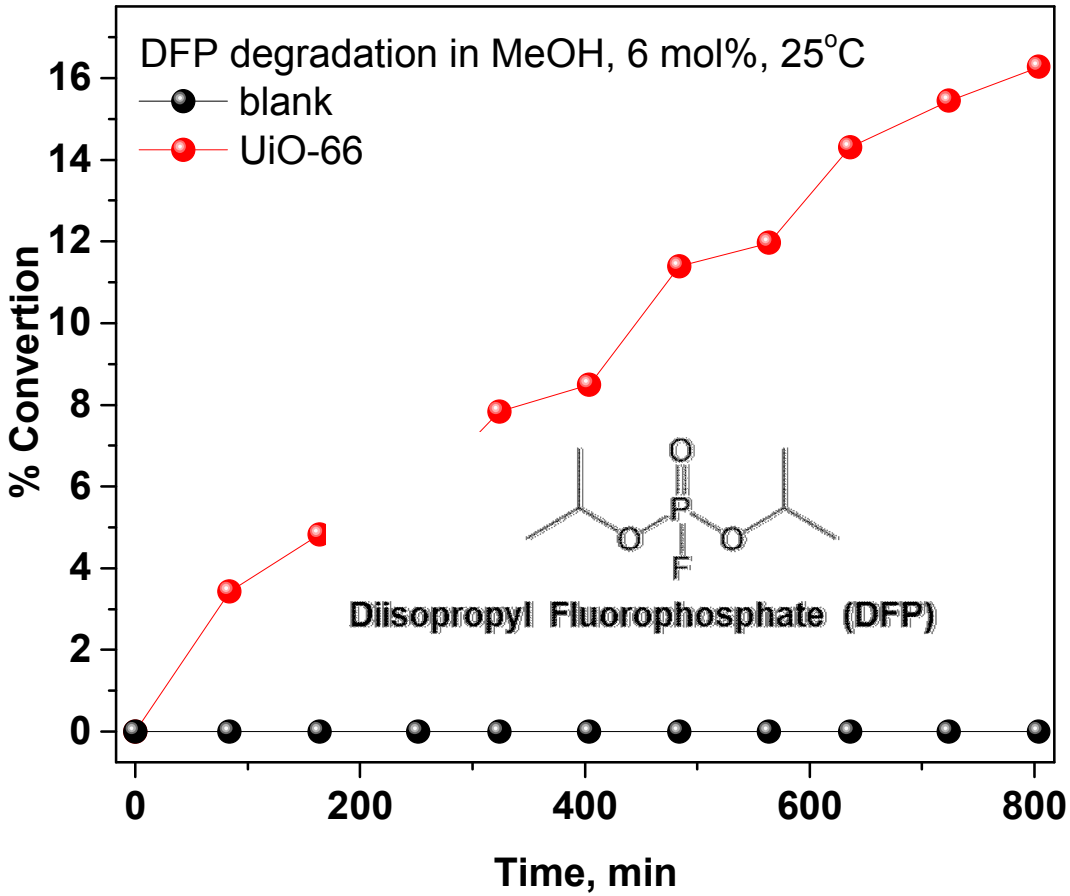
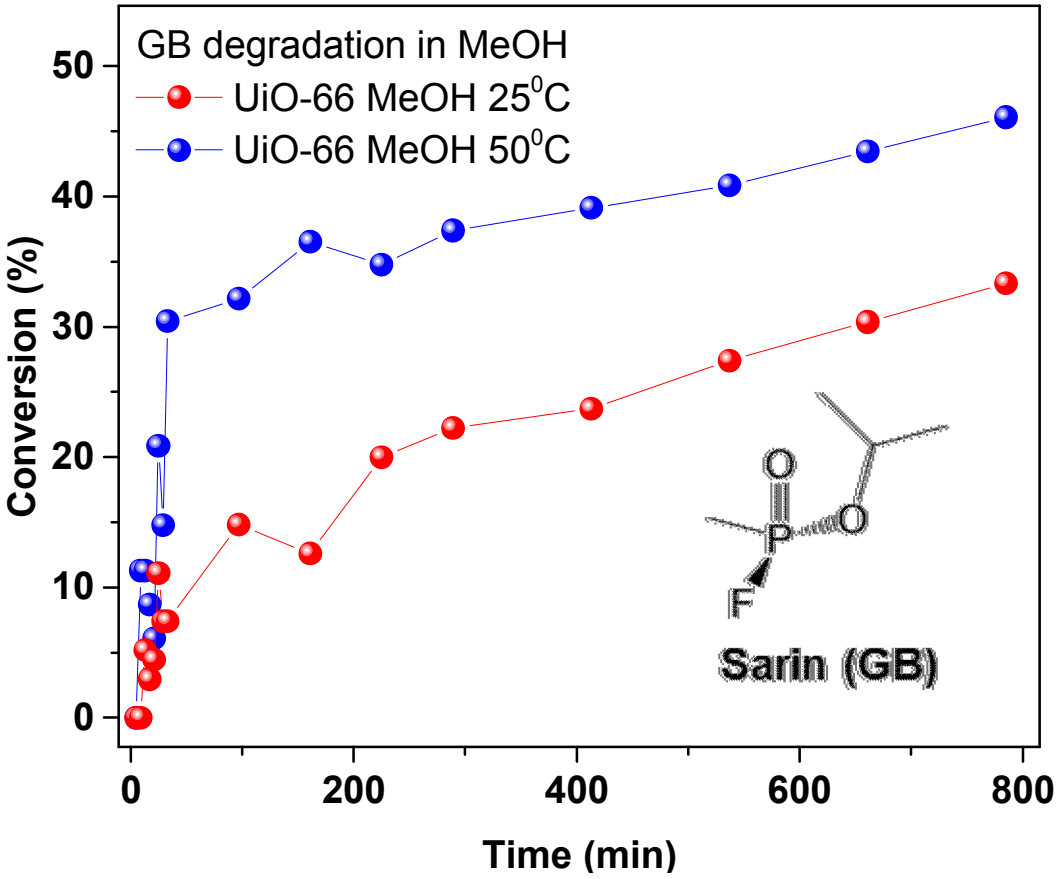
Room temperature DFP methanolysis: comparable with DMNP reaction kinetics



Sample	$t_{1/2}$, min
MeOH	N/A
UiO-66	1380.56

Significant differences noted in the reactivity as function of chloro- vs. fluorophosphates chemistry

GB methanolysis as facilitated by UiO-66

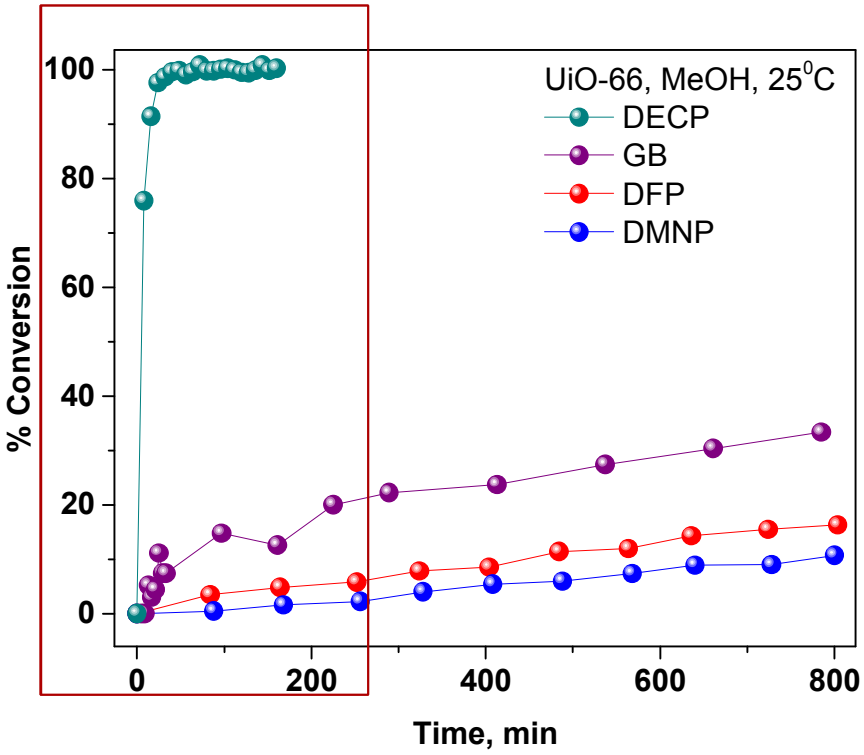


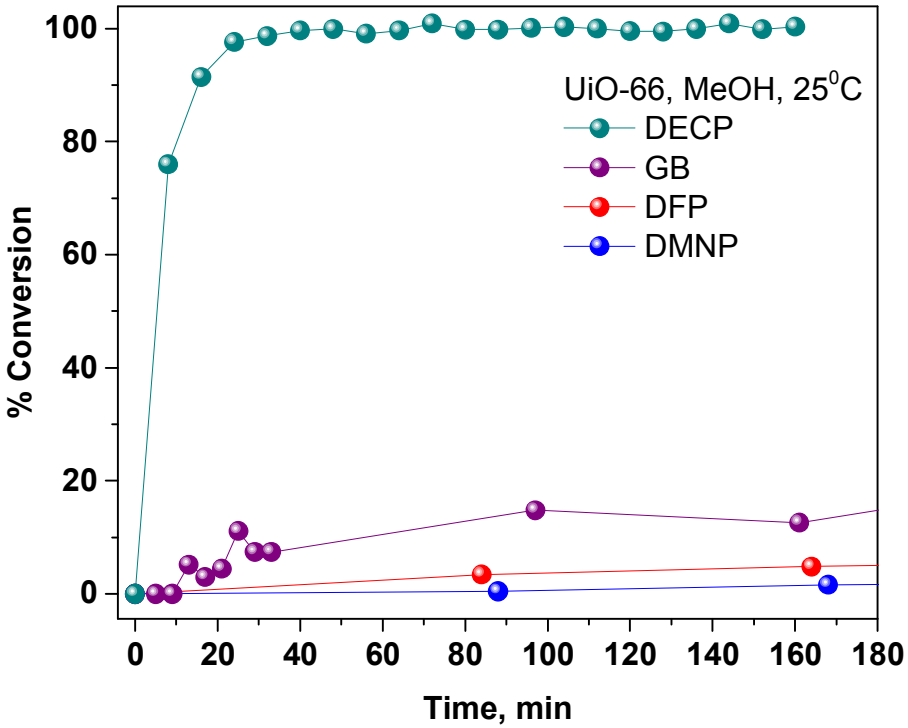
In collaboration with Jared Decoste, ECBC

Sample	$t_{1/2}$, min
UiO-66, 25°C	1386
UiO-66, 50°C	990

The reactivity profiles at RT and 50^{0}C are comparable, with an initial spike the first 30 min followed by much slower kinetics afterwards- perhaps catalyst poisoning?

Room temperature methanolysis trends: DECP>GB>DFP>DMNP





- The methanolysis of GB is faster than that of both DFP and DMNP at room temperature
- The reactivity of GB, DMNP and DFP runs in parallel, indicating related conversion mechanisms

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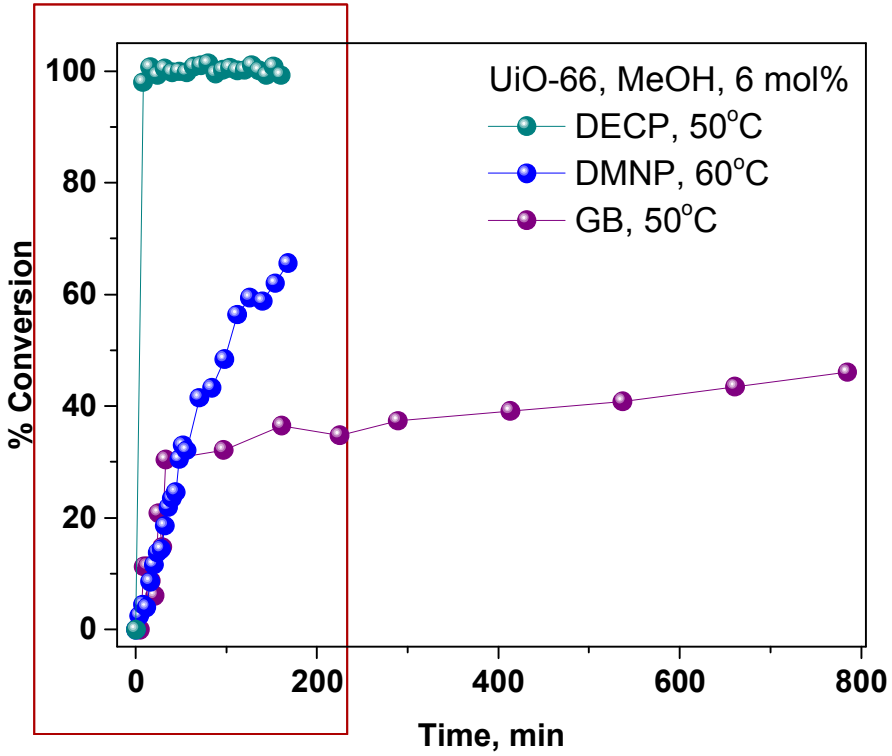
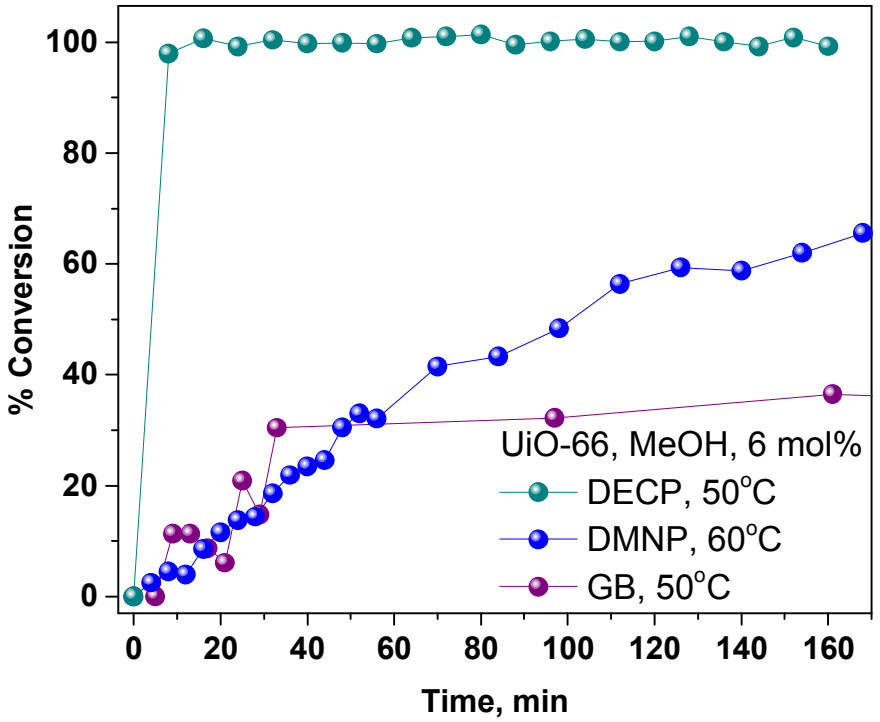
Degradation kinetics are significantly improved with temperature: DECP>DMNP>GB





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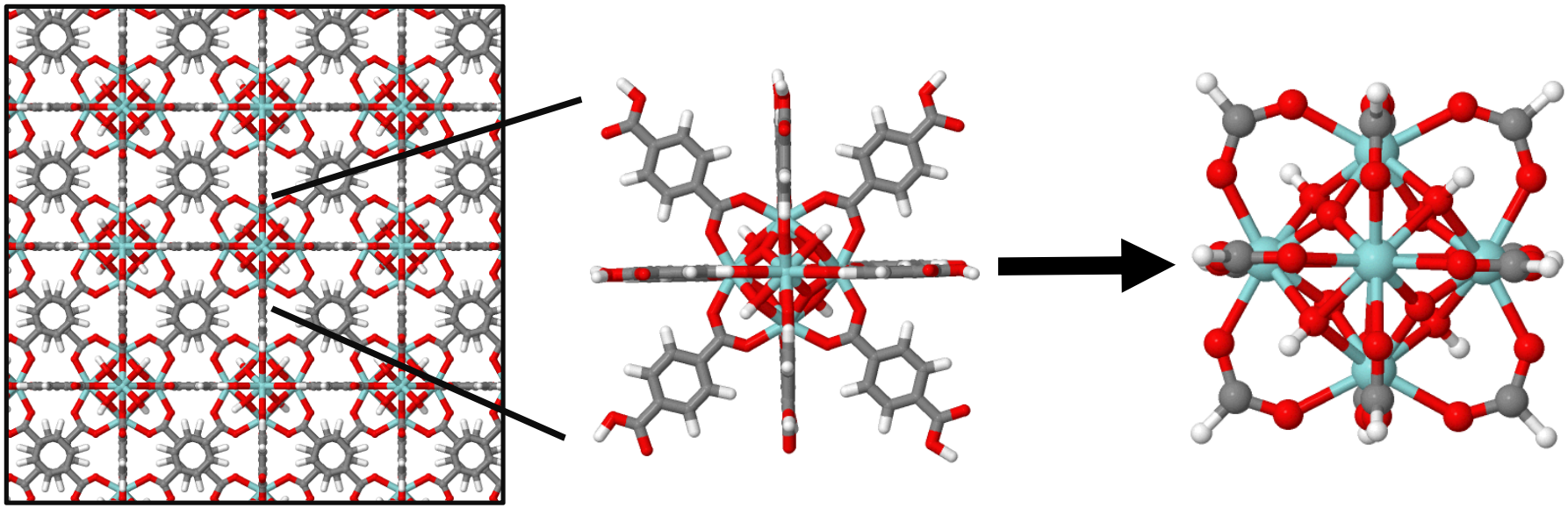
Computational Methods

Gas Phase Cluster DFT:

- Clusters generated from VASP optimized structure
- Clusters optimized with MO6-L functional, def2-SVP basis set for all non-metal atoms and SDD ECP and psuedopotential for metal atoms
- Model ”idealized” ligands as formate ligands



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Considering defects in the Zr cluster

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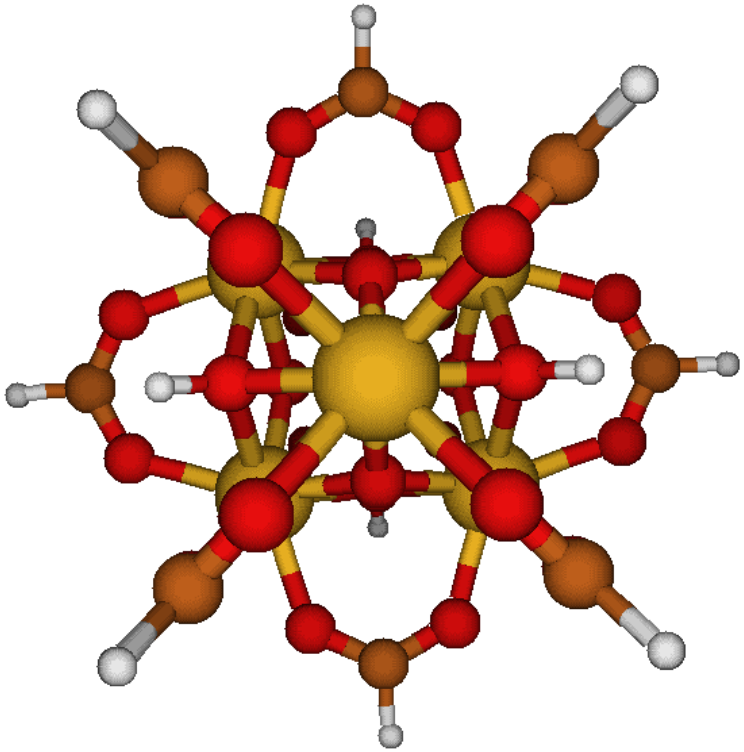
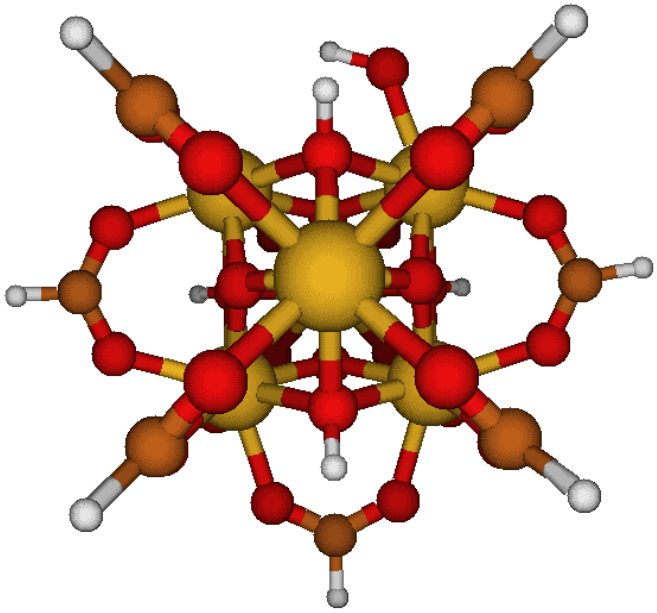
Defect-free Zr cluster



$- CHO_2$

$+ H_2O$

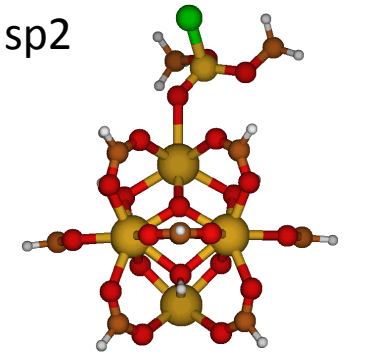
Missing linker Zr cluster

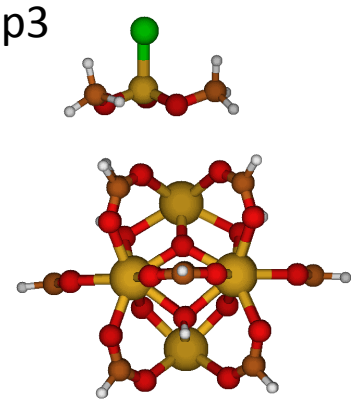


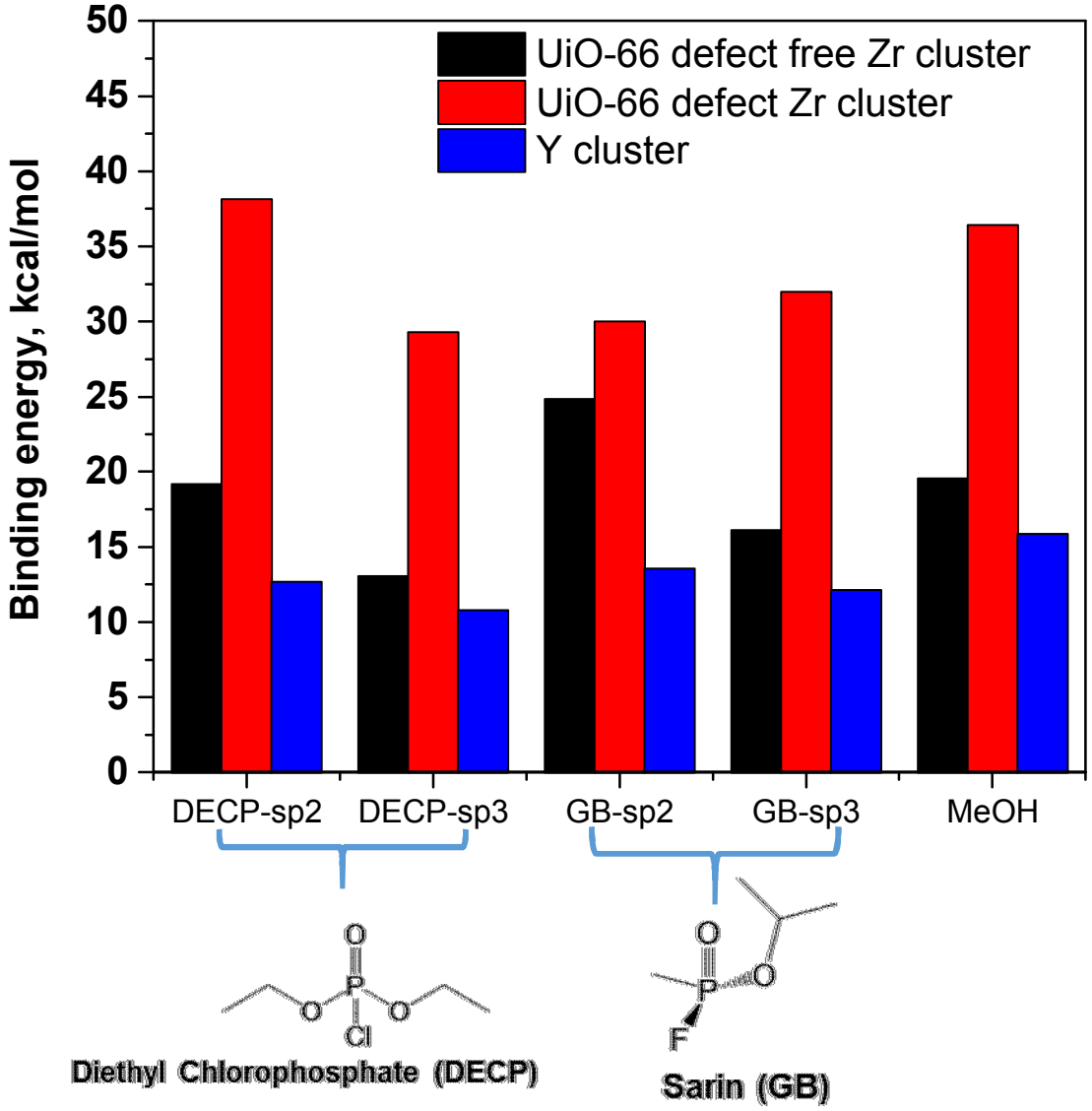
- Remove a ligand and add water → 8 coordinated Zr and 7 coordinated Zr

Angew. Chem. Int. Ed. **2015**, 54, 11162-11167
Chem. Sci. **2016**, 7, 4706-4712

Binding energy significantly increased in clusters with defects

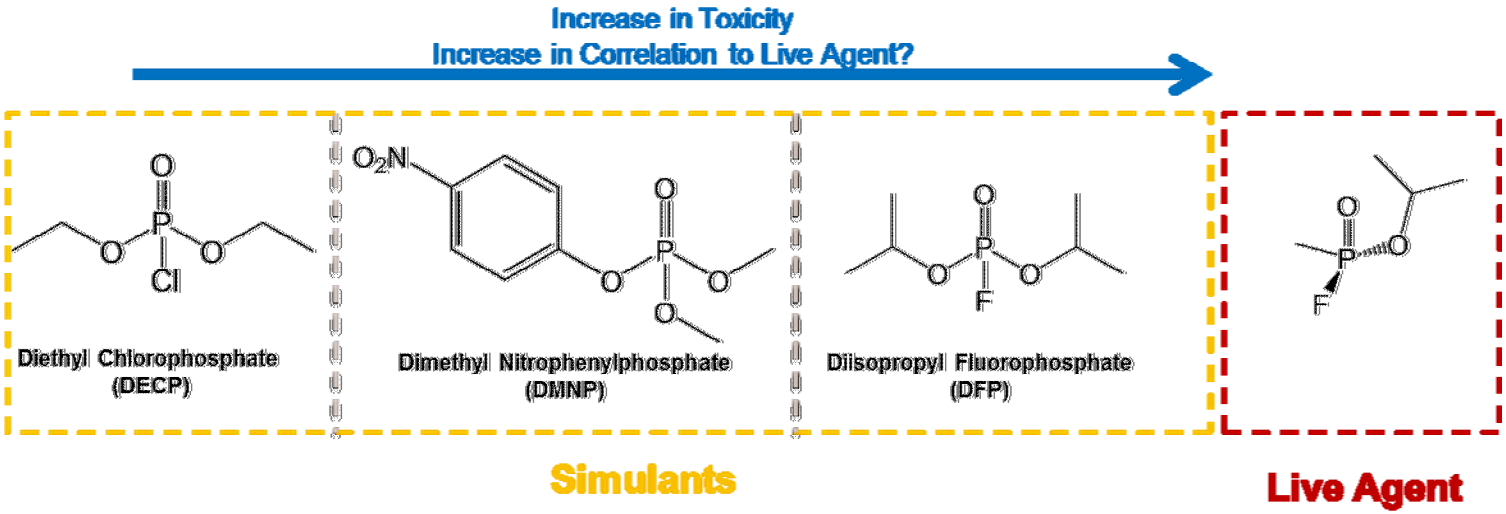






Summary

- Significant differences in the chemistry of chloro- vs. fluorophosphates
- DECP appropriate choice to downselect best performing candidates
- DECP is not an ideal surrogate molecule to characterize the GB methanolysis
- DMNP and DFP have much more relatable reaction kinetics with GB in methanol
- DFT binding energies in progress to better inform future experiments



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