Enhancing catalytic activity and mitigating poisoning of active sites within MOFs in organophosphate hydrolysis through post-synthetic modification

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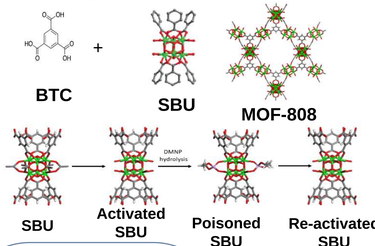
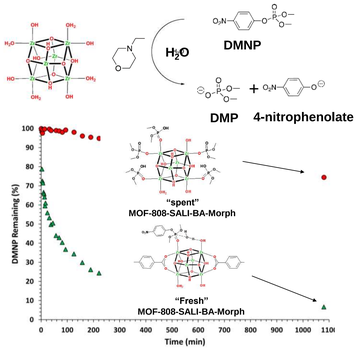
Relevance

- Toxic Chemicals, such as organophosphates pose a dangerous threat
- Extremely toxic to nervous system; they covalently bind to the acetylcholinesterase enzyme causing a build up of acetylcholine, which prevents contraction of respiratory muscles which eventually leads to death by asphyxiation or cardiac arrest
- Certain enzymes can render organophosphates inactive but are only effective under certain conditions, however, susceptible to degradation[1]
- Stable materials capable of fast organophosphate hydrolysis within a gas mask or protective suits are greatly needed
- Catalysis is often poisoned through the by-products of hydrolysis, hence, circumventing this issue is critical for active protection

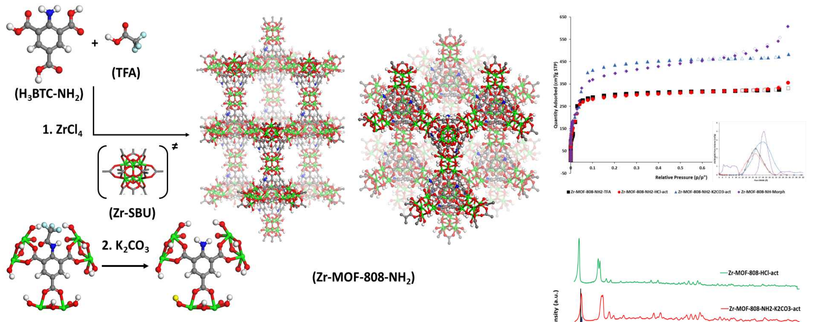
Metal-Organic Frameworks (MOFs)

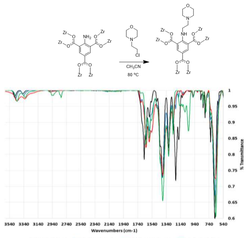
- Metal-organic frameworks (MOFs) are porous materials comprised of organic struts which are connected to metal-containing nodes named secondary building units (SBUs)
- Zirconium based MOFs are comprised SBUs that can be connected with a maximum of 12 bridging carboxylate organic linkers, however, 10, 8, 6 and 4-connected SBUs can be obtained.[2] SBUs with < 12 connectivity have missing-linkers Zr(OH)(H_2O) sites
- While missing-linker sites can facilitate organophosphate hydrolysis under buffered reaction conditions, they are inactive under non-buffered solely aqueous or humid conditions [3]

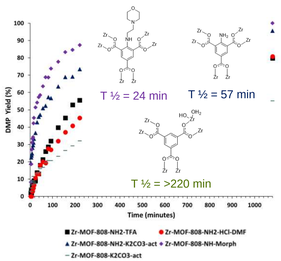


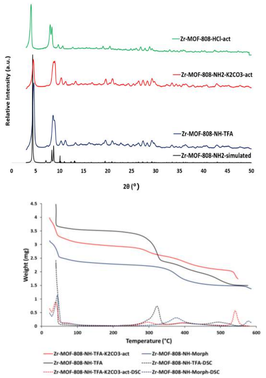


Synthesis and modification of MOF-808-NH_2



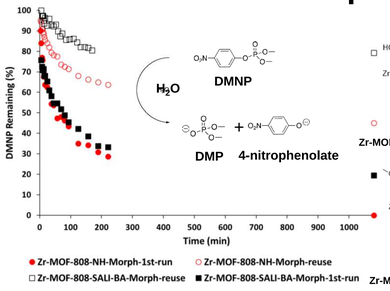


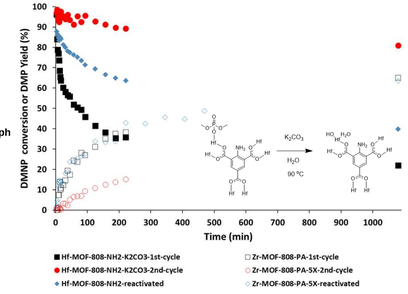




- H_3-BTC-NH_2 was utilized to synthesize an amine functionalized Zr-MOF-808 and Hf-MOF-808 analogs
- K_2CO_3 activation facilitated removal of TFA from SBU and amine on BTC linker
- Post-synthetic modification of Zr-MOF-808-NH_2 with 4-(2-chloroethyl)morpholine generated a morpholino functionalized MOF
- Zr-MOF-808-NH-Morph outperformed other MOFs in the hydrolysis of DMNP under non-buffered conditions

Re-use and re-activation of poisoned sites





- K_2CO_3 activation of spent aggregated Zr-MOF-808-PA facilitated removal of DMP from SBUs and fully restored initial hydrolysis activity
- K_2CO_3 activation of spent Hf-MOF-808-NH_2 only partially restored initial activity, mass loss observed during activation and solvent exchanging of the highly disperse MOF particles

Conclusions and Future Directions

- Incorporation of amine functionalities within MOF-808 through *de novo* or PSM accelerate catalytic organophosphate hydrolysis without the need for volatile caustic buffer
- Morpholino groups attached to the strut within Zr-MOF-808-NH-Morph reduces DMP poisoning upon re-use relative to non-functionalized Zr-MOF-808
- Poisoned spent MOFs can be reactivated with dilute basic aqueous washings
- Our newly synthesized highly active catalysts along with our regenerative basic post-treatment activation technique are critical advancements for the practical and recyclable utilization of MOFs as organophosphate hydrolysis catalyst within fibers or composites for protection.

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