

# Controlling the heterogeneous catalysis of zirconium clusters within porous scaffolds

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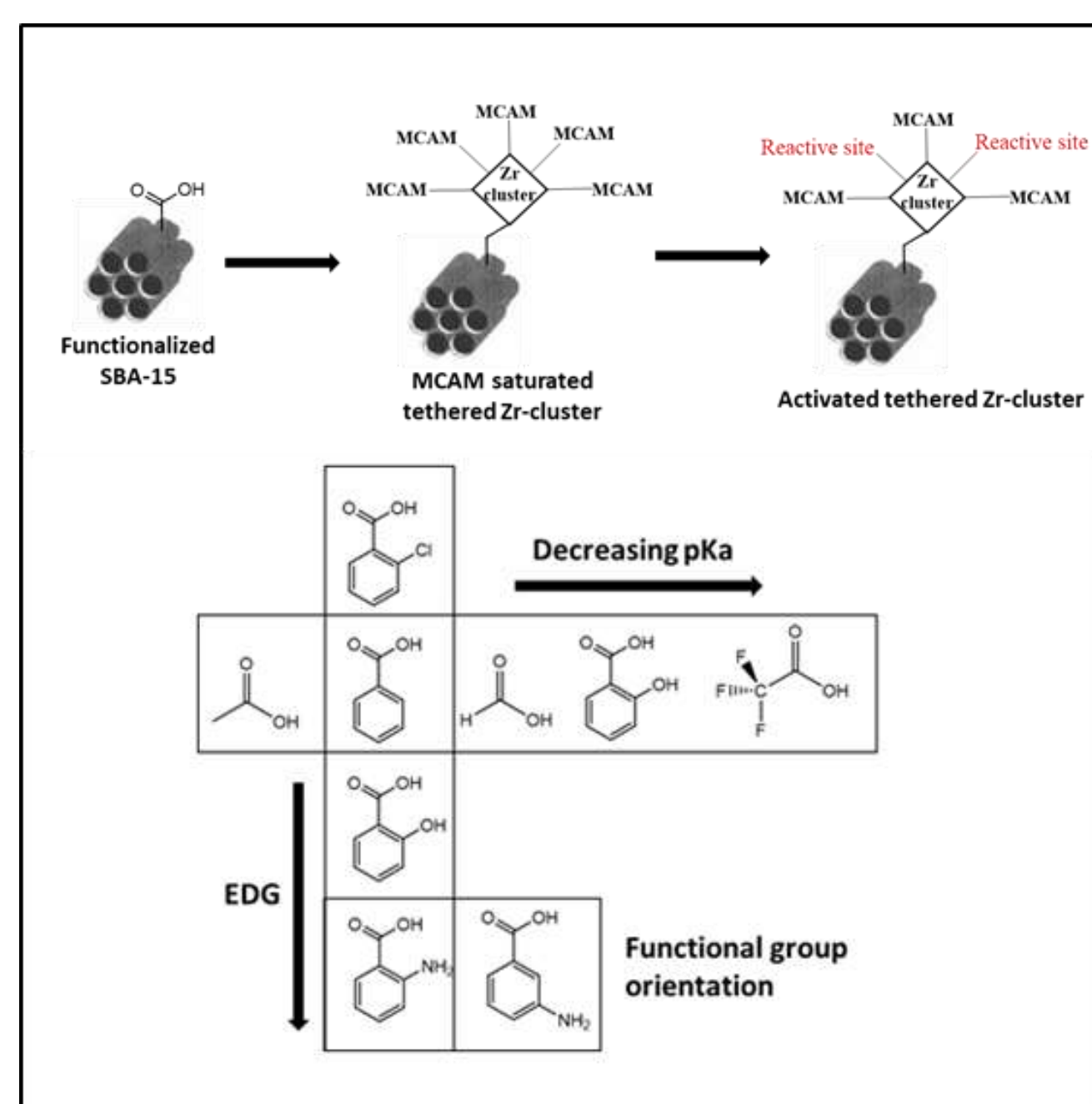
**BLUF:** MOFs with Zr-SBUs have shown promise for protection and self-decontamination of toxic chemicals. However, due to the many variables inherent to MOF structures and synthesis processes, these materials are difficult to scale and activity is not fully understood. Therefore, a basic study on factors that impact the local environment of the reactive site (zirconia cluster) is needed to guide development of an optimized and scalable porous catalytic material.

## ABSTRACT

Metal-organic frameworks (MOFs) with Zr-based secondary building units (SBUs) have shown promise as materials for catalytic degradation of toxic chemicals. In particular, Zr-based SBUs have been previously determined to be the primary reactive component in these materials for catalytic hydrolysis reactions. However, the multitude of variables inherent to MOF structures (e.g. pore size, pore structure, connectivity, crystal size, functional groups, and monocarboxylic acid modulators, MCAMs, used in synthesis) complicate the understanding of the reactivity of the material, especially the role of the SBU. In this work, we have explored the reactivity of a simplified system consisting of Zr<sub>6</sub> and Zr<sub>12</sub> clusters grafted onto silica supports to better understand the reactivity of the SBU component of the MOF independent of the other variables inherent to MOF structures. Silica supports (SBA-15) functionalized with sulfuric acid or phosphoric acid groups were used to tether individual Zr clusters to the surface. The final products were characterized by PXRD and N<sub>2</sub> isotherm to confirm porosity of the material and retained crystallinity of the Zr cluster post-attachment. Hydrolysis reactivity of these materials was assessed through <sup>1</sup>H NMR experiments under buffered and non-buffered conditions in the presence of dimethyl nitrophosphate (DMNP). The use of buffering moieties on either the MCAM or the SBA-15 support were also explored to enhance reactivity of the materials under neutral aqueous conditions.

## HYPOTHESIS

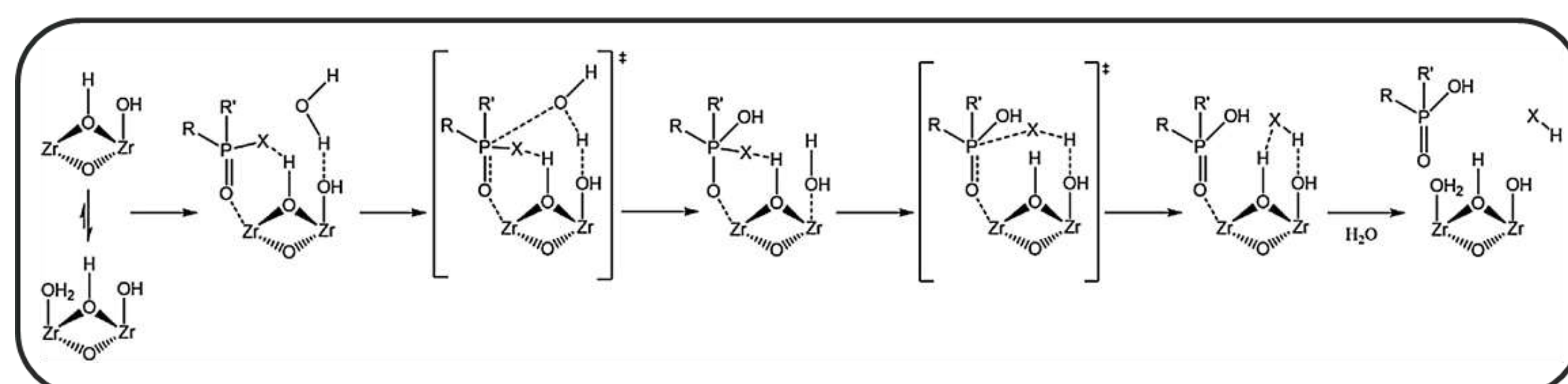
Functionalized silica supports will provide a scaffold to tether active Zr clusters with varying MCAMs to study the impact of the local chemical environment on hydrolysis reactivity.



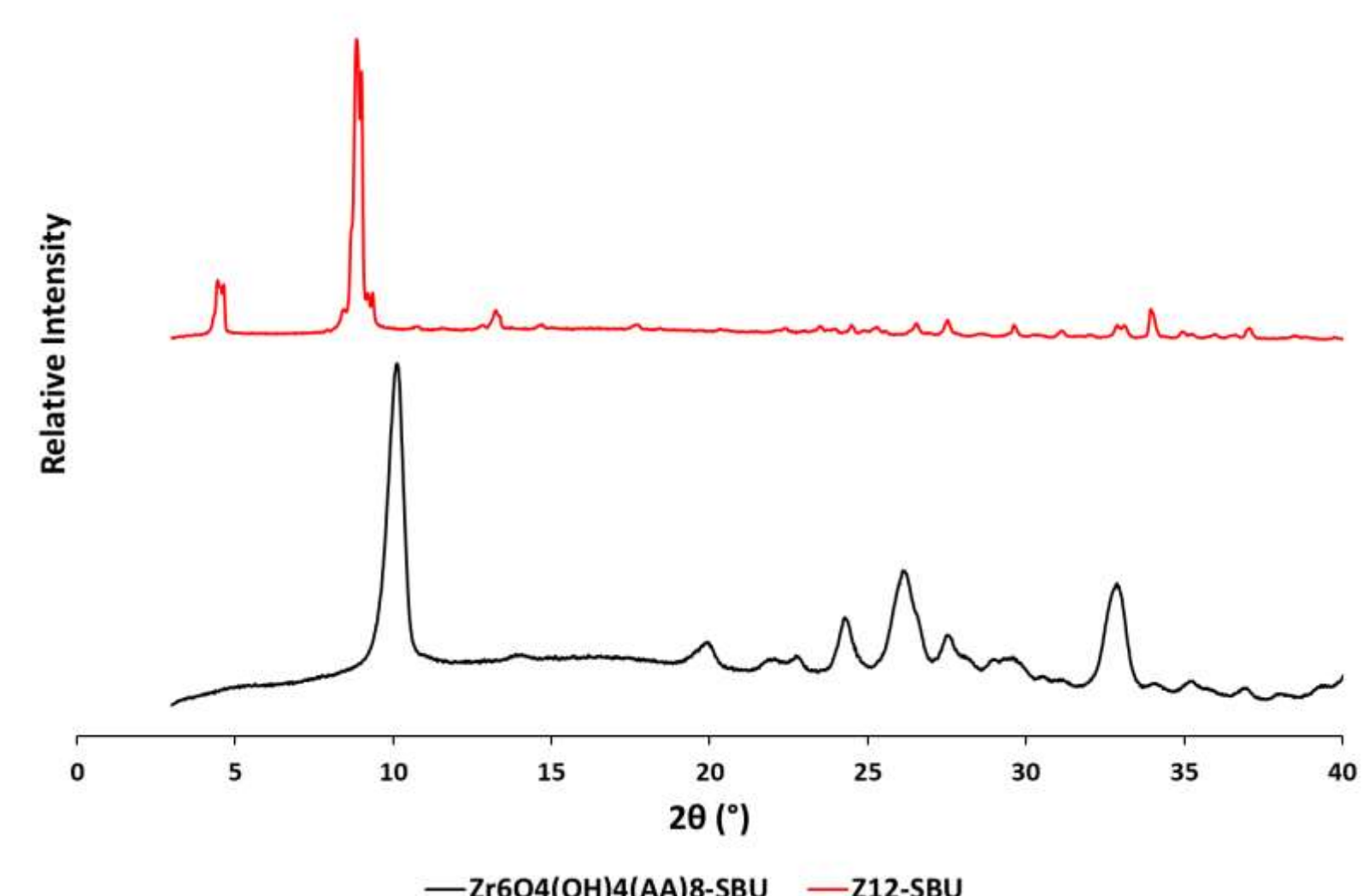
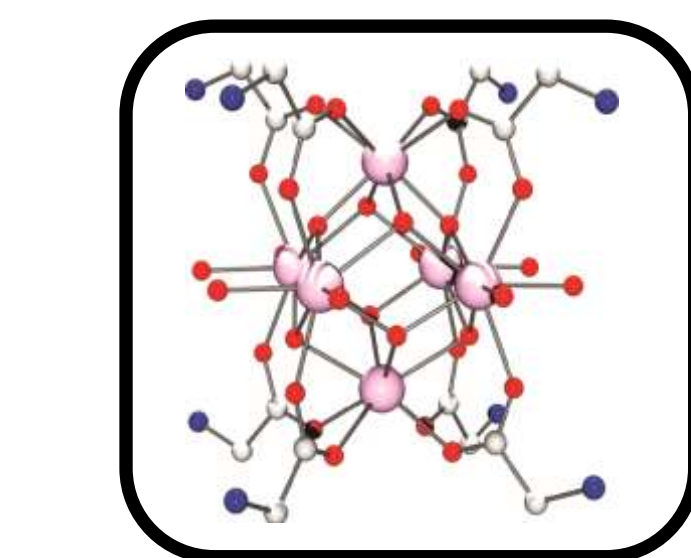
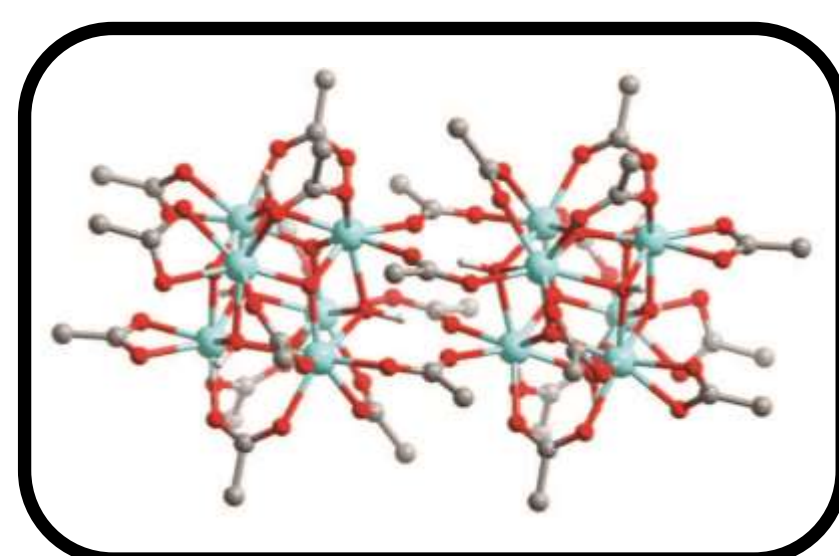
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## TASK 1: SYNTHESIS OF ZIRCONIA CLUSTERS

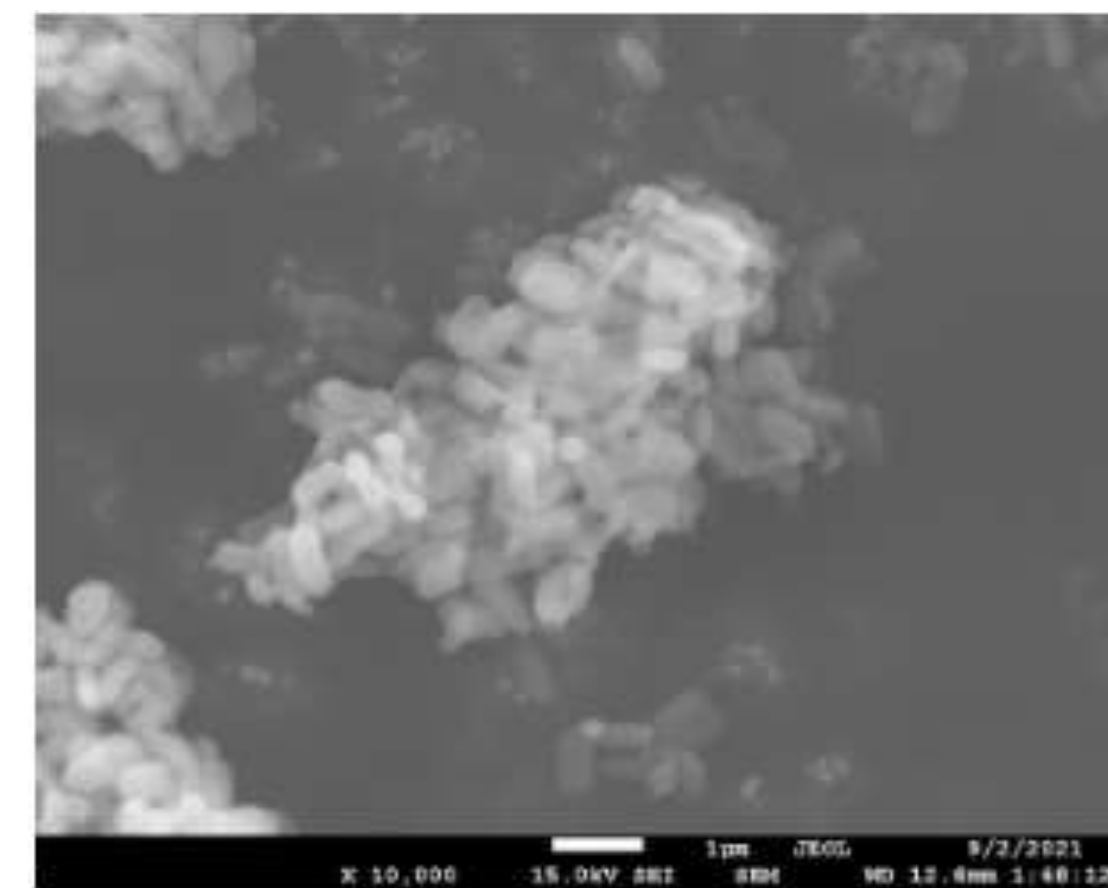
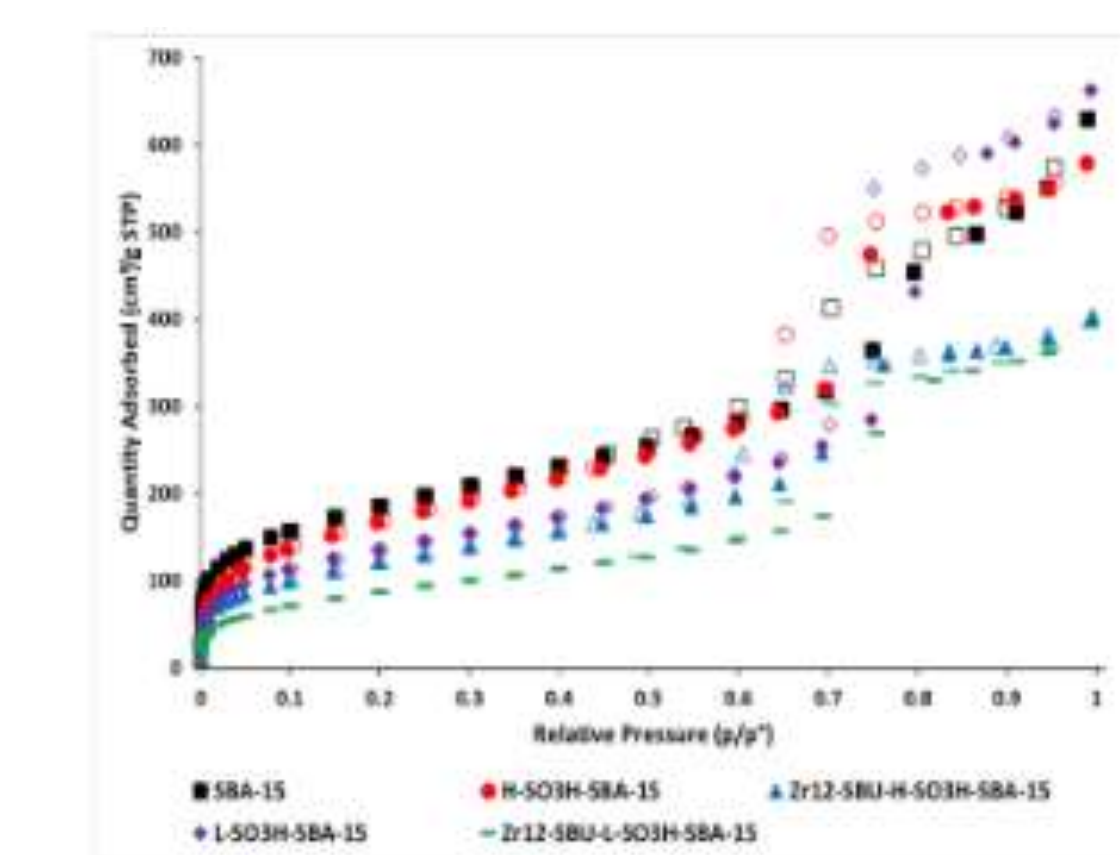


Zr clusters are the active catalytic site for nerve-agent hydrolysis.



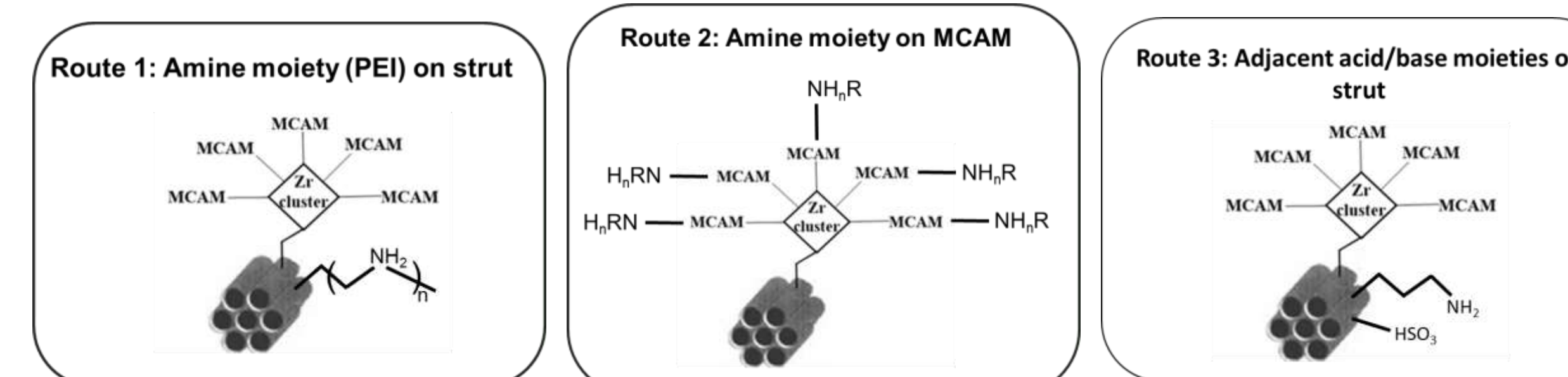
## TASK 2: INCORPORATE ZIRCONIA CLUSTERS ONTO POROUS SUPPORTS

Sulfonic and phosphoric acid functionalized SBA-15 were synthesized according to literature via in-situ and post synthetic methods respectively. Zr<sub>6</sub> and Zr<sub>12</sub> clusters were deposited resulting in upto a 20 wt% Zr material that maintains porosity. Final materials characterized by N<sub>2</sub> isotherm to ensure porosity and SEM-EDx to measure Zr content.



## TASK 3: INCORPORATION OF PROTON SINKS

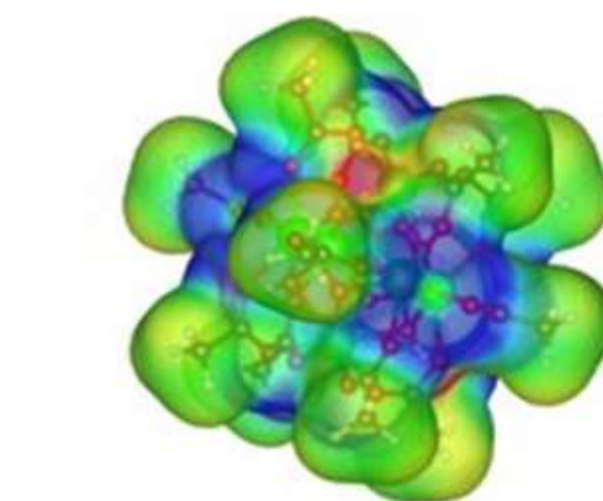
Many Zr-MOFs have shown promising hydrolysis reactivity in buffered solution but do not maintain performance under purely aqueous conditions that would better simulate real world conditions. One method to enhance purely aqueous reactivity has been to introduce solid buffering moieties, typically amine groups, into catalysts. 3 strategies are shown below of attempts to introduce solid proton sinks capable of providing buffering capacity in these materials.



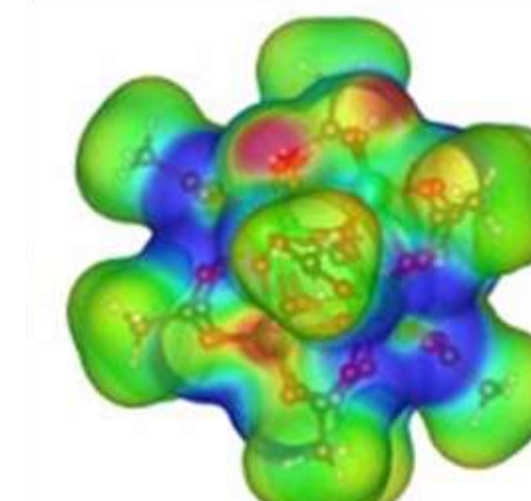
## TASK 4: MOLECULAR SIMULATION OF ZR CLUSTERS IN SOLUTION AND ON POROUS SUPPORTS

DFT calculations were used to predict the optimized structure of the Zr clusters based on PXRD patterns. Amorphous silica was modeled using a melt quench method and then functionalized with the Zr. Electrostatic mapping was performed to predict enhanced binding and reactivity.

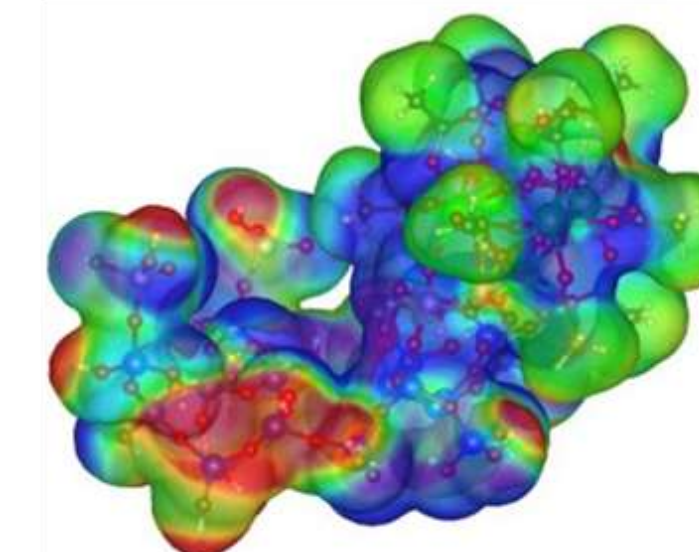
Zr<sub>6</sub>-(acetic acid)<sub>8</sub>



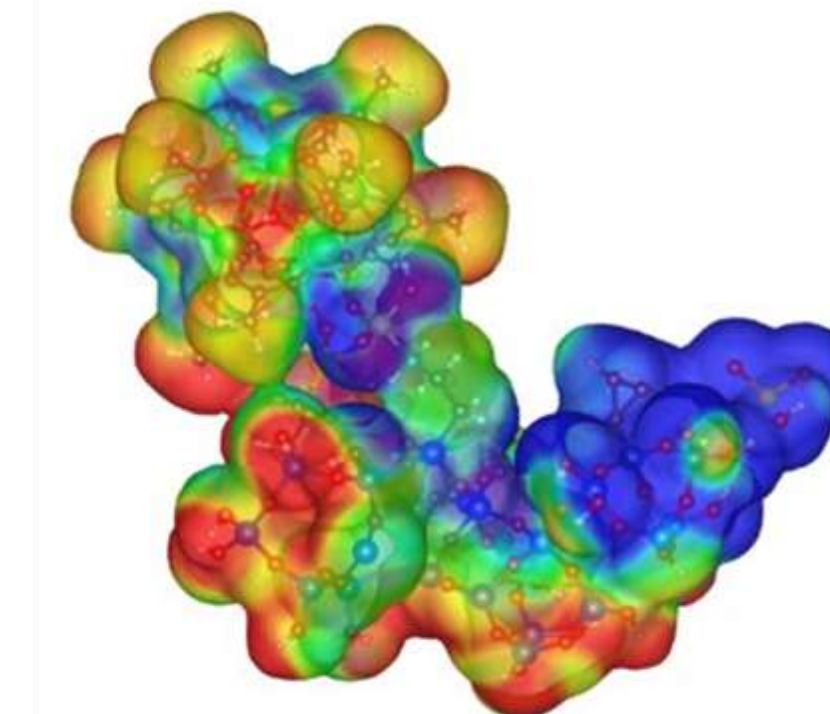
Zr<sub>6</sub>-(acetic acid)<sub>7</sub>-(OH)



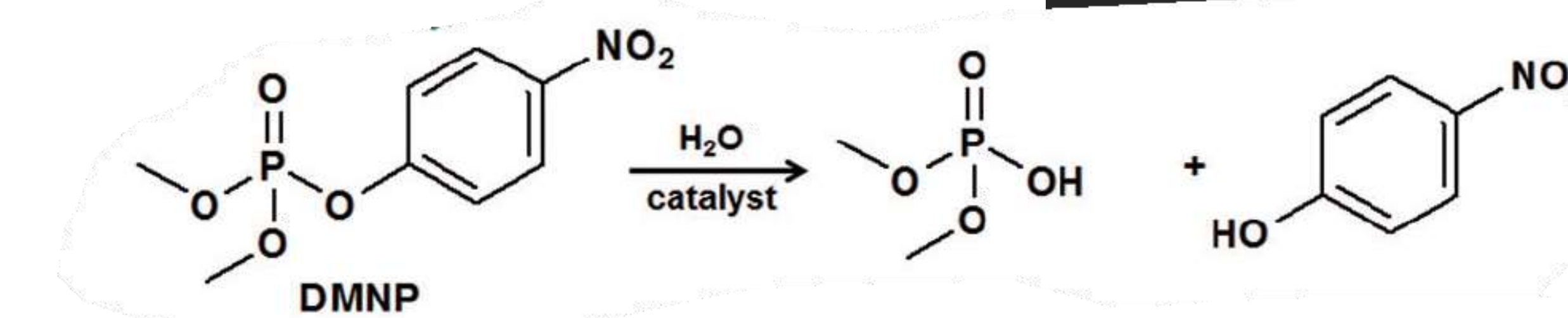
Zr<sub>6</sub>-acetic acid-PO<sub>3</sub>H-SBA-15



Zr<sub>6</sub>-acetic acid-L-SO<sub>3</sub>H-SBA-15



## TASK 5: REACTIVITY TESTING



DMNP hydrolysis monitored by <sup>1</sup>H NMR is used to test catalytic activity.

Material	Half-life (min), DMNP, water	Half-life (min.), DMNP, 0.45 M NEM buffer
Zr <sub>12</sub> -(acetic acid)	N.R.	12
Zr <sub>6</sub> -(glycine)	N.R.	69
Zr <sub>6</sub> -(acetic acid)	N.R.	17
Zr <sub>6</sub> -(benzoic acid)	N.R.	20
HCl activated Zr <sub>12</sub> -(acetic acid)	N.R.	7
Zr <sub>6</sub> -(BA-CH <sub>2</sub> NH <sub>2</sub> )	1000	69
Zr <sub>6</sub> -(BA-CH <sub>2</sub> -morpholine)	1000	<2

Material	Half-life (min), DMNP, water	Half-life (min.), DMNP, 0.45 M NEM buffer
P-SBA-15		>220
H-SO <sub>3</sub> H-SBA-15		1080
L-SO <sub>3</sub> H-SBA-15-(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	~20% (18 h)	550
SBA-15-(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	>1080	>550
Zr-SBA-15		>550
Zr <sub>12</sub> -acetic acid-SBA-15-(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	>1080	>550
Zr <sub>12</sub> -acetic acid-P-SBA-15		69
Zr <sub>12</sub> -acetic acid-H-SO <sub>3</sub> H-SBA-15		13
Zr <sub>6</sub> -benzoic acid-L-SO <sub>3</sub> H-SBA-15		24
Zr <sub>6</sub> -acetic acid-L-SO <sub>3</sub> H-SBA-15		18
Zr <sub>12</sub> -acetic acid-L-SO <sub>3</sub> H-SBA-15	~10% (18 h)	15 (+/- 2)
Zr <sub>12</sub> -acetic acid-L-SO <sub>3</sub> H-SBA-15-PEI	~20% (18 h)	
Zr <sub>12</sub> -acetic acid-L-SO <sub>3</sub> H-SBA-15-(CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	~50% (18 h)	

**Conclusions/future work:** Zr clusters were successfully synthesized and deposited onto functionalized silica supports. Reactivity of Zr clusters and supported Zr clusters were measured in buffered and aqueous solutions. Based on a normalized Zr wt%, the supported Zr clusters were much more highly active. Molecular simulation of electrostatic potential agreed well with reactivity results. The best materials included amine groups as proton sinks for solid buffering capacity. More spectroscopic characterization is needed to better understand the local environments and predict better materials to test in the future.

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