

The Use of POMs in Photocatalytic CO₂ Reduction

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Research Question: How can atmospheric CO₂ be converted into useful products through the use of a POM photocatalyst?

Background Information

- A POM (polyoxometalate) is a type of inorganic cluster compound composed of transition metal oxides linked together by oxygen atoms. ⁽²⁾
- These compounds have unique properties and can play a role in the conversion of CO₂ to useful fuels through light absorption. In this lab, the researchers will modify variables within the POM's, such as the metal centers, in order to examine the effect on the desired products of the reduction. By using POM's, this lab hopes to contribute to the mitigation of climate change.
- POMs are unique inorganic catalysts for water oxidation due to their stability and ability to facilitate reversible electron transfer reactions without altering their structure. ⁽²⁾

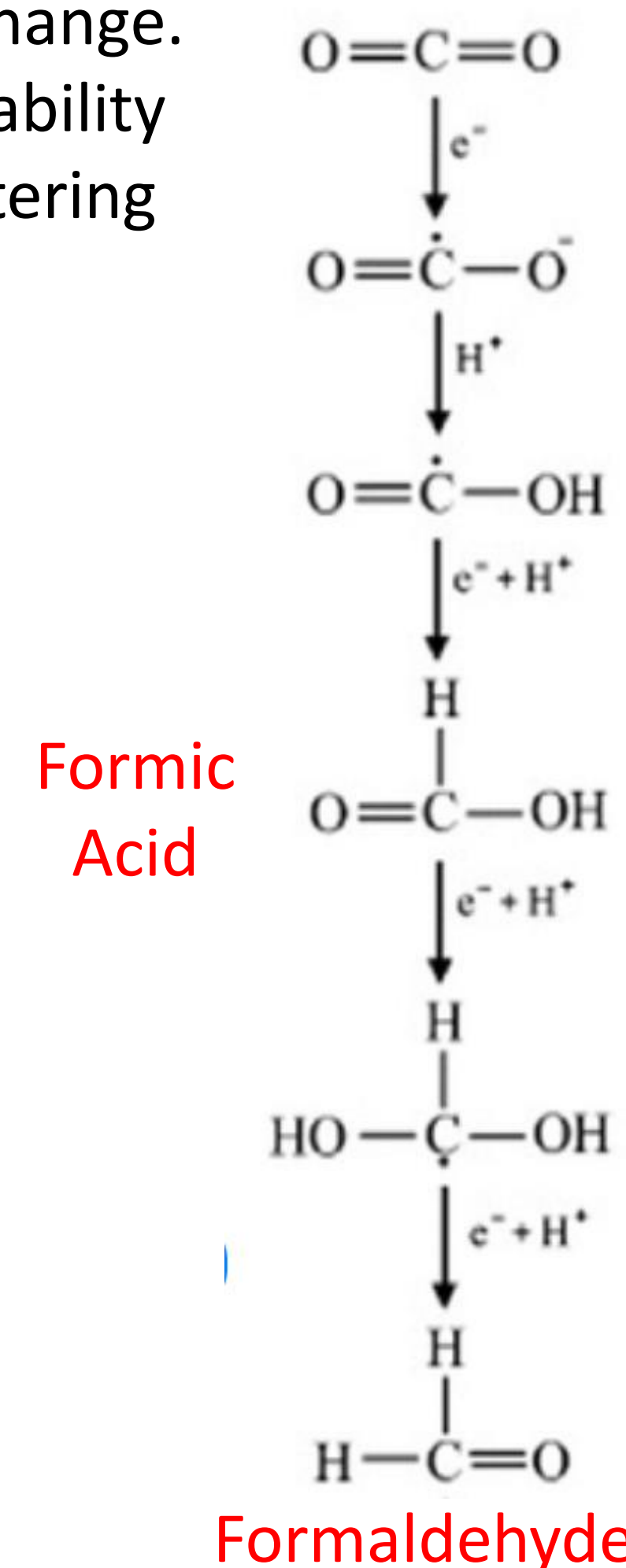
Research Methods: This lab is in the stage synthesizing basic POM's.

A couple batches of a molybdenum-based POM have been synthesized and the tungsten-based POM will be next. The lab will then focus on working with metal centers for controlling electron transfer and reaction activity. These factors will facilitate further testing on the selectivity of the products within the reduction of CO₂.

Obstacles Faced: The synthesis of the molybdenum-based POM has yielded an impure product, so multiple batches had to be made. In addition, the research for this conversion can be difficult because more complex photocatalyst structures are an area that hasn't been fully studied. Some of these niche areas of study could prove useful for a reaction such as this one with challenging energy parameters.

Basis of Study (Metal Centers)

- POM's vary greatly in structure and may involve multiple or different metal centers. Two examples of common structures are Keggin and Wells-Dawson. ^(3,5)
- Different metal centers can facilitate different reaction pathways. This is important for CO₂ catalytic conversion because the selectivity of products is one of the main challenges of this research. In the case of this lab, formaldehyde is one of the desired products.
- Two of the most common core metals in a Keggin POM are Tungsten (XW₁₂O₄₀)ⁿ and Molybdenum (XMo₁₂O₄₀)ⁿ. An example of these structures can be seen below. ^(2,4)



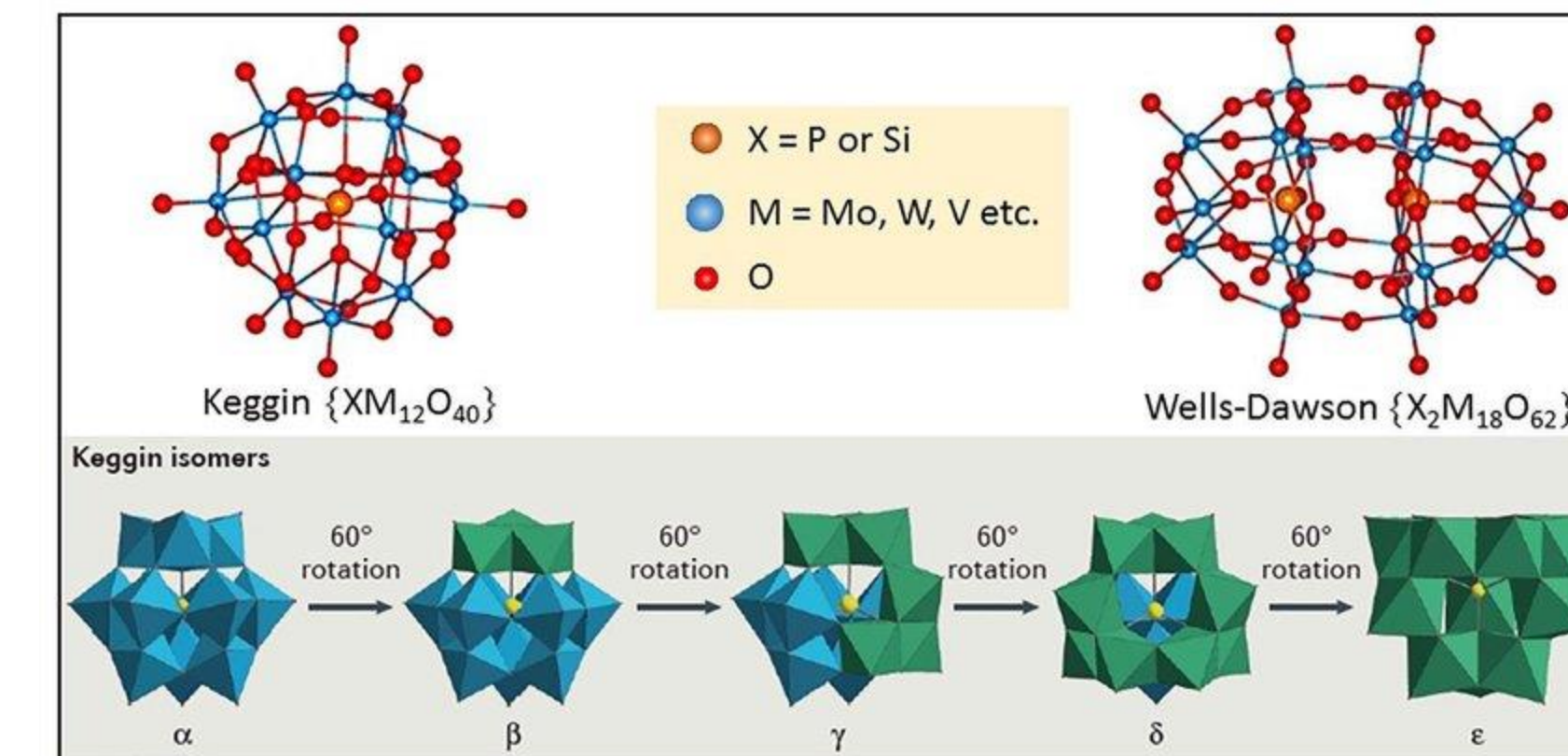
1) CO₂ conversion pathway for POM

Process of POM CO₂ Reduction

- The POM absorbs photons and goes into an excited state.
- Water gets oxidized forming e⁻ and H⁺ (electrons and protons stored in cluster). Cluster gets more reduced which enhances its reducing power.
- The e⁻ and H⁺ transfer to CO₂ reducing the structure to form products.

(In the reduction process, water acts as sacrificial e⁻ donor) ^(1,3)

* An example of the CO₂ reaction pathway can be seen to the left, with several products



2) POM structure and isomer (Keggin and Wells-Dawson)

Acknowledgements and References

- X. Huang, X. Liu, Applied Surface Science 2020
- ACS Appl. Mater. Interfaces 2017, 9, 13, 11689–11695
- S. Barman, S. S. Sreejith, S. Garai, R. Pochamoni, S. Roy, ChemPhotoChem 2019, 3, 93.
- Horn, Michael (POMs): from Electroactive Clusters to Energy Materials VL - 14 DO - 10.1039/D0EE03407J JO - Energy & Environmental Science
- Azmani, Khalid, et al. "Understanding Polyoxometalates as Water Oxidation Catalysts (WOC) through Iron vs. Cobalt Reactivity." Chem. Sci., vol. 8755, Feb. 2021,