The Interaction Between Brooker's Merocyanine and Linde Type L Zeolite

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Abstract

Materials chemistry looks at the characterization and application of materials with useful or interesting properties. Zeolites are an example of this, and are a porous host material that can contain other molecules and show unique properties. Zeolites can be used as energy transfer materials or as a microreactor due to their ability to organize other guest molecules. The focus of this research aims to clarify the understanding of how Linde Type L zeolite interacts with a guest molecule, specifically Brooker's Merocyanine, which was chosen due to its zwitterionic character. These chemicals have been studied at length on their own, but together not a full fundamental understanding is well established. When combined, experimental spectroscopic results indicate that the dye is adsorbed to the zeolite. However, BET analysis, which is a gas measurement of internal surface area of the zeolite pores, indicates that the dye is not found within the pores of the host material. My research project modeled a zeolite L crystal with a Brooker's Merocyanine molecule located at various locations through computational methods to determine the binding energy difference of the zeolite pore compared to the outer surface.

Zeolites

Zeolites are crystal structures composed of silicon, aluminum, and oxygen bonds that form into channels, which allow the zeolite to adsorb smaller molecules. These host-guest properties allow for zeolites to act in multifaceted ways, including acting as a catalyst or ion exchange reactions.

Zeolites have specific applications[1], including

- petroleum refining
- oil cracking
- gas purification
- biomass conversion
- carbon dioxide capture
- water purification
  - One reason for this is due to their charge and pores
  - Zeolites are capable of capturing smaller molecules and allowing for local chemical reactions

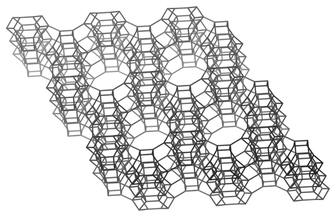

Figure 1. Structure of Zeolite L[2]

Brooker's Merocyanine

Brooker's Merocyanine is a dye molecule that has two forms, the quinoidal and zwitterion form.

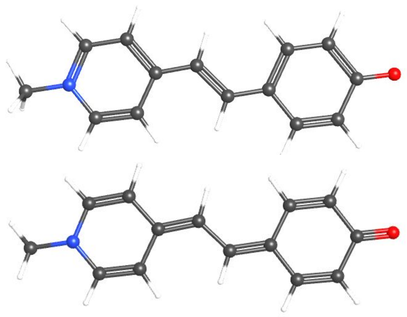

Figure 2. Quinoidal (A) and zwitterion (B) forms of the Brooker's Merocyanine

- A zwitterion has unique properties in that it can form chains of molecules due to the partially charged ends
- These molecules can exhibit second harmonic generation when aligned
- When the zeolite and dye are combined, we expect that the dye will enter the channels

BET Analysis

	Micropore volume (cm^3/g)
Zeolite L (1-d channel)	0.00439
Zeolite L/BM	0.00437
% Change	negligible
ZSM-5 (2-d channel)	0.152
ZSM-5/BM	0.118
% Change	22.4%

BET analysis uses the adsorption of inert gas molecules on a solid surface in order to measure the available pore volume.

- We used BET to test whether the dye entered the channels by looking at the pore volume change between loaded and unloaded zeolite

Although ZSM-5 was noted to have a significant change in micropore volume, LTL was found to have a negligible change in volume.

Thionine Test

Thionine can be used to determine if the zeolite can adsorb substances in its channels because the thionine changes color when the zeolite is dye-loaded.

- 5 minutes of boiling resulted in the sample with zeolite turning blue-violet
  - This is because thionine aggregates in solution but links together as monomer units when in the zeolite channels

Figure 3. Thionine solution (left) and zeolite with thionine (right)

Computational Analysis

Computational analysis is the study of modeling molecules through computational techniques.

- This includes heat of formation, binding energies, structure optimization, and visualization of orbital overlap, and allows for geometry optimizations while freezing atoms and optimizing the dye
- The downfall of computational analysis is that it is only as effective as it is realistic
  - This leads to high vs low theory and the necessity for both

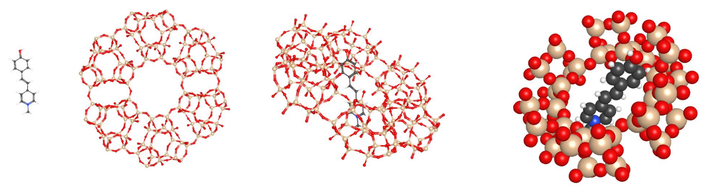

Figure 3. The zeolite and dye molecule optimized separately (left) and the combined dye and zeolite (middle). The right is showing a space filling model of the combined dye and zeolite.

Using computations, we hope to find the binding energy of the dye on the outer surface of the zeolite and compare that to the binding energy while the dye is inside the pore.

ONIOM

- Our own N-layered Integrated molecular Orbital and molecular Mechanics
- ONIOM is a technique for geometry optimizations that uses multiple levels of theory
  - This is in order to stay realistic while also keeping the processing time and memory cost down
  - It is difficult to model hundreds of atoms together and see how they all optimize at a realistic level
  - ONIOM calculations have not converged to self-consistency due to weak dye-zeolite interactions

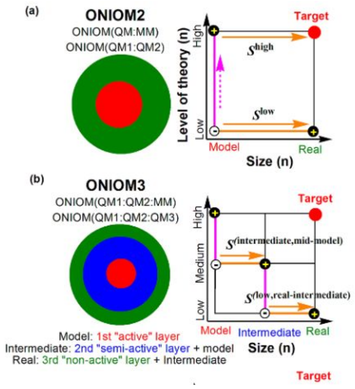

Figure 4. Visualization of the layers of the ONIOM method[3]

Results

- The Brooker's Merocyanine can physically fit into the channels of the pore
- BET analysis suggested that the dye molecule is not adhering to the channels
- Individual dye and zeolite structures have been fully optimized, but the ONIOM calculation for the dye-zeolite combination have not yet converged.

Future Directions

- We will expand our computational analysis to include molecular dynamics in order to determine the path to the lowest energy conformation of the dye within the channel
- We will expand this study to other zeolites to determine if there is strong or weak dye adsorption
- Although ONIOM optimizations have proven challenging, we plan to continue to refine our techniques.

References

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[2]Database of Zeolite Structures. https://america.iza-structure.org/IZA-SC/framework_3d.php?STC=LTL, (accessed 2024-03-12).

[3]Lung Wa Chung, W. M. C. Sameera, Romain Ramozzi, Alister J. Page, Miho Hatanaka, Galina P. Petrova, Travis V. Harris, Xin Li, Zhuofeng Ke, Fengyi Liu, Hai-Bei Li, Lina Ding, and Keiji Morokuma, Chemical Reviews 2015 115 (12), 5678-5796 DOI: 10.1021/cr5004419

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