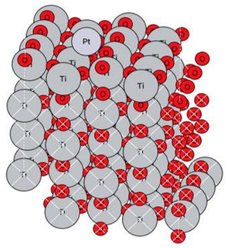
Analyzing Metal Support Interactions over TiO_2

Daniel Zheng, Sharada Lab
Polytechnic School, Class of 2025
USC Viterbi Department of Chemical Engineering, SHINE 2023

Single-Atom Catalysis



Look at different metal heterogenous catalysts to determine the best binding site on the surface

TiO_2 : Solid material.
Pt: Active site

Pt bound to different sites (A1, A2, H1, Oba_{vac} , etc..)

Plan: To analyze and calculate key characteristics relating to different sites when transition metals are bound to the surface of TiO_2 and how different interactions change the binding of CO to Pt

Computational Methods

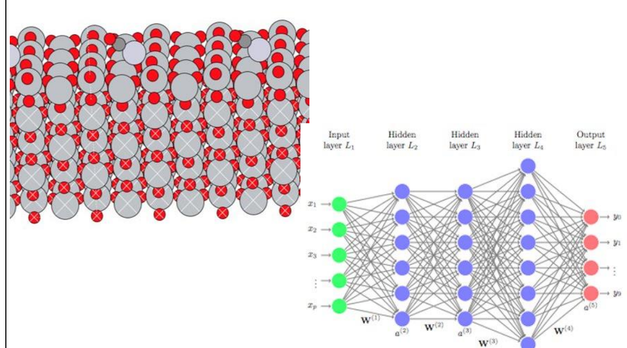
Software: VASP, ASE, CP2K

Calculation Methods: DOS, and DFT

Energy Analysis: EDA

$$\Delta E_{tot} = \Delta E_{deform} + \Delta E_{frozen} + \Delta E_{pol} + \Delta E_{CT}$$

Machine Learning: Random Forest, FFNN



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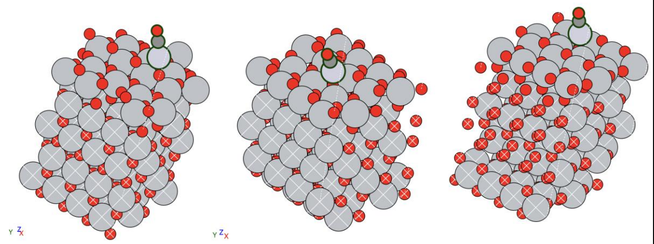
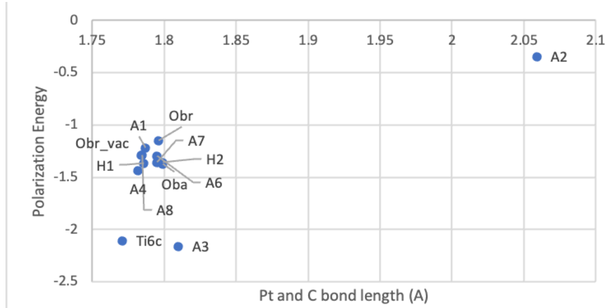
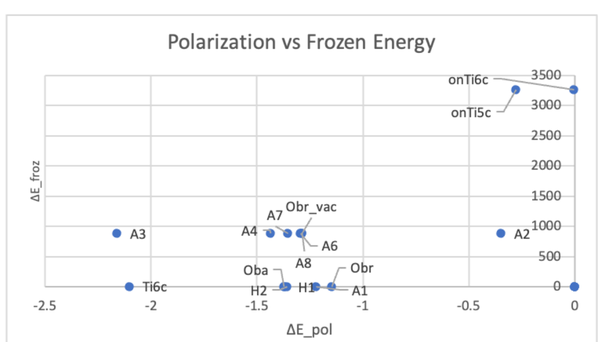
Energy Decomposition Analysis



CO and Pt bind differently depending on which site CO interacts with. This produces a variety of binding energies, frozen energies, polarization energies, deformation energies, and charge transfer interactions.

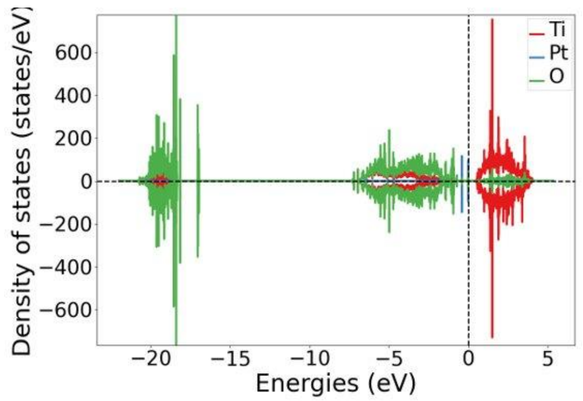


Scatterplot of the bond length of Pt and C compared to Polarization Energy. Clustering appears around 1.8Å and -1.35 eV. There could be a relationship between stronger ΔE_{pol} and shorter bond length.

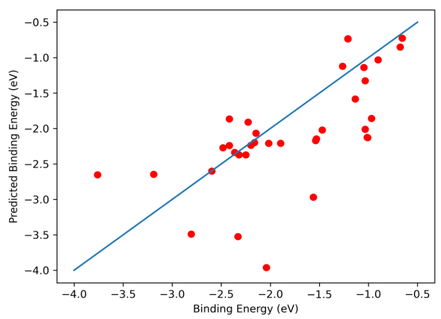


Pristine sites Ti5c and Ti6c have the highest frozen energy penalty. There appears to be clustering around –1 and –1.5 ΔE_{pol}. Some values cluster around 800 and 3 eV on the ΔE_{froz} section.

Density of States and Machine Learning



A partial DOS, showing contributions of each element in the system. There are multiple overlaps of orbitals, signifying hybridization at –19 eV, -4 eV, and 4 eV. The energy requirement for an electron to jump up a level is around 1 eV.



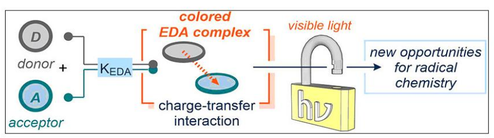
A parity plot comparing the predicted binding energy to the true binding energy of metals. The mean square error was 0.45.

Conclusions

- There seems to be a correlation between certain sites and clustering in the EDA graphs
- Random Forest is relatively effective on predicting binding energies
- Observed orbital overlap of Pt to nearby Oxygen

Further Works

- Acquiring BSSE data to implement Charge Transfer into the total interaction energy
- Fully analyze and compare all characteristics of CO interaction with Pt
- Apply DOS on more sites on the TiO2 surface
- Use a Feed Forward Neural Network on the dataset to try and observe a higher accuracy.
- Perform Lobster calculations to obtain ICOHP



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Citations

1: *Feedforward Deep Learning Models*. Feedforward Deep Learning Models · UC Business Analytics R Programming Guide. http://uc-r.github.io/feedforward_DNN
2:Synthetic methods driven by the photoactivity of electron donor https://pubs.acs.org/doi/10.1021/jacs.0c01416
3:Staub R, Iannuzzi M, Khaliullin RZ, Steinmann SN. Energy Decomposition Analysis for Metal Surface-Adsorbate Interactions by Block Localized Wave Functions. J Chem Theory Comput. 2019 Jan 8;15(1):265-275. doi: 10.1021/acs.jctc.8b00957. Epub 2018 Dec 7. PMID: 30462497.
4: Humphrey, N., Bac, S., & Mallikarjun Sharada, S. (2020). Ab initio molecular dynamics reveals new metal-binding sites in atomically dispersed Pt1/TiO2 catalysts. *The Journal of Physical Chemistry C*, *124*(44), 24187-24195.

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