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Tuning oxo formation energies using spectator ligands in the MIL-100 metal organic framework

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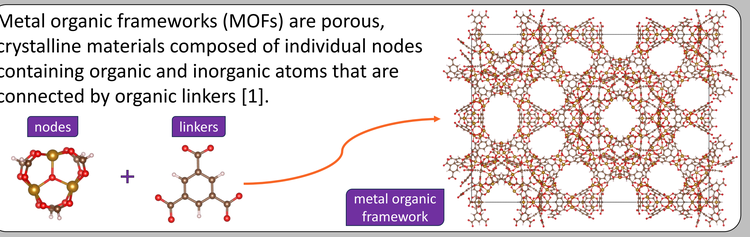
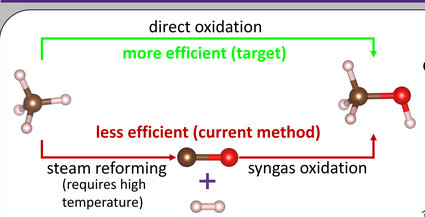
CLEMSON UNIVERSITY
CHEMICAL AND BIOMOLECULAR ENGINEERING

Metal Organic Frameworks (MOFs)

Metal organic frameworks (MOFs) are porous, crystalline materials composed of individual nodes containing organic and inorganic atoms that are connected by organic linkers [1].



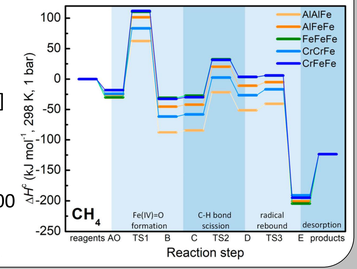
MOFs as Catalysts for the Direct Oxidation of CH_4



Developing an efficient and economical way to convert methane to methanol (MTM) requires catalysts capable of selectively breaking H-CH_3 bonds [2].

The MIL-100 Fe MOF has proven to be a selective catalyst for the MTM conversion. [3]

Different reaction pathway energies for the catalyzed oxidation reaction were observed when varying the metal composition of MIL-100 [4], suggesting an opportunity to tune both conversion and selectivity in MTM reactions.

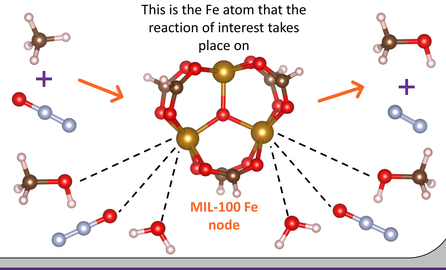


Research Question

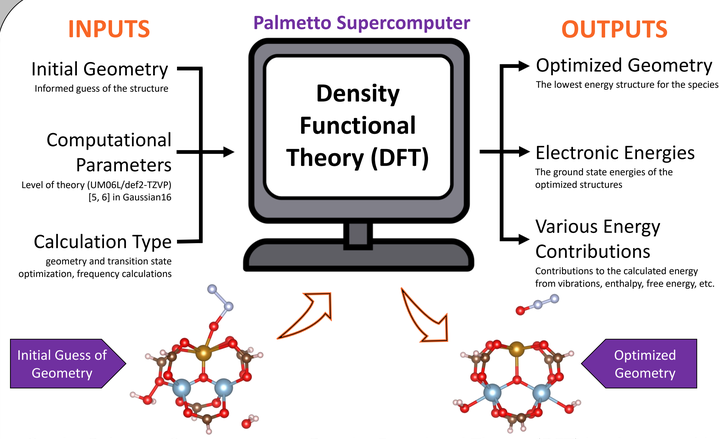
How sensitive are the MTM reaction pathway energies to different spectator ligands and MIL-100 node metal compositions?

Spectating Ligands
These are molecules that are coordinated to the MOF, but indirectly participate in the reaction of interest

Active Site
This is the Fe atom that the reaction of interest takes place on



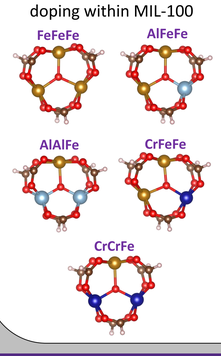
Computational Methodology



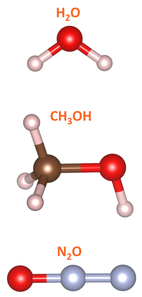
On the Palmetto Supercomputer, Density Functional Theory (DFT) implemented in the Gaussian16 software [7] computed the electronic energies for the N_2O activation reaction intermediates in order to calculate the reaction thermodynamic and kinetics.

Modeling of MIL-100 Node Variants Tested

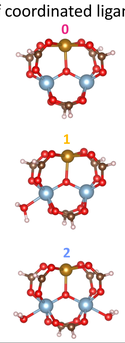
MIL-100 Variant (M):
Considered Al and Cr doping within MIL-100



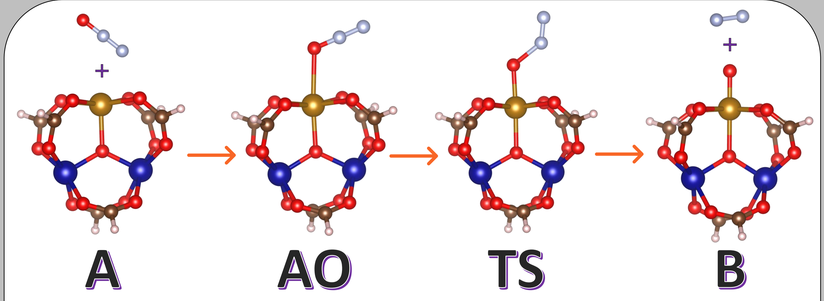
Ligands (L)
Considered 3 different ligands from gas environment



Number of Ligands (n)
Considered 3 different amounts of coordinated ligands

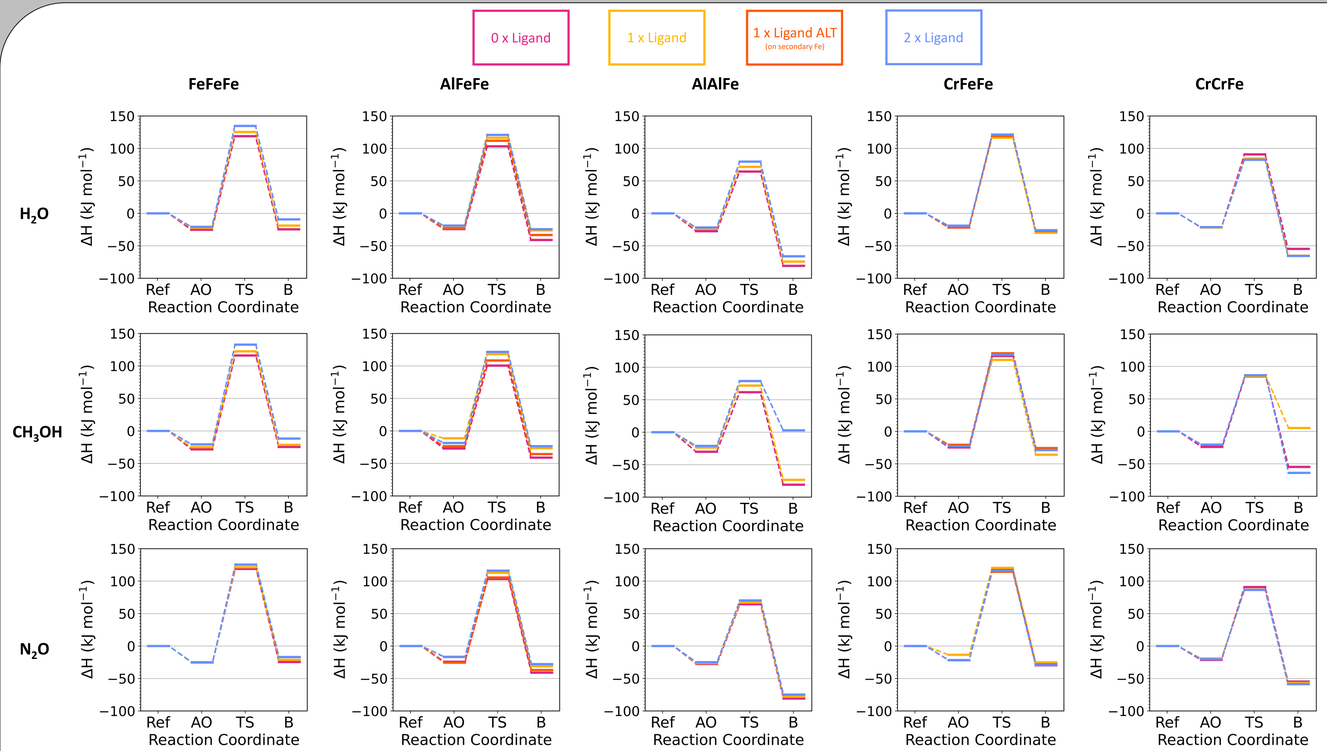


Reaction Overview for Formation of Oxo Species



$FeM_1M_2 \cdot nL + N_2O \rightarrow FeM_1M_2 \cdot nL + N_2$

Results



Binding Enthalpies (kJ/mol)

	A	B
FeFeFe	-75.5 | -71.7	-69.7 | -62.1
AlFeFe	-94.1 | -63.3	-79.3 | -61.5
AlAlFe	-84.4 | -81.6	-77.7 | -73.4
CrFeFe	-91.0 | -63.3	-94.6 | -59.4
CrCrFe	-79.4 | -85.1	-89.8 | -85.6

Key: $\Delta H_{0\rightarrow1}$ | $\Delta H_{1\rightarrow2}$

Binding Enthalpies (kJ/mol)

	A	B
FeFeFe	-79.3 | -76.8	-76.1 | -67.1
AlFeFe	-99.0 | -65.6	-84.4 | -62.6
AlAlFe	-89.9 | -76.9	-82.4 | -0.7
CrFeFe	-89.0 | -70.7	-98.8 | -63.5
CrCrFe	-86.9 | -85.1	-27.0 | -154

Key: $\Delta H_{0\rightarrow1}$ | $\Delta H_{1\rightarrow2}$

Binding Enthalpies (kJ/mol)

	A	B
FeFeFe	-24.9 | -24.7	-21.5 | -20.4
AlFeFe	-29.7 | -22.7	-19.8 | -19.3
AlAlFe	-22.6 | -20.3	-19.6 | -17.1
CrFeFe	-36.4 | -13.8	-35.2 | -18.3
CrCrFe	-29.5 | -28.1	-31.6 | -30.0

Key: $\Delta H_{0\rightarrow1}$ | $\Delta H_{1\rightarrow2}$

N_2O activation is influenced by H_2O and CH_3OH spectator ligands; however, the trends are different depending on the spectator ligand and MIL-100 metal doping.

N_2O is not influenced by the presence of additional N_2O spectator ligands.

Potential Descriptors For Spectator Ligand Influence

Species	Exp Dipoles	O Charge (CM5)
H_2O	1.857	-0.643
CH_3OH	1.672	-0.458
N_2O	0.161	-0.070

Conclusions and Future Works

On certain MIL-100 nodes, the MTM reaction pathway energies are highly sensitive to spectator ligands coordinated at secondary metal sites within the node.

Present finding suggests that the presence of these spectator ligands (combined with different metal-doping) could be used to tune the MTM reaction mechanisms.

Ongoing calculations into the full reaction pathways for MTM are necessary to determine the influence of spectator ligands throughout the reaction mechanism, in order to tune the chemical reactivity using spectator ligands and metal doping.

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References

1. Zhou, H-C, et al., *Chem. Rev.* (2012), 673–674, 112(2).
2. Blanksby, S. and Ellison, G., *Acc. Chem. Res.*, (2003), 255–263 36(4).
3. Kholdeeva, O., *Catal. Today*, (2014), 54-61, 238.
4. Vitillo et al., *ACS Catalysis*, (2019), 2870-2879, 9(4).
5. Zhao, Y., *Theoretical Chemistry Accounts*, (2008), 215-241, 120.
6. Weigend, F., *PCCP*, (2006), 1057-1065.
7. Gaussian 16, Revision C.02, M. Frisch Et. Al, Gaussian, Inc., Wallingford CT, 2019.