Theory Group Meeting

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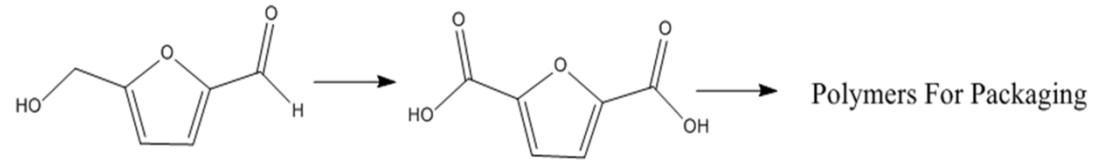
Introduction

- Project Title: Computer simulation of nano supported catalysts for the production of chemical feedstocks from plant waste.

- HMF – Derived from dehydration of sugars and also cellulose.

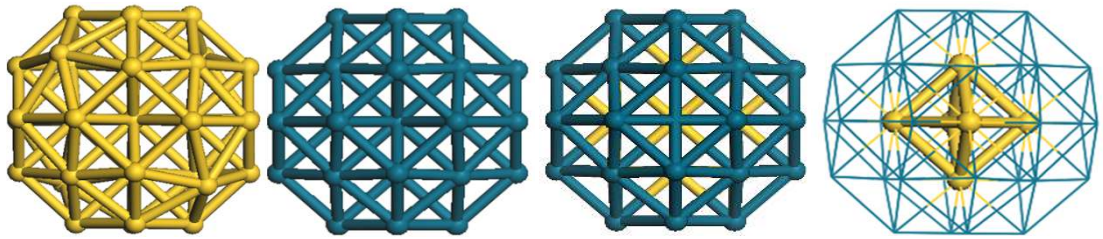


Hydroxymethylfurfural (HMF) 2,5-Furandicarboxylic Acid (FDCA)

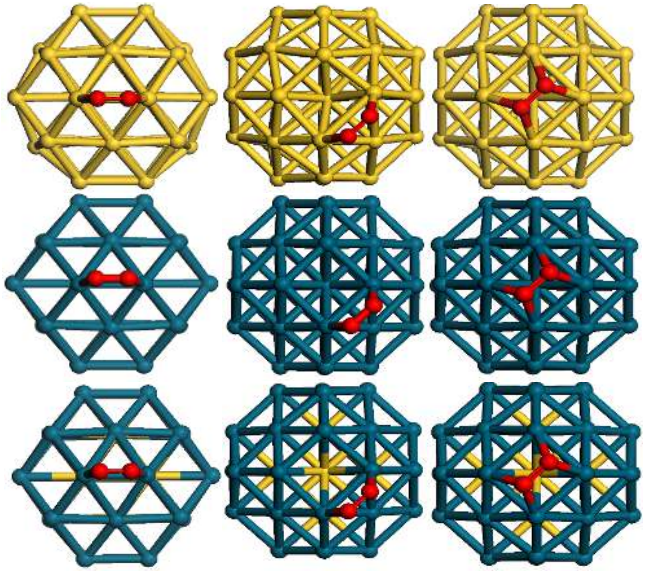
- Reaction performed using gold nanoparticles in the presence of atmospheric oxygen (mild reaction conditions)
- Little known regarding mechanism – Molecular modelling required.
- Debate surrounding oxygen interaction with nanoparticles.

Interaction of oxygen with metal particles

$E_{ads} = E_{(cluster+o2)} - (E_{(cluster)} + E_{(o2)})$



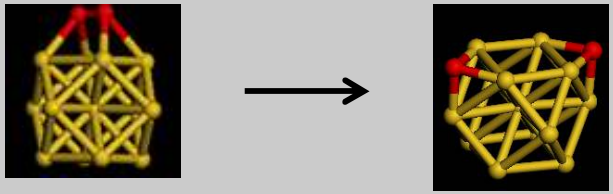
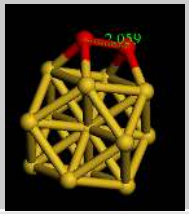
Highly ordered M_{38} clusters chosen to perform investigation on.



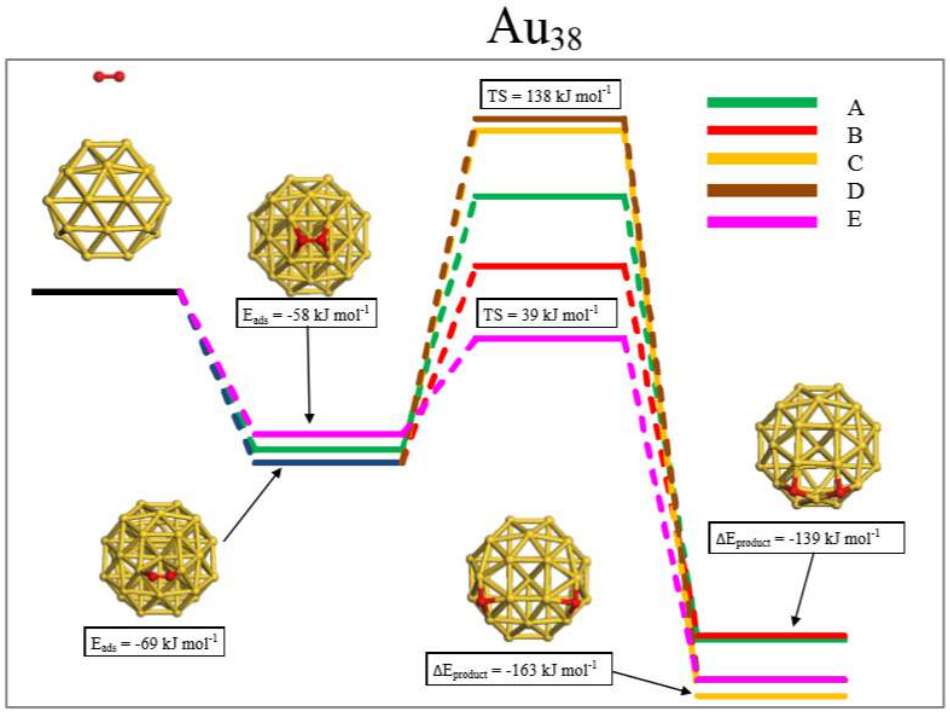
	E_{ads} / kJ mol^{-1}			$q(O_2)$ / e		
	a	**b**	**c**	**a**	**b**	**c**
Au_{38}	-64	**-69**	**-58**	-0.57	-0.59	**-0.81**
Pd_{38}	-123	-121	**-152**	-0.53	-0.51	-0.73
Au_6Pd_{32}	-139	-141	**-167**	-0.51	-0.52	-0.73

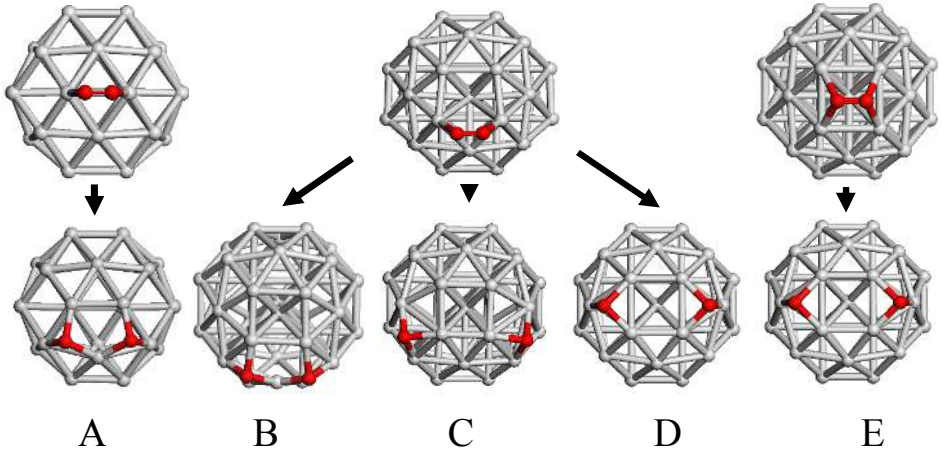
Bader analysis confirms adsorption in position c in all clusters studied exhibits greatest degree of charge transfer from metal to the oxygen molecule.

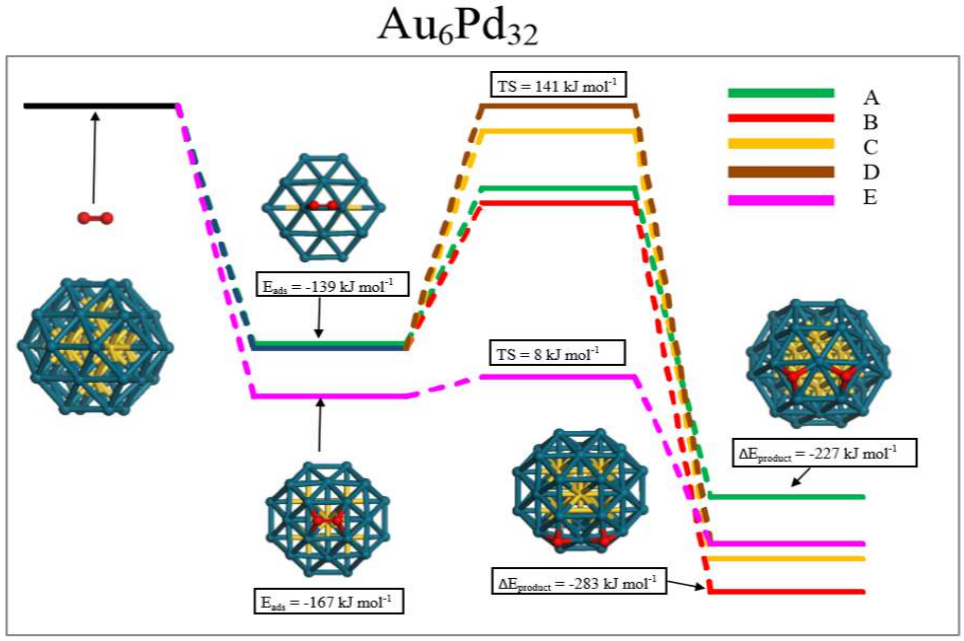
Determining Barriers to Oxygen Dissociation

Nudged Elastic Band (NEB)	Improved Dimer Method (IDM)
	
• Interpolation to generate 24 intermediate images from start to finish. • Typically require 384 cores and 72 hours for one NEB run to complete. • Up to 10 restarts are required to obtain barrier to dissociation. • Frequency job to verify TS.	• Initial “guess” of transition state required. • IDM optimiser minimises in each direction except most unstable direction. • Comparable to a Gaussian TS optimisation. • Over 900 iterations were required during some tests.
• Overall determined to be most reliable method.	• Overall this method proved unreliable. Barrier to ammonia inversion proved accurate however O_2 dissociation barriers varied substantially.

Oxygen Dissociation



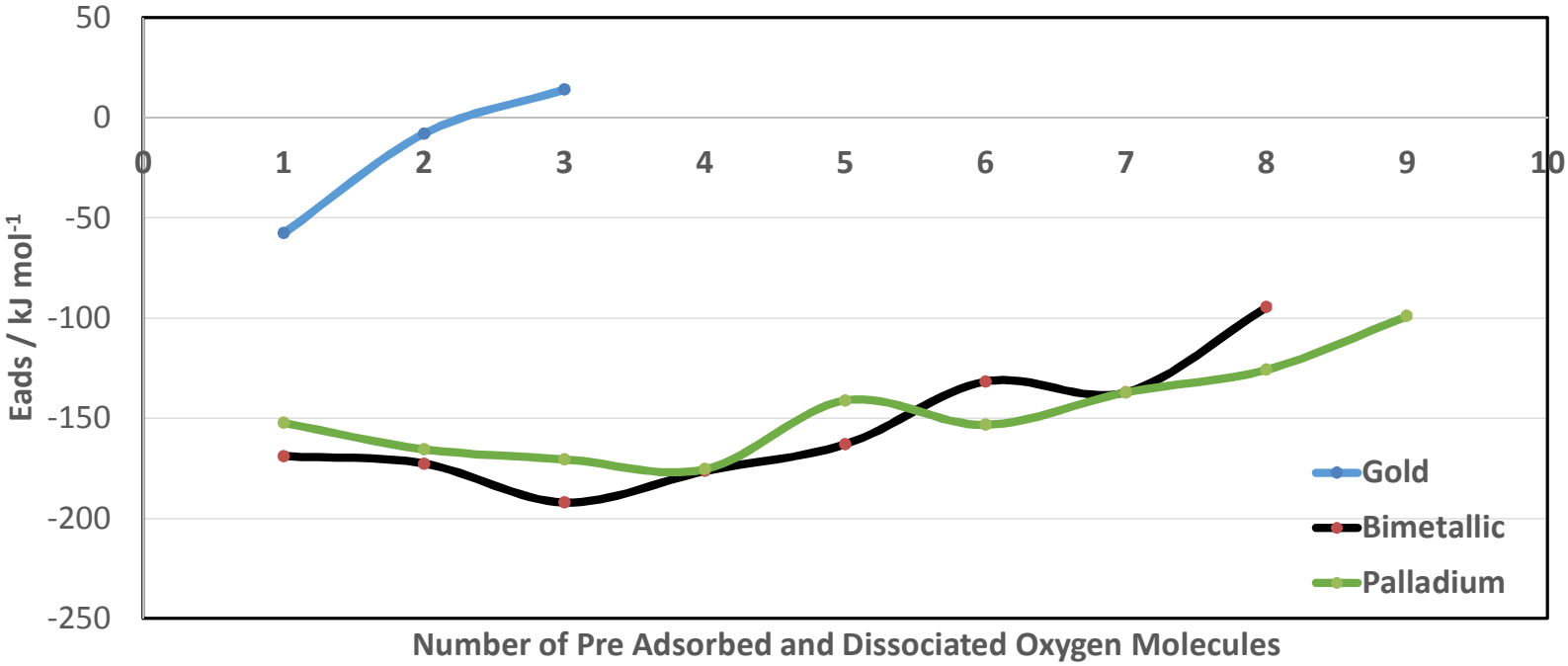


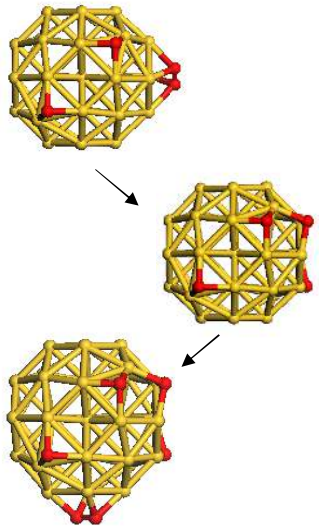


Dissociation via pathway E is clearly favourable in both Au_{38} and Au_6Pd_{32} clusters. All other dissociation pathways have a barrier to dissociation greater than adsorption energy therefore dissociation unlikely. Pd_{38} exhibits trend similar to Au_6Pd_{32}.

Multiple Oxygen Dissociation

- How many oxygen molecules can these clusters dissociate?





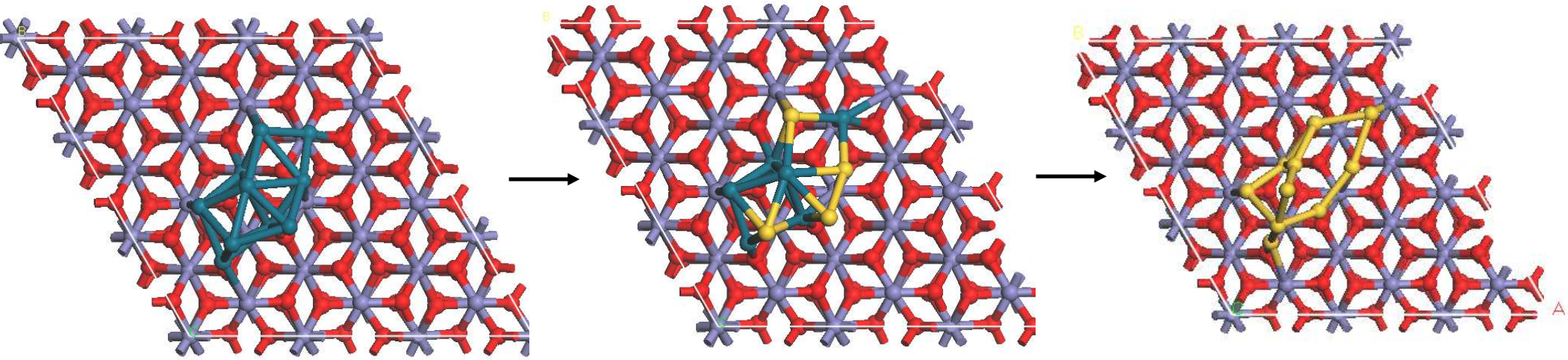
Barriers to dissociation remain approximately constant as a function of coverage however adsorption energy varies which prohibits more than 2 oxygen molecules from dissociating on Au_{38}. Pd_{38} and Au_6Pd_{32} clusters continue oxidation (currently at nine)

Au_6Pd_{32}

- Simple representation of a core shell particle.
- Experimental evidence demonstrates enhanced reactivity if Au is randomly alloyed into particle.
- Need to generate a random alloy cluster model.

S.O.D Program			**KLMC**		
Site occupancy disorder. Allows for substitutions of atoms into a system.	Generated 1041 structures for $Au_6Pd_{32.}$ Physically unfeasible to optimise using DFT.	Tried to categorize structures. Measured Pd-Pd, Au-Au, Au-Pd distances per confirguration to look for similarities.	Knowledge Led Master Code. Aims to generate global minima from any given composition of atoms.	KLMC first uses potential based approaches (GULP) to "roughly" obtain energies of clusters and then tightly optimise within DFT (VASP)	Difficult to obtain accurate potentials for bimetallic clusters.

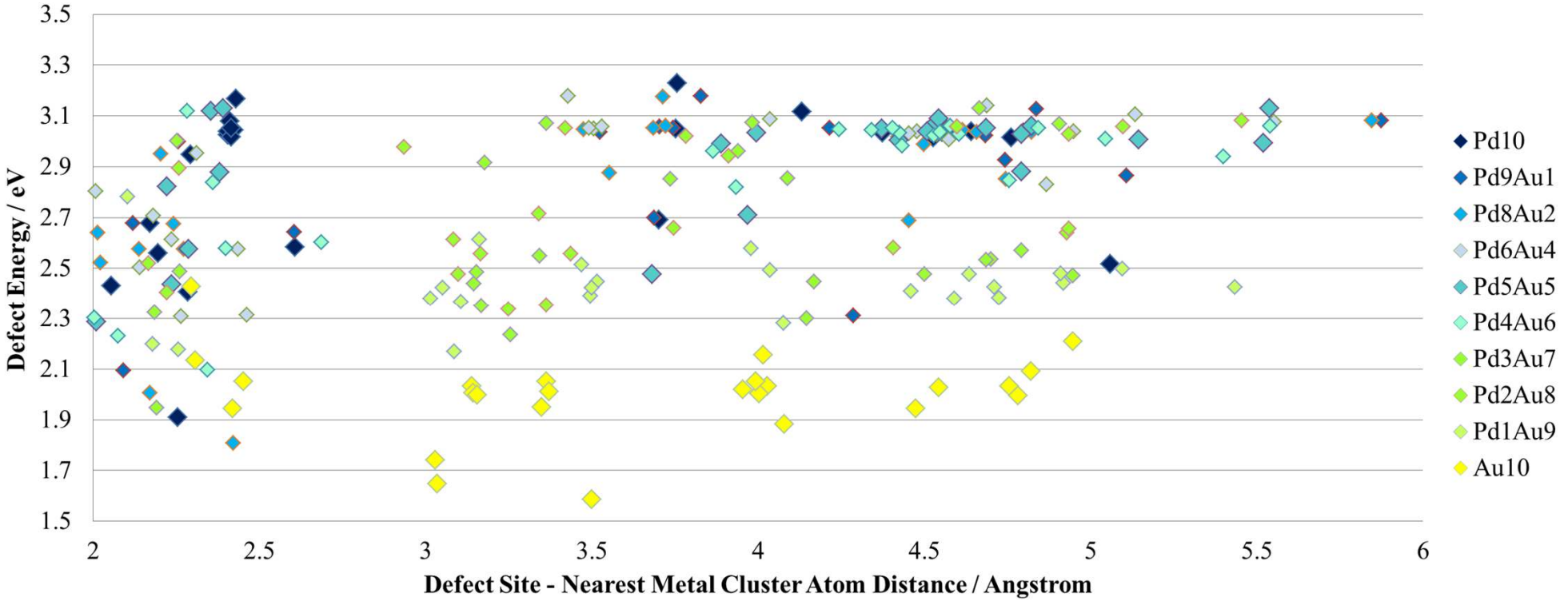
Fe_2O_3 (0001) surface oxygen defects.



Surface oxygen defect energies calculated at cluster compositions from Pd_{10} to $Au_{10.}$

DFT + U, Ueff = 6eV for Fe. Alternating spin throughout layers present in slab. Top layer free to relax.

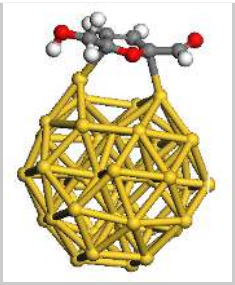
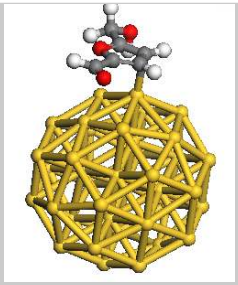
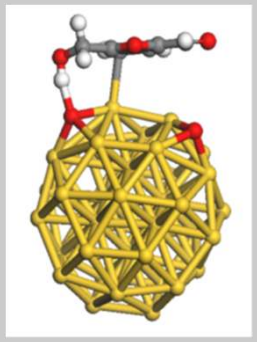
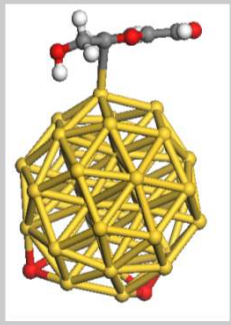
Fe_2O_3 Mars-van Krevelen Defect Energies

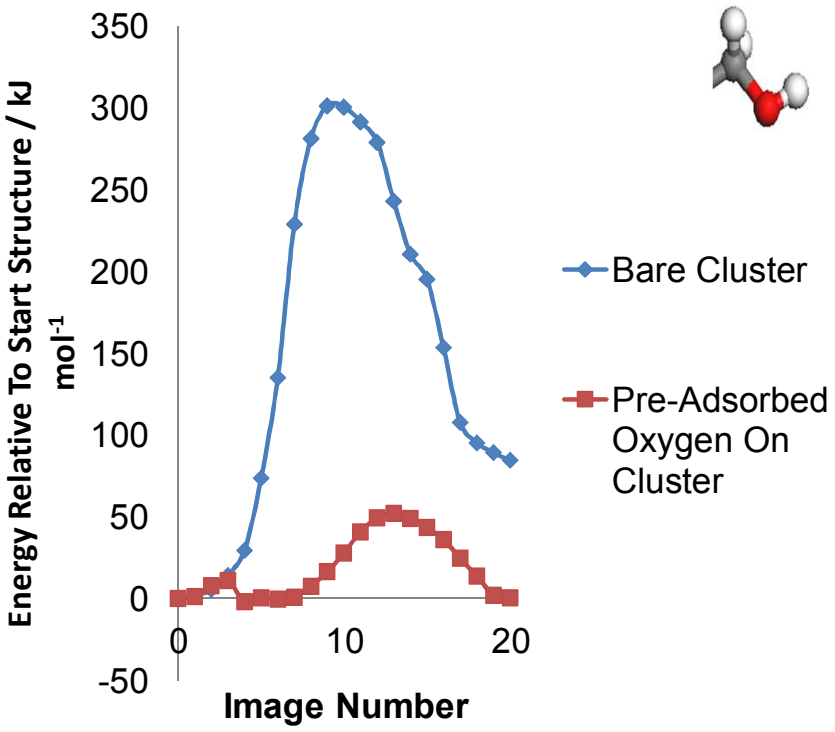


Defect energy primarily determined by proximity to metal cluster. However Pd_1Au_9 and Au_{10} cluster compositions give rise to substantially lower defect energies.

HMF Oxidation

- To date work focussed on HMF interaction with unsupported bare and partially oxidised clusters.

Eads = -63 kJ mol^{-1}	Eads = -43 kJ mol^{-1}
	
Eads = -48 kJ mol^{-1}	**Eads = -31 kJ mol^{-1}**
	



Outreach Events

- "Chemistry in the 3rd Dimension"

- Pilot held at Cardiff University November 2013.
- Students complete a workshop designed to allow them to predict geometry and estimate bond strength within chemical systems.
- Awarded £1500 to purchase 3D projector to enable workshop to be made portable.
- Volunteers welcomed to help develop workshop to make it a permanent addition to outreach events offered at Cardiff University.

Conclusions

- Au_{38} capable of adsorbing and dissociating 2 oxygen molecules.
- Pd_{38} and bimetallic cluster exhibits greater ability to dissociate molecular oxygen.
- Simple core / shell model for Au_6Pd_{32} needs improvement for random alloy modelling.
- Oxygen vacancy defects on $M_{10}Fe_2O_3$ depends largely on proximity to cluster however Au_{10} cluster is flexible and stabilises defect site.
- Pre adsorbed and dissociated oxygen species required to activate O-H bond of HMF (proposed rate limiting step of reaction)

Future Work

- Pursue mechanism for HMF oxidation on $Pd_{13,}$ $Au_{13,}$ $Pd_{38,}$ Au_{38} and Au_6Pd_{32} with and without support. Include D2 within calculations.
- Complete oxidation of metal cluster study (up to 12 dissociated oxygen molecules)
- Use semiempirical methods for mechanistic study of LA to gVL and include a Cu/Zr support (NOVACAM)
- Quantify shape of clusters through moment of inertia analysis.

Acknowledgements

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- Dr Dayna Mason for outreach event organisation.
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- Thank you for listening.