

Posters

Non-linear moments modelling of metal, oxygen and hydrogen binding to metallic surfaces

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e05-surfin-shu

The adsorption energy E_{ads} of metal, oxygen and hydrogen adsorbed on a series of strained FCC and HCP transition metal surfaces has been modelled using the first four moments $\mu_{(1-4)}$ of the clean surface d-states [1-2]. For compressive and tensile surface strains of between -5% and +10% the adsorption energy E_{ads} has been shown to be effectively modelled by a degree 6 polynomial expansion of $\mu_{(1-4)}$.

The physical justification for these models is discussed in terms of the distortion of the surface d-states during bonding, and extends the effectiveness of the conventional d-band model which only uses first adsorption moment $\mu_{(1)}$ i.e. the centre of the surface d-band, to cases where the surface is controllably distorted. The current work discusses the changes to the width, skewness, and bimodality of the surface electronic states of the Pt-block metals under strain, and also shows the non-linear character of adsorption under strain.

[1] Non-linear moments modelling of metal, oxygen and hydrogen binding to strained FCC (111) and (100) surfaces. I. G. Shuttleworth, *Chem. Phys. Letts.* **813** (2023) 140310.

<https://doi.org/10.1016/j.cplett.2023.140310>

[2] Moments analysis of the binding of metal, oxygen and hydrogen atoms to strained Co(0001), Ru(0001) and Os(0001). I. G. Shuttleworth, *Chem. Phys.* **566** (2023) 111788

<https://doi.org/10.1016/j.chemphys.2022.111788>

Advances in sustainable catalysis: A computational perspective

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e05-react-cat

The urgent need for society to move towards a greener and more sustainable future presents a very exciting opportunity for catalytic chemists. Many of the necessary changes in resource management and increased energy efficiency will be propelled by the directed design of new catalysts, for which a detailed theoretical understanding of the activity of current catalysts is a crucial part. Many very different computational techniques are being applied across Hub project's to the characterization of novel catalysts as a preliminary step to the engineering of new and much greener chemical route to important products. This poster will depict the implementation of a QM/MM protocol to explore the bioengineering potential of OleTJE, in order to increase its selectivity toward olefin production. There will also be a demonstration of the use of restricted cluster model calculations to investigate the ability of HOD to catalyze spin-forbidden oxygen activation.

An example of sustainable homogenous catalysis will be a study explored the reactivity of a novel μ -nitrido-bridged diiron-oxo porphyrin that was able to catalyze the methane to methanol reaction under very mild conditions. This study used unrestricted DFT methods to determine that the acidity of the FeO anion was mostly responsible for its increased activity over the related mono-oxygen porphyrin catalysts. The final example explored in this poster will concern several periodic DFT studies into the electronic properties and catalytic abilities of the low-index facets of early transition metal carbides. These studies point to the possibility of green catalytic routes towards the production of fuels and useful chemicals from the utilization of the green-house gas carbon dioxide; as well as the potential for these materials to be used as catalysts in hydrogen fuel cells. Taken together these example will demonstrate some of the powerful computational studies preformed as part of the UK Catalysis Hub's remit to model the next generation of powerful catalytic systems for a future circular economy.

Capturing the ground state electronic and magnetic properties of Cobalt containing metal and mixed metal oxides using density functional theory (DFT).

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e05-surfin-log

The Fischer-Tropsch (FT) reaction is important to mitigate chemical waste and produce sustainable hydrocarbon fuels. Hydrogenation of CO is an endothermic reaction, and so requires the use of catalysts to make the process economically viable. Transition metals like Ru, Fe, Co, and Ni have been demonstrated, yet further work is needed to understand the catalyst efficacy.¹ Cobalt-containing metal oxides (e.g. Co₃O₄) have been used as a catalytic precursor and reduced to obtain the active catalysts for Fischer-Tropsch (FT) synthesis, along with transition metal ions such as Mn²⁺ that act as promoters.² The active catalyst species is the Co metal atom obtained by reducing the metal oxides, which are dispersed in form of clusters across a support such as TiO₂, SiO₂, or Al₂O₃.³ In the Mn-promoted Co/TiO₂ FT reaction, an increase in Mn loading enhances the selectivity towards alcohols (oxygenates) and olefinic products. Advanced characterization techniques reveal the presence of spinel-like structures, with the formula Co_xMn_{3-x}O₄, in the catalyst precursor, indicating transition metal interactions.⁴ However, the nature of the interactions between Co, Mn and the support, contributing to enhanced Co metal dispersion and oxygenate selectivity is still evasive.

As a result, understanding the effect of Mn promoters in the formation of active catalyst would require an accurate description of the properties of metal oxide species involved in catalyst synthesis, from Co₃O₄ to Co_xMn_{3-x}O₄ and finally to Co metal. The magnetic properties of Co²⁺, Mn²⁺ and Mn³⁺ ions in these metal oxides add an additional dimension to the problem. Our simulations of antiferromagnetic (AFM) CoO and MnO, having a rocksalt structure show distortions during geometry optimizations, reducing the symmetry from cubic to rhombohedral. Additionally, equation of state (EOS) calculations show that the antiferromagnetic (AFM) state is energetically preferable. The ordering of the magnetic moments within the crystal systems, like CoO and MnO, significantly distorts the geometry (lattice parameters) below their respective Neel (T_N) or Curie (T_c) temperatures as observed experimentally.⁵ Our findings lay the groundwork for the development of models of precursor nanoparticles, with future work focusing on the impact of spin on surface structures.

References:

(1) Zhang, Qinghong, et al. *ChemCatChem* 2, no. 9 (2010): 1030-1058. (2) Paterson, James, et al. *ChemCatChem* 10.22 (2018): 5154-5163. (3) Jacobs, Gary, et al. *Applied Catalysis A: General* 233.1-2 (2002): 263-281. (4) Morales, Fernando, et al. *Physical Chemistry Chemical Physics* 7.4 (2005): 568-572. (5) Schrön, A., et al. *Physical Review B* 86.11 (2012): 115134.

Modelling hole trapping in hydrogen-related defects at the c-Si/a-SiO₂ and c-Si/a-SiO₂/a-HfO₂ interface

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e05-surfin-shl

The performance metal-oxide-semiconductor field-effect transistors (MOSFETs) is affected by random telegraph noise and bias temperature instability. These effects are caused by the trapping and release of holes and electrons in the dielectric oxide layer, but the atomistic nature of these processes is unclear. This research is focused on the DFT modelling of the effect of Negative Bias Temperature Instability (NBTI) in c-Si/a-SiO₂/a-HfO₂ devices. We aim to evaluate the accuracy of the Reaction Diffusion Drift (RDD) model, which suggests that the hole-induced dissociation of hydrogen-passivated defects can explain the trap generation kinetics in many types of devices.

We investigate how H-related defects in amorphous SiO₂ can be involved in hole trapping and hydrogen release, making them possible candidates for NBTI. Using non-local density functional we investigate how H-passivated oxygen vacancies and 3-coordinated silicon centres trap holes and release protons in bulk a-SiO₂ by reporting barriers for proton dissociation and defect charge transition levels with respect to the Si/SiO₂ interface using the rigid band approximation. We also probe the effect of trap levels of pre-existing defects with respect to the distance to the interface using models of c-Si/a-SiO₂/a-HfO₂ stacks to simulate both thick and thin film devices. Distributions of one-electron levels are calculated for oxygen vacancy centres and H-induced defects as a function of the distance to the interface. The thermodynamic nature of interstitial hydrogen is studied with respect to its position in the Si/SiO₂/HfO₂ stacks to assess its behaviour according to the RDD model. The charge state of interstitial H depends on the material in which it is present, and it can drift toward HfO₂ with a low energy barrier, as proposed by the RDD model.

Computational Infrared and Raman Spectroscopy in ChemShell

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e05-sok

To aid the interpretation of experimental vibrational spectra, we developed and implemented computational infrared and Raman facilities in the ChemShell computational chemistry environment using hybrid quantum mechanical and molecular mechanical approach. Density functional theory for the electronic structure calculations and classical forcefields for the environment are employed. Computational vibrational spectra for chemical active sites are reported using electrostatic and fully polarizable embedding to achieve more realistic vibrational signatures of material systems, including solvated molecules, proteins, zeolites and metal oxide surfaces, providing useful insight into the effect of the chemical environment on the signatures obtained from experiment. This work has been facilitated by the efficient task-farming parallelism implemented in ChemShell for high-performance computing platforms.

References:

- [1] Guan, Jingcheng, et al. *Philosophical Transactions of the Royal Society A* 381.2250 (2023): 20220234.
- [2] Abdul Nasir, Jamal, et al. *Journal of the American Chemical Society* (2022).

Catalytic Partial Oxidation of Methane using an Yttria-Stabilized Zirconia Catalyst

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e05-react-cat

This project is about discovering the catalytic cycle for Catalytic Partial Oxidation of Methane (CPOM) via using Yttria-Stabilized Zirconia (YSZ). The partial oxidation of methane is an important industrial process for upgrading natural gas into syngas, a mixture of CO and H₂ which is widely used in the industrial field. The reaction of CPOM occurs on the (111) plane of YSZ, in which the methane is physisorbed and oxidized into formaldehyde, before decomposing into syngas and other by-products. The surface model in this project is large symmetric slab model, which consists of 4*4 supercell with 96 ZrO₂ formula units. The thickness, width and vacuum separation of the slab are respectively 16.36Å, 14.6 Å and ~15Å. The concentration of Y₂O₃ is 14.3 mol% on the surface, which fits the experimental observation of 10-14 mol%.

The surface was firstly pre-oxidized via the removal of one lattice oxygen and absorption of the oxygen molecule in the atmosphere. Thus, the pre-oxidized 'YSZ+O' model was prepared for further reaction. Then the research discussed the process of methane absorption and oxidation into surface formaldehyde on the YSZ, with various routes and reactions being analyzed. To be specific, the results mainly indicated a possible method which led to the decomposition of surface formaldehyde through H-Zr interaction. Proper structures were discovered with lower potential energy compared with the initial structure, which suggested that CO may be desorbed firstly. When the CO was abstracted at first, the remaining hydrogen could form a surface hydroxyl and an isolated proton located at the surface vacancy. The electronic structures are simulated based on the Density Functional Theory (DFT) via VASP, to achieve its configuration and polarization if possible. Besides, other routes such as abstracting H₂ initially were also discussed, with higher energy barrier in the end.

Potential thermoelectric materials: zinc-based oxychalcogenides $\text{SrZn}_2\text{Ch}_2\text{O}$ (Ch = S, Se)

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e05-power-dos

In the process of primary energy consumption, a large amount of waste heat is generated. Thermoelectric materials can convert waste heat energy into electric energy, which is crucial to solving the current energy crisis and global warming. In general, the performance of thermoelectric materials can be determined by the dimensionless figure of merit, ZT, that is evaluated by electronic and thermal properties. However, it is difficult to maximize ZT due to the interaction between different parameters. Although some high ZT thermoelectric materials such as Bi_2Te_3 and PbTe have been found, they have not been widely used because they contain rare or toxic elements.^{1,2}

Recently, $\text{SrZn}_2\text{S}_2\text{O}$ was proposed as a novel photocatalyst for water splitting applications.³ Because of its complex structure, relatively high thermal stability, and the low toxicity and easy synthesis of oxides, we think that $\text{SrZn}_2\text{S}_2\text{O}$ may be a potential thermoelectric material. Using density functional theory (DFT), we first studied the phononic stability of $\text{SrZn}_2\text{S}_2\text{O}$ and its variant - $\text{SrZn}_2\text{Se}_2\text{O}$. Then based on the $\text{SrZn}_2\text{Ch}_2\text{O}$ (Ch = S, Se) electronic structure calculated with hybrid-DFT, electronic transport properties were calculated using AMSET⁴. Our calculation results indicate that both oxychalcogenides may become thermoelectric materials for high-temperature applications.

References

- 1 Y. Z. Pei, A. D. LaLonde, N. A. Heinz and G. J. Snyder, *Adv. Energy Mater.*, 2012, **2**, 670-675.
- 2 M. Saleemi, M. Toprak, S. Li, M. Johnsson and M. Muhammed, *J. Mater. Chem.*, 2012, **22**, 725-730.
- 3 S. Nishioka, T. Kanazawa, K. Shibata, Y. Tsujimoto, H.-C. Loye and K. Maeda, *Dalton T.*, 2019, **48**, 15778–15781.
- 4 A. M. Ganose, J. Park, A. Faghaninia, R. Woods-Robinson, K. A. Persson and A. Jain, *Nat. Commun.*, 2021, **12**, 2222.

Intrinsic defects in amorphous Ga₂O₃

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e05-bulk-shl

Ga₂O₃ is a promising material for power electronics devices and solar blind UV photodetectors, owing to its high breakdown electric field and wide bandgap (~5 eV). However, defects that occur during the growth, fabrication, or operation of Ga₂O₃-based devices can affect their performance and electronic properties.

In this study, we used classical dynamics (MD) and density functional theory (DFT) with the Gaussian plane-waves method to model amorphous phase of Ga₂O₃ and investigate the impact of point defects, such as oxygen vacancies and hole trapping on the electronic properties of Ga₂O₃. We employed the PBE0-TC-LCR functional, a non-local functional, to obtain more accurate and reliable predictions for the geometry relaxation and charge transition levels of the defects.

Our findings revealed that oxygen vacancy defects in amorphous Ga₂O₃ exhibit additional charge transition levels (CTLs) compared to those observed in the crystalline phase. This behavior indicates that additional electrons tend to become trapped around oxygen vacancies. Furthermore, we discovered that hole trapping in amorphous Ga₂O₃ is highly localized and occurs at deeper trapping energy compared to the crystalline phases. Our study could provide insights for designing Ga₂O₃-based electronics by understanding the impact of defects on the material's electronic properties.

Developing Standardised Modelling Workflows for QM/MM Simulations of Metal Oxides

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Modelling plays a key role in advancing our understanding of materials, assisting in both the discovery of novel condensed phase systems and development of their applications. Thus, models of solid state materials need to be both accurate and efficient, yet there is often a compromise between accuracy and computational cost. QM/MM (Quantum Mechanical/Molecular Mechanical) simulations achieve high accuracy with good computational efficiency by limiting the full quantum mechanical calculation to a small region of interest where preserving physicality is critical; the interactions with the quantum region are then modelled through coupling to an environment of classical charges.^[1] QM/MM has advantages over periodic density functional theory (DFT) simulations; the latter method can be resource inefficient, scale poorly with increasing sizes of cells and require corrections for nonphysical interactions, such as defect interactions, due to limitations in cell size.^[2]

We have performed calculations on neutral and charged defects in bulk MgO, employing QM/MM simulations (validating these against periodic DFT calculations) to develop a full workflow for producing accurate and realistic simulations. Our initial methodology is based on the simple system of bulk magnesium oxide (MgO) to facilitate accurate model development, allowing us to design heuristics for easily setting up embedding simulations.^[3-6] Currently, we are exploring the optimal size/shape of the QM and MM regions for accurate and efficient simulation, building on previous work in this area that suggests using a unit cell based partitioning approach over the simpler radial partitioning method.^[7, 8] A study by Shushko, Shluger and Catlow explored MgO surfaces with a similar but distinct embedding method, and we hope to be able to replicate their results using our newer models.^[9] The outcomes of this will show if the best method of partitioning can be rigorously identified from chemical observables of the bulk periodic system. In the future, we hope to use this work to investigate species that are more challenging to model for their applications to photocatalytic hydrogen production.

[1] A. Warshel, M. Levitt, *Journal of Molecular Biology* **1976**, 103, 227-249.

[2] S. Lany, A. Zunger, *Physical Review B* **2008**, 78, 235104.

[3] M. Causa, R. Dovesi, E. Kotomin, C. Pisani, *Journal of Physics C: Solid State Physics* **1987**, 20, 4983.

[4] A. De Vita, M. Gillan, J. Lin, M. Payne, I. Stich, L. Clarke, *Physical Review B* **1992**, 46, 12964.

[5] A. Gibson, R. Haydock, J. P. LaFemina, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **1992**, 10, 2361-2366.

[6] S. Pugh, M. Gillan, *Surface science* **1994**, 320, 331-343.

[7] M. Kick, H. Oberhofer, *J. Chem. Phys.* **2019**, 151, 16.

[8] B. X. Shi, V. Kapil, A. Zen, J. Chen, A. Alavi, A. Michaelides, *The Journal of Chemical Physics* **2022**, 156, 124704.

[9] P. V. Sushko, A. L. Shluger, C. R. A. Catlow, *Surface Science* **2000**, 450, 153-170.

Study of three-phase contact angles via DPD simulations

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e05-surfin

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The removal of oil droplets from solid substrates is the core problem in numerous applications of home and personal care products. When surfactants adsorb at an oil-water interface, they lower the interfacial tension, which is a key driver for oily soil detergency [eg E. Kissa, *Textile Res. J.* 45, 736-41 (1975)]. Thus, understanding and predicting the effect of surfactants on the three-phase contact angles of solid—oil—water systems is paramount in wash formulation design.

In this work, we use dissipative particle dynamics (DPD) to study solid—oil—water systems, where the substrate is represented as a continuous wall. A collection of systems with different wall interactions is prepared to portray hydrophobic and hydrophilic cases. Our aim is to predict the equilibrium contact angle of the oil droplets using Young's equation. The required interfacial tensions are obtained from oil—water and solid—liquid systems. The approach is validated by the slower simulation of explicit cylindrical droplets, which involves multiple boxes of different size to extrapolate the contact angle at infinite droplet radius. We report a good agreement between both methodologies for different surface interactions. We will then work towards more real world situations where surfactants and other surface properties need to be considered.

Influence of Solvent on Selective Catalytic Reduction of Nitrogen Oxides with Ammonia over Cu-CHA Zeolite

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e05-react-sok

In this new study, we made a comparison between water- and ammonia-solvated and bare Cu species [1]. Our results show the promoting effect of solvent on the oxidation component of the NH₃-SCR cycle since the formation of important nitrate species is found to be energetically more favourable on the solvated Cu. Conversely, both solvent molecules are predicted to inhibit the reduction component of the NH₃-SCR cycle. Diffuse reflectance infrared fourier-transform spectroscopy (DRIFTS) experiments exploiting (concentration) modulation excitation spectroscopy (MES) and phase-sensitive detection (PSD) identified spectroscopic signatures of Cu-nitrate and Cu-nitrosamine (H₂NNO), important species which had not been previously observed experimentally. This is further supported by the QM/MM-calculated harmonic vibrational analysis. Additional insights are provided into the reactivity of solvated active sites and the formation of key intermediates including their formation energies and vibrational spectroscopic signatures, allowing the development of a detailed understanding of the reaction mechanism. Further, we made a significant addition to the just-published work and now extended the study to Fe Beta-zeolite. The new results are significantly promising since we found the formation of key intermediates in a system containing Fe-framework is highly exothermic as compared to Al-Framework zeolite.

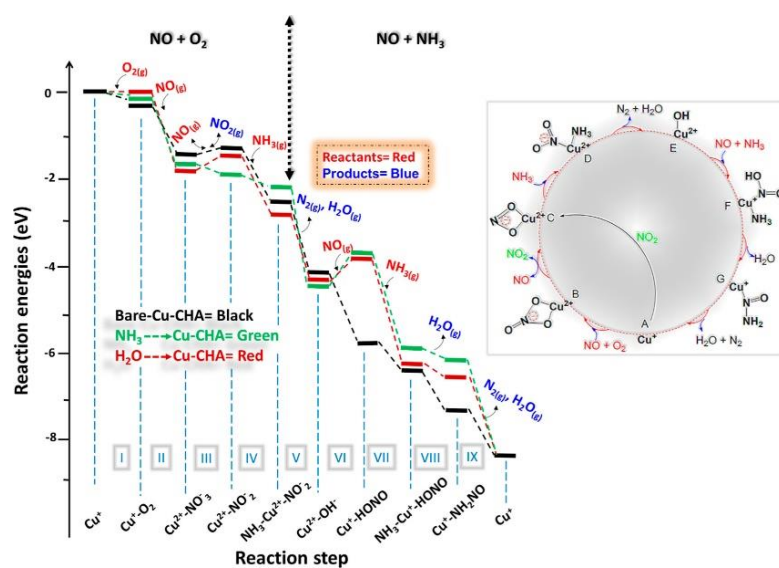


Figure 1. Potential reaction-energy landscape for NH₃-SCR on the activated Cu-CHA site and (black) on the bare site, (green) with physisorbed ammonia and (red) with physisorbed water. Inset right: NO-activated NH₃-SCR of the NO_x catalytic cycle.

References

- [1] Abdul Nasir, J, et al. J. Am. Chem. Soc. 2023, 145, 1, 247–259

Removal of VOCs in cooking fumes via adsorption method on zeolites

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e05-enviro-cat

The growth of public awareness of hazard from gaseous pollutants emitted by cooking activities spawned the implement of new laws and regulations as well as new technologies for cooking fumes emission control. Considering the emission characteristics of large air volume and intermittence of cooking fumes, MFI zeolites were applied as an efficient adsorbent for enriching the low-concentrated complex humid volatile organic compounds (VOCs) from cooking fumes. In order to illustrate the superiority of Ti-O-Si framework as a cooking VOCs adsorbent, zeolites with the same MFI topology to TS-1 but different framework compositions of Si-O-Al (ZSM-5) and Si-O-Si (silicalite-1, hereinafter referred as S-1) were also investigated for comparison. Related characterizations were performed to reveal the difference among three zeolites. It was found that textural properties, surface silanol density and defect content significantly affect the adsorption site accessibility, water resistance as well as organophilicity of zeolites adsorbents, all of which play a decisive role in the adsorption process of cooking fumes. Furthermore, adsorption energy between water/VOCs molecular and zeolites with Si/Al/Ti center was calculated through hybrid quantum mechanical/molecular mechanical (QM/MM) technique, revealing the adsorption interaction between different framework and VOCs as well as the water resistance.

Thermoelectric properties of the *Pnma* and *R3m* phases of GeS and GeSe

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e05-power-ske

As the impact of climate change becomes ever more apparent, coupled with dwindling fossil fuel reserves and an ever-growing demand for more energy, there is an intense focus on finding technologies that can provide clean and sustainable energy. As large amounts of current energy usage is wasted as heat (60 %), using thermoelectric generators to capture waste heat and recover it as useful electrical energy could significantly enhance efficiency and sustainability. Furthermore, thermoelectric generators are easily scalable to a wide range of applications including in the automotive, manufacturing and power industries.

Tin monoselenide SnSe is one of the most promising TE materials and was reported to have a very high ZT of 2.6 at 923 K. The germanium analogues GeS and GeSe have also been predicted to have good TE performance, and, recently, the rhombohedral (*R3m*) phase of GeSe, was reported to have a ZT value > 1 . However, the TE properties of *R3m* GeS, a structural analogue of *R3m* GeSe, have not yet been investigated.

We have used first-principles modelling to perform a comprehensive evaluation of the structural and electronic properties of the orthorhombic (*Pnma*) and *R3m* phases of GeS and GeSe. Our results show that n-type *Pnma* GeSe can support a large ZT of 2.23 at 940 K, due to a combination of its low lattice thermal conductivity and comparatively high electrical conductivity. This suggests that, if n-type doping of *Pnma* GeSe is possible, it could be a good match for p-type semiconducting material (e.g., SnSe) in a thermoelectric couple device.

Stability of Ru@Sn₉ Zintl cluster on a CeO₂ (111) surface and its catalytic activity in Water-Gas-Shift (WGS) reaction.

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e05-react-mcg

Cerium Oxide (CeO₂) is one of the most efficient compounds, supporting surface, because of the facile changes in oxidation state between Ce⁴⁺ to Ce³⁺, and is widely used in high-performance oxygen storage applications and catalytic redox reactions, solid oxide fuel cells, water-gas shift reactions, etc. The use of Zintl clusters or metalloids rather than isolated noble metal atoms as the catalytic centre offers the potential to exploit the interactions between transition and main-group metal to achieve low-barrier reactions, and recent work from our collaborators in Tianjin suggests that Zintl clusters are effective catalysts for the water gas shift (WGS) reaction. Recently, Sun et al. have reported the selective reduction of CO₂ over highly dispersed RuSnO_x sites, derived from a [Ru@Sn₉]⁶⁻ Zintl cluster but an atomic-level understanding of mechanism, and how it relates to the electronic properties of the cluster remain unclear.¹

In this work, we firstly investigate the stability of the Ru@Sn₉ Zintl cluster on the CeO₂ surface by comparing the optimised energy of the cluster on the surface with a dispersed structure where the Ru and Sn atoms are dispersed on the surface, using periodic Density Functional Theory (DFT). Interestingly, in many cases clusters prove not to be stable on surface, but rather are disrupted by strong metal-support interactions (SMSI).² An important first objective therefore is to establish the stability of the Ru@Sn₉ cluster on the surface under normal reaction conditions. It has been found that Ru@Sn₉ cluster will disperse over the surface and accumulate in a monolayer where Ru would prefer to stay at the edge. Later, we report some initial studies on the RuSn₉/CeO₂ (111) catalyst for WGS reaction where possible reaction mechanisms have been explored and activation energy barriers calculated. This catalyst shows a significantly lower energy barrier using different reaction path, compared to other reported heterogeneous catalysts such as Au, Pt, Cu nanoparticles on supported surfaces.

1 Wang, Y.; Zhang, C.; Wang, X.; Guo, J.; Sun, Z.; Zhang, H. Site-Selective CO₂ Reduction over Highly Dispersed Ru-SnO_x Sites Derived from a [Ru@Sn₉]⁶⁻ Zintl Cluster. *ACS Catal.* **2020**, *10*, 7808-7819.

2 Diebold, U. The surface science of titanium dioxide. *Surface Science Reports* **2003**, *48*, 53-229.

Utilisation of Machine Learning for Lithium Titanium Sulphate (LTS) Solid Solutions Energy Prediction

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e05-algor-smw

Battery development is critical for the transition from fossil fuels to renewable and more sustainable energy as rate of climate change is rapidly increasing. However, traditional material discovery methods are time-consuming and resource intensive. An ideal approach would be to study the desired properties to identify a potentially suitable material. While computational methods have been successful in assisting material discovery using this 'inverse design' method, ab-initio methods, such as DFT and Hartree Fock, requires significant computational cost and time.

To address these challenges, Machine Learning is used to facilitate the material discovery of Lithium Titanium Sulphide for batteries. DFT were used to generate the energies of the structures which are used as the labels for training the machine learning model, while descriptors were used to represent the structures generating features.

The data obtained showed Many Body Tensor Representation (MBTR) descriptor to have the most consistent performance with all machine learning model whilst Smooth Overlap of Atomic Orbital (SOAP) have the lowest mean absolute error (MAE) overall when paired with support vector regression (SVR). This project showcases the potential of Artificial Intelligence in accelerating material discovery and advancing the development of sustainable battery technology.

Effects of Electronic Polarization on the Convergence of Mott-Littleton Calculations of BaSnO₃

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e05-bulk-smw

Barium Stannate (BaSnO₃) is a perovskite oxide material with a wide range of applications in various electronic devices thanks to its attractive electronic and thermal properties. Point defects in such materials can introduce additional charge carriers, modify band structures, and affect carrier mobility, resulting in changes in conductivities as well as catalytic activities. Understanding and controlling point defects in perovskite materials is crucial for tailoring their properties to specific applications and advancing their technological potential. The Mott-Littleton method evaluates the defect energy accurately by calculating the energy difference between the perfect and the defective crystals using interatomic potentials, which require significantly less computational resources, compared to *ab initio* methods. Partitioning the regions around the defect centre also provide straightforward and intuitive interpretations on defect energies based on factors that affect the formation and stability of the defect.

We show that converging the defect energy in Mott-Littleton calculations can be challenging due to effects of electronic polarization due to the charged point defect, even for simple crystal structures in bulk phase, and analysing charge distributions in localised cluster can provide further insights on how the model can be improved and adapted to surfaces and interfaces, where addressing defect-induced dipole and quadrupole effects remains problematic.

Ketonisation of Carboxylic Acids over ZrO₂-based catalysts for Biomass Valorisation: The Role of Surface Acid-Base Sites

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e05-react-cat

Production of liquid fuels from biomass have gained increasing industrial and academic attention as alternative energy source to fossil-based fuels. Biofuels are usually obtained as a mixture of organic species with high content of oxygenated derivatives, which required chemical upgrading for improvement of its physicochemical properties prior to their use as fuels.¹ Acid–base bifunctional catalysts are particularly desirable in this context, which can be tuned by different approaches in order to optimise their activity and selectivity.² Here, we investigate how the reaction mechanism and energy profile of the ketonisation of carboxylic acids are affected by modification of the acid-base properties of zirconia-based catalysts.

The ketonisation reaction has been proposed to occur via several putative mechanisms. Currently, the β -ketoacid mechanism is the most plausible one based on previous experimental and computational results.¹ The two most important steps of the β -ketoacid mechanism are investigated here: enolisation of the adsorbed carboxylic acid and C-C coupling step to afford α -hydroxy γ -carboxy alkoxide intermediate. These reaction steps were studied over pristine c-ZrO₂ (111) and t-ZrO₂ (101) surfaces, as well as over three modified surfaces: Ca- and Y-doped c-ZrO₂ (111), and, sulfated t-ZrO₂ (101). We show that distinct strengths of the acid-base sites on the surface of these catalysts can influence the adsorption modes and protonation state of the reactants and intermediates, resulting in significant changes in the computed energy barriers and the identity of the rate-determining step in the ketonisation of organic acids.

¹B. Boekaerts, B. F. Sels, Appl. Catal. B: Environm. 2021, 283, 119607; ²M. Delarmelina, C. R. A. Catlow, R. Soc. Open Sci. 2021, 9:211423.

Computational investigation of CO₂ hydrogenation over Rh-based catalysts

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e05-react-cat

The alleviation of CO₂ emissions has become an urgent issue, requiring the development of technology for carbon dioxide capture, storage and utilization. Energy-efficient catalytic CO₂ conversion using renewable energy, has attracted considerable attention worldwide as a potentially feasible means to mitigate CO₂ emissions, and sustainably produce commodity fuels and chemicals. It is thermodynamically feasible to convert CO₂ through hydrogenation processes to produce hydrocarbons. Among them, methane (CH₄) is an attractive target molecule as it can be directly injected into the existing natural gas infrastructure for distribution and storage. In addition, CO₂ hydrogenation to CH₄ is regarded as a feasible process for the long term chemical storage of electricity produced from renewable sources. Among the metal catalysts, Rh has exhibited high activity for CO₂ hydrogenation and selectivity towards methane. However, the various mechanistic routes for CO₂ hydrogenation to CH₄ are multiple and complex. A powerful tool for exploring the reaction mechanisms under realistic conditions is provided by the combination of Density Functional Theory (DFT) and kinetic Monte Carlo (kMC) simulations which can complement operando experimental techniques and identify descriptors of activity and selectivity for CO₂ hydrogenation.

In this context, we aim to investigate all the mechanistic pathways for CO₂ hydrogenation over Rh surfaces, providing a valuable benchmark study to inform the rational design of high-performance catalysts for CO₂ hydrogenation. Here, DFT simulations have been used to explore the reaction mechanisms for CO₂ hydrogenation over the Rh(111) surface, including 53 reversible reaction steps, 6 desorption steps, CO₂ adsorption, and all the relevant intermediates. It has been found that the Rh catalyst can promote the CO₂ activation and H₂ dissociation based on the geometric and electronic analysis of the adsorption structures for CO₂ and H₂ and lower activation energies for H₂ dissociation. Based on the present work, we plan to carry out kMC simulations to explore the product distributions and the dominant reaction pathways involved in CO₂ hydrogenation over the Rh surface, which will provide an in-depth insight into the reaction mechanisms for the CO₂ hydrogenation over the Rh surface under experimental conditions.

High-dimensional neural networks for interatomic potentials: Applications to metal organic frameworks

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Machine learning interatomic potentials (MLIP) are revolutionising our way of describing and understanding how atoms and molecules interact. Precise simulations of atomic and molecular chemical systems is hampered by the poor scalability of first principles methods such as Density Functional Theory (DFT), or by the limitations of classical force fields due to their empirical nature. A major challenge in the development of MLIPs is creating a training set that allows the system to learn all of the relevant physics and chemistry of a given system. Active learning is a technique that can solve this problem by building a training set that systematically explores phase space. In this work we use neural network potentials and active learning to study UiO-66 metal organic framework (MOF), a system of interest due to its stability, pores and filtration abilities. We compare the radial distributions functions of configurations from simulations using our system with simulations using DFT methods and explore the scalability and transferability of our potential.

USING POTENTIALS FOR MODELLING COMPOUNDS THAT UNDERGO THE METAL – INSULATOR PHASE TRANSITION

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e05-bulk-smw

The metal-insulator phase transition is the process by which a compound that conducts electricity becomes an insulator (or vice versa) by means of a change in its atomic and electronic structure. One of the most studied compounds is vanadium dioxide (VO_2). The computational method most widely used for its study is DFT since the process has its origin in a Peierls distortion caused by the presence of a d^1 electron in vanadium. Moreover, there are other dioxides that undergo the same process by means of a Peierls distortion: NbO_2 and TaO_2 , being both niobium and tantalum in the same group as vanadium (Group V).

Interatomic potentials are a convenient computational method since they allow to study large systems and/or a high number of configurations without being too computationally expensive. Considering that DFT is a computationally expensive one, interatomic potentials are a good alternative for studying and optimising the structure of these compounds. All in all, this project aims to adapt the potentials used in VO_2 for using them also in NbO_2 and TaO_2 with the finality of analysing the effect of their differences in the parameters of the potentials and developing an easy-going approach to study the elements in the same group. The potentials that are being used are Buckingham Potential (for optimising the general structure), Morse Potential and Double-Well Morse Potential (for reproducing the Peierls distortion) using the Package GULP.

Electronic and Structural Properties of the 2D Photocatalyst $g\text{-C}_3\text{N}_4$

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e05-surfin-jbu

Increased efficiency in the performance of photocatalytic materials can be effected by the formation of nanocomposites, often with carbon-based 2D systems. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) has shown great promise for photocatalytic water splitting when combined with semiconductor materials such as TiO_2 . It is highly stable, semiconducting and has favourable electronic properties. However, much is not understood about the properties of the material and the mechanisms by which it facilitates photocatalytic processes. We survey different density functional theory approaches to model $g\text{-C}_3\text{N}_4$ in order to understand fundamentally its structural and electronic properties. We also study the effects of applied strain on its properties, to simulate realistic structures when the 2D system is interfaced on a semiconductor surface. Our results help us understand catalytic processes that are observed by our experimental collaborators who grow samples and measure their activity.

Modeling the Effect of OSDA on Nucleation Process of TS-1 Zeolite

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e05-nano-cat

Zeolites are porous materials that come in many topologies and have multiple catalytic functions. The majority of zeolite synthesis relies on organic structure-directing agents (OSDAs). However, most OSDAs designs are based on trial and error, chemical intuition, or large-scale screenings rather than rational design. Thus, this empirical labor-intensive task makes the design of OSDA a significant technical threshold. In this study, we analyzed the effects of over 80 different OSDAs on the nucleation process using TS-1 zeolite as an example. Through high-throughput computational simulations, literature mining, synthesis, and characterization, we revealed the energetic, geometric, and electrostatic descriptor effects of OSDAs on the entire nucleation process.

High-throughput computational design and discovery of conductive materials in the CSD MOF subset

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e05-power

MOFs are innovative porous materials, and have been widely studied for the past two decades for applications in different areas including gas storage, gas separation and catalysis. Here, we aim to study electrical conductivity in MOFs, a less explored but interesting property that can bring promising opportunities in energy storage and sensing application. Due to their high porosity and surface area, MOFs are poor electrical conductors. Here, to identify promising conductive structures, we performed high-throughput screening of the existing ca. 90,000 structures in the CSD MOF subset¹— characterising the band gap and examining the presence or absence of metallic behavior. The first set of selection criteria was developed based on the nature of MOFs' surface chemistry with a focus on the type of the secondary building unit and the ligand. We focused on MOFs containing open shell metals, metal clusters and highly conjugated linkers that can facilitate through-linker charge transfer between metals. The second set of criteria involved the presence of linkers containing metal-S, or -N coordination, redox-active linkers, π - π stacking, and mixed valence metals. For the ca. 1000 structures shortlisted, we then performed DFT calculations to derive useful insights into structure-conductivity relationships in MOFs, identify top-performing conductive MOFs, and to delineate key chemical and physical features in MOFs that influence their conductive properties for the first time. The results guide MOF researchers to assess and design conductive structures for electronics, energy storage and sensing applications.

Reference:

[1] Peyman Z. Moghadam *et al.* (2017) *Chemistry of Materials*, 29, 2618–2625