Chem4Energy Annual Conference
Materials and Processes for a Sustainable Energy Future
Monday 7 – Friday 11 April 2025

Conference Programme (may be subject to amendment)

Tuesday 8 April 2025

08:50 – 09:00	*Chair's comments*	*Professor Cornie van Sittert, North-West University, South Africa*
09:00 – 09:45	**Keynote** Current challenges in catalytic science to achieve a net zero world	**Professor Graham Hutchings, Cardiff University, UK**
09:45 – 10:10	LDHs catalysts for SCR of reduction of NH_3 to NO and NO_2	Professor Ateeq Rahman, University of Namibia
10:10 – 10:35	OER catalysts (IrM oxides) are characterized for green hydrogen production via PEM water electrolysis	Dr Shawn Gouws, Nelson Mandela University, South Africa
10:35 – 10:50	Synthesis of Ni-Al LDHs by Co-Precipitation method: Their role in hydrogen production	Meameno-Etuna Tweufilwa, University of Namibia
10:50 – 11:20	*Refreshment break*	
11:20 – 11:45	Investigation into support influence on rWGS activity of Fe_3Ni catalysts using metal oxide-overlayered alpha-Al_2O_3 supports	Professor Nico Fischer, University of Cape Town, South Africa
11:45 – 12:10	Improving Pd-based alloy catalysts for CO_2 hydrogenation with DFT and AI analysis	Dr Igor Kowalec, Cardiff University, UK
12:10 – 12:25	Photocatalytic degradation of Rhodamine B dye using Cu_4O_3 nanoparticles under visible Light	Jacobina Nangombe, University of Namibia
12:30 – 13:40	*Lunch*	
13:40 – 13:45	*Chair's comments*	*Professor Richard Catlow, University College London, UK*
13:45 – 14:30	**Keynote** Density functional theory study of catalytic materials in metal-air batteries	**Professor Khomotso Maenetja, University of Limpopo, South Africa**
14:30 – 14:55	Theoretical investigation of optoelectronic properties of Ru-dyes for solar cell application	Dr Willem Pendukeni Nashidengo, University of Namibia

Tuesday 8 April 2025 continued

14:55 – 15:20	Amide-rich NaH as a highly active catalyst for ammonia synthesis	Dr Michael Higham, University College London, UK
15:20 – 15:35	DFT study of oxidative addition to mononuclear gold(I) complexes for sustainable energy	Zinhle Mtshali, University of Stellenbosch, South Africa
15:35 – 16:05	*Refreshment Break*	
16:05 – 16:30	Structure prediction of energy materials: Results obtained on a supercomputer and a Quantum Annealer Computer	Professor Scott Woodley, University College London, UK
16:30 – 16:55	Ruthenium *fcc* surfaces and nanoparticles for hydrogen production	Dr Marietjie Ungerer, University of Leeds, UK
16:55 – 17:10	Exploring the impact of spin coupling on properties of Manganese Oxide Cathode Materials: A DFT study	Mogau Kgasago, University of Limpopo, South Africa
17:10 – 17:25	Modelling the leaching of Fe-Cr alloys for redox flow battery applications	Cherise Thesner, North-West University, South Africa
17:30	*Close of Session*	

Current challenges in catalytic science to achieve a net zero world

Graham J. Hutchings

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Designing new catalysts is a topic of intense research interest in the scientific community. Catalysis is crucial for the manufacture of many of the materials we use and need in our everyday lives. However, most chemicals are made from fossil carbon and there is now a move to transition to sources of carbon that are renewable. This presents many challenges and this presentation will introduce some of these. The presentation will then introduce some of the latest research using gold and palladium catalysts; namely the recently discovered cooperative redox enhancement (CORE) effect and the use of in situ generation of hydrogen peroxide to produce chemicals.

Biography

Graham Hutchings is Regius Professor of Chemistry at Cardiff University He studied chemistry at University College London. His early career was with ICI and AECI Ltd where he became interested in gold catalysis. In 1984 he moved to academia and has held chairs at the Universities of Witwatersrand, Liverpool and Cardiff. He was elected a Fellow of the Royal Society in 2009, a Member of Academia Europaea, in 2010 a Founding Fellow of the Learned Society of Wales, a Fellow of the Royal Academy of Engineering in 2023 and an Honorary Fellow of the Chinese Chemical Society in 2023. He was awarded the Davy Medal of the Royal Society in 2013, the ENI Award for Advanced Environmental Solutions in 2017, a CBE in 2018 and the Michel Boudart Award in 2021. He has over 950 research papers.

LDHs catalysts for SCR of reduction of NH_3 to NO and NO_2

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Introduction

There is increasing focus on the applications of layered doubled hydroxides (LDHs) in many fields results from the exceptional structural properties and chemical composition of LDHs. The general formula of LDHs is $[M^{1-x}$ II M^{x} III $(OH)_2]$ $[Ax/n\ n-]\cdot mH_2O$, where M (II) and M (III) resembles to divalent and trivalent metal ions, while A n− represents non-organic or organic interlayer anions [1]. The natural hydrotalcite reproduces a brucite-like structure, in which Mg^{2+} cations are moderately replaced with Al^{3+} cations. The positive charge generated by this substitution is typically balanced by carbonate anions (CO_3^{2-}), which co-exist in the interlayer space with water molecules [2]. However, the synthetic LDHs are synthesized by various procedures, e.g., sol-gel, rehydration, urea hydrothermal, and co-precipitation [3].

Materials and Methods

X-Ray diffraction, Scanning Electron Microscopy, TPR, and FT-IR spectrophotometer is used determine the morphology and other functionality of LDHs catalysts.

Results and Discussion

The selection and synthesis of LDHs is very crucial for NH_3 denitrification reactions. Wu et al. [4] reported that TiO_2 to modify NiO and obtained two NiTi mixed oxides (NiTi-IMP, NiTi-LDO) through the solution impregnation method, one-pot sol–gel method etc. It was found that compared to NiTi-IMP. NiTi-LDO had the best selective catalytic reaction (SCR) performance, with more than 90% NO_x conversion rate at 240~360 °C and around 95% at 150~390 °C. Various catalysts for NH_3 reaction such as MnO_2 modified MgAl oxides, and $MnNiTiO_2$-LDO. The LDO catalyst, effectively evades the coverage of active centers, thus promoting the efficiency of reduction reaction's [5].

References

1. *Cavani, F.; Trifirò, F.; Vaccari, A. Hydrotalcite-type anionic clays: Preparation, properties and applications. Catal. Today 1991, 11, 173–301.*
2. *Kooli, F.; Rives, V.; Ulibarri, M.A. Preparation and Study of Decavanadate-Pillared Hydrotalcite-like Anionic Clays Containing Transition Metal Cations in the Layers. Samples Containing Nickel-Aluminum Prepared by Anionic Exchange and Reconstruction Inorg. Chem. 1995, 34, 5114–5121.*
3. *Szymaszek, A.; Samojeden, B.; Motak, M.The Deactivation of Industrial SCR Catalysts—A Short Review Energies 2020, 13, 3870.*
4. *Wu, X.; Wang, R.; Du, Y.; Zou, C.; Meng, H.; Xie, X. Performance enhancement of* NH_3*-SCR via employing hydrotalcite-like precursor to induce the decoration of NiO by* TiO_2 *phase Mol. Catal. 2019, 467, 150–160.*
5. *Du, Y.; Liu, J.; Li, X.; Liu, L.; Wu, X. SCR performance enhancement of NiMnTi mixed oxides catalysts by regulating assembling methods of LDHs-Based precursor.Appl. Organomet. Chem. 2020, 34, e5510.*

OER catalysts (IrM oxides) are characterized for green hydrogen production via PEM water electrolysis.

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Introduction

Large quantities of industrial hydrogen are produced from fossil fuels, which leads to a large carbon footprint; therefore, a need arises to reduce the carbon footprint in numerous industrial processes such as methanation, methanol, and ammonia.[1-2] One possible route my group is investigating is using proton exchange membrane water electrolyzers to produce green hydrogen for these industrial processes.[3-5]

Materials and Methods

This study used XRD, XRF, and TEM analysis together with electrochemical techniques such as cyclic voltammetry, linear voltammetry, and chronopotentiometry for stability and durability study to determine the kinetic rate and overpotential. The ink was prepared using metal chloride reduction to the metal oxides using the Adams method.

Results and Discussion

Our research shows that the preliminary results for IrM (M=Ru, Ti, and Au) bimetallic mixtures show that similar robustness could be obtained for iridium only as the oxygen evolution reaction catalysts. Although most of these studies are ex-situ, the next step will be to start in-situ membrane electrode assembly studies.

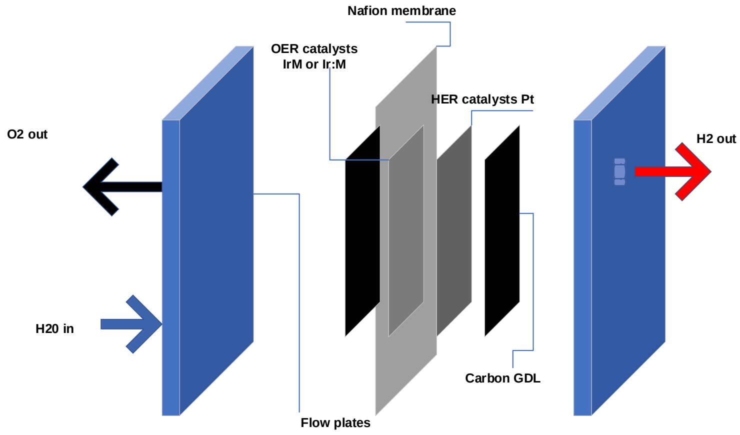

Illustration diagram of an expanded PEM electrolyzer.

References

1. F. Dawood, M Anda, and G.M. Shafiullah, Hydrogen production for energy: An overview, Int. Jour. of Hydrogen Energy, 45, (2020) 3847-3869.
2. Y.K Salkuyeh, B.A. Saville, and H.L. Maclean, Inter. Jour of Hydrogen Energy, 42, (2017), 18894-18909.
3. Minguzzi, et al, Electrocatalysts, ACS Catal., 5, (2015), 5104– 5115.
4. W. Huimin, C. et al., Journal of the American Chemical Society,143 (12), (2021) 4639-4645.
5. Gouws, Shawn and Mackay, Jason. Pure and Applied Chemistry, 96, (2024), 1383-1401.

Synthesis of Ni-Al LDHs by Co-Precipitation Method: Their Role in Hydrogen Production

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Introduction

The growing global demand for clean renewable energy sources has led to a growing interest in efficient hydrogen generation techniques, particularly solar-driven photocatalytic water splitting[1]. Nickel-Aluminium Layered Double Hydroxides (Ni-Al LDHs) are being explored as potential photocatalysts due to their adjustable composition, stratified structure, and advantageous catalytic characteristics[2]. This research explores the synthesis and characterization of Ni-Al LDHs using the co-precipitation method.

Materials and Methods

This study synthesised NiAl layered double hydroxides (LDHs) via a co-precipitation approach, meticulously controlling synthesis parameters including molar ratio, temperature, and salt selection to enhance catalytic characteristics[2,3]. The materials characterisation involved scanning electron microscopy (SEM) to evaluate the surface properties, including particle size, morphology, and uniformity of the Ni-Al LDHs[4]. Fourier-transform infrared spectroscopy (FTIR) was employed to ascertain the atomic groups and ions in the Ni-Al layered double hydroxide and Ni-Al Oxides[4,5]. TGA, XRD, SAXS, TEM, and BET investigations will be utilized to clarify phase stability, particle size distribution, and surface area[3].

Results and Discussion

The synthesis of Ni-Al LDH was achieved effectively through the co-precipitation method. The analysis through SEM of the synthesized materials revealed that higher synthesis temperatures (65°C) resulted in particles exhibiting improved crystallinity and larger sizes, whereas lower temperatures (5°C) produced smaller and less-defined structures. The calcination process enhanced the stability of the LDH structure, as indicated by the reduced hydroxyl signals observed in FTIR, which confirms the increased thermal stability of the calcined samples.

References

1. *K. Maeda, J. Photochem. Photobiol. C: Photochem. Rev., 12, (2011), 237–268.*
2. *C. Li, et al, Nanomaterials, 12, (2022), 3525.*
3. *J. Kameliya, et al, Inorganics, 11, (2023), 121.*
4. *Y. Li, et al, AIChE Journal, 69, (2023), e18006.*
5. *H. Zhao, et al, New J. Chem., 46, (2022), 20235–20249.*

Investigation into support influence on rWGS activity of Fe_3Ni catalysts using metal oxide-overlayered γ-Al_2O_3 supports

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CO_2 emissions, primarily due to anthropogenic activities, have led to an increased atmospheric concentration of this potent greenhouse gas. Carbon capture and utilization (CCU) which leverages CO_2 as a carbon source for value-added chemical production. Current CCU technologies utilize a negligible fraction of the CO_2 emitted globally.[1, 2] Power-to-Liquid (PtL) processes, which target the production of liquid fuels using captured CO_2 with green H_2 via routes like the reverse Water-Gas Shift (rWGS) coupled with the Fischer-Tropsch synthesis (FTS), can fill this gap but face significant technical and catalyst design challenges. The endothermic rWGS reaction is severely thermodynamically limited and catalyst systems need to suppress competing reaction pathways such as methanation.

Supported Fe_3Ni-based catalysts have shown promise in the rWGS.[3, 4] The supports studied in the present work are metal oxide overlayers of Cr, Ga, Sm, Ti, V and Zr on a common γ-Al_2O_3. This approach was chosen to limit the investigation to the electronic properties of the metal oxide rather than structural differences such as pore volume and surface area.

The rWGS performance was studied at 600 °C, with an equimolar feed. With all catalysts and bare supports achieving greater than 99.5% CO selectivity, the results indicate that the presence of the Fe_3Ni alloy does not necessarily lead to an increase in CO_2 conversion for all supports, however there is a clear synergistic effect between the alloy and the Al_2O_3, CrOx@ Al_2O_3, GaOx@ Al_2O_3 and VOx@ Al_2O_3 supports. Temperature-programmed CO_2 activation experiments provide some insight into the observed synergy on these systems, while analyses of the reduced materials are used to gain insight into the differences in stability observed across the samples. STEM-EDX analysis suggests a support specific formation of an iron oxide - FexNi alloy interface forming the active phase under reaction conditions.

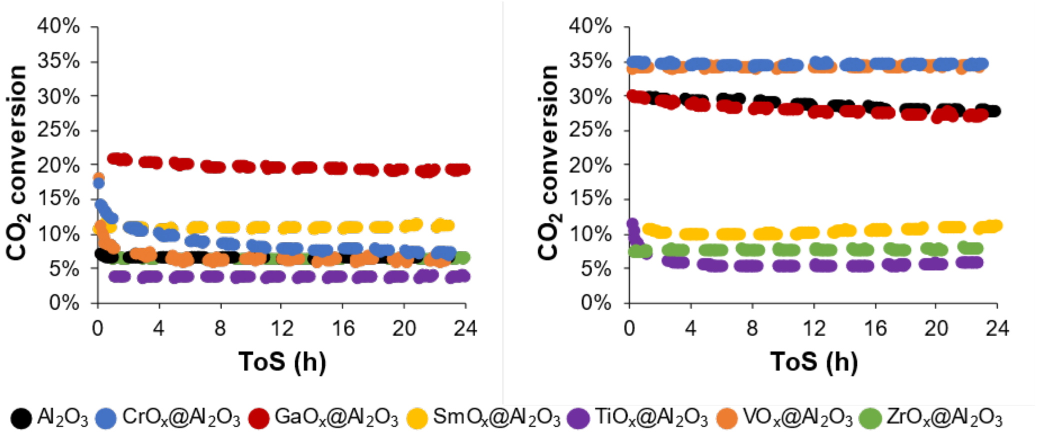

Figure 1. CO_2 conversion under rWGS conditions of bare Al_2O_3 and MOx@Al_2O_3 supports (left) and Fe_3Ni/ Al_2O_3 and Fe_3Ni/MOx@Al_2O_3 catalysts (right).

1. *Alper, E. et al., Petroleum, 3, 2017, 109-126.*
2. *Zhu, Q. et al., Clean Energy, 3, 2019, 85-100.*
3. *Yan, B. et al., Journal of Catalysis, 374, 2019, 60-71.*
4. *Raseale, S. et al., Catalysis Today, 441, 2024, 114884.*

Improving Pd-based alloy catalysts for CO_2 hydrogenation with DFT and AI analysis

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Introduction

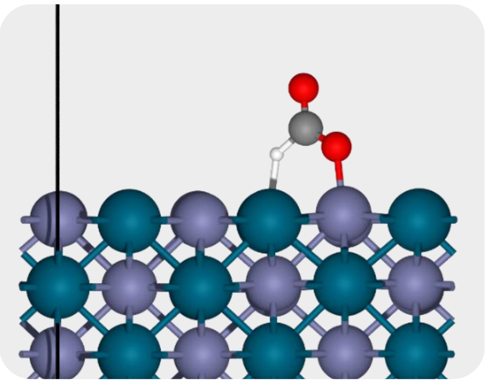
Methanol synthesis by direct hydrogenation of anthropogenic CO_2 is recognized as a potential route towards sustainable fuels and achieving net-zero emissions.[1] Supported Pd-based alloy catalysts, such as PdZn, are potent for CO_2 activation and hydrogenation to methanol.[2] Combined experimental and density functional theory (DFT) studies show that the monodentate formate, $HCOO^{m*}$, is a key intermediate in CO_2 hydrogenation on Pd surfaces.[3]

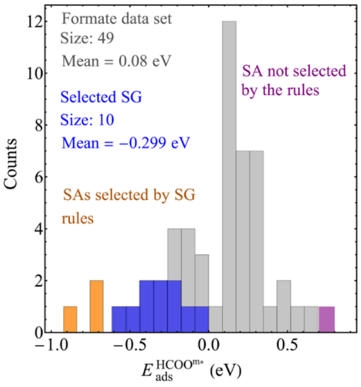
Materials and Methods

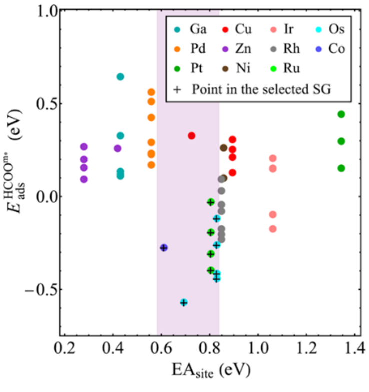
The initial CO_2 reactivity on CuPd and PdZn alloys, and Pd-based single atom alloy (SAA) surfaces is studied *via* periodic DFT simulations and subgroup discovery (SGD) supervised artificial intelligence (AI) analysis.[4] SGD identifies “rules" for subsets of data associated with a statistically outstanding distribution of a certain target of interest, here linked to desired chemical reactivity.

Results and Discussion

A linear correlation was observed between the adsorption energy of $HCOO^{m*}$, $\boldsymbol{E_{ads}^{HCOO^{m*}}}$, and the activation energy required for hydrogenation of CO_2 to formate across the investigated surfaces of metals and alloys. Combined DFT and SGD analysis shows that the single atom (SA) dopant electron affinity (EA), an intrinsic material property, can be used to predict SAs facilitating $HCOO^{m*}$ adsorption. The work shows a potent strategy for virtual high-throughput screening of catalysts for sustainable fuel synthesis from CO_2 at a greatly reduced computational cost.







References

1. *G. J. Hutchings et al., Sustainable synthetic fuels for transport, Royal Society, 2019.*
2. *N. Lawes et al., Catalysis Letters, 2024, 154, 1603–1610.*
3. *T.-W. Jiang et al., Applied Catalysis, B, 2023, 334, 122815.*
4. *H. I. Rivera-Arrieta et al., ChemRxiv. 2024; DOI:10.26434/chemrxiv-2024-1dr10.*

Photocatalytic degradation of Rhodamine B dye using Cu_4O_3 nanoparticles under Visible Light

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Introduction

As a potential solution to the global energy and environmental pollution, design and synthesis of artificial photocatalysts with high activities have attracted scientific interests worldwide.[1,2] In this study, the photocatalytic activities of Cu_4O_3 was evaluated toward a degradation of Rhodamine B (Rh-B) dye in the aqueous solution under visible light irradiation.

Materials and Methods

Cu_4O_3 powders were synthesized using a hydrothermal method adapted from Zhao *et al.*[3] The as-synthesized products were characterized by X-ray Diffractometer (XRD), Fourier transform Infrared (FT-IR) spectroscopy and Ultraviolet-Visible diffuse reflectance (UV-Vis DRS) spectroscopy. The photocatalytic dye degradation activities of the catalysts were investigated by measuring the absorbance of Rh-B at $\lambda_{max} = 555$ nm.

Results and Discussion

Pure Cu_4O_3 (A2) and Cu_4O_3 with a trace of $Cu_2(OH)_3NO_3$ (A3) powders were synthesized. The XRD data revealed that both (A2) and (A3) have high crystallinity with particle sizes of 27.7 nm and 6.9 nm respectively. The optical band gap energies were found to be 1.98 eV (A2) and 1.81 eV (A3). Photocatalytic tests showed that A3 exhibited a much higher degradation rate (91%) of Rh-B dye compared to pure Cu_4O_3 (4%). The improved performance of A3 is likely due to the presence of $Cu_2(OH)_3NO_3$, which facilitates the electron hole charge separation hence, inhibiting fast recombination which will ultimately enhance the photocatalytic activity[4], or due to large surface area because more active sites are available for photocatalytic reactions.[5]

References

1. J.P.S., Pradeeba, S. and K. Sampath, "Depollution of Synthetic dyes From Wastewater Using Polyazomethine/TiO2 and Polyazomethine/ZnO Nanocomposites Via Photocatalytic Process", Global NEST Journal, (2022), 24(3).
2., H.K. Khalilova, et al, Photocatalytic removal of organic pollutants from industrial wastewater using TiO_2 catalyst. Journal of Environmental Protection, (2018). 9(6),1047-1056.
3. L. Zhao, et al, "Facile Solvothermal Synthesis of phase-pure Cu4O3 Microsphres and their Lithium storage properties.," Chemistry of Materials, (2012).vol. 24, 1136-1142.
4. Q. Su, et al, A Review on Cu_2O-Based Composites in Photocatalysis: Synthesis, Modification, and Applications. Molecules (Basel, Switzerland), (2023), 28(14), 5576.
5. C. Mondal, Recent Progress in Copper Based Photocatalysts. Oriental Journal of Chemistry (2024), 40(2).

Density functional theory study of catalytic materials in metal-air batteries

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Introduction

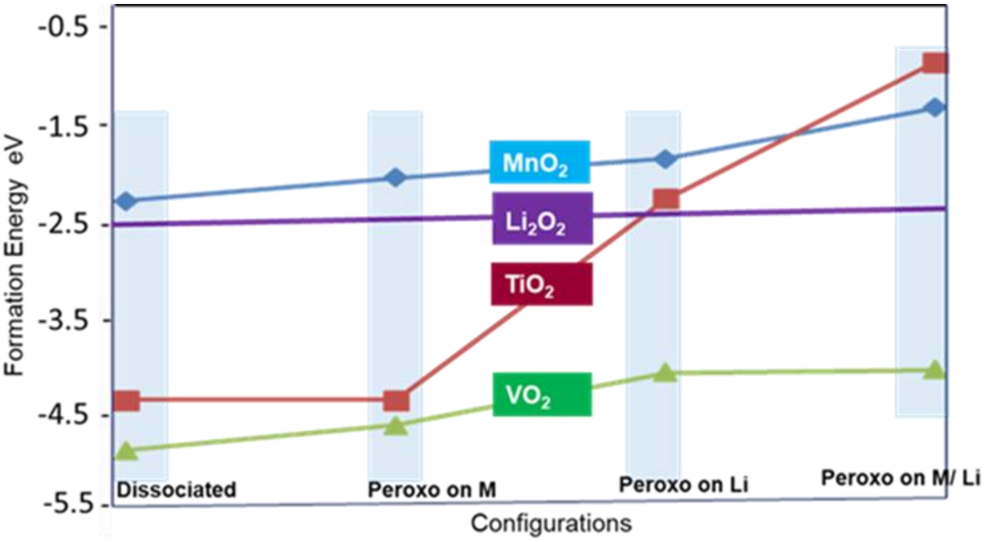
The metal-air battery has the potential to provide energy densities up to three times those of traditional lithium-ion batteries used in electronics gadgets, not to mention the upcoming wave of electric vehicles [1]. Catalytic materials have been proposed and synthesized to promote the oxygen reduction reactions and oxygen evolution reactions ORR/OER process, which can be mainly classified into three groups: carbon-based materials noble metal/metal oxides, and transition metal oxides [2]

Materials and Methods

Density functional theory (DFT) study is employed in order to investigate the surfaces of, metal oxides which act as catalysts in metal-air batteries. Adsorption and co-adsorption of metal and oxygen on the most stable surface is investigated, which is important in the discharging and charging of metal–air batteries.

Results and Discussion

The surface lithium peroxide for MO_2 simulated produces clusters with oxygen-oxygen bond lengths that are comparable to the calculated bulk and monomer discharge products reported in literature.



References

1. *K. M. Abraham. et al. The Electrochemical Society 217th Meeting Abstract 0745 (2010), 1.*
2. *K. Sakaushi, T. Fellinger, and M. Antonietti, Chem. Sus. Chem., 8, (2015), 1156.*

Theoretical investigation of optoelectronic properties of Ru-dyes for solar cell application

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Introduction

The ruthenium bipyridyl-based molecular systems, known as dye sensitizers for solar cells (DSSCs) applications[1,2], were used in the study. The systems were designed to optimize the capture of light (photons) through, firstly the implementation of the antenna effect (by introducing antennas in the molecular system) for signal modulation, and secondly through the variation of bridging ligands and the molecular dye areas of DSSCs for electronic coupling, which ensure optimized charge transfer mechanisms, as well as extending the absorption functional range of the dyes[3]. Improvement of the Ru-dye properties is expected to optoelectronic properties. A computational approach was used to predict potential dye sensitizers, ideal for solar cells, while eliminating dyes with poor or low potentials.

Materials and Methods

DFT and TD-DFT theory at the B3LYP/6-31G* level was used for analysing the photo response and the effect of solvents on the light harvesting properties of the designed molecules. LANL2DZ basis set was used for the ruthenium core and the valence orbitals[1,2].

Results and Discussion

The results, showed that variations of bridging ligands and antenna systems had a great influence on the photo-response properties of the dye molecules and could be of potential use in the DSSCs[4]. The functionality of the dyes was characterized by enhanced molar absorptivity and functional ranges towards NIR. In addition, solvatochromic effect of different solvents provided an insight of which particular solvent was suited for the specific Ru-dye systems used, acetonitrile was a suitable solvent system among others[5,6]. The DSSCs designed and studied, have provided a baseline for experimental work to be carried out using these dyes.

References

1. *R. E. Smalley, 30, (2005), 412-417*
2. *T. W. Hamann, et al., Energy Environ Sci, 1(1), (2008), 66–78, doi: 10.1039/b809672d.*
3. *C. C. Chiu, et al., ACS Omega, 3(1), (2018) 433–445, doi: 10.1021/acsomega.7b01589.*
4. *N. Robertson, Angew.Chem, (2006), 2338–2345, doi: 10.1002/anie.200503083.*
5. *M. Grätzel, Inorganic Chemistry, 44(20), (2005), 6841–6851, doi: 10.1021/ic0508371.*
6. *S. Aghazada and M. Nazeeruddin, Inorganics (Basel), 6(2), (2018), 52, doi: 10.3390/inorganics6020052.*

Amide-Rich NaH as a Highly Active Catalyst for Ammonia Synthesis

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Introduction

Ammonia synthesis is also one of the most environmentally challenging industrial processes, with ammonia production being responsible for an estimated 1.8% of global energy consumption[1]. Recent experimental studies have revealed that the $NaNH_2$ catalyst is highly active for ammonia cracking, and may also be a highly active catalyst for ammonia production[2]. It is believed that active phase resembles a NH_2-rich sodium hydride phase. Hence, in the present work, DFT techniques are applied to model the proposed active phase, and investigate surface reaction processes to determine the likely reaction mechanism.

Materials and Methods

Plane-wave DFT calculations using the VASP code[3,4]. In order to approximate the predominant active phase identified from the experimental results, a model was constructed based on a NaH(100) (2x2) surface facet with NH_2 amide species substituting a fraction of lattice hydride, in order to represent an amide-rich hydride phase. The PBE exchange-correlation functional with a D3 dispersion correction (with Becke-Johnson damping) was applied, along with a 600 eV plane-wave cut-off energy; k-point sampling with performed using a 6x6x1 Monkhorst-Pack grid. Geometric optimization was performed until forces were converged to within 0.01 eVÅ-1. Transition states were obtained using the Nudged Elastic Band (NEB method) and dimer methods.

Results and Discussion

The calculations reveal that surface hydride/amide vacancies can facilitate N_2 activation, with N_2 adsorbing exothermically with elongation of the N-N bond. Whilst hydrogenation of N_2 requires adjacent H/NH_2 vacancies, dissociation of intermediates such as $NHNH_2$ is facile. NH is readily hydrogenated to regenerate NH_2, the NH_2 species is highly stable, and its hydrogenation to yield ammonia is highly energy-demanding. The calculations demonstrate how H/NH_2 vacancies on the NaH(100) surface can facilitate ammonia synthesis via a Mars-van-Krevelen type mechanism.

References

1. *Ammonia: Zero-Carbon Fertiliser, Fuel and Energy Store, https://royalsociety.org/-/media/policy/projects/green-ammonia/green-ammonia-policy-briefing.pdf,*
2. *W. I. F. David et al. J. Am. Chem. Soc. 2014, 136, 38, 13082–1308*
3. *G. Kresse and J. Hafner, Phys. Rev. B: Condens. Matter Mater. Phys., 1993, 47, 558–561*
4. *G. Kresse and J. Hafner, Phys. Rev. B: Condens. Matter Mater. Phys., 1994, 49, 14251–14269*

DFT study of oxidative addition to mononuclear gold(I) complexes for sustainable energy

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Introduction

The efficient storage of solar energy in chemical fuels, such as hydrogen, is essential for the large scale use of solar energy systems.[1] Water splitting has been a popular hydrogen method production, however due to water scarcity hydrogen-halide (HX) splitting has been suggested as an alternative method for sustainable hydrogen production.[2] The purpose of this research is to develop a homogeneous gold-based catalyst for photocatalytic hydrogen production through oxidative addition of HX (X= Halogens).

Materials and Methods

Optimisation of the structure of series of the mononuclear gold(I) complexes in the gas phase in the presence of HX was undertaken using density functional theory at the B3LYP-D3/cc-pVTZ level with the aid of Gaussian09. Frequency calculations confirmed that energy minima had been obtained. Counterpoise corrected calculations of the interaction energies and Atoms in Molecules analysis of the optimised structures was undertaken at the same level of theory.

Results and Discussion

A series of Au(L)$_2$·HX complexes where X = (F, Br, Cl and) were optimised where the HX approaches the gold to form either a hydrogen or halogen bond.. In Figure 1 the series of Au(diethylamine)$_2$·HX shows that the HF complex forms a stronger hydrogen bond interaction energies whereas the other hydrogen halides form halogen bonds. Counterpoise corrected and Atoms in Molecules calculations further show whether halogen or hydrogen bonding is favoured. Understanding the nature of these interactions will help us build a gold catalyst for sustainable energy production.

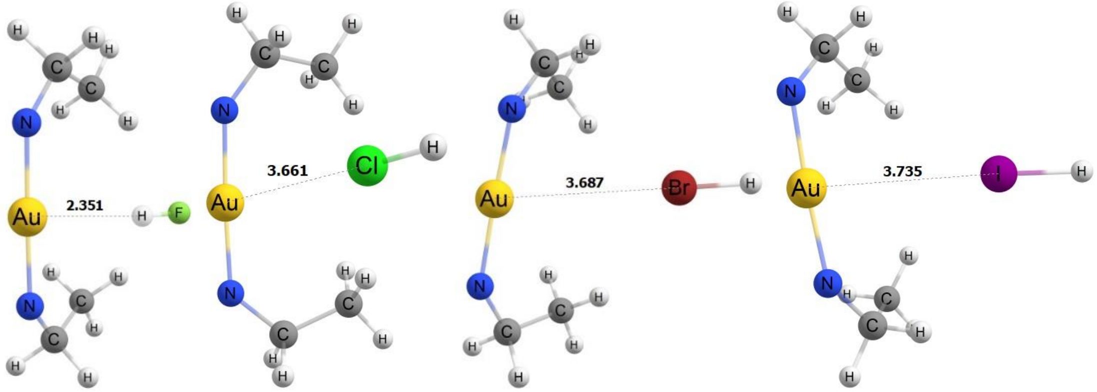

Figure 1 The optimised geometries of a series of Au(diethylamine)$_2$·HX, where X =F, Cl, Br and I

References

1. *R. R. Beswick, et al, ACS Energy Lett, 6, (2021), 3167*
2 .*T. S. Teets, et al, J. Am. Chem. Soc, 131, (2009), 7411*

Structure Prediction of Energy Materials: Results Obtained on a Supercomputer and a Quantum Annealer Computer

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Introduction

Structure prediction is one of the fundamental optimisation tasks in the field of materials modelling. Once the atomic structure is known, then the properties of the material can be calculated and, with a suitable workflow, predicted candidate structures discovered that have properties tuned to enhance or optimise the suitability of the material when used in a targeted application, e.g., part of a battery, heat pump or solar cell. Both the prediction of these structures and the calculation of their properties often require large compute resources: a larger supercomputer will enable the investigation of larger system sizes (more atoms) and/or more configurations, as well as the use of more accurate models (definition of the energy cost function). Thus, practitioners in this field are often exploiting the latest available supercomputer.

In preparation for the arrival of an exascale (10^{18} flops) supercomputer, as part of the Excalibur funding programme (see https://excalibur.ac.uk) the UK have invested in projects that address one or more of four key pillars: separation of concerns, co-design, data science, and people, with the aim to deliver the next generation of high-performance simulation software for the highest-priority fields, which includes materials modelling, in UK research. The Excalibur project started in October 2019 and ran through until March 2025, redesigning high priority computer codes and algorithms to meet the demands of both advancing technology and UK research. In this presentation, I will describe two new methods[1,2] for predicting the atomic structure of materials, which were developed by two of the Research Software Engineers funded by two Excalibur projects: PAX-HPC and QEVEC.

Materials and Methods

The targeted materials are Li doped MnO_2, which is employed as a cathode material[1] and solid solutions like $Al_{1-x}Ga_xN$. In the PAX-HPC project we pursued a method of sampling many configurations and obtaining thermodynamical properties from first computing the partition function. The KLMC software was refined to enable an efficient and easy workflow suitable for evaluating many configurations on a supercomputer. In the QEVEC project we pursued an approach that uses nature's ability to anneal a system to, typically, its ground state as opposed to trying to simulate the annealing process. We employ the D-wave quantum annealer to perform the annealing[2] and here I will describe how we map our system of interest on to this hardware and how we read off the results. The pros and cons of both approaches will be discussed.

Results and Discussion

Interestingly, in the PAX-HPC project we were able to use our KLMC approach to gain an insight into the mechanism of lithium charging and discharging MnO_2. For the QEVEC project we were able to derive thermodynamical properties and replicate the bandgap bowing seen when doping AlN with Ga.

References

1. *W. Jee, et al., Chemistry of Materials, 36, (2024), 8737.*
2. *B. Camino, et al., Journal of Applied Physics, 22 (2023), 133.*

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Ruthenium *fcc* surfaces and nanoparticles for hydrogen production

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Introduction

Hydrogen is a major sustainable energy vector, which is set to play a leading role in attaining a net zero carbon economy. More recently, global research efforts have shifted towards storing hydrogen in condensed phases, i.e cryogenic condensation or compressed at high pressures at room temperature or stored as liquid organic hydrogen carriers (LOHC) and particularly systems involved in generating and storing hydrogen via water electrolysis.[1] Despite the emergence of new technologies, the storage and transportation of hydrogen pose considerable challenges that need to be addressed, including the low gravimetric energy density, the flammability and diffusivity of hydrogen. Ammonia is now being studied as a potential solution for long-term energy storage, going beyond its traditional uses as a fertilizer.

Materials and Methods

We have carried out density functional theory (DFT) calculations with long-range dispersion corrections to investigate the interaction of various gas phase species on Ru nanoparticles and surfaces.[2,3] Electronic structure techniques based on the density functional theory (DFT) with long-range dispersion corrections [DFT-D3-(BJ)] were used to calculate fundamental properties of the catalysts, e.g. the lattice parameters, surface energies and work functions of the (001), (011) and (111) surfaces of Ru, Pd and Pt in the *fcc* phase, induced magnetisation the electronic structures, work functions, the chemical bonding and electron transfer occurring during the adsorption of hydrogen.[2,3] For the adsorption of hydrogen on the Ru surfaces, both H atoms and the optimised H_2 molecule were added to the surface at various adsorption sites and in different configurations.

Results and Discussion

The surface energies followed the observed trend (111) < (001) < (011) for both Ru and Pd with all three methods, which is comparable to experimental data. The work function followed the trend of Φ (111) < Φ (001) < Φ (011) for all three metals and calculated by all three methods.
An isolated H atom adsorbs preferentially in H_{4F}, H_{B1} and H_{fcc} positions on the (001), (011) and (111) surfaces, respectively, where Bader analysis shows that charge transfer of between 0.17 and 0.27 e− occurs from the surface to the adsorbate. When an H_2 molecule is adsorbed, dissociation occurs readily but a few meta-stable sites were found where hydrogen binds molecularly. We have investigated surface coverages of H up to monolayer coverage, where Eads/H decreased with increasing H coverage on all three surfaces. The highest coverage was obtained on the (001) and (011) surfaces, followed by the (111) surface.

References

1. 1 G. Petitpas, S. Aceves, Hydrogen Storage Technology: Materials and Applications, (CRC Press 2013).
2. Ungerer, M.J.; De Leeuw, N.H., Catalysts 2022, 12(10), 1287.
3. Ungerer, M.J.; De Leeuw, N.H., Nanomaterials 2023, 13(6), 1118.

Exploring the Impact of Spin Coupling on Properties of Manganese Oxide Cathode Materials: A DFT Study

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Introduction

$LiMn_2O_4$ stands out as a sustainable, affordable, and thermally stable alternative[2] to cobalt-rich[1] cathodes. Although it faces stability challenges due to Jahn-Teller distortion and phase transitions[3], combining it with layered structures enhances its stability[4]. The current study aims to design core-shell architectures of $LiMn_2O_4$ and ($LiMn_2O_3$/$LiMnO_2$). As such the initial efforts are dedicated towards exploring antiferromagnetic (AFM) and ferromagnetic (FM) spin configurations to identify one that describes the properties of core-shell candidates more accurately.

Materials and Methods

The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) scheme, along with a Hubbard U correction, was used to describe the exchange-correlation functional, as implemented in the VASP code. Spin-polarized calculations were performed, utilizing both antiferromagnetic (AFM) and ferromagnetic (FM) configurations.

Results and Discussion

The antiferromagnetic (AFM) configuration shows greater stability with lower total energy and closely matches experimental lattice parameters (within 1%), making it the preferred ordering for $LiMn_2O_4$, Li_2MnO_3, and $LiMnO_2$. In $LiMnO_2$, FM suggests half-metallicity, but AFM shows metallic behavior with a 0 eV band gap, consistent with experiments. These findings highlight the importance of magnetic ordering in accurately modeling Mn-based lithium oxides, enabling the design of more efficient Mn-based cathode materials for lithium-ion batteries.

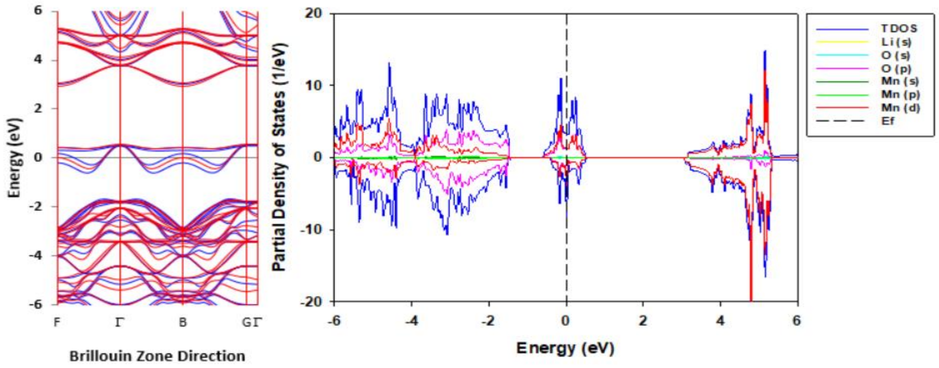

Figure 1: The calculated (a) electronic band structure and (b) the partial density of states for the $LiMnO_2$ spinel bulk structure using AFM ordering.

References

[1] *J Ma, et al, Advanced Science, 11, (2024), 1-20.*
[2] *RS Ledwaba, et al, Materials Today Communications, 27, (2021), 1-5.*
[3] *D Hlungwani, et al, Materials, 15, (2022), 1-16.*
[4] *RC Longo, et al, ACS Applied Material Interfaces, 10, (2018), 19226−34.*
[5] *G Kresse, et al, Physical Review B, 49, (1994) 14251 - 69.*

Modelling the leaching of Fe-Cr alloys for redox flow battery applications

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Introduction

Due to the energy crisis experienced in the world today, the need for energy storage has led to a metal dependency in terms of battery production. Hydrometallurgy is a method for extracting metals from ores, minerals, alloys, and waste through chemical reactions in aqueous solutions. It can efficiently recover and purify metals for battery production.[1] There are three main steps followed in any hydrometallurgical process, namely, leaching, separation and purification, and precipitation and reduction.[2] Computational methods like density functional theory (DFT) and molecular dynamics (MD) can enhance our understanding of phase interactions in hydrometallurgy, leading to improved methods.[4] This study focuses on the first process, namely leaching. A computational model for solid-liquid interactions is being developed to simulate the leaching of Fe-Cr alloys to form electrolytes for iron-chromium redox flow batteries (ICRFBs).

Materials and Methods

DFT-based calculations for optimising bulk and surface slab models of Fe and Cr were used to benchmark the k-point grid and cut-off energy for the alloy leaching model. Using the Supercell program,[4] several configurations for Fe_xCr_{1-x} precursor alloys, namely Fe_7Cr_3, FeCr, Fe_4Cr_6, and Fe_3Cr_7, were constructed and unique configurations were identified. These unique configurations were submitted to GULP[5] optimisations and then subjected to thermodynamic and statistical calculations to identify the unique configurations with the highest probability to exist. These configurations were optimised with settings identified for the alloy leaching model.

Results and Discussion

The bulk computational model developed during benchmarking with Fe and Cr by varying k-point grids and cut-off energy resulted in an identified k-point grid of 11×11×11 and cut-off energy of 550 eV. The k-point grid falls into the literature range for Fe and Cr studies. In contrast, the cut-off energy was higher than observed previously in the literature. For the surface slab computational model, a k-point grid of 11×11×1 and a cut-off energy of 550 eV were identified during benchmarking. Using Supercell program[4] thirteen unique configurations for Fe_7Cr_3, Fe_4Cr_6, and Fe_3Cr_7 and fifty-two for FeCr were obtained.

References

1. *Shamsuddin, M. Hydrometallurgy. In Physical Chemistry of Metallurgical Processes, 2, (2021), 429.*
2. *Nicol, M. Introduction. In Hydrometallurgy: Theory; Elsevier, 1, (2022), 1*
3. *Yu, T., et al., Molecular Dynamics Simulation Study on the Interaction Mechanisms of Leaching Solutions and LiCoO2 Surface. Sep Purif Technol (2024), 339.*
4. *Okhotnikov et al., Supercell Program: A Combinatorial Structure-Generation Approach for the Local-Level Modeling of Atomic Substitutions and Partial Occupancies in Crystals. J Cheminform 8 (1), (2016), 17.*
5. *Gale, J. D., et al., The General Utility Lattice Program (GULP). Mol Simul, 29 (5), 2003, 291*