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Book of Abstracts



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Preface

Catalysis, a central discipline in modern chemistry, has been pivotal in the development of countless industrial and scientific processes. However, beyond its practical applications, the theoretical study of catalysis has emerged as an indispensable field for deeply understanding the underlying mechanisms that govern catalytic reactions. Theory, with its ability to unravel the fundamental principles of the interactions between catalysts and reactants, provides the conceptual foundation upon which new approaches are built and existing processes are optimized.

The International Conference on the Theoretical Aspects of Catalysis (ICTAC) is a biennial conference series that began in 1986 in Lyon, France. Since then, it has been hosted by various cities across Europe, Japan, and the USA. The current 19th edition is being held in Seville, Spain, from September 2nd to 6th, 2024. The organizers are delighted and honored to host this event and wish you a successful congress, both scientifically and personally, in the outstanding environment that the city of Seville offers its visitors.

This book of abstracts is a compilation of the works presented at ICTAC-2024. Throughout these pages, you will find recent advancements in computational modeling, molecular dynamics, density functional theory (DFT), AI-assisted techniques, and other theoretical approaches that are redefining our understanding of how catalysts function at the molecular level.

Each abstract included in this volume stands as a testament to the relevance and sophistication of theoretical analysis in modern catalysis. These works not only offer predictions and explanations of catalytic phenomena but also enable the rational design of new catalysts and the optimization of key reactions. Theory, in its role as a guide for experimentation and development, is presented here as a fundamental tool for advancing the field.

This compilation is intended to serve as a source of inspiration and reference for researchers and students interested in the theoretical aspects of catalysis. We hope that this compendium will spark new ideas, foster collaboration between theorists and experimentalists, and serve as a foundation for future research that expands the horizons of our knowledge in catalysis.



Javier Fdez. Sanz
Chairman of ICTAC-2024

Monday, September 2

Key Lecture 1 Nuria López. CO₂ electrocatalytic conversion from first principles.

Key Lecture 2 Manos Mavrikakis. On the nature of the active site in heterogeneous catalysis.

CO₂ electrocatalytic conversion from first principles

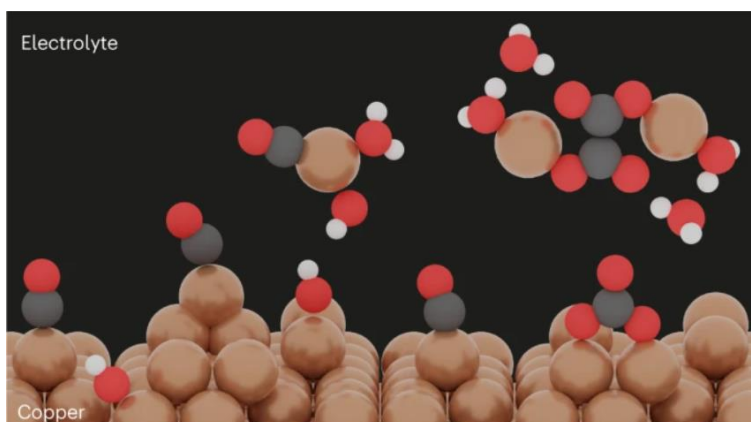
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Keywords: electrocatalysis, CO₂, reaction conditions, electrolyte

In the talk, I will present the advances in the search for electrocatalytic materials that can go beyond the formation of C₂ product. I will highlight the evolution of the material under reaction conditions and the role of the electrolyte in electrocatalysis [1-4].



References

- [1] Z. Lian, F. Dattila, N. López *Nat Catal* **7**, 401–411 (2024).
- [2] H. Ma, E. Ibáñez-Alé, R. Ganganahalli, R. Ganganahalli, J. Pérez-Ramírez, N. López, and B. Siang Yeo *J. Am. Chem. Soc.* **145**, 24707–24716, (2023)
- [3] J. Vavra, G.P.L. Ramona, F. Dattila, A. Kormányos, T. Priamushko, P. P. Albertini, A. Loiudice, S. Cherevko, N. López and R. Buonsanti *Nat. Catal.* **7**, 89–97 (2024)
- [4] R. C. Oglou, T. G. U. Ghobadi, F. S. Hegner, J. R. Galán-Mascarós, N. López, E. Ozbay, F. Karadas *Angew. Chem, Int. Ed.* **62**, e202308647 (2023)

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On the nature of the active site in heterogeneous catalysis

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Keywords: STM, DFT, KMC, atom-ejection; cluster sties

Adsorption of reactants and reaction intermediates on solid catalytic surfaces can lead to significant changes of the surface, including ejection of metal atoms and formation of metal clusters while the reaction is taking place. Depending on the specific system, these clusters provide new, more favorable reaction paths than the typically considered active sites. In this talk, we will attempt to provide a more realistic picture of the catalyst's surface and its active sites as a function of reaction conditions and the identity of reactants and that of key intermediates. Insights derived from our analysis can inform the design of new catalysts with improved activity, selectivity, and stability characteristics.

References

- [1] L. Xu, K. G. Papanikolaou, B. A. J. Lechner, L. Je, G. A. Somorjai, M. Salmeron, M. Mavrikakis, *Science*, **380**, 70-76 (2023)
- [2] L. Xu, M. Mavrikakis, *Journal of the American Chemical Society Au*, **3**, 2216-2225 (2023)

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Tuesday, September 3

Key Lecture 3 Gianfranco Pacchioni. Can we predict the properties of single-atom catalysts?

Oral contribution Ning Cao. Probing Cu(II)-oxyl Formation Mechanisms: Insights from Combined Static and Dynamic Calculations.

Oral contribution Alexander Kolganov. Unravelling the active site in supported organometallic catalysts via automated configurational space exploration.

Oral contribution Gerard Bru. Insights into metal-catalysed reverse Water-Gas Shift reaction through reactive force fields.

Focus Topic 1 Marie Laure Bocquet. Reactivity of functionalized graphene with Single Atom Catalyst in liquid water: an ab initio dynamic study.

Oral contribution Michael Badawi. Accessing accurate activation energies for catalysis with Machine Learning Thermodynamic Perturbation Theory.

Oral contribution Hector Prats. Computational design of carbide-based catalysts for efficient CH₄ and CO₂ conversion.

Oral contribution Dipanshu Kumar. Hybrid QM:QM methods for adsorption of ethanol in H-MFI.

Oral contribution Rubén Pérez. Defect identification in Ceria systems with High Resolution Atomic Force Microscopy, Simulations and water markers.

Emerging Researcher Romain Reocreux. Ten-Electron Count Rule and Atomic Charges rationalise the Catalytic Properties of Single-Atom Alloy Catalysts.

Oral contribution Jingcheng Guan. Theoretical Developments in Py-ChemShell for Calculating Anharmonic Vibrational Signatures of Catalysts.

Oral contribution Pablo Lustemberg. Unraveling the Role of Peroxo Species in Surface Chlorine Transformation during HCl Oxidation on CeO_{2-x} (111).

Oral contribution Fabian Berger. Two are Better than One: Exploring Single and Dual Active Sites in the Novel Material Class of Highly Dispersed Ternary Alloys.

Short Communication José M. González-Acosta. Ultra-high Metal Loading Heterogeneous Single Atom Catalysts based on Palladium-Phthalocyanine Covalent Organic Frameworks for CrossCoupling Reactions.

Short Communication Joshua Sims. Morphology of Ru nanoparticles at titania-water interface – A computational study.

- Short Communication Samantha McIntyre. Electroreduction of NO_3^- to N_2 on Pt(111) and Pd(111). Surfaces.
- Short Communication Weitian Li. Elucidating the Reactivity of Oxygenates on Single-Atom Alloy Catalysts.
- Short Communication Rafał Stottko. Can Machine Learning Predict the Reaction Paths in Catalytic CO_2 Reduction on Small Cu/Ni Clusters?
- Short Communication Fileto Rodríguez. Unraveling Silicate Cluster Formation: Cutting-Edge Insights from Theoretical Spectroscopy.
- Short Communication Eleonora Romeo. Analyzing Activity and Selectivity Trends for NO Hydrogenation Using "Catalytic Matrices".

Can we predict the properties of single-atom catalysts?

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Keywords: Single atom catalysts, transition metals, electrocatalysis

In the past, single atom catalysts (SACs) could not be clearly visualized and characterized due to the limitations associated with instrumental resolution. Today this is a new frontier in heterogeneous catalysis due to the high activity and selectivity of SACs for various catalytic reactions. This has opened various questions for theory. One is where are the atoms and what is the stability of SACs in working conditions. In order to address these questions, we discuss the nature of isolated Rh, Ru and Pt species deposited on two representative oxide surfaces, anatase TiO₂ (a reducible oxide), and tetragonal ZrO₂ (a non-reducible oxide) [1-3]. These systems have been characterized experimentally using high-resolution scanning transmission electron microscopy (STEM), Fourier transform infrared spectroscopy (FTIR), and temperature programmed desorption (TPD) spectra of adsorbed CO probe molecules. Combining these data with extensive Density Functional Theory (DFT) calculations one can provide an unambiguous identification of the stable single-atom species present on these supports and of their dynamic behavior.

The other question that can be addressed by theory is the prediction of the behavior of SACs in electrocatalytic processes such as the oxygen reduction (ORR), the oxygen evolution (OER) and the hydrogen evolution (HER) reactions. In this context we assist to a rapidly growing number of DFT studies and of proposals of universal descriptors that should provide a guide to the experimentalist for the synthesis of new catalysts, in particular related to graphene-based SACs. We will critically analyze some of the current problems connected with these DFT predictions: accuracy of the calculations, neglect of important contributions in the models used, physical meaning of the proposed descriptors, inaccurate data sets used to train machine learning algorithms, not to mention some severe problems of reproducibility. It follows that the “rational design” of a catalyst based on some of the proposed universal descriptors or on the DFT screening of large number of structures should be considered with some caution [4-6].

References

- [1] H. V. Thang, G. Pacchioni, L. De Rita, P. Christopher, “Nature of stable single atom Pt catalysts dispersed on anatase TiO₂”, *J. of Catalysis*, 367, 104-114 (2018).
- [2] H. V. Thang, S. Tosoni, L. Fang, P. Brujininx, G. Pacchioni, “Nature of sintering-resistant, single-atom Ru species dispersed on zirconia-based catalysts. A DFT and FTIR study of CO adsorption”, *ChemCatChem*, 10, 2634-2645 (2018).
- [3] L. De Rita, J. Resasco, S. Dai, A. Boubnov, H. V. Thang, A. S. Hoffman, I. Ro, G. W. Graham, S. R. Bare, G. Pacchioni, X. Pan, P. Christopher, “Structural evolution of atomically dispersed Pt catalysts dictates reactivity”, *Nature Materials*, 18, 746-751 (2019).
- [4] G. Di Liberto, Luis A. Cipriano, G. Pacchioni, “Role of Dihydride and Dihydrogen Complexes in Hydrogen Evolution Reaction on Single-Atom Catalysts”, *J. of the American Chemical Society*, 143, 20431–20441 (2021).
- [5] G. Di Liberto, Luis A. Cipriano, G. Pacchioni, “Universal principles for the rational design of single atom electrocatalysts? Handle with care”, *ACS Catalysis*, 12, 5846-5856 (2022).
- [6] G. Di Liberto, S. Tosoni, L. A. Cipriano, G. Pacchioni, “A Few Questions about Single Atom Catalysts: When Modeling Helps”, *Accounts of Materials Research*, submitted.

Probing Cu(II)–oxyl Formation Mechanisms: Insights from Combined Static and Dynamic Calculations

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Keywords: Reaction mechanism, AIMD simulations, CREST, copper complexes, DFT

Inspired by the selective C–H bond cleavage abilities of monooxygenases such as pMMOs and LPMOs, which contain a 'histidine brace' and copper species, our group synthesized a Cu–UiO–67 metal-organic framework (MOF) with histidine ligands (see Figure 1a).^[1] H₂O₂ is widely utilized to activate Cu MOFs. However, the reaction mechanism of the Cu(I) oxidation reaction remains controversial (see Figure 2b). Following O–O bond cleavage on the copper, Cu(II)–OH·OH species form, leading to subsequent steps such as hydrogen transfer between hydroxyls to generate Cu(II)–oxyl or hydroxyl dissociation.

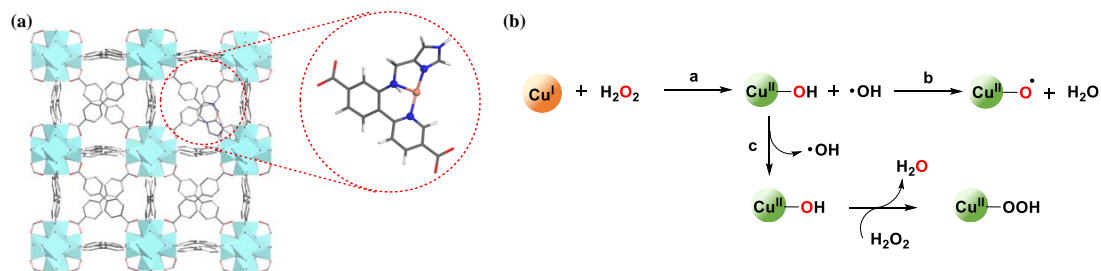


Figure 1(a) Schematic representation of Cu–N,N,N UiO-67 MOFs and the local copper site and (b) Possible Cu(II)–oxo species generated through activation of Cu(I) complex by H₂O₂.

In this work, we employed AIMD simulations along with static DFT calculations to elucidate the crucial role of a Cu(II)–2OH intermediate in Cu(II)–oxyl formation. Additionally, we investigated the impact of solvent, specifically water and acetonitrile, on the reaction mechanism using AIMD simulations. A conformational search tool, CREST,^[2] was also used to explore different Cu-intermediates and coordination numbers leading to Cu(II)–oxyl. Our results show that some intermediates prefer reacting with the ligand rather than forming a Cu(II)–oxyl, providing guidance for catalyst design.

References

- [1] Gerz, I. Bioinspired Copper Complexes for Incorporation into UiO-67.
- [2] Pracht, P.; Bohle, F.; Grimme, S. Physical Chemistry Chemical Physics 2020, 22 (14), 7169–7192

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Unravelling the active site in supported organometallic catalysts via automated configurational space exploration

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Keywords: surface organometallic catalysis, configurational space exploration, amorphous silica, DFT, *ab initio* molecular dynamics

Surface organometallic catalysts (SOMC) are promising systems that combine the advantages of heterogeneous catalysts with the “well-defined” nature of molecular systems. However, the strained and inhomogeneous nature of commonly used amorphous supports can create a plethora of microcoordination environments and active site configurations.[1] Thus, sampling the ensemble of catalyst states is required to gain a comprehensive understanding of the principles defining catalyst behavior. We present an autonomous method for configurational space exploration of SOMC through the combination of *ab initio* molecular dynamics (aiMD) methods and a graph-theory-based post-processing tool. We focused on the amorphous silica-supported zirconocene hydride ($^R\text{Cp}_2\text{ZrH}_2@SiO_2-700$), as these type of systems are versatile, serving both as catalysts for olefin polymerization and plastic upcycling.

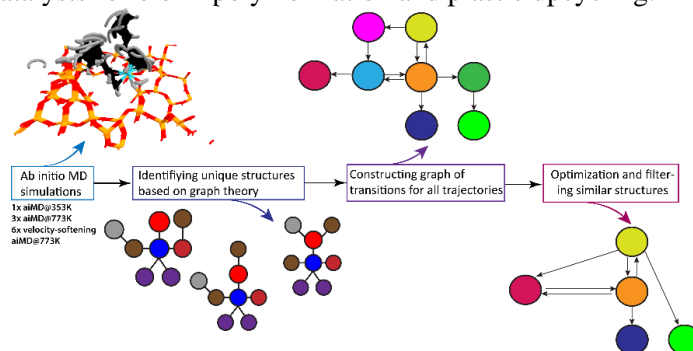


Figure 1. (a) Workflow implemented in this study.

The general workflow is schematically illustrated in Figure 1. We carried out multiple *aiMD* simulations, including velocity-softening *aiMD*, which accelerates trajectories to cross small barriers rapidly. Graph-theory based analysis was employed to extract unique structures from MD trajectories. [2] A key advantage of graph theory lies in its ability to map transitions between different states. The unique structures identified through these analyses were then further optimized using DFT, and the graph network was “trimmed” to remove any duplicates. This workflow allowed us to automatically discover various-type sites which could be formed after the interaction of the $^R\text{Cp}_2\text{ZrH}_2$ with amorphous silica, either through interactions with different surface sites or due to surface relaxation.

References

- [1] B. R. Goldsmith et al, *ACS Catalysis*, 2017, **7**, 7543-7557.
 [2] S. Bougueroua et al., *Mol. Phys.*, 2023, **121**, e2162456.

Insights into metal-catalysed reverse Water-Gas Shift reaction through reactive force fields

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Keywords: ReaxFF; Molecular Dynamics; reverse Water-Gas Shift; CO₂ conversion; metal catalysis

The reverse Water-Gas Shift reaction (rWGS) offers a way to convert CO₂, a greenhouse gas, into CO, a more reactive molecule, which can be transformed into e-fuels. Ni-based catalysts are active for rWGS, however, they are not fully selective, with methanation side reaction taking place.¹

To understand the influence of reaction conditions and Ni morphology on the reaction outcome, we have performed ReaxFF reactive force field simulations.² A new Ni/C/O/H force field (FF) was developed, with parameters describing the main rWGS and side methanation reaction. Machine-learning-based optimization algorithms were used to train the FF,³ with DFT results as input data.

At first, we studied the effects of temperature, pressure, and feed compositions (CO₂:H₂ ratio) by performing molecular dynamic simulations with Ni(100). We observed an increase in CO₂ conversion when increasing temperature, pressure, and H₂ content in the feed. Considering the selectivity towards CO, it increased with the increase of temperature but decreased with H₂ content in the feed. The simulation results of the reaction at various temperatures also allowed us to calculate the apparent activation energy of the reaction. Further, we have focused our studies on the influence of Ni morphology, with simulations on Ni(100), Ni(111) surfaces and with a Ni₅₆₁ nanoparticle (NP). Ni(100) and Ni₅₆₁ NP have shown better activity than the close-packed Ni(111) surface, however, with lower selectivity, as more hydrogenated precursors of methanation were observed (see Figure 1).

Our results agree with experimental data and demonstrate that ReaxFF simulations can be used to point out optimal reaction conditions. Having this proof of performance predictions, the studies can be taken a step further, towards investigations of bimetallic systems, more selective in the rWGS reaction,⁴ for which we will also present our first attempts.

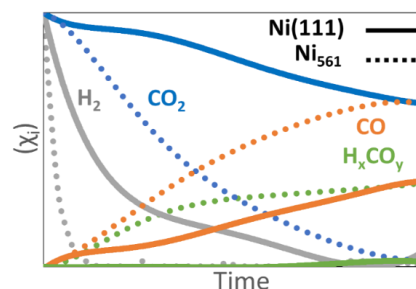


Figure 1. Evolution of species on different Ni topologies

References

- [1] K-J. Lee, Y. Ye, H. Su, B. S. Mun, E. J. Crumlin, *ACS Catal.*, **13**, 9041-9050 (2023)
- [2] P. Senftle, S. Hong, S. Md. M. Islam, S. B. Kylasa, Y. Zheng, Y. K. Shin, C. Junkermeier, R. Engel-Herbert, M. J. Janik, J. M. Aktulga, T. Verstraelen, A. Grama, A. C. T. van Duin, *npj Comput. Mat.*, **2**, 15011-15025 (2016)
- [3] A. Salom-Català, E. Strugovshchikov, K. Kaźmierczak, D. Curulla-Ferré, J.M. Ricart, J. J. Carbó, *J. Phys. Chem. C*, **128**, 2844-2855 (2024)
- [4] E. Gioria, P. Ingale, F. Pohl, R. Naumann d'Alnoncourt, A. Thomas, F. Rosowski, C, *Catalysis Science & Technology*, **12**, 474-487 (2022)

Reactivity of functionalized graphene with Single Atom Catalyst in liquid water : an ab initio dynamic study

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Keywords: DFT, graphene, SAC, liquid-solid interface, ab initio molecular dynamics

Graphene and hBN are materials known to be inert in neat water (in the absence of water ions) and this has been verified at the quantum level using ab initio molecular dynamics. In contrast when these prototypical materials become “activated” with single defects (like single vacancies in hBN or oxygenated chemical groups in graphene oxide (GO) sheets for example [1]) they do chemically interact with interfacial water.

Following this line we are now exploring the reactivity of another type of activated graphene when a single metallic atom M is embedded into a graphene sheet which is pre-doped by N heteroatoms to enable fourfold M-N₄ Single Atom Catalyst (SAC) motives. After an initial screening of a few late metallic atoms like Pt, Ni and others, we end up choosing Fe as a more sustainable metal and we investigate two different defect motives in hydrated graphene either of pyridine type or porphyrin type.

Using spin polarized ab initio molecular dynamics, we show that both Fe SACs spontaneously adsorb two interfacial water molecules from the solvent on opposite sides. Interestingly, we unveil a different catalytic reactivity of the two hydrated SAC motives: while the Fe-porphyrin defect eventually dissociates an adsorbed water molecule under a moderate external electric field, the Fe-pyridine defect does not convey water dissociation.[2] Such favorable water activation into its self-ions permitted by the Fe-porphyrin SAC defect becomes therefore of great importance to guide the next generation of sustainable electrocatalysts.

References

[1] F. Mouhat, F.X. Coudert, M.-L. Bocquet, *Nat. Comm.* **11**, 1566 (2020)

[2] L. Scalfi, M. R. Becker, R. R. Netz and M. -L. Bocquet, *Commun.Chem.* **6**, 236 (2023).

Acknowledgments

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Accessing accurate activation energies for catalysis with Machine Learning Thermodynamic Perturbation Theory

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Keywords: RPA; MLPT; cracking; biased molecular dynamics; machine learning

The accurate determination of free energy barriers of relevant steps in catalysis requires the combination of enhanced *ab initio* molecular dynamics (AIMD) with a sufficiently high level of theory, such as RPA, which is currently out of reach. Herein, we make this combination feasible thanks to a recently developed Machine Learning thermodynamic Perturbation Theory (MLPT^{1,2}) approach. As a prototypical case, we selected the cracking and isomerization reactions of C₇ alkenes catalyzed by zeolites (here chabazite), that are building blocks of many chemical transformations in petroleum refining or biomass conversion, and for which a large set of AIMD data has been previously collected at the GGA level.^{3,4} Incorporation of the GGA rate constants in a single event kinetic model was helpful to construct a robust kinetic model, but adjustment of some inaccurate rate constants turned out to be necessary to reproduce the experimentally observed relative selectivities of cracking and isomerization reactions.³ Based on this adjustment strategy, the difference between the free energy of activation for type B isomerization reactions minus type B1 cracking should be close to +10 kJ/mol. The latter value was overestimated to be about 15 kJ/mol at the PBE+D2 level of theory.⁵

The MLPT method allows us, in some way, to rebuild a Molecular Dynamics trajectory at the high level using the low-level MD data and energies from a few single points calculations performed at the high level.^{1,2} In this work we demonstrate that the RPA was able to reach chemical accuracy and bridge the gap between experimental and computed values (Figure 1)². Although the MLPT methodology is presented here for a specific case of hydrocarbon conversion reactions, it can be directly applied to any other type of chemical reaction.

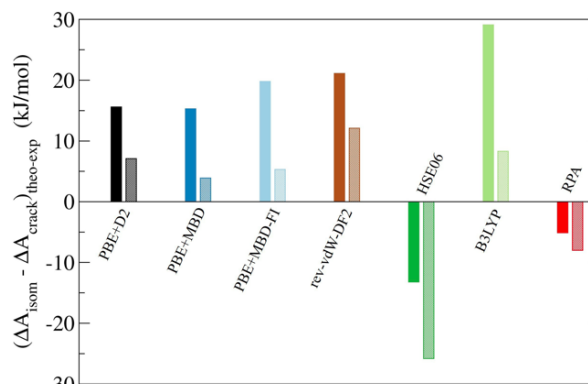


Figure 1. Deviation with respect to experiment⁵ of the difference of the free energies of activation at the various levels of theory investigated for the isomerization and cracking reactions (dark bars: isomerization between tertiary dibranched to tribranched cations; light bars: the backward reaction).

References

- [1] T. Bučko, M. Gešvandtnerova, D. Rocca, *J. Chem. Theory Comput.*, **16**, 6049 (2020)
- [2] J. Rey, C. Chizallet, D. Rocca, T. Bučko, M. Badawi, *Angew. Chem. Int.*, **63**, e202312392 (2024)
- [3] J. Rey, A. Gomez, P. Raybaud, C. Chizallet, T. Bučko, *J. Catal.* **373**, 361 (2019)
- [4] J. Rey C. Bignaud, P. Raybaud, T. Bučko, C. Chizallet, *Angew. Chem. Int.* **132**, 19100 (2020)
- [5] J.-M. Schweitzer, J. Rey, C. Bignaud, [...], T. Bučko, C. Chizallet, *ACS Catalysis*, **12**, 1068 (2022)

Acknowledgments

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Computational design of carbide-based catalysts for efficient CH₄ and CO₂ conversion

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Keywords: TMC, KMC, computational screening, CO₂ conversion, CH₄ reforming

Small particles of transition metals (TM) supported on transition metal carbides (TMC) - TM/TMC- provide a plethora of design opportunities for catalytic applications due to their highly exposed active centres, efficient atom utilisation and the physicochemical properties of the TMC support [1]. To date, however, only a very small subset of TM/TMC catalysts have been tested experimentally and it is unclear which combinations may best catalyse which chemical reactions. Herein, we develop a high-throughput screening approach to catalyst design for supported nanoclusters based on Density Functional Theory, and apply it to elucidate the stability and catalytic performance of all possible combinations between nanoclusters of 7 metals (Rh, Pd, Pt, Au, Co, Ni and Cu) supported on 11 stable surfaces of TMCs with 1:1 stoichiometry (TiC, ZrC, HfC, VC, NbC, TaC, MoC and WC) towards CH₄ and CO₂ conversion technologies [2, 3]. We analyse the generated database to unravel trends or simple descriptors of the clusters' resistance towards metal aggregate formation and sintering, oxidation, stability in the presence of adsorbate species, and study their adsorptive and catalytic properties [4]. We identify Pt/HfC as the most promising combination and perform Kinetic Monte Carlo (KMC) simulations to assess its catalytic activity and selectivity for several catalytic processes involving CH₄ and/or CO₂ to validate the screening results. The results of the KMC simulations confirm the predictions of the computational screening and elucidate the strong synergies between the Pt clusters and the HfC support.

References

- [1] H. Prats, M. Stamatakis, *J. Phys. Chem. Lett.*, **just accepted**, DOI: 10.1021/acs.jpcclett.3c03214 (2024)
- [2] H. Prats, M. Stamatakis, *J. Mat. Chem. A*, **10**, 1522-1534 (2022)
- [3] H. Prats, M. Stamatakis, *Nanoscale Adv.*, **5**, 3214-3224 (2023)
- [4] H. Prats, M. Stamatakis, *Catal. Sci. Technol.*, **13**, 4635-4639 (2023)

Acknowledgments

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Hybrid QM:QM methods for adsorption of ethanol in H-MFI

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Keywords: Adsorption, Molecular Dynamics, H-MFI, Active Sites, Spectroscopy

Understanding the mechanism behind the adsorption of molecules in zeolites is crucial given their wide range of applications in industries such as petrochemicals. Numerous theoretical studies have been done in the past to quantify the free energies of adsorption in zeolites but reaching chemical accuracy (< 4 kJ/mol) is still challenging. With the advances in computational modeling, mechanically embedded hybrid high-level/low-level (QM:QM) quantum mechanical method is becoming a viable path to get chemically accurate free energy of adsorption for larger systems like zeolites.

I will present our work on ethanol adsorption on different active sites of H-MFI zeolite using hybrid QM:QM static calculations and molecular dynamics (MD) simulations. To reach chemical accuracy, we couple the QM:QM - MD with the recently developed MD-based theoretical methodology (DOS-P) of Galimberti et al. [1] to compute free energies. This allows us to calculate anharmonic enthalpies and entropies term corrected at the B3LYP+D2 and ω B97X level. While sampling the free energy surface by Molecular Dynamics (MD) requires longer simulations (> 50 ps), DOS-P allows us to obtain converged thermodynamic terms from vibrational partition functions based on the (anharmonic) VDOS using a set of short trajectories (< 3 ps). The results will be critically assessed by comparison with previous theoretical calculations [2] and experiments [3]. I will show how the hybrid QM:QM approach is essential to correctly describe the system at the atomic level in terms of chemically accurate adsorption energies and vibrational spectra.

References

- [1] D. Galimberti and J. Sauer, *J. Chem. Theory Comput.*, 17, 5849–5862 (2021)
- [2] G. Piccini, M. Alessio and J. Sauer, *Phys. Chem. Chem. Phys.*, 20, 19964-19970 (2018)
- [3] K. Alexopoulos, M. Lee, Y. Liu, Y. Zhi, Y. Liu, M. Reyniers, G. Marin, V. Glezakou, R. Rousseau, and J. Lercher, *J. Phys. Chem. C*, 120, 7172–7182 (2016)

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Defect identification in Ceria systems with High Resolution Atomic Force Microscopy, Simulations and water markers

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Keywords: ceria, oxygen vacancies, atomic force microscopy, water, DFT

A lot of experimental and theoretical effort has been devoted to determine the most energetically favorable place for the creation of O vacancies in Ceria (CeO₂) and the location of the two associated Ce³⁺ ions. Carbon monoxide, CO, in connection with infrared (IR) vibrational spectroscopy, is a promising alternative to pinpoint the defect sites[1], but the precise assignment of the different CO vibrational bands is rather complex [2]. Here, we propose an alternative for the identification of the defect sites, inspired by our previous work on the (101) anatase surface [3], that combines experiments using water molecules as markers and high resolution atomic force microscopy (HR-AFM) with sophisticated simulations of the HR-AFM images. HR-AFM, using metal tips functionalized with closed-shell molecules like CO [4] or with an O-terminated Cu tip obtained by soft nano indentation [5] provides images with truly unprecedented resolution. Recent HR-AFM experiments at NIMS using O-terminated tips and a very low dose have found that water molecules do not show the expected triangular symmetry, predicted by us [6], but a boomerang-like shape spanning two of the three equivalent O sites. Furthermore, the images show a complex contrast on the surrounding areas. Detailed spectroscopy measurements provide clearly distinguishable force versus distance curves on different Ce and O sites. Preliminary DFT calculations motivated by these experiments suggest a preferential binding of water to Ce³⁺ ions on the surface compared to the Ce⁴⁺ sites. Our working hypothesis is that water can be used as a marker for the location of Ce³⁺ and that the asymmetry in the water image is associated with the location of the other Ce³⁺ associated with the presence of a subsurface O vacancy. This methodology can contribute significantly to the characterization of few-atom catalysts based on ceria and other complex and technologically relevant oxide surfaces.

References

- [1] Y. Wang and C. Wöll, *Chem. Soc. Rev.*, **46**, 1875–1932 (2017)
- [2] P. G. Lustemberg et al., *J. Chem. Phys.*, **159**, 034704 (2023)
- [3] O. Stetsovych et al., *Nat. Comm.*, **6**, 7265 (2015)
- [4] L. Gross, et al.: *Angew. Chem., Int. Ed.*, **57**, 3888 (2018)
- [5] H. Monig et al., *ACS Nano*, **10**, 1201 (2016)
- [6] D. Fernandez-Torre et al., *J. Phys. Chem. C*, **116**, 13584 (2012)

Acknowledgments

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Ten-Electron Count Rule and Atomic Charges rationalise the Catalytic Properties of Single-Atom Alloy Catalysts

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Keywords: Single-Atom Alloys, DFT, molecular orbitals, descriptors, catalysis

Embedding single atoms of transition metals into the surface of coinage metals has emerged as an effective atom-efficient approach to create active and selective catalysts. These so-called Single-Atom Alloys (SAAs) have proven to perform chemistries deemed as unattainable with pure transition metal catalysts [1]. This unique behaviour results from the SAAs' ability to escape decades-old models (d-band model, scaling relationships) that have successfully predicted the reactivity of more traditional metal catalysts [1]. With no predictive models, however, the design of new SAA catalysts is confined to trial-and-error approaches. Via two high throughput campaigns, we show here that atomic charges and electron count rules are better suited for the identification of potentially active SAA catalysts [2-3].

Following the experimental evidence of localised electrostatic charges on the dopant of SAAs [1], we have first determined the dopant charges of Cu, Ag and Au surfaces doped with Rh, Ni, Pd and Pt. Computed dopant charges show large differences among SAAs (-0.63e on PtCu vs +0.32e on NiAu) and could play a role in the binding of adsorbates [2]. To test this hypothesis, we have computed the binding energies of a large range of catalytically relevant adsorbates. We have shown that the binding energies correlate with the dopant charges for a subset of adsorbates, namely electron rich Lewis bases such as H₂O, OH, and NH₃, suggesting that the binding energy can be decomposed into an electrostatic contribution (dominating in this subset) and a covalent contribution. By linearly combining the dopant charge (electrostatic descriptor) and the binding energy of carbon (proxy for the covalent term), we reproduce the DFT data within 0.06 eV mean absolute error and 0.07 eV standard deviation. We also propose an adsorbate classification based on the relative importance of the two identified terms.

Although this classification already provides a very intuitive theoretical framework for the rationalisation of reactivity trends on SAA catalysts, the covalency descriptor only gives indirect information about the dopants and ignores their electronic structure [3]. In our attempt to identify an electronic descriptor, we have extended our high throughput approach to most of the d-block elements as potential dopants (3d, 4d and 5d). The obtained trends reveal that the extremal binding energy is reached when the total number of valence electrons of both the dopant and the adsorbate reach 10. Further electronic structure analyses show that this corresponds to the saturation of the dopant's d-orbitals. Finally, we illustrate how this 10-electron rule can be used to identify promising SAA catalysts (in particular Mo, W and Re based SAAs) for the reduction of nitrogen to ammonia, a reaction of industrial significance.

[1] Réocreux R.; Stamatakis M. *Accounts of Chemical Research*, **55**, 87-97 (2022)

[2] Réocreux R.; Sykes E. C. H.; Michaelides A.; Stamatakis M. *JPCCL*, **13**, 7314-7319 (2022)

[3] Schumann J.; Stamatakis M.; Michaelides A.; Réocreux R., *submitted*, (ChemRxiv:10.26434/chemrxiv-2022-d5hhf)

Theoretical Developments in Py-ChemShell for Calculating Anharmonic Vibrational Signatures of Catalysts

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Keywords: QM/MM, Catalysis, DFT, TDDFT, VSCF, IR, Raman

We report the development of a fully anharmonic method for the calculation of vibrational signatures for chemical systems modelled by hybrid QM/MM approaches. Interested systems of catalysis include transition metal-containing zeolites, metallic oxide surfaces, and solvated biomolecules [1]. The method is based on the vibrational self-consistent field (VSCF) method applied to normal and local modes in chemical active sites [2], but also considers the effects of the chemical environment. The infrastructure has been implemented as a new module in Py-ChemShell [3, 4] and is scalable using partitioned taskfarming parallelism. This work builds on recent extension to Py-ChemShell for calculations of infrared and Raman intensities using the double harmonic approximations [1]. Our VSCF implementation tackles intrinsic anharmonicities, mode couplings and delocalization of normal modes, which are recognized as key challenges for first-principle computations of vibrational properties. We consider the assignment of band positions for intermediates of catalysis using the new infrastructure, for example over pyridine adsorption at Brønsted acid sites in zeolite MFI and hydrogenation on polar ZnO surfaces, and calculate anharmonic infrared and Raman signatures of active species in systems of interest. We conclude with a discussion of further intermodal correlation, thermal and evolution effects using VSCF in hybrid QM/MM.

References

- [1] Guan J, et al. *Philos. Trans. R. Soc. A* 2023, 20220234.
- [2] Cheng X, et al. *J. Chem. Phys.* 2014, 141.10, 104105.
- [3] Lu Y, et al. *J. Chem. Theory Comput.* 2019, 1317-1328.
- [4] Lu Y, et al. *PCCP* 2023, 21816-21835.

Acknowledgments

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Unraveling the Role of Peroxo Species in Surface Chlorine Transformation during HCl Oxidation on CeO_{2-x}(111)

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Keywords: Deacon process, CeO₂, peroxo species, DFT, reaction pathways

The Deacon process offers a sustainable method for recovering chlorine from HCl, a toxic air contaminant, through its oxidation with molecular oxygen. CeO₂-based catalysts have shown promise as cost-effective alternatives to commercial RuO₂-based materials in HCl oxidation [1,2]. Previous density functional theory (DFT) model calculations [1] suggested that a crucial step in this process involves the displacement of tightly bound chlorine at a vacant oxygen position on the CeO₂(111) surface (Cl_{vac}) toward a less strongly bound cerium on on-top (Cl_{top}) position, which is highly endothermic by more than 2 eV. In this study, based on DFT investigations of the reoxidation of a chlorinated single-crystalline Cl_{vac}-CeO_{2-x}(111)-(3 × 3)R30° surface structure, we offer valuable insights into the complex steps of the HCl oxidation process on CeO₂-based catalysts, which are supported by experimental observations. The Cl_{vac} species are found to be strongly bound with an adsorption energy exceeding 2 eV [3]. Our DFT results suggest that the HCl oxidation involves three crucial steps [4]: (i) Diffusion of subsurface vacancies to the surface with an activation energy of 0.80 eV. (ii) Adsorption of O₂²⁻ at the surface vacant site within an energy range of 0.3–0.7 eV. (iii) Dissociation of O₂²⁻ species, leading to the displacement of Cl_{vac} to Cl_{top}. This step is exothermic by 0.60 eV with an activation barrier of 1.04 eV and occurs even at 500 K. This provides an energetically favorable alternative explanation compared to that reported by Armute et al. [1] and highlights the importance of peroxo species for catalytic oxidation reactions on CeO₂-supported catalysts.

References

- [1] A. P. Amrute, C. Mondelli, M. Moser, G. Novell-Leruth, N. López, D. Rosenthal, R. Farra, M. E. Schuster, D. Teschner, T. Schmidt, et al. *J. Catal.*, **286**, 287–297 (2012).
- [2] M. Capdevila-Cortada, G. Vilé, D. Teschner, J. Pérez-Ramírez, N. López, *Appl. Catal., B*, **197**, 299–312 (2016).
- [3] V. Koller, C. Sack, P. Lustemberg, M. V. Ganduglia-Pirovano, H. Over, *J. Phys. Chem. C*, **126**, 13202–13212 (2022).
- [4] V. Koller, P. Lustemberg, A. Spriewald-Luciano, S. M. Gericke, A. Larsson, C. Sack, A. Preobrajenski, E. Lundgren, M. V. Ganduglia-Pirovano, H. Over, *ACS Catal.*, **13**, 12994–13007 (2023).

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Two are Better than One: Exploring Single and Dual Active Sites in the Novel Material Class of Highly Dispersed Ternary Alloys

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Keywords: Single Atom Alloys, Dual Atom Alloys, Catalysis, Surfaces, Transition Metals, Segregation, Aggregation, DFT

Heterogeneous catalysis plays a vital role in reshaping how we address the ever-growing demand for energy, fuels, and chemicals. A major challenge for catalysis is the high stability and thus inertness of readily available feedstocks such as carbon dioxide or water. Activation of such unreactive molecules requires highly active catalysts which typically comes at the cost of reduced selectivity. Single atom alloy (SAA)^[1] catalysts, which are composed of catalytically very active elements (dopants) atomically dispersed in a less active but more selective host metal, offer an exciting solution to overcome this activity-selectivity tradeoff.

Binary alloys consist of one dopant and one host element. They can form either individual single atom dopant sites (SAAs) or dopant dimers (homodimers). Ternary alloys contain two different dopant elements and one host element. They can form two individual dopant sites in a sample, an SAA with two different active site types, or homodimers as well. Yet, they can also feature active sites based on heterodimers containing two different dopant elements (dual atom alloys, DAAs). Hence, ternary alloys show the promise to surpass the capabilities of binary alloys as they will enable catalytic reactions with two rate-determining steps that require different dopant elements as active sites. In addition, DAAs containing heterodimers can facilitate bond cleavage or formation if each of the dopant atoms stabilizes one of the fragments, as recently demonstrated by our collaborators.^[2]

So far, even a basic understanding of the fundamental properties such as aggregation and segregation energies of ternary alloys is lacking. Nevertheless, these are highly important properties that determine whether an active site is accessible for reactions at the surface and whether ternary SAAs or homo or hetero DAAs are formed. To address this crucial knowledge gap, we provide segregation and aggregation energies for all 3d, 4d, and 5d transition metals (TMs) and their combinations as obtained with the optB86b-vdW functional. To understand the effects of the host metal element and surface facet, we explore all SAAs and DAAs on the Cu(100), Cu(111), and Ag(111) surfaces. We identify general trends across the periodic table for the type and location of active sites. In binary alloys, very early and late TM dopants do not form homodimers but SAAs, e.g. ScCu(111) and PdCu(111). Combining these TMs in a ternary alloy leads to the preferential formation of heterodimers, e.g. ScPdCu(111). In contrast, "central" 4d and 5d TMs, e.g. Mo or Re, tend to form dimers with "central" TMs and therefore also easily form homodimers in binary as well as ternary alloys.

These insights lay the foundation for future catalysis research and will for the first time enable experimentalists and theoreticians to make a rational choice of dopants for a particular reaction of interest based on a data set that comprises all transition metals.

References

- [1] R. T. Hannagan, G. Giannakakis, M. Flytzani-Stephanopoulos, E. C. H. Sykes., *Chem. Rev.*, **120**, 12044-12088, (2020).
- [2] P. L. Kress, S. Zhang, Y. Wang, V. Çınar, C. M. Friend, E. C. H. Sykes, M. M. Montemore, *J. Am. Chem. Soc.*, **145**, 8401–8407, (2023).

Ultra-high Metal Loading Heterogeneous Single Atom Catalysts based on Palladium-Phthalocyanine Covalent Organic Frameworks for Cross-Coupling Reactions.

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Keywords: SACs, DFT, Suzuki, Palladium, COFs

Suzuki-Miyaura cross-coupling is a valuable reaction for synthesizing biaryl compounds by coupling aryl halides with boronic acid, facilitated by a palladium catalyst [1]. This reaction is widely utilized in organic synthesis due to its mild reaction conditions, broad substrate scope, and high functional group tolerance, making it a versatile tool for constructing complex organic molecules. However, since the reaction typically relies on rare-earth metals for catalysis, there is a growing need for sustainable alternatives.

In this line, Single Atom Catalysts (SACs) represent a sustainable forefront in catalysis, holding exceptional atom efficiency and selectivity in diverse chemical reactions [2]. Leveraging SACs, researchers have improved the metal loading which also contributes to a better transformative cross-coupling process [3].

Ultra-high density SACs have been obtained based on palladium porous polyphthalocyanine covalent organic framework (COFs). This synthesis generates an almost continuous range of metal coordination environments, making it difficult to precisely characterize the catalyst. Nevertheless, they achieve similar yields to its homogeneous analogue while ensuring full catalyst recovery making them a better sustainable alternative. Our findings pave the way for the development of high-performance catalysts with well-defined nature for organic synthesis.

References

- [1] Yin, L. & Liebscher, J., *Chem. Rev.* **107**, 133–173 (2007).
- [2] Li, W.-H., Yang, J., Wang, D., & Li, Y., *Chem*, **8**, 119-140 (2022)
- [3] Z. Chen, E. Vorobyeva, S. Mitchell, E. Fako, M. A. Ortuño, N. López, S. M. Collins, P. A. Midgley, S. Richard, G. Vilé, *Nature Nanotechnology*, **13**, 702-707 (2018)

Acknowledgments

This work was supported by funding from the Generalitat de Catalunya and the European Union under Grant 2024FI. The Spanish Ministry of Science and Innovation is acknowledged for financial support (RTI2018–101394–B–I00) and Severo Ochoa Grant (MCIN/AEI/10.13039/501100011033 CEX2019–000925–S) and the Barcelona Supercomputing Center–Mare Nostrum (BSC–RES) for providing generous computer resources.

Morphology of Ru nanoparticles at titania-water interface – A computational study

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Keywords: grand canonical sampling, nanoparticle, ruthenium, TiO₂, biomass

Biomass conversion requires the ability to transform highly oxidized molecules into value added molecules, this requires hydrogenation, often using Ru supported over TiO₂. This catalyst is that it is used in water, making its surface state hard to determine.

Prior research into the surface state of the Ru-water interface¹ has shown that in the presence of water and under realistic reaction conditions (500K), adsorbed water molecules fully dissociate. This prior research paves the way for investigating more realistic systems, in particular subnanometric (~10 atoms) Ru nanoparticles adsorbed on support such as titania.

Global optimization was performed by using the PGOPT² program to generate numerous and varied nanoparticle morphologies (Ru₁₀ supported on TiO₂ anatase 101) with different combinations of water molecules and varying degrees of splitting of these water molecules. Several thousand structures were thus generated and optimized using the CP2K DFT software (PBE functional), allowing for the free energy of the system to be studied according to different structural parameters. A typical structure obtained through this method is shown in Fig. 1.

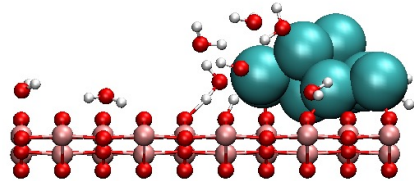


Fig. 1. Ru₁₀ supported on TiO₂ (anatase 101) with 9 unsplit water molecules.

	0	1	2	3	4	5	6	7	8
0	0,00	-1,78	-3,44	-4,12	-7,03	-6,14	-7,46	-9,38	-10,47
1		-1,92	-3,44	-4,74	-4,81	-6,34	-7,29	-9,40	-9,97
2			-1,56	-3,30	-4,00	-5,21	-6,35	-7,90	-9,46
3				-1,86	-4,50	-6,64	-6,36	-9,69	-7,44
4					-0,41	-3,79	-4,74	-9,40	-8,49
5						-2,52	-5,73	-9,10	-9,10
6							-1,65	-4,02	-6,81
7								-2,25	-4,97
8									-0,80

Fig. 2. Free energy (eV, at 500K and water saturation pressure) of the most stable configuration obtained according to the number of water molecules adsorbed on the nanoparticle (horizontal axis) and the number of broken bonds on the water molecules (vertical axis), i.e. the degree of water dissociation.

The stability of nanoparticles is analyzed according to the number of water molecules adsorbed, the potential splitting of these water molecules and morphological parameters.

Fig. 2 shows the free energy of the most stable configuration obtained for different numbers of water molecules and differing degrees of water dissociation.

This establishes the presence of OH adsorbed on the nanoparticles, a key species used to explain reaction mechanisms on Ru nanoparticles but for which there has been no direct of evidence of its presence up until this point.

References

- [1] M. A. Ramzam *et al.*, *J. Phys. Chem. Lett.*, **14**, 4241(2023)
- [2] H. Zhai, A. N. Alexandrova, *J. Phys. Chem. Lett.*, **9**, 1696 (2018)

Acknowledgments

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Electroreduction of NO_3^- to N_2 on Pt(111) and Pd(111) Surfaces

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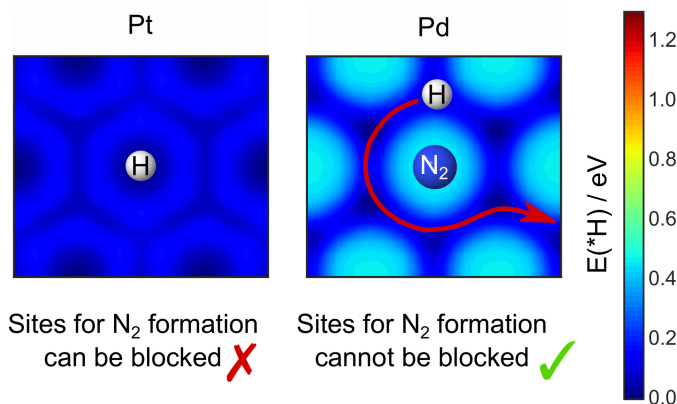
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Keywords: nitrate reduction, Pt(111)/Pd(111), selectivity, hydrogen coverage, statistical modelling

In recent years, reactive nitrogen species have become prevalent pollutants in the biosphere with nitrate (NO_3^-) in particular, causing substantial contamination of terrestrial waterways and ground water.¹ Therefore, research has focused on designing catalysts which are able to reduce nitrate levels by converting these threatening pollutants into benign products such as N_2 .^{1,2} One method which has shown promise is the electrocatalytic reduction of NO_3^- to N_2 under acidic conditions using a Pd(111) surface.² Curiously, while Pd and Pt exhibit similar catalytic behaviour for many reactions, the Pt(111) surface does not behave similarly with respect to the selective nitrate reduction, and produces only NH_4^+ and N_2O , with little to no N_2 produced.³

In this work, density functional theory is used to study the formation of N_2 from NO on both Pt(111) and Pd(111). It is found that both metals exhibit a similar mechanism and energy profile for N_2 formation. However, they exhibit key differences in hydrogen adsorption behaviour. Therefore, hydrogen coverage as a function of electrode potential is explored in more detail to see whether surface hydrogen atoms may inhibit the formation of N_2 on Pt(111), explaining the differences in observed selectivity.



References

- [1] M. Duca, and M. Koper, *Energy Environ. Sci.* **5**, 9726-9742 (2012).
- [2] A. de Vooy, M. Koper, R. Van Santen, and J. Van Veen, *J. Catal.* **202**, 387-394 (2001).
- [3] A. de Vooy, M. Koper, R. Van Santen, and J. Van Veen, *Electrochim. Acta.* **46**, 923-930 (2001).

Acknowledgments

This work was supported by the University of Otago and the MacDiarmid Institute for Advanced Materials and Nanotechnology.

Elucidating the Reactivity of Oxygenates on Single-Atom Alloy Catalysts

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Keywords: single-atom alloy, catalyst screening, linear scaling, Brønsted–Evans–Polanyi relation, methanol dissociation, DME synthesis

Doping isolated transition metal atoms into the surface of coinage-metal hosts forming single-atom alloys (SAAs) can significantly improve the catalytic activity and selectivity of their monometallic counterparts [1-2]. To date, however, only a very small subset of chemical reactions on SAAs has been investigated, and it is unclear which combinations may best catalyse which chemical reactions.

In this study, we investigate the catalytic properties of SAAs with different bimetallic combinations (Ni-, Pd-, Pt-, and Rh-doped Cu(111), Ag(111), and Au(111)) for chemistries involving oxygenates relevant to biomass reforming with the help of Density Functional Theory (DFT) calculations.

We calculate and compare the formation energies of species such as methoxy (CH₃O), methanol (CH₃OH), and hydroxymethyl (CH₂OH), thereby elucidating the stability of these adsorbates on SAAs and exploring the validity of thermochemical linear scaling relations (TCS) on these surfaces [1].

For the reactions, we choose the dehydrogenation of CH₃OH towards formaldehyde (CH₂O) to investigate C-H and O-H activation, while dimethyl ether (CH₃OCH₃) formation from methyl (CH₃) and CH₃O is chosen to study C-O coupling. Activation energies and reaction energies for each of the aforementioned elementary steps are then computed, and the pertinent Brønsted–Evans–Polanyi (BEP) relationships are explored [1].

Our analysis of the data in terms of the TCS and the BEP relationships shows that SAAs with particular metallic combinations have the potential to combine weak binding with low activation energies, thereby exhibiting enhanced catalytic behavior over their monometallic counterparts for key elementary steps of oxygenate conversion.

References

[1] W. Li, S. E. Madan, R. Réocreux, M. Stamatakis, *Acs Catal.*, **13**, 15851-15868 (2023)

[2] M. T. Darby, R. Réocreux, E. C. H. Sykes, A. Michaelides, M. Stamatakis, *Acs Catal.*, **8**, 5038-5050 (2018)

Acknowledgments

The authors gratefully acknowledge the use of the UCL High Performance Computing Facilities Kathleen@UCL and Myriad@UCL in the completion of the simulations of this work. We are grateful to the U.K. Materials and Molecular Modelling Hub, which is partially funded by EPSRC (EP/P020194/1), for computational resources (HPC facility Young). We also thank Dr Hector Prats and Dr Julia Schumann for helpful discussions.

Can Machine Learning Predict the Reaction Paths in Catalytic CO₂ Reduction on Small Cu/Ni Clusters?

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Keywords: nanoparticle, CO₂ reduction, machine learning, interactions, metallic cluster

Our study delves into the catalytic reduction of CO₂ on 13-atom bimetallic (CuNi) nanoclusters with icosahedral geometry. Given the varied configurations possible with copper and nickel atoms, including their positioning and distribution, conducting simulations for each permutation becomes time-consuming and impractical. To address this, we've devised a machine learning model tailored to predict the energy of specific bimetallic clusters and their interactions with CO₂ reduction intermediates. While the model doesn't offer precise energy predictions, it effectively identifies candidates for further optimization with a reasonable degree of certainty (MAE = 0.2 eV). Additionally, we've uncovered that the stability of these complexes correlates with the central atom type within the nanoparticle, despite its lack of direct interaction with intermediates. Using our model, we were able to analyse the catalytic pathway of CO₂ reduction without performing any optimization of the bimetallic cluster and come to conclusions that are consistent with previous literature reports [1, 2].

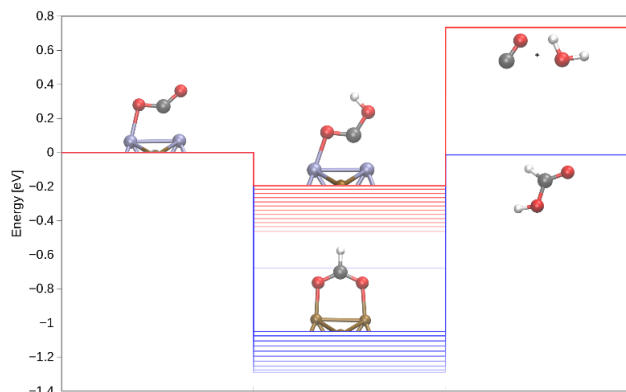


Figure 1. Predicted potential energy profiles for the carboxyl (red) and formate (blue) pathways. The intensity of the color represents the composition of the nanocluster—the darker the color, the greater the Ni content.

References

- [1] R. Kortlever, J. Shen, K.J.P Schouten, F. Calle-Vallejo, M.T.M Koper, *J. Phys. Chem. Lett.*, **6**, 4073–4082 (2015)
- [2] C. Liu, T.R. Cundari, A.K. Wilson, *Phys. Chem. C* **116**, 5681–5688, (2012)

Acknowledgments

This research was carried out with the support of the Interdisciplinary Centre for Mathematical and Computational Modelling University of Warsaw (ICM UW) grant no. g92- 506. We gratefully acknowledge Poland's high-performance Infrastructure PLGrid (HPC Center ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2023/016617. This article/publication is based upon work from COST Action CA18234 (CompNanoEnergy), supported by COST (European Cooperation in Science and Technology).

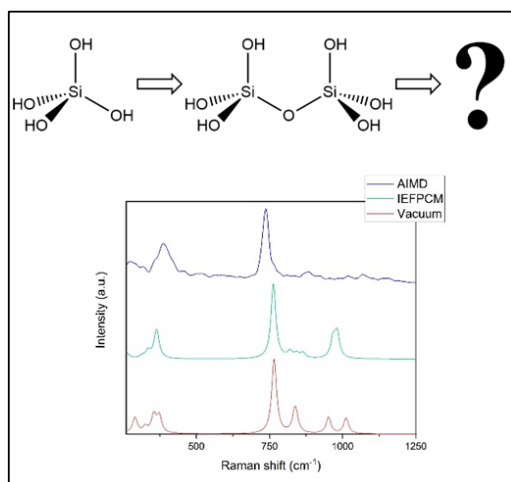
Unraveling Silicate Cluster Formation: Cutting-Edge Insights from Theoretical Spectroscopy

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Keywords: Raman, theoretical spectroscopy, DFT, AIMD, zeolites, nucleation

Part of the increasing attention received by Raman spectroscopy during the last decades stems from the versatility of the technique. Among all the capabilities that it offers, growing interest has been drawn to its capacity to capture the spectra of species in aqueous solutions.



Therefore, Raman spectroscopy has been established as a strong candidate to address the longstanding challenge that nucleation of silicates in solution presents.¹ When this reaction starts significant quantities of a wide variety of oligomeric species start to be formed. The resulting myriad of species provides a mixed Raman signal where the identification of individual signals is not possible. To allow a reliable use of Raman spectroscopy to follow these reactions in solution, we computed the individual Raman spectra of these species with state-of-the-art methodologies.

In our work we show how implicit solvent models or in-vacuum computations are insufficient for accurately computing the Raman spectra of this species, as most of the solute-solvent interaction is formed by hydrogen bonds. On top of it, the conformations that solvent and solute can take also affect the Raman spectra. With the aim to obtain the most precise spectra possible we used the autocorrelation function (ACF) formalism for the computation of spectroscopic properties,² whose results we compared with our previous results and with the scarce experimental data. For the computation of the electromagnetic moments, we used the radical Voronoi tessellation scheme. Based on our ACF computations, we demonstrate firstly the crucial role of the solvent in the spectroscopy signal of silicate species in solutions. We also created a collection of high-quality Raman spectra for selected silicate oligomers which can be used to unravel the complex mixture of species created during the nucleation of this materials.

References

- [1] P. K. Dutta, D.-C. Shieh, *Appl. Spectrosc.*, **39**, 343–346 (1985)
- [2] Thomas M., Brehm M., Kirchner B., *Phys. Chem. Chem. Phys.*, 2015, **17**, 320 (2014)

Acknowledgments

This work was supported by the EU H2020 Project, “Characterisation and Harmonisation for Industrial Standardisation of Advanced Materials” (CHARISMA), under Grant Agreement no. 952921. Computational resources were provided by the Flemish Supercomputer Center.

Analyzing Activity and Selectivity Trends for NO Hydrogenation Using "Catalytic Matrices"

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Keywords: Nitric oxide reduction, Nitric oxide hydrogenation, Electrocatalysis, Structural sensitivity, Reaction mechanism, DFT

Anthropogenic activities have increased oxidized nitrogen compounds (NO_x) in the biosphere, unbalancing the nitrogen cycle. Electrocatalytic NO_x reduction, especially in converting NO to NH₄⁺/NH₃, is promising to help restore equilibrium [1]. However, the first hydrogenation of NO is usually potential limiting and details about selectivity to *NHO or *NOH and the active sites remain unknown, impeding catalyst development [2,3].

In this contribution, I will use "catalytic matrices" to classify the selectivity and activity of late transition metals for *NO hydrogenation [4]. For transition metals in groups 9, 10 and 11, catalytic matrices reveal high *NO hydrogenation activity for the elements of group 11 (Cu, Ag, Au), and moderate activity in (100) facets. Besides, *NHO is statistically favored over *NOH. Cu electrodes, often used for NO reduction to ammonia, should generally have undercoordinated active sites. Furthermore, multivariate regression based on coordination number, group number, and period in the periodic table can reproduce areas of high activity in catalytic matrices. Finally, I will show the use of catalytic matrices for CO hydrogenation [5].

In conclusion, catalytic matrices are valuable tools for conducting statistical analysis and provide qualitative and quantitative insights. For NO electroreduction, they indicate that effective catalysts should generally contain undercoordinated Cu sites and proceed via *NHO.

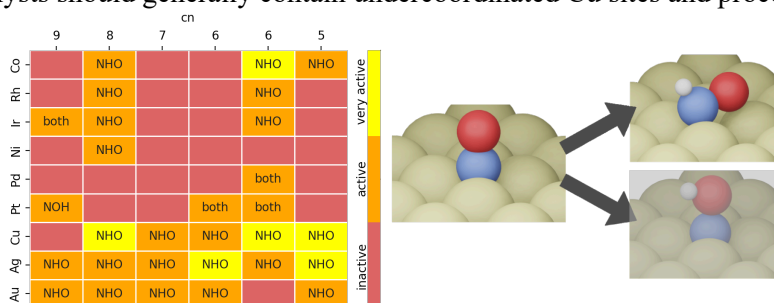


Figure 1. Left: catalytic matrix for *NO Hydrogenation. Right: *NO and its two hydrogenation products.

References

- [1] P. H. van Langevelde, I. Katsounaros, M. T. M. Koper, *Joule*, **5**, 290–294 (2021).
- [2] V. Rosca, M. Duca, M. T. de Groot, M. T. M. Koper, *Chem. Rev.*, **109**, 2209–2244 (2009).
- [3] C. A. Casey-Stevens, H. Ásmundsson, E. Skúlason, A.L. Garden, *Appl. Surf. Sci.*, **552**, 149063 (2021).
- [4] E. Romeo, M. F. Lezana-Murales, F. Illas, F. Calle-Vallejo, *ACS Appl. Mater. Interfaces*, **15**, 22176–22183 (2023).
- [5] F. Calle-Vallejo, *Curr. Opin. Electrochem.*, **42**, 101409 (2023).

Wednesday, September 4

Key Lecture 4 María Verónica Ganduglia-Pirovano. Breaking Scaling Relations through Metal-Oxide Interactions on Metal-CeO₂ Interfaces: Implications for the Conversion of Methane to Fuels.

Oral contribution Georgi Vayssilov. Carbon Monoxide Oxidation on Platinum Species Supported on Cerium Dioxide – Density Functional Study.

Oral contribution Michael Walter. CO₂ hydrogenation mechanism on inverse ZnO/Cu catalysts.

Oral contribution Pablo Gamallo. DFT-based kMC simulations of CO₂ hydrogenation in Ni₄/CeO₂ catalyst. The role of Eley-Rideal reactions.

Focus Topic 2 Mercedes Boronat. Approaching enzymatic catalysis with zeolites: an ab initio and experimental study of alkylaromatics competing reactions.

Oral contribution Torstain Fjermestad. Synergy between experiment and multiscale modelling to gain insight into the zeolite catalysed methanol-to-DME reaction.

Oral contribution Martine Castellà-Venture. Theoretical Study of the Steric Hindrance Effects on Methyl Pyridine Derivatives Adsorption in H-ZSM5 Zeolite.

Oral contribution Stepan Sklenak. Mechanism of the direct oxidation of methane to methanol by dioxygen on the distant binuclear Fe(II) cationic sites over the zeolite of the ferrierite topology.

Oral contribution Dorota Rutkowska-Zbik. Is the ability of distant metal ions to activate dioxygen specific only for zeolite materials?

Emerging Researcher John Mark Martinez. Quantum mechanical insights into light-driven reactions on metallic nanoparticles.

Oral contribution Sai Sharath Yadavalli. Elucidating the role of potassium in methane steam reforming using first-principles-based kinetic Monte Carlo simulations.

Oral contribution Stefano Vaghi. Revisiting intermediates and mechanism producing (MMA-ran-DMAEMA)_n copolymers via ARGET-ATRP catalyzed by Cu complexes.

Oral contribution Luis Enrique Sansores. A study of the absorption of Li on γ -graphyne monolayers materials doped with X (X=N, B, P, Al, and Si) heteroatom.

Short Communication Simone Puricelli. Kinetic influences on a process considered under thermodynamical control: acid resin catalysed self- and cross-aldolic condensation of cyclic ketones.

- Short Communication Henning Windeck. Internal H–Bond Formation of Brønsted Acid Sites in the Zeolites H–MOR, H–FER, and H–MFI: Predictions of Structures and Stabilities beyond DFT.
- Short Communication Christopher Mills. Elucidating the Electrolytes Involved in the Solvation of Vanadium Ions in the Catalytic Reactions within Redox Flow Batteries.
- Short Communication Julian Beßner. Theoretical evaluation of CuFeO_2 and CuBi_2O_4 as possible catalysts for N_2 Reduction.
- Short Communication Robert M. Narvaez. Adsorption and spectra validation studies through DFT of Metal-Phosphonate properties in NU-1000 structure.
- Short Communication Eduardo Oliveira. Exploring the Formation of Reactive Oxygen Species on Amorphous Silica Through DFT-MD.

Breaking Scaling Relations through Metal-Oxide Interactions on Metal-CeO₂ Interfaces: Implications for the Conversion of Methane to Fuels

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Keywords: DFT, scaling relations, CH₄ activation, metal-ceria, CH₄ to CH₃OH

In the field of C1 chemistry, the reaction between CH₄ and CO₂ to produce syngas (CO/H₂), known as methane dry reforming (MDR), is gaining significant attention due to its environmentally friendly nature. Additionally, the direct conversion of CH₄ to CH₃OH is a highly desirable goal in catalytic chemistry. Metal-ceria systems have emerged as promising catalysts for MDR. In this presentation, we will discuss recent findings on metal (Ni, Co, Pt, Cu, NiCu)/CeO₂(111) model catalysts and compare them with results obtained from extended (111) metal surfaces, as well as metal/CeO₂ powder catalysts.¹⁻⁴ The focus will be on theoretical investigations, utilizing the DFT+U approach implemented in the VASP simulation package, in conjunction with experimental techniques such as in situ/operando methods (AP-XPS, XRD, and XAFS) and catalytic testing. Special attention will be given to examining the effects of metal loading and metal-ceria interactions.

A key finding is that a low metal loading, combined with the ability of reducible ceria to stabilize oxidized metal species on the CeO₂ surface by re-localizing electrons on localized *f*-states, is crucial for enabling CH₄ activation, even at room temperature, and facilitating CH₄ reforming efficiently at relatively low temperatures (700 K). The room-temperature activation of methane on low-loaded metal/CeO₂ is particularly noteworthy as it deviates from simple linear scaling relationships.⁵ These results shed light on how this nanomaterial escapes the "tyranny of linear scaling" for the dissociative adsorption of methane, presenting a potential strategy for overcoming scaling relations to develop active and stable catalysts for methane activation and conversion.

Furthermore, we will present compelling evidence demonstrating that low Ni loadings on a CeO₂(111) support can facilitate a direct catalytic cycle for methanol generation at low temperatures (450 K) using oxygen and water as reactants.⁶ This process exhibits a higher selectivity than previously reported for ceria-based catalysts. Additionally, we will discuss the role of active site isolation in the reactivity of Ni_{1-x}Cu_x/CeO₂ systems for C–H bond cleavage.⁷

References

- [1] Liu Z. et al. *Angew. Chem. Int. Ed.*, **55**, 7455–7459 (2016)
- [2] Liu Z. et al. *Angew. Chem. Int. Ed.*, **56**, 13041–13046 (2017)
- [3] Lustemberg, P. G. et al. *J. Phys. Chem. Lett.*, **11**, 9131–9137 (2020)
- [4] Zhang, F. et al. *ACS Catal.*, **11**, 1613–1623 (2021)
- [5] Latimer, A. A. et al. *Phys. Chem. Chem. Phys.*, **19**, 3575–3581 (2017)
- [6] Lustemberg P. G., et al. *J. Am. Chem. Soc.*, **140**, 7681–7687 (2018)
- [7] Lustemberg P. G., et al., *J. Phys. Chem. Lett.*, **13**, 5589–5596 (2022)

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Carbon Monoxide Oxidation on Platinum Species Supported on Cerium Dioxide – Density Functional Study

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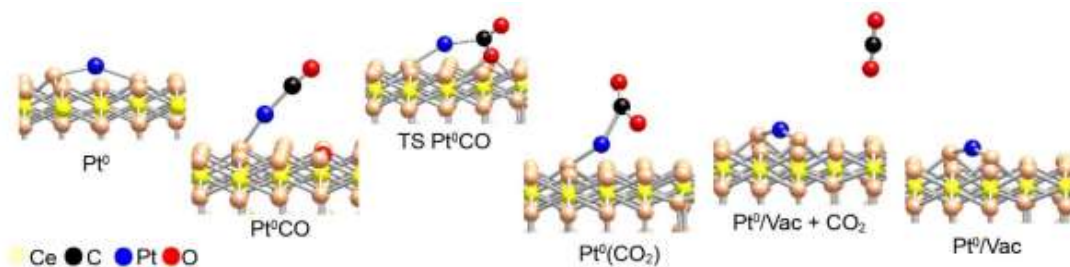
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Keywords: DFT, cerium dioxide, platinum, carbon monoxide, reaction mechanism

Cerium dioxide is a reducible oxide, which often is crucial component in various adsorption or catalytic systems for removal of gas pollutants including adsorption and conversion of carbon monoxide. In order to contribute to clarification of the mechanism of CO oxidation on platinum supported on cerium dioxide we modeled the process on various platinum containing species: mononuclear platinum in different oxidation states and Pt clusters employing density functional method [1]. Among all modelled mechanisms on ceria support, the lowest activation barriers for CO oxidation are calculated for the reaction paths via $\text{Pt}^{2+}(\text{CO})_2$ or $\text{Pt}^{4+}(\text{CO})$ complexes: 22 – 35 kJ/mol. Via the dicarbonyl complexes, $\text{Pt}^{2+}(\text{CO})_2$, the activation barriers for the first and second CO oxidation steps are 24 and 40 kJ/mol, while the barriers for the healing oxygen vacancies with O_2 are somewhat higher, 49 and 69 kJ/mol. Under oxidative conditions, in presence of Pt^{4+} , the activation barriers for CO oxidation are 35 and 53 kJ/mol on ceria surface, and 22 and 27 kJ/mol on ceria nanoparticle.

The CO oxidation on platinum clusters occurs with relatively low activation barriers when the clusters are completely covered by CO, namely 40 and 50 kJ/mol on ceria surface and 47 or 19 kJ/mol on ceria nanoparticle. In this case, the first step involves surface oxygen anion, while the second step is with an additional oxygen center from an O_2 molecule located in the formed oxygen vacancy. The results are compared with platinum supported on alumina.

The calculations were performed with DFT+U approach using periodic code VASP with the gradient corrected PW91 exchange-correlation functional.



Optimized stationary points for CO oxidation on Pt^0 at $\text{CeO}_2(111)$ surface.

References

[1] I. Z. Koleva, H. A. Aleksandrov, G. N. Vayssilov, *ACS Catal.*, **13**, 5358-5374 (2023)

Acknowledgments

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CO₂ hydrogenation mechanisms on inverse ZnO/Cu catalysts

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Keywords: CO₂ reduction, energy storage, methanol, inverse catalyst, DFT, global optimization, ab initio thermodynamics

Mankind is facing considerable challenges in their quest to secure sufficient energy supply for the future based on renewables. These are often produced when they are not needed while their production is low at times of large demand. Therefore, large scale effective energy storage is needed. The synthesis of the base chemical methanol from the greenhouse gas CO₂ and green H₂ is a promising strategy as methanol is liquid and can thus be easily stored, transported and processed further.

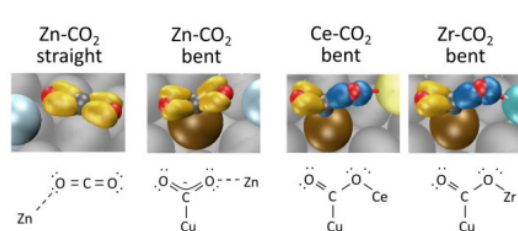


Figure 1: Wannier orbitals and formal Lewis structures representing the different activation modes of CO₂ bound to Zn, Ce and Zr (from [1]).

We study the formation of methanol on ZnO/Cu catalysts gradient corrected density functional theory (DFT). The catalytically active region is modeled as a minimum size inverse catalyst represented by Zn_xO_y(H) clusters of different size [1] and a ZnO nano-ribbons [1,3] on an extended Cu(111) surface. We apply an extensive and systematic approach combining global optimization based on an evolutionary algorithm with atomistic ab initio thermodynamics to identify the ZnO₃ motif as the elementary building block [2]. Comparison to a high level wave function method reveals that DFT systematically underestimates reaction barriers, but nevertheless conserves energetic ordering. In contrast to other metal-supported oxides like ceria and zirconia, the reaction proceeds through the formation of formate on ZnO_x/Cu, thus avoiding the CO intermediate. The difference between the oxides is attributed to variance in the initial activation of CO₂ (Figure 1). The energetics of the formate reaction pathway is insensitive to the exact environment of undercoordinated Zn active sites pointing to a general mechanism for Cu-Zn based catalysts.

References

- [1] T. Reichenbach, K. Mondal, M. Jäger, T. Vent-Schmidt, D. Himmel, V. Dybbert, A. Bruix, I. Krossing, M. Walter, M. Moseler, *J. Catalysis*, **360**, 168-174 (2018)
- [2] T. Reichenbach, M. Walter, M. Moseler, B. Hammer, A. Bruix, *J. Phys. Chem. C*, **123** 30903-30916 (2019)
- [3] K. Mondal, Megha, A. Banerjee, A. Fortunelli, M. Walter, M. Moseler, *J. Phys. Chem. C*, **126**, 764-771 (2022)

DFT-based kMC simulations of CO₂ hydrogenation in Ni₄/CeO₂ catalyst. The role of Eley-Rideal reactions.

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Keywords: CO₂ conversion, heterogeneous catalysis, hydrogenation, kinetic Monte Carlo, Eley-Rideal reactions

CO₂ hydrogenation into light fuels represents a promising avenue for addressing climate change, enhancing energy sustainability, and fostering economic development. In this study we performed a comprehensive analysis of the CO₂ hydrogenation mechanism on a well-defined Ni/CeO₂ catalyst model system utilizing a multiscale approach. The methodology integrates periodic density functional theory (DFT) calculations with kinetic Monte Carlo (kMC) simulations considering the role of Eley-Rideal reactions, often ignored in conventional catalytic studies.

DFT calculations conducted on a Ni₄ cluster supported on CeO₂ (111) surface reveal favourable adsorption energies and low energy barriers, suggesting the catalyst's potential for high-selectivity CO₂ methanation. Furthermore, kMC simulations demonstrate a synergistic effect between the two three-fold hollow sites, with certain elementary reactions predominating in one site over another. Notably, this effect is more pronounced when explicitly considering Eley-Rideal steps.

The simulations unveil that CO is primarily formed via the dissociative pathway of the reverse water-gas shift reaction, whereas methane is generated through a CO₂ → CO → HCO → CH → CH₂ → CH₃ → CH₄ mechanism. Overall, our findings underscore the significance of incorporating Eley-Rideal reactions and highlight the efficacy of small Ni clusters supported on CeO₂ (111) surfaces as promising catalysts for high-selectivity CO₂ methanation under mild conditions, while exhibiting enhanced activity and selectivity towards CO formation at elevated temperatures.

References

[1] P. Lozano, P. Gamallo, R. Sayós, F. Illas, *ACS Catal.*, **14**, 2284-2299 (2024)

Acknowledgments

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Approaching enzymatic catalysis with zeolites: an ab initio and experimental study of alkylaromatics competing reactions

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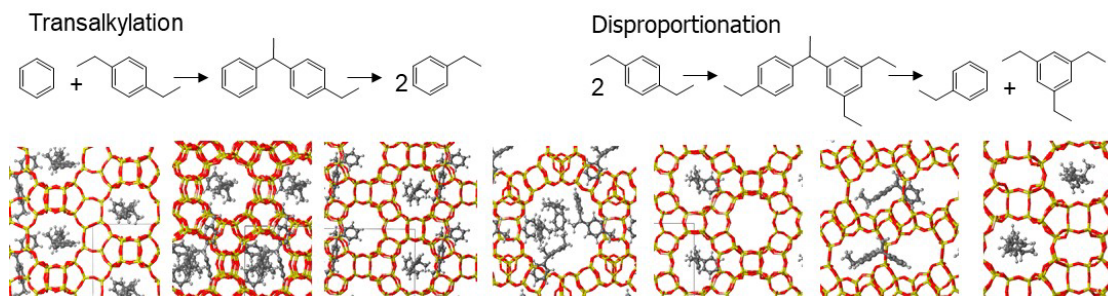
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Keywords: DFT, zeolite, confinement, mechanism, selectivity

Zeolites are microporous aluminosilicates largely employed in industry as efficient Brønsted acid heterogeneous catalysts.¹ The stabilization of reaction intermediates and transition states inside the zeolite microporous voids by weak Van der Waals interactions is very sensitive to the fit of the adsorbed species with the surrounding environment, but approaching the level of molecular recognition of enzymes with solid catalysts is a challenging goal.² In this work, we focus on the competing transalkylation and disproportionation of diethylbenzene (Scheme 1), where the key diaryl intermediates for the two competing reactions only differ in the number of ethyl substituents in the aromatic rings. By combining a fast high-throughput screening of all zeolite structures able to stabilize the key intermediates with a more computationally demanding periodic DFT study of the mechanism on the most promising candidates, a series of potentially selective zeolite structures are theoretically proposed and experimentally synthesized and tested. The results presented demonstrate that subtle changes in the zeolite architecture can modulate the preferred reaction pathways, leading to a precise control of the host-guest interactions as it occurs in enzymatic catalysis.³



Scheme 1. Reactions considered and key intermediates confined in selected zeolites.

References

- [1] P. del Campo, C. Martínez, A. Corma, A. *Chem. Soc. Rev.*, **50**, 8511 (2021)
- [2] M. Moliner, M. Boronat, *Microporous Mesoporous Mater.* **358**, 112354 (2022)
- [3] P. Ferri, Ch. Li, D. Schwalbe-Koda, M. Xie, M. Moliner, R. Gómez-Bombarelli, M. Boronat, A. Corma, *Nature Communications* **14**, 2878 (2023)

Acknowledgments

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Synergy between experiment and multiscale modelling to gain insight into the zeolite catalysed methanol-to-DME reaction.

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Keywords: Multiscale modelling, fixed-bed reactor, computational fluid dynamics, DFT, microkinetic modelling, methanol-to-DME, H-ZSM-5

With the aim to understand the complicated trends in species concentrations and formation rates throughout a reactor, we did a combined multiscale simulation[1] and experimental study. We carried out the zeolite catalysed methanol-to-DME reaction in a fixed bed reactor containing a catalyst bed of length 1 cm and measured the methanol conversion in the temperature range 423 to 523 K.

We reproduced the experimental trend by constructing a 3D model of the reactor and catalyst bed (Figure 1) and modelled the relevant transport and reaction processes.

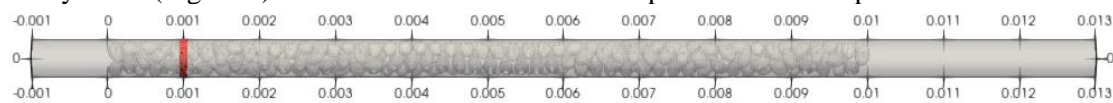


Figure 1. 3D model of the reactor and catalyst bed. The location of the cross-section shown in Figure 2 is indicated in red.

At 523 K, the rate of methanol consumption is largest at the start of the catalyst bed, and to gain more insight into the reactivity of the system, we computed the DME mass fraction (Figure 2a) and formation rate (Figure 2b) on a cross-section located 1 mm from the start of the catalyst bed (see red slab in Figure 1). We see that DME is formed close to the surface and has accumulated inside the catalyst pellets.

In conclusion, we have shown that the products of the reaction are formed close to the surface and accumulate inside the catalyst pellets. Knowledge of how the species are distributed in the pellets is important because it allows us to understand what shape the catalyst pellets should have in a more efficient catalytic system.

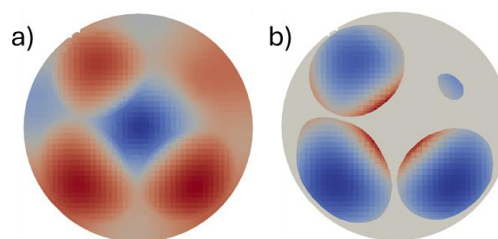


Figure 2. Cross-section at 1 mm from the start of the catalyst bed. a) Mass fraction of DME. Min. value (blue) 0.03; max. value (red) 0.05. b) Formation rate of DME, max. value (red) 535 and min. value (blue) 349 mol m⁻³ s⁻¹

References

[1] T. Maffei, G. Gentile, S. Rebughini, M. Bracconi, F. Manelli, S. Lipp, A. Cuoci, M. Maestri, Chem. Eng. J., **283**, 1392-1404 (2016).

Theoretical Study of the Steric Hindrance Effects on Methyl Pyridine Derivatives Adsorption in H-ZSM5 Zeolite

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Keywords: methyl pyridine derivatives; H-ZSM-5; PBE-D3 calculations; chemisorption complexes; confinement effect; steric constraint

The theoretical study of the adsorption of pyridine (PY) and of its methyl derivatives (isomers of methyl and dimethyl pyridines) on the Brønsted acid sites (BAS) of H-ZSM-5 zeolite cavity by cluster and periodic models, using PBE-D3 calculation method has been investigated. In this study, realistic cluster models extracted from the siliceous crystallographic ZSM-5 structure have been used. The substitution of one Si atom in different tetrahedral crystallographic T-sites by aluminum atom within the ZSM-5 cavity has been considered. The confinement effects resulting from van der Waals dispersion interactions and steric constraints on the energetic and vibrational properties of the adsorption complexes formed have been thoroughly examined.

Our DFT-D3 calculation results clearly show that upon adsorption of any PY derivative, a proton transfer occurs spontaneously from BAS to adsorbed molecule leading directly to the formation of an ion pair complex. Whatever the adsorption complex considered, the calculated structure reflects a compromise between the repulsive interactions due to steric hindrance and the attractive van der Waals dispersion interactions between the atoms of the adsorbed molecule and those of the wall zeolite cluster. Although the isomers of methyl pyridine derivatives have the same stability and the same proton affinity, the stability of their complexes and the adsorption energy of their isomers essentially depend on their steric hindrance due to the fact that for some sites of adsorption, the methyl group of some isomers does not fit well in the void space of the zeolite cavity. Whatever the adsorbed molecule considered, the calculated vibrational frequencies and frequency shifts are in satisfactory agreement with the experimental results available in the literature.

References

- [1] M. Castellà-Ventura, A. Moissette, E. Kassab, *Phys. Chem. Chem. Phys.*, **20**, 6354-6364 (2018)
- [2] M. Castellà-Ventura, A. Moissette, E. Kassab, *Computation*, **8**, 81 (2020)

Acknowledgments

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Mechanism of the direct oxidation of methane to methanol by dioxygen on the distant binuclear Fe(II) cationic sites over the zeolite of the ferrierite topology

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Keywords: selective oxidation of methane, direct oxidation of methane, distant binuclear cationic sites, DFT, cationic sites, silicon-rich zeolites

The distant binuclear cationic sites were firstly identified using theoretical modeling in the context of the study of the N₂O decomposition over the Fe(II) cation exchanged zeolites of the ferrierite, beta, and MFI topologies. The first chemical step of the N₂O decomposition is the formation of the Alpha–oxygen species [1] [i.e., (Fe(IV)=O)²⁺] which exhibits unique oxidation properties reflected in an outstanding activity in the oxidation of methane to methanol at room temperature. Moreover, we firstly predicted using the power of periodic DFT calculations that these distant binuclear cationic sites were able to split dioxygen to yield pairs of the distant Alpha–oxygen species. Subsequently, experiments were performed at room temperature and the theoretical prediction of a cleavage of dioxygen to give a pair of the distant Alpha–oxygen atoms was confirmed experimentally and thus splitting dioxygen was discovered [2]. A pair of the formed distant Alpha–oxygen species exhibits unique oxidation properties reflected in an outstanding activity in the oxidation of methane to methanol at room temperature [2].

In this contribution, we report on our periodic DFT calculations of the two detailed plausible mechanisms of the direct oxidation of methane to give methanol on the distant binuclear Fe(II) cationic sites in the zeolite of the ferrierite topology. An impediment of one of the two Alpha–oxygen atoms forming a pair of the distant Alpha–oxygen species is proposed to reconcile the results of our DFT calculations and the expectations of Professor S.L. Scott of UCSB [3] with our experiments. The most likely mechanism features a blockage of one of the two Alpha–oxygen atoms forming a pair of the distant Alpha–oxygen species. Firstly, a molecular oxygen reacts with one of the two Alpha–oxygen atoms forming a pair to yield an FeO₃ site. The formation of these FeO₃ sites were predicted by our DFT calculations to be responsible for the experimentally observed isotope exchange of ¹⁶O=¹⁶O with Fe=¹⁸O [4]. Subsequently, the rebound mechanism [5] occurs on the other Alpha–oxygen atom. Another possibility is a simultaneous reaction of two methane molecules with a pair of the distant Alpha–oxygen atoms via the rebound mechanism [5].

References

- [1] E. Tabor, M. Lemishka, Z. Sobalik, K. Mlekodaj, P. C. Andrikopoulos, J. Dedecek, S. Sklenak, *Communications Chemistry*, **2**, 71 (2019)
- [2] E. Tabor, J. Dedecek, K. Mlekodaj, Z. Sobalik, P. C. Andrikopoulos, S. Sklenak, *Science Advances*, **6**, eaaz9776 (2020)
- [3] S. L. Scott, *Science*, **373**, 277-278 (2021)
- [4] P. C. Andrikopoulos, Z. Sobalik, J. Novakova, P. Sazama, S. Sklenak, *ChemPhysChem*, **14**, 520-531 (2013).
- [5] F. Göltl, C. Michel, P. C. Andrikopoulos, A. M. Love, J. Hafner, I. Hermans, P. Sautet, *ACS Catalysis*, **6** 8404-8409 (2016).

Is the ability of distant metal ions to activate dioxygen specific only for zeolite materials?

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Keywords: dioxygen, porphyrin, zeolite, DFT, oxidation

It was recently discovered that distant binuclear iron sites stabilized in aluminosilicate zeolite matrices can activate molecular oxygen by splitting the O₂ molecule [1]. As a result, a pair of the so-called α -oxygen ((Fe=O)²⁺) active sites is formed, which have strong oxidative properties manifesting in the ability to oxidise methane to methanol at room temperature. In this context, we explored the reactivity of the active sites composed of by Fe, Ni, Co, and Mn porphyrin (Por) dimers towards the dioxygen molecule.

The process of O₂ activation by two distant cooperating transition metal ions was studied using the model consisting of two metal(II) porphyrin species which were placed in parallel one to another at a varied distance (from 7.5 to 4.0 Å). Such a selection of the organic model follows from the fact that the iron porphyrins (being a single iron site) are widely known for their binding and activation of O₂ in enzymes, e.g., from cytochrome P450 family. The calculations were done within Density Functional Theory using Turbomole v6.3 using def2-TZVP basis with PBE functional with D3 dispersion correction proposed by Grimme.

Our calculations show that all investigated metal ion pairs can bind the oxygen molecule located between them, what is manifested by elongation of the O-O bond. The ability to activate O₂ increases in the following order: Ni < Co < Mn \approx Fe. For the Fe(II) ions this effect is the strongest, allowing for the O-O bond dissociation and formation of the high-valent oxo species, similar to those found in zeolites. The performed calculations allowed to determine the energy barriers connected with the O-O bond splitting and their dependence on the distance between the ions.

In summary, we demonstrate the ability of distant binuclear metal(II) sites, iron in particular, to activate dioxygen by its splitting despite the nature (aluminosilicate, organic) of the “matrix” employed for the stabilization of Fe(II) ions. Our study opens up the possibility for new systems for oxygen activation for selective oxidation reactions.

References

[1] Tabor, E., J. Dedecek, K. Mlekodaj, Z. Sobalik, P. C. Andrikopoulos, S. Sklenak, *Sci. Adv.*, 6, eaaz9776 (2020)

Acknowledgments

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Quantum mechanical insights into light-driven reactions on metallic nanoparticles

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Keywords: nanoplasmonics, plasmonic catalysis, density functional theory, embedded correlated wavefunction theory, photocatalysis

The nearly-free-electron-like valence electrons in some metallic nanoparticles (MNPs) facilitate their enhanced ability to scatter/absorb light by means of local surface plasmon resonances (LSPRs). When the incident light has a frequency resonant with the MNP's LSPR, amplified electric fields are generated within and surrounding the MNPs that can lead to hot charge-carrier generation, induce local heating, or cause excitations of molecules or other materials nearby. Photocatalysis mediated by MNPs exploits this unique optical phenomenon. First-principles quantum mechanics can aid in understanding such light-driven chemistry, but the methods used must properly account for both electronic excitations and surface reactions. We therefore used embedded correlated wavefunction (ECW) theory to simulate chemical reactions on metallic surfaces and calculate their ground- and excited-state energy curves. ECW calculations of a variety of reactions on pure and surface-doped metals reveal that enhanced kinetics can occur on excited-state reactive potential energy surfaces accessed via plasmon-enhanced light absorption or resonance energy transfer between the MNP and the surface-active site. Our calculations explain experimentally observed enhanced rates and, in some cases, modification of product selectivity, due to plasmon-driven electronic transitions.

Elucidating the role of potassium in methane steam reforming using first-principles-based kinetic Monte Carlo simulations

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Keywords: Methane steam reforming, Ni catalyst, coke formation, potassium loadings, KMC simulations, activity, stability and adsorbate-adsorbate interactions.

In the chemical industries, potassium is commonly employed as a promoter to reduce coke formation on the Ni catalyst surface, and has been demonstrated to significantly improve the productivity of the MSR reaction.¹ Despite numerous theoretical/experimental studies, there is a lack of detailed understanding on the potassium effect at steam reforming conditions. In this contribution, we developed a first-principles-based KMC model of MSR on Ni(111) and potassium-doped Ni(111) surfaces. The cluster expansion (CE) methodology (implemented in graph-theoretical KMC²) was employed to systematically capture the adsorbate-adsorbate interactions of MSR species on Ni and potassium sites. We performed KMC simulations with different loadings of potassium (0.5-3%) on Ni(111) to understand its effect on macroscopic coverages and net MSR turnover rates. A thorough examination of the KMC process statistics was carried out to rationalise the effect of potassium on MSR kinetics. At high operating conditions, we found that the potassium strongly promotes the oxidation of CH and carbon adsorbates. For instance, at 1273 K and 10 bar, we observe that the net MSR turnover rate on potassium-doped Ni(111) system is 3 times higher than Ni(111). The KMC process statistics analysis reveals that the key oxidation events/steps such as CHO formation, CHOH formation, COH formation and CO formation occur significantly faster on the potassium sites than Ni(111). Furthermore, a detailed flux analysis has been performed to identify the dominant MSR pathways on Ni(111) and potassium-doped Ni(111) surfaces. At high temperatures, the CHO pathway and CO pathway occurring on the potassium sites contribute substantially to the net flux of MSR (these pathways constitute around 33% of the net flux). The aforementioned results provide a deeper mechanistic level understanding of the role of potassium in MSR. Overall, our KMC simulations can potentially aid in the design of next-generation Ni-based catalysts that exhibit high activity and stability at MSR conditions.

References

- [1] M. Carlsson, *Johnson Matthey Technology Review*, **59**, 313-318 (2015)
- [2] J. Nielsen, M. d'Avezac, J. Hetherington and M. Stamatakis, *The Journal of Chemical Physics*, **139** (2013)

Acknowledgments

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Revisiting intermediates and mechanism producing (MMA-ran-DMAEMA)_n copolymers via ARGET-ATRP catalyzed by Cu complexes

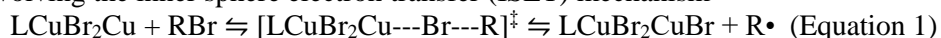
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Keywords: ATRP, Mechanism, TS, Cu, DFT

Atom Transfer Radical Polymerization (ATRP) is an increasingly popular and versatile technique whose hypothesised mechanism involves a homolytic cleavage of Br-C bonds by action of a Cu complex; the so formed radical species may add to olefinic groups growing polymeric chains^[1]. Despite this general characteristic of the process, copolymerization of monomers with similar olefinic groups may not closely follow the expected dependence of the final composition on their feed ratio. In this respect, the P(MMA-ran-DMAEMA)_n copolymer, which interests us for its modulable responsive properties^[2], incorporated far more DMAEMA than expected^[3], a finding tentatively attributed to DMAEMA coordination to Cu-based catalysts. In this work, electronic structure calculations and NMR experiments supported DMAEMA coordination and suggested the formation of peculiar ion pairs with redox potential differing from commonly suggested species. Kinetic Monte Carlo was also employed to simulate copolymerizations, the kinetic constants having been estimated basing on an activation step involving the inner sphere electron transfer (ISET) mechanism^[3]



whose endothermicity markedly depended on L (= bipyridine (BPY), BPY₂, Me₆TREN), and on DMAEMA or solvent (e.g. CH₃CN) coordination. Given the open shell nature of the products, PES scans and TS searches employed a broken symmetry approach at B3LYP/6-31++G(d,p)/SMD level of theory. The calculated structures, albeit different in shape, share a C-Br distance around 2.7 Å, similar spin densities and activation energies <20 kcal/mol. Apart from supporting the ISET hypothesis as ATRP activation, our results evidenced the possibility of exploiting CH₃CN Cu-coordination capability to modulate DMAEMA copolymer contents.

References

- [1] J.-S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 6, 5614–5615 (1995).
- [2] M. Mella, A. Tagliabue, S. Vaghi, L. Izzo, *Colloids Surf., A* **620**, 126525 (2021)
- [3] M. Mella, M. V. La Rocca, Y. Miele, L. Izzo, *J. Polym. Sci. Part A* **56**, 1366 (2018).
- [4] Fang, C. Fantin, M. Pan, X. de Fiebre, K. Coote, M. L. Matyjaszewski, K. Liu, P, *J. Am. Chem. Soc.*, **141**, **18**, 7486–7497 (2019).

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A study of the adsorption of Li on γ -graphyne monolayers materials doped with X (X=N, B, P, Al, and Si) heteroatoms

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Keywords: γ -Graphyne, Impurities, Electronic Structure, Two-Dimensional, DFT.

Pristine γ -graphyne (γ -GY) is a widely recognized two-dimensional system known for its high adsorption capacity of lithium (Li), sodium (Na), and potassium (K), along with high energy barriers for the diffusion of such metal ions. In this study, we performed calculations using density functional theory to investigate the electronic structure effect of impurities (X=B, N, Al, Si, P and Au) in γ -graphyne monolayers on the adsorption of Li. Our model considers the presence of 2 and 4 X ions in substitutional positions, as well as γ -GY without the C \equiv C bond. Geometry optimization reveals that the planar structure of γ -GY is not always preserved, as it depends on both the position and type of impurity present. The planar structure of γ -GY is consistently preserved in the presence of B and N impurities. However, for all other impurities, the planar structure is lost when 4 ions are included.

The adsorption of Li is also considered, in this case, the lowest energy structure is when the Li ion is located at the center of the 12 member ring. There is also a local minimum when the Li is located in the center of the 6 member ring.

In this work we present our results for the structure, electronic structure, energy of formation and adsorption energy for all structures. We also analyze the orbitals involved in the bonding between the carbons and the impurities, as well as the charge transfer and the electrostatic potential.

Acknowledgments

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Kinetic influences on a process considered under thermodynamical control: acid resin catalysed self- and cross-aldolic condensation of cyclic ketones.

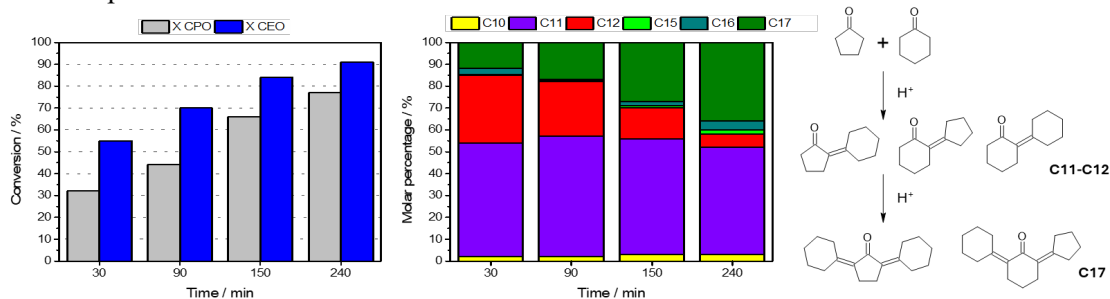
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Keywords: Condensation, Acid Resin, Mechanism, Heterogeneous Catalysis, DFT

Aldol condensation reactions allow molecular upgrading generating precursors of high-quality biofuels. In fact, the self- and cross-condensation reaction involving cyclopentanone (CPO) and cyclohexanone (CEO), molecules obtained from biomasses, is shown to produce both dimers (C10-C12) and trimers (C15 -C18) [1] [2] when reacted in presence of heterogeneous acid catalysts such as resins. The latter are preferable to homogeneous catalysts for several economic, environmental and plant engineering reasons. The conversion of CPO is commonly found lower than for CEO in both self- and cross-condensation reactions while using identical conditions. Furthermore (*vide* figures), the prevalent formation of C12 over C10, the low concentration of C15 compounds from CPO, and the absence of C18 species were also apparent. Thus, the primary C12 product does not react with a third CEO molecule, producing instead C17 compounds with additional CPO molecules.



In the attempt of rationalizing the distribution patterns obtained during the condensation, the energetics of all possible intermediates was investigated at the B3LYP/6-311G** level, the results of such analysis agreeing with the experimental data relative to the absence of C18, the substantial production of C11 or C17, as well as of a lower quantity for C16. A different propensity in forming C10 over C12, or C16 over C17, was instead indicated by the thermodynamical analysis, which hinted at a kinetic control. With the investigation of transition state energetics not involving resin functional groups having met only a partial success in rationalizing data, models including sulfonate groups appear needed.

References

- [1] G. Nie, H. Wang, Q. Li, L. Pan, *et al.*, *Appl. Catal. B: Environ.* 292, 120181 (2021)
- [2] Q. Li, G. Nie, H. Wang, *et al.* *Appl. Catal. B: Environ.* 325, 122330 (2023)

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This work was supported by Università degli Studi dell'Insubria with a p.H.D. studentship to SP and SV and fundings to MM and CL.

Internal H–Bond Formation of Brønsted Acid Sites in the Zeolites H–MOR, H–FER, and H–MFI: Predictions of Structures and Stabilities beyond DFT

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Keywords: Infrared spectroscopy (IR), Nuclear magnetic resonance spectroscopy (NMR), QM:QM methods, Zeolites, Hydrogen bonding, Brønsted acid sites

Understanding site heterogeneity in zeolites, i.e. type and framework position of active sites, is a prerequisite for the design of catalysts and catalytical processes. The catalytic activity of acidic zeolites stems from framework Brønsted acid sites (BAS, Al–O(H)–Si). Their acidic protons can either point into empty pore space (unperturbed BAS) or form an H–bond with a Si–O–Si acceptor site (H–bonded BAS). While both unperturbed and H–bonded BAS are observed in the zeolite H–MFI, only unperturbed BAS are observed in the zeolites H–MOR and H–FER.

This work aims to identify the origin of this qualitative difference between zeolite frameworks. We calculate relative stabilities for all unperturbed and H–bonded BAS in the zeolites H–MFI, M–MOR, and H–FER. Further, we calculate ¹H–NMR and IR signals and verify the peak assignment of experimental spectra. To overcome the limitations of standard DFT calculations at the generalised gradient approximation level and to reach chemical accuracy, we use a hybrid high–level QM:low–level QM methodology (QM = quantum mechanics). We combine second order Møller–Plesset perturbation theory (MP2) on cluster models with dispersion–augmented DFT on periodic models to obtain accurate structures. Finally, we add energy corrections based on coupled cluster theory with singles, doubles, and perturbatively treated triples substitutions (CCSD(T)). Thus, we reach CCSD(T)–accuracy for periodic systems.

We find various structures of both unperturbed and H–bonded BAS for all investigated zeolites. This signifies that H–bonded BAS are in fact structurally feasible not only in H–MFI, but also in H–MOR and H–FER. Our chemically accurate relative stabilities show that H–bonded BAS are as stable as unperturbed BAS only for H–MFI, whereas H–bonded BAS are less stable than unperturbed BAS for H–MOR and H–FER. This indicates a subtle interplay between stabilisation through H–bonding and destabilisation through framework distortion upon H–bond formation. We could only achieve this understanding by using the chemically accurate hybrid QM:QM methodology for the prediction of both relative stabilities and spectroscopic (IR and NMR) features. Standard DFT calculations severely overestimate the H–bond strength and predict that H–bonded BAS are more stable than unperturbed BAS for all three investigated zeolites. They fail to correctly describe the interplay between stabilisation through H–bonding and destabilisation through framework distortion.

References

- [1] E. Brunner, K. Beck, M. Koch, L. Heeribout, H. G. Karge, *Microporous Materials*, **3**, 395–399 (1995)
- [2] C. Schroeder, V. Siozios, C. Mück–Lichtenfeld, M. Hunger, M. R. Hansen, H. Koller, *Chemistry of Materials*, **32**, 1564–1574 (2020)
- [3] H. Windeck, F. Berger, J. Sauer, *Angewandte Chemie*, **62**, e202303204 (2023)

Elucidating the Electrolytes Involved in the Solvation of Vanadium Ions in the Catalytic Reactions within Redox Flow Batteries

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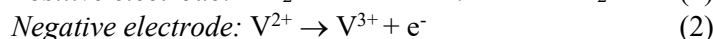
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Keywords: Vanadium, Redox, Solvation, Computational, Flow Batteries

This project focuses on the development of vanadium redox flow batteries (VRFBs) as a storage solution for energy generated via renewable energy sources, such as wind and solar. VRFBs are an efficient energy solution that utilises the redox states of soluble vanadium species which contribute to their beneficial properties such as high energy densities, lifespans exceeding 50 years, and the ability to almost completely discharge.¹ Despite their capacity for large scale energy storage, VRFBs are not commercially viable due to slow reaction rates at the catalytic electrode surfaces.^{1,2} Hence, VRFBs have yet to be widely adopted.

In a VRFB, two different redox reactions occur, one at the positive electrode ($\text{VO}_2^+/\text{VO}^{2+}$) and the other at the negative electrode ($\text{V}^{2+}/\text{V}^{3+}$), as shown below:²



One significant challenge in vanadium redox flow batteries (VRFBs) is understanding the underlying mechanisms of their reactions.² Current understanding suggests that reactions at the positive and negative electrodes follow outer- and inner-sphere mechanisms, respectively, likely due to differences in their solvated structures.² Therefore, it is essential to comprehend the solvated structure of vanadium ions before delving into electrode surface reactions. This project investigates the solvated structures, including those with commonly employed electrolytes, of the four vanadium ions present in VRFBs using a range of computational techniques, including ab initio and classical molecular dynamics, as well as density functional theory. This investigation is crucial for gaining a deeper understanding of solvation spheres, which has the potential to influence reaction kinetics. Subsequently, both previously proposed and novel reaction mechanisms will be examined using pristine and functionalized carbon-felt models. Additionally, surface modification techniques, such as surface functionalization, to enhance catalytic activity will be explored.

References

[1] J. P. Barton, D. G. Infield, *IEEE Trans. Energy Convers.* 19, 441-448 (2004).

[2] C. Choi, H. Noh, S. Kim, R. Kim, J. Lee, J. Heo, H. Kim, *J. Energy Storage* 21, 321-327, (2019).

Acknowledgments

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Theoretical evaluation of CuFeO_2 and CuBi_2O_4 as possible catalysts for N_2 reduction

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Keywords: photoelectrochemistry, density functional theory, nitrogen reduction reaction, transition metal oxides, computational hydrogen electrode

Ammonia is the most important component in fertilizers, as 80% of the worldwide production goes into fertilizers.^[1] Currently, the energetically expensive Haber–Bosch process is used to break the triple bond of N_2 .^[1] In the last years, the photoelectrochemical (PEC) reduction of nitrogen has gained attention, providing an alternative route to produce ammonia more affordable and sustainable. Despite beneficial properties of binary copper oxides as photocathodes for catalytic reactions such as the nitrogen reduction reaction (NRR), their stability and Faradaic efficiency suffers under reaction conditions.^[2]

To this end, the ternary copper oxides CuFeO_2 and CuBi_2O_4 are investigated as materials for photocathodes as promising alternatives for the conversion of solar energy into chemical fuels.^[3, 4] In this work we performed Density Functional Theory calculations (DFT+*U*) to analyze their electronic properties, thermodynamic stability of different surfaces and adsorption energy trends for NRR intermediates. Beyond that, we investigated diverse defects in thermodynamically stable surfaces for both materials and their impact on the NRR mechanism. Furthermore, the influence of an aqueous surrounding on the stability of the surfaces and reaction intermediates thereon will be investigated using the hybrid QMMM simulation approach (SAFIRES^[5]) implemented in ASE and GPAW, which to this end will be extended to be compatible with periodic surface models.

References

- [1] V. Smil. *Scientific American* **277**, 76-81 (1997).
- [2] Y. J. Jang, A. E. Lindberg, M. A. Lumley, and K.-S. Choi, *ACS Energy Letters* **5** (6), 1834-1839 (2020).
- [3] F. E. Oropeza, N. Y. Dzade, A. Pons-Martí, Z. Yang, K. H. L. Zhang, N. H. de Leeuw, E. J. M. Hensen, and J. P. Hofmann, *The Journal of Physical Chemistry C*, **124** (41), 22416-22425 (2020).
- [4] M. Ferri, J. D. Elliott, M. F. Camellone, S. Fabris, and S. Piccinin, *ACS Catalysis* **11** (4), 1897-1910 (2021).
- [5] B. Kirshhoff, E. Ö. Jónsson, A. O. Dohn, T. Jacob, and H. Jónsson, *Journal of Chemical Theory and Computation* **17** (9), 5863-5875 (2021).

Acknowledgments

This work was supported by Elvar Örn Jónsson from the University of Iceland.

Adsorption and spectra validation studies through DFT of Metal-Phosphonate properties in NU-1000 structure.

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Keywords: DFT, NU-1000, PhPA, Adsorption, NMR, IR, XPS, MOF.

Metal-organic frameworks (MOFs) have emerged as a revolutionary class of materials with remarkable versatility and wide-ranging applications across multiple scientific disciplines. MOFs, consisting of metal nodes interconnected by organic linkers, possess exceptional tunability, high surface areas, and intriguing porosity. These distinctive characteristics bestow upon MOFs extraordinary properties, making them highly desirable for diverse applications encompassing gas storage and separation, catalysis, sensing, and drug delivery systems.

Amid the extensive assortment of MOFs, the NU-1000 structure has garnered substantial attention due to its exceptional properties and potential in various fields. NU-1000 is an exceptionally sturdy and highly stable MOF characterized by a well-defined structure comprising 558 atoms (264 C, 180 H, 96 O, 18 Zr) within its unit cell. The deliberate design and synthesis of NU-1000 provide a platform for investigating the fundamental principles governing MOF behaviour and offer a pathway for the development of advanced functional materials.

In this study, density functional theory (DFT) calculations are employed to investigate the functionalization of cluster-nodes with a focus on the catalysis, adsorption energies, and structural parameters of the NU-1000 metal-organic framework (MOF) in the presence of phenyl phosphonic acid (PhPA) molecules adsorbed on its metallic nodes. Molecular dynamics simulations, accounting for temperature effects, are utilized to compute infrared (IR) spectra, while nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) spectra are also calculated. A comparison between the simulated and experimentally measured spectra establishes the reliability of the DFT calculations. This work, conducted as part of the PHOSPORE project, advances the understanding of MOFs and facilitates the tailored design of MOFs for a wide range of applications in catalysis and functional materials.

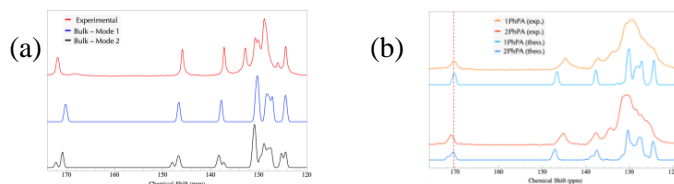


Figure 1. Comparison of theoretical-experimental ¹³C NMR spectra of the bulk structure (a) and in presence of PhPA adsorbed on the cluster-nodes (b).

Acknowledgments

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Exploring the Formation of Reactive Oxygen Species on Amorphous Silica Through DFT-MD

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Keywords: DFT, Molecular Dynamics, ROS, Formation, Heterostructure

Previous research has demonstrated that both Ag nanoparticles and Ag nanoparticles/SiO₂ heterojunctions (a combination of metal and semiconductor) can effectively eliminate viruses and other pathogens, even when integrated into polymeric matrices. This development has opened up exciting possibilities for the creation of safe, everyday protection technologies. These innovative materials were proving to be a valuable tool in the fight against the last pandemic (SARS-CoV-2). Our current study aims to delve further into the biocidal activity of Ag nanoparticle/SiO₂, utilizing advanced quantum mechanical methods and techniques. The main objectives are twofold: (i) to gain a deeper understanding of the factors that control the stability, physical and chemical properties of Ag nanoparticles/SiO₂; and (ii) to study the interaction of Ag nanoparticle/SiO₂ with O₂ and H₂O to analyze the generation of pairs of electrons (e⁻) and holes (h⁺) on the surface of these materials. By doing so, we will be able to analyze the formation and progression of reactive oxygen species (ROS), which are responsible for the biocidal activity.

References

1. Tremiliosi, G. C. *et al.* Engineering polycotton fiber surfaces, with an antimicrobial activity against *S. aureus*, *E. Coli*, *C. albicans* and SARS-CoV-2. *Japan J. Med. Sci.* **1**, 47–58 (2020).
2. Assis, M. *et al.* PVC-SiO₂-Ag composite as a powerful biocide and anti-SARS-CoV-2 material. *J. Polym. Res.* **28**, 1–7 (2021).
3. Assis, M. *et al.* SiO₂-Ag composite as a highly virucidal material: A roadmap that rapidly eliminates SARS-CoV-2. *Nanomaterials* **11**, 1–19 (2021).
4. Deraet, X. *et al.* Reactivity of Single Transition Metal Atoms on a Hydroxylated Amorphous Silica Surface: A Periodic Conceptual DFT Investigation. *Chem. - A Eur. J.* **27**, 6050–6063 (2021).

Acknowledgments

This work was supported by Generalitat Valenciana (Conselleria de Innovación, Universidades, Ciencia y Sociedad Digital) and the postdoctoral contract (CIAPOS/2022/162).

Thursday, September 5

Key Lecture 5 Stephan Steinmann. Computational Heterogeneous Electrocatalysis: From Developments to Applications.

Oral contribution Liana Savintseva. Theoretical insight into the mechanism of Shono electrocatalytic oxidation.

Oral contribution Bartek Szyja. Ru-pincer complexes as charge transfer mediators in CO₂ electroreduction.

Oral contribution Isabela Man. Exploring the activity of the graphene quantum dots (GQDs) for the electrochemical Oxygen Reduction Reaction using DFT.

Focus Topic 3 Feliu Maseras. Selected examples in multimetallic homogeneous catalysis.

Oral contribution Adarsh Kalikadien. Automated homogeneous catalyst design: Navigating the catalytic chemical space (and getting lost in the forest?).

Oral contribution Oscar Jiménez-Halla. Activation of Small Molecules and Catalytic Activity in the Formation of Heterocycles Mediated by Boron.

Oral contribution Estefanía Fernández-Villanueva. Elucidating the reaction mechanism of selective CO₂ hydrogenation to methanol over Cu/MgO catalysts: Synergistic effects of water and Cu⁺.

Oral contribution Julen Munárriz. A Quantum Chemical Topology perspective on Ammonia Fixation via Metal-Ligand Cooperation.

Emerging Researcher Ángel Morales. Influence of Water in the structure and the band edges of photoactive titania nanoparticles: Implications in Photocatalysis.

Oral contribution Albert Solé-Daura. Applying the Marcus theory to estimate the kinetics of energy-transfer events in photocatalysis.

Oral contribution Auguste Tetenoire. Simulation of photoinduced reaction of CO oxidation on Ru(0001).

Oral contribution Tobias Schäfer. Coupled Cluster Theory for Solids: Applying the “gold standard” of Quantum Chemistry to Heterogeneous Catalysis.

Computational Heterogeneous Electrocatalysis: From Developments to Applications

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Keywords: Electrocatalysis, DFT, QM/MM, HER, developments

Modelling heterogeneous electrocatalysis is key to gain atomistic insights into the mechanism of various catalytic reactions that are expected to become large-scale industrial processes in the future such as the hydrogen evolution reaction, CO₂ electroreduction or biomass electro-oxidation. In particular, grand-canonical density functional theory (GC-DFT) has been developed over the last ten years to a practical tool for investigations of electrocatalytic reactions.^[1] Still, modelling of electrocatalysis remains challenging: the interfaces need to be of sufficient sizes to account for the liquid nature of the electrolyte and diffusion is slow at the solid/liquid interface.

In this presentation I will present the background and recent developments, with a particular emphasis going beyond generalized gradient approximations density functionals^[2] and on implicit solvent models, their limitations and how a QM/MM approach can provide a competitive alternative.^[3-4] This will be complemented by applications: I will first discuss the impact of using the random-phase approximation (RPA), instead of GGAs, for a model system composed of carbon monoxide and copper.^[2] Second, I will revisit the hydrogen evolution reaction over Earth-abundant molybdenum sulfide electrocatalysts. Finally, the electro-oxidation reaction of 5-(hydroxymethyl)furfural (HMF) over NiOOH in alkaline conditions will be tackled. This reaction constitutes an attractive alternative to the oxygen evolution reaction, as its thermodynamics suggest lower onset potentials. I will present the reaction mechanism and discuss the origin of the significant overpotential.

References

- [1] N. Abidi, K. R. G. Lim, Z. W. Seh, S. N. Steinmann, *WIREs Comput Mol Sci*, **11**, e1499 (2021).
- [2] Z. Wei, F. Göttl, S. N. Steinmann, P. Sautet, *J. Phys. Chem. Lett.*, **13**, 6079 (2022).
- [3] P. Clabaut, B. Schweitzer, A. W. Götz, C. Michel, S. N. Steinmann, *J. Chem. Theory Comput.* **16**, 6539 (2020).
- [4] N. Abidi, S. N. Steinmann, *ACS Appl. Mater. Interfaces*, **15**, 25009 (2023).

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Theoretical insight into the mechanism of Shono electrocatalytic oxidation

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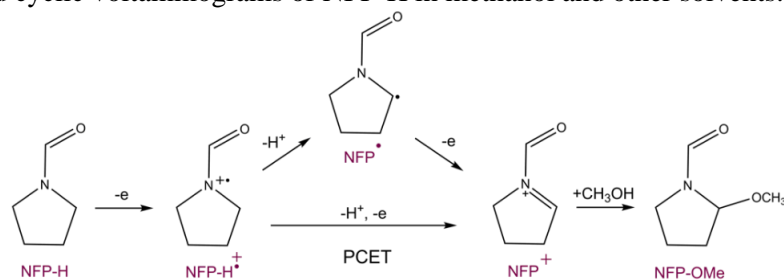
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Keywords: Shono oxidation, electrocatalysis, cyclic voltammetry, electron transfer, DFT

While chemical synthesis often requires harsh experimental conditions and the use of specific and often toxic catalysts, electrooxidation offers an alternative approach for milder experiments. Thus, electrochemical late-stage functionalization of α -position to amino-group is of interest, especially in the pharmaceutical industry. Such functionalization can be carried out by Shono-type electrooxidation [1]. Theoretical analysis can shed light on the mechanism of this reaction, as two possible mechanisms of reaction flow are discussed in the literature: four-step ECEC (*electrochemical-chemical-electrochemical-chemical*) mechanism and three-step mechanism, where the second chemical step and the third electrochemical step are combined into one - PCET (*proton-coupled electron transfer*) [2] (Scheme 1). Herein, we investigated the mechanism of N-formylpyrrolidine (NFP-H) Shono-type electrooxidation using DFT approach and simulated cyclic voltammograms of NFP-H in methanol and other solvents.



Scheme 1. Two discussed mechanisms of the Shono oxidation in methanol

Density functional theory (M06/def2-TZVP) with dispersion correction and implicit solvation was used for the determination of transition state energies of chemical steps as well as evaluation of formal potentials of electrochemical steps (vs. Fc^+/Fc reference electrode). The combination of Marcus theory with Butler-Vollmer approach allows us to perform comprehensive study of electrochemical process. Theoretical cyclic voltammograms were simulated using a numerical approach [3] and useful insights on the mechanism were obtained.

References

- [1] T. Shono, Y. Matsumura, K. Tsubata, *Tetrahedron Letters*, **22** (34), 3249-3252 (1981)
- [2] L. F. T. Novaes, J. S. K. Ho, et. al. *JACS*, **144** (3), 1187-1197 (2022)
- [3] J. H. Brown. *Journal of Chemical Education*, **92** (9), 1490-1496 (2015)

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Ru-pincer complexes as charge transfer mediators in CO₂ electroreduction

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Keywords: pincer complex, CO₂ reduction, constrained DFT, graphene, charge transfer

In this work, we unravel the role of the system components in the charge transfer (CT) processes occurring in the 2-electron reduction of CO₂. We focus our analysis on the pincer-complex/graphene composite system in order to explain the role of the donors of the pincer ligands in the elementary charge transfer processes. To achieve this goal, we have used the unique combination of the constrained DFT method and computational hydrogen electrode approach.

The results obtained this way allowed us to conclude that the catalytic performance of the system depends to a great extent on the electron-donating properties of the Ru-pincer complex. We have determined, that the optimal charge transfer in the system is due to the easy, single-step transfer to the activated CO₂ molecule and the energies required for such transfer are comparable to the overpotential of the reaction.

We have observed the trend in which the first coordination sphere of the Ru cation directly influences the CT energy – the more imine ligands coordinating the Ru, the lower ECT is, regardless of the transfer direction. This trend fits in the Hard/Soft Acids and Bases (HSAB) theory, according to which imine ligands are considered harder donors than carbenes. On the contrary, the overpotentials determined for the Ru-CCC, Ru-CNC, Ru-NCN and Ru-NNN pincers did not show the same trend, which implies that the interactions of the Ru site and the CO₂ reactant do not change linearly, but rather are characterized by the optimum interaction strength.

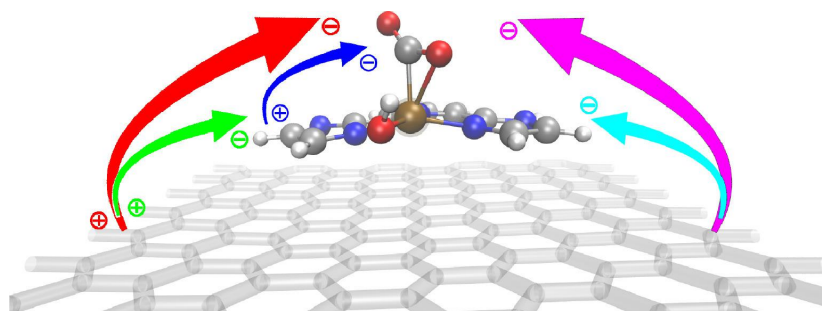


Figure 1. Charge transfer directions

References

- [1] B.M. Szyja, J. Zasada, E. Dziadyk-Stopyra, *Molecular Catalysis*, **555**, 113875 (2024)

Exploring the activity of the graphene quantum dots (GQDs) for the electrochemical Oxygen Reduction Reaction using DFT

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Keywords: DFT, ORR, GQD, N-GQD, volcano plot

The study was carried out in the context of the ongoing research aimed at discovering more effective catalysts for the oxygen reduction reaction (ORR) in PEM fuel cells such as to replace the best-performing one, Pt that is scarce and expensive. Graphene quantum dots (GQDs) are gaining attention for this application, due to low dimensionality, abundance in edge sites, quantum confinement. [1]. In this study we investigate at theoretical level using density functional theory (DFT), the possible activities towards ORR of undoped and N-doped GQDs of various shapes (triangular, rhombohedral, hexagonal) and sizes (C13-C114) with zigzag and armchair terminations under the effect of the implicit water model as implemented in GPAW software. For the undoped ones, the edges of the triangular and of the largest rhombohedral shapes with zigzag terminations present the highest potential activities (predicted low onset overpotentials ($\eta_{th,onset}$) blue and dark yellow points in Figure 1a) [2]. For the other shapes we predict low activities, especially for the armchair terminated ones (purple, pink, cyan points – Figure 1a). For the N-doped structures, an inversion of the activity is observed (Figure 2b). Structural changes in some of the N-doped structures takes place when O* moiety is formed during the reaction (see red point in Figure 1a). A correlation between the strength of adsorption and the p electronic states of the carbon sites was established.

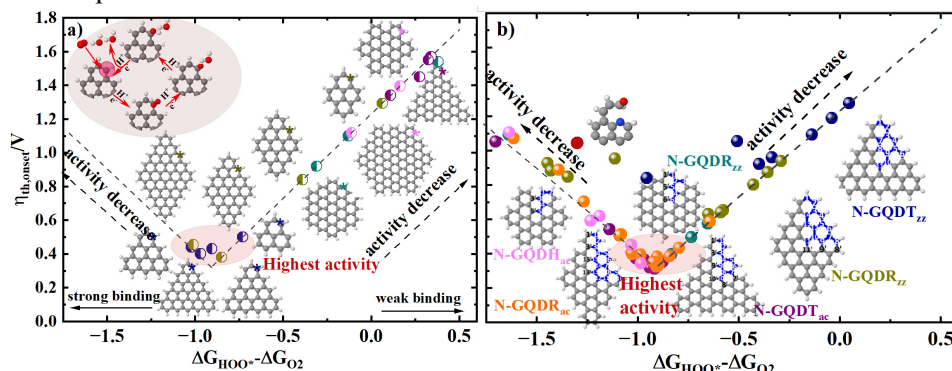


Figure 1 Theoretical onset overpotential ($\eta_{th,onset}$) for a) the edges of undoped GQDs of various shapes and sizes b) the N-GQDs with N in all inequivalent positions (C-gray, N-blue, O-red)

References

- [1] M. Favaro et al, *ACS Catal*, **5**, 1,129-144, (2015);
 [2] D.L. Isac et. al, *Carbon*, **222**,118942,(2024);

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Selected examples in multimetallic homogeneous catalysis

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Keywords: DFT; microkinetic modeling; bimetallic complexes; copper; nickel

Multimetallic catalysis is an emerging field of research further expanding the frontiers of homogeneous catalysis [1] (Figure 1). The simultaneous activation of two substrates by different catalytic entities can be responsible for rate acceleration and modified selectivity, and may ultimately lead to the synthesis of novel compounds. The eventual control of both activation and coupling may open the way for the design of novel synthetic routes proceeding in mild conditions. Such control of conditions will be more easily achievable is a detailed mechanistic understanding is available, but this is difficult to acquire from purely experimental methods.

DFT calculations can be very useful in this concern. Theoretical models can provide fundamental insights on the substrate activation by metals as well as on the interactions between the different catalysts. This will allow the deciphering at the atomic level of the preferential pathways leading to different reaction products. In this contribution, we discuss a series of representative examples of multimetallic cooperative processes described by means of molecular modelling [2, 3].

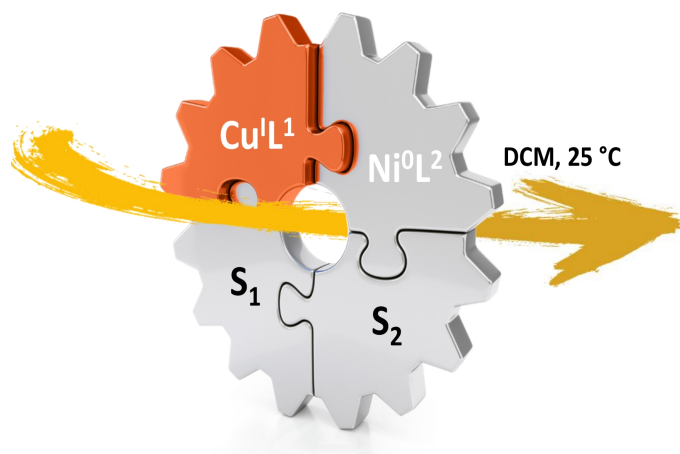


Figure 1: A typical set-up for multimetallic catalysis.

References

- [1] G. Sciortino, F. Maseras, *Top. Catal.* **65**, 105-117 (2022).
- [2] I. Funes-Ardoiz, F. Maseras, *Angew. Chem. Int. Ed.* **55**, 2764-2767 (2016).
- [3] G. Sciortino, F. Maseras, *Chem. Commun.* **59**, 6521-6524 (2023).

Automated homogeneous catalyst design: Navigating the catalytic chemical space (and getting lost in the forest?)

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Keywords: homogeneous catalysis, machine learning, organometallics, density functional theory, hydrogenation

Homogeneous catalysis with transition metal (TM) complexes is key to numerous synthetic methodologies for the preparation of chiral compounds. Conventionally, the development of new catalysts for enantioselective conversions follows an experimental trial-and-error search, largely guided by serendipity and intuition of the chemist. An automated computational strategy to guide the experimental efforts may not only save resources and costs in the catalyst design campaign, but also expand the scope of the catalyst search. This creates an opportunity for unexpected discoveries. However, such an approach requires understanding at the molecular level. Luckily, TM-based catalysts have a relatively well defined chemical structure.

For TM-based catalysts, performance optimization usually becomes a ligand optimization task [1]. To design and optimize these chiral ligands, a common strategy is the 3D correlation of steric and electronic free-energy relationships [2]. Modern data science approaches are enabling a shift from linear to polynomial or non-linear fitting for the prediction of stereo-selectivity and design of new chiral ligands. In collaboration with an experimental high-throughput experimentation (HTE) lab, we applied our newly developed computational tools to a digitalized set of ~200 chiral ligands and a selection of substrates. This DFT-based computational data is used to create many predictive models for reactivity and selectivity, using our machine learning pipeline. This presentation will provide an overview of our integrated workflows [3-5], including key features, as well as critical insights that were gained from this case study on industrially relevant homogeneous transition metal catalysts.

References

- [1] T. Gensch, G. dos Passos Gomes, P. Friederich, E. Peters, T. Gaudin, R. Pollice, K. Jorner, A. Nigam, M. Lindner-D'Addario, M. S. Sigman and A. Aspuru-Guzik, *J. Am. Chem. Soc.*, **144**, 1205–1217 (2022)
- [2] M. S. Sigman, K. C. Harper, E. N. Bess and A. Milo, *Acc. Chem. Res.*, **49**, 1292–1301 (2016)
- [3] I. Chernyshov, <https://github.com/EPiCs-group/epic-mace/tree/master> (2023)
- [4] A. V. Kalikadien, E. A. Pidko and V. Sinha, *Digital Discovery*, **1**, 8–25 (2022)
- [5] A. V. Kalikadien, A. Mirza, A. Najl Hossaini, A. Sreenithya, E. A. Pidko, *ChemPlusChem*, e202300702 (2024)

Activation of Small Molecules and Catalytic Activity in the Formation of Heterocycles Mediated by Boron

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Keywords: Multiple bonds, FLPs, reaction mechanisms, DFT calculations, boron

Boron is a non-metal element with interesting electronic and structural properties, and it can exhibit behavior reminiscent of transition metals in certain chemical reactions.^[1] Some boron-containing compounds can form complexes with other molecules, similar to the coordination complexes formed by transition metals.^[2] Boron compounds, particularly organoboron compounds, have been explored for their ability to mimic the reactivity and coordination chemistry of transition metal complexes. In this work, we will focus on how the electron-deficient nature of boron can be exploited for catalytic applications and in reactions that involve the transfer of electron pairs.^[3] Our recent theoretical investigations at the DFT level showcase the ability of boron to mediate chemical transformations similarly to transition metal catalysts.

References

- [1] M.-A. Légaré, C. Pranckevicius, H. Braunschweig, *J. Am. Chem. Soc.*, **119**, 8231-8261 (2019)
- [2] W.-J. Tian, W.-J. Chen, M. Yan, R. Li, Z.-H. Wei, T.-T. Chen, Q. Chen, H.-J. Zhai, S.-D. Li, L.-S. Wang, *Chem. Sci.*, **12**, 8157-8164 (2021)
- [3] T. Oishi, L.I. Lugo-Fuentes, Y. Jing, J.O.C. Jimenez-Halla, J. Barroso-Flores, M. Nakamoto, Y. Yamamoto, N. Tsumoji, R. Shang, *Chem. Sci.*, **12**, 15603-15608 (2021)

Acknowledgments

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Elucidating the reaction mechanism of selective CO₂ hydrogenation to methanol over Cu/MgO catalysts: Synergistic effects of water and Cu⁺

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Keywords: CO₂, Methanol, Copper, MgO, H₂O, Hydroxylated, DFT, Mechanism

CO₂ hydrogenation stands at the forefront of research efforts aimed at transforming CO₂ into less harmful and valuable carbon forms, such as methanol. While Cu-doped and Cu-supported catalysts on non-redox metal oxides (SiO₂, MgO, Al₂O₃) have shown some activity for this process, their efficacy is limited, necessitating the addition of promoters for enhancement.¹ Furthermore, layered double hydroxides resembling hydrotalcite (HT) have emerged as oxide precursors, facilitating the dispersion of metal species and demonstrating notable catalytic activity for CO₂ hydrogenation.² In a previous study combining experimental and theoretical approaches,³ monodentate formate species stabilized on Cu⁺ sites were identified as intermediates in the reaction mechanism on Cu/MgO HT-derived catalyst. However, the precise role of these species remained elusive. In this work, we employed density functional theory (DFT) calculations to gain a molecular-level understanding of how surface water and hydroxyl groups facilitate spontaneous CO₂ activation at Cu⁺ sites and the subsequent formation of monodentate formate species. Specifically, we developed a hydroxylated Cu/MgO computational model to investigate the intricate interactions involved in the CO₂ hydrogenation reaction. Our study assumes that hydrogen dissociation and spillover primarily occur at existing Cu nanoparticles and that the reaction proceeds through the formate pathway, with monodentate species being observed primarily at Cu⁺ single-atom sites. Through our computational analysis, we elucidate the critical synergy between Cu⁺ species and water/hydroxyl groups, which not only promotes the facile formation and stabilization of monodentate formates but also mitigates the formation of intermediates that could potentially lead to CH₄ production. This synergistic effect enhances the selectivity towards methanol.

References

- [1] E. Lam, G. Noh, K. Larmier, O. V. Safonova, C. Copéret *J. Catal.* **394**, 266-272 (2021).
- [2] N. Dewangan, W. M. Hui, S. Jayaprakash, A-R. Bawah, A. J. Poerjoto, T. Jie, A. Jangam, K. Hidajat, S. Kawi, *Catal. Today* **356**, 490-513 (2020).
- [3] J. Cored, J. Mazarío, C. Cerdá-Moreno, P. G. Lustemberg, M. V. Ganduglia-Pirovano, M. E. Domine, P. Concepción, *ACS Catal.* **12**, 3845-3857 (2022).
- [4] E. Fernández-Villanueva, P. G. Lustemberg, M. Zhao, J. Soriano Rodríguez, P. Concepción, M. V. Ganduglia-Pirovano, *JACS* **146**, 2024-2032 (2024).

Acknowledgments

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A Quantum Chemical Topology perspective on Ammonia Fixation via Metal-Ligand Cooperation

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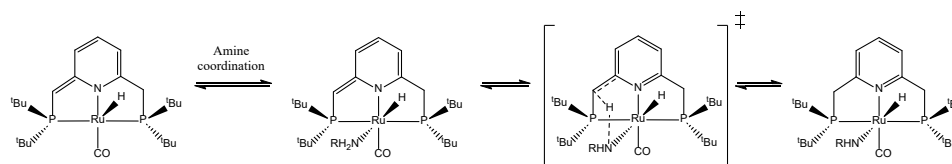
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Keywords: Ammonia Fixation, Metal-Ligand Cooperation, Chemical Bonding, Quantum Chemical Topology, Energy Decomposition

The functionalization of N–H bonds of amines is a pivotal step in the synthesis of compounds of significant economic importance like pharmaceuticals [1]. However, attaining this by using metal complexes is difficult due to the tendency of amines to form stable Werner complexes, and the high strength of N–H bond. A promising approach relies on metal-ligand cooperation (MLC), which employs a heterolytic mechanism that does not alter the oxidation state of the metal [2]. In this regard, the original PNP-Ru(II) complex proposed by Milstein, which was considered a milestone in ammonia fixation, is shown in Scheme 1 [3]. However, the examples of systems able to carry out ammonia fixation are still very scarce.

In this contribution, we took as a reference the previous system, and analysed the kinetics and thermodynamic features of the process by considering several amines and substituents in the PNP scaffold. Namely, we applied the Electron Localization Function (ELF) to unravel electron flows that take place along the reaction pathway; and Interacting Quantum Atoms (IQA) energy decomposition scheme to provide the energy counterpart of the metal–amine interaction and analyse electronic variations within the ligand structure. This way, we expect to identify the electronic factors leading to more active systems and facilitate a rational design of new systems with improved properties.



Scheme 1. Ammonia fixation via the Ru-PNP complex proposed by Milstein *et al.*

References

- [1] Y. Wang, P. M. Tran, M. E. Lahm, Y. Xie, P. Wei, E. R. Adams, J. N. Glushka, Z. Ren. V. V. Popik, H. F. Schaefer III, G. H. Robinson, *J. Am. Chem. Soc.* **144**, 16325-16331 (2022).
- [2] C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **44**, 588-602 (2011).
- [3] E. Khaskin, M. A. Iron, L. J. W. Shimon, J. Zhang, D. Milstein, *J. Am. Chem. Soc.* **132**, 8542-8543 (2010).

Acknowledgments

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Influence of Water in the structure and the band edges of photoactive titania nanoparticles: Implications in Photocatalysis

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Keywords: Density Functional Theory, Titania, Nanostructures, Band Edges

Heterogeneous photocatalysis emerges as one of the key processes to sustainable future. The design of robust and selective heterogeneous photocatalysts, based on insights from fundamental studies, may have a great impact for our society. Establishing synergies between experiments and computational analysis is fundamental to achieve this challenge. The influence of structural features can be observed through experiments, but a deep understanding and, more importantly, a systematic rationalization of the structure-property relationship are not straightforward and requires relying on large-scale atomistic simulations based on accurate theoretical methods and realistic structural models. [1]

In water splitting process is essential to understand the interaction of water with photoactive nanostructures. Thus, we focus on well-defined experimentally synthesized titania (TiO₂) nanoparticles and detailed realistic nanoparticle models to measure and computed infrared spectra of the surface hydroxyls generated by hydration. [2] The surface-induced change in the distribution of atomic environments due to the presence of water promotes structural and electronic properties. Titania nanoparticles without crystallinity behave as those reported by anatase-like nanostructures. [3] Finally, the combined effects of hydroxylation through ligand-induced dipole effect, electronic stabilization and inter-ligand interactions will be discussed to rationalize their effect on the electronic band edge position in titania nanostructures. [4]

References

- [1] Á. Morales-García, F. Viñes, C. Sousa, F. Illas, *J. Phys. Chem. Lett.*, **14**, 3712-3720 (2023).
- [2] L. Mino, Á. Morales-García, S. T. Bromley, F. Illas, *Nanoscale*, **13**, 6577-6585 (2021).
- [3] M. Recio-Poo, Á. Morales-García, F. Illas, S. T. Bromley, *Nanoscale*, **15**, 4809-4820 (2023).
- [4] M. Recio-Poo, Á. Morales-García, F. Illas, S. T. Bromley, *Under Review*.

Acknowledgments

This work was supported by MCIN/AEI/10.13039/501100011033 through projects PID2020-115293RJ-I00, PID2021-126076NB-I00, PID2021-127957NB-I00, TED2021-129506B-C22, TED2021-132550B-C22 and the María de Maeztu CEX2021-001202-M project. M. R.-P. acknowledges the Ministerio de Ciencia e Innovación (MICIN) for a FPI fellowship (PRE2019-087627).

Applying the Marcus theory to estimate the kinetics of energy-transfer events in photocatalysis

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Keywords: photocatalysis, energy transfer, alkene isomerization, DFT, Marcus Theory

Photocatalysis taps the reactivity of excited states to unlock the synthesis of essential molecular scaffolds crucial to industries like fine chemicals, which are otherwise inaccessible in the ground state. However, the high energy-laying nature of singlet excited states in readily-available nonactivated substrates precludes their direct excitation. In this regard, Energy Transfer (EnT) photocatalysis has recently emerged as a powerful strategy to enable the indirect sensitization and excited-state reactivity of nonactivated compounds using solar light as a renewable energy source, as illustrated in **Figure 1**.^[1] While EnT processes hold great potential and are gaining increasing interest, they still represent a largely unexplored area for computational chemistry.

Here, we propose a handy and cost-effective strategy to estimate the kinetics of EnT processes using computational methods. This strategy relies on the application of the Marcus theory^[2] in conjunction with reorganization energies derived from DFT calculations, which has proven successful for the estimation of single-electron transfer kinetics,^[3] albeit its application

to EnT events has not been explored thus far. Taking the indirect sensitization of alkenes for subsequent E/Z isomerization as a representative example,^[4] we demonstrate that the proposed strategy allows for accurate prediction of EnT free-energy barriers, with errors of less than 2 kcal mol⁻¹ compared to experimental values derived from rate constants.

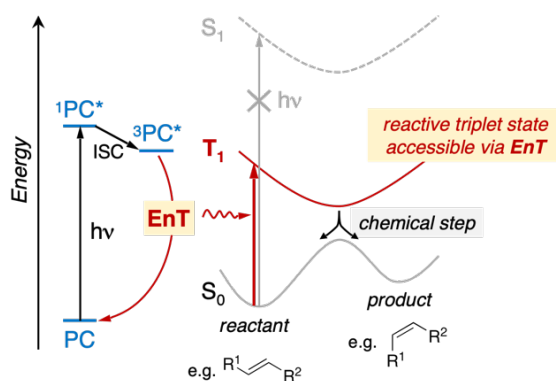


Figure 1. Schematic overview of EnT photocatalytic processes. PC stands for photocatalyst.

References

- [1] F. Strieth-Kalthoff, F. Glorius, *Chem.*, **6**, 1888-1903 (2020)
- [2] R. A. Marcus, *J. Chem. Phys.*, **24**, 966-978 (1956)
- [3] A. Solé-Daura, Y. Benseghir, M.-H. Ha-Thi, M. Fontecave, P. Mialane, A. Dolbecq, C. Mellot-Draznieks, *ACS Catal.*, **12**, 9244-9255 (2022)
- [4] T. J. B. Zähringer, M. Wienhold, R. Gilmour, C. Kerzig, *J. Am. Chem. Soc.*, **145**, 21576-21586 (2023)

Acknowledgments

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Small molecule reactivity for Catalysis on organic-coated gold nano-objects

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Keywords: Semi-empirical, Reactivity, Catalysis, Gold-nanoparticle, Coated-Nanoparticle

Over the last decade, the deliberate surface modification of nanoparticles (NPs) has emerged as a promising strategy to increase their catalytic and electrocatalytic performances [1]. In particular, the reductive grafting of diazonium salts has led to excellent electrocatalytic properties [2,3], specifically with calix[4]arenes molecules (*i.e.* organic macrocycles) grafted on AuNPs for applications in direct methanol fuel cells [4]. However, the interface of those object is not well known. Typically, characterization with Raman spectra can elucidate the nature of the interface.

In this work, we use Density Functional Tight binding (DFTB) method to investigate the interface between calix[4]arene molecules and nanoparticles. This method has proven its efficiency in simulating gold-supported organic molecules at a low computational cost [5]. Furthermore, compared to DFT Raman calculation, it allows to overcome the limit of the size of the system to go beyond the cluster model [6]. The results of Raman spectra calculations combined with the experimental findings shed light on the grafting process. Next, the structuration of the interface between calix[4]arenes and the facets of the nano-object is investigated. This allows to understand the reactivity of small molecules with organic-coated gold nano-object.

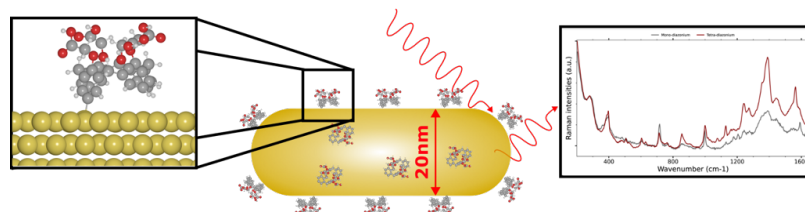


Figure 1: Representation of a capped nanoparticle with calix[4]arene macrocycle, and the different analysis performed to characterize the interface.

References

- [1] L. Lu *et al.*, *ACS Catal.* **2021**, *11*, 6020.
- [2] A. Mattiuzzi *et al.*, *Nat. Commun.* **2012**, *3*, 1–8 ;
- [3] L. Troian-Gautier *et al.*, *Chem. Commun.* **2016**, *52*, 10493–10496.
- [4] Q. Lenne *et al.*, *Adv. Mater. Interfaces* **2020**, *7*, 2001557.
- [5] A. Fihey *et al.*, *J. Comput. Chem.* **2015**, *36*, 2075–2087.
- [6] L. Laurentius, *et al.* *ACS Nano* **2011**, *5*, 4219–4227.

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Coupled Cluster Theory for Solids: Applying the “gold standard” of Quantum Chemistry to Heterogeneous Catalysis

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Keywords: coupled-cluster, many-electron, CCSD(T), SAC, SAA

Despite the widespread use of density functional theory (DFT) and, more recently, machine-learned atomistic potentials as computational tools in catalysis, systematically improvable many-electron correlation methods remain essential for generating highly accurate reference results [1].

I will report recent advancements for applying the highly-accurate coupled cluster (CC) approach to periodic systems, crucial for modelling processes in heterogeneous catalysis. Specifically, I will show our recent results for adsorption energies [2,3] and vibrational spectra of molecules on surfaces. Our ongoing research extends to surfaces with defects and polarons, single-atom catalysis, as well as single-atom alloys, and aims at reaction pathways in these scenarios using coupled cluster theory.

From a methodological perspective, I will outline the main challenges complicating reliable and converged coupled cluster calculations so far and how we address them. These challenges include (i) reaching the thermodynamic limit of the surface model, (ii) reaching the basis-set limit, and (iii) reaching convergence with respect to the included excitation operators in coupled cluster theory. In particular for metals, problem (iii) prevented applications of the “gold standard” CCSD(T) to metals due to an infrared divergence. Our new method CCSD(cT) [4] resolves this problem, enabling robust applications of coupled cluster theory to metallic scenarios.

References

- [1] T. Schäfer, N. Daelman, N. López, *J. Phys. Chem. Lett.* **2021**, 12, 27, 6277–6283 (2021)
- [2] T. Schäfer, A. Gallo, A. Irmeler, F. Hummel, A. Grüneis, *J. Chem. Phys.* **155**, 244103 (2021)
- [3] T. Schäfer, F. Libisch, G. Kresse, A. Grüneis, *J. Chem. Phys.* **154**, 011101 (2021)
- [4] N. Masios, A. Irmeler, T. Schäfer, A. Grüneis, *Physical Review Letters* **131**, 186401 (2023)

Acknowledgments

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Friday, September 6

Key Lecture 6 Anastassia Alexandrova. Interfacial fluxionality in electrocatalysis: in and out of equilibrium.

Oral contribution Lucas García-Verga. Exploring Adsorption Site Ensembles on Equimolar Bimetallic Oxides.

Oral contribution Oliver Loveday. Automated Chemical Reaction Network Generation for Heterogeneous Catalysis.

Oral contribution Reisel Millan. Mobility of solvated Cu cations in Cu-CHA predicted by machine learning accelerated molecular dynamics.

Focus Topic 4 Miguel Ángel San-Miguel. Computational Insights into Semiconductor Materials for Reactive Oxygen Species Generation.

Oral contribution Michael Higham. Mechanism of NH₃ Synthesis on Fe₃Mo₃N (111).

Oral contribution Fernando Ruetze. Molecular hydrogen interaction with a maghemite (001) surface. Physisorption and reduction by vacancy formations. A theoretical study using the DFT method.

Oral contribution Alberto Roldan. Advances in the Rational Approach for Modelling Supported Catalysts.

Interfacial fluxionality in electrocatalysis: in and out of equilibrium

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Keywords: electrocatalysis, grand canonical DFT, grand canonical genetic algorithm, CO₂ reduction, hydrogen evolution reaction

Electrocatalytic interfaces under applied potential and in the presence of adsorbates dramatically reshape, as seen, for example, in *in situ* STM. I will present a theoretical framework to describe the dynamics of electrocatalytic interfaces, combining grand canonical DFT, global optimization under potential and adsorbate coverage, and the network of concurrent reaction pathways constituting the catalytic mechanism. Conditions radically reshape the interface, and change the accessible reaction mechanisms. To illustrate this, I will discuss size-selected supported Pt cluster electrocatalysts for HER. By combination of theory and experiment, we demonstrate that these clusters have exhibit strong fluxionality of structure and coverage as a function of voltage and the stage of the catalyzed reaction.^{1,2} Metastable local minima are involved in the mechanism. The nature of the active sites strongly depends on the potential. This behavior inevitably leads to breaking scaling relations.³ I will further show how fluxionality can actually be used as a tool in cluster electrocatalyst design.⁴ While clusters are particularly fluxional, bulk interfaces are also prone to ongoing dynamism. The Cu cathode in the presence of CO and H and CO, characteristic of CO(2)RR, strongly restructures. Theory can describe this, and propose viable active sites for CO₂RR and the parasitic HER reactions.^{5,6} Simulated STM images agree with and interpret the experiment. Finally, limitations of the theoretical approach will be discussed.

References

- [1] Z. Zhang, T. Masubuchi, P. Sautet, A. N. Alexandrova, *Angew. Chem.* **62**, e2-2218210 (2023)
- [2] J. Munarriz, Z. Zhang, P. Sautet, A. N. Alexandrova, *ACS Catal.* **12**, 14517-14526 (2022)
- [3] B. Zandkarimi, A. N. Alexandrova, *J. Phys. Chem. Lett.* **10**, 460-467 (2019)
- [4] Z. Zhang, B. Zandkarimi, J. Munarriz, C. E. Dickerson, A. N. Alexandrova, *ChemCatChem* **14**, e202200345 (2022)
- [5] Z. Zhang, Z. Wei, P. Sautet, A. N. Alexandrova, *J. Am. Chem. Soc.* **144**, 19284-19293 (2022)
- [6] D. Cheng, A. N. Alexandrova, P. Sautet, *J. Phys. Chem. Lett.* **15**, 1056-1061 (2024)

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Exploring Adsorption Site Ensembles on Equimolar Bimetallic Oxides

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Keywords: Oxygen Evolution Reaction, Adsorption Site Ensemble, Bimetallic Oxides, Electrocatalysis, Active Sites

The growing impacts of climate change associated with the energetic demands of our modern lifestyle impose an urgent need for technologies that generate renewable fuel sources. The generation of hydrogen from water splitting on electrolyzers powered by renewable energy sources is a promising technology to aid the development of such carbon neutral economy. Nowadays, iridium oxide (IrO_2) is the commercially available catalyst for the anodic oxygen evolution reaction (OER). However, the high cost and scarcity of iridium makes the discovery of efficient, stable, and cheap OER catalysts mandatory for large-scale deployment of such technology. The generation of mixed oxides could reduce the iridium content for state-of-the-art catalysts, while maintaining, or even enhancing, the observed OER activity.

Recent studies in computational catalysis have contributed to the screening of mixed oxides as catalysts candidates for OER.¹ A common approach is to study ordered bulk mixed oxides, cleave surfaces from such ordered bulk models, and select adsorption sites from surfaces with low surface energies as representative models. However, adsorption site ensembles with different chemical ordering could also be present and contribute to experimentally measured catalytic activity. At the same time, the high computational cost of density functional theory makes it intractable to calculate all possible adsorption sites ensembles when searching for representative or most active adsorption sites for a given system.

Here, we explore $\text{Ir}_x\text{Ti}_{1-x}\text{O}_2$ bimetallic oxides to compare distinct approaches to generate representative catalytic sites. We explore surfaces cleaved from ordered bulk models and special quasirandom structures. We also implement a data-driven approach to select surface sites by i) using smooth overlap of atomic positions (SOAP)² vectors as fingerprints for distinguishing sites, ii) randomly generating surfaces to maximize the number of distinct sites with a given composition, iii) selecting representative sites from the pool of distinct ensembles through clustering algorithms and limiting potentials calculated using a graph neural network interatomic potential.³ Our results show $\text{Ir}_x\text{Ti}_{1-x}\text{O}_2$ systems with comparable activity and improved stability as compared to IrO_2 and present a framework that leverage from recent machine learning developments to model mixed alloys as catalysts candidates.

References

- [1] G. T. K. K. Gunasooriya and J. K. Nørskov, *ACS Energy Letters*, **5**, 3778-3787, (2020)
- [2] A. van de Walle, P. Tiwary, M. de Jong, D.L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.-Q. Chen, Z.-K. Liu, *Calphad*, **42**, 14-18 (2013)
- [3] J. Gasteiger, M. Shuaibi, A. Sriram, S. Günnemann, Z. Ulissi, C. L. Zitnick, A. Das, *Transactions on Machine Learning Research*, (2022)

Acknowledgments

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Automated Chemical Reaction Network Generation for Heterogeneous Catalysis

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Keywords: heterogeneous catalysis, computational chemistry, chemical reaction networks, automation, machine learning

The study of reaction mechanisms in heterogeneous catalysis has traditionally relied on chemical intuition for proposing paths and density functional theory (DFT) simulations to evaluate them. While this approach has been key in explaining experimental trends, it overlooks alternative paths that could likely have a key role in the overall process and it finds its limits when applied to complex mechanisms. To overcome this limitation and target a more realistic description of catalytic systems, new strategies involving automation and machine learning (ML) tools are key to obtain a more complete construction and evaluation of chemical reaction networks (CRNs).¹

Herein we present a framework capable of (i) automatically identify and generate all the potentially involved species and reactions, (ii) evaluate the ground-state and transition state energies for the species via a built-in graph neural network (GNN), GAME-Net,² able to provide robust predictions comparable to DFT and, (iii) the inclusion of a mean-field microkinetic model (MKM) to further expand the analysis. To showcase its capabilities, several case studies are investigated and features such as catalytic activity, selectivity and breaking the limits of traditional methodologies by studying previously untreatable complex CRNs are achieved, paving the way towards the exploration and analysis these kind of catalytic processes.

References

- [1] M. Wen, et al., *Nat. Comput. Sci.*, **3**, 12 (2023)
- [2] S. Pablo-García, S. Morandi, et al., *Nat. Comput. Sci.*, **3**, 433 (2023)

Acknowledgments

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Mobility of solvated Cu cations in Cu-CHA predicted by machine learning accelerated molecular dynamics.

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Keywords: Heterogeneous catalysis, diffusion, chabazite, machine learning, DFT.

Cu-exchanged zeolites play a crucial role in the chemical industry as redox catalysts, for instance, in the abatement of NO_x emissions with the selective catalytic reduction (SCR) using NH₃ as reductant.¹ These materials rely on mobile solvated Cu⁺ cations for their catalytic activity, but the effect of the framework composition (e.g Si/Al ratio) and the nature of the ligands (NH₃, H₂O, etc) in diffusion is not fully understood². Ab initio molecular dynamics simulations can provide quantitative atomistic insight but are too computationally expensive to explore large length and time scales or diverse compositions. We report a machine-learning interatomic potential that accurately reproduces ab initio results allowing multianosecond simulations and diverse chemical compositions.

The training of Neural Network potentials was based on the PaiNN architecture which uses equivariant message-passing for the ground truth prediction. The acquisition of training data was performed using active learning (AL) with a query-by-committee approach with an ensemble of four potentials. The final dataset contains 70k geometries with Si/Al ratios ranging from 5 to 50 for CHA framework and different Cu cationic species.

Simulations at several temperatures in the NVT ensemble show that while two ammonia molecules are sufficient to mobilize Cu⁺, a higher water concentration is needed to fully detach Cu⁺ from the framework. In general, the mobility of Z₂Cu²⁺, ZCu²⁺(OH)⁻ species is lower compared with Cu⁺ regardless of the nature of the ligand. Our results demonstrate the power of combining high-throughput DFT calculations, machine learning, and molecular dynamics simulations for simulating transport in nanoporous catalysts.

References

- [1] C. Peden, *Journal of Catalysis*, **373**, 384 (2019)
- [2] R. Millan, E. Bello-Jurado, M. Moliner, M. Boronat, R. Gomez-Bombarelli, *ACS Central Science*, **9**, 2040-2056 (2023)

Acknowledgments

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Computational Insights into Semiconductor Materials for Reactive Oxygen Species Generation

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Keywords: Semiconductor surfaces; Reactive Oxygen Species (ROS); DFT calculations; molecular adsorption; Silver-based materials

Microorganisms, including bacteria, fungi, and viruses, are major causes of disease globally, leading to significant outbreaks and health crises. Antibiotic resistance is a growing issue as bacteria evolve to counteract antibiotics. This necessitates the development of non-antibiotic antimicrobial therapies. Advanced materials, especially those leveraging nanotechnology, are being explored to prevent the transmission and entry of pathogens. In our group, we investigate the enhanced degradation process and bactericidal activity of Ag-based semiconductor materials because of their ability to generate reactive oxygen species (ROS)¹⁻⁴.

Recently, utilizing experimental results and density functional theory (DFT) free energy profiles, we propose a novel mechanism for the multifunctional capabilities of the Ag₃PO₄(110) surface⁵. Our findings reveal that co-adsorbed H₂O and O₂ molecules facilitate an energetically favorable pathway that efficiently activates the dissociation of H₂O and stabilizes the reactive oxygen species (ROS) precursors, specifically hydroxyl (\bullet OH) and superoxide (\bullet O²⁻) radicals. This work serves as a proof of concept to interpret surface reactions on Ag₃PO₄ and provides a new perspective for understanding the catalytic mechanisms involved in the initial stages of ROS production on metal oxide semiconductor surfaces at the atomic level.

References

- [1] A. F. Gouveia, R. A. Roca, N. G. Macedo, L. S. Cavalcante, E. Longo, M. A. San-Miguel, A. Altomare, G. S. da Silva, J. Andrés, *Journal of Materials Research and Technology*, **21**, 4023-4051 (2022).
- [2] L. H. da S. Lacerda, E. Longo, J. Andrés, M. A. San-Miguel, *Journal of Solid State Chemistry*, **305**, 122670 (2021).
- [3] L. K. Ribeiro, M. Assis, L. R. Lima, D. Coelho, M. O. Gonçalves, R. S. Paiva, L. N. Moraes, L. F. Almeida, F. Lipsky, M. A. San-Miguel, L. H. Mascaro, R. M. T. Grotto, C. P. Sousa, I. L. v. Rosa, S. A. Cruz, J. Andrés, E. Longo, *The Journal of Physical Chemistry B*, **125(38)**, 10866–10875 (2021).
- [4] F. Lipsky, L. H. da S. Lacerda, S. R. de Lazaro, E. Longo, J. Andrés, M. A. San-Miguel, *RSC Advances*, **10(51)**, 30640–30649 (2020).
- [5] F. Lipsky, L. H. da S. Lacerda, L. Gracia, B. G. Foschiani, M. Assis, M. Oliva, E. Longo, J. Andrés, M. A. San-Miguel, *The Journal of Physical Chemistry C*, **127(48)**, 23235–23245 (2023).

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Mechanism of NH₃ Synthesis on Fe₃Mo₃N(111)

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Keywords: Ammonia Synthesis, DFT, Metal Nitrides, Heterogeneous Catalysis,

Plane-wave DFT techniques are applied to investigate two distinct reaction mechanisms for ammonia (NH₃) synthesis over a thin-film model Fe₃Mo₃N(111) surface¹, namely an associative Mars van Krevelen mechanism and the conventional, dissociative, Langmuir Hinshelwood mechanism. The η-carbide structured Fe₃Mo₃N is experimentally reported to be highly active for NH₃ synthesis², in common with the isostructural Co₃Mo₃N³. Experimental studies revealed that lattice N is much more active in Co₃Mo₃N, in contrast to Fe₃Mo₃N⁴, and computational studies showed that the presence of surface lattice N vacancies can enhance N₂ activation and NH₃ synthesis over Co₃Mo₃N⁵. Hence, the present work aims to provide a complementary investigation of the Fe₃Mo₃N system in order to elucidate the similarities and differences between the two systems.

The computed reaction profiles show that, like the isostructural Co₃Mo₃N system, the Fe₃Mo₃N system affords low activation barriers for ammonia synthesis via the ER–MvK mechanism. The present work will inform future catalytic studies and furthermore provides a benchmark for subsequent investigations concerning promotion or doping of the Fe₃Mo₃N which may enhance catalytic activity.

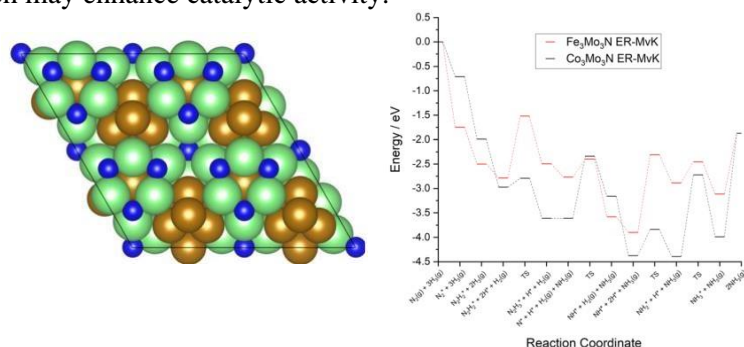


Figure 1: Graphic illustrating the model (left). Key: Fe, brown; Mo green; N, blue. Computed reaction profiles (right) comparing the ER–MvK mechanism for ammonia synthesis on Fe₃Mo₃N (red) and for Co₃Mo₃N (black).

References

- Higham, M.D.; Zeinalipour-Yazdi, C.D.; Hargreaves, J. S. J.; Catlow, C. R. A., *Faraday Discuss.*, **2023**, 243, 77-96
- Jacobson, C. J. H. *Chem. Commun.*, **2000**, 1057.
- Hargreaves, J. S. *Applied Petrochemical Research*, **2014**, 4, 3
- Daisley, A; Hargreaves, J. S. J, *Journal of Energy Chemistry*, **2019**, 170–175
- Zeinalipour-Yazdi, C. D.; Hargreaves, J. S. J.; Catlow, C. R. A., *J. Phys. Chem. C*, **2018**, 11, 6078

Molecular hydrogen interaction with a maghemite (001) surface. Physisorption and reduction by vacancy formations. A theoretical study using the DFT method.

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Keywords: maghemite, DFT, vacancy, hydrogen dissociation, hydrogen activation

The study of the interaction of H₂ on the oxidized surface of maghemite suggests that the possible physisorption and also the formation of an oxygen vacancy is feasible through two reaction pathways. The first pathway occurs by interaction at one site on oxygen atom and proceeds through energy barriers in the range of 1.65 to 2.20 eV. The second pathway occurs at two-center sites (Fe-O) and is a two-step reaction pathway. In the first step, a heterolytic dissociation of H₂ occurs, forming an intermediate with new O-H and Fe-H bonds on the surface, with energy barriers of 0.45 to 0.87 eV. It means a high activation of the H-H bond in the H₂ molecule. In the second step, the diffusion of Fe-bound hydrogen to nearby O takes place with energy barriers between 0.25 and 0.65 eV. The formation of the oxygen vacancy leads to a reduction in surface area due to a gain in electron density observed from changes in charge and electronic states. A comparison of the projected density of states (PDOS) of the outermost shell atoms is performed between the oxidized and reduced surfaces.

Advances in the Rational Approach for Modelling Supported Catalysts

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Keywords: Cluster Models, Atomic Fingerprint, Machine Learning, Supported Metal Catalysts

Catalysis is crucial in a world with high energy and commodity demands. However, current linear economy catalysts need to be replaced with sustainable alternatives. Innovation in catalysis will transform manufacturing, promote sustainability, and aid the transition to a net zero-carbon economy.

Commonly, the computational work done on supported NPs considers their morphologies in their geometric ground state, i.e., the global energy minimum, which in many cases needs to be found using stochastic global optimisation and intelligent sampling techniques [1]. The energies of these nanoscale structures are often evaluated using density functional theory (DFT) and interatomic potentials (IP). This is problematic because (i) small moieties have a relatively large number of low-lying energy configurations [1, 2], making the number of DFT calculations to map their stabilities overly demanding [3, 4], and (ii) the energy contribution from each atom depends on its position in the supported cluster, making the parametrisation of standard IPs unable to describe energies accurately [1].

We have developed an atom-centred machine-learned IP and stochastic approach to map the energy and morphology of multi-metallic supported catalysts. This allows for accurate representations of supported catalysts and consideration of their predominant morphologies under specific temperature conditions. The atoms in supported clusters are surrounded by diverse environmental factors and are located in different electronic structure sites. We have developed a universal fingerprint based on Behler's symmetry functions [5] and structural features from graph theory that unequivocally identifies each atom. We assigned atomic energies and forces to each fingerprint to train a simple neural network model. This led to accurate predictions with mean absolute errors of $0.003 \text{ eV}\cdot\text{atom}^{-1}$ and $0.035 \text{ eV}\cdot\text{\AA}^{-1}$ in mono- and bimetallic structures. Using this, we generated and evaluated thousands of supported metal structures. We classified clusters' shapes using continuous symmetry measurements and analyzed the prevalent morphologies under specific temperatures.

The work presented here leads to crucial protocols for the accurate atomistic modelling of supported catalysts, especially those in the sub-nanometre scale.

References

- [1] G. Carchini, N. Almora-Barrios, G. Revilla-Lopez, L. Bellarosa, R. Garcia-Muelas, M. Garcia-Melchor, S. Pogodin, P. Błóński, N. Lopez *TopCatal*, **56**, 1262 (2013)
- [2] F. Baletto. *JPhysCondensMatter*, **31**, 113001 (2019).
- [3] J. Engel, S. Francis, A. Roldan *PCCP*, **21**, 19011-19025 (2019).
- [4] J. Engel, E. Schwartz, C.R.A. Catlow, A. Roldan *JmatChemA*, **8**, 15695-15705 (2020).
- [5] J. Behler, M. Parrinello, *PRL*, **98**, 146 (2007).

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Posters

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- P2 *Daniel Barrena Espés.* Triazole-based scaffolds: a multifaceted topological approach of reactivity.
- P3 *Fabian Berger.* Bringing Molecules Together: Coadsorption at Dopant Sites of Single Atom Alloys.
- P4 *Ramón Bergua.* Ab-initio molecular dynamics to study the fluxionality of metal nanoclusters: Pt₈ as a case of study.
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- P6 *Annika Enss.* Theoretical investigation of the reactivity of Lewis acidity of extra-framework aluminium sites in H-ZSM-5.
- P7 *R. Farris.* Optimization and Analysis of Nanoalloys: Introducing the NanoParticleLibrary for Computational Studies.
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- P14 *Isabela Man.* Quantum chemical modeling of Oxygen Evolution Reaction Pathways Mediated by Co_{1-x}Fe_xO₄ oxide clusters.
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- P21 *Elena Rodríguez Remesal*. Role of non-metal doping on the formation doped and reduced titania nanostructures: (TiO₂)₈₄ nanoparticle as a case of study.
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- P27 *Silvio Pipolo*. Real-Time Formulation of Atomistic Electromagnetic Models for Plasmonics.
- P28 *Bssim Mounsef Jr.*. Temperature Trend for Anharmonic Corrections to the Free Energy of Adsorption of Methanol over H-SSZ-13 Probed by DFT-based MD and Thermodynamic Integration.

Investigation of the Water Splitting Reaction on Photoactive ZnO Surfaces in the Excited State

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Keywords: Semiconductors, zinc oxide, photocatalysis, water splitting, excited states, heterogeneous photocatalysis, DFT.

Water splitting reaction over semiconductors has been extensively studied since the seminal work published in 1972, by Fujishima and Honda.[1] There, authors achieved water decomposition into hydrogen (H₂) and oxygen (O₂) gases using titanium oxide (TiO₂) as electrode by applying ultraviolet (UV) light. During the last decades, such photocatalytic activity has been computationally studied over different materials,[2,3] focusing mainly on the reaction in the ground state (S₀). Unlike other investigations, the present work focused on the study of the overall water splitting reaction on ZnO surfaces in the triplet excited state (T₁), assuming an excitation by solar radiation. The reaction pathway has been thermodynamically and kinetically described with the location of the most stable sites for the adsorbates, and the transition states between them, getting an accurate description of the reaction evolution in both ground and excited triplet state.

The most stable wurtzite zinc oxide surfaces have been explored for the study, according to the lowest Miller indices values, corresponding to (000 $\bar{1}$) and (0001) polar surfaces, and (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) non-polar surfaces. For all cases, *c*(2x2) supercells have been used, except a *c*(4x2) for (10 $\bar{1}$ 0) surface, to avoid lateral interactions of the adsorbates. All optimizations have been performed using PBE functional with Grimme's D3 dispersion correction, using Climbing-Image Nudged Elastic Bands (CI-NEB) and Dimer methods to locate transition states. Triplet excited state (T₁) single point calculations have been carried out on top of these structures using PBE and Hubbard +*U* correction. The results show high adsorption energies for H and O atoms on (000 $\bar{1}$) and (0001) surfaces due to its polar termination in O and Zn atoms, respectively, and no major preference for any specie on the non-polar surfaces. This influences the reaction paths, with high activation energies on polar surfaces, and highly endothermic paths on the non-polar surfaces, on both S₀ and T₁ states. No major differences have been seen on limiting steps between S₀ and T₁ paths, regardless using PBE or PBE+*U* functionals.

References

- [1] A. Fujishima, K. Honda, *Nature*, **238**, 37-38 (1972).
- [2] Q. Zhang, C. S. Dandeneau, X. Zhou, G. Cao, *Advanced materials*, **21**, 4087-4108 (2009).
- [3] M. Nolan, A. Iwaszuk, A. K. Lucid, J. J. Carey, M. Fronzi, *Advanced materials*, **28**, 5425-5446 (2016).

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Triazole-based scaffolds: a multifaceted topological approach of reactivity

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Keywords: Quantum Chemical Topology, Interacting Quantum Atoms, Chemical Bonding, Organometallic Chemistry, Ligand design

The involvement of molecular structure in chemical properties is a phenomenon of paramount importance in the field of catalysis. This way, ligand design plays a crucial role in the development of organometallic chemistry. Their characteristics, such as the strength of the coordination bonding towards a metal centre, the donor/acceptor capacity, or their spatial arrangement in the complex, dominates the reactivity of the catalyst.

Within this fertile field, the wide variety of triazole-based polydentate scaffolds stands out for showing unique hemilabile electronic properties [1]. We have focused the discussion on the novel benzotriazole-based species as bidentate P-N ligands.

Understanding their electronic properties, at the instance of the chemical bonding that shape their molecular properties, sheds light on the most intricate aspects of reactivity. To this end, we propose a topological study guided by the IQA energy decomposition scheme, keeping chemically meaningful domains at the same time the scheme remains independent of any arbitrary reference. The results illustrate the possible coordination of these species, according to the experimentally verified structural arrangement, giving a qualitative interpretation from a topological point of view.

References

[1] B. Schulze, U. S. Schubert, *Chem. Soc. Rev.* **43**, 2522-2571 (2014).

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Bringing Molecules Together: Coadsorption at Dopant Sites of Single Atom Alloys

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Keywords: Single Atom Alloys, Catalysis, Coadsorption, Surfaces, Transition Metals, DFT

The development of improved catalysts for industrially relevant processes has evolved into a pivotal task for chemists, as most catalysts used today were developed in the 20th century, a time when climate change was not a prominent concern. To design more efficient and less wasteful catalysts, a reliable and accurate understanding of the fundamental reaction mechanisms is required. While the stabilization of transition states and the associated lowering of reaction barriers is a key property of catalysts, another essential aspect is their ability to bring reactants together at an active site. Yet, molecules such as CO naturally tend to remain apart from each other due to repulsive lateral interactions when no hydrogen bonds or strong dispersion interactions are involved. The novel material class of single atom alloys (SAA),^[1] which are composed of catalytically very active elements (dopants) atomically dispersed in a less active but more selective host metal, are promising candidates.

We show that coadsorption is favored on SAAs due to the considerably stronger interactions between adsorbates and the transition metal (TM) dopant sites compared to the rather weak interactions with the more inert host surfaces. This conclusion is grounded on the pure and mixed coadsorption of CO, NO and H on a wide range of SAAs, including all 4d TM dopants incorporated into the Cu(111) and Ag(111) surfaces. The computationally observed trends are verified by demonstrating their insensitivity to the density functional theory (DFT) functional used. Many-body energy decomposition reveals that repulsive lateral interactions between coadsorbates are more than compensated for by the enhanced binding with the dopant site. This general phenomenon holds true even for the prototypical coadsorption of CO, which has rarely been observed so far,^[2] as strong repulsive lateral interactions are usually present.

Furthermore, SAAs with early TM dopants are promising for the coadsorption of hydrogen with CO and NO, which could open a new route for the reduction of these molecules. Coupled with the relatively weak adsorption and the resulting facilitated desorption of products on early TMs (compared to later TMs, not the host surface), these so far underexplored SAAs represent interesting candidates for future catalysis research.

References

- [1] R. T. Hannagan, G. Giannakakis, M. Flytzani-Stephanopoulos, E. C. H. Sykes., *Chem. Rev.*, **120**, 12044-12088, (2020).
[2] Y. Wang, J. Schumann, E. E. Happel, V. Çınar, E. C. H. Sykes, M. Stamatakis, A. Michaelides, R. T. Hannagan, *J. Phys. Chem. Lett.*, **13**, 6316–6322, (2022).

Acknowledgments

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Ab-initio molecular dynamics to study the fluxionality of metal nanoclusters: Pt8 as a case of study

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Keywords: Platinum, nanocatalyst, gas, ab initio molecular dynamics.

Platinum is a great catalyst for the dehydrogenation reactions of aliphatic compounds. Recently, to achieve the maximum efficiency during the reaction, instead of the metal surface or large nanoparticles, small nanoclusters can be used to maximize the number of active sites available to the reactants. Moreover, small platinum nanoclusters may adopt several structures at a given temperature. Also the metallic delocalized bonding within these clusters allows them to visit many structures at a given temperature, the so-called fluxionality[1].

We have carried out a theoretical study of the dynamic properties of Pt8 sub-nanoclusters in gas phase showing that the unpaired electrons play an important role in the ability of transition among the structures of the ensemble. First, through a global minima search methodology we have determined a variety of isomers energetically accessible. Second, using the most relevant isomers of the ensemble as a starting point, we have performed Born-Oppenheimer molecular Dynamics (BO-MD)[2] to gain an insight into the fluxional character of these structures.

Through the analysis of trajectories we discovered that some transitions are likely to occur because of the structural similarity between the isomers, while some enantiomers might be kinetically trapped. We discovered that the role of unpaired electrons is key in such structural changes.

References

- [1] H. Zhai, A. N. Alexandrova, *J. Phys. Chem. Lett.* **9**, 7, 1696-1702 (2018)
- [2] T-H. Chen, D. G. Vlachos, S. Caratzoulas *J. Phys. Chem. C*, **127**, 39, 19778-19787 (2023)

Acknowledgments

This work was supported by Grant No. PID2020-114754GA-I00 funded by MCIN/AEI/10.13039/501100011033 and Gobierno Vasco-Eusko Jaurlaritza (Grant No. IT1254-19, IT1553-22). DIPC and SGI-IZO-SGIker (UPV/EHU) are acknowledged for their technical support and the generous allocation of computational resources, as well as the computer resources at MareNostrum and the technical support provided by the Barcelona Supercomputing Center.

Computational Mechanistic Analysis of Catalyzed CO₂ Cycloaddition: Impact of the Catalyst Structure on Efficiency.

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Keywords: Zinc complexes - Carbon dioxide - Cyclic carbonates - DFT calculations – Computational catalysis

Density Functional Theory (DFT) computations have been used to explore and understand the mechanism of the CO₂ cycloaddition to propylene oxide to form cyclic carbonate. We have studied the reaction catalysed by Zn(II) complexes [Zn(N4R)Cl₂] with N4R-chelating ligands bearing a phenanthroline bis(aniline) skeleton.[1] Our results show that there are two competing reaction pathways, interconnected at each step, differing in the number of chlorides coordinated due to the labile nature of these ligands. These outcomes support that epoxide ring opening is the rate determining step and takes place through the dichloride catalyst. Eventually, the CO₂ insertion and ring closure takes place preferentially along the mono-chloride catalyst pathway given that the substrate coordination favours the Cl⁻ release. Thus, the ability of the [Zn(N4R)Cl₂] for coordination/decoordination of a chloride makes the catalyst more adaptable and able to perform the reaction with lower barriers.

We have also studied the mechanism with different substituents, R=ⁱPr and H in the ortho-aniline position, to analyze the reasons of their effect in the catalytic efficiency. A thorough structural analysis has disclosed that the catalyst with the bulkiest substituent group exhibits the highest catalytic activity thanks to steric effects and non-covalent interactions. Additionally, we have investigated the impact of the N4R skeleton by replacing the phenanthroline moiety by bipyridine.

We have employed a microkinetic model to take into account the different experimental concentrations of the species involved in the reaction.

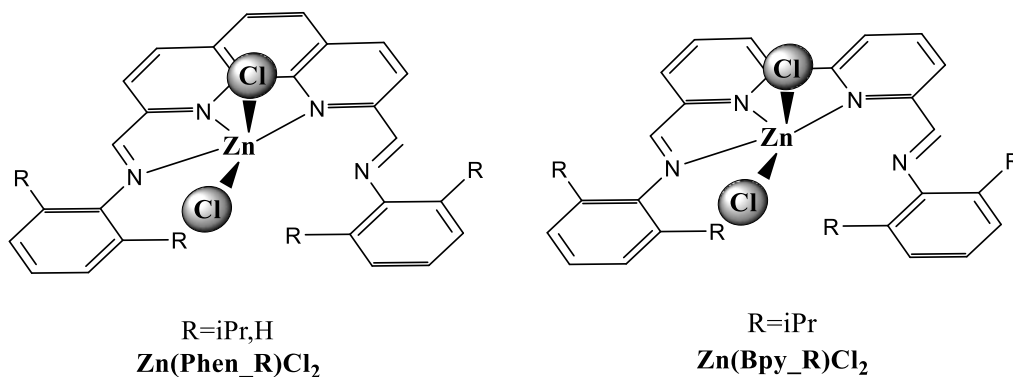


Figure 1. Chemical structures of the studied systems by means of DFT.

References

[1] N. El Aouni., C. López Redondo, M.B Yeamin, A. Aghmiz, M Reguero, A.M Masdeu-Bultó, *Mol. Catal.*, **538**, 112992 (2023)

Theoretical investigation of the reactivity of Lewis acidity of extra-framework aluminium sites in H-ZSM-5

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Keywords: methanol-to-olefins, zeolites, Lewis acidity, extra-framework aluminium, hydrogen transfer

Acidic zeolites are important catalysts for industrial applications like the methanol-to-olefins (MTO) process. The active sites can be both Brønsted and Lewis acid sites (BAS and LAS), which differ in acid strength and reactivity. LAS can be found in the bulk as extra-framework aluminum sites (EFAl). Several possible structures were discussed in literature, like AlO^+ , AlOH^{2+} or Al^{3+} . Some reactions in the MTO process are believed to involve LAS rather than BAS², therefore investigating the reactivity of LAS is relevant to understand the full catalytic activity of zeolites.

In the present study, we investigate EFAl structures in H-ZSM-5 (see Fig. 1), which were found by Khramenkova et al. by use of genetic algorithms³, in terms of stability and Lewis acidity. Pyridine serves as a probe molecule to access Lewis acidity by investigating vibrational frequencies of the adsorbed molecule. We further employed the LAS models to calculate reaction barriers related to the MTO process, as we did in previous work for surface LAS⁴. Of specific interest are those reactions that involve hydrogen transfer steps and are thought to be the precursor for the formation of aromatics.

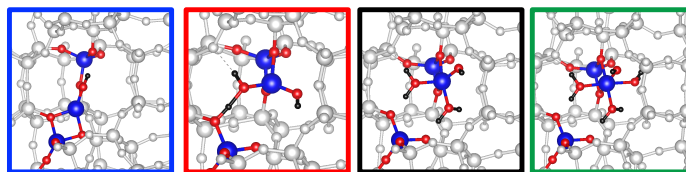


Figure 1: Optimized structures of EFAl sites in H-ZSM-5 with general composition $\text{AlOH}(\text{H}_2\text{O})_2^{2+}$, $x=0-3$. Color code: blue=Al, red = O, black = H.

References

- [1] D. L. Bhering, A. Ramirez-Solis, C. J. A. Mota, *J. Phys. Chem. B*, **107**, 4342-4347 (2003)
- [2] S. Müller, Y. Liu, F. M. Kirchberger, M. Tonigold, M. Sanchez-Sanchez, J. A. Lercher, *J. Am. Chem. Soc.*, **138**, 15994-16003 (2016)
- [3] E. V. Khramenkova, H. Venkatraman, V. Soethout, E. A. Pidko, *Phys. Chem. Chem. Phys.*, **24**, 27047-27054 (2022)
- [4] A. E. Enss, P. N. Plessow, F. Studt, *J. Phys. Chem. C*, submitted (2024)

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Optimization and Analysis of Nanoalloys: Introducing the NanoParticleLibrary for Computational Studies

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Keywords: Nanoparticles, Nanoalloys, Chemical Ordering, Global Optimization, Machine Learning,

The understanding of the chemical and physical properties of nanostructured materials is often precluded by the complexity of their structure, which also poses a challenge for constructing representative structural models in computational studies. For nanoalloys, this challenge also involves predicting the most stable arrangement of the two elements, as well as the chemical properties of the resulting surface sites.

Stable chemical orderings of bimetallic nanoparticles can be determined with global optimization approaches, which typically evaluate hundreds or thousands of candidate structures algorithmically. Given the unaffordable computational cost of evaluating the stability of such a large number of structures with approximations based on the predominant density functional theory, global optimization algorithms often rely on surrogate energy models that are fit to reproduce energies of bimetallic particles calculated at this accurate level of theory [1, 2]. Similarly, surrogate energy models can be used to approximate the binding energies on a large number of inequivalent sites and thus explore the behaviour of nanoalloys under reaction conditions.

Here we present an Open Source-Python Package, the NanoParticleLibrary (NPL, <https://github.com/reac-nps/NanoParticleLibrary>), which has been developed for computational studies of nanoalloys. The library is a wrapper around the popular Atomistic Simulation Environment and includes a flexible energy pipeline for different surrogate energy models of nanoparticles, site recognition algorithms, and various global optimization algorithms. The surrogate energy models can be imported or trained within the library, and used with a Genetic Algorithm, Markov Chain Monte Carlo, and a recently developed Optimal-Exchange algorithm [3].

We showcase the capacity of this library by presenting different case studies involving the optimization of the shape, element ordering, and response to reaction conditions of different technologically relevant bimetallic nanoparticles.

References

- [1] S. M. Kozlov, G. Kovács, R. Ferrando, and K. M. Neyman, *Chemical Science*, **6**, 3868–3880 (2015)
- [2] Z. Yan, M. G. Taylor, A. Mascareno, and G. Mpourmpakis, **18**, 2696–2704 (2018)
- [3] F. Neumann, J.T. Margraf, K. Reuter, A. Bruix, *ChemRxiv*, 10.26434/chemrxiv-2021-26ztp.

Accurate Adsorption Free Energies of Oxygen-Containing Species on Pt(111) Surface: Beyond Harmonic Oscillator Approximation

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Keywords: MLFF, Thermodynamic integration, adsorption, free energy, heterogeneous catalysis, anharmonicity

An accurate description of adsorption processes is of paramount importance for understanding heterogeneous catalytic processes. Current approaches to calculating adsorption free energies either provide insufficient entropic contributions or are very complex and/or computationally expensive. For example, the harmonic oscillator approximation (HA), the most frequently used thus far, is reportedly prone to significant deviations [1].

Herein, we introduce a new approach that allows for accurate calculations of adsorption free energies at an affordable computational cost. Specifically, we employ the λ -path thermodynamic integration (TI) methods [2,3] to account for the system's anharmonic contribution that results from the deviation from the harmonic model. The phase space samplings for TI are accelerated by means of machine learned force fields (MLFFs), which have been trained on the fly [4]. The use of MLFFs provides adequate insight into the dynamics of adsorption processes at significantly lower costs while maintaining near DFT accuracy. The accuracy at DFT level is guaranteed by additional reliable free energy perturbation theory (FEPT) calculations with high phase space overlaps.

The adsorptions of oxygen-containing species on the Pt(111) surface, which are highly relevant to catalytic reactions in fuel cells and water-splitting processes, are investigated, and the accurate anharmonic free energy diagrams are reported. We show that the anharmonic effects in the adsorption of hydroperoxyl (OOH) and hydroxyl (OH) on Pt surface are required to be evaluated for accurate estimations of the OER and ORR overpotentials, respectively.

References

- [1] G. Piccini, M. Alessio, and J. Sauer, *Phys. Chem. Chem. Phys.* **20**, 19964–19970 (2018).
- [2] J. Amsler, P.N. Plessow, F. Studt, T. Bučko, *J. Chem. Theory Comput.* **17**, 1155 (2021).
- [3] J. Amsler, P.N. Plessow, F. Studt, T. Bučko, *J. Chem. Theory Comput.* **19**, 2455 (2023).
- [4] R. Jinnouchi, F. Karsai, C. Verdi, G. Kresse, *J. Chem. Phys.* **154**, 094107 (2021)

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N-doped GQDs for ORR - a theoretical approach

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Keywords: ORR, DFT N-doped GQD, volcano plot, PDOS.

Oxygen reduction reaction (ORR) plays a key role in controlling performance PEM-fuel cells. Efficient electrocatalysts should have low overpotentials, rich catalytic sites and low cost. [1] Metal-free-graphene-based are considered promising alternatives to state-of-the-art precious Pt catalysts. [2] Factors like size, doping, surface functionalization and regulation of the number of the available active sites in graphene quantum dots (GQDs)s play an important role in ORR efficiently control. By N-doping, these drastically alter their electronic characteristics, offering more electrocatalyzing active sites. [3] We investigate, using DFT, the thermodynamic ORR activity of N-doped GQDs of various shapes (triangle, rhombohedral, hexagonal), having zigzag/armchair terminations and N-located in all inequivalent positions, by following the $4e^-$ pathway mechanism. The most active sites are placed closer to the edges than to the basal plane of the quantum dots. Also, the most active sites are placed on the armchair terminated shapes and on the zigzag hexagonal one, while on the triangular and rhombohedral with zigzag terminations, no activity is predicted. By correlating ORR intermediates adsorption energies to the corresponding PDOS of each closest N-doping carbon neighbour, all sites of weakest adsorption present band gaps, comparing to much stronger adsorption sites having semi-metallic/metallic behaviour. After N-doping, O adsorption makes structural changes in several triangle structures, e.g. C-N breaking bond, creating other possible active sites within the zigzag structures. (Fig.1 illustrates top-view structures)

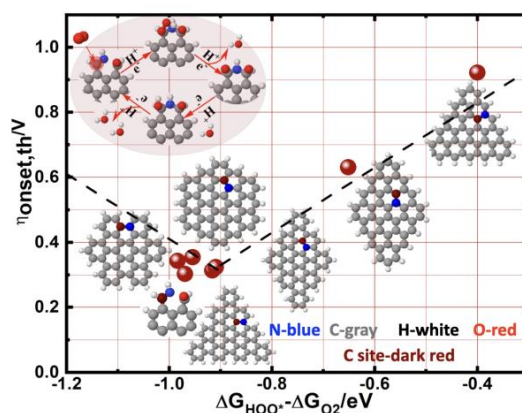


Fig. 1 – Best active sites on volcano plot by fitting theoretical onset overpotential to O_2 protonation free energy.

References

- [1] Z. Du et al., *Phys. Chem. Chem. Phys.*, **25**, 13913-13922 (2023).
- [2] Y. Jiao et al., *J. Am. Chem. Soc.*, **136**, 4394–4403 (2014).
- [3] M. Goswami et al., *Sci Rep*, **13**, 5182 (2023).

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Removal of a pharmaceutical pollutant from wastewater by heterogenous photocatalysis TiO₂ under solar light irradiation

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Keywords: TiO₂, UV-solar light, Pharmaceutical pollutant, photocatalytic degradation, Wastewater treatment.

Drugs such as antibiotics administered to living beings are incompletely metabolized, excreted and released at low concentrations in the different compartments of the environment [1]. Antibiotics are bioactive, persistent and accumulate in soils, sediments and water. The presence of these contaminants in the environment constitutes a threat to human health and a negative impact on aquatic and terrestrial ecosystems. These pharmaceuticals have already been detected in wastewater effluents, surface water, ground water and even in drinking water because they are not eliminated by conventional wastewater treatment plants [2]. It is, therefore, necessary to develop new technologies effective in removing pharmaceuticals from water.

For this purpose, the photocatalytic degradation of an antibiotic largely used in human and veterinary medicines was studied. The titanium oxide (P25 Degussa) was used as catalyst and photodegradation was carried out in aqueous solution under solar light irradiation. The influence of the solar-light irradiation time, the catalyst amount, the pollutant initial concentration and the pH of the aqueous solution under treatment was investigated. The experimental results show that for an initial concentration of 20 ppm, more than 96 % of the pollutant disappears after six hours of irradiation when using 40 mg/L of catalyst. The photocatalysis process is applied even at low concentrations. Kinetic of this photocatalytic degradation corresponds to the first order reaction, Langmuir-Hinshelwood model [3] serves as a basis for the photodegradation process. The removal efficiency of the photocatalytic degradation highly depends on the aqueous solution pH which affects both the speciation of the antibiotic molecule and the electrostatic charges at the surface of the catalyst. Thereby, it affects the interfacial electron transfer, the photo redox process and the release of oxidizing species [4]. A maximum of photocatalytic degradation was observed for a pH close to neutral. A photodegradation mechanism of the antibiotic was proposed. It seems that this pharmaceutical pollutant went through a gradual transformation into small molecules and was eventually transformed into water, carbon dioxide and nitric acid. This study reveals that Photocatalysis TiO₂/UV-solar could be considered as a promising environmentally friendly technology for the treatment of wastewater containing hard-to-remove organic compounds such as pharmaceuticals.

References

- [1] K. Kümmerer, *Chemosphere*, **75**, 417–434 (2009)
- [2] E. Felis, E. Kalka, J. Sochacki, A. Kowalska, K. Sylwia Bajkacz, M. Harnisz, E. Korzeniewska, *European Journal of Pharmacology*, **866**, 172813 (2020)
- [3] C. Turchi, D. Ollis, *Journal of Catalysis*, **122**, 178-192 (1990)
- [4] M. Chong, B. Chow, C. Saint, *Water Research*, **44**, 2997-3027 (2010)

Revealing the Unique Role of Water in the Formation of Benzothiazoles

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Keywords: Benzothiazoles, Water-Catalyzed reaction, Solvent-effect, Free-energies, Metadynamics

Benzothiazoles are promising compounds for their anti-cancer, anti-microbial, and anti-rheumatic properties. However, they are usually synthesized in harsh conditions like high temperatures, pressure, strongly acidic conditions, catalysts, or combinations thereof. Targeting a greener route for the synthesis of this important class of bioactive molecules, we reveal the role of the solvent in the formation of 2-Methylbenzothiazole using either water alongside a reducing agent as the reaction medium or in combination with stoichiometric amounts of a weak acid, instead of the harsh conditions and catalysts previously reported.

DFT Molecular Dynamics simulations coupled with enhanced sampling techniques (metadynamics) provide a clear understanding of this catalytic role of water. I will show how protic solvent, and in particular water, not only supports the benzothiazole formation but plays a dominant role as it strongly catalyzes the reaction [1].

Water is a highly versatile and multiform player in a reaction. Depending on the specific reaction, it, e.g., stabilizes the transition state, acts as dielectric screening, or provides an alternative reaction path through the Grotthuss mechanism. Here, I will demonstrate how bulk water in this case - due to its extended network of hydrogen bonds and an efficient Grotthuss mechanism - provides a reaction path that strongly reduces the reaction barriers compared to aprotic environments, namely more than 80 kJ/mol for the first reaction step i.e. formation of hydroxybenzothiazolidine and 250 kJ/mol for the second i.e. the elimination of water. Finally, I will discuss the influence of different aliphatic and aromatic substituents with varying electronic properties on chemical reactivity.

References

[1] D. Kumar, P. F. Kuijken, T. van de Poel, K. Neumann and D. R. Galimberti, *Chem. Eur. J.*, e202302596, 30 (2024)

Effects of Pd doping and oxygen vacancy on CO₂ hydrogenation over Pd/In₂O₃ Surface

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Keywords: DFT, In₂O₃, reduced surface, CO₂ hydrogenation, catalysis

The hydrogenation of carbon dioxide to synthesize methanol has been recognized as an intriguing method for CO₂ utilization [1]. In₂O₃-based catalysts have been extensively studied in this reaction due to their high selectivity for methanol production, particularly when doped with metals, to enhance catalytic performance [2]. This study investigated the effects of composite systems (Pd/In₂O₃) on the solid surface, focusing on oxygen vacancy formation (Ov) and the energetic parameters of the CO₂ hydrogenation reaction. The calculations utilized the density functional theory (DFT) method with the PBE-D3 exchange-correlation functional and the mixed Gaussian and plane-wave method (GPW) with a DZVP-MOLOPT-GTH basis set and Goedecker-Teter-Hutter pseudopotential (GTH), including BSSE correction, implemented in the CP2K package. The perfect Pd/In₂O₃(110) and Pd/In₂O₃(111) surfaces were modeled and optimized. Surface oxygen atoms were removed from different sites to create and optimize the defective Ov surface. The calculated adsorption energy between a Pd₄ cluster and the defective surfaces D1 and D2 on In₂O₃(111) is -7.8 kcal mol⁻¹ and -8.3 kcal mol⁻¹, respectively (Figure 1b and 1c), compared to -6.4 kcal mol⁻¹ for the perfect surface. These preliminary results indicate an increase in the metal-support interaction with oxygen vacancy. Hirshfeld charge analysis results indicate that electron transfer from the defective In₂O₃(111) surface to the Pd₄ cluster is more effective when the vacancy (D1) is formed close to the cluster. The electronic localization function (ELF) highlights the charge density deformation for both perfect Pd/In₂O₃ and defective Pd/In₂O₃ surfaces (D1 and D2). In D1, an increase in electronic density is observed for the oxygen atom linked to palladium. However, this is not observed in D2, where the oxygen with increased electronic density is farther from the Pd cluster. Projected density of states (PDOS) calculations were performed to understand the effect of surface oxygen vacancy on the electronic structure of the Pd₄ cluster. The d-band center shifted closer to the Fermi level upon creation of the oxygen vacancy, indicating enhanced reactivity of the Pd₄ cluster on the defective surface. Pd/In₂O₃(110) will also be investigated, and CO₂ adsorption will be studied for both surfaces prior to calculating the energetic parameters of CO₂ hydrogenation to form methanol. These results will underscore the significance of oxygen vacancies in activating the metal. The vacancy site near the cluster may facilitate CO₂ adsorption, potentially enhancing hydrogenation.

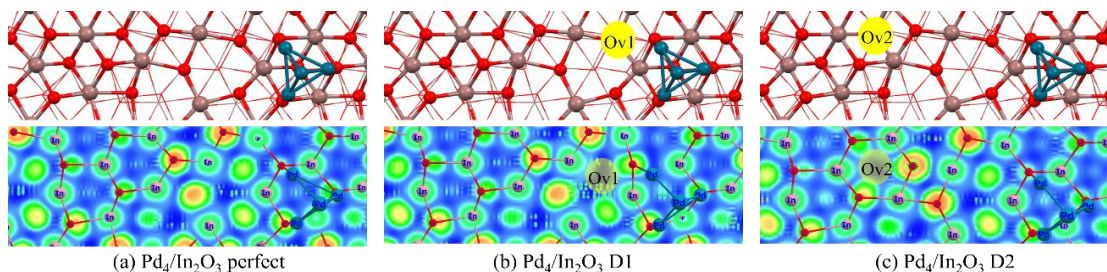


Figure 1. Optimized surfaces and ELF's contours.

References

- [1] D. Cai, Y. Cai, K. B. Tan, G. Zhan, *Materials*, **16**(7), 2803 (2023)
 [2] N. Rui, Z. Wang, K. Sun, J. Ye, Q. Ge, C. Liu, *Appl. Catal. B*, **218**, 488-497 (2017)

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The authors acknowledge Petrogal Brasil SA for the research fellowship grant to Milena D. Lessa and project ID a20006/LNCC for the computational facility.

Quantum chemical modeling of Oxygen Evolution Reaction Pathways Mediated by $\text{Co}_{1-x}\text{Fe}_x\text{O}_4$ oxide clusters

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Keywords: DFT, OER, Oxide Clusters

Water electrolysis in Proton Exchange Membrane Water Electrolyser (PEMWE) in which water is converted by the aid of electricity obtained from the renewable sources of energies in H_2 ($2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + \text{H}_2(\text{g})$), the high storage energy molecule it still represents a promising technology. Oxygen side of the system plays a limiting role. Hence identifying alternative materials to the expensive precious metal oxides catalysts (eg. $\text{RuO}_2/\text{IrO}_2$) it is impetuous. In this direction earth abundant non precious metals (e. Co, Mn based ones) are of interest. The present study uses quantum chemical calculations to explore the abilities of the $\text{Co}_x\text{Fe}_{1-x}\text{O}_4$ clusters ($x=3$) to proceed OER on the metal sites (see the inset structures in Figure 1 – the skeleton of the oxide cluster is composed of the three metal atoms (Co/Fe) and of the four oxygen atoms marked with the dark red color). The calculations provide insight into the mechanistic details (nucleophilic attack (Figure 1a) and intramolecular coupling (Figure 1b) of this process and the impact of the coordination environment and substituting metal atom on the ability to catalyze OER. The coordination environment is represented by the HO^* and H_2O attached to the clusters and by the arrangement of the metal atoms in the cluster (see the inset pictures in Figure 1)

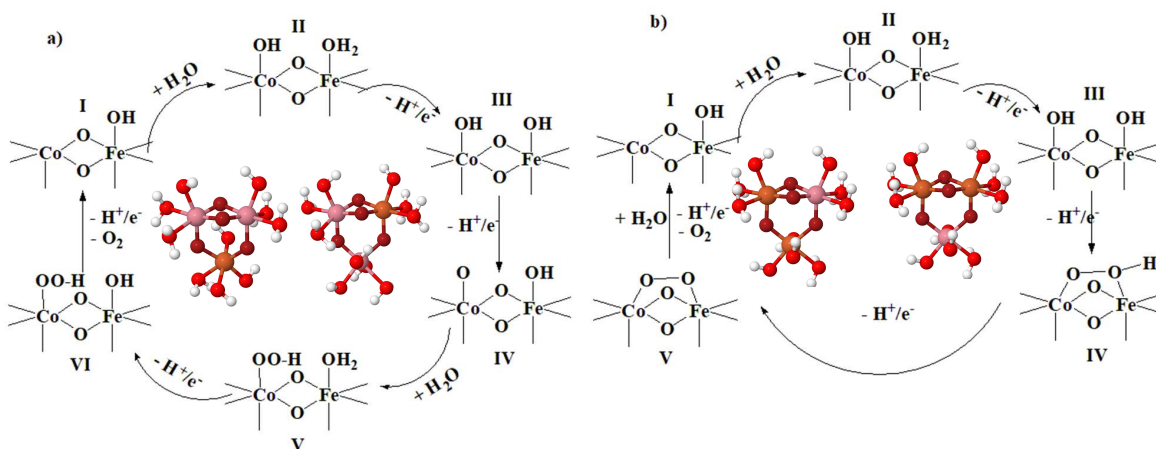


Figure 1 Schematic representation of the catalytic cycle for oxygen evolution pathway (a) water nucleophilic attack (WNA) and b) intramolecular coupling (IMC) pathway. The inset pictures represent the Co_2FeO_4 and CoFe_2O_4 clusters – : Co-pink, Fe-orange, O-dark red, red.

References

- [1] S.Shiva, H. Lim, *Energy Reports*, (2022), 8, 13793;
- [2] Q. Wu et. al, *Mater.Chem. Front.*, (2023), 7, 1025;

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Artificial Intelligence-Driven Materials for Solar Thermochemical Hydrogen Generation

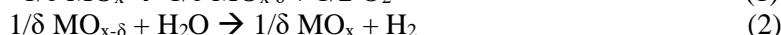
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Keywords: Artificial Intelligence, Machine Learning, Thermochemical Cycle, Solar Hydrogen.

Thermochemical cycles are a promising technology for converting solar heat into hydrogen through a two-step process. Initially, the metal oxide (MO_x) is reduced using high-temperature heat (eq. 1), followed by hydrogen generation via water splitting, which reoxidizes the reduced material (eq. 2):



While CeO₂ serves as the current state-of-the-art material used for this process, perovskites hold potential as candidates to outperform ceria due to their inherent versatility. Their ABO₃ structure allows for various combinations at the A and B sites, enabling fine-tuning of their properties and the discovery of novel materials with improved characteristics. A crucial determinant of their efficacy in hydrogen production is the oxygen vacancy formation enthalpy (Δh_o). If this value exceeds 500 kJ/mol, excessively high temperatures would be needed in the reduction step 1 [1]. Conversely, if it falls below 242 kJ/mol, it would not provide sufficient energy to break water molecules in the oxidation step 2 (this being the energy requirement at 25°C with no phase change [2]). Hence, materials with Δh_o energies falling within the 242-500 kJ/mol range are deemed acceptable. In this study, we screened over 2000 potential compositions of doped perovskites with an AA'BB'O₃ structure to identify the most promising candidates for high-efficiency hydrogen production. Our approach involved: i) computational chemistry (using DFT+U calculations) to build a database comprising the Δh_o (and other pertinent properties) of more than one hundred double and simple perovskite compositions, ii) employing artificial intelligence (AI) to train a Machine Learning (ML) algorithm on the established database, enabling prediction of the Δh_o values for the 2000 new perovskite compositions and iii) lab tests on the most promising candidates. Our database construction followed the criteria outlined by Vieten *et al* [3] and Baldassarri *et al* [4] criteria, while the ML model was implemented using the R language in Rstudio. The resulting ML model exhibited an impressive accuracy of 87%, indicating its capability of explaining 87% of the data deviation. This high level of accuracy can be attributed to the precision and variability present within the constructed database.

References

- [1] A. Bayon, A. de la Calle, E. Stechel, C. Muhich. *Energy Tech.*, **10**, 2100222 (2022).
- [2] C.Muchic, B. Ehrhart, V.Witte. *Energy Environ. Sci.*, **8**,3687 (2015).
- [3] J.Vieten, B.Bulfin. *Energy Environ. Sci.*, **12**, 1369 (2019).
- [4] B.Baldassarri, J.He, A.Gopakumar, C.Wolverton, *Chem.Mater.*, **35** (24), 10619-10634.

Acknowledgments

This work was supported by Comunidad de Madrid, SmartSolFuel project of “Programa de Atracción de Talento” (ref. 2020-T1-AMB-19884).

Structure and oxidation properties of Pt-Zr binary nanoclusters

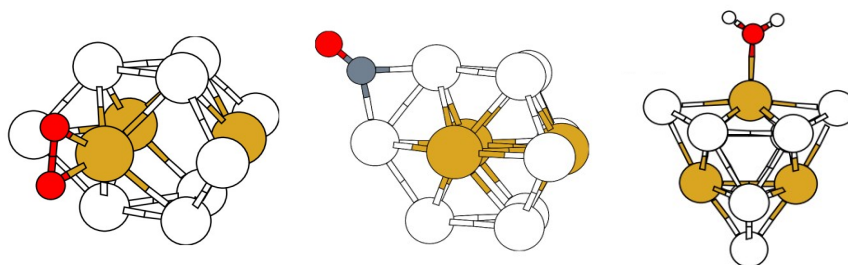
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Keywords: Clusters, DFT, CO oxidation, Platinum, Catalysis

The strong binding of CO to platinum nanoclusters can result in poisoning effects, a major problem during a variety of oxidation reactions. One interesting way to solve this problem is adding to these clusters small quantities of other metals, to induce a weakening of the CO-Pt bonds. In this contribution, using DFT simulations we have studied both the structure and chemical reactivity of platinum clusters doped with approximately 25% of Zr atoms (Pt₃Zr). At this concentration, a very stable alloy with high melting point is formed. After performing an extensive study for the structure of clusters with varying sizes, we have chosen the Pt₉Zr₃ cluster to simulate the adsorption of oxygen and carbon monoxide, and their reaction to form CO₂. The results show that the presence of Zr greatly enhances tendency towards a complete oxidation of the cluster. Also, it causes sizable changes to the CO binding energies at the Pt sites. Finally, the interaction between CO and adsorbed oxygen takes place with moderate barriers, indicating that these clusters will be active for the CO oxidation reaction.



Relaxed structures for adsorption of O₂, CO and H₂O at Pt₉Zr₃ cluster

Selective Catalytic Reduction of Nitrogen Oxides with Ammonia over Cu-CHA and Fe-BEA Zeolite

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Keywords: NH₃-SCR; Zeolites, de-NO_x, QM/MM; Reaction Mechanism; Catalysis

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.

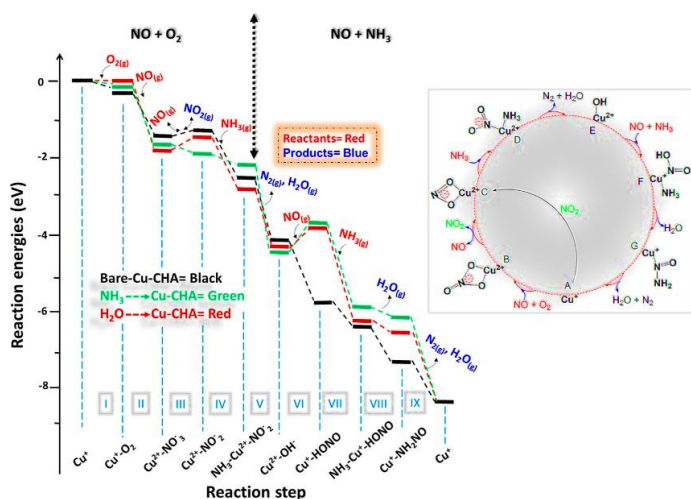


Figure 1. Potential reaction-energy landscape for NH₃-SCR on the activated Cu-CHA site and (black) on the bare site, (green) with physisorbed ammonia and (red) with physisorbed water. Inset right: NO-activated NH₃-SCR of the NO_x catalytic cycle.

References

1. Abdul Nasir, J., Guan, J., Keal, T.W., Desmoutier, A.W., Lu, Y., Beale, A.M., Catlow, C.R.A. and Sokol, A.A. J. Am. Chem. Soc. 2023, 145, 1, 247–259.

Molecular modelling study of the ozone-iodide reaction

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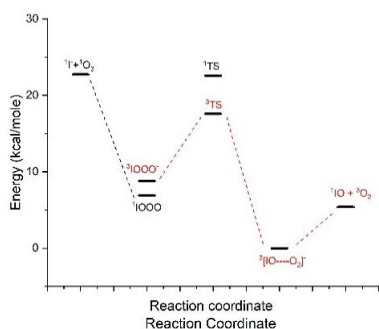
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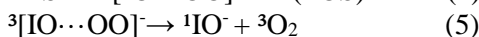
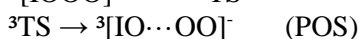
Keywords: Iodide, Ozone and DFT Calculation

The expansion of human activities has led to an increase in greenhouse gases concentration in the atmosphere, resulting in notable changes such as the global warming [1]. Halogens, including iodine, play a vital role in tropospheric chemistry. Ozone depletion might be primarily caused by the reaction between ozone and iodide. A previous study based on thermodynamic data, showed that the formation of IOOO^- is the crucial step in the overall reaction [2]. In this work, we investigated the pathway for the $\text{I} + \text{O}_3$ reaction using DFT level with hybrid functional B3LYP and the def2-TZVP basis set. All geometry optimizations on reactants, TS, PRE, POS reactive complexes and products were computed on triplet and singlet states.

Fig 1: Reaction profile for the iodide-ozone reaction



The pathway for the reaction between ozone and iodide is presented through 1, 2, 3 and 4 reactions, considering the triplet state as the lowest energy.



The calculations are consistent in predicting an exoergic reaction on the triplet surface. The estimated I-O bond length in the ${}^3\text{TS}$ closely resembles that reported by Gálvez et al. After the formation of ${}^1[\text{IOOO}]$, it is possible for the reaction to undergo a spin-crossing reaction by passing through the triplet transition state (red dotted line).

References

- [1] K. Darkwah Williams et al., Greenhouse effect: greenhouse gases and their impact on global warming. Journal of Scientific Research and Reports, **2018**, *17*, 1-9
 [2] Ó. Gálvez, M. Teresa Baeza-Romero, M. Sanz, L. F. Pacios, A theoretical study on the reaction of ozone with aqueous iodide. Physical Chemistry Chemical Physics **2016**, *18*, 7651-7660.

Acknowledgments

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Unlocking the Catalytic Chemistry Behind Bio-Based Reductive Amination

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Keywords: Amination, biomass, DFT, heterogenous catalysis, furfural.

Comprehensive DFT reaction profiles for the reductive amination of furfural derivatives over Pd(111) and Ru(0001) were constructed in VASP. Using the improved dimer method,¹⁻³ over 100 possible structures corresponding to transition states were optimised, which were then validated with vibrational analysis. In agreement with experiment,⁴ the activation energy for the ring hydrogenation step was twice as large over Ru (+134.1 kJ mol⁻¹) as it was over Pd (+69.5 kJ mol⁻¹). When bound to Pd, the substrate favoured strong interactions with the furan ring (Figure 1), facilitating hydrogenation, whereas Ru catalysis was dominated by the oxophilicity of the surface, prioritising interactions with the carbonyl and ring oxygens.

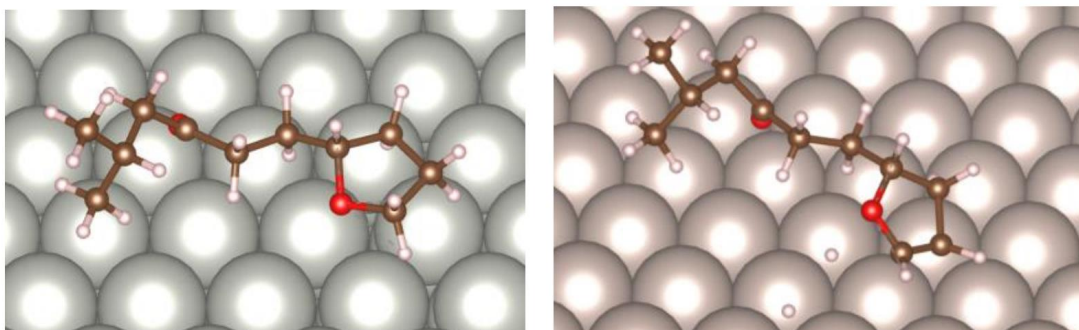


Figure 1: Ring hydrogenation intermediates over Pd(111) (left) and Ru(0001) (right).

References

- [1] G. Henkelman, H. Jónsson, *J. Chem. Phys.*, **111**, 7010–7022 (1999)
- [2] G. Henkelman, H. Jónsson, *J. Chem. Phys.*, **113**, 9978–9985 (2000)
- [3] A. Heyden, A. T. Bell, F. J. Keil, *J. Chem. Phys.*, **123**, 224101 (2005)
- [4] S. Jiang, C. Ma, E. Muller, M. Pera-Titus, F. Jérôme, K. De Oliveira Vigier, *ACS Catal.*, **9**, 8893–8902 (2019)

Acknowledgments

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Understanding how water affects excited states in Titania Nanoclusters using Nonadiabatic Molecular Dynamics Simulations: Implications in Photocatalysis

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Keywords: Titania, Nanoclusters, Heterogeneous Photocatalysis, Excited States, NAMD

Titania (TiO₂) has gained considerable attention over the last few decades in the field of photocatalysis due to its unique electronic and optical properties.^[1-3] As a wide-bandgap semiconductor, titania can absorb ultraviolet (UV) light and generate electron-hole pairs that can be used for redox reactions at its surface. However, TiO₂ has two significant drawbacks for applications using sunlight: 1) a relatively large bandgap (i.e., 3.2 eV for the anatase bulk phase) implying that its activation requires UV-light, and 2) a rapid recombination of electron-hole pairs that facilitates catalyst deactivation, rendering redox reactions unfeasible. Various strategies, such as nanostructuring, have been proposed to overcome these limitations. Factors such as morphology, size, and composition play a crucial role in defining the electronic structure, and can help mitigate these limitations.

Here, we employ nonadiabatic molecular dynamic (NAMD)^[4, 5] simulations to investigate the dynamics of the excited states of in (TiO₂)₄ and (TiO₂)₈ nanoclusters, with different degrees of hydration. Through a systematic analysis, we assess the suitability of using: i) either classical or *ab initio* MD to obtaining the trajectories, ii) single-particle or TDDFT states for computing the nonadiabatic couplings (NACs), and iii) explore a variety of trajectory surface hopping methods for running NAMD simulations aimed at predicting the lifetime of the electronic states of interest. This detailed study not only shed light on the dynamics of various excited states of the selected TiO₂ models, but also constitutes an initial methodological assessment of NAMD dynamics recipes for further use in larger titania nanostructures with different hydration degree.

References

- [1] M. A. Fox, M. T. Dulayme, *Chem. Rev.*, **93**(1), 341-357 (1993)
- [2] A. Fujishima, X. Zhang, D. A. Tryk, *Surf. Sci. Rep.*, **63**(12), 515-582 (2008)
- [3] K. Hashimoto, H. Irie, A. Fujishima, *Jpn. J. Appl. Phys.*, **44**(12R), 8269 (2005)
- [4] B. Smith, M. Shakiba, A. V. Akimov, *J. Chem. Theory Comput.*, **17**, 678-693 (2021)
- [5] B. Smith, A. V. Akimov, *J. Phys. Chem. Lett.*, **11**, 1456-1465 (2020)

Acknowledgments

M. Recio-Poo acknowledges the Ministerio de Ciencia e Innovación (MICIN) for a *Formación Personal Investigador* (FPI) fellowship (PRE2019-087627).

Organic photosensitizers for photocatalytic reduction of CO₂: mapping the landscape of their photoactivated excited states

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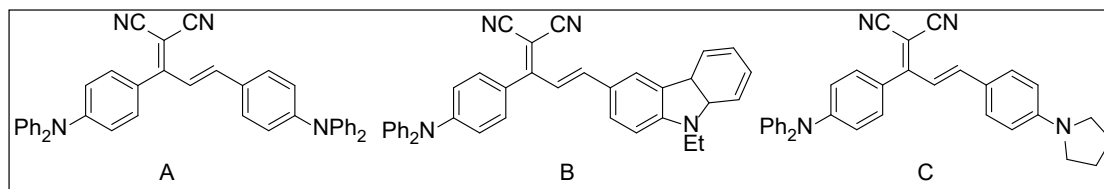
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Keywords: Photocatalysis; Organic photosensitizers; CO₂ photoreduction; Excited state PES; DFT calculations

In photocatalytic systems, organic photosensitizers (PS) are an interesting alternative to rare metal complexes, more expensive and pollutant. However, to improve the efficiency of the first ones it is necessary to understand their photophysics and the factors that determine it.

The 1,1-dicyano-2,4-diaryl-1,3-butadienes (DDB) are a family of push-pull chromophores with interesting luminescence properties.^{1,2} They have been tested as photosensitizers in the photocatalytic reaction of CO₂ reduction to CO. Surprisingly, it has been found that, while some members of the family show a significant efficiency (p. e. A in Figure), some others seem to be inactive (B and C in Figure).³



These substantial differences in such similar molecules provide a valuable area of study to elucidate the factors that contribute to the efficiency of PSs. This knowledge can help in the design of more effective photocatalytic systems.

For this reason, we have studied computationally the DDB family to determine the photophysical properties of these compounds, by elucidating the sequence of events that occur in the excited states populated after irradiation.

We have mainly used density functional (DFT) methods to explore the topography of the potential energy surfaces of the lowest singlet and triplet excited states and determine the interplay between them. We have identified two low-lying intramolecular charge transfer states and a locally excited one with several minima. The relative energies between these states are not very different in the different members of the family studied, what indicates the subtle factors that determine the efficiency of a PS coupled with a given catalysts.

References

- [1] M. Yahya, N. Seferoglu, A. Barsella, S. Achelle, Z. Seferoglu, *Spectrochimica Acta A*, **248**, 1-7 (2021)
- [2] M.M. Raikwar, E. Mathew, M. Varghese, I.H. Joe, N.N. Sekar, *Photochem. Photobiol.* 931-945, **95** (2019)
- [3] N. El Aouni, A. Aghmiz, M. Reguero, A. M. Masdeu-Bultó, *Submitted*

Role of non-metal doping on the formation doped and reduced titania nanostructures: (TiO₂)₈₄ nanoparticle as a case of study

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Keywords: heterogeneous photocatalysis, nanoparticles, nitrogen dopand, carbon dopand, titanium oxide.

Semiconducting photocatalysts have generated great expectation during last decades due to their potential applications in different areas, including energy and environmental. In particular, titania (TiO₂) has become the workhorse in the field of heterogeneous photocatalysis. However, its restrictive light absorption in the UV region hinders several commercial applications. Different strategies have been proposed to overcome this drawback, including crystal facet engineering, tailoring size and morphology of photoactive nanostructures and either metal or non-metal doping, just to name a few. The common objective of all of them is to reduce the energy gap promoting the activation of the nanostructures in the VIS region. Among these, we focus here on doping with non-metal elements, this incorporation to the photoactive framework reduces the energy gap by creating intermediate energy levels between valence and conduction bands. In particular, we pay attention to structural modifications with carbon and nitrogen as doping agent (C-doped and N-doped TiO₂).

C atoms in the TiO₂ framework promotes the activation in the VIS region as experiments and theoretical analysis in anatase and rutile bulk systems and also in anatase surfaces extended surfaces had shown [1-3]. However, all these models involve situations that are not sufficiently representative of the experimental photoactive finite nanostructures where several active regions such as corners or edges are missing. Thus, the aim of the present study is to investigate C and N doping on a (TiO₂)₈₄ nanoparticle exposing the experimental realistic bipyramidal morphology and a size within the scalable regime [4].

Our results show the formation of N-doped titania nanostructures is more feasible thermodynamically speaking than the formation of the C-doped counterparts. On the other hand, the reduction of titania nanostructure by creating neutral oxygen vacancies (O_{vac}) is favored when the N doping agent is substituting an O atom in the framework. This reducibility is easier to reach when the nonmetal doping agent is the N atom, which promotes lower formation energies than the C atom. A plausible correlation between the vacancy formation and the distance between the O_{vac} and N atom suggesting a low formation energy as $d(\text{O}_{\text{vac}}\text{-N})$ decreases. From a electronic viewpoint, the presence of N doping agent reduces the energy gap observed in the undoped structure making in principle these N-doped structure more effective for photocatalytic purposes. Clearly, the atomic environment and structure of titania framework can play an important role in the stability of non metal-doping as shown by these studies.

[1] C. Di Valentin, G. Pacchioni and A. Selloni, *Chem. Mater.*, **17**, 6656-6665(2005)

[2] H. Heffner, R. Faccio and I. López-Corral, *Appl. Surf. Sci.*, **551**, 149479 (2021)

[3] M. Curti, C. B. Mendive, T. Bredow and D. W. Bahnemann, *J. Phys. Chem. C*, **125**, 24263. (2021)

[4] Á. Morales-García, A. M. Escatllar, F. Illas and S. T. Bromley, *Nanoscale*, **11**, 9032 (2019)

[5] E. R. Remesal, A. Morales-García, *Phys. Chem. Chem. Phys.*, **24**, 21381-21387(2022)

[6] E. R. Remesal, A. Morales-García, F. Illas *J. Phys. Chem. C*, **127**, 40, 20128–20136 (2023)

Mechanism of N₂O decomposition catalysed by Cu-exchanged zeolites

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Keywords: DFT, AIMD, chabazite, mechanism, redox cycle, environmental catalysis

Cu-exchanged zeolites are promising catalysts for the decomposition of N₂O, a compound with a global warming potential ~300 times larger than CO₂ and whose emissions will increase significantly if the maritime industry substitutes oil-based fuels by ammonia-based fuels.¹ The reaction, 2N₂O → 2N₂ + O₂, follows a Cu⁺ / Cu²⁺ redox catalytic cycle and can generate NO or NO₂ as undesired by-products. Understanding the full reaction network and the dynamic stability of the Cu⁺ and Cu²⁺ active sites under reaction conditions is key to improve their efficiency.^{2,3} In this work, we apply periodic DFT calculations using VASP and *ab initio* molecular dynamics (AIMD) simulations using CP2K to investigate the complete mechanism of N₂O decomposition on Cu-CHA models containing isolated and dimeric active sites in different environments of the CHA crystallographic structure. The competition between NO and O₂ formation is studied in detail, since the final objective is to find the optimum catalyst composition and reaction conditions for this challenging process.

All calculations are carried out at the PBE+D3 level of theory. The static DFT mechanistic study shows several possible routes for the formation of O₂, NO and N₂ as well as spectroscopically observed intermediate structures (Cu⁺-O, Cu²⁺-NO₃)⁴. Calculated activation energies of the order of 30 kcal/mol (Fig. 1) indicate that the N₂O decomposition is feasible for Cu-CHA catalysts under typical experimental conditions (T ≈ 350 °C, P ≈ 1 atm).

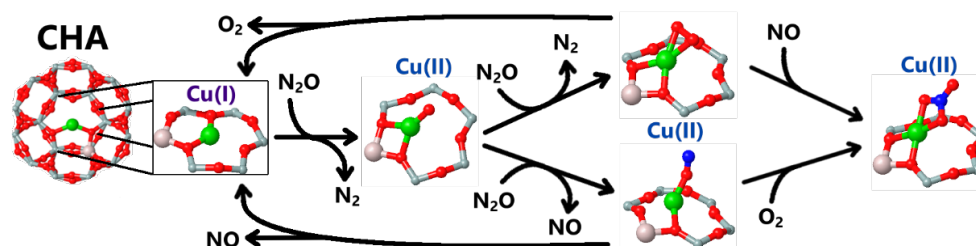


Figure 1: Simplified mechanism for the decomposition of N₂O in Cu(6r) sites in Cu-CHA.

References

- [1] W. Winiwarter, L. Höglund-Isaksson, Z. Klimont, W. Schöpp, M. Amann, *Environ. Res. Lett.*, **13**, 014011 (2018)
- [2] R. Millan, P. Cnudde, V. van Speybroeck, M. Boronat, *JACS Au* **1**, 1778 (2021)
- [3] R. Millan, E. Bello-Jurado, M. Moliner, M. Boronat, R. Gómez-Bombarelli, *ACS Central Science* **9**, 2044 (2023)
- [4] M. V. Konduru, S. S. C. Chuang, *J. Catal.* **196**, 271 (2000)

Acknowledgments

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A DFT study of the mechanism of CO₂ methanation on Ru-based catalysts

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Keywords: Ruthenium, oxide, hydrogenation, reaction mechanism, oxidation state

A highly active and selective catalyst for low temperature CO₂ methanation consisting of a combination of metallic ruthenium (Ru⁰), ruthenium oxide (RuO₂) and a ruthenium oxycarbonate phase (RuO_xC_y) formed by interstitial carbon doped into RuO₂ has been recently described.^{1,2} To maintain its long-term catalytic performance it is key to understand the detailed reaction mechanism and the competing processes leading to catalyst deactivation, such as reduction of RuO₂ to form Ru⁰ nanoparticles. In this work we investigate by means of periodic DFT calculations at the PBE level the mechanism of H₂ dissociation and CO₂ hydrogenation to methane on four different catalyst models: the (110) surface of RuO₂, the (102) surface of RuO_xC_y (with Ru₁₆O₃₂C₈ composition), and Ru₆ clusters supported on both RuO₂ and RuO_xC_y.

All calculations are performed with the VASP code, using four-layers slab models to simulate the different materials. The calculations indicate that H₂ dissociation is fast on RuO₂ and supported Ru₆ clusters, and difficult on RuO_xC_y. On the other hand, CO₂ adsorbs forming carbonate species on RuO₂ and RuO_xC_y, is activated on Ru₆/RuO_xC_y as a bent molecule that releases CO, and does not even adsorb on Ru₆/RuO_xC_y (Figure 1). The ongoing mechanistic study suggest that both Ru⁰ and RuO_xC_y are necessary for the reaction to proceed smoothly.

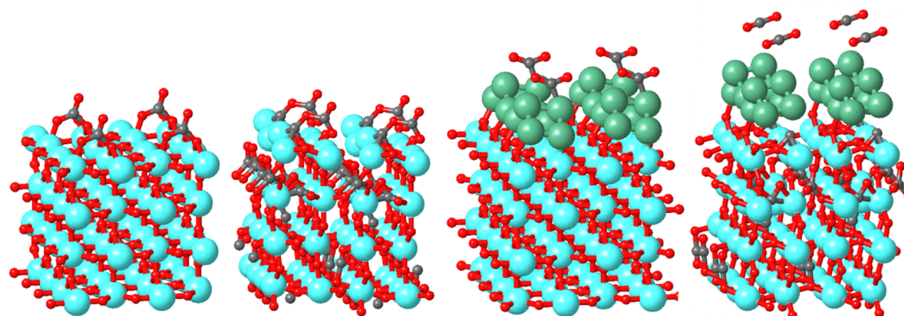


Figure 1. CO₂ adsorption on RuO₂, RuO_xC_y, Ru₆/RuO₂ and Ru₆/RuO_xC_y models. Gray, red, blue and green balls represent C, O, cationic Ru and metallic Ru, respectively.

References

- [1] C. Tébar-Soler, V. Martin-Diaconescu, L. Simonelli, A. Missyul, V. Perez-Dieste, I. J. Villar-García, J. B. Brubach, P. Roy, M. Lopez Haro, J. J. Calvino, P. Concepción, A. Corma, *Nat. Mater.* **22**, 762-768 (2023).
- [2] C. Tébar-Soler, V. Martin-Diaconescu, L. Simonelli, A. Missyul, V. Perez-Dieste, I. J. Villar-García, D. Gómez, J. B. Brubach, P. Roy, A. Corma, P. Concepción, *ACS Catal.* **14**, 4290–4300 (2024)

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Flexibility of Na-Y faujasite zeolite upon water adsorption/desorption: application of GCMC & Machine Learning Potentials

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Keywords: zeolite, cation mobility, Monte Carlo, MLP, adsorption

Zeolite Y exchanged with various cations is a widely studied and applied material, commonly used as a catalyst in petrochemical industry and in separation processes. To better describe the fundamental properties of zeolite Y, the understanding of cations mobility and distribution inside the framework is essential. The migration of cations upon water adsorption/desorption has been studied before with theoretical and experimental tools, however many works overlook the framework flexibility and so far, the computational methods have lacked quantum accuracy.¹⁻³

In this research we aim at understanding the interactions between zeolite framework, cations, and water as guest molecule. Firstly we have applied Monte Carlo (MC) method⁴ for a preliminary study of water adsorption (*Figure 1*). Subsequently we incorporated Machine Learning Potentials (MLPs)⁵ in the computational workflow. With this novel method, the Potential Energy Surface (PES) is described by a numerical potential, which is trained based on underlying quantum mechanical data by means of a deep neural network. It allows us to study the cations and water mobility in zeolite, as well as the response of the zeolite framework. Additionally, we performed *in situ* dehydration of zeolite Na-Y while monitoring crystal structure parameters with XRD. The individual sodium occupancies were calculated with parametric Rietveld refinement.

Computational results are in agreement with experimental data, and highlight the need for more advanced theoretical methods, especially for intricate and computationally heavy systems. We describe complex interactions between zeolite framework, cations, and guest species. Finally, we present the evidence that water adsorption/desorption in zeolite Na-Y initiates migration of the sodium cations, which results in framework deformation, emphasizing the flexibility of zeolite catalyst.

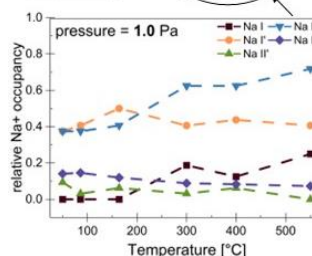
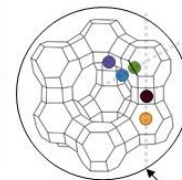


Figure 1. Cations migration during water adsorption, captured with GCMC method.

References

1. Louisfremea, W. *et al. J. Phys. Chem. C* **120**, 18115–18125 (2016).
2. Louisfremea, W. *et al. Mol. Simul.* **41**, 1371–1378 (2015).
3. Beauvais, C. *et al. ChemPhysChem* **5**, 1791–1793 (2004).
4. Dubbeldam, D. *et al. Mol. Simul.* **42**, 81–101 (2016).
5. Vandenhoute, S. *et al. Npj Comput. Mater.* **9**, 1–8 (2023).

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Integrated DFT-Monte Carlo approach to modelling Co nanoparticles

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Keywords: Fischer-Tropsch, Cobalt nanoparticles, Sites, Surface reconstruction, Sintering

Despite its history spanning over almost a century, the Fischer-Tropsch (FT) process has recently gained renewed interest from the scientific community in light of its potential to speed-up the energy transition. In fact, by converting syngas into a wide variety of hydrocarbon products, this technology makes it possible to produce fundamental chemical commodities from renewable feedstocks.

Supported cobalt catalysts are particularly suitable for the FT synthesis as they showcase high activity under mild process conditions, with operating temperatures usually not exceeding 500 K.

While supported Co nanoparticles (NP) larger than 10 nm are generally reported to be structure insensitive, a positive correlation between turnover frequency (TOF) and particle size is often recorded for NPs smaller than 10 nm [1]. Hence, understanding how the NP structure evolves over this size range is important to unravel the reaction mechanism and might ultimately lead to the formulation of new strategies to produce better-performing catalysts.

In this work, we employed a paired DFT–Monte Carlo approach to generate low-energy structures of Co NPs in the 2-10 nm size range under operating conditions. In particular, both unsupported and Al₂O₃-, SiO₂- and TiO₂- supported FCC Co NPs were simulated and the site distribution over the considered size range was investigated. With growing size, the percentage of B5-A sites, generally considered to be the active ones for CO activation, was shown to increase mostly at the expenses of B3 terrace sites. This was linked to the experimentally observed increase in TOF over this size range.

Additionally, the effect of the exposure of the Co NPs to typical FT CO partial pressure was considered and was shown to induce major surface reconstruction, as previously reported in experimental and theoretical works [2,3].

Finally, the obtained structures were used as inputs to model γ -Al₂O₃- and TiO₂-mediated Ostwald ripening. In this context, CO was shown to play a prominent role as it favors formation of the migrating Co subcarbonyl species responsible for sintering. Furthermore, by applying the rate equation described in [4], we investigated how the size distribution of a generic ensemble of particles evolves over an industrially meaningful time span.

References

- [1] J. van de Loosdrecht et al., *Comprehensive Inorganic Chemistry II (Second Edition): From Elements to Applications*, 525–557 (2013)
- [2] J. Wilson, C. de Groot, *J. Phys. Chem.*, **99**, 7860–7866, (1995)
- [3] A. Banerjee, V. Navarro, J. W. M. Frenken, A. P. van Bavel, H. P. C. E. Kuipers, M. Saeys, *Journal of Physical Chemistry Letters*, **7**, 1996–2001 (2016)
- [4] S. C. Parker, C. T. Campbell, *Physical Review B*, **75**, (2007)

Small molecule reactivity for Catalysis on organic-coated gold nano-objects

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Keywords: Semi-empirical, Reactivity, Catalysis, Gold-nanoparticle, Coated-Nanoparticle

Over the last decade, the deliberate surface modification of nanoparticles (NPs) has emerged as a promising strategy to increase their catalytic and electrocatalytic performances [1]. In particular, the reductive grafting of diazonium salts has led to excellent electrocatalytic properties [2,3], specifically with calix[4]arenes molecules (*i.e.* organic macrocycles) grafted on AuNPs for applications in direct methanol fuel cells [4]. However, the interface of those object is not well known. Typically, characterization with Raman spectra can elucidate the nature of the interface.

In this work, we use Density Functional Tight binding (DFTB) method to investigate the interface between calix[4]arene molecules and nanoparticles. This method has proven its efficiency in simulating gold-supported organic molecules at a low computational cost [5]. Furthermore, compared to DFT Raman calculation, it allows to overcome the limit of the size of the system to go beyond the cluster model [6]. The results of Raman spectra calculations combined with the experimental findings shed light on the grafting process. Next, the structuration of the interface between calix[4]arenes and the facets of the nano-object is investigated. This allows to understand the reactivity of small molecules with organic-coated gold nano-object.

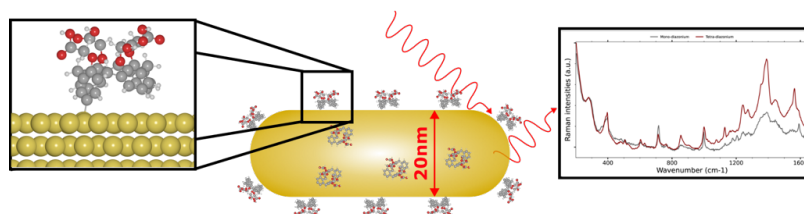


Figure 1: Representation of a capped nanoparticle with calix[4]arene macrocycle, and the different analysis performed to characterize the interface.

References

- [1] L. Lu *et al.*, *ACS Catal.* **2021**, *11*, 6020.
- [2] A. Mattiuzzi *et al.*, *Nat. Commun.* **2012**, *3*, 1–8 ;
- [3] L. Troian-Gautier *et al.*, *Chem. Commun.* **2016**, *52*, 10493–10496.
- [4] Q. Lenne *et al.*, *Adv. Mater. Interfaces* **2020**, *7*, 2001557.
- [5] A. Fihey *et al.*, *J. Comput. Chem.* **2015**, *36*, 2075–2087.
- [6] L. Laurentius, *et al.* *ACS Nano* **2011**, *5*, 4219–4227.

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Real-Time Formulation of Atomistic Electromagnetic Models for Plasmonics

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Keywords: plasmonics, atomistic models, real-time dynamics, subnanometres junctions, metals

Time-dependent approaches for nanoplasmonics permit shedding light on the dynamic optical properties of plasmonic nanostructures that are intrinsically connected with their applications in photochemistry and photoreactivity. In this work [1] we propose a real-time extension of recently developed atomistic approaches named omegaFQ and omegaFQFmu [2]. They are found to successfully reproduce quantum size effects in metal nanoparticles, including plasmon shifts for both simple and d-metals, even below the quantum size limit. Moreover because of their atomistic nature and given that they can phenomenologically include quantum tunneling effects, they can effectively describe the optical response of subnanometer junctions [3]. In this work we incorporate real-time dynamics in this family of approaches, providing an efficient framework for studying the time-dependent optical behavior of metal nanostructures, including the decoherence of plasmon excitations, and paving the way to future studies in the field of photochemistry and plasmon-assisted catalysis via Molecular Dynamics.

References

[1] P. Lafiosca, L. Nicoli, S. Pipolo, S. Corni, T. Giovannini, C. Cappelli, <https://arxiv.org/abs/2406.10926> (2024).

[2] Giovannini, T.; Rosa, M.; Corni, S.; Cappelli, C. *Nanoscale*, **11**, 6004-6015 (2019).

[3] Giovannini, T.; Bonatti, L.; Lafiosca, P.; Nicoli, L.; Castagnola, M.; Illobre, P. G.; Corni, S.; Cappelli, C., *ACS photonics*, **9**, 3025-3034, (2022).

Temperature Trend for Anharmonic Corrections to the Free Energy of Adsorption of Methanol over H-SSZ-13 Probed by DFT-based MD and Thermodynamic Integration

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Keywords: methanol, zeolites, DFT, molecular dynamics, thermodynamic integration

Entropy losses in the formation of adsorbates constitute a large part of the free energy changes along reaction paths in heterogeneous processes. This effect becomes more pronounced at practical temperatures used in heterogeneous catalysis, above 400K, and accurate methods for the calculation of adsorption free energies are crucial for the correct estimation of reaction energy barriers.

Obtaining such adsorption free energies has proven a challenge within the confines of the harmonic approximation¹. Alternatives to the harmonic approximation usually rely on continuous-path methods, which cannot be applied to the problem of adsorption and imply the accumulation of errors along a reaction path.

In this work, we employ the recently-developed λ -path integration method^{2,3} to evaluate the anharmonic effects on methanol confinement within acid SSZ-13. Four temperatures were studied in order to probe trends in adsorption free energies: 300 K, 440 K, 600 K and 800 K. The case of methanol adsorption is particularly relevant, as it is a precursor which allows for methylation of olefins, a process which is increasingly relevant as an alternative to oil-derived chemistry.

References

- [1] G. Piccini, M. Alessio, J. Sauer, *Physical Chemistry Chemical Physics*, 19964–19970, **20** (2018)
- [2] J. Amsler, P. N. Plessow, F. Studt, T. Bučko, *Journal of Chemical Theory and Computation*, 1155–1169, **17** (2021)
- [3] J. Amsler, P. N. Plessow, F. Studt, T. Bučko, *Journal of Chemical Theory and Computation*, 2455–2468, **19** (2023)

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