CSI 2024

Cluster-surface interactions
for energy applications

Bernried, Germany, 7 – 10 April 2024

Book of Abstracts

Bernried with yacht harbour at Lake Starnberg (Image: pwmotion)

About the Conference

CSI 2024 is the latest in a series of topical international conferences on cluster-surface interactions. It provides a platform for scientific exchange and discussions on experimental and theoretical results on different aspects of clusters on surfaces. This year, a special focus lies on:

- Energy conversion and storage
- Exotic fundamental properties of clusters
- Thermal catalysis on clusters
- Dynamics of clusters

Conference Organizers

- Barbara A J Lechner, TU Munich
- Ueli Heiz, TU Munich

Steering Committee

- Scott Anderson, University of Utah
- Riccardo Ferrando, University of Genoa
- Paolo Milani, University of Milan
- Atsushi Nakajima, Keio University
- Richard Palmer, Swansea University
- Stefan Vajda, J. Heyrovsky Institute

Conference Venue

Hotel Seeblick
Tutzinger Str.9
82347 Bernried
Germany
www.seeblick-bernried.de

Cluster–surface interactions for energy applications

Bernried, Germany, 7 – 10 April 2024

Sunday, 7 April

16:00 - 18:00   Registration

18:00 - 20:00   *Dinner*

20:00 - 22:00   Scientific Discussion

Monday, 8 April

9:00 - 9:05   Opening Remarks, Barbara A. J. Lechner

Session 1: Thermal catalysis on clusters (Chair: Barbara A. J. Lechner)

9:05 - 9:50   **Scott Anderson**, University of Utah
"Physical and electrocatalytic properties of Pt/carbon electrodes prepared by energy- and size-selected Ptn deposition on HOPG"

9:50 - 10:35   **Joanna Olszowka**, J. Heyrovsky Institute
"Metal-support tango – catalytic assembly for dry methane reforming"

10:35 - 11:05   *Coffee Break*

11:05 - 11:50   **Alessandro Fortunell**i, University of Pisa
"ML-Accelerated DFT Conformal Sampling of Interfacial Activated Processes"

11:50 - 12:35   **Štefan Vajda**, J. Heyrovsky Institute
"Size- and Composition-Selected Subnanometer Cluster Catalysts in Oxidative Dehydrogenation Hydrogenation Reactions under Realistic Conditions: From Controlling Activity up to Switching Selectivity by Atom a Time"

12:35-14:00   *Lunch*

Session 2: Dynamics of clusters (Chair: Ueli Heiz)

14:00 - 14:45   **Bjørk Hammer**, Aarhus University
"Machine learning for surface structure determination"

14:45 - 15:30   **Friedrich Esch**, TU Munich
"Does Cluster Encapsulation Inhibit Sintering? Stabilization of Size-Selected Pt Clusters on Fe3O4(001) by SMSI"

15:30 - 16:00   *Coffee*

16:00 - 16:45   **Florian Kraushofer**, TU Munich
"Dynamics of encapsulated clusters and nanoparticles"

16:45 - 17:30   **Marc Willinger**, TU Munich
"Non-equilibrium dynamics of simple reaction systems observed by multi-scale operando electron microscopy"

17:30 - 18:15   **Richard Palmer**, Swansea University
  "Nanoparticles in the real world: Atomic structure, dynamics and energetics from aberration-corrected electron microscopy"

18:30 - 20:00   *Dinner*

20:00 - 22:00   **Poster Session**

Tuesday, 9 April

Session 3: Energy conversion and storage (Chair: Scott Anderson)

9:00 - 9:45   **Ib Chorkendorff**, DTU
  "Single crystals and mass-selected nanoparticles for ammonia synthesis"

9:45 - 10:30   **Ewald Janssens**, KU Leuven
  "Catalysts for energy applications made by beam deposition of bimetallic clusters"

10:30 - 11:00   *Coffee Break*

11:00 - 11:45   **Albert Bruix**, Universitat de Barcelona
  "Modeling the response of supported particles to reaction conditions

11:45 - 12:30   **Fengqi Song**, Nanjing University
  "Electrically controlled nonvolatile switching of single-atom magnetism in a Dy@C84 single-molecule transistor"

12:30   *Group Photo*

12:40 - 14:00   *Lunch*

Session 4: Exotic fundamental properties of clusters (Chair: Gereon Niedner-Schatteburg)

14:00 - 14:45   **Veronique Dupuis**, Université Lyon
  "Epitaxy and Interfacial coupling of FeRh clusters deposited on perovskite oxide"

14:45 - 15:30   **Emanuele Telari**, Sapienza Università di Roma
  "Charting nanocluster structural landscape via convolutional neural networks"

15:30 - 16:00   *Coffee Break*

16:00 - 16:45   **Atsushi Nakajima**, Keio University
  "Superatom Periodicity of Metal-Atom Encapsulated Silicon Cage Nanoclusters on Organic Substrates"

16:45 - 17:30   **Paolo Milani**, University of Milan
  "Cluster-assembled Computers"

17:30 - 18:15   **Francesca Baletto**, University of Milan
  "Born differently: how the formation process affects catalytic properties"

18:30 - 20:00   *Dinner*

Session 5: Recent news and developments in cluster science (Chair: Atsushi Nakajima)

20:00 - 20:45   **Alessandro Baraldi**, University of Trieste
"Oxygen adsorption on the topmost layer of graphene supported Pt clusters"

20:45 - 21:10   **Hot topic talk: Andreas Walz**, pureions/TU Munich

"Mass selected ions in vacuum: unexploited synergies in nanoscience"

21:15 - 22:00   Scientific Discussion

Wednesday, 10 April

COST action "COSY" satellite meeting

Session 6 (Chair: Alessandro Fortunelli)

9:00 - 9:45   **M. Arturo López-Quintela**, University of Santiago de Compostela
"Wet-chemical synthesis and catalytic properties of metal clusters of small atomicity without protecting ligands"

9:45 - 10:30   **Maciej Rogala**, University of Lodz
"Defect Migration Behind Resistive Switching at Metal Oxides Surfaces"

10:30 - 11:00   *Coffee Break*

Session 7 (Chairs: Joanna Olszowka & Giacomo Melani)

11:00 - 11:30   **Sandra Gómez**, University of Salamanca
"Time evolution of PAHs and molecular crystals upon light irradiation"

11:30 - 12:00   **Junjie Shi**, TU Wien
"Direct Conversion of Methane to Methanol on Metal Clusters Functionalized Ceria Surfaces: Metal-Support Interactions"

12:00 - 12:30   **Lenard Carrol**, IFF-CSIC
"Confinement and Dimerization of Cu5 on Graphene"

12:30 - 14:00   *Lunch*

Session 8 (Chairs: Sandra Gómez & Junjie Shi)

14:00 - 14:15   **Hot topic talk: Giacomo Melani**, CNR-ICCOM
"The effect of solvation on the properties of pristine and defective oxide interfaces for solar water splitting: Insights from the BiVO4(010) surface"

14:15 - 16:00   CSI/COSY Round Table with Francesca Baletto, Joanna Olszowka, Richard Palmer and Alessandro Fortunelli

16:00   *Departure*

Physical and electrocatalytic properties of Pt/carbon electrodes prepared by energy- and size-selected Pt_n deposition on HOPG

Tsugunosuke Masubuchi,[a] Zihan Wang,[a] Sooyeon Hwang,[b] Paulo Perez,[c] Scott Anderson[d]

[a]*Chemistry Dept., University of Utah, 315 S 1400 E, Salt Lake City, UT 84112 USA*
[b]*Center for Functional Nanomaterials, Brookhaven National Lab, Upton, NY 11973*
[c]*U of Utah Nanofab, 36 S. Wasatch Dr., Salt Lake City, UT 84112, USA*

Sub-nano Pt_n clusters on conductive oxide supports are highly active electrocatalysts for both alcohol oxidation [1,2] and reduction reactions such as hydrogen evolution (HER) [3,4] and oxygen reduction (ORR) [5], but the oxide supports are poorly characterized, difficult to treat theoretically, and unstable outside a narrow potential range. This talk will focus on sub-nano Pt_n deposited on highly oriented pyrolytic

graphite (HOPG), which are found to be even more active than the same clusters on oxide electrodes, and thus far more active than bulk-like Pt nanoparticles. The Pt_n HOPG system is also interesting from the cluster deposition/dynamics perspective because HOPG is a weakly interacting support, and the sticking probability, sinter stability, and structure of the resulting clusters are highly dependent on deposition energy. The talk will present combined results from electrocatalysis, XPS, ISS, and S/TEM to address the effects of impact energy on cluster structure, and the resulting effects on catalytic activity.
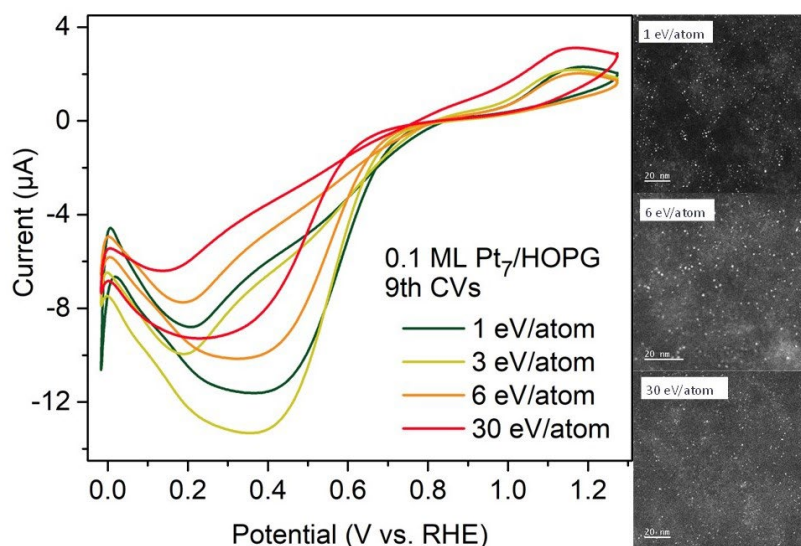
[1] von Weber, A., et al. Phys. Chem. Chem. Phys. 17, 17601-17610 (2015)

[2] von Weber, A., et al. Acc. Chem. Res. 49, 2632–2639 (2016)

[3] Kumari, S., et al. J. Am. Chem. Soc. 145, 5834-5845. (2023)

[4] Zhang, Z., et al. Angew Chem Int Ed Engl, 135, e202218210. (2023)

[5] von Weber, A., et al. J. Phys. Chem. C 119, 11160–11170 (2015)

Metal-support tango – catalytic assembly for dry methane reforming

<u>Joanna E. Olszowka</u>,[1] Abdul Selim,[1] Shashikant A. Kadam,[1] Juraj Jasik,[1] Mykhailo Vaidulych,[1] Karolina Simkovicova,[1] Stanislav Valtera,[1] Magda Zlamalova,[2] Ladislav Kavan,[2] Hana Tarabkova, [2] Martin Mergl,[3] Martin Kalbac,[3] Jaroslava Moravkova,[4] Muntaseer Bunian,[5] Yu Lei,[5] Ali Rinaldi,[6] Marc G. Willinger,[6] Armin Kleibert,[7] Stefan Vajda[1]

[1]*Department of Nanocatalysis,* [2]*Department of Electrochemical Materials,* [3]*Department of Low-dimensional Systems,* [4]*Department of Structure and Dynamics in Catalysis, J. Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic,* [5]*Department of Chemical & Materials Engineering, University of Alabama, Huntsville, Alabama, USA,* [6]*Department of Chemistry, Technical University of Munich, Munich, Germany,* [7]*Paul Scherrer Institute, Villigen, Switzerland*

In dry methane reforming (DMR), the two greenhouse gases CO_2 and CH_4 are simultaneously converted to the syngas (CO and H_2). Highly active Ni-based catalysts are often used for this reaction, yet their application is hampered due to susceptibility to sintering as well as deactivation caused by coke formation. The modulation of the metal-surface interactions offers control of the oxidation state, stability and performance of the catalyst over time. In this study, well-defined model catalysts are investigated to identify structure-function relationships derived from
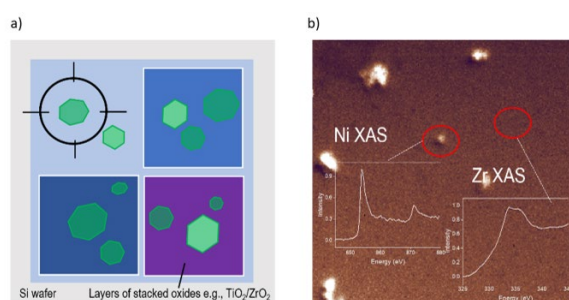

Figure 1. Spatially arranged array of oxides for spectro-microscopic analysis (a), and XPEEM image of the sample with Ni NPs (bright features) on the ZrO_2 support. The insets show local XAS extracted from encircled nanoparticle and the support (b).

support effects to leverage the gained insights for the design of real-world catalysts. Vital information about the oxidation state of the catalyst components under working conditions was acquired with synchrotron-based XPEEM (X-ray Emission Electron Microscopy) and XPS (X-ray Photoemission Spectroscopy) with single particle resolution under a flow of CO_2 or CH_4 and their mixture to mimic conditions of DMR. Distinct behavior in the reducibility of Ni nanoparticles is observed when on different supporting materials under DMR conditions. During sequential experiments, a reoxidation of Ni nanoparticles on ZrO_2 is observed by CO_2, followed by subsequent reduction by CH_4. In-situ experiments under DMR conditions reveal a reduced Ni and in-situ XPS C1s spectra suggest different distribution of the C impurities on the Ni nanoparticles and support material before the reaction, which unifies under high-temperature conditions. SEM images collected on various catalysts after the reaction often reveal a formation of additional carbon deposit over Ni nanoparticles in an encapsulating form of carbon, which might be connected with the porosity of the Ni nanoparticles and the high density of available nucleation sites. Microscopic analysis reveals that in the case of TiO_2 deposited on SiO_2, the thin oxide film can restructure under reaction conditions into islands and depending on the composition of the reactant gas mixture a reduction of TiO_2 to metallic Ti can take place. The presentation will detail correlations between particle size, and the effect of the support and oxidation state of Ni as main parameters for balancing and optimizing performance and stability.

[1] J. Vijayakumar et al., Nat. Commun. 14, 174 (2023)

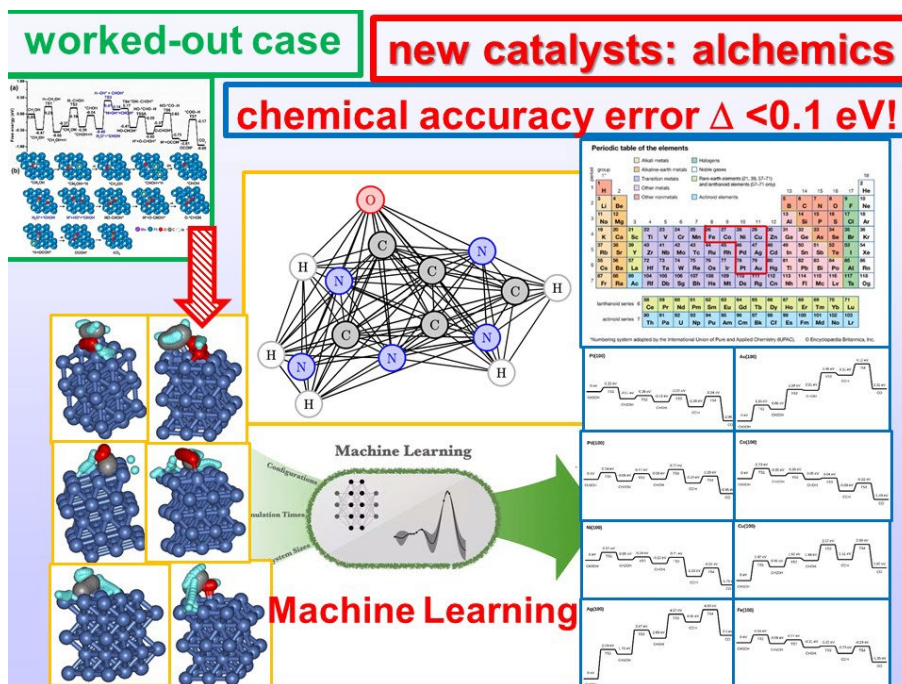# ML-Accelerated DFT Conformal Sampling of Interfacial Activated Processes

T. Roongcharoen, G. Conter, G. Melani, L. Sementa, and <u>A. Fortunelli</u>*

[1] *Consiglio Nazionale delle Ricerche, CNR-ICCOM&IPCF, Pisa, Italy*
E-mail: alessandro.fortunelli@cnr.it

I will present our recent results on how to accelerate first-principles computational predictions of reactive processes at heterogeneous interfaces by exploiting Machine-Learning (ML) and conformal techniques.

We combine stochastic sampling of activated mechanisms with ML force-fields in the form of Neural Network Potential (NNP), coupled with conformal transfer of databases to exploit as much as possible information from existing data. We use methanol decomposition (of practical interest as hydrogen production process) as a test of double-ended search. Starting from fully worked-out Pt-based systems, we construct conformal databases that are exported to other systems to quickly derive a first-generation MACE (Multi-Atomic Cluster Expansion) NNP, including cases exhibiting a change in adsorption sites as successful tests of simple catalytic path modifications. The so-derived NNP is then improved with 2 steps of active learning, leading to accurate DFT-accuracy-level predictions.

This is part of an integrated set of codes to provide a versatile and general tool to study activated processes at interfaces in materials science and catalysis. The codes operate (optionally) via the LAMMPS interface, exploit (optionally) existing simulation environments and tools, such as ASE and PLUMED, and run on traditional HPC cpu systems as well as more modern gpu-accelerated machines such as the "Leonardo" supercomputer in Bologna, Italy.

[1] T. Roongcharoen, et al. (in preparation)

Size- and Composition-Selected Subnanometer Cluster Catalysts in Oxidative Dehydrogenation Hydrogenation Reactions under Realistic Conditions: From Controlling Activity up to Switching Selectivity by Atom a Time

<u>Štefan Vajda</u>

Department of Nanocatalysis, J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic, stefan.vajda@jh-inst.cas.cz

The focus of the presentation will be on catalysts by supported monodisperse subnanometer clusters made of a handful of atoms, supported on technologically relevant oxide- and model carbon-based supports.

The performance of Co, Cu, Pd and CuPd clusters in the oxidative dehydrogenation of cyclohexene and cyclohexane will be discussed [1-4], where the atomic precision design of mono- and bimetallic clusters allows for the fine-tuning of their activity and selectivity by varying the composition of the clusters in an atom-by-atom fashion and by support effects.
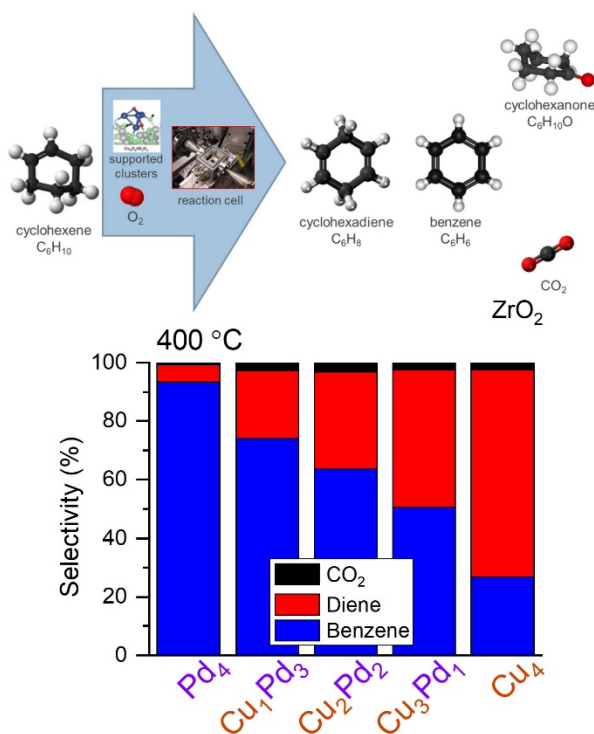
[1] Jašík, J.; Valtera, S.; Vaidulych, M.; Bunian, M.; Lei, Y.; Halder, A.; Tarábková, H.; Jindra, M.; Kavan, L.; Frank, O.; Bartling, S.; Vajda, Š. Oxidative dehydrogenation of cyclohexene on atomically precise subnanometer Cu_4-nPd_n (0≤n≤4) tetramer clusters: The effect of cluster composition and support on performance. Faraday Discuss. 2023, 242, 70-93. DOI: 10.1039/D2FD00108J

[2] Valtera, S.; Jašík, J.; Vaidulych, M.; Olszówka, J.E.; Zlámalová, M.; Tarábková, H.; Kavan, L.; Vajda, Š. Atom by Atom Built Subnanometer Copper Cluster Catalyst for the Highly Selective Oxidative Dehydrogenation of Cyclohexene. J. Chem. Phys. 2022, 156, 114302-114310. DOI: 10.1063/5.0065350

[3] Halder, A.; Ha, M.-A.; Zhai, H.; Yang, B.; Pellin, M.J.; Seifert, S.; Alexandrova, A.N.; Vajda, S. Oxidative Dehydrogenation of Cyclohexane by Cu vs Pd Clusters: Selectivity Control by Specific Cluster Dynamics. ChemCatChem. 2020, 12, 1307–1315. DOI: 10.1002/cctc.201901795
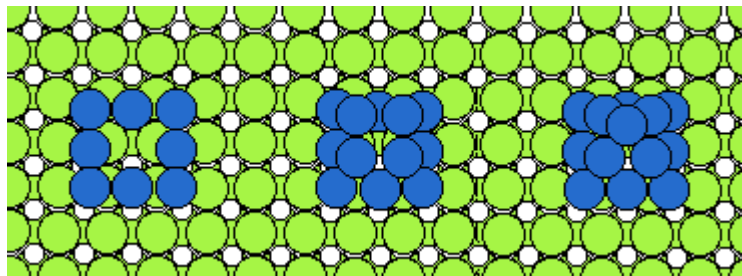
[4] Lee, S.; Halder, A.; Ferguson, G.A.; Seifert, S.; Winans, R.E.; Teschner, D.; Schlögl, R.; Papaefthimiou, V. ; Greeley, J.; Curtiss, L.A.; Vajda, S. Subnanometer Cobalt Oxide Clusters as Selective Low Temperature Oxidative Dehydrogenation Catalysts. Nat. Commun. 2019, 10, Article number: 954, p. 1-9. Published online February 27, 2019, DOI: 10.1038/s41467-019-08819-5, Communication

Machine learning for surface structure determination

Bjørk Hammer

Department of Physics and Astronomy, Aarhus University, Denmark

In recent years, machine learning interatomic potentials (MLIPs) have been developed to a stage, where they are replacing Density Functional Theory (DFT) in e.g. molecular dynamics calculations [1]. For structure determination some challenges remain since the MLIPs may be applied to structures far from the data they are based on. This renders the MLIPs less reliable and calls for their on-the-fly learning, where new DFT training data are provided to improve the MLIPs, while the searches progress. In this work, strategies for such learning are presented, including protocols for when to when to update the MLIP [2] and for how to collect the training data following Bayesian statistics [3]. Examples will be given of a surprising hollow pyramid structure of a Pt_{13} cluster supported on MgO [2] and of a complex ultra-thin surface oxide on Pt_3Sn [4]. Our computer codes are available as an open-source python package, AGOX [5, 6].

[1] Z. Tang, S.T. Bromley, B Hammer, The Journal of Chemical Physics **158**, 224108 (2023)

[2] E. L. Kolsbjerg, A. A. Peterson, and B. Hammer, Phys. Rev. B 97, 195424 (2018)

[3] M. K. Bisbo and B. Hammer, Phys. Rev. Lett. **124**, 086102 (2020)

[4] L. R. Merte et al., Angew. Chem., Intl. Ed. **61**, e202204244 (2022)

[5] M.-P. V. Christiansen, N. Rønne, and B. Hammer, J. Chem. Phys. **157**, 054701 (2022)

[6] N. Rønne, et al, J. Chem. Phys., J. Chem. Phys. **157**, 174115 (2022)

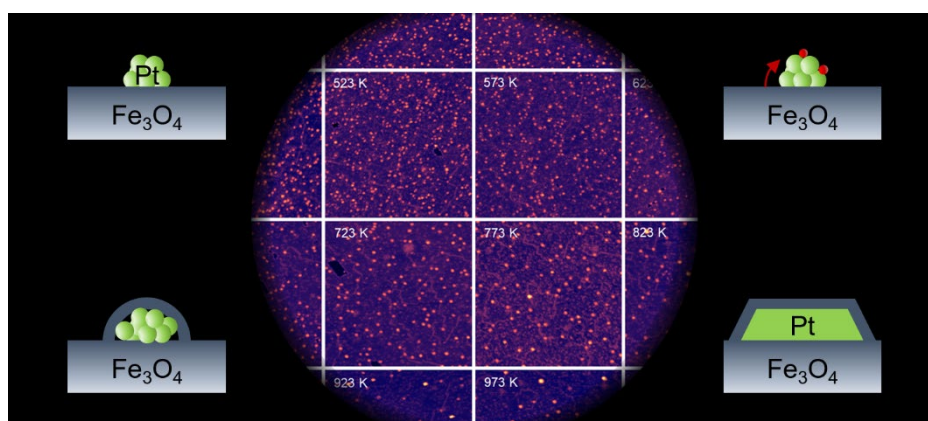## Does Cluster Encapsulation Inhibit Sintering? Stabilization of Size-Selected Pt Clusters on Fe_3O_4(001) by SMSI

Sebastian Kaiser[ab], Johanna Reich[b], Matthias Krinninger[b], Andrey Shavorskiy[c], Suyun Zhu[c], Ueli Heiz[a], Barbara A. J. Lechner[b] and <u>**Friedrich Esch**</u>**[a]**

[a] *Chair of Physical Chemistry and Catalysis Research Center, Department of Chemistry, TUM School of Natural Sciences, Technical University of Munich, 85748 Garching, Germany*
[b] *Functional Nanomaterials Group and Catalysis Research Center, Department of Chemistry, TUM School of Natural Sciences, Technical University of Munich, 85748 Garching, Germany*
[c] *MAX IV Laboratory, Lund University, Lund 221 00, Sweden*

The metastability of supported metal nanoparticles limits their application in heterogeneous catalysis at elevated temperatures due to their tendency to sinter. One strategy to overcome these thermodynamic limits on reducible oxide supports is encapsulation via strong metal–support interaction (SMSI). While annealing-induced encapsulation is a well-explored phenomenon for extended nanoparticles, it is as yet unknown whether the same mechanisms hold for sub-nm clusters, where concomitant sintering and alloying might play a significant role. Here, we explore the encapsulation and stability of size-selected Pt_5, Pt_{10}, and Pt_{19} clusters deposited on Fe_3O_4(001). In a multimodal approach using temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM), we demonstrate that SMSI indeed leads to the formation of a defective, FeO-like conglomerate encapsulating the clusters. By stepwise annealing up to 1023 K, we observe the succession of lattice oxygen reverse spillover, encapsulation, cluster coalescence, and Ostwald ripening, resulting in square-shaped crystalline Pt particles, independent of the initial cluster size [1,2]. The respective sintering onset temperatures scale with the cluster footprint and thus size. Remarkably, while small, encapsulated clusters can still diffuse as a whole, atom detachment and thus Ostwald ripening is successfully suppressed up to 823 K, i.e., 200 K above the Hüttig temperature that indicates the thermodynamic stability limit. Finally, we developed a new atom tracking setup that allows us to follow individual diffusing Pt_5 clusters at the verge of encapsulation [3].

[1] S. Kaiser, F. Maleki, K. Zhang, W. Harbich, U. Heiz, S. Tosoni, B.A.J. Lechner, G. Pacchioni, and F. Esch, ACS Catalysis **11**, 9519 (2021)

[2] S. Kaiser, J. Plansky, M. Krinninger, A. Shavorskiy, S. Zhu, U. Heiz, F. Esch, and B.A.J. Lechner, ACS Catalysis **13**, 6203 (2023)

[3] C. Dri, M. Panighel, B.A.J. Lechner, F. Esch et al., Ultramicroscopy, 205, 49 (2019)

Dynamics of encapsulated clusters and nanoparticles

Florian Kraushofer**, Matthias Krinninger, Sebastian Kaiser, Johanna E. Reich, Friedrich Esch, Barbara A.J. Lechner**

Technical University of Munich, TUM School of Natural Sciences, Department of Chemistry, 85748 Garching, Germany

Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and reducing treatments on this encapsulation layer remains controversial, partly due to the 'pressure gap' between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and scanning tunneling microscopy (NAP-STM) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a $TiO_2(110)$ support, different sintering and encapsulation dynamics are observed in O_2, H_2 and CO_2 environments, respectively, and we show that the degree of support reduction plays an important role. We also compare the encapsulation of nanoparticles, which is well established, with that of small clusters, where no satisfying atomistic model exists to date. On $Fe_3O_4(001)$, encapsulation stabilizes small Pt clusters against sintering [1]. Moreover, the cluster size and the cluster footprint on the support affect its diffusivity and can therefore be used to tune the sintering mechanism. Interestingly, small clusters of up to 10 atoms even still diffuse intact after encapsulation, and we can observe and track this diffusion in real time using our FastSTM [2].

[1] S. Kaiser et al., *ACS Catalysis* 13, 6203-6213 (2023)

[2] C. Dri et al., *Ultramicroscopy* 205, 49-56 (2019)

Non-equilibrium dynamics of simple reaction systems observed by multi-scale operando electron microscopy

Marc Willinger

Department of Chemistry, School of Natural Sciences, Technical University of Munich, Lichtenbergstrasse 4, Garching, Germany

Our aim is to understand processes that lead to the emergence of catalytic function. We use a combination of operando scanning and transmission electron microscopy to investigate and correlate processes and dynamics that dominate at different length and time scales. Taking the example of simple redox reactions that are catalyzed by non-noble metals, we find that the active catalyst operates near a phase boundary where metallic and oxidized phases coexist [1]. Real-time imaging reveals fascinating oscillatory redox dynamics that increase in complexity as the chemical potential of the gas-phase increases [2]. Moving from simple model catalysts to industrially relevant metal nanoparticles supported on reducible oxide supports, we use in-situ transmission electron microscopy to study effects related to a strong metal-support interaction (SMSI) under reactive conditions [3,4]. Correlative operando electron microscopy clearly shows that catalysis cannot be understood based on the study of static atomic arrangements. Instead, we must consider complex non-equilibrium dynamics in which oscillatory behavior near phase boundaries are providing conditions for continuous re-generation of active sites and catalytic turn-over.
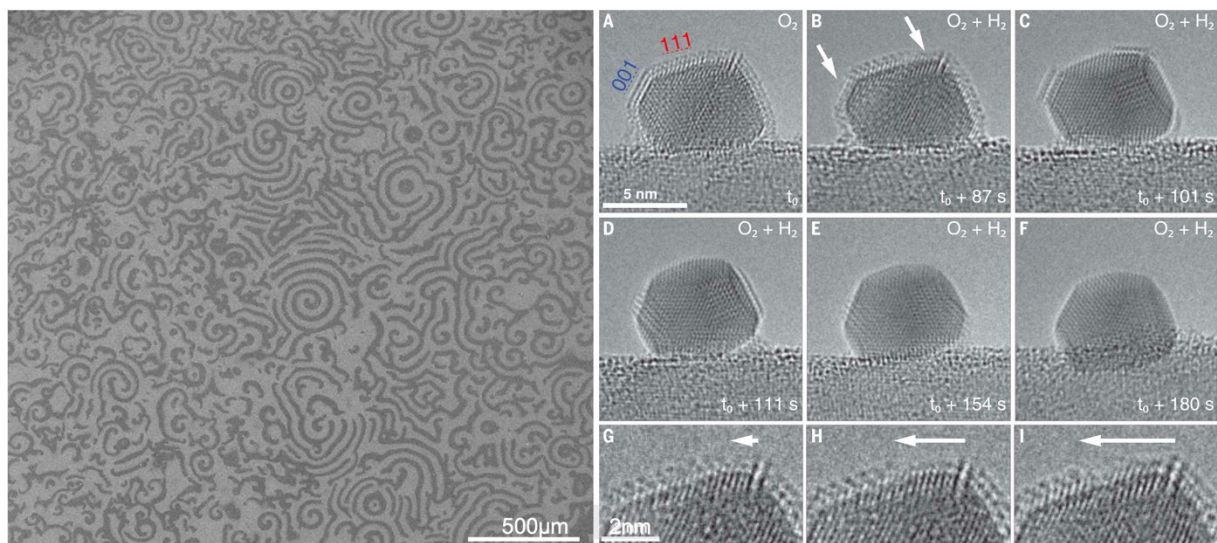
Left: Dynamics of a simple redox reaction on the surface of a nickel foil observed by operando SEM. Right: Changes in the encapsulated state of a titania supported platinum particle with changing environment as revealed by operando TEM.

[1] Barroo C. et al. Nat Catal **3**, 30–39 (2020)

[2] Huang X. et al. Adv. Mater. 2101772 (2021)

[3] Beck A. et al. Nat. Catal **4**, 488-497 (2021)

[4] H. Frey, A. et al., Science **376**, 982-987 (2022)

Nanoparticles in the real world: Atomic structure, dynamics and energetics from aberration-corrected electron microscopy

<u>Richard E. Palmer</u>

Nanomaterials Lab, Swansea University, Bay Campus, Swansea SA1 8EN, UK
R.E.Palmer@swansea.ac.uk - swanseanano.uk

Compared with the hypothetical case of an isolated nanoparticle (atomic cluster) at T=0, as addressed in some foundation theoretical treatments, two key factors will shape the behaviour of nanoclusters in the real world, where we make experimental measurements. (i) The radiative environment (including the sample temperature and interaction with charged beams) and (ii) the material environment (including pressure/reactive gas and support). We will discuss four examples of the influence of these (coupled) factors.
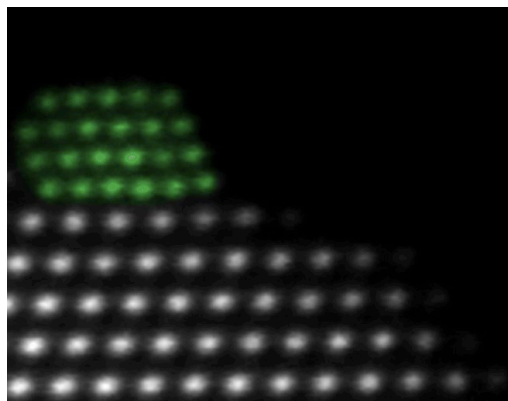
(1) Aberration-corrected electron microscopy at variable elevated temperature probes the melting and **energy differences between isomers** of arrays of size-selected gold clusters bound to point defects on a carbon surface (while subject to irradiation by 200keV electrons) [1,2]. This is pre-Covid work forms a brief basis for the talk.

(2) **Video imaging of a single** deposited gold cluster on carbon at room temperature shows dynamic fluctuations between competing structures (isomers) for different cluster sizes <1000 atoms [3]. Measurements at variable temperature enable equilibrium properties, branching ratios and relative barrier heights in the potential energy surface to be explored. The first such measurements will be reported.

(3) A study of 1 nm silver clusters (on carbon) compares clusters stored in vacuum versus those **exposed to ambient** before TEM. The work shows dramatic differences in the isomer proportions (fcc dominant versus Ih dominant), probably due to the effect of sulphur contaminants on the structural energetics [4].

(4) The **role of the support** is probed by studies of Au clusters assembled on carbon from sputtered gold atoms, where the transition from 2D to 3D morphology versus size appears to be delayed substantially compared with the free cluster. For Pt_{130} clusters on cerium oxide, the 2D versus 3D competition depends on **which facet** of ceria supports the cluster [5].

I will also briefly report progress on the **scale-up** of nanoparticle beam deposition towards manufacturing levels. For example, implantation of lead clusters from the scaled-up MACS cluster beam into porous carbon creates an electrode architecture, illustrated by electrochemical generation of oxidising species for water treatment [6].

[1] D.M. Foster, R. Ferrando, R.E. Palmer, Nature Comms. **9** 1323 (2018)

[2] D.M. Foster, T. Pavloudis, J. Kioseoglou, R.E. Palmer, Nature Comms. 10 2583 (2019)

[3] M. Dearg, C. Roncaglia, D. Nelli, E. El Koraychy, R. Ferrando, T.J.A. Slater, R.E. Palmer, Nanoscale Horiz. 9, 143 (2024)

[4] J. Vernieres, N. Tarrat, S. Lethbridge, E. Watchorn-Rokutan, T. Slater, D. Loffreda, R.E. Palmer, Communications Chemistry 6 19 (2023)

[5] H. Eliasson, Y. Niu, R.E. Palmer, H. Gronbeck, R. Erni, Nanoscale 15 19091 (2023)

[6] E. Kazimierska, Y. Niu, J. McCormack, C. Tizaoui, R.J. Cobley, R.E. Palmer, J. Nanoparticle Research 25 1 (2023)

Session 3: Energy conversion and storage (Chair: Scott Anderson)

Single crystals and mass-selected nanoparticles for ammonia synthesis

Ib Chorkendorff

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One of the most challenging processes in catalysis is the activation of molecular nitrogen [1], which is essential for life, as it constitute a part of all amino acids and nucleic acid. Despite substantial progress in producing ammonia electrochemically at ambient conditions [2] the process is today based on the Haber-Bosch which is very centralized due to the high cost of operating plants at 150-200 bars. Sustainable energy is produced de-centrally and ammonia is used de-centrally mainly as fertilizer. Thus, it would be highly desirable if the process could be made decentralized, but that would require substantial reduction of the pressure and thus reduction of temperature for equilibrium reasons. But reducing temperature means reduced rates and we therefore need roughly 50 times more active catalysts than those use today. In this presentation will we give an overview of the recent state-of-the-art of the ammonia synthesis and present different new routes of preparing catalysts. It will be shown how catalysts can be prepared by introducing promotors in situ [3] allowing for use of promotors that never could be reduced thermally and therefore not prepared by the conventional routes and therefore may not have been found despite enormous efforts in this field. It will be shown how such new classes of promotors works by suppressing the spin difference in magnetic elements [4] and how a new reaction mechanism for ammonia synthesis can be revealed by using mass-selected Cobalt nanoparticles [5] in combination with a new method of measuring activity in combination with Ultra High Vacuum and cluster sources [6].

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[3] V. Shadravan, et al., Energy & Environnemental Science 15 3310-3320 (2022)

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Catalysts for energy applications made by beam deposition of bimetallic clusters

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Beam deposition of bimetallic clusters produced in a gas-aggregation source is used to grow model thermo-, electro-, or photocatalysts for different environmentally relevant reactions.

First, strong enhancement of the methanol electro-oxidation mass activity is found on size-selected pure Au clusters dispersed on a conducting fluorine-doped tin oxide. This is attributed to the high density of exposed under-coordinated Au atoms at the surface of the faceted Au NCs [1]. Next, PtNi bimetallic clusters on inert flat oxides are shown to drive low temperature methanol dehydrogenation in temperature programmed desorption experiments. Subsurface Ni atoms weaken the Pt-CO interaction and improve the catalytic performance compared to pure Pt clusters [2]. The photocatalytic degradation of stearic acid degradation activity under solar light of bimetallic AuAg clusters, soft-landed on TiO_2 nanoparticles, was shows a strong composition dependence, which could be related to the overlap of the the clusters' plasmon resonance with the solar spectrum [3].

With the objective to close the gap between surface science and catalysis approaches, we recently developed a microreactor for the assessment of the reactivity of minute quantities of well-defined nanoparticles under industrially relevant pressure and temperature conditions (up to 250°C and 40 bar). First results obtained with this microreactor, namely CO_2 hydrogenation on PdZn nanoclusters, will be shown.

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[2] T.W. Liao, A. Yadav, P. Ferrari, Y. Niu, X.K. Wei, J. Vernieres, K.J. Hu, M. Heggen, R.E. Dunin-Borkowski, R.E. Palmer, K. Laasonen, D. Grandjean, E. Janssens, P. Lievens, Chem. Mater., 31, 10040 (2019)

[3] V. C. Chinnabathini, F. Dingenen, R. Borah, I. Abbas, J. van der Tol, Z. Zarkua, F. D'Acapito, T.H.T. Nguyen, P. Lievens, D. Grandjean, S.W. Verbruggen, E. Janssens, Nanoscale, 15, 6696 (2023)

Modeling the response of supported particles to reaction conditions

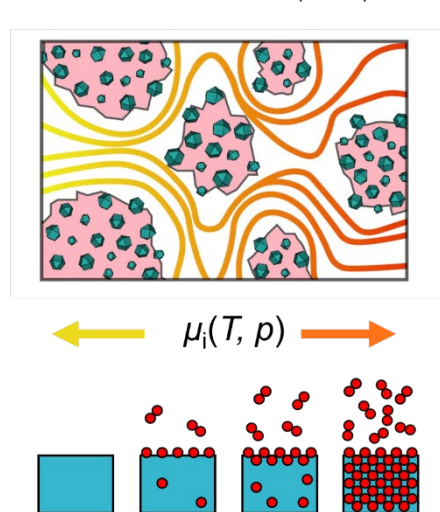**J. E. Quinlivan Domínguez, P. Castro Latorre, R. Farris, K. Neyman, and A. Bruix**

Departament de Ciència de Materials i Química Física and Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, 08028 Barcelona, Spain

The improvement of spectroscopic techniques has enabled the *in-situ* characterization of catalysts under operating conditions, often revealing a highly dynamic behavior of the active phase. For example, metals and metal-oxides usually employed as catalysts frequently undergo significant chemical and structural transformations during operation. In contrast, the conceptual framework and structural models used to rationalize the catalytic
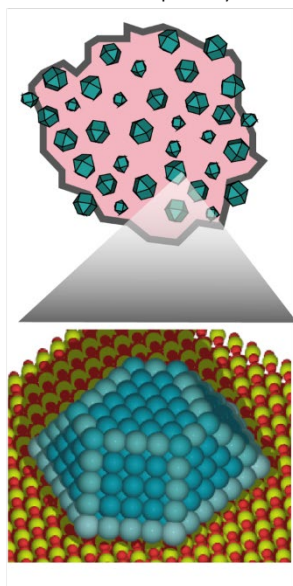
properties of such materials has traditionally relied on a rather static picture of the catalyst substrate. In addition to this so-called environmental complexity, the structural complexity of such these nanostructured materials further hinders the characterization of their response to reaction conditions [1].

Establishing reliable structural models of working catalysts is particularly relevant in computational modeling studies relying on quantum mechanical calculations. To overcome these challenges, novel computational approaches have been developed to determine the structure and composition of targeted materials and conditions, combining quantum mechanics, structure prediction (i.e. global optimization) algorithms, ab initio thermodynamics, and, more recently, also machine-learning methods [2].

During my talk, I will introduce some of these approaches and showcase their capacity by presenting different case studies involving the characterization of the structure and oxidation states of supported and catalytically relevant nanostructures [3, 4].

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Electrically controlled nonvolatile switching of single-atom magnetism in a Dy@C$_{84}$ single-molecule transistor

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Single-atom magnetism switching is a key technique towards the ultimate data storage density of computer hard disks and has been conceptually realized by leveraging the spin bistability of a magnetic atom under a scanning tunnelling microscope [1-2]. However, it has rarely been applied to solid-state transistors, an advancement that would be highly desirable for enabling various applications. Here, we demonstrate realization of the electrically controlled Zeeman effect in Dy@C$_{84}$ single-molecule transistors, thus revealing a transition in the magnetic moment from 3.8 μ_B to 5.1 μ_B for the ground-state G$_N$ at an electric field strength of 3−10 MV/cm. The consequent magnetoresistance significantly increases from 600% to 1100% at the resonant tunneling point. Density functional theory calculations further corroborate our realization of nonvolatile switching of single-atom magnetism, and the switching stability emanates from an energy barrier of 92 meV for atomic relaxation. These results highlight the potential of using endohedral metallofullerenes for high-temperature, high-stability, high-speed, and compact single-atom magnetic data storage.
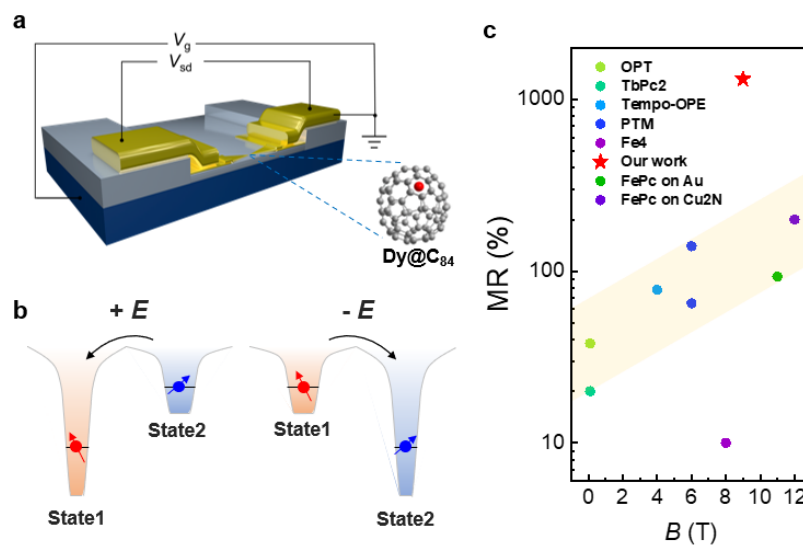

Figure 1. Electrically tunable molecular magnetism and giant magnetoresistance in Dy@C$_{84}$ single-molecule transistors

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A universal way to provide oxidization resistance for atomic precise clusters with alternative elements and atom numbers

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A serious obstacle that limits the applications of clusters is that many clusters are sensitive to environmental factors like oxidization [1] and aggregation [2], leading to functional failure. Up to now great efforts have been made to create robust cluster-based species [3,4] but a universal approach is still in urgent need.

Here we report a universal and facile way to acquire oxidization-resistant atomically precise clusters by combining beam implantation technique with gas-tight polymers, using magnetron sputtering gas phase condensation cluster beam source. Mass-selected clusters with various elements and atom numbers ranging from 2057 to 2 are packaged in PMMA with uniform size distribution and show long-term oxidization resistant for over a month, which are confirmed by XPS spectra and STEM. The mechanism of this oxidization resistance is investigated to be synergistic effect of chemical bonding of clusters to PMMA and its physical isolation. Moreover, the steric hinderance effect by PMMA also suppress agglomeration between clusters even when we dissolve the cluster-PMMA nanocomposite in anisole. This help pave the way for applications of oxidizable non-noble metal clusters in magnetism, optics and other fields.

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Epitaxy and Interfacial coupling of FeRh clusters deposited on perovskite oxide

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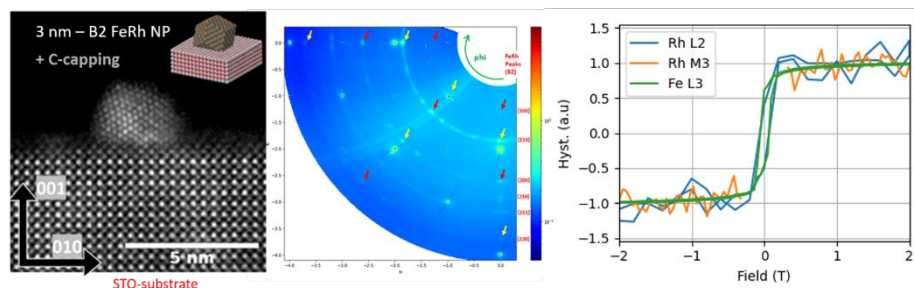[3] Institut des Nanotechnologies de Lyon (INL), CNRS UMR5270 ECL INSA, F-69622 Villeurbanne
[4] Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin – BP, F-48 91192 Gif-sur-Yvette
[5] Université Grenoble Alpes, CEA, IRIG/MEM/NRS, F-38000 Grenoble
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Near equiatomic composition, FeRh bulk alloys in the CsCl-type (B2) chemically ordered phase present a metamagnetic transition from the antiferromagnetic (AFM) state at low temperature to the ferromagnetic state (FM) above a critical transition temperature of 370 K, accompanied by a 1% volume expansion. Despite the high FeRh material cost, the competition near room temperature between both magnetic orders holds great potential applications including magnetocaloric refrigeration and ultrafast spintronics. Although their magnetic properties have been extensively studied over the last 25 years, the mechanism behind the AFM to FM transition is still widely debated and not well understood [1]. Beyond previous studies on continuous FeRh films [2,3], here we propose to explore metamagnetic phase transition in nanogranular film, made of FeRh clusters preformed in the gas phase using the Low Energy Cluster Beam Deposition (LECBD) technique. We present experimental results obtained on mass-selected FeRh clusters with 3 nm and 7 nm in diameter deposited on TiO_3 based substrate and subsequently UHV annealed at 700°C to reach the B2 phase [4, 5]. We clearly observed epitaxial relationships from STEM-HAADF on single nanoparticle of B2 FeRh deposited on oxide perovskite substrate with carbon capping but also from grazing incidence X-ray diffraction (GIXRD) on clusters assemblies, which is also accompanied by a Fe (resp. Rh induced) magnetic moment evolution visible from X-ray magnetic circular dichroism (XMCD) measurements at Fe L (resp. Rh M) edge under synchrotron facilities. The systematic study of such hybrid multiferroïc nanostructures (0D/2D) reveal a strong interplay between surface chemical reactivity, configuration, morphology and magnetic state.

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Session 4: Exotic fundamental properties of clusters (Chair: Gereon Niedner-Schatteburg)

Charting nanocluster structural landscape via convolutional neural networks

E. Telari, A. Tinti, M. Settem, L. Maragliano, R. Ferrando, A. Giacomello

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A general method to obtain a representation of the structural landscape of nanoparticles in terms of a limited number of variables is proposed. The method is applied to a large data set of parallel tempering molecular dynamics simulations of gold clusters of 90 and 147 atoms, silver clusters of 147 atoms, and copper clusters of 147 atoms, covering a plethora structures and temperatures. The method leverages convolutional neural networks to learn the radial distribution functions of the nanoclusters and distills a low-dimensional chart of the structural landscape. This strategy is found to give rise to a physically meaningful and differentiable mapping of the atom positions to a low-dimensional manifold in which the main structural motifs are clearly discriminated and meaningfully ordered. Furthermore, unsupervised clustering on the low-dimensional data proved effective at further splitting the motifs into structural subfamilies characterized by very fine and physically relevant differences such as the presence of specific punctual or planar defects or of atoms with particular coordination features. The method has been successively enhanced in order to use the low dimensional description for the biasing of molecular simulations. In such a way, it made it possible to force and sample structural transitions in molecular dynamics simulations and to perform free energy calculations over the structural landscape of a system composed of 147 gold atoms.

Superatom Periodicity of Metal-Atom Encapsulated Silicon Cage Nanoclusters on Organic Substrates

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Among the family of nanocluster (NC) superatoms (SAs) that mimic atomic-like properties due to their symmetrical geometric structures and closed-shell electronic states, the tantalum atom-encapsulating silicon 16-mer ($Ta@Si_{16}$) and aluminum 13-mer (Al_{13}) exhibit alkali-like and halogen-like superatoms (SAs), respectively [1-4]. $Ta@Si_{16}$ SAs exhibit superatomic behavior characterized by an interplay between electron shell closure (68 e) and geometrical packing within a Si_{16} cage in a cationic state. Conversely, Al_{13}^- SAs exhibit superatomic behavior with electron shell closure (40 e) and geometrical packing (I_h symmetry) in an anionic state. The fabrication of SA assemblies necessitates the tunability of electron counting in SAs along with substrate properties to optimize the cluster–surface interaction.

Metal-encapsulating Si_{16} cage NCs ($M@Si_{16}$) emerge as promising SAs for designing tunable properties by altering the central metal atom: halogen-like, rare-gas-like, and alkali-like characteristics appear for central metal atom of groups 3, 4, and 5, respectively [1]. Moreover, group 6 metal atom of W forms $W@Si_{16}$, exhibiting alkaline earth-like characteristics [5]. Notably, $M@Si_{16}$ SAs (M = Lu, Hf, Ta, and W) can be controllably immobilized on a substrate; halogen-like $Lu@Si_{16}$ SAs can be soft-landed on organic substrates pre-deposited with *p*-type hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (HB-HBC, $C_{66}H_{66}$), while alkali-like $Ta@Si_{16}$ and alkaline earth-like $W@Si_{16}$ SAs can be soft-landed on *n*-type C_{60} substrates. For structural analysis of non-crystalline $M@Si_{16}$ SAs, the extended x-ray absorption fine structure (EXAFS) analyses presents a promising avenue, where the EXAFS vibrations are simulated by FEFF analysis of candidate structures with quantum chemical calculations.

Furthermore, halogen-like Al_{13}^- and $B@Al_{12}^-$ SAs can be soft-landed on organic substrates pre-deposited with *p*-type HB-HBC substrates, and the electronic states are characterized as chemically robust SAs by X-ray photoelectron spectroscopy [2,3]. Comparing $Ta@Si_{16}/C_{60}$ and Al_{13}/HB-HBC, $Ta@Si_{16}/C_{60}$ is more stable for fabricating uniformly decorated substrates with SA assemblies [4]. These results underscore the significance of organic molecule selection in controlling the NC assembled materials through optimizing the cluster–surface interaction.

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[2] M. Shibuta, T. Inoue, T. Kamoshida, T. Eguchi, A. Nakajima Nat. Commun. 13, 1336 (2022)

[3] T. Inoue, M. Hatanaka, A. Nakajima J. Am. Chem. Soc. 145, 23088 (2023)

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Cluster-assembled Computers

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Self-assembled nanoparticle or nanowire networks have recently come under the spotlight as systems able to obtain brain-like data processing performances by exploiting the memristive character and the wiring of the junctions connecting the nanostructured network building blocks.

Recently we demonstrated that nanostructured Au films, fabricated by the assembling of gold clusters produced in the gas phase, have non-linear and non-local electric conduction properties caused by the extremely high density of grain boundaries and the resulting complex arrangement of nanojunctions. Starting from the characterization of this system, we proposed and formalized a generalization of the Perceptron model to describe a classification device based on a network of interacting units where the input weights are non-linearly dependent. This model, called ''Receptron'', provides substantial advantages compared to the Perceptron as, for example, the solution of non-linearly separable Boolean functions with a single device.

Here I present and discuss the practical application of the Receptron model to the realization of electronic components for the classification of Boolean function without previous training and the fabrication of arithmetic logic unit circuits based on cluster-assembled devices.

Born differently: how the formation process affects catalytic properties

<u>Francesca Baletto</u>[1,2], **Mirko Vanzan**[1], **Sofia Zinzani**[1], **Leticia Finger-Basso**[1,4], **Kevin Rossi**[2,3], **Vagner Rigo**[4,1]

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[3] *Mechanical Engineering, TU Delft, Netherlands*

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This talk focuses on how to model the formation process of metallic and bimetallic nanoparticles (nanoalloys) -as supposed to occur inside gas aggregation sources- can affect their chemo-physical properties. Based on classical molecular dynamics simulations, we discuss how we can model the formation nanoparticles, often far from their global minimum [1]. We focus on Au and Pt-based nanoalloys as AuRh and AuPd. The latter have naïve optical properties related to the local chemical arrangement, which might affect their plasmocatalytic behaviour [2]. We discuss the implication of surface re-organisation on the catalytic properties of nanoparticles, adopting a multiscale approach, nanoCHE. As paradigmatic examples, we consider oxygen reduction on Pt-nanoparticles and the conversion of CO_2 in methane on Cu-nanoparticles [3]. If time allows, we discuss the adsorption of ethanol and how the description of adsorption sites is affected [4].
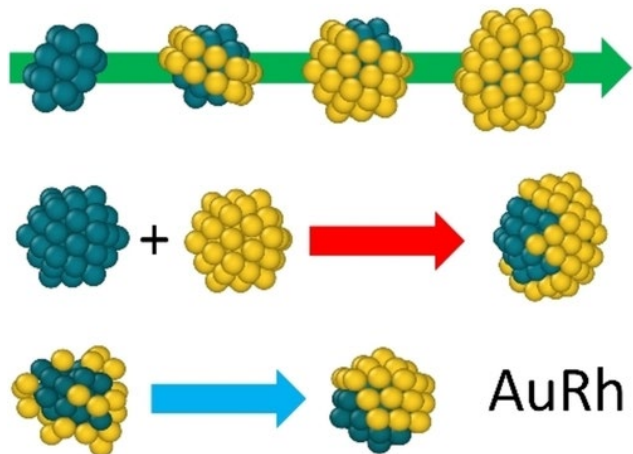
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Oxygen adsorption on the topmost layer of graphene supported Pt clusters

F. Loi[1], L. Bignardi[1], D. Perco[1], A. Berti[1], P. Lacovig[2], S. Lizzit[2], A. Kartouzian[3], U. Heiz[3]. D. Alfè[4], and A. Baraldi[1,2]
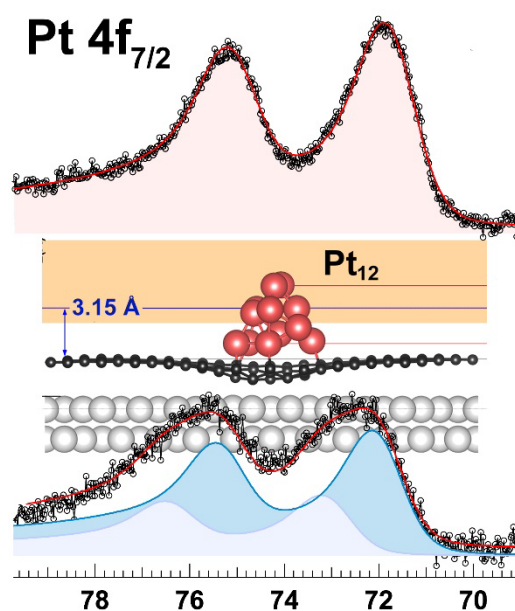
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[2]*Elettra Sincrotrone Trieste, AREA Science Park, 34149 Trieste, Italy*
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The science of surfaces and interfaces has always garnered significant interest in the understanding of the adsorption sites of atoms and molecules which, originating from the gas phase, interact with solids. The diversity of properties that molecules assume in different configurations (bond energy, vibrational frequencies, etc.) proves to be of utmost importance for an in depth understanding of chemical reactions. While the ability to distinguish adsorption sites on a wide variety of crystalline surfaces has become a common feature of several surface science experimental techniques, understanding the positioning of atoms and molecules on clusters composed of only a few atoms, which do not exhibit a crystalline structure, is much more complicated. In this work, which combines high-resolution core-level photoemission experiments with ab initio calculations, we show how oxygen, resulting from a photodissociation process, tends to adsorb on the upper layers of small size-selected Pt clusters. The reasons for these results can be found in the particular pinning process of the graphene layer on which the Pt clusters are deposited and in the non-uniform and layer-dependent electronic charge redistribution in the clusters.

Mass selected ions in vacuum: unexploited synergies in nanoscience

<u>Andreas Walz</u>[1,2], Annette Huettig[1,2], Michael Walz[1,2], Hartmut Schlichting[1,2], and Johannes V. Barth[1]

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[2] *pureions GmbH, Germany*

Cutting-edge research in the field of nanoscience – electronics, solar, catalysis, or bioresearch – requires an unbiased understanding of the structure-related properties of its building blocks. Ions, sorted by mass-, charge- or structure-recognizing methods, play an increasing role in these experiments. Common substances span a wide range in size – metal atoms, clusters, nanoparticles; (bio) organic molecules up to MDa proteins, DNA and viruses. Numerous ionization methods such as electrospray, MALDI, and plasma techniques e.g. laser ablation or magnetron sputtering are established. This multidimensionality led to a highly branched community with individual, often self-built tools. Potential synergies, so far undiscovered, are worth to be exploited. One shared feature of most devices is collimation of ions to a beam, typically at elevated pressure, and their transfer to higher vacuum for mass selection.

In-line with this, we present an ion beam deposition device currently supplied by an ESI-source. The main body contains RF-driven high-transmission (>80% efficiency) ion guides - stacked ring and high order multipole - allowing for lowest residual gas loads and small beam diameters down to < 2 mm. Digital square-wave supply electronics for ion guides and the quadrupole mass filter with adjustable amplitude and frequency provide a virtually unlimited m/z-range - so far tested from m ≈ 200 Da - 2 MDa and m/z ≈ $10^2 – 10^5$. The QMF reaches high resolving power $R_{max} > 650$ and transmission $T_{max} > 80\%$. Overall efficiency of an ion from the source to be mass selectively deposited in UHV is about 25 % ($I_{source} \approx 10$ nA, $I_{depo} \approx 2.5$ nA, limited by the ESI source) within an almost benchtop sized system (50 x 100 cm).

The highly efficient and modular ion guidance and mass selection is broadly adaptable to any ion/beam size. All components/electronics may be used stand-alone or in combination with existing systems and new devices to foster nanoscience.

Wet-chemical synthesis and catalytic properties of metal clusters of small atomicity without protecting ligands

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Metal nanoclusters show very different properties than both, nanoparticles, and bulk, due to the quantum confinement of the free electrons [1]. Such nanoclusters can be seen as super-atoms (or molecules) in which atoms are linked by strong covalent bonds [2]. In the past decade, we have developed wet-synthetic methods, based on kinetic control without binding ligands, to produce monodisperse nanoclusters (mainly of Au, Ag and Cu) of small atomicity ($<\approx$ 20 atoms) at pilot scale ($>\approx$ g/day) [3]. In this talk we will describe the background of this technique and analyze some of their catalytic activities for both, unsupported clusters in solution and supported on different substrates. Among the main outcomes we can highlight that Au_5 clusters display high catalytic activities for the aerobic oxidation of thiophenol to disulphide [4]. Very recently, we have also reported exceptional catalytic activities of Ag_5 clusters for the irreversible aerobic oxidation of thiols [5]. We observed that there is a volcano-type behavior for the size-dependent catalytic activities in the size range 2-10, being the highest catalytic activity around 5 atoms. There is also an increasing catalytic activity in the series $O_2 < H_2O_2 < OH$ radicals, which was used to demonstrate a new catalytic approach to cancer therapy [5]. Ag_5 and Cu_5 were also used as catalytic radical scavengers in industrially relevant processes involving detrimental free radical formation such as polymer stabilization [6] and as catalyst/photocatalyst in the production of pure hydrogen by a novel photo-thermal looping process [7]. Finally, we will briefly comment on the use of Cu_5 clusters for the activation of 2D polymerization on insulating surfaces reducing the polymerization temperatures by $\approx$ 100ºC [8].

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Defect Migration Behind Resistive Switching at Metal Oxides Surfaces

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University of Lodz, Faculty of Physics and Applied Informatics, Lodz, Poland

Titanium dioxide serves as a model material within the category of transition metal oxides, due to its significance in illustrating the fundamental mechanisms of redox processes. A comprehensive understanding of the physical phenomena inherent in this material is imperative for advancing the optimization of its diverse applications. Particularly, TiO_2 has gained attention as a memristive material, where resistive switching phenomena offers potential for information storage, presenting notable implications for neuromorphic computing. Our investigation successfully demonstrated the feasibility of achieving high-density data storage within the surface layer of TiO_2 [1]. This accomplishment is directly linked to the generation of quasi-homogeneous switchable regions near the surface. Moreover, we describe the origins of crystallographic defects responsible for the electronic properties of the material [2]. Our findings highlight that thermal treatment under ultra-high vacuum conditions serves as merely the initial step in surface reduction, rendering it electrically active. Importantly, we establish that additional internal processes play a crucial role in shaping the final properties of the surface layer, thereby influencing its applicability. Utilizing X-ray photoelectron spectroscopy in conjunction with computational calculations, our investigation provides insights into the phenomena governing the spatial distribution of the final stoichiometry of TiO_{2-x}. Additionally, we discern the determinants of the localization of defect structures crucial for investigating the material's electrical properties.

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[2] M. Rogala, et al. Sci. Rep. 9, 12563 (2019)

Time evolution of PAHs and molecular crystals upon light irradiation

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Can quantum dynamics methods be used to predict the behaviour of extended conjugated materials or molecular crystals after photo-excitation? Is quantum dynamics, usually used to describe low dimensionality molecules in gas phase, ready to take a step forward towards big systems?
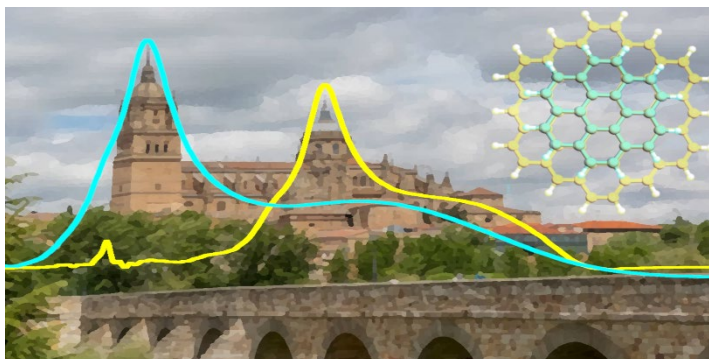
The first part of the presentation explores what happens after shining UV light on coronene and circumcoronene, small models for graphene dots and polycyclic aromatic hydrocarbons (PAHs).

The ML-MCTDH quantum dynamics method [1] is used to understand how these molecules evolve over time after being excited. The movements of breathing and tilting drive the excited states towards their deactivation independantly of the size of the system. This exciting finding suggests that coronene can be used as a simple model to understand how larger molecules like graphene sheets or nanoflakes behave after light irradiation [2].

In the second part, efforts made in the group to understand the photoexcited behaviour of molecular crystals that have photosensitizing potential will be covered. In particular, molecular crystals of tetraphenylpyrazine -known to present fluorescence enhancement due to their aggregation state- are presented and the deactivation mechanisms towards the emissive state will be explored [3].

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[3] J. Hernández-Rodríguez, A. Martín Santa Daría, S. Gómez-Carrasco, S. Gómez, in preparation

Direct Conversion of Methane to Methanol on Metal Clusters Functionalized Ceria Surfaces: Metal-Support Interactions

<u>Junjie Shi</u>[1,2*], Wen Li[2], Yigit Nevzat[1], Yong Qin[2], Günther Rupprechter[1]

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The direct conversion of CH_4 to CH_3OH is viewed as a "holy grail" in chemistry. It is been considered a dream reaction for industry, as methanol is a useful fuel and building block for many chemicals. However, grand challenge arises not only from the activation of the inert C−H bonds in CH_4 but also from the overwhelmingly higher reactivity of CH_3OH compared to CH_4. Recent ultra-high vacuum (UHV) model study demonstrates that metal-oxide interfaces ($CeO_x/Cu_2O/Cu(111)$, $Ni/CeO_2(111)$) can catalyze the direct conversion of methane to methanol at 300-450K upon exposure to a gas mixture of CH_4, O_2 and H_2O with high selectivity. Inspired by this, we conducted research under ambient conditions using the ceria-based catalyst in continuous flow reactor. Our results point that CH_3OH can be produced continuously on Cu/CeO_2, Au/CeO_2 at ambient pressure with high selectivity (~100%). The CH_3OH yields is around 7μmol/h/g on Cu/CeO_2 at 500 °C, which is around 7 times of Au/CeO_2. Both O_2 and H_2O play key roles in promoting the CH_4 conversion to CH_3OH, with either of them no CH_3OH can be produced. The state-of-the-art operando characterization methods (In-situ DRIFTS, NAP-XPS) will be used to identify and track the structural changes of the active sites under "working" conditions, in the same time, the reaction mechanism can be analyzed.
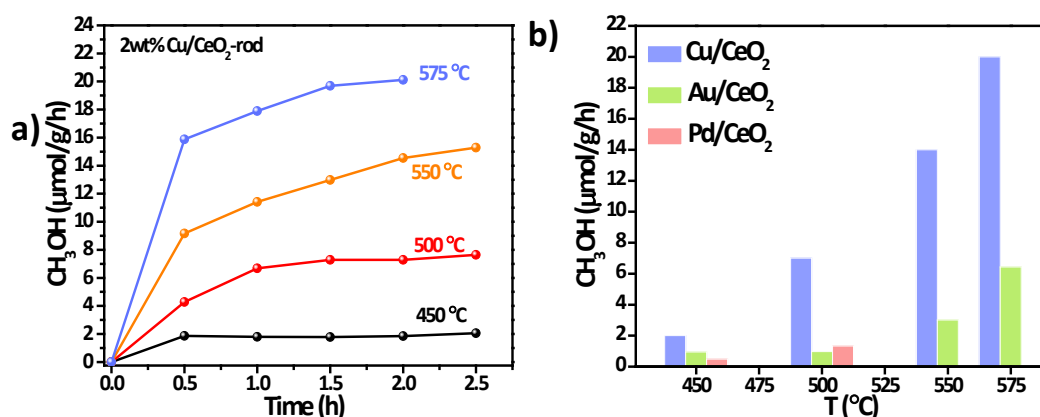

Figure 1. a) Steady-state temperature profiles of 2wt% Cu/CeO₂-rod catalyst for the direct CH₄→ CH₃OH reaction (28 vol% CH₄/9.4 vol% O₂/53 vol% H₂O/9.6 vol% N₂, 160 mL/ min, m_catal = 200 mg, space velocity 48000 mL h⁻¹ g_cat⁻¹); b) Compare activities of Cu/CeO₂, Au/CeO₂ and Pd/CeO₂ for the direct CH₄→ CH₃OH reaction.

[1] J. Shi, G. Rupprechter et al., Appl. Catal. B. 2022, 301, 120789

[2] Z. Zuo, P. Liu, J. Rodriguez et al., J. Am. Chem. Soc. 2016, 138, 13810–13813

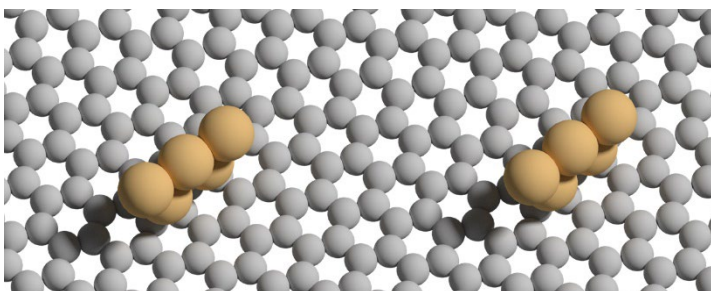[3] V. Sushkevich, J. van Bokhoven et al., Science. 2017, 356, 523–527

Confinement and Dimerization of Cu₅ on Graphene

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Atomically precise metal clusters (AMCs) are nanoscale structures known for their impressive properties and applications [1,2]. Graphene, a two-dimensional material with high stability and remarkable conductivity, is a suitable candidate as an ideal support for AMCs [3]. Our study delves into the interaction between two Cu₅ clusters on a single graphene sheet, pristine and defective. In particular, we examine how carbon vacancies influence the clusters' stability, configuration and confinement through ab initio molecular dynamics simulations, while the dimerization of the two clusters on pristine graphene are studied, with density functional theory results validated by more refined post Hartree-Fock methods. The quantum mechanical computations were executed via ORCA [4], MOLPRO [5], and the VASP software [6], with the CP2K code specifically employed for ab initio molecular dynamics simulations, known for its efficiency [7]. The Langevin ensemble and adaptive-Langevin thermostat were used in these simulations, with a time step of 2 fs. The AIMD simulations were performed using a single gamma point sampling of the Brillouin zone, while 5×5×1 k-points of the Monkhorst-Pack method were chosen for the DFT computations. The results revealed that while separate planar Cu₅ clusters typically dimerize into a larger Cu₁₀ dimer with a three-dimensional structure on a pristine graphene surface, when carbon vacancies are present, this traps the Cu₅ clusters, causing them to optimized to a trigonal bipyramidal 3D structure and remain isolated as individual clusters. This confinement substantially stabilizes the clusters, leading to a significantly favorable adsorption energy of the Cu₅ clusters onto the graphene. Note that similar behavior for confinement and particularly dimerization are noticed at varrying tempratures (300, 400 and 600 K).

[1] F. Dhayal et al. Dalton Trans. 48, 3531-3538 (2019)

[2] H. Zhai et al. ACS Catal. 11, 6210-6224 (2017)

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[4] F. Neese, Wiley Interdiscip. Rev. Comput. Mol. Sci. 2, 73-78 (2012)

[5] H.J. Werner et al. MOLPRO, version 2021.2, a package of ab inito programs, see https://www.molpro.net

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[7] T. Kühne et al. J. Chem. Phys. 152, 194103 (2020)

The effect of solvation on the properties of pristine and defective oxide interfaces for solar water splitting: Insights from the BiVO$_4$(010) surface

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Solar water splitting holds immense promise for sustainable energy production, with semiconductor/water interfaces playing a pivotal role in the process. Understanding the influence of solvation on electronic band edges is crucial for optimizing such interfaces, particularly for the oxygen evolution reaction (OER). This study investigates the impact of solvation on the electronic properties of the bismuth vanadate BiVO$_4$(010) surface, a promising photoanode material for photo-electrochemical water splitting [1]. Employing first-principles molecular dynamics simulations (FPMD) at the strongly constrained and appropriately normed (SCAN) level of theory, we delve into the intricate interplay between surface composition, water adsorption, hydroxylation, and electronic band alignment including effects due to structural fluctuations. Our findings reveal that surface composition (stoichiometric vs bismuth-rich) significantly influences the band edges of the oxide/water interface [2], with water adsorption and hydroxylation modulating band alignment crucial for efficient charge transfer during the OER. Additionally, we highlight the pronounced effects of surface defects and their behavior at finite temperature, particularly neutral oxygen vacancies, on shifting and altering the band gap of BiVO$_4$.

Doping induced by these defects strongly influences the semiconductor's photoelectrochemical performance. Furthermore, employing FPMD simulations allows us to predict structural and vibrational properties of the aqueous interfaces, in agreement with X-ray photoelectron spectroscopy (XPS) measurements, strengthening the reliability of our simulations [3].

These atomistic insights pave the way for designing rules of new photocatalysts starting from Earth-abundant substrates, such as ZnO, TiO$_2$, or α-Al$_2$O3, leveraging optimal oxygen vacancy concentrations to tailor band alignment for water oxidation, and advancing sustainable energy solutions. For such photo-catalysts a combination of DFT-based simulations with advanced-machine learning techniques is being developed.

[1] D. Lee, W. Wang et al. Nat. Energy (2020)

[2] W. Wang et al. J. Am. Chem. Soc., (2022)

[3] G. Melani, W. Wang, C. Zhou, M. Liu, K.-S. Choi, G. Galli, *in preparation* (2023)

Characterizing temperature, charging and adsorption dynamics of single nanoparticles [01]

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Single nanoparticle (NP) techniques allow to probe intrinsic properties of nanoparticles, but typically rely on surface deposition. Instead, we develop the analysis of single NPs in the gas phase using a cryogenic radio-frequency ion trap and UV/Vis [1,2] or IR action spectroscopy. Absorption is indirectly monitored using NP mass spectrometry (NPMS): the produced heat causes the loss of messenger atoms or molecules that are adsorbed to the particle surface. Here, we present current progress on controlling and characterizing the charge state, temperature and surface coverage of single trapped NPs that will ease the implementation and quantitative analysis of future experiments.

Inducing charge changes is crucial for absolute mass determination and facilitates control in long experiments ($\sim$ days). Using a filament to emit electrons for electron attachment or charge transfer — mediated by different collision gases at different pressures — we demonstrate full control of the charge state of positively charged silica NPs.

Characterizing binding sites and energies is an important goal for NP characterization and essential for quantitative action spectroscopy. Extensive adsorption measurements on silica NPs are presented and we demonstrate in situ fluorescence thermometry for semiconductor quantum dots. We will report on the latest progress to simultaneously measure temperature and adsorption on single fluorescent nanoplatelets

[1] B. Hoffmann et al., J. Phys. Chem. Lett. 2020, 11, 15, 6051 (2020)

[2] B. Hoffmann et al., Molecular Physics, 122:1 (2024)

Diffusion of Pt atoms on epitaxial graphene: a combined experimental and ab initio study [02]

A. Berti[1], R. Bergua[3], D. Perco[1], L. Bignardi[1], S. Lizzit[2], P. Lacovig[2], E. Jimenez-Izal[3] and A. Baraldi[1,2]

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[2]*Elettra Sincrotrone Trieste, AREA Science Park, 34149 Trieste, Italy*

[3]*Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia Saila Kimika Fakultatea Euskal Herriko Unibertsitatea (UPV/EHU) & Donostia International Physics Center (DIPC), Euskadi, Spain*

Platinum-nanoparticle-based catalysts are widely used to fabricate high-performance heterostructure devices, such as fuel cells. The possibility to employ carbon-based supports such as graphene opens up promising applications due to the prospect to control and enhance the catalytic properties of Pt. To accomplish this goal, it is key to achieve a deep understanding of the diffusion dynamics of Pt atoms on the support [1-3], as graphene often interacts very weakly with adatoms. In this study, using a novel approach based on high resolution core-level spectroscopy combined with *ab initio* density functional theory, we systematically investigate the low-temperature diffusion of Pt monomers on epitaxial graphene, to shed light on the formation of small Pt clusters with different atomic sizes. Our approach involves a real-time investigation of the evolution of Pt on graphene grown on Ir(111) [4], from deposited single Pt atoms to nucleated sub-nanometer clusters. Thanks to the energy resolution and photon flux achieved in the X-ray photoelectron spectroscopy measurements and to the extended set of DFT calculations, we disentangle the contribution arising from the different Pt species forming on graphene, which mainly results in the appearance of shifted spectral components. The combination of experimental results and *ab initio* calculations is crucial to shed light on the diffusion processes behind this system.
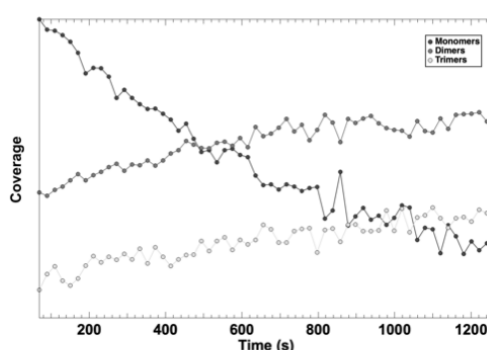
(a) Uptake curves for the monomers, dimers and trimers species.
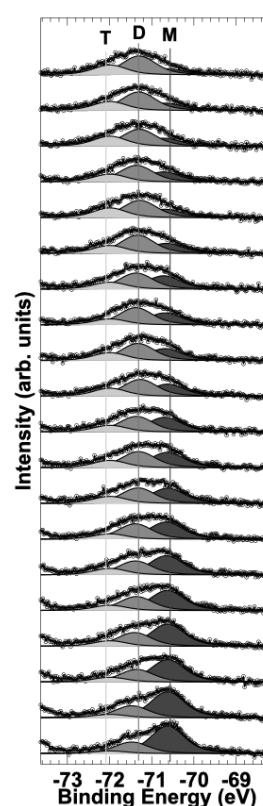
(b) Evolution of the Pt 4f$_{7/2}$ core level acquired in real-time during the diffusion process

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[2] Petrov, I.; Barna, P. B.; Hultman, L.; Greene, J. E., J. Vac. Sci. Technol., A 21, S117–S128 (2003)

[3] Sarakinos, K., Thin Solid Films 688, 137312 (2019)

[4] L. Bignardi, P. Lacovig, R. Larciprete, D. Alfè, S. Lizzit, A Baraldi, Surf. Sci. Rep. 78, 100586 (2023)

Reactive Machine Learning Potential for Sub-Nanometre Cluster Migration Dynamics in Zeolites and Silica [03]

Tereza Benešová, Lukas Grajciar, Andreas Erlebach, <u>Christopher Heard</u>

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Popular techniques to enhance the stabilization of small noble metal clusters against sintering and deactivation include pinning to (hydroxylated) metal oxide surfaces or encapsulation within zeolite micropores [1]. However, particle diffusion, agglomeration and redispersion processes occur on a timescale too short for many experimental characterisation methods and too long for traditional computational modelling methods. We have tackled the problem of modelling the initial stages of cluster deactivation via growth of clusters up to around 1 nm, through the development of flexible, transferrable reactive neural network potentials [2,3]. These potentials reproduce density functional theory (DFT) with low energy and force errors (< 6 meV/atom and < 150 meV/Å, respectively). This development allows us to perform near-exhaustive, unbiased global structure optimization, long term (ns-scale) dynamical simulations, and characterization of dynamical processes *via* biased dynamics simulations.

In this contribution, I will summarize our recent methodological developments and the atomistic insights that can be obtained through enhanced sampling of clusters with reactive MLPs, including:

a) The importance of reactive interactions with hydroxylated silica supports on the preferred particle structure and mobility of small Pt clusters
b) The non-monotonic effects of cluster size on the cluster migration and agglomeration pathways on silica supports
c) Confinement effects in zeolite micropores

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[2] A. Erlebach, P. Nachtigall, L. Grajciar*, NPJ Comput Mater 174, (2022)

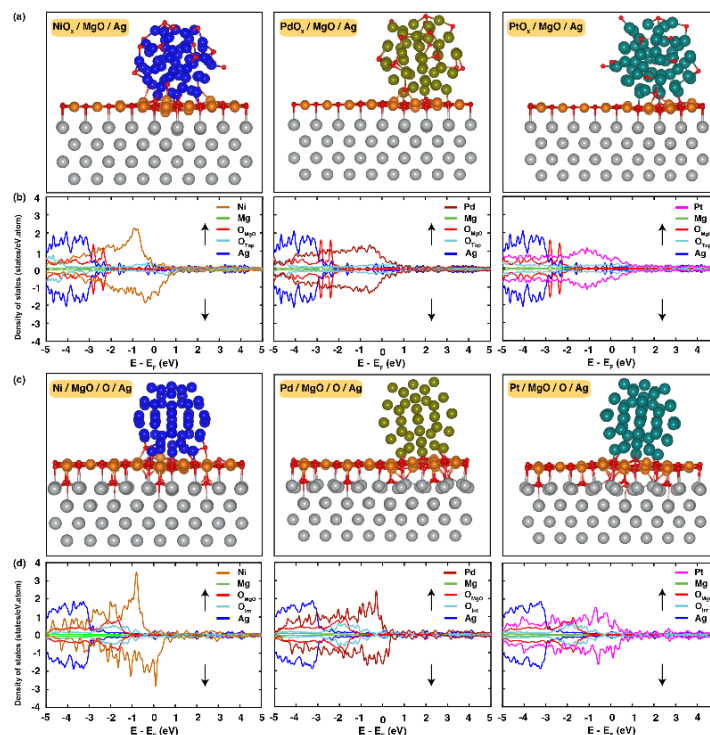[3] Heard, Erlebach, Grajciar, 10.26434/chemrxiv-2023-9g3fn (2024)

Density Functional Theory Investigation of X55 (X: Ni, Pd, and Pt) Nanoclusters on MgO (100) and MgO (100)/Ag(100) Support: Unraveling the Impact of Oxidation [04]

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In this computational study, we employ Density Functional Theory (DFT) to explore the geometrical features and electronic structure of X_{55} (X: Ni, Pd, and Pt) nanoclusters (NCs) on MgO (100) and on an MgO (100)/Ag (100) substrate. Initially, these NCs are deposited on a 3-layer thick MgO (100). The results show a strong covalent between the surface of MgO and NCs. By going down the NCs of group X, the bonding strength and magnetization reduces. Furthermore, these NCs are deposited on MgO/Ag ultrathin films (one monolayer MgO and 4 layers Ag), and results show similar trends in magnetic and electronic properties to those of the systems with a bare MgO film. Analysis of Ab initio molecular dynamics (AIMD) simulations at T= 200 K, simulating the experimental conditions of growth, reveals that these deposited NCs are thermally stable and can preserve their crystalline morphology at elevated temperatures. In addition, by systematically exploring the interaction between the nanoclusters and the MgO/Ag substrates under oxidizing conditions, we provide insights into the mechanisms influencing their energetic stability and electronic properties. The MgO (100)/Ag(100) support system is specifically examined to assess its role in modulating the oxidation dynamics. Our findings contribute to a comprehensive understanding of the interplay between nanocluster materials, oxide supports, and oxidation processes, offering valuable guidance for the design and optimization of catalytic systems in various applications.

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[2] Savio, Letizia, Marco Smerieri, Luca Vattuone, Sergio Tosoni, Gianfranco Pacchioni, and Mario Rocca. "Interface Oxygen Induced Internal Structures of Ultrathin MgO Islands Grown on Ag (100)." *The Journal of Physical Chemistry C* 124, no. 16 (2020): 8834-8842

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(Photo-)conversion of greenhouse gases on TiO$_2$-based catalysts [05]

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CH_4, CO_2 and N_2O are amongst the most prominent greenhouse gases accelerating the climate crisis, one of the major threads of the 21st century [1]. Therefore, capture and utilization of such gases, e.g. by (photo-)conversion to more valuable compounds is desirable.

The well-known photocatalytic properties of the widely available TiO$_2$ polymorphs anatase and rutile, combined with the high reactivity of defects such as Ti^{3+} towards oxygen-containing molecules renders TiO$_2$ as an ideal model system to investigate cost-effective conversion of these greenhouse gases [2,3]. Also TiO$_2$ is known to form efficient hybrid catalysts with metal particles or metal-chalcogenide-clusters like nanostructured copper particles, $(WO_3)_3$ clusters or 2D TMDCs nanoparticles, e.g. MoS_2 to name only few examples [4-6].

In this work we present model studies of the (photo-)conversion of small molecules such as CO_2 and N_2O on a TiO$_2$ Rutile (110) system with and without different types of co-catalysts present. To gain a comprehensive understanding, herein spectroscopic techniques (such as X-ray photoelectron spectroscopy (XPS) and FT Infrared Reflection Absorption Spectroscopy (FT-IRRAS)) will be combined with temperature- programmed desorption (TPD) experiments to probe the population of different reaction pathways and adsorption sites.

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[2] M. Osmić, L. Mohrhusen, K. Al-Shamery, *J. Phys. Chem. C* 2019, *123*, 7615–7626

[3] J. Strunk, in *Metal Oxides in Energy Technologies* (Ed.: Y. Wu), Elsevier, Amsterdam, 2019, 275–301

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(Photo-)conversion of greenhouse gases on TiO$_2$-based catalysts [05]
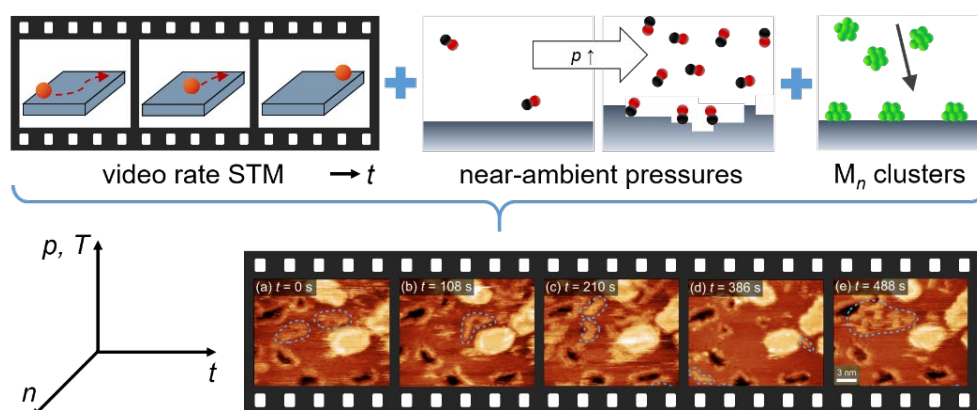
Observing dynamic cluster catalysts [06]

Florian Kraushofer,[1] Matthias Krinninger,[1] Sebastian Kaiser,[1] Johanna E. Reich,[1] Moni Blum,[2] Friedrich Esch,[1] Barbara A. J. Lechner[1]

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[2] Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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Catalyst particles and in particular small clusters are typically highly dynamic during an ongoing reaction. In our group, we investigate structural and chemical changes under reactive gas atmospheres in order to get an atomistic picture of the stability and activity of cluster catalysts. Time-resolved scanning tunneling microscopy (STM) from ultra-high vacuum to the mbar regime, i.e. near ambient pressures (NAP-STM), allows us to systematically study the influence of different gas atmospheres on the surface structure. The microscopy data is complemented by information on chemical composition and oxidation state from NAP X-ray photoelectron spectroscopy (NAP-XPS).

In the CO_2 conversion catalyst In_2O_3/Pd(111), for example, we could follow the evolution of cluster catalysts and capture the catalytically active phase, a mixed oxide phase. The surface chemical, compositional and structural dynamics can be reversibly regulated by switching the atmosphere between reducing and oxidizing environments [1].

In another example, we could disentangle the influence of the reduction state of a reducible oxide support, of the cluster size, and of the gas phase on the strong metal-support interaction (SMSI) induced encapsulation of Pt clusters. By tuning the O_2 pressure, we could drastically change the kinetics of the encapsulation on rutile TiO_2(110) [2]. Changing the reduction state of the rutile support, we could further influence the overlayer growth and the stoichiometry of the encapsulating layer. On Fe_3O_4(001), we observed the diffusion of tiny size-selected Pt clusters even after they became encapsulated [3]. At the same time, we could show that their encapsulation suppresses Ostwald ripening significantly, thus stabilizing the clusters against sintering.

[1] X. Zhang et al., under review

[2] P. Petzoldt et al., *J. Phys. Chem. C* 126, 16127 (2022)

[3] S. Kaiser et al., *ACS Catalysis* 13, 6203 (2023)

## Novel polymerization reaction catalyzed by silver clusters [07]

Xinran Lu[1], **Pilar Prendes González**[2], **Senén Paz Abuín**[2], **David Buceta**[3], **Carlos Vázquez Vázquez**[1], **M. Arturo López Quintela**[1]

[1] *Laboratory NANOMAG, iMATUS, University of Santiago De Compostela (Spain)*
[2] *Dpt I+D+i of GAIRESA (Valdoviño, Spain)*
[3] *NANOGAP (Milladoiro, Spain)*

Metallic nanoclusters, typically less than 1-2nm in size, display different chemical properties than metallic materials in bulk and nanoparticles, attributable to quantum confinement effects. Due to their tiny size, clusters can act as individual active sites in catalysis, which makes them of particular interest.
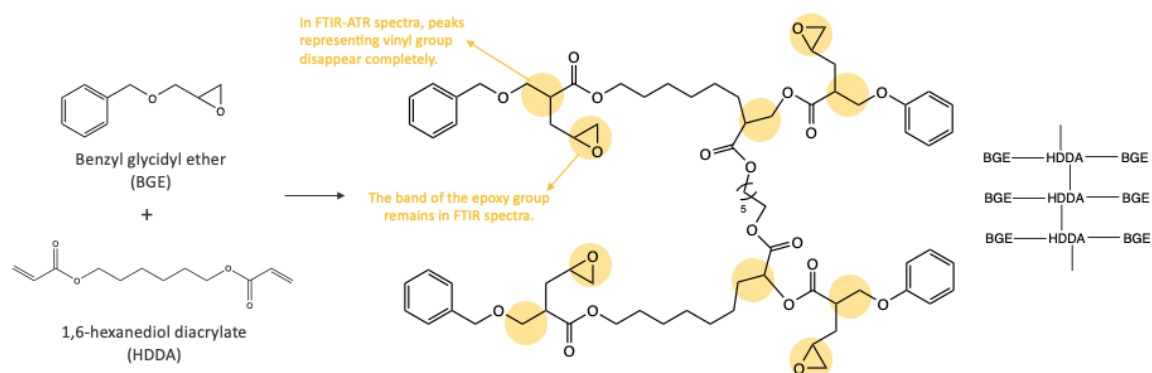
In this work, we report the catalytic activity of silver clusters (Ag_5-Ag_{15}) dispersed in hexanediol diacrylate (HDDA) in a new type of polymerization reaction with diglycidyl ether of bisphenol A (DGEBA). Studies by infrared spectroscopy, nuclear magnetic resonance and differential scanning calorimetry reveal that with Ag clusters the reaction between HDDA and DGEBA seems to proceed via a novel type of mechanism preserving the epoxy groups, contrary to the usual epoxy polymerization. Ag clusters selectively activate the oxygens of ether and ester groups in the presence of a nearby epoxy group, facilitating their reaction with the vinyl group of HDDA. Similar reactions happen with other molecules, such as benzyl glycidyl ether, glycidyl ester of neodecanoic acid, etc. The figure shows the proposed reaction of benzyl glycidyl ether. This new mechanism could be important to the curing of epoxy resin, as the Ag clusters enable it to form a new curing system with HDDA that preserves epoxy groups. Moreover, experimental results suggest that these epoxy groups can further react with traditional hardeners, like amines.

The results demonstrate the prospect of a novel thermostable polymer, setting the stage for broad applications of these new type of cured resins through further research. Since the clusters act as catalysts for the reaction, they also form part of the final product, potentially giving additional properties to the polymer. These properties may include antibacterial activity or potential utility in degradation processes. Further studies pursuing these goals will be conducted in subsequent work.

The effect of solvation on the properties of pristine and defective oxide interfaces for solar water splitting: Insights from the $BiVO_4(010)$ surface   [08]

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Solar water splitting holds immense promise for sustainable energy production, with semiconductor/water interfaces playing a pivotal role in the process. Understanding the influence of solvation on electronic band edges is crucial for optimizing such interfaces, particularly for the oxygen evolution reaction (OER). This study investigates the impact of solvation on the electronic properties of the bismuth vanadate $BiVO_4(010)$ surface, a promising photoanode material for photo-electrochemical water splitting [1]. Employing first-principles molecular dynamics simulations (FPMD) at the strongly constrained and appropriately normed (SCAN) level of theory, we delve into the intricate interplay between surface composition, water adsorption, hydroxylation, and electronic band alignment including effects due to structural fluctuations. Our findings reveal that surface composition (stoichiometric vs bismuth-rich) significantly influences the band edges of the oxide/water interface [2], with water adsorption and hydroxylation modulating band alignment crucial for efficient charge transfer during the OER. Additionally, we highlight the pronounced effects of surface defects and their behavior at finite temperature, particularly neutral oxygen vacancies, on shifting and altering the band gap of $BiVO_4$.

Doping induced by these defects strongly influences the semiconductor's photoelectrochemical performance. Furthermore, employing FPMD simulations allows us to predict structural and vibrational properties of the aqueous interfaces, in agreement with X-ray photoelectron spectroscopy (XPS) measurements, strengthening the reliability of our simulations [3].

These atomistic insights pave the way for designing rules of new photocatalysts starting from Earth-abundant substrates, such as ZnO, TiO_2, or α-Al_2O3, leveraging optimal oxygen vacancy concentrations to tailor band alignment for water oxidation, and advancing sustainable energy solutions. For such photo-catalysts a combination of DFT-based simulations with advanced-machine learning techniques is being developed.

[1] D. Lee, W. Wang et al. Nat. Energy (2020)

[2] W. Wang et al. J. Am. Chem. Soc. (2022)

[3] G. Melani, W. Wang, C. Zhou, M. Liu, K.-S. Choi, G. Galli, *in preparation* (2023)

Model Photo(-electro)catalysis in the Liquid Phase [09]

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Hydrogen production via photocatalytic oxidation of organic compounds is considered a promising alternative to conventional steam reforming [1]. While alcohol photoreforming on TiO_2 has been extensively studied at different conditions at ambient pressure [2, 3] and in ultra-high vacuum (UHV) [4], several mechanistic aspects remain unsolved to date, which are highly relevant for bridging the pressure and material gap between the investigated systems. The developed liquid phase setup is specifically tailored for the comprehensive characterization of liquid and gas phase photoproducts in small sample concentrations by an online gas chromatograph.

Herein, we illustrate the technical aspects, particularly relevant for the evaluation of model catalysts, which are often available only in low quantities. We discuss possible applications in photo(-electro)catalysis, namely ethanol photooxidation on Pt/TiO_2 and oxygen evolution arising from photoelectrocatalytic water splitting on $BiVO_4$ thin films.

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Hunting Oxygen in MoS$_2$-based hydrotreatment catalysts for biooils: Combined insights from STM & XPS from UHV to o*perando* conditions   [10]

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Hydrotreatments of (fossil) oils using promoted MoS$_2$-based catalysts are well-established industrial processes, primarily for the removal of heteroatoms (S, N, O, …) [1-3]. The process is currently becoming more relevant in the energy transition, e.g. for upgrading of biooils from sustainable feedstocks such as sewage sludge or biomass pyrolysis. However, such biooils appear as complex feedstocks that are rich in impurities and heteroelements (O, N) and thus remain challenging due to stability problems and catalyst deactivation [4].

In contrast to the established use in (oxygen free) hydrodesulphurization (HDS), where in-situ formed S vacancies act as active sites, the sulphide catalyst will be exposed to nitrogenates and oxygenates in the desired hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) processes. Thus, S atoms may be partially exchanged by N or O, triggering an active site blocking and strong catalyst degradation on the long term [5,6].

As a well-defined model system, this work investigates 2D MoS$_2$ nanoparticles on Au (111) surfaces (fig. 1) being exposed to H$_2$ and N or O containing molecules at relevant temperatures to mimic hydrotreatment conditions. Herein, we present combined insights from scanning tunnelling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) from UHV to near-ambient pressure (NAP) conditions to elucidate the underlying processes at an atomistic level. Our results show that the MoS$_2$ nanoparticles are generally surprisingly robust but respond to elevated H$_2$O levels by a small uptake of oxygen starting from the particle corners and edges, leading to an ongoing restructuring of the catalyst under ongoing phase separation. The oxidation-reduction equilibrium can be steered by the presence of hydrogen in the feed.
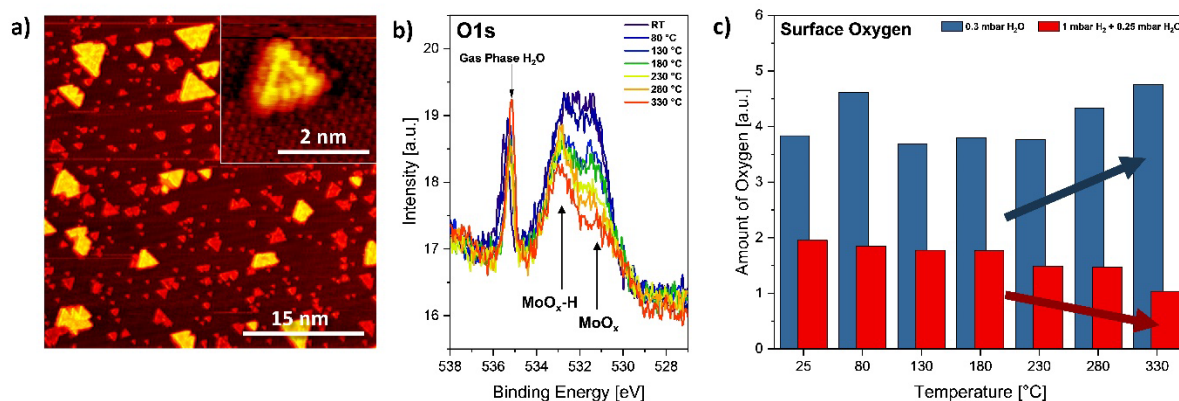
Figure 1: a) Scanning tunneling micrograph of 2D MoS$_2$ nanoparticles on a Au(111) support. b) operando O1s NAP-XPS of MoS$_2$/Au(111) in H$_2$ and H$_2$O. c) Analysis of surface oxidation.

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Investigation of electrical properties of MoO$_{3-x}$ nanoclusters for ReRAM applications [11]

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α phase MoO$_3$ exhibits a layered orthorhombic crystalline structure with intriguing electronic and optical properties. Its n-type semiconducting properties, wide bandgap and high relative permittivity render it suitable for diverse electronic and optoelectronic devices, such as in energy and memory storage, catalysis, sensors and organic light-emitting diodes.

Here we study electrical properties of molybdenum trioxide two-dimensional (2D) nanoclusters epitaxially grown on highly oriented pyrolytic graphite (HOPG) [1, 2]. In presented investigations the bottom HOPG substrate serve as conductive electrode, facilitating electrical measurements. Atomic force microscopy measurements were conducted using a conductive AFM probe as the top movable electrode, allowing for local electrical characterization with high spatial resolution. The obtained conductive maps provide insights into the heterogeneity of electrical properties and the presence of defects within the MoO$_{3-x}$ 2D clusters. Furthermore, current-voltage curves were acquired at various points across the sample surface, revealing the non-homogeneous conductivity behavior [3].

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Photoreforming of Alcohols at Ambient Conditions in a Newly Designed μ-Reactor [12]

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The production of hydrogen from water or alcohols using solar light is a sustainable alternative to currently dominating fossil fuel energy carriers.

While extensive studies on photoreforming alcohols in ultra-high vacuum (UHV) using model catalysts provide new conceptual insights, transferring these findings directly to applied conditions remains questionable. In contrast, gaining a mechanistic understanding from studies at ambient conditions in the liquid phase on powder catalysts is challenging due to the material's intrinsic heterogeneity.

Hence, we investigate low surface area planar substrates in a well-defined environment under ambient conditions in the gas phase to directly link specific material properties to catalytic activity. Our newly developed micro-dimensional reactor, operating with wavelengths of the solar spectrum, allows for sensitive and time-resolved product detection by mass spectrometry, which is achieved by a lid-integrated capillary defining the low reactant flow through the reactor. Additionally, the reversible sealing of the reactor enables catalyst characterization in situ and post-reaction.

First experiments on photoreforming alcohols over Pt-loaded TiO_2 already showed similar product selectivities as in UHV suggesting the absence of a pressure gap, which enables a comprehensive interpretation of the surface photochemistry of both systems.

Metal cluster mediated N₂ activation and cleavage [13]

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It is generally understood that transition metal clusters (TMC) may serve as model systems for chemical active surfaces, as they occur e.g. on catalytically active nano particles. Our group is conducting an ongoing research program that utilizes atomically precise TMCs and characterizes their surface morphologies through molecular interactions with N_2 and H_2. We found cases of dinitrogen (N_2) activation and spontaneous cleavage even under isothermal cryo conditions [1,2,3]. By this contribution we will report on the current state of understanding and on new findings which elucidate the influence of cluster charge state, and which identifies collaborative effects amongst multiple adsorbate molecules on the surfaces of the investigated clusters. We discuss the validity of the across edge – above surface (AEAS) mechanism of N_2 cleavage [1], and we will report on the current insights on the underlying interactions. We will also present some results of ongoing work on dihydrogen (H_2) activation, and we give reference to our initial experiments on $H_2 – N_2$ co-adsorption [4].
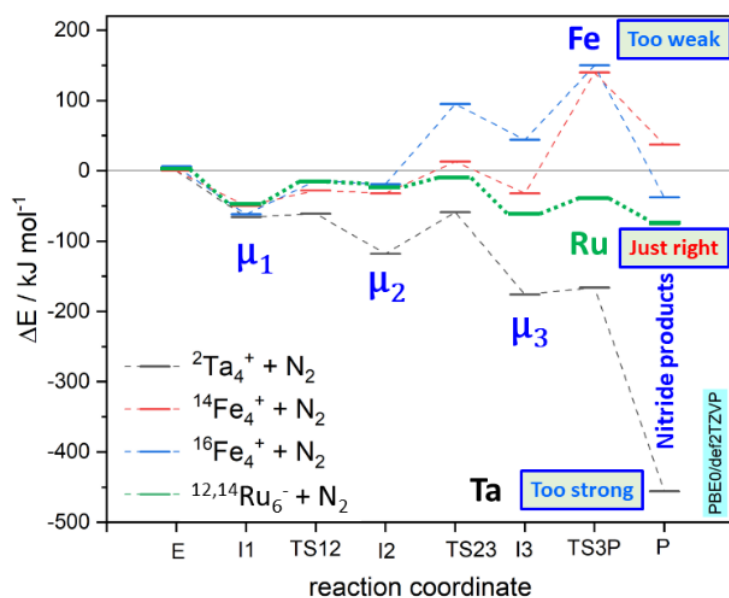
The observed spontaneous N_2 cleavage by Tantal clusters found interpretation by the AEAS mechanism that invokes consecutive $\mu_1 – \mu_2 – \mu_3$ – chains of N_2 coordination. DFT modelling of conceivable N_2 activation by Iron clusters and by similar Ruthenium clusters points towards most similar reaction pathways but strong variation of interaction strengths.

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Caesium-sputtering cluster source for small (N<10 atoms) cluster deposition at Paris Nord [14]

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This poster describes a mass-selected cluster deposition source recently transferred from Swansea University to Université Sorbonne Paris Nord to study metal clusters on semi-conducting substrate and their interactions with light.

The Cs-ion sputtering (Alton) source produces small, mass-selected clusters of atoms by direct sputtering without gas condensation. Caesium also coats the sputtered target and thus reduces the work function so the yield of negative cluster ions is high (nA). The source, originally built by Hall and Palmer in the 1990s [1], is designed to be compact and portable and the absence of gas condensation reduces the need for differential pumping when it is attached to an ultrahigh vacuum (UHV) deposition system [1]. Following recent refurbishment in Swansea, the sputter source can now produce, mass-select and deposit a beam of negative clusters, clusters with variable impact energy. Mass selection employs a compact Wien velocity filter, significantly reducing the source's size. A 10° beam deflector is placed behind the Wien filter to prevent neutral clusters from landing on the sample. The source can produce small clusters ranging from 1 to 10 atoms per cluster, focused on a 3 mm² area. The source can produce beams of a wide range of materials, including noble metals, carbon and silicon [2] and established a new collaboration between Swansea and Paris Nord in functional nanomaterials.
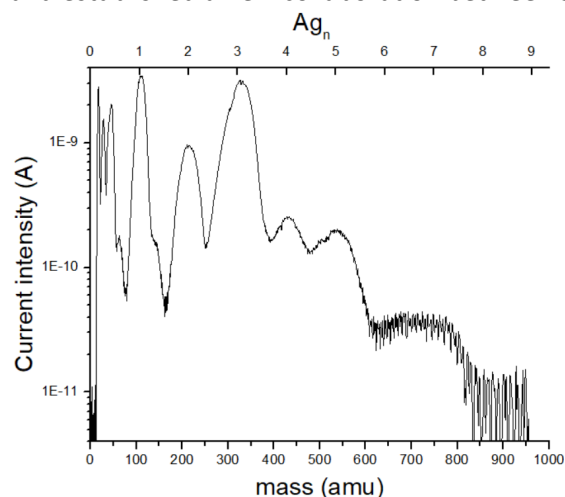

Figure 1 - Mass spectrometry performed with a Ag target. X-axis is the mass in atomic mass units. Vertical axis represents the current collect on the deposition plate (logarithmic scale) and the top axis indicates Ag cluster size.

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The Role of Metal Clusters in Heterogeneous Photocatalysis: Alcohol Photooxidation on Pt_n/TiO_2(110) [15]

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Heterogeneous photocatalysis offers the prospect of utilizing solar energy for the environmentally benign production of valuable chemicals such as hydrogen. In order to improve the efficiency of photocatalytic materials, researchers usually focus on driving forces on charge carriers, hereby adopting a purely thermodynamic view on the catalytic reactions. In comparison, the surface chemistry and reaction kinetics of these materials are commonly neglected, even though their crucial role is self-evident in thermal catalysis. Addressing this important aspect, we employ surface science methods to study photocatalysts under highly defined conditions using single crystal semiconductors and atomically precise noble metal clusters to obtain mechanistic insights on the molecular scale.

In this presentation, we focus on the photocatalytic hydrogen evolution from alcohols over rutile TiO_2(110) loaded with Pt cluster co-catalysts. Our experimental evidence reveals a new reaction mechanism, which substantially differs from the generally assumed model of independent redox reactions [1,2]. By individually changing active sites for both the alcohol oxidation and the hydrogen evolution reaction, we further show that the overall photoactivity strongly depends on the equilibrium of a reaction network of several elementary photo- and thermal reaction steps. Our results provide new mechanistic insights into the photocatalytic hydrogen evolution from Pt loaded TiO_2 and illustrate the importance of a comprehensive understanding of the photocatalysts' (surface) chemistry.

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Atomically Precise Supported CuPd Clusters: Catalysts for CO$_2$ Conversion

[16]

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The production of value-added products (e.g., methane, methanol, etc.) from carbon dioxide and hydrogen offers a promising avenue for sustainable energy production and CO$_2$ utilization. However, under mild conditions, CO$_2$ hydrogenation presents a significant challenge due to the high stability of the CO$_2$ molecule. In recent years, significant research efforts have been devoted to exploring novel catalytic systems for this conversion process. Among these, subnanometer-sized supported clusters have emerged as particularly intriguing candidates. By tailoring the size and composition of clusters, the electronic and geometric properties of the clusters can be fine-tuned, thereby enabling the proper adjustment of their catalytic activity and selectivity. This can be further enhanced by the synergy of different metals within bimetallic clusters [1]. Hence, it was already shown that Cu$_4$ clusters are active in methanol synthesis [2] Moreover, a recently published DFT study on bimetallic tetramer clusters predicted that the substitution of one Cu atom with an atom of Pd can efficiently tailor the catalytic properties of the cluster-based catalysts [3].

In this study, we investigate atomically precise CuPd clusters supported on ZrO$_2$ as a promising catalyst for low-pressure methanol synthesis from CO$_2$. Catalytic studies were carried out in a continuous flow reactor under atmospheric pressure conditions and temperatures ranging from 25°C to 350°C. The results of catalytic testing indicate that fine-tuning the atomic composition of the bimetallic clusters has a substantial effect on the catalytic activity and selectivity. Hence, CuPd catalysts exhibited catalytic activity in CO$_2$ conversion into methanol, with Cu$_3$Pd$_1$ being the most active. Our ongoing work aims to elucidate the underlying mechanisms governing the CO$_2$ hydrogenation reaction on these nanoscale catalysts and assess their potential as efficient and selective catalysts for CO$_2$ conversion.

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Exploring the Impact of Pt Cluster Size and Support on CO Oxidation   [17]

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In-situ characterization of subnanometer cluster-based catalysts remains a challenging task. Here, we compare the evolution of the oxidation state of Pt_{40} and Pt_{13} clusters, supported on thin tin oxide (SnO_2) and titania (TiO_2) films, during CO oxidation using in-situ NAP-XPS. Both Pt cluster sizes displayed catalytic activity on SnO_2 support, with Pt_{13} clusters exhibiting enhanced activity at higher temperatures, achieving approximately 30% CO total conversion. This difference in CO conversion may arise from both cluster size and the influence of strong metal support interaction (SMSI) for different Pt cluster sizes.

X-ray photoelectron spectra of the as-prepared samples under a 2 mbar He atmosphere revealed significant differences in size and support. While on TiO_2, only metallic Pt was observed with BE = 71.7 eV for Pt_{40} and slightly higher BE = 71.8 eV for Pt_{13}, on SnO_2, the spectra showed a predominant composition of Pt^{2+} (approximately 90%), while the remaining 10% can be attributed to a more oxidized form of Pt^{4+}, with no contribution of metallic Pt^0.

During heating in a CO + O_2 atmosphere, a shift of the Pt 4f components towards lower binding energies and their narrowing were observed, suggesting mostly by change of oxidation state but also but could be also affected by changes in the metal-support interaction, cluster geometry [1], charge transfer [2], partial agglomeration, or the cluster environment could be affected by possible overgrowth of oxide support over the particle [3,4].

For Pt clusters supported on SnO_2, a change in oxidation state towards fully reduced metallic Pt^0 was observed for Pt_{13}, whereas for Pt_{40}, 5% of Pt^{2+} oxide remained. This could hypothetically explain why Pt_{13} is more active than Pt_{40}, as the metallic state is known to be more favorable for oxidation of CO. Additionally, smaller clusters provide a higher surface area for the adsorption and activation of CO and O_2.

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Mass selected ions in vacuum: unexploited synergies in nanoscience   [18]

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Cutting-edge research in the field of nanoscience – electronics, solar, catalysis, or bioresearch – requires an unbiased understanding of the structure-related properties of its building blocks. Ions, sorted by mass-, charge- or structure-recognizing methods, play an increasing role in these experiments. Common substances span a wide range in size – metal atoms, clusters, nanoparticles; (bio) organic molecules up to MDa proteins, DNA and viruses. Numerous ionization methods such as electrospray, MALDI, and plasma techniques e.g. laser ablation or magnetron sputtering are established. This multidimensionality led to a highly branched community with individual, often self-built tools. Potential synergies, so far undiscovered, are worth to be exploited. One shared feature of most devices is collimation of ions to a beam, typically at elevated pressure, and their transfer to higher vacuum for mass selection.

In-line with this, we present an ion beam deposition device currently supplied by an ESI-source. The main body contains RF-driven high-transmission (>80% efficiency) ion guides - stacked ring and high order multipole - allowing for lowest residual gas loads and small beam diameters down to < 2 mm. Digital square-wave supply electronics for ion guides and the quadrupole mass filter with adjustable amplitude and frequency provide a virtually unlimited m/z-range - so far tested from m ≈ 200 Da - 2 MDa and m/z ≈ $10^2 - 10^5$. The QMF reaches high resolving power $R_{max} > 650$ and transmission $T_{max} > 80\%$. Overall efficiency of an ion from the source to be mass selectively deposited in UHV is about 25 % ($I_{source} ≈ 10$ nA, $I_{depo} ≈ 2.5$ nA, limited by the ESI source) within an almost benchtop sized system (50 x 100 cm).

The highly efficient and modular ion guidance and mass selection is broadly adaptable to any ion/beam size. All components/electronics may be used stand-alone or in combination with existing systems and new devices to foster nanoscience.

Poster Session

UHV compatible thermal reactor for model ammonia synthesis catalysts - from single crystals to size selected clusters [19]

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The current primary use of ammonia is in the production of fertilizer. Roughly 1% of world energy consumption is used in the production of ammonia [1] Ammonia is also a promising candidate as hydrogen carrier [2].

Industrial catalysts have a surface area of around 10 m^2/g, however model systems often only have a surface area of around 1 cm^2.

Model catalysts however can be used for very accurately studying different active sites on a catalyst and their intrinsic activity. To enable this however a very sensitive setup is needed. Ammonia catalysts are also very sensitive to contaminants found in air such as water and sulphur. We have developed a new design for a reaction cell that is compatible with UHV vacuum systems for catalyst synthesis and characterisation. For synthesis we use a magnetron sputtering based cluster source, producing ligand free clusters, which are mass selected with an accuracy of 2-5% [3].

The build-up of ammonia concentration in the cell during a test has been modelled to show the evolution over time can be explained by ammonia synthesis on the catalyst surface and diffusion out of the cell. The activity measurements have also been benchmarked against literature data on commercial catalysts and have been found to match [4].

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