

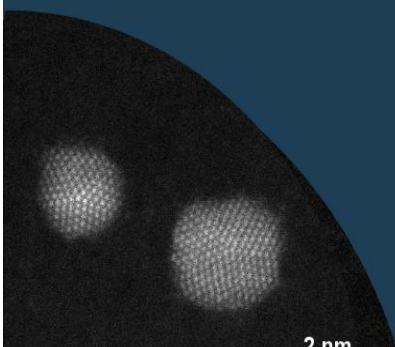
ClusterCat 2024:

Cluster-based Catalysis for CO₂ valorization

*A conference focused on cluster science
from production, characterization,
theoretical modelling to catalysis*



CONFERENCE PROGRAM AND ABSTRACTS



Time	Tuesday 16/01/2024	Wednesday 17/01/2024	Thursday 18/01/2024	Friday 19/01/2024
		Chair: Pavol Mikolaj, Esperanza Sedano Varo	Chair: Bárbara Jamora Yusti, Imran Abbas	Coffee
9:00 - 9:40		Dr. David Buceta	Dr. K. Doblhoff-Dier	
9:40 - 10:20		Dr. Tom Burdyny	Hot topic presentation: 9.40 - Bárbara Zamora Yusti 10.00 - Sumant Phadke	Skills training Analytical Storytelling
10:20		Coffee	Coffee	
10:40 - 11:20		Prof. Jos Oomens	Prof. Chris Binns	
11:20 - 12:00			Hot topic presentation: 11.20 - Olga Lushchikova 11.40 - Maximilian Winzely	Hot topic presentation: 11.20 - Vana Chinnappa 11.40 - Avni Nandkisho
12:00-13:00	Lunch 12.00 - 13.00	Lunch 12.00 - 13.00	Prof. Malte Behrens	Lunch 12.00 - 13.00
13:00 - 13:40	Chair: Sumant Phadke, Dimitra Papamichail 13.00 - Welcome: Dr. Joost Bakker (Catchy representative) 13.10 - Esperanza Sedano Varo (Representative organisation committee) 13.20 - Prof. Britta Redlich (director HFML-FELIX)	Chair: Deema Balalta, Filippo Romeggio Poster session	Lunch 12.40 - 13.40	
13:40 - 14:20	Prof. Emiel Hensen		Visit to Felix 13.40 - 16.00	
14:20 - 15:00	Hot topic presentation: 14.20 - Pavol Mikolaj 14.40 - Ilyas Muhammad	Hot topic presentation: 14.20 - Imran Abbas 14.40 - Rikke Egeberg Tankard		
15:00	Coffee	Coffee		
15:20 - 16:00	Dr. Florian Kraushofer	Dr. Rui Gao		
16:00 - 17:30	Welcome activity	SB meeting		
19:00		Event dinner		

Important information:

Address for FELIX: Toernooiveld 7, 6525 ED Nijmegen NL

Address for Huygens building: Heyendaalseweg 135, Nijmegen



Oral and Poster presentation abstracts

Nanoscale Control in Heterogeneous Catalysis

for a Sustainable Future

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Abstract

Efficient utilization of transition metals is one of the most important requirements for heterogeneous catalysts. Design rules for nanoparticle catalysts are well established and often imply that sub-optimal metal dispersion is desired for high activity. Metal-support interactions can have a strong impact on the catalytic performance of metal nanoparticles. Specific sites at the metal-support interface can give rise to unusual high reactivity. In this contribution, I will review structure sensitivity for monometallic and bimetallic catalysts and demonstrate the possibility to tune metal-support interfaces towards high CO₂ hydrogenation and CO oxidation activity. The approach entails experimental work involving synthesis of uniform active phases, operando characterization, transient kinetic analysis augmented with density functional theory calculations of mechanism and microkinetics simulations.

The first example deals with approaches to break structure sensitivity. For this, we use cobalt dispersed on ceria-zirconia support materials. We first establish how the size of the support crystallites can stabilize cobalt nanoparticles. Then, we investigate how incomplete reduction of cobalt oxide can lead to cobalt-cobalt oxide interfaces with a much higher CO₂ methanation activity than conventional cobalt nanoparticle catalysts. This work shows the promise of very small metal clusters stabilized on an oxide for achieving high CO₂ methanation activity.

Second, I will show how tuning the size of CeO₂ crystallites can strongly affect the stability and reactivity of single metal atoms. The improved reducibility displayed by CeO₂ particles of a few nanometer as contrasted to bulk CeO₂ with a size of tens of nanometers translates in retention of single Pd atoms with improved kinetics for low-temperature CO oxidation.

Keywords: Catalysis, Structure sensitivity, Metal, Support, CO₂ hydrogenation

Key references:

- Parastaev, E.J.M. Hensen et al. *Nat. Catal.* 2020, **3**, 526-533
- V. Muravev, E.J.M. Hensen et al. *Nat. Catal.* 2021, **4**, 469-478
- V. Muravev, E.J.M. Hensen et al. *Angew. Chem. Int. Ed.* 2022, e202200434
- Parastaev, E.J.M. Hensen et al. *Nat. Catal.* 2022, **5**, 1051-1060
- V. Muravev, E.J.M. Hensen et al. *Science* 2023, **380**, 1174-1178

Activation of CO₂ by free metal oxide clusters

Pavol Mikolaj

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Motivated by the performance of the industrially employed Cu/ZnO catalyst for direct CO₂ hydrogenation, the European training network CATCHY seeks to develop new and high-performance cluster-based catalysts. As part of this project, we utilize transition metal oxide clusters in the gas phase as model systems to study the fundamental driving forces that determine the reactive and catalytic properties of such catalysts.

So far, we have investigated the interaction of CO₂ with small copper oxide, cobalt oxide, and yttrium oxide clusters via infrared multiple-photon dissociation (IR-MPD) spectroscopy (collaboration with J. Bakker, FELIX laboratory). Clusters were produced by laser ablation of a metal target in the presence of He carrier gas seeded with O₂. Independent of the metal, cluster formation appears to be strongly charge dependent, with cations preferably forming oxygen-rich clusters, while anions tend to form stoichiometric and oxygen-deficient clusters. To study the cluster-CO₂ interaction, a CO₂/He mixture was subsequently introduced in an adjacent flow tube reactor and the resulting reaction products were investigated via infrared spectroscopy.

In the case of cationic copper and cobalt oxide complexes, the characteristic Fermi dyad of CO₂ is observed, indicating the presence of physisorbed, unactivated linear CO₂. In contrast, all anionic cluster complexes show bands which are characteristic for an activated bent CO₂ molecule. Most interestingly, the IR-MPD spectra of yttrium oxide-CO₂ complexes appear to be more complex than the spectra of the copper and cobalt oxide complexes, potentially indicating different CO₂ binding motifs.

Energy Transitions at Hapag-Lloyd

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Hapag-Lloyd operates 250 Vessels, consuming more than 4.3 million tons of fuel oil, emitting 15.7 mil. ton CO₂e WTW per year. We have an ambition to be net-zero carbon by 2045 and reduce CO₂ intensity of the entire fleet by 30% by 2030 EEOI vs. 2019. In addition to possible efficiency and optimization measures, we will need green fuels to meet these targets. We are already bunkering biofuels and LNG but to meet our decarbonization targets, we will need to increase our biofuels consumption, switch from fossil LNG to bio-LNG and secure offtake of future green fuels. In this talk, I will explain different production pathways for green fuels, their certification requirements, maritime regulations and challenges.

Dynamic catalyst restructuring observed in NAP-STM: Substrate and environment effects

Florian Kraushofer

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Understanding the atomic-scale composition, structure and the nature of the active sites of heterogeneous catalysts is a prerequisite to improving established systems, and can provide the basis for intelligent design of new catalysts. However, it is now well established that characterizations performed in ultra-high vacuum (UHV) often do not capture the full complexity of these systems. Instead, real catalysts typically exhibit dynamic restructuring to a working state under the reactive gas environment and at elevated temperatures, but may revert back to an inactive state when they are removed from that environment. To gain a true understanding of the involved atomic-scale structural dynamics and active site formation, in situ or operando measurements are required.

In this talk, I will present results from two different systems exhibiting such restructuring, which were studied using a combination of near-ambient pressure scanning tunnelling microscopy (NAP-STM) and x-ray photoelectron spectroscopy (NAP-XPS). The first is an $\text{In}_2\text{O}_3/\text{Pd}(111)$ inverse model catalyst, which is active for CO_2 hydrogenation already at room temperature. Immediate reduction and restructuring is observed when exposing the catalyst to the reaction atmosphere, but the original state can be restored by annealing in oxygen. Second, I will show the effect of reducing and oxidizing atmospheres on the SMSI-state of cluster and nanoparticle Pt catalysts on rutile TiO_2 at pressures from UHV up to 1 mbar. Depending on the gas environment, we observe qualitative differences in oxidation state and thickness of the encapsulating layers being formed. We also find a strong dependence on the degree of reduction in the support.

Tuning catalytic activities with low-atomicity clusters for CO₂ valorization

David Buceta

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Low atomicity clusters are composed of a small number of metal atoms (less than ≈ 15 atoms). They present novel properties such as fluorescence, catalysis, photocatalysis, and biomedical properties that differ from larger clusters, nanoparticles, and the same metal in bulk. These properties strongly depend on cluster size. It is well known that AQC's have strong catalytic activities for different reactions, presenting enhanced selectivities and new mechanisms over those of nanoparticles and bulk, and more tunability to different reactions compared to single atoms. In this talk, several illustrative examples of how catalytic activity for CO₂ valorization can be tuned by changing cluster and support interactions.

Spatial Modulation of CO₂ and Internal CO Reduction Leads to High Selectivity and Product Functionality in CO₂ Electrolysis

Tom Burdyny

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Carbon dioxide (CO₂) electrolysis to produce hydrocarbons and oxygenates using copper (Cu) based catalysts has attracted substantial interest due to the direct production of versatile C₂₊ feedstocks. Inside the reactor, however, CO₂ electrolyzers produce C₂₊ compounds occur via a two-step tandem CO₂ to CO and CO to C₂₊ steps. Such knowledge has been utilized in catalyst and cathode-to-anode reactor design, but sparingly in the in-plane design of the system. Here we use the knowledge that CO₂ reduction on copper is primarily a tandem reaction, and through modulation of the reactor flow rate achieve C₂₊ selectivity 84% at CO₂ utilizations of 31%, exceeding theoretical CO₂ utilization efficiencies of 25% for C₂₊ products. We show that higher utilizations are possible when a subset of the reactor performing only CO reduction, instead of CO₂ reduction, preventing excess CO₂ conversion to carbonates. Through use of varied flow field (serpentine, parallel, interdigitated) and pure CO-fed electrolysis, we link these our results to CO residence time. Notably we find that while ethylene production is constant with flow rate (~40%), oxygenates increase substantially at lower flow rates, reaching 45% at 10 SCCM. Finally, we posit that researchers should switch to combined ethylene + ethanol selectivity as a qualifying metric due to the ease of dehydrating ethanol to form ethylene and a demonstrated inability to fully control ethylene:oxygenate branching pathways. Efforts should then shift to the removal of ethanol from membrane electrode assembly systems and downstream recovery through existing commercial processes.

IR spectroscopy of protonated fullerenes

Jos Oomens

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The presence of C₆₀ and C₇₀ in the interstellar medium had long been hypothesized, but was firmly established by spectroscopic evidence a little more than a decade ago [1-3]. It is then a small step to accept that also fullerene derivatives must be present. In fact, already in the 1980's, Sir Harold Kroto himself contemplated on the presence of these fullerene derivatives; in particular, he suggested that protonated fullerenes were perhaps the most likely candidates [4]. However, for a long time, decent laboratory spectra for these protonated fullerene derivatives have been unavailable. Interestingly, the symmetry-breaking effects of fullerene derivatization are – quite obviously – significant and are expected to be reflected in the spectra; computational spectra alone are therefore not sufficient and laboratory spectra are crucial to confirm their influence on the spectra.

Using the FELIX free-electron laser, we reported the first IR spectra of C₆₀H⁺ (see Figure 1) and C₇₀H⁺, using IR multiple-photon dissociation (IRMPD) spectroscopy in an ion trap mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) source [5,6]. Indeed, the attachment of a proton and the inherent symmetry lowering alter the IR spectra entirely as compared to their neutral analogues. With the experimental spectra in hand, we can comment on the performance of density functional theory calculations in predicting the IR spectra. We find that the B3LYP functional and a sufficiently large basis set reproduce the experimental spectra accurately.

The protonated fullerenes possess exactly one fundamental CH stretch band in the 3 μm spectral range. Our earlier experiments were unable to detect this band due to the limited pulse energy of FELIX, as well as of our OPO laser source. Recent updates to the FELIX beamline now allow us to access the 3 μm range with much higher laser power, which has enabled us to record these diagnostic IR bands. We will show that the band position deviates significantly from the value that we had earlier estimated from the scaled harmonic frequency predicted by the DFT calculations [5]. We also contrasted our laboratory IR spectra against astronomical spectra of objects known to feature abundant emission bands of neutral C₆₀. In addition to the four well-known C₆₀ bands, these objects show partly resolved emission bands that deviate clearly from typical PAH emission spectra. Our overlay shows that protonated fullerenes, as well as other low-symmetry fullerene derivatives, may indeed explain much of this partly resolved envelope [5,6].

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Exploring CO₂ interactions with Cu clusters in superfluid helium nanodroplets

Olga Lushchikova

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Copper-based catalysts hold promise for CO₂ utilization but face inefficiency and high-energy demands, exacerbating emissions. Understanding CO₂ interaction at a molecular level is key for better catalyst design. Our research uses copper clusters mimicking active sites to explore their impact on CO₂ structure. Prior work delved into cationic Cu clusters' role in CO₂ hydrogenation via IR spectroscopy at FELIX using laser ablation sources. [1,2] We now demonstrate formation of charged clusters through metal doping of multiply charged superfluid helium nano-droplets (mc-HNDs), serving as ultracold (0.4 K) nano-reactors for studying cluster reactions with CO₂. This study involves verifying cluster structure with He as a probe before studying their reaction with CO₂. [3] Further, we analyze cluster-CO₂ complexes using collision-induced dissociation and photo-fragmentation spectroscopy of He-tagged ions to gather insights into their structure and binding energies.

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An Electrochemical Cell for Operando Grazing-Incidence X-ray Absorption Spectroscopic Studies of Low-Loaded Electrodes

Maximilian Winzely

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X-ray absorption spectroscopy (XAS) is a powerful technique that can provide element specific information on the local electronic and structural properties of newly developed electrocatalysts, especially when performed under operating conditions (i.e., operando). However, the large amounts of catalyst typically needed to achieve sufficiently high spectral quality and temporal resolution can result in working electrodes of several micrometers in thickness. This can in turn lead to an inhomogeneous potential distribution across the electrode, delamination and/or incomplete utilization of the catalyst layer, severe bubble formation and accumulation due to poor mass transport properties.[1, 2] In addition, the activity and selectivity of a catalyst are often measured in a different cell geometry (e.g., using rotating disk electrodes (RDEs)), leading to uncertainties in comparison with the results inferred from spectroscopic data.[3] To tackle these problems we have developed a new spectroelectrochemical XAS flow cell that enables spectral acquisition in fluorescence mode using an X-ray beam incidence angle of $\leq 0.1^\circ$ with regards to the working electrode's substrate plane, i.e., in a so called grazing incidence (GI) configuration. In this acquisition configuration we successfully tracked the formation of palladium hydride with a time resolution of 10 seconds per spectrum while using a Pd-loading as low as $20 \mu\text{gPd}\cdot\text{cm}^{-2}$. Moreover, the careful design of the working electrode flow field allows the study of faradaic processes (e.g., O_2 -reduction) under mass-transport controlled conditions entailing currents comparable to those attained in RDE measurements ($\leq 10 \text{ mA}\cdot\text{cm}^{-2}$).

The combination of these features with an ion-conductive membrane to separate the working- and counter-electrode compartments additionally enables the detection of gaseous products (e.g., from CO_2 -electroreduction) by degassing them out of the electrolyte and analysing them in time-resolved fashion by means of mass spectrometry[4].

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High pressure microreactor designed for testing minute quantities of catalysts deposited on planer surfaces: A case study of CO₂ hydrogenation on PdZnO_x clusters

Imran Abbas

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This study introduces a microreactor designed for the assessment of minute quantities of nanoparticles, specifically synthesized using cluster beam deposition technology. The primary aim of this microreactor is to enable the testing of well-defined nanoparticles under industrially relevant conditions, thereby closing the gap between surface science and catalysis approaches.

The microreactor, featuring a precisely engineered microchannel measuring $48 \times 16 \times 0.070$ mm, serves as a controlled environment for evaluating the catalytic performance of Pd_{0.5}Zn_{0.5}O_x nanoparticles produced via CDB and deposited on planer substrates. These nanoparticles exhibit remarkable activity in the CO₂ hydrogenation process, particularly in the reverse water gas shift reaction.

Stable mass-selected AuTiO_x nanoparticles for CO oxidation

Rikke Egeberg Tankard

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Stability under reactive conditions poses a common challenge for cluster- and nanoparticle based catalysts. Since the catalytic properties of < 5 nm gold nanoparticles were first uncovered, optimizing their stability at elevated temperatures for CO oxidation has been a central theme. Here we report direct observations of improved stability of AuTiO_x alloy nanoparticles for CO oxidation compared with pure Au nanoparticles on TiO₂. The nanoparticles were synthesized using a magnetron sputtering, gas-phase aggregation cluster source, size-selected using a lateral time-of-flight mass filter and deposited onto TiO₂-coated micro-reactors for thermocatalytic activity measurements of CO oxidation. The AuTiO_x nanoparticles exhibited improved stability at elevated temperatures, which is attributed to a self-anchoring interaction with the TiO₂ substrate. The structure of the AuTiO_x nanoparticles was also investigated in detail using Ion Scattering Spectroscopy, X-ray Photoelectron

Spectroscopy, and Transmission Electron Microscopy. The measurements showed that the alloyed nanoparticles exhibited a core-shell structure with an Au core surrounded by an AuTiO_x shell. The structure of these alloy nanoparticles appeared stable even at temperatures up to 320°C under reactive conditions, for more than 140 hours. The work presented confirms the possibility of tuning catalytic activity and stability via nanoparticle alloying and self-anchoring on TiO₂ substrates and highlights the importance of complementary characterization techniques to investigate and optimize nanoparticle catalyst designs of this nature.

Magnetic Fields Enhance Mass Transport During Electrocatalytic Reduction of CO₂

Rui Gao

Flemish Institute for Technological Research (VITO)

The selectivity of electrocatalytic reduction of CO₂ (CDR) is dictated not only by the intrinsic reactivity of the catalyst but also by the transport of reactants to the catalyst (i.e., mass transport). Current methods for increasing mass transport in CDR rely upon either (1) mechanical agitation or (2) use of gas-diffusion electrodes and are unable to eliminate concentration polarization completely. We have shown that magnetic fields can be used to increase mass transport in electrochemical systems through magnetohydrodynamic effects (MHD). The Lorentz force acting upon ions moving in the solution generates fluidic convection that enhances mass transport and modifies the observed reactivity. We demonstrated that magnetic fields parallel to the surface of the cathode can help increase mass transport and increase the selectivity for the reduction of CO₂ compared to the reduction of protons to hydrogen.

Zooming into electrochemical interfaces: an atomistic view from simulations

Katharina Doblhoff-Dier

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The structure of the electrode and the electrode – electrolyte interface are pivotal in electrochemistry, as they determine the electrocatalytic activity of an electrocatalyst. Unfortunately, it is difficult to study this interface under in situ conditions. By supplementing experimental observations with computer simulations, density functional theory calculations, ab initio molecular dynamics and force field molecular dynamics, we can gain insight into the atomistic structure at the interface and the physical mechanisms underlying an experimental observation.

In this talk, I will take you for a stroll through the atomistic world of simple electrochemical interfaces including Pt and Au single crystal surfaces, but also touching on more complex substrates such as NiOOH. We will study the structure of the interface and elucidate the interaction between ions, adsorbates, and electrode (surfaces) as well as the capacitive response of the interface.

CO₂ and H₂ activation on zinc-doped copper clusters

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Here we systematically investigate the CO₂ and H₂ activation and dissociation on small Cu_nZn^{0/+} (n=3-6) clusters using Density Functional Theory. We show that Cu₆Zn is a superatom, displaying an increased HOMO-LUMO gap and is inert towards CO₂ or H₂ activation or dissociation. While other neutral clusters weakly activate CO₂, the cationic clusters preferentially bind the CO₂ in monodentate nonactivated way. Notably, Cu₄Zn allows for the dissociation of activated CO₂, whereas larger clusters destabilize all activated CO₂ binding modes. Conversely, H₂ dissociation is favored on all clusters examined, except for Cu₆Zn. Cu₃Zn⁺ and Cu₄Zn, favor the formation of formate through the H₂ dissociation pathway rather than CO₂ dissociation. These findings suggest the potential of these clusters as synthetic targets and underscore their significance in the realm of CO₂ hydrogenation.

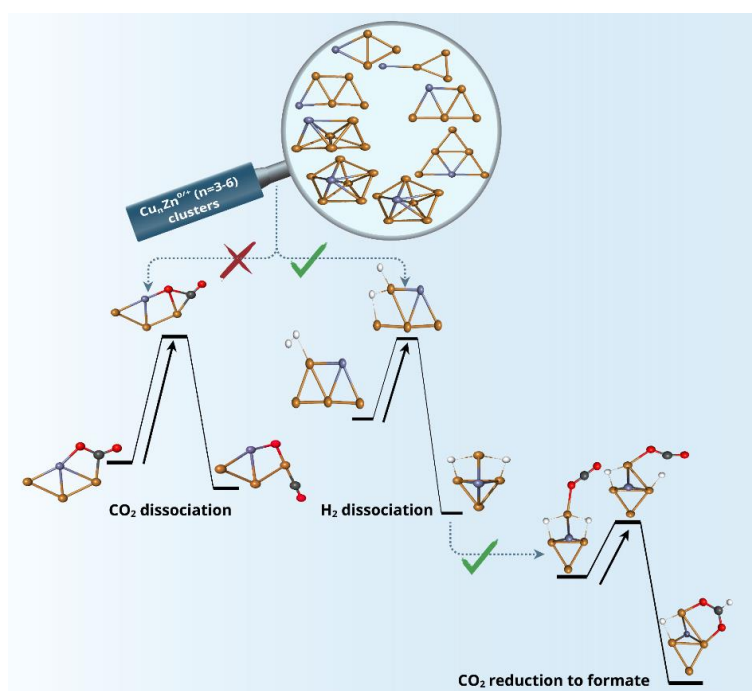


Figure 1: Structural search of Cu_nZn (n=3-6) clusters and the CO₂ and H₂ dissociation reactions mechanisms.

Zamora, B.; Nyulászi, L.; Höltzl, T. CO₂ and H₂ Activation on Zinc-Doped Copper Clusters. *ChemPhysChem* 2024, 25 (1), e202300409. <https://doi.org/10.1002/cphc.202300409>.

Gas-phase Pd Clusters-modified Mesoporous Copper Oxide Hollow Spheres as Electrocatalysts for CO₂ Reduction to C₂₊ products

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Renewable energy-driven electrochemical CO₂ conversion to value-added chemicals is a prospective strategy for addressing global carbon emission and energy consumption issues worldwide. Herein, we report a novel highly efficient electrocatalyst for CO₂ conversion in C₂₊ products based on mesoporous oxygen-rich copper hollow spheres prepared by a colloid templating method, whose surface is uniformly modified by the deposition of different loadings of well-defined Pd clusters of ca. 3 nm diameter using the laser ablation cluster beam deposition (CBD) technology. Primary electrochemical results show that these electrodes are able to reduce CO₂ to ethylene with a faradaic efficiency of more than two times higher than that of commercial Cu₂O nanoparticles under the same reaction conditions. A clear phase transition from CuO to Cu₂O and metallic Cu is occurring under CO₂ electro-reduction conditions as highlighted by XRD. These remarkable performances are likely originating from the facile gas charge transport via the mesoporous structure of the oxygen-rich copper spheres as imaged by SEM as well as from their high surface area, which allows a high catalytic activity and a uniform accommodation of the metallic clusters. As CBD is a versatile technique that allows the deposition of virtually any type of well-defined cluster on a large variety of support, this work provides an attractive avenue to achieve stable selective multicarbon products via rational electrode design.

Designed Nanoparticles by Gas Phase Synthesis

Chris Binns

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The talk will describe various methods to produce size selected nanoparticles with flexible choice of materials by gas phase synthesis. It will include the production of complex multi-element nanoparticles with alloy, core-shell or Janus structures. Potential applications and the possibility of scale-up will also be presented.

Gas phase deposition of well-defined bimetallic gold-silver clusters for photocatalytic applications

Vana Chinnappa Chinnabathini^{1,2,3}, Fons Dingenen^{2,3}, Rituraj Borah^{2,3}, Imran Abbas¹, Johan van der Tol¹, Zviadi Zarkua¹, Francesco D'Acapito⁴, Thi Hong Trang Nguyen¹, Peter Lievens¹, Didier Grandjean¹, Sammy W. Verbruggen^{2,3}, Ewald Janssens¹

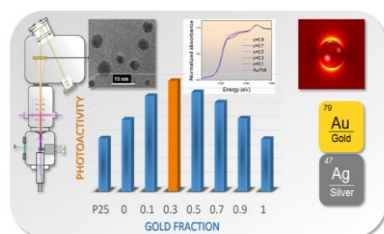
1. QSP, Department of Physics and Astronomy, KU Leuven, Belgium.

2. Sustainable Energy, Air & Water Technology (DuEL), University of Antwerp, Belgium.

3. NANOLab Center of Excellence, University of Antwerpen, Groenenborgerlaan 171, 2020, Antwerpen, Belgium.

4. CNR-IOM-OGG c/o ESRF LISA CRG - The European Synchrotron, Grenoble, France.

Cluster beam deposition is employed for fabricating well-defined bimetallic plasmonic photocatalysts to enhance their activity while facilitating a more fundamental understanding of their properties. $\text{Au}_x\text{Ag}_{1-x}$ clusters with compositions ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9$ and 1) spanning the metals miscibility range were produced in the gas-phase and soft-landed on TiO_2 P25-coated silicon wafers with an optimal coverage of 4 atomic monolayer equivalents. Electron microscopy images show that at this coverage most clusters remain well dispersed whereas EXAFS data are in agreement with the finding that the deposited clusters have an average size of *ca.* 5 nm and feature the same composition as the ablated alloy target. A composition-dependant electron transfer from Au to Ag that is likely to impart chemical stability to the bimetallic clusters and protect Ag atoms against oxidation is additionally evidenced by XPS and XANES. Under simulated solar light, $\text{Au}_x\text{Ag}_{1-x}$ clusters show a remarkable composition-dependent volcano-type enhancement of their photocatalytic activity towards degradation of stearic acid, a model compound for organic fouling on surfaces. The Formal Quantum Efficiency (FQE) is peaking at the $\text{Au}_{0.3}\text{Ag}_{0.7}$ composition with a value that is twice as high as that of the pristine TiO_2 P25 under solar simulator. Under UV the FQE of all compositions remains similar to that of pristine TiO_2 . A classical electromagnetic simulation study confirms that among all compositions $\text{Au}_{0.3}\text{Ag}_{0.7}$ features the largest near-field enhancement in the wavelength range of maximal solar light intensity, as well as sufficient individual photon energy resulting in a better photocatalytic self-cleaning activity. This allows ascribing the mechanism for photocatalysis mostly to the plasmonic effect of the bimetallic clusters through direct electron injection and near-field enhancement from the resonant cluster towards the conduction band of TiO_2 . These results not only demonstrate the added value of using well-defined bimetallic nanocatalysts to enhance their photocatalytic activity but also highlights the potential of the cluster beam deposition to design tailored noble metal modified photocatalytic surfaces with controlled compositions and sizes without involving potentially hazardous chemical agents.



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Engineering of synergistic materials for upscaling electrochemical CO₂ reduction in advanced electrolyzers

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In a progressively electrified world, electrochemical CO₂ conversion has emerged as a promising technology for sustainable energy conversion, enabling the utilization of greenhouse gases. Leveraging surplus power generated from sources such as wind and solar, the process of CO₂ reduction can be effectively harnessed with the aid of a catalyst. However, despite the promise, the electrochemical CO₂ reduction reaction (CO₂RR) encounters obstacles, including limited *CO coverage, high energy barriers, sluggish kinetics, and product selectivity issues. The industrial utilization of CO₂ electroreduction hinges on the presence of sturdy electrocatalysts that exhibit both high activity and selectivity. Notably, functional materials with hetero interfaces have recently emerged as a promising class of electrocatalysts for CO₂ reduction. Emphasizing the need for customized catalyst engineering, varying metal tendencies toward oxygen and hydrogen play a pivotal role in shaping catalytic dynamics. Additionally, the utilization of innovative electrolyzer cell designs for CO₂ reduction presents a promising avenue for improving reaction kinetics and current densities, overcoming limitations associated with conventional aqueous systems. The ECOMATEs project seeks to contribute to the advancement of bimetallic catalyst-based electrode materials and pioneering electrolyzer setups for efficient and stable electrochemical CO₂ conversion, aiming to pave the way for a sustainable and impactful carbon management approach. Through this proposed research we aim to effectuate a substantial breakthrough in the electrochemical conversion of CO₂ innovative designs for electrolyzer cells, with a specific focus on the synthesis of high-value-added products, especially C₂₊. This presentation aims to highlight the ongoing efforts in developing efficient bimetallic catalyst-based electrode materials and state-of-the-art reactor designs, ultimately contributing to the progression of sustainable and effective electrochemical CO₂ conversion technologies.

New insight into an old catalyst: the many faces of copper in methanol synthesis

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Cu/ZnO-based catalysts are applied in industrial methanol synthesis and show great potential in CO₂ hydrogenation. The synergetic and complex interplay of Cu- and Zn-species promotes the conversion of formate intermediates and their activity has been can be further tuned by different electronic and structural promoters. The presentation will cover the materials chemistry of state-of-the-art catalysts and discuss potential future directions for the hydrogenation of CO₂ to methanol on modified catalysts.

Recent advances in copper chalcogenides for CO₂ electroreduction

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Transforming CO₂ through electrochemical methods into useful chemicals and energy sources may contribute to solutions for global energy and ecological challenges. Copper chalcogenides exhibit unique properties that make them potential catalysts for CO₂ electroreduction. In this review, we provide an overview and comment on the latest advances made in the synthesis, characterization, and performance of copper chalcogenide materials for CO₂ electroreduction, focusing on the work of the last five years. Strategies to boost their performance can be classified in three groups: (1) structural and compositional tuning, (2) leveraging on heterostructures and hybrid materials, and (3) optimizing size and morphology. Despite overall progress, concerns about selectivity and stability persist and require further investigation. This review outlines future directions for developing the next-generation of copper chalcogenide materials, emphasizing on rational design and advanced characterization techniques for efficient and selective CO₂ electroreduction.

Nanoparticles synthesis via thermal annealing of physically deposited thin films

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In recent years, the development of advanced materials with tailored properties has become paramount in various fields (including catalysis). This study focuses on a novel approach to synthesize nanoparticles from magnetron sputtered thin films through high-temperature annealing processes. The technique capitalizes on the precision and versatility of magnetron sputtering, offering a robust platform for creating thin films with controlled compositions and microstructures. Through systematic annealing at elevated temperatures, these thin films can be transformed into nanoparticles, potentially showcasing unique morphological and chemical characteristics.

The significance of this project lies in its potential to revolutionize nanomaterial synthesis. Successful implementation of this method would yield nanoparticles with precisely engineered properties, enabling breakthroughs in diverse applications.

By utilizing magnetron sputtering, a low-impact deposition technique, and transforming thin films into nanoparticles, this research minimizes material wastage, energy, and time consumption, contributing to the advancement of green nanotechnology. The knowledge gained from this study could also lead to the development of scalable and cost-effective manufacturing processes for tailored nanoparticles, thereby fostering innovation in the industrial sector.

High-Pressure Cell for *In Situ* Grazing Incidence XAS Characterization of Model Catalysts on Planar Supports under CO₂ Hydrogenation Conditions

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Well-defined model catalysts studied under realistic CO₂-to-methanol hydrogenation conditions offer structure-activity insights, which enable a more profound understanding and a better design of methanol synthesis catalysts. In contrast to conventionally prepared catalysts, physical synthesis methods such as cluster beam deposition (CBD) can produce model nanoparticles of precise atomic structure and composition [1]. Depositing such nanoparticles on various planar substrates at very low metal loadings (0.1 – 10 µg/cm²) provides an opportunity to understand particle size's effects and the catalyst's support on the reactivity. However, such model catalysts also present a challenge for *in situ* structural characterization using bulk-sensitive methods, such as X-ray absorption spectroscopy (XAS), since they are optimized for studying catalysts with about three to four orders of magnitude higher metal loading [2]. To address this, we have developed a grazing incidence (GI) *in situ* XAS cell that enables the study of the structure of these model catalysts under CO₂-to-methanol hydrogenation conditions at relevant temperatures and pressures.

We have successfully measured *in situ* XAS data for nanoparticles deposited on flat substrates using fluorescence detection. In particular, we obtained high-quality Pd K- and Au L₃-edge XAS data in 30-60 min for Pd and Ag_{0.7} Au_{0.3} nanoparticles with ca. 0.96 – 10 µg/cm² loading at 230°C temperature and 20 bar pressure of reactive gases (CO₂:3H₂:Ar). The mono- and bimetallic nanoparticles proved to be stable and are resistant to sintering even under harsh reaction conditions. With this proof-of-concept, we now intend to investigate innovative bimetallic systems produced by gas-phase cluster deposition and contribute to a rational design of CO₂ hydrogenation catalysts.

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Tuning the reactivity of bimetallic clusters towards CO₂

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The increasing atmospheric CO₂ concentration leads to global warming and climate destabilization. One potential way to mitigate CO₂ emissions is by converting CO₂ into useful chemicals. In industry, for example, methanol is produced by direct hydrogenation of CO₂ over a Cu-ZnO-Al₂O₃ catalyst. A detailed understanding of the reaction mechanisms is required for a rational design of more active and selective catalysts.

Gas-phase metal clusters can form an idealized model system for the active sites of the complex catalysts. We investigate how the doping of clusters with foreign elements affects their reactivity, by IR spectroscopically characterizing the reaction products of adsorption of CO₂ and H₂ onto first-row transition metal-doped clusters, complemented by DFT calculations. For this, we present a newly commissioned dual-laser, dual-target cluster source and show how the doping of cationic cobalt clusters by single vanadium atom affects the adsorption mode of CO₂.

Graphene supports for electron microscopy investigation of atomic catalytic clusters

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The graphene's monolayer of carbon atoms makes it an optimum support for metallic atomic clusters during Scanning Transmission Electron Microscopy (STEM) characterization. For high-quality images, this 2D material provides a noise-free background for imaging clusters while achieving high-resolution and multi-dimensional imaging.^[1] Moreover, its excellent mechanical properties make it a great eventual candidate for in situ STEM, which is usually based on MEMS chips with relatively thick SiN_x windows.^[2]

We prepared Au clusters in a Leica EM ACE600 high vacuum sputter coater and deposited them directly on SiN_x and graphene grids simultaneously with no size selection. The clusters on the SiN_x support have a narrower size distribution and a more homogenous deposition compared to the graphene where the clusters' deposition followed a certain pattern.

In addition, the electron beam activation of the clusters can result in structural changes and rotation of the clusters or diffusion of atoms to new sites. The bonding sites on a graphene support and their effect on the clusters' stability are yet to be explored and this can be a crucial point for future STEM investigation of catalytic clusters.

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Ethylene activation by Pd single atom catalysts supported on C60

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Ever increasing energy demands require more efficient catalytic processes in the chemical industry. In heterogeneous catalysis increasing the available surface area of a catalyst will lead to a more efficient use of the catalyst. The ultimate form of this is when a single atom acts as a catalyst. However, in order to maintain the characteristics and advantages of heterogeneous catalysis, namely high throughput and easy reusability [1], the single atom catalysts (SAC) need a support structure. This support structure however is known to have an influence on the catalytic activity of the SAC [2]. In order to disentangle the intrinsic activity of a single atom and the effects a support structure has on that activity in more detail, we study the reactivity of gas-phase palladium atomic ions towards ethylene and compare that to the activity of gas-phase Pd-C60 complexes. The SAC and supported SAC are reacted with ethylene to investigate its activation for use in hydrogenation reactions. The produced complexes are characterized using IR multiphoton dissociation (IRMPD) spectroscopy and complemented by DFT calculations.

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Unravelling Structure-Activity Relations in CO₂ Electroreduction: Size Studies of Au and Cu Nanoparticles

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Nanoparticles are extensively utilized in various industrial processes due to their enhanced catalytic performance resulting from a high surface-to-bulk ratio. Modulating the size of these nanoparticles allows for manipulation of their activity and selectivity, which is particularly intriguing in the context of CO₂ electroreduction, a process yielding 16 different products where enhancing selectivity is of significant interest. However, investigating these minute catalysts in electrochemistry poses considerable challenges, given the multitude of parameters that influence apparent selectivity.

In this study, we thoroughly examine the intrinsic selectivity of size-selected nanoparticles by meticulously controlling all relevant parameters, including size, loading, impurities, and shape. Our methodology aims to meticulously manage these variables to establish experimental structure-activity relationships and generate reliable, transferable knowledge applicable to other catalytic studies, both fundamental and experimental. Here, we present several parameters with significant impacts on the selectivity and activity of the nanocatalysts, along with the results demonstrating the influence of these controlled parameters on the accuracy of size-based performance studies of the nanoparticles.

Gas-Phase CuPd Bimetallic Cluster-Modified Electrodes as Model Electrocatalysts for CO₂ Conversion

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Copper-based electrocatalysts possess the unique ability to convert CO₂ to multicarbon products such as ethylene – a precursor in many industrial processes. However, their stability and product selectivity remain insufficient. A promising approach to overcome these shortcomings and design better CO₂RR electrocatalysts is to tune Cu selectivity by forming bimetallic Cu-M systems [1] while establishing their detailed structure-selectivity relationship. To achieve this, we used laser ablation Cluster Beam Deposition (CBD) [2] to produce well-defined bimetallic cluster-modified electrodes [2]. More specifically, CuPd clusters with an original average size of 3 nm and mass loadings of 1-2 μg cm⁻² were deposited onto a carbon support. To produce a model catalyst which allows the independent investigation of the electronic and geometric structural effects induced to Cu by the second element, a Cu_{0.9}Pd_{0.1} composition was selected [3]. CuPd cluster-decorated electrodes were tested for CO₂ electrolysis and methane (C₁), and ethylene (C₂) were found among the products. As it is shown from the electrocatalytic activity trends, the evolution of C₂ products is correlated with the cluster mass loading. In addition, the cluster coverage influences the onset of the competitive H₂ evolution; with the lowest cluster-loaded electrodes presenting more intense H₂ production due to limited cluster coverage of the carbon substrate. High resolution (Scanning) Transmission Electron Microscopy ((S)TEM) coupled with Energy-dispersive X-ray spectroscopy (EDX), and X-ray Photoelectron Spectroscopy (XPS) analyses of the as-prepared cluster-modified electrodes, are used to explore the role of Pd in CuPd.

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Magnetic field effect on cluster growth

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Cluster production using physical methods provides several advantages compared with chemical routes, such as better control of the size distribution and the minimised impact on the environment. On the other hand, their slow deposition rate has inhibited the physical approaches from being used more widely. To address this issue, we have systematically studied the influence of aerodynamics on the efficiency of cluster transportation in a cluster source [1]. Another important factor that needs to be considered is the influence of magnetic field configuration on the magnetron sputtering device.

In the 1980s, it was found that by tuning the unbalance degree of the magnetic field configuration, one can significantly increase the number of electrons escaping from the plasma sputtering region, increase the ion flux and the associated high ion bombardment on the substrate and thus produce very dense thin films [2]. Subsequently, simulations have been carried out to better understand how the unbalanced magnetic field influences the sputtering parameters [3].

Although significant progress has been made in the understanding of how the magnetic field influences the magnetron sputtering process, there are very few reports about its influence on cluster formation. An exception is a recent work by Vaidulych et al [4], where it is argued that a decrease in the magnetic field assisted with an increase in the flow of the carrier gas greatly improves the deposition rate of the nanoparticles. However, in this approach, the sputtering rates across experiments were not strictly maintained, which might influence the results in an unexpected way. Furthermore, a concrete explanation of how this magnetic field affects cluster growth is still missing.

In this work, preliminary simulation results on the influence of different magnetic field configurations are shown. The electromagnetic modelling software package OPERA was used to optimise the magnetic field configuration, and the configurations of the magnetic field on a magnetron were physically varied to validate the simulation results. Plasma density was measured at different magnetic configurations in an attempt to investigate its influence on the density of charged particles surrounding the target. A hypothesis will be proposed to explain cluster growth mechanisms under the influence of different plasma spatial distributions.

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