FemChem

Scientific Workshop

Book of Abstracts
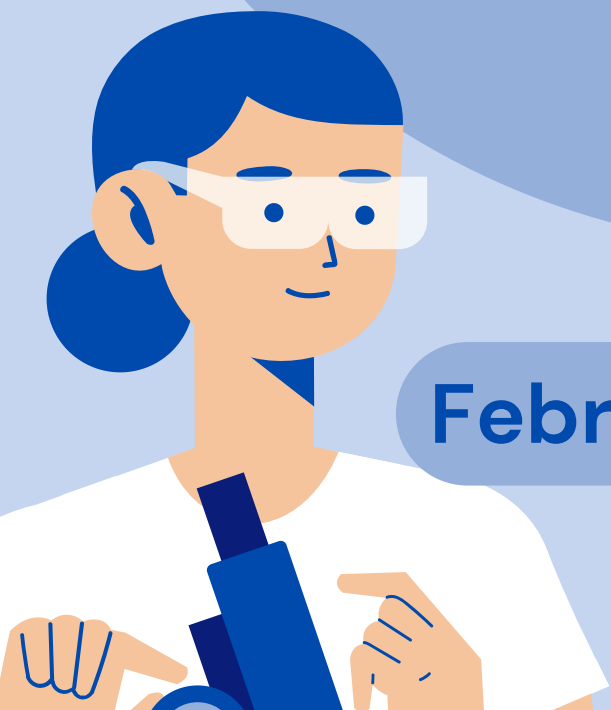
February 27, 2024

Table of Contents

OPENING

08:45 AM – 10:00 AM

9:00   Opening words

9:30   Ulrike Diebold

SESSION 1

10:20 AM – 11:40 AM

10:20   Papaplioura

Substituting Gaseous Reagents for Solid Alternatives

10:35   Ammann

Tackling recyclability in stereolithographic 3D printing via ring-opening photo–copolymerization

10:50   Pfennigbauer

Development of clickable N–heterocyclic carbenes for biosensing applications

11:05   Abbas

Prospective economic and environmental assessment for developing a superstructure based multi–objective optimization framework for biorefinery system

11:20   Toussaint

The Sweet Potential of Rare Monosaccharides: Tin–organic frameworks for the Synthesis of Rare Monosaccharides and Product Recovery by Adsorptive Separation

Substituting Gaseous Reagents for Solid Alternatives

Eleni Papaplioura, Michael Schnürch

Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163, 1060 Wien, Austria

Keywords: Heck-coupling, quaternary ammonium salts, vinylation

The functionalization of short carbohydrate chains is a significant challenge in organic synthesis, primarily due to the low reactivity of alkylhalides and the impractical use of short-chain olefins as alkylating/alkenylating agents.

This study is centered on the development of a convenient Heck vinylation protocol that circumvents the need of ethylene gas as a coupling partner. Olefins and especially arylethenes are powerful precursors in organic synthesis used for the synthesis of bioactive compounds as well as polymers. The versatility of the alkene moiety renders them excellent substrates for the construction of more complex molecules. However, conventional methodologies utilize olefins that are gaseous at room temperature or elaborate high pressure equipment, and therefore in this type of transformation, ethylene and other gaseous olefins are often avoided, primarily for practical and safety reasons.

A sustainable and safe approach that can tackle this issue involves the use of solid and easy to handle sources of alkenes and in situ generation of the required reactive coupling partners as illustrated by the use of quaternary ammonium salts as alkenyl sources. [1] The practicality of this method, characterized by its convenience and safety in a one-pot reaction renders it attractive for applications in a research and discovery context.
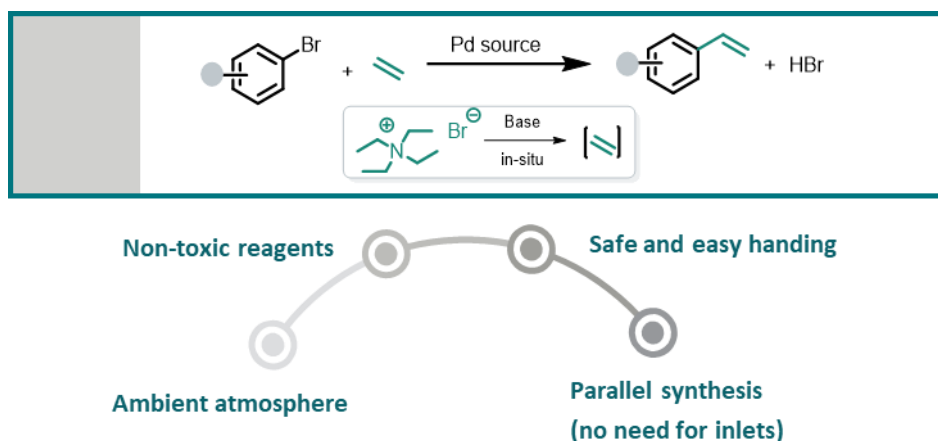

Figure 1: Mizoroki-Heck coupling using tetraethylammonium salt as ethylene precursor

[1]   M. Spettel, R. Pollice, M. Schnürch, Org. Lett. 2017, 19, 4287-4290.

Tackling recyclability in stereolithographic 3D printing via ring–opening photo–copolymerization

Theresa Ammann, Katharina Ehrmann, Robert Liska

Institute for Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria

Keywords: Polyesters, Photoinitiation, Degradability, Ring-Opening Copolymerization

3D printing is a versatile tool since it allows ecologically and economically favorable production of complex customized parts with minimal energy efforts and lead times. When using photoinitiation, a liquid formulation is cured into a thermoset polymeric material upon irradiation. Thermosets are irreversibly hardened during the curing process. However, the scope of accessible materials is still narrow, so more research into developing new and better systems has to be done. Especially the fact that most of the 3D printed materials are not degradable is a major drawback.

In recent years, degradability and recyclability of thermosets has been increasingly researched in order to reduce plastic waste in the environment and offer chances for recycling processes and medical applications. In this regard, pure polyester networks offer an ideal opportunity since they contain hydrolysable ester bonds and usually afford benign degradation products.

Polyesters are commercially produced by condensation reactions of multifunctional carboxylic acids with multifunctional alcohols or by ring-opening polymerization (ROP) of cyclic esters. However, the relatively novel ring-opening copolymerization (ROCOP) of epoxides and anhydrides offer a more advantageous approach towards recyclable polyesters. A diverse monomer scope for easy tuning of the final polyesters is readily available, and the mild reaction conditions and living behavior of the reaction lead to homogeneous network formation, which is expected to provide good thermomechanical properties.

Furthermore, obtaining the starting monomers from the degradation products and thus closing the recycling circle is possible.

Previous reports of this photopolymerization have focused on organometallic catalysts, organic bases and Lewis base/Lewis acid pairs. However, no attempts of using photocatalysts for ROCOP have been reported to date.

Therefore, we have identified photoacid generators (PAGs) and photobase generators (PBGs) as possible catalysts for this ROCOP reaction, which would enable light-based 3D printing of the polyester materials. We have confirmed experimentally that both PAGs and PBGs are able to initiate ROCOP.

However, significant amounts of side products, e.g. from homopolymerization of the epoxide, make PAGs unsuitable for producing pure polyester networks. Therefore, we have optimized linear photopolymer systems using PBGs as catalyst. The influence of temperature, light intensity, PBG concentration, and monomer and PBG structures regarding the stability of the formulations and the properties of the produced polyesters have been investigated. Subsequently, polymer networks using multifunctional epoxides were produced. Preliminary degradation studies demonstrate the successful full degradation of these polymer networks. Accelerating the photocatalyzed ROCOP to use it in a printing process is focus of ongoing work.
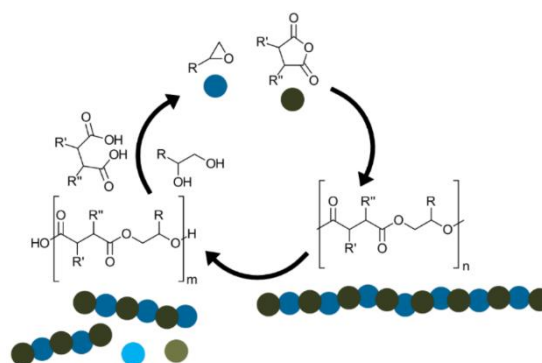
Development of clickable N–heterocyclic carbenes for biosensing applications

Katharina Pfennigbauer, Dorian Bader, Brigitte Holzer

Keywords: biosensing, N-heterocyclic carbenes, surface chemistry, click chemistry, surface plasmon resonance.

N-heterocyclic carbenes (NHCs) have been introduced as a stable alternative to thiolate-based self-assembled monolayers (SAMs). The straightforward preparation of NHC-based SAMs from their corresponding hydrogen carbonate [1] or triflate salts in combination with a mild base [2], allows the introduction of addressable functional groups. For biosensors not only the stability of the surface anchor molecules plays a pivotal role in their performance but also the surface density, and orientation of the receptor on the sensor surface. [3] Employing click chemistry instead of the commonly used amide coupling of the molecule of interest with the surface anchors will allow controlled 1 to 1 interaction which increases the sensitivity of the sensor.

This work describes the development of a synthetic route towards a variety of NHC-based compounds bearing clickable groups (Figure (1a)). Variations in the core moiety and the spacer length will allow the optimization of the SAM surface density. Furthermore, click reactions in solution and on surface will be shown to confirm the addressability of the functional groups as well as the possibility to modify the final system on demand, e.g. with photo- or electroactive tags (Figure (1b)).

Exemplarily selected compounds are tested in biosensing applications by comparing the protein surface coverage of NHC- and commonly used thiolate-based SAMs upon amide coupling and copper-catalyzed azide-alkyne click (CuAAC) reaction on gold sensor surfaces with surface plasmon resonance (SPR) spectroscopy.

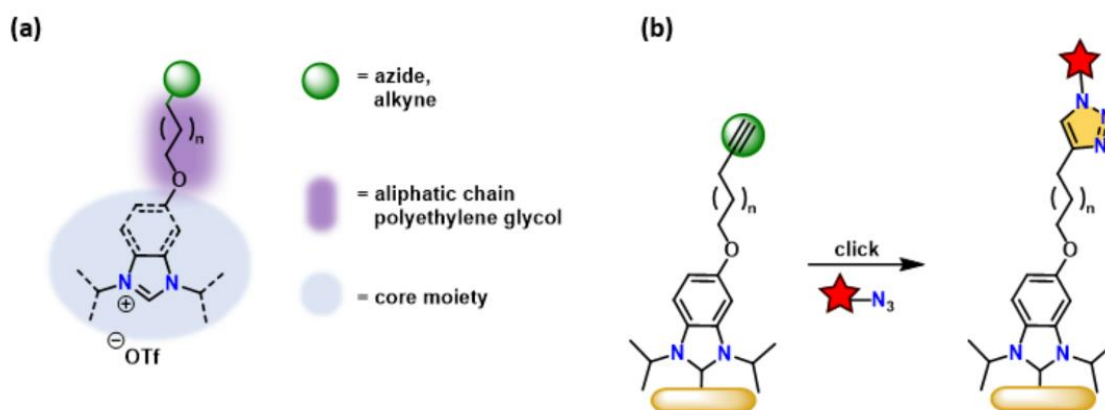**Figure 1: (a) Structural design of NHC precursors. (b) Schematic illustration of surface modification by applying click chemistry.**

[1]   Crudden, C. M. et al., Nat. Commun. 7, 1–7 (2016). DOI: 10.1038/ncomms12654
[2]   Salorinne, K. et al., Angew. Chem. 29, 6294 –6298 (2017). DOI: 10.1002/anie.201701605
[3]   Steen Redeker, E. et al., Bioconjugate Chem., 24, 11, 1761–1777 (2013). DOI: 10.1021/bc4002823

Prospective economic and environmental assessment for developing a superstructure based multi–objective optimization framework for biorefinery system

Safdar Abbas, Stavros Papadokonstantakis

Institute of Chemical, Environmental and Bioscience Engineering, TU Wien,1060 Wien, Austria

Keywords: Prospective LCA, learning by doing, integrated assessment models, shared socio-economic pathways, multi-objective optimization

Sustainable technology has become increasingly important as a result of global environmental issues. Meanwhile, new technologies tend to be more expensive and have larger environmental impacts than established technologies. The reason is a first-time production process is less smooth than a production process that has been in operation for years. Biorefinery system requires a significant investment in terms of capital expenditures (CAPEX) as well as feedstock inputs. Therefore, R&D and experience are important in estimating the cost-saving potential of building a growing number of biorefinery plants which are comprised of a mix of established and innovative technologies.

To the best of our knowledge, this study is the first to describe how superstructure-based biorefineries could grow in the future by integrating prospective LCA with scenario methodology and prospective economic analysis explained by learning effects. It can provide valuable information to stakeholders about the estimated economic investment and environmental assessment to achieve the European Commission's goals in 2050. In this study we employ a theoretical framework for prospective economic assessments based on the "learning curve theory" to estimate cost reduction due to technological implementation, measured in terms of numbers or capacities of units. In this framework learning theory is employed through a multi-component analysis approach. This approach involves systematically breaking down the complete production process. The aim is to pinpoint both established and innovative technological components. These components are then analysed in depth using the corresponding techno-economic data.

Prospective LCA, which tries to analyse the environmental performance of technologies in the future, has recently received a lot of attention. The evolution of the future background scenarios that result from a combination of the ecoinvent database and the integrated assessment models (IAMs) has a significant impact on the outcome of LCA studies. IAMs, such as the shared socio-economic pathways (SSPs), often execute globally consistent future scenarios that span probable evolutions of society and ecosystems over a century timeline. Scenarios development is a systematic and documented approach that includes the steps of aim and scope determination as well as inventory analysis. An open source software Activity-Browser (AB) is used to conduct the prospective LCA. The core part of the applicable technique is scenario generation during the inventory analysis phase, which represents both descriptions of possible future states and descriptions of events influencing both the LCI's foreground and background data.

GAMS software is used to solve the multi-objective optimization model in terms of economic and environmental perspective. These prospective strategies could lead in a clearer view on the environmental effect and cost structure of new technology, as well as a more equitable comparison basis with traditional technologies, thus leading in faster acceptance and shorter time to market for sustainable solutions.

[1]   R. Sacchi et al., "Prospective EnvironMental Impact asSEment (premise): A streamlined approach to producing databases for prospective life cycle assessment using integrated assessment models", Renewable and Sustainable Energy Reviews, vol. 160, p. 112311, 2022, DOI: 10.1016/j.rser.2022.112311.

The Sweet Potential of Rare Monosaccharides: Tin–organic frameworks for the Synthesis of Rare Monosaccharides and Product Recovery by Adsorptive Separation

V. Toussaint, T. Röper, L. Pavlis, I. Delidovich

Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Vienna, Austria.

Keywords: Porous organic frameworks, epimerization, zeolites, boronic acid polymers.

Nowadays, the interest in biomass valorization in technological areas such as chemical, fuel and food industry is rapidly increasing. In this regard, the conversion of abundant into rare monosaccharides with significant application potential in medical and pharmaceutical industry is of great interest.[1] Element-organic frameworks are a young class of nanoporous inorganic-organic hybrid materials. Recently, catalytic activity for epimerization of monosaccharides of Lewis acidic porous tin-organic frameworks (Sn-OF) was uncovered. [2a]

In this work, a few Sn-OFs were synthesized via corresponding lithium intermediates starting from a bifunctional linker as shown in Fig. 1a. The synthesized materials were characterized by elemental analysis, low-temperature N_2 physisorption, ^1H, ^{13}C, and ^{119}Sn MAS NMR, EXAFS, XANES, IR spectroscopy, and SEM. We currently work on elucidating structure performance relations of the Sn-OFs. High reaction rates were achieved for epimerization of monosaccharides, i.e. glucose and xylose, whereas transformation rate of lactose disaccharides was two orders of magnitude lower. We explain this result by inaccessibility of the active sites located in micropores.The Sn-OFs were applied to convert readiliy available monosaccharides into rare and expensive products. The epimerizations of D-glucose to D-mannose, L-ribose to L-arabinose, D-xylose to D-lyxose, D-galactose to D-talose, and L-rhamnose to L-quinovose were explored. With Sn-OF-1 equilibrium yields with selectivity of 77-90% were reached at 100 °C after 1.5 h (Fig. 1b).[2] The rare monosaccharides are highly demanded as precursors in pharmaceutical and food industries.[4]
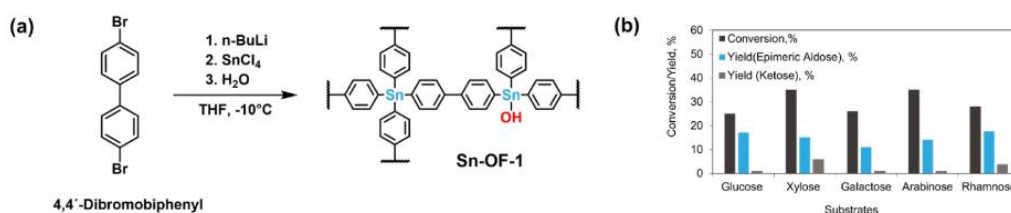
Figure 1: (a) Synthesis of Sn-OF-1. (b) Conversion of aldoses and yields of the correspondig epimeric aldoses and ketoses of catalytic tests with Sn-OF-1 (100 mg Sn-OF-1, 10 wt% sugar in H_2O:EtOH (50:50); 100°C, 1.5h, 750 rpm).

Development of an efficient product recovery presents a key element of process design. We work on product separation via adsorption, focusing on elaborating materials with high affinity towards the desired products. Suitable materials for adorptive separtion are zeolites in Ca2+ form and boronic acid polymers.[5] For instance, L-ribose is selectively separated over CaY zeolite from L-arabinose-L-ribose, with separation factor up to 2.2, owing to complexation of the eq-ax-eq motive of D-ribose with Ca2+ ions. In comparison, the complexation with boronic acid polymers by covalent bonding leads to a separation factor of 4.1. The results of this project will provide a knowledge-driven basis for manufacture of rare saccharides.

[1]   I. Delidovich, R. Palkovits, ChemSusChem 2016, 9, 547.
[2]   a.I. Delidovich, A. Hoffmann, A. Wil ms, M. Rose, ACS Catal. 2017, 7, 3792-3798.; b.V. Toussaint, et al., Manuscript in preparation.
[4]   a.T. Ma, S. B. Pai, Y. L. Zhu, J. S. Lin, K. Shanmuganathan, J. Du, C. Wang, H. Kim, M. G. Newton, Y. C. Cheng, J. Med.Chem. 1996, 39, 2835-2843.; b.Y. Takagi, K. Nakai, T. Tsuchiya, T. Takeuchi, J. Med. Chem. 1996, 39, 1582-1588.
[5]   I. Delidovich and V. Toussaint, Green Chem., 2024, doi.org/10.1039/D3GC04049F.

SESSION 2

12:40 PM – 13:45 PM

12:40   Alexander K. Opitz

13:00   Rauchenwald

Freeze–casting of polymer–derived ceramics for CO2 utilization

13:15   Hulaj

Photocathode design for visible light–driven photoelectrochemical reduction of CO_2

13:30   Horvath

Thermoanaerobacter kivui as workhorse in hot syngas fermentation

Freeze–casting of polymer–derived ceramics for CO₂ utilization

Katharina Rauchenwald[1,2], Philipp Miksovsky[3], Katharina Bica-Schröder[2,3], Karin Föttinger[2,4] and Thomas Konegger[1,2]

[1] *Institute of Chemical Technologies and Analytics, TU Wien*

[2] *Doctoral College CO2Refinery, Faculty of Technical Chemistry, TU Wien*

[3] *Institute of Applied Synthetic Chemistry, TU Wien*

[4] *Institute of Materials Chemistry, TU Wien*

Keywords: Polymer-derived ceramics, Freeze-casting, Heterogeneous Catalysis

To target climate goals, CO_2 should be considered a valuable carbon resource rather than vicious waste. Innovative catalyst support materials based on freeze-cast, polymer-derived silicon oxycarbides (SiOCs) are a promising materials concept for CO_2 utilization applications. Polymer-derived ceramics use silicon-based polymeric precursors and come with the benefit that preceramic polymers can be chemically modified and shaped in the polymeric state, with a subsequent heat-treatment to obtain ceramic materials. Freeze-casting, in contrast, is a method that uses the phase separation of a solvent from the preceramic solution for pore templating, whereas by controlled solidification and subsequent sublimation of solidified solvent, various pore morphologies ranging from dendritic to prismatic in the approximate size range of 1-100 μm are available. Freeze-cast SiOCs provide immense versatility in terms of shaping and structural tailorability and are overall compatible with the wet impregnation technique to deposit catalytically active sites on their inner surface for catalytic tests in monolithic microreactors.

In this work, the conversion of CO_2 to fuels like CH_4 as well as higher value products like cyclic carbonates is tackled, where suitable carrier structures are required for high catalytic performance. To adress the specific material requirements for diverse heterogeneous catalysis concepts, a versatile processing approach by combining freeze-casting with the polymer-derived ceramic route is applied.

In a first example, the development of catalytic reactors for CO_2 methanation is discussed: By depositing 25 wt.% Nickel onto dendritically structured freeze-cast SiOC, CO_2 to CH_4 conversions up to 58 % were reached at temperatures of 400 °C, demonstrating suitability of this specific materials concept at elevated temperatures. The second application example involves the development of SiOC-supported ionic liquids for the highly selective production of limonene carbonate by cycloaddition of CO_2 to bio-based epoxides. Here, the ability to modify the affinity of porous, freeze-cast SiOC monoliths to water by interrupting the pyrolysis at different conversion states promoted the ionic liquid deposition and, subsequently, the performance of these supported catalysts.

The presented results on freeze-cast SiOCs for a variety of CO_2 conversion processes links the in-depth knowledge about the chemistry and shapeability of polymer-derived ceramics with promising CO_2 utilization technologies, and thus indicates their versatility and suitability in various fields and applications of heterogeneous catalysis.

Photocathode design for visible light–driven photoelectrochemical reduction of CO$_2$

B. Hulaj[1], D. Apaydin[2], D. Eder[2], K. Bica-Schröder[1]

[1]*Institute of Applied Synthetic Chemistry, TU Wien, Vienna, Austria*

[2]*Institute of Materials Chemistry, TU Wien, Vienna, Austria*

Keywords: CO$_2$ valorization, photoelectrochemistry, polymers

The valorization of carbon dioxide (CO$_2$) emerges as a promising approach to tackle global challenges, mitigate atmospheric impact, and align with sustainability objectives. However, achieving this goal requires efficient catalytic systems due to significant thermodynamic and kinetic barriers hindering the conversion of CO$_2$ into value-added chemicals.[1]

In this study, we describe the design of photocathodes coated with a conductive polymer, optionally doped with ruthenium and rhenium. By integrating these compounds into a cohesive photoelectrocatalytic framework, the study aims to explore optimal conditions for CO$_2$ reduction.

The synthesis methodology prioritizes simplicity, setting itself apart from the complexities associated with various polymeric CO2 reduction strategies. The incorporation of ruthenium and/or rhenium introduces a synergistic enhancement of both photo- and electrocatalytic properties, resulting in increased selectivity for carbon monoxide formation with relatively low overpotentials.[2]

Preliminary analytical data validates the successful deposition of a conductive polymer layer and optional doping with ruthenium and/or rhenium. Comprehensive elemental analysis is enabled through various mass spectrometry techniques, including Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

[1]   Rosen, B.A.; Salehi-Khojin, A.; Thorson, M.R.; Zhu, W.; Whipple, D.T.; Kenis, P.J.A.; Masel, R.I. *Science* **2011**, *334*, 643 –644.
[2]   Kamata, R.; Kumagai, H.; Yamazaki, Y.; Higashi, M.; Abe, R.; Ishitani, O. *J. Mater. Chem. A*, **2021**, *9*, 1517 –1529.

Thermoanaerobacter kivui as workhorse in hot syngas fermentation

Josef Horvath, Maja Stumptner, Julia Reichebner, Stefan Pflügl

Keywords: Syngas, carbon capture and utilization, biotechnology

Climate change is becoming a greater threat every day. Therefore, it is undoubtedly one of the greatest challenges for the human species to use our knowledge in order to create the turn-around we need to save our planet for future generations. To make that possible, one promising route is carbon capture and utilization (CCU), a technique to use atmospheric and industrial CO_2 as a sustainable resource.

We believe that gas fermentation can be a way to capture CO_2 and utilize it. This technology uses syngas from waste biomass, to feed it to anaerobic bacteria. The bacteria are capable of converting the components of such gases, like CO, CO_2 and H_2, into valuable chemicals.

Gas fermentation has only recently made it to commercialization and there is still big potential for further characterization. Direct coupling of syngas production plant to an active fermentation vessel has not been shown before and the biocatalysis is not fully characterized yet.

We chose Thermoanaerobacter kivui as our workhorse for syngas conversion. T. kivui uses one of the oldest metabolic pathways to naturally capture and convert CO_2 to acetate. At this moment the kinetics of T. kivui as catalyst in a continuous gas fermentation process are poorly studied. The first aim of this work therefore is to study its metabolism and find key parameters that drive the conversion of syngas to acetate. Therefore, T. kivui´s behavior was monitored in continuous bioproduction under different syngas compositions. It was found that T. kivui will utilize different mixtures of CO, H_2 and CO_2 and is able to co-utilize all three of those gasses, as well as just CO alone.

With exact measurement of all the flows in this process, a metabolic model of T. kivui could be generated. In the future, this knowledge could help with engineering the strain to produce more valuable products.

Next to the metabolic study, scale up with T. kivui in syngas fermentation was also demonstrated. A bubble column reactor, which is the most economical tool for syngas fermentation, was used to set up a continuous bioprocess. This pilot plant at a scale of 16L was directly coupled to the syngas plant at TU Wien. In this proof-of-concept experiment we could show that T. kivui convert syngas from wood pellets, continuously for at least 24 hours.

Both undertakings were big steps in establishing T. kivui as workhorse for hot syngas fermentation. The strain was shown to be viable for growth on syngas directly from a syngas plant and with new insights into its metabolism, the strains product spectrum could also be enhanced in the future. As such, bioconversion of syngas could potentially proof to be an economic and efficient process for biomass upgrading into chemicals and fuels.

SESSION 3

14:10 PM – 15:15 PM

14:10   Noelia Barrabés

14:30   Naghdi

Advances in MOF Design: Optimizing Metal–Organic Frameworks Pores for High–Efficiency Water Purification

14:45   Mößlacher

Study of Au11 and Au25 nanoclusters catalysts in the selective hydrogenation of phenylethylene: effect cluster size, ligand and oxide support material

15:00   Magenheim

Automated Quantum Chemical Microsolvation in Arbitrary Solvents

Advances in MOF Design: Optimizing Metal–Organic Frameworks Pores for High–Efficiency Water Purification

Shaghayegh Naghdi[1], Mohammad Zendehbad[2], Pablo Ayala[1], Alexey Cherevan[1], Rémy Guillet-Nicolas[3], Santu Biswas[4], Thomas Haunold[1], Günther Rupprechter[1], Maytal C. Toroker[4], Freddy Kleitz[3], Dominik Eder[1]

[1] Department of Material Chemistry, Technische Universität Wien, 1060 Vienna, Austria,

[2] Department of Water, Atmosphere, and Environment, University of Natural Resources and Life Sciences Vienna, Austria,

[3] Department of Inorganic Chemistry- Functional Materials, Faculty of Chemistry, Universität Wien

[4] Technion - Israel Institute of Technology, Haifa 3600003, Israel.

Keywords: Meta-organic frameworks, Hierarchical pores, MOF-based water purification, Photocatalysis

In the realm of environmental and energy technologies, Metal-Organic Frameworks (MOFs) have emerged as a focal point of interest due to their unique combination of tunable light-harvesting, catalytic functionalities, and exceptional adsorption properties. Recognizing the limitations imposed by the small micropores of MOFs in liquid-phase dynamics, particularly in terms of reactant diffusion, we have pioneered a novel approach. This involves the strategic introduction of mesopores into mixed- ligand MOFs via selective ligand removal (SeLiRe) through thermolysis.

Our methodology has led to the creation of photoactive MOFs within the MIL-125-Ti family, boasting two types of hierarchical pore structures: expansive cavities and intricate branching fractures. Remarkably, these tailored pore geometries have enhanced the Hydrogen Evolution Reaction (HER) rates by up to 400%, presenting a groundbreaking tool for designing hierarchical MOFs with heightened functionality in liquid environments [1].

Our research further explored the effects of selective ligand removal on the adsorption properties of MOFs. We concentrated on eliminating organic pollutants from water. The presence of unsaturated Ti–OH groups, coupled with enhanced accessibility—as a result of SeLiRe—significantly improved adsorption efficiency. In fact, these modified MOFs demonstrated adsorption rates up to four times greater than those of the original mixed-ligand and single-ligand MOFs [2].

In a significant stride forward, we introduce two new mixed-ligand Cu-based MOFs, named TUW-1 and TUW-2. These have been synthesized as superior adsorbents for rapid and highly effective nitrate removal from water and real wastewater. Notably, these MOFs stand as the most stable in aqueous conditions, maintaining structural integrity for over 365 days. Additionally, both TUW-1 and TUW-2 demonstrate rapid adsorption kinetics and unprecedented nitrate adsorption capacities (119.42 mg g^{-1} for TUW-1 and 105.93 mg g^{-1} for TUW-2), outperforming all known adsorbents, even at neutral pH levels. These studies highlight the potential of MOFs as promising materials for efficient and sustainable water purification.

[1]   Naghdi et al., Nature Communications 2022, 13 (1), 282.
[2]   Naghdi et al., Advanced Functional Materials 2023, 195, 6.

Study of Au11 and Au25 nanoclusters catalysts in the selective hydrogenation of phenylethylene: effect cluster size, ligand and oxide support material

Sebastian Mößlacher, Rareş Banu, Noelia Barrabés

ClusCat Lab, Institute of Materials Chemistry, TU Wien

Keywords: Au-nanocluster, selectivity, hydrogenation

The selective hydrogenation of alkynes is of particular importance as it plays a decisive role in fine chemistry and polymer production. A catalyst that efficiently and selectively converts alkynes to alkenes while avoiding overhydrogenation to alkanes is essential. This capability is crucial for the removal of trace amounts of alkynes prior to alkene polymerisation or the conversion of alkynes into fine chemicals.Recently, gold catalysts have emerged as a promising alternative, showing superior selectivity and high activity compared to Pd. In order to understand the relationship between activity, selectivity and structural properties of catalysts, the use of atomically precise and controlled nanocatalysts is essential.Atomically precise gold nanoclusters in catalysis is an emerging field, opening up new perspectives for precise studies of size-dependent properties, effects of atomic structure and reaction mechanisms in catalysis.

In our study, the synergistic effects between the cluster size/structure, the nature of the ligand and the oxide employed has been explored. We investigated two different ligand-protected gold nanoclusters, phosphine-protected ($Au_{11}(PPh_3)_7Br_3$) and thiolate-protected ($Au_{25}(SC_2H_4Ph)_{18}$), supported on MgO as alkaline, Mg- and Al-oxide hydrotalcite (HT) as slightly basic and Al_2O_3 as acid carrier material, in the selective hydrogenation of phenylacetylene to styrene.

Regarding not only the protection of the cluster but also the supporting materials, strong differences have evolved in selectivity and activity. For the determination of the influence from the ligands on the reaction, the catalysts have undergone thermal pretreatment to be compared to the not treated samples.

While high selectivity and general activity have been observed without pretreatment, a thermal conditioning has resulted in an decrease in not only selectivity but also production when looking at Au25 on HT (Figure 1). The preliminary analysis of the spectroscopy studies revealed that the reaction itself brings more change to the binding sites on the catalyst in comparison to just the pretreatment.

Furthermore, the acidity of the supports indicated that acidic nature is not enhancing selectivity. Until now Au25 on HT and Au11 on MgO were the most effective catalysts regarding selectivity while keeping high acitivity.
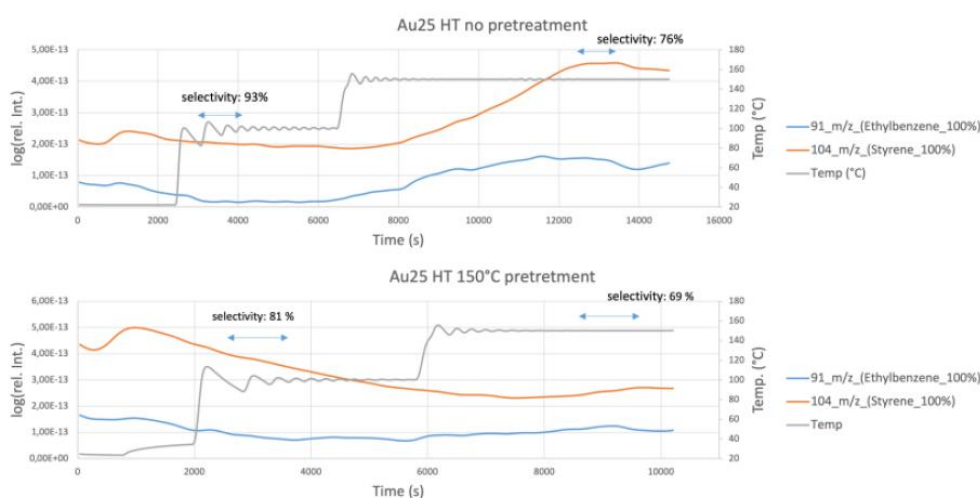
Figure 1: comparison reactor data (MS) of Au25 HT with and without pretreatment

Automated Quantum Chemical Microsolvation in Arbitrary Solvents

Lukas Magenheim, Radu A. Talmazan and Maren Podewitz

Institut für Materialchemie, TU Wien, Getreidemarkt 9, 1060 Wien, Austria

Molecules in solution, typically denoted as solutes, are surrounded by solvent molecules with which they interact. These interactions have a direct influence on the properties and reactivity of the solute at hand. To obtain a more accurate chemical model, as well as improve the description of the system behaviour, it is vital that solvent effects are taken into account.

In quantum chemical descriptions, those solvent effects are either treated implicitly, accounting for bulk properties only – in its simplest way by an electrical permittivity – or explicitly, by defining an arbitrary number of solvent molecules around the solute. This approach poses two questions:

- Where and how should those solvents be placed?
- How many are needed to capture most of the relevant interactions while minimizing the computational workload?

In a previous work [1] we devised a protocol for systems solvated in water, that extracts energetic and entropic information from MD simulation derived data. This protocol makes use of the Grid Imhomogenous Solvation Theory (GIST) [2,3] to determine solute-solvent interaction on a grid. Here, we present the completely revised and extended protocol, which is now fit to evaluate favorable solvation sites for a larger set of rigid solvents, such as dichloromethane or DMSO.[4] We showcased the applicability of our methodology at several examples ranging from solvatochromic substances to transition-metal containing bioinorganic compounds such as Vitamin B12.

[1]   M. Steiner, T. Holzknecht, M. Schauperl, M. Podewitz, Molecules 2021, 26, 1793.
[2]   C. N. Nguyen, T. Kurtzman Young and M. K. Gilson, J. Chem. Phys., 2012, 137, 044101.
[3]   D. R. Roe and T. E. Cheatham 3rd, J. Chem. Theory Comput. 2013, 9, 3084.
[4]   L. Magenheim, R. A. Talmazan, M. Podewitz, manuscript in preparation (2024).

SESSION 4

15:40 PM – 17:00 PM

15:40   Golta Khatibi

16:00   Wodak

The Influence of Metallic Nanoparticles on the Properties of Hybrid Solder Joints

16:15   Ricchiuti

On-chip Photothermal Spectroscopy (PTS) for the detection of a PMMA thin film on Silicon Nitride

16:30   Umfahrer

Classification of Late-Antique Glass: Tandem-LIBS-LA-ICP-MS Analysis and Machine Learning Approach

16:45   Closing

The Influence of Metallic Nanoparticles on the Properties of Hybrid Solder Joints

Irina Wodak, Golta Khatibi, Andriy Yakymovych, Farzad Khodabakhshi

Institute of Chemical Technologies and Analytics

Keywords: Hybrid Solder Joints, Metallic Nanoparticles, Intermetallic Compound (IMC), Morphology, Mechanical Properties

Since lead containing Sn-Pb solders as potential health-hazards have been systematically phased out from industrial applications, Sn-based solders such as e.g. Sn-Ag-Cu (SAC), Sn-3.5Ag have risen as the predominant alternative. Although they are considered leading solder alloys, they have some drawbacks, such as a higher melting temperature compared to Sn-Pb and a pronounced growth of brittle intermetallic compounds (IMC) at the substrate/solder interface, which deteriorates the mechanical reliability of solder joints.

The aim of this research is the employment of Fe-Nanoparticles in the solder material which act as diffusion barrier with respect to the formation of IMCs as well as grain growth. The influence of other metal nanospheres, such as Ni and Co, will be investigated in later stages. Previous studies revealed that doping solder pastes with metal NPs results in substantial agglomeration, likely attributed to the considerable overall NP amount. Consequently, a diminished positive effect is observed. To address this, the concept of mixing NPs with commercial flux has emerged. This strategy concentrates their growth-inhibiting effect on the interface, requiring a reduced overall NP amount.

In the early period of work different synthesis methods for metal nanoparticles were investigated. The as-synthesized nanoparticles were further analyzed with SEM, TEM, EDX and XRD measurements. Different amounts of the NPs are then used to produce hybrid solder (solder/NPs doped flux/solder) joints. Subsequently, the microstructure and mechanical properties of the hybrid solder joints in the initial state and after heat treatment are investigated. Additionally, SEM, FIB/TEM, and EDX analyses are conducted to investigate the chemical reactions between metal NPs and the solder matrix, influencing phase formation, grain growth, and intermetallic compound (IMC) growth.

Further investigation involves scrutinizing the alteration in viscosity of the flux following the addition of nanoparticles and evaluating their influence on the wettability of the solder. Additionally, prospective work will focus on studying mechanical properties of the hybrid solder joints through stress-relaxation tests as well as microhardness measurements. Finally, the performance of the hybrid solder joints will be compared with conventional solder joints and the influence of the different metal NPs as well as the different NP concentrations on the properties and stability of the microstructure will be investigated.

On–chip Photothermal Spectroscopy (PTS) for the detection of a PMMA thin film on Silicon Nitride

Giovanna Ricchiuti[1,2,3], Jesús Hernán Mendoza Castro[4,1], Anton Walsh[2,3], Artem Vorobev[4,2,3], Marco Grande[4], Bernhard Lendl[1] and Liam O'Faolain[2,3]

[1] Institute of Chemical Technologies and Analytics, TU Wien, Getreidemarkt 9/164-UPA, 1060, Vienna, Austria

[2] Centre for Advanced Photonics and Process Analysis, Munster Technological University, T12 T66T Bishopstown, Cork, Ireland

[3] Tyndall National Institute, T12 PX46 Cork, Ireland

[4] Department of Electrical and Information Engineering, Polytechnic University of Bari, 4, 70126 Bari, Italy

Keywords: Photothermal Spectroscopy, QCL sources, mid-IR

In this study, we report on a compact photothermal sensor that relies on Photonics Integrated Circuits (PICs). In detail, we use a silicon nitride (S3N4) micro ring resonator (MRR) as a transducer, combined with a dual-beam transversal photothermal detection scheme. As a proof-of-principle we detect a Polymethylmethlyacrylate (PMMA) thin film as an analyte. A 160 nm PMMA layer is spin-coated on top of the 33 µm radius MRR with four rectangular partially transmitting elements (PTE) in the gap region, engineered to achieve high Q-factor and high slope Fano resonance features. PMMA absorption peak is positioned at $v\sim$ ~1730 cm^{-1}. In PTS, modulated light absorption by the analyte under investigation is photoinduced by a periodic modulation of the sample's temperature and in turn of its refractive index. Photothermal phenomenon is directly proportional to the optical power of the excitation source and for this reason it benefits from recent developments of powerful mid-IR laser sources, such as Distributed Feedback lasers (DFB) and/or Quantum Cascade Lasers (QCL).

In our setup we use a tunable NIR laser to tune the MRR at the inflection point of a picked resonance within the transmission spectrum, aiming for maximized shift sensitivity, and an External Cavity (EC)-QCL that emits between 1560-1770 cm^{-1}, covering the spectral region in which the polymer absorbs. The MIR source is focused on top of the waveguide via a Cassegrain reflector such that the beam spot-size (~ 20 µm) is collected only on top of the ring under measurement. PTS enables to gain a qualitative spectral information of the target analyte by sweeping the pump laser in pulsed mode on the chip and recording the lock-in amplifier (LIA) demodulated signal using the pulse rate as a reference trigger. The polymer periodically heats up and cools down, provoking a periodical shift proportional to the generated thermal gradient ΔT.

Based on the thermal properties and relaxation time of the overall chip coated with PMMA, the PTS signal was optimized in terms of pulse repetition rate and pulse width. This in turn permits to maximize the PT signal's magnitude. In post-processing, the PT signal is normalized by the optical power of the excitation laser, recorded via an MCT detector. This way a qualitative spectrum, proportional to PMMA absorption feature, is obtained and benchmarked against FTIR spectrometer's record.

Moreover, as the PT signal is inversely proportional to the interaction area between the probe and pump laser, this sensing scheme holds great promises for realizing miniaturized and highly sensitive sensors to be exploited for several different analytes and applications.

Classification of Late–Antique Glass: Tandem–LIBS–LA–ICP–MS Analysis and Machine Learning Approach

Barbara Umfahrer[1], Lukas Brunnbauer[1], Sabine Ladstätter[2], Pamela Fragnoli[2], Andreas Limbeck[1]

[1]TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-I²AC, 1060 Vienna, Austria

[2]Österreichisches Archäologisches Institut, Georg-Coch-Platz 2, 1010 Wien

Keywords: Tandem-LIBS-LA-ICP-MS, historical glass, classification

Determining the provenance of an artifact found at a specific location can give insight into ancient societies' economies and industries. In archaeology elemental fingerprinting is a common approach to reveal the beforementioned provenance of discovered artifacts since raw materials come with a distinct geological pattern of major, minor, and trace elements.

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is commonly used to analyze historical glass, as it provides fast analysis and the required sensitivity for most constituents of interest. However, various elements, which are major and minor components of glass, such as Si, K, Ca, Fe, and Al are challenging to measure with conventional quadrupole ICP-MS due to isobaric and polyatomic interferences. This study aims to explore the advantages of incorporating Laser-Induced Breakdown Spectroscopy (LIBS) into the measurement setup, using Tandem-LIBS-LA-ICP-MS.

This contribution presents the results of analyzing 46 late-antique glass samples, excavated at Hemmaberg, Austria. Quantification was carried out using Tandem-LIBS-LA-ICP-MS and the reference materials NIST® SRM® 610 and NIST® SRM® 612. Comparing the results of both LIBS and LA-ICP-MS with the composition from a reference liquid analysis, it was demonstrated that LIBS is superior in analyzing certain elements (e.g. Ca, Al).

Finally, a database containing the elemental composition and origin of glass samples reported in the literature was built and used as a training dataset for a k-nearest neighbor (k-NN) classification model, which enables assigning the origin and the glass type of the samples under investigation.

POSTER CONTRIBUTIONS

Poster contributions in alphabetical order

Achleitner	Realisation of a lIBS method to determine the degree of imidization of polyimides
Banu	Origins of Chirality in Gold Nanoclusters
Cazorla	Activity of Cu/CeO2 and Cu/CexZr1–xO2 catalysts for the reverse water gas shift reaction
Chen	Bottom–Up Synthesis of Medium/High Entropy Sulfides and their Use in Photocatalysis
Eisenköck	Maximizing efficiency in the chemical recovery of the pulp and paper industry through spectroscopic monitoring
Fritz	Vibrational spectroscopy – a valuable PAT tool for crystallization monitoring
Iebed	Elucidating the Role of Posttranslational Modifications of HMGN1 in DNA Packaging
Kronlachner	Characterization of ceramic nanoparticles using Laser Ablation–Single Particle–ICP–MS.
Pavlis	Selective Product Recovery of D–Mannose from its mixture with D–Glucose by Adsorptive Separation over CaY Zeolites
Pinto	Long wavelength distributed feedback tapered quantum cascade lasers
Rabl	Synergistic advances in electrocatalytic CO2 reduction: enhancing the performance of [AgSePh]∞ through innovative counter electrode optimization
Riedlsperger	Optimizing Protein Analysis with QCL–based Multi–Pathlength Mid–IR Spectroscopy
Tampieri	A bizarre cubic/tetragonal phase transition behaviour in copper ferrite
Templ	Mashing up Tsuji–Trost Allylation – a mechanochemical approach
Unglert	Neural–network force field backed nested sampling: Predicting phase diagrams
Vijayakumar	Teaching an old dog new chemometrics: laser–based mid–IR spectroscopy coupled to chemometrics as a tool for continuous monitoring of protein unfolding
Walk	Dynamic Modeling for Enhanced Process Simulation and Optimization in Steel Production
Weisweiller	Photocatalytic generation of solar fuels and simultaneous oxidation of microplastics

Realisation of a lIBS method to determine the degree of imidization of polyimides

Birgit Achleitner[1], Laurie Girault[2], Silvia Larisegger[3], Michael Nelhiebel[4], Patrick Knaack[2] and Andreas Limbeck[1]

[1]*TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164, 1060 Vienna, Austria*

[2]*TU Wien, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163, 1060 Vienna, Austria*

[3]*KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Argentinierstraße 8, 1040 Wien, Austria*

[4]*KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Technologiepark Villach Europastraße 8, 9524 Villach, Austria*

Keywords: Laser Induced Breakdown Spectroscopy, Polymer Analysis, Degree of Imidization

Due to their excellent chemical and physical properties, polyimides are widely used in industrial applications including automotive, aerospace and electronics. Because they are non-soluble and due to their high thermal stability, the shaping is done via a chemical reaction or thermal treatment of a soluble precursor, the poly(amic acid). During this treatment the conversion of the amic acid group into imide is achieved, which is reflected in the degree of imidization. The degree of imidization of a polyimide is also closely related to the final properties of the polymer. IR is a well-established technique to determine this characteristic feature but lacks the possibility of analyzing depth profiles. As a consequence, polymerization studies are limited to the sample surface.

In this work, we present a LIBS method for the investigation of the imidization degree of a self-synthesized poly(4,4'-oxydiphenylene-pyromellitimide) (PMDA-ODA). To confirm the LIBS method, IR measurements served as a reference and a good agreement between those two techniques was found. Furthermore, the investigation of variably imidized samples is shown as an example of use.

Origins of Chirality in Gold Nanoclusters

Rareş Banu, Adea Loxha, Noelia Barrabés

Keywords: chirality, nanoclusters, spectroscopy

Chirality, a ubiquitous natural phenomenon, has long fascinated scientists due to its far-reaching implications. Its precise control is a key objective across various disciplines, notably in medicine and catalysis. In the pharmaceutical industry, the meticulous management of chirality is crucial for ensuring the quality of drugs. Achieving this control requires a fundamental understanding of the synthetic and catalytic processes leading to chiral products.

Among the intriguing materials that have emerged in recent times are thiolate-protected gold nanoclusters, representing a relatively novel class with exquisite properties, notably chirality. These nanoclusters, characterized by atomically controlled size and structure, exhibit chiral features at multiple levels, encompassing their core, ligand arrangement, and ligands themselves. This inherent tunability offers the prospect of tailoring the origin of chirality in these structures to align with specific applications. [1-4]

This study focuses on the synthesis of three nanoclusters, each manifesting distinct levels of chirality, employing a novel chiral ligand. The investigation of these nanoclusters is conducted through electronic and vibrational circular dichroism (ECD and VCD, respectively) spectroscopy. The results unveil several significant findings, including a remarkable enhancement in the nanocluster synthesis yield and an enantioselective synthesis, leading to the first experimental ECD and VCD spectra for one of the studied clusters.

All in all, the study sheds light on how different nanocluster structures impact their chiroptical properties. These findings offer valuable insights into the origins of chirality in such systems, opening the doors for nanoclusters to be used in various life-science fields, such as drug production and bio-medicine.
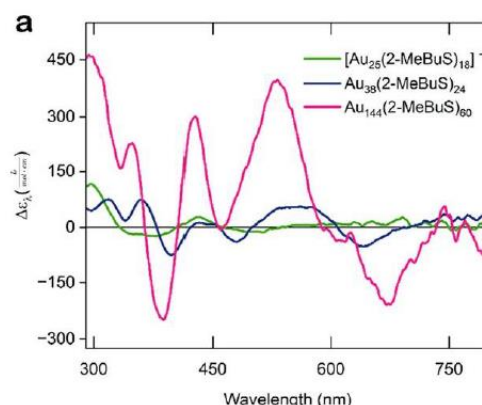
Figure 1: ECD signal of the three synthesized nanoclusters

[1]   Directing Intrinsic Chirality in Gold Nanoclusters: Preferential Formation of Stable Enantiopure Clusters in High Yield and Experimentally Unveiling the "Super" Chirality of Au144. Vera Truttmann, Adea Loxha, Rareş Banu, Ernst Pittenauer, Sami Malola, María Francisca Matus, Yuchen Wang, Elizabeth A. Ploetz, Günther Rupprechter, Thomas Bürgi, Hannu Häkkinen, Christine Aikens, and Noelia Barrabés. ACS Nano 2023 17 (20), 20376-20386 DOI: 10.1021/acsnano.3c06568

[2]   Dolamic, I., et al., First enantioseparation and circular dichroism spectra of Au38 clusters protected by achiral ligands. Nature Communications, 2012. 3(1): p. 798.

[3]   Barrabés, N., B. Zhang, and T. Bürgi, Racemization of Chiral Pd2Au36(SC2H4Ph)24: Doping Increases the Flexibility of the Cluster Surface. Journal of the American Chemical Society, 2014. 136(41): p. 14361-14364.

[4]   Wang, Y., B. Nieto-Ortega, and T. Bürgi, Amplification of enantiomeric excess by dynamic Inversion of enantiomers in deracemization of Au38 clusters. Nature Communications, 2020. 11(1): p. 4562

Bottom–Up Synthesis of Medium/High Entropy Sulfides and their Use in Photocatalysis

Yan Chen, Martin Nastran, Bernhard Fickl, Jakob Rath, Stephen Myakala, Alexey Cherevan, Dominik Eder, Bernhard C. Bayer

Institute of Materials Chemistry, TU Wien

Keywords: high entropy sulfide, hydrogen evolution reaction, photocatalysis

In the pursuit of sustainable energy sources, the spotlight shines brightly on innovative materials that hold the potential to revolutionize the landscape of energy conversion. Among these materials, two-dimensional (2D) and non-2D medium and high entropy sulfides (MESs/HESs) stand out as promising candidates in the domain of photocatalytic hydrogen evolution reaction (HER). These compounds, characterized by their intricate compositions and distinctive structures, present a captivating multi-functional avenue for exploring new frontiers in renewable energy.

In this work, we introduce $(MoWCoNi)S_x$ and $(MoWCoNiFe)S_x$ - medium and high entropy sulfides that encapsulate a symphony of molybdenum (Mo), tungsten (W), cobalt (Co), nickel (Ni), and occasionally iron (Fe) as effective (co-)catalysts for light-driven HER. We explore their bottom-up synthesis method to gain CdS-supported medium and high entropy sulfide hybrids. Instead of prior introduced high-temperature method to get HESs, a novel low-temperature solvothermal synthesis has been applied to construct medium and high entropy sulfides directly.

We demonstrate that the compositions and synthesis pathways of medium and high entropy sulfides could affect the crystal structure and the performance of photocatalytic process. Our work shows the potential of medium and high entropy materials in constructing photosystems for catalytic H2 production and delves into understanding their structure-property relationships.

Maximizing efficiency in the chemical recovery of the pulp and paper industry through spectroscopic monitoring

Miranda Eisenköck[1], Barbara Weiß[1], Anna Katharina Schwaiger[2], Wolfgang Fuchs[2], Bernhard Lendl[3], Michael Harasek[4], Martin Kraft[1], Karin Wieland[1]

[1] *Competence Center CHASE GmbH, Vienna, Austria*

[2] *Sappi Europe | Gratkorn Mill, Gratkorn, Austria*

[3] *Institute of Chemical Technologies and Analytics | TU Wien, Vienna, Austria*

[4] *Institute of Chemical, Environmental and Bioscience Engineering | TU Wien, Vienna, Austria*

Keywords: PAT, pulp and paper, chemical recovery, circular economy, Raman spectroscopy

The recovery of chemicals after the extraction process of cellulose from wood in the pulp and paper industry is a key step towards circular process streams including ecological and economic benefits. The main chemical ingredient of the "cooking liquor" used here in the solubilization is $Mg(HSO_3)_2$. After the cooking step the residual material is incinerated and SO_2 is recovered from the hot flue gas in a cascade of Venturi scrubbers. Reiterated interactions of the hot gas with fresh $Mg(OH)_2$ slurry lead to the reformation of the magnesium bisulfite cooking liquor via a 2-step reaction process. Due to harsh conditions (temperatures > 60 °C, pH 4-7, high ionic strength) and complex interactions between gas and liquid phase, the formation of insoluble salts causes clogged pipes and unscheduled downtimes.

A key step in achieving higher recovery efficiency is a deepened understanding of the chemical interplay occurring in the Venturi scrubbers. Raman spectroscopy is used as a non-destructive, in-situ process monitoring tool. In combination with multivariate regression models, the spectral data is translated into critical process-relevant parameters. Continuous monitoring of variables such as free SO_2, total SO_2, sulfate and monosulfite based on the Raman spectral fingerprint allows tight process control of the interaction between the SO_2 gas and $Mg(OH)_2$ slurry.

We demonstrate the efficient use of Raman spectroscopy as a valuable tool in the chemical recovery of the pulp and paper industry. We establish and optimize a multivariate regression model based on several hundred at-line reference spectra to predict multiple target variables. Based on our approach, critical process parameters can be determined within seconds. Effects on the chemical system due to a change in the process control strategy may be corrected or averted by early countermeasures. Hence, long downtimes and loss of valuable chemicals due to unwanted precipitation are reduced.

Vibrational spectroscopy – a valuable PAT tool for crystallization monitoring

Markus Fritz[1], Karin Wieland[1], Thomas Linder[2], Bernhard Sandig[2], Martin Kraft[1] and Peter Pöchlauer[2]

[1]Competence Center CHASE GmbH, Vienna, Austria

[2]Patheon Austria GmbH & Co KG, Linz, Austria

Keywords: Crystallization process monitoring, PAT, vibrational spectroscopy

Crystallization is used in many chemical manufacturing processes to separate, purify, and isolate products from reaction mixtures. This is especially important when different polymorphic forms may be formed along the way. Typically, only one of the forms exhibits the desired physical (e.g. solubility, stability, melting point, etc.) and chemical (chemical reactivity) properties. Hence, the production of the wrong polymorph can have a significant impact on the properties of the final product and can thus affect its suitability for the intended use. Consequently, careful control of the crystallization process is key to ensuring the formation of the correct polymorph.

Vibrational spectroscopy enables real-time analysis of the crystallization process. Together with uni- or multivariate analysis, concentration profiles can be extracted and used for e.g. reaction end-point determination. Raman and FTIR spectroscopy can both be employed for polymorph screening and crystallization progress monitoring but exhibit different advantages and disadvantages; Raman spectroscopy is a weak scattering effect and is typically hampered by fluorescent samples while IR spectroscopy in aqueous environment suffers from strong water absorptions. Both vibrational spectroscopy techniques, however, are affected by temperature changes in terms of band shifts, broadening or intensity. Hence, the effect of temperature needs to be considered in data analysis.

Spectroscopy-based continuous monitoring of crystallization processes is a critical tool for optimizing process performance and ensuring product quality. We show results using a combined approach of Raman and FTIR in-line spectroscopic monitoring during a crystallization process with changing temperature. Along with this multi-sensor approach, valuable process information can be extracted in combination with multivariate data analysis.

Elucidating the Role of Posttranslational Modifications of HMGN1 in DNA Packaging

Dina Iebed, Anne Conibear

Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria

Keywords: Protein semi-synthesis, Posttranlational modifications, Intrinsically disordered proteins, Protein NMR spectroscopy

DNA packaging in eukaryotes is a tightly regulated mechanism involving a number of different proteins. Among them is HMGN1, a member of the intrinsically disordered high mobility group proteins. HMGN1 is modulated by its posttranslational modifications (PTMs), mainly lysine acetylations and serine phosphorylations. Understanding the specific influence of PTMs on the biological function of HMGN1 is a challenge, because of the difficulties of accessing homogeneous site-specifically modified HMGN1 variants. Here we present our synthetic approach to accessing HMGN1 variants bearing site-specific fluorophores, and PTMs in the nucleosome binding domain and nuclear localization signal. We investigated several semi-synthetic strategies and native chemical ligation sites for their feasibility, synthetic accessibility and efficiency. The site-specifically modified HMGN1 variants will be used to investigate the effect of the PTMs on the binding of HMGN1 to nucleosomes, the localization of HMGN1 in the cell, and conformational changes. PTM crosstalk, in which the effects of multiple PTMs interact, will be explored as well. Understanding how PTMs influence the behavior of HMGN1 in DNA packaging has the potential to provide insights into how this fundamental cellular process is regulated.

Characterization of ceramic nanoparticles using Laser Ablation–Single Particle–ICP–MS

Laura Kronlachner, Zuzana Gajarska and Andreas Limbeck

TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-I²AC, 1060 Vienna, Austria

Key words: nanoparticle, single-particle, ICP-MS

Nanotechnology is rapidly gaining importance as an emerging scientific field, thanks to the extraordinary chemical and physical attributes displayed by materials at the nanometer scale. These properties diverge significantly from those found in bulk materials, rendering nanomaterials invaluable for many applications across diverse scientific and industrial sectors. For example, ceramic nanoparticles are applied in energy production, as well as in photonics, optoelectronics and catalysis [1] but also find use in biomedical applications such as drug delivery and are applied in orthopedic therapy [2].

The widespread utilization of nanoparticles calls for reliable and robust analytical methods for comprehensive material characterization. A deep understanding of nanoparticle properties and characteristics is indispensable for purposes such as engineering, research and development, quality control, and the successful implementation of innovative applications. This entails gathering precise information about the elemental compositions of the particles, as well as crucial data such as average size, size distribution, and particle number concentration. In recent years, single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has emerged as a powerful analytical tool for nanoparticle characterization [3].

To overcome the limitations of the conventional SP-ICP-MS analyzing nanoparticles in liquid suspensions, which include problems with sample stability and sample introduction efficiency, the combination of laser ablation and SP-ICP-MS has been developed. Using laser ablation as the sampling method incorporates vital solid sampling benefits [4,5].

In this work, we present the use of in-house manufactured polymer thin films with defined element concentrations as calibration standards, avoiding the need for certified nanoparticle reference material. This is especially useful for nanomaterials where reference material is not commercially available. Ceramic nanoparticles were analyzed and sized using the laser ablation approach with thin film calibration standards created in-house.

Summary: Spin coating is a feasible method for the preparation of nanoparticle samples as well as spiked thin films as calibration standards for the analysis with Laser-Ablation-ICP-MS. No commercially available standard material, which is often not available, is necessary, and Single-Particle-ICP-MS can be combined with all the benefits solid sampling with laser ablation offers.

[1]   R. D'Amato, M. Falconieri, S. Gagliardi, E. Popovici, E. Serra, G. Terranova and E. Borsella, J. Anal. Appl. Pyrolysis, 2013, 104, 461–469.
[2]   A. I. Moreno-Vega, T. Gómez-Quintero, R. E. Nuñez-Anita, L. S. Acosta-Torres and V. Castaño, J. Nanotechnol., , DOI:10.1155/2012/936041.
[3]   D. Mozhayeva and C. Engelhard, J. Anal. At. Spectrom., 2020, 35, 1740–1783.
[4]   S. Yamashita, Y. Yoshikuni, H. Obayashi, T. Suzuki, D. Green and T. Hirata, Anal. Chem., 2019, 91, 4544–4551.
[5]   D. Metarapi, M. Šala, K. Vogel-Mikuš, V. S. Šelih and J. T. Van Elteren, Anal. Chem., 2019, 91, 6200–6205.

Activity of Cu/CeO$_2$ and Cu/Ce$_x$Zr$_{1-x}$O$_2$ catalysts for the reverse water gas shift reaction

Mireia Palma[1], Christian Schröder[1], Noelia Barrabés[2], Maricruz Sanchez-Sanchez[1]

[1]*Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Getreidemarkt 9/166, Vienna 1060, Austria*

[2]*Institute of Materials Chemistry, TU Wien, Getreidemarkt 9/165, Vienna 1060, Austria.*

Keywords: Reverse water-gas-shift, Cerium Oxide, Copper, CO2 utilization, Zirconium Oxide

Reverse water gas shift (RWGS) have received recently attention as a way to utilize CO$_2$ to produce syngas. Among RWGS catalysts, inexpensive Cu-based materials are of interest because they have shown high activity and selectivity .[1] The nature of the support can affect the catalytic performance and, in particular, reducible oxides have been reported to improve the catalytic performance of Cu sites.[1] CeO$_2$ as catalyst support has been used to investigate the RWGS reaction because of its ability to form oxygen vacancies and its oxygen storage and release capacity, which have been demonstrated to assist in the conversion of CO$_2$ to CO.[2, 3] ZrO$_2$ is known to enhance oxygen mobility when added to CeO2. [4] In this work we study the effect of adding adding ZrO$_2$ on the activity in RWGS of Cu/CeO2 catalysts with different metal loadings.

The CuO/CeZrO$_2$ catalysts have been synthetized with diferent loadings of ZrO$_2$ and CuO. The co-precipitation method was used to synthesize the CeO$_2$-ZrO$_2$ supports. Cu was then introduced by impregnation of the supports with Cu nitrate solutions, followed by calcination at 500°C for 4 hours. Activity tests were performed in a 3 mm diameter quarz reactor, after reduction of the catalyst at 300°C to generate Cu metal. Activity was measured in the lower temperature range (250°C to 350°C) in order to work at differential conversions and obtain the kinetics parameters. The gas products were analyzed by gas chromatography. The characterization of the catalysts has been performed by different spectroscopies and temperature-programmed reductions (TPR).

The tests in RWGS show that among the catalysts tested, Cu supported on CeO$_2$ has the highest activity. On the other hand, the characterization by XRD shows that the presence of Zr in the CeO$_2$ support stabilizes the Cu particles against sinterization. Further studies on the CeO$_2$-ZrO$_2$ support will lead to insights on the role of support on the activity of Cu particles for RWGS.

[1]   Zhang, Y.; Liang, L. et al. Applied Surface Science. 2020, 516, 146035.
[2]   Zhou, G.; Dai, B. et al. Journal of CO2 utilization. 2017, 21, 292-301.
[3]   Yang, S.; Pang, S. et al. ACS Catal. 2018, 8, 12056-12066.
[4]   Duprez, D.; Descorme, C. et al. Topics in Catalysis. 2001, Vols. 16/17, 49-56.

Selective Product Recovery of D–Mannose from its mixture with D–Glucose by Adsorptive Separation over CaY Zeolites

Loretta Pavlis, Valérie Toussaint, Irina Delidovich

Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, 1060-Vienna, Austria

Keywords: zeolites, adsorptive separation, monosaccharides.

Nowadays, D-mannose (D-Man) presents one of the most highly demanded sugars on the world market. D-Man is used in food industry in supplements or sweeteners and plays a crucial role in the pharmaceutical industry.[1] D-Man is available from biomass as a monomer of hemicelluloses, one of the main components of lignocellulose.[2]

Recently, an environmentally friendly method for D-Man production was uncovered. The epimerization of D-glucose (D-Glc) to D-Man in the presence of tin organic frameworks (SnOFs) produces D-Man with high selectivity, with an equilibrium mixture D-Glc:D-Man of 80:20.[3] Methods for D Man recovery by means of conventional techniques such as chromatography exhibit several drawbacks due to large amounts of eluent, long separation times and large columns, and highly diluted fractions of saccharides. In this work, adsorptive separation with calcium-exchanged NaY zeolites was explored as a cost-effective, sustainable, and selective separation method to recover D-Man.

First, the commercially available NaY zeolite was exchanged with Ca2+ ions to obtain CaY zeolites. Using CaY as adsorbent, a highly selective uptake of D-Man from its solution with D-Glc could be achieved. The loading could be increased in ethanol-water solutions compared to aqueous solutions. For the competitive adsorption from a 50:50 D-Man:D-Glc in a 70:30 ethanol:water mixture, a separation factor of 4.2 was determined. Higher adsorption of D-Man on CaY is probably due to the more stable tridentate complexation of the Ca2+ ions with the axial-equatorial-axial hydroxy groups of D-Man.[4] D-Man could be nearly fully desorbed by addition of water at room temperature. Our current research focuses on the combination of both, synthesis and adsorptive separation for the development of a production process of D-Man. Currently, we explore the product recovery of other monosaccharides such as D-lyxose and L-ribose from their mixtures with D-xylose and L-arabinose, respectively.

[1] X. Hu, Y. Shi, P. Zhang, M. Miao, T. Zhang, B. Jiang, Compr. Rev. Food Sci. Food Saf., 2016, 15, 773-785.
[2] L. Negahdar, I. Delidovich, R. Palkovits, Appl. Catal. B Environ., 2016, 184, 285-298.
[3] I. Delidovich, A. Hoffmann, A. Willms, M. Rose, ACS Catal., 2017, 7, 3792-3798
[4] H. Caruel, L. Rigal, A. Gaset, J. Chromatogr. A, 1991, 558, 89-104

Long wavelength distributed feedback tapered quantum cascade lasers

Davide Pinto[1,2], Kumar Kinjalk[2], Ariane Meguekam[2], Michael Bahriz[2], Bernhard Lendl[1] and Alexei N. Baranov[2]

[1]*Institute of Chemical Technologies and Analytics, Technische Universität Wien, Getreidemarkt 9/164, 1060 Vienna, Austria*

[2]*Institute of Electronics and Systems, UMR 5214 CNRS – Université de Montpellier, 34095 Montpellier, France*

Keywords: Quantum Cascade Lasers, Tapered Laser, Long wavelength Mid-IR

Short abstract: We present an investigation on the electrical, optical, and spectral properties of distributed feedback tapered quantum cascade lasers emitting at 14-15 μm, based on the InAs/AlSb material system. Tapered lasers provide higher power outputs without degrading the beam quality. Devices with different taper angles were tested and compared with conventional ridge waveguide lasers.

Mid-infrared Quantum Cascade Lasers (QCLs) have drastically improved the quality of research and technology in many applications, such as free space communication, chemical sensing or imaging, and high-resolution spectroscopy. In some application, such as in photoacoustic and photothermal spectroscopy, high-power sources and good beam quality are two pre-requisites to achieve high performance. Within this context, tapered QCLs benefit from bigger active zone volume without degrading the quality of the fundamental transverse mode. The wider front facet further improves the quality of the beam along the slow axis, reducing its divergence angle [1].

In this work we present an investigation of tapered QCLs with taper angles ranging between 0° and 3°. The QCL was based on the InAs/AlSb material system emitting around 14-15 μm [2]. In this spectral range, BTEX compounds exhibit strong absorption, making such laser sources extremely interesting for environmental sensing applications. The presented devices feature an active zone composed of an InAs/AlSb superlattice sandwiched between undoped InAs spacers and highly-doped InAs cladding layers. The wafer grown by molecular beam epitaxy on an InAs substrate was processed into deep mesa ridge lasers using optical photolithography and wet chemical etching. Electron beam lithography and dry etching were employed to pattern Bragg gratings on top of the ridge waveguide. The periodicity of the grating was designed according to the Bragg law $\lambda_0 = 2n_{eff}\Lambda$, where Λ is the grating period, λ_0 is the vacuum wavelength at the gain peak and n_{eff} is the TM mode effective index obtained by simulation of the ridge waveguide. A grating periodicity of 2080 nm was used. A gold layer was deposited to provide electrical contact.

In Fig. 1(a) a scanning-electron microscope image of a straight device is shown. The devices were tested and compared in terms of electrical and optical properties, and in terms of spectral purity. Single-longitudinal mode operation was obtained, with a side-mode suppression ratio (SMSR) greater than 20 dB. In Fig. 1(b), emission spectra of a straight QCL, measured at different temperatures in CW operation, are portrayed.

In terms of optical properties, tapered device with higher taper angles provide a greater power output. An improvement of the slope efficiency is observed, which can be justified by the higher collection efficiency of the system towards higher taper angle devices. The larger front facet of tapered lasers reduces the divergence angle along the slow axis, allowing to collect more light. The far-field intensity profiles were measured in order to determine the beam divergence and estimate the devices brightness.
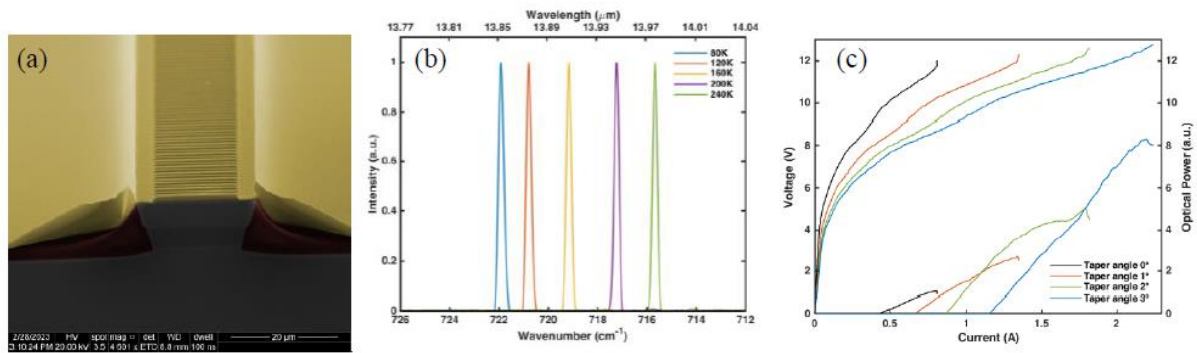
Figure 1: (a) Scanning electron microscope image of the DFB-QCL. In yellow the gold layer, in brown the insulation layer and in dark grey the active zone of the device. (b) Representative straight DFB spectra, exhibiting single mode emission with a SMSR greater than 20 dB. The device was tested in CW operation at different temperatures. (c) Voltage-Light-Current curves for tapered devices, from 0° to 3° taper angles.

[1]   L. Nähle, J. Semmel, W. Kaiser, S. Höfling, A. Forchel, "Tapered quantum cascade lasers," Applied Physics Letters. 91, 181122 (2007).

[2]   K. Kinjalk, D.A. Díaz-Thomas, Z. Loghmari, M. Bahriz, R. Teissier, A.N. Baranov, "InAs-based quantum cascade lasers with extremely low threshold," Photonics. 9, 747 (2022).

Synergistic advances in electrocatalytic CO$_2$ reduction: enhancing the performance of [AgSePh]$_\infty$ through innovative counter electrode optimization

Hannah Rabl, Stephen Nagaraju Myakala, Pablo Ayala, Jakob Blaschke, Stefan Pfaffel, Dorottya Varga, Alexey Cherevan, Doğukan Apaydın, Dominik Eder

Keywords: CO$_2$RR, MOCHAs, MOCs, electrocatalysis

Electrocatalytic reduction of carbon dioxide (CO$_2$) emerges as a promising strategy for mitigating the greenhouse gas effect, offering a potential solution to combat global warming and attenuate climate change. Nevertheless, the electrolysis of CO$_2$ in aqueous environments at room temperature frequently faces challenges, particularly the concurrent hydrogen evolution reaction, presenting a persistent obstacle. The pursuit of cost-effective, selective, and stable electrocatalysts continues to be a significant impediment in advancing electrocatalytic CO$_2$ reduction reactions (CO$_2$RR).

Metal Organic Chalcogenolate Assemblies (MOCHAs), characterized by crystalline coordination polymers with 1D or 2D structures, have undergone extensive study for their structural and optoelectronic properties over the past five years []. Our innovative microwave-assisted synthesis method has enabled the scalable production of MOCHAs, facilitating subsequent material testing applications4. Importantly, our investigations have unveiled the catalytic activity of MOCHAs containing silver, such as [AgSePh]$_\infty$ and [AgSPh]$_\infty$, for electrocatalytic syngas formation under ambient conditions4.

We went on to suggest a novel and highly effective approach to enhance cathodic CO2 reduction by redirecting attention to the counter side reaction. The maintenance of an inert atmosphere on the counter side resulted in a noteworthy transformation in the reproducibility and selectivity of CO formation, elevating the Faradaic Efficiency for CO from 65% to 95%. Additionally, our exploration signifies a departure from the conventional use of expensive Pt-counter electrodes, favouring the more economical and abundant BiVO4 photoanode. Notably, the competitiveness of BiVO4 is highlighted in comparison to the standard Pt-counter electrode.

Encouragingly, our comprehensive examinations into the stability of [AgSePh]$_\infty$ have revealed intriguing insights. Prolonged exposure to elevated potential weakens the Ag-Se bond within [AgSePh]$_\infty$, resulting in the release of benzeneselenol into the gas phase. These findings elucidate the intricate behavior of our catalyst under varying conditions.

In summary, this study not only makes a significant contribution to the field of electrocatalytic CO2 reduction but also introduces innovative avenues for catalyst development and optimization. Through improvements in selectivity, exploration of alternative counter electrode materials, and enhancements in stability, we move closer to a sustainable solution for reducing carbon emissions and promoting green energy—an imperative challenge in our time.

[1]   Schriber, E. A.; Paley, D. W.; Bolotovsky, R.; Rosenberg, D. J.; Sierra, R. G.; Aquila, A.; Mendez, D.; Poitevin, F.; Blaschke, J. P.; Bhowmick, A.; Kelly, R. P.; Hunter, M.; Hayes, B.; Popple, D. C.; Yeung, M.; Pareja-Rivera, C.; Lisova, S.; Tono, K.; Sugahara, M.; Owada, S.; Kuykendall, T.; Yao, K.; Schuck, P. J.; Solis-Ibarra, D.; Sauter, N. K.; Brewster, A. S.; Hohman, J. N. Chemical Crystallography by Serial Femtosecond X-Ray Diffraction. Nature 2022, 601 (7893), 360–365. https://doi.org/10.1038/s41586-021-04218-3.

[2]   Paritmongkol, W.; Sakurada, T.; Lee, W. S.; Wan, R.; Müller, P.; Tisdale, W. A. Size and Quality Enhancement of 2D Semiconducting Metal–Organic Chalcogenolates by Amine Addition. J. Am. Chem. Soc. 2021, 143 (48), 20256–20263. https://doi.org/10.1021/jacs.1c09106.

[3]   Maserati, L.; Refaely-Abramson, S.; Kastl, C.; Chen, C. T.; Borys, N. J.; Eisler, C. N.; Collins, M. S.; Smidt, T. E.; Barnard, E. S.; Strasbourg, M.; Schriber, E. A.; Shevitski, B.; Yao, K.; Hohman, J. N.; Schuck, P. J.; Aloni, S.; Neaton, J. B.; Schwartzberg, A. M. Anisotropic 2D Excitons Unveiled in Organic–Inorganic Quantum Wells. Mater. Horiz. 2021, 8 (1), 197–208. https://doi.org/10.1039/C9MH01917K.

[4]   Rabl, H.; Myakala, S. N.; Rath, J.; Fickl, B.; Schubert, J. S.; Apaydin, D. H.; Eder, D. Microwave-Assisted Synthesis of Metal-Organic Chalcogenolate Assemblies as Electrocatalysts for Syngas Production. Commun Chem 2023, 6 (1), 43. https://doi.org/10.1038/s42004-023-00843-3.

Optimizing Protein Analysis with QCL–based Multi–Pathlength Mid–IR Spectroscopy

Lisa Riedlsperger, Alicja Dabrowska, Bernhard Lendl

Mid-infrared spectroscopy, with its fixed transmission pathlength design, has long been a well-established method for the analysis of proteins and polypeptides in solution. Research shows that the optimum transmission of a solvent should be approximately $1/e$, resulting in an optimal absorbance of ~0.4 (or $\log_{10} e$). Achieving this value for a strong absorbing matrix proves challenging due to the varied background absorbance across different wavelengths. Proteins with their characteristic amide I (1700 – 1600 cm^{-1}) and amide II (1600 – 1500 cm^{-1}) bands are especially difficult to distinguish with spectroscopic analysis in aqueous solutions due to the strong water absorption in this region. In this work, we demonstrate a system that measures samples simultaneously at different pathlengths to determine the most optimal pathlength for each characteristic band of the solute. To achieve this, we employ an external-cavity quantum cascade laser (EC-QCL) that serves as a powerful source of IR radiation. The laser beam is subsequently expanded to a line and directed through the wedge-shaped transmission cell hosting pathlengths from ~10 μm to 400 μm. The transmitted radiation is then detected by a pyroelectric linear array with 256 elements. The hereby proposed configuration combines the advantages of QCLs over conventional thermal emitters while also providing the capability to cover a wider dynamic range of absorbance values. Consequently, it is possible to increase the signal-to-noise ratio for measurements of proteins in aqueous solutions and provide greater insight into the investigated sample.

A bizarre cubic/tetragonal phase transition behaviour in copper ferrite

A. Tampieri[1], T. Lederer[1], S. Loiha[2], S. Wannapaiboon[3], K. Deekamwong[4], P. Tawachkultanadilok[4], J. Wittayakun[4], K. Föttinger[1]

[1]Institute of Materials Chemistry, TU Wien, Vienna, Austria

[2]Materials Chemistry Research Center, KKU, Khon Kaen, Thailand

[3]Synchrotron Light Research Institute, Nakhon Ratchasima, Thailand

[4]School of Chemistry, Suranaree University of Technology, Nakhon Ratchasima, Thailand

Spinels are generally cubic, but copper ferrite is distorted due to the Jahn-Teller effect and, as a result, is tetragonal below 400 °C. We synthesised a copper ferrite material that has an additional low-temperature tetragonal-to-cubic transition and displays an oscillatory transition behaviour starting as a tetragonal at room temperature, going to cubic, then reverting to tetragonal, then cubic again, as observed by in situ XRD. Synchrotron in situ XAS studies indicate the presence of a distortion in the tetrahedral site, which may be due to a shifted inversion parameter. The distorted M-O bonds may have interesting applications in catalysis: our material exhibits a higher activity and lower onset temperature in CO oxidation than an annealed copper ferrite.

Mashing up Tsuji–Trost Allylation – a mechanochemical approach

Johanna Templ, Michael Schnürch

Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163, 1060 Vienna, AUSTRIA

The palladium-catalyzed Tsuji-Trost allylation is a versatile and fundamental reaction with widespread application in organic synthesis. By eliminating a leaving group in the allylic position, various allylic compounds can form a π-allyl metal complex with a Pd(0) species, which in turn can be attacked by a range of nucleophiles, resulting in the formation of allylated products.

An alternative approach to achieve nucleophilic allylation is through the use of allyl bromide. However, this conventional allylating agent presents significant health concerns, such as high toxicity and mutagenicity. Additionally, its high flammability poses hazards during reaction setup.
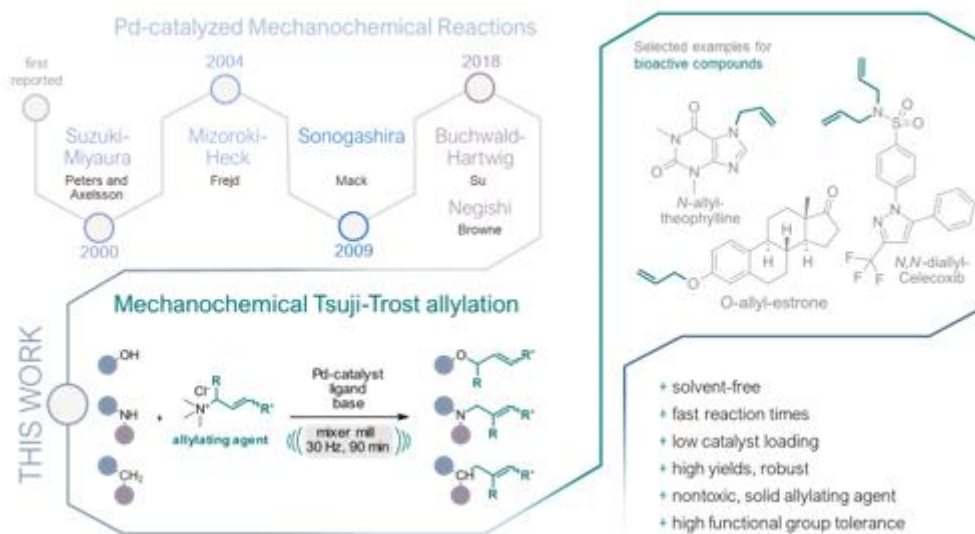

Figure 1: Previously published Pd-catalyzed mechanochemical reactions *(left, top)* and the recently reported mechanochemical Tsuji-Trost reaction *(left, bottom)* suitable for a late-stage modification of bioactive compounds *(right, top)* and the method's outstanding features *(right, bottom)*.

Given the aforementioned toxicological and safety issues, we were encouraged to expanded our previous research on the use of quaternary ammonium salts as safe and non-toxic alkylating agents [1] to allylation reactions. We have identified allyl trimethyl ammonium chloride as an ideal allylating agent for various *O*-, *N*-, and *C*-nucleophiles in a Pd-catalyzed, mechanochemical Tsuji-Trost reaction. This reaction can be performed solvent-free in a ball mill and exhibits short reaction times (90 minutes), very low catalyst loadings (0.5 mol%), and mild basic conditions. During the oxidative addition step of the catalytic cycle, solely trimethylamine is released as a gaseous by-product, eliminating the need for an additional separation step. This environmentally friendly approach employs easy-to-handle and non-toxic reagents, providing access to numerous allylated substrates. The high yields, excellent functional group tolerance, and broad applicability of this novel method are expected to facilitate late-stage functionalization of complex natural products and pharmaceutically active compounds, paving the way for a more sustainable approach in allylation.

[1]   J. Templ, M. Schnürch, J. Org. Chem. 2022, 87, 6, 4305–4315. 2J. Templ, E. Gjata, F. Getzner, M.Schnürch, Org. Lett. 2022, 24, 40, 7315–7319.

Neural–network force field backed nested sampling: Predicting phase diagrams

N. Unglert[1], J. Carrete[2,1], L. B. Pártay[3], and G. K. H. Madsen[1]

[1]*Institute of Materials Chemistry, TU Wien, 1060 Vienna, Austria*

[2]*Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain*

[3]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*

Keywords: Machine Learning, Nested Sampling, Neutral Networks

Nested sampling is a promising method for calculating phase diagrams of materials [1]. However, the computational cost limits its applicability if ab-initio accuracy is required. In the present work [2], we report on the efficient use of a neural-network force field [3] in conjunction with the nested-sampling algorithm. We train our force fields on a recently reported database of silicon structures and demonstrate our approach on the low-pressure region of the silicon pressure-temperature phase diagram between 0 and 16 GPa. The simulated phase diagram shows a good agreement with experimental results, closely reproducing the melting line. Furthermore, all of the experimentally stable structures within the investigated pressure range are also observed in our simulations. We point out the importance of the choice of exchange-correlation functional for the training data and show how the r2SCAN meta-GGA plays a pivotal role in achieving accurate thermodynamic behaviour. We furthermore perform a detailed analysis of the potential energy surface exploration and highlight the critical role of a diverse and representative training data set.

[1]   Pártay B., L.; Csányi, G.; Bernstein, N. Eur. Phys. J. B 2021, 94, 159.
[2]   Unglert, N.; Carrete, J.; Pártay, L. B.; Madsen, G. K. H. Phys. Rev. Materials 2023, 7, 123804.
[3]   Montes-Campos, H.; Carrete, J.; Bichelmaier, S.; Varela, L. M.; Madsen, G. K. H. J. Chem. Inf. Model. 2022, 62,88–101.

Teaching an old dog new chemometrics: laser–based mid–IR spectroscopy coupled to chemometrics as a tool for continuous monitoring of protein unfolding

Shilpa Vijayakumar, Andreas Schwaighofer, Georg Ramer, Bernhard Lendl

Research Division of Environmental Analytics, Process Analytics and Sensors, Institute of Chemical Technologies and Analytics, TU Wien, Getreidemarkt 9, Vienna, 1060, Austria.

Keywords: Mid-infrared spectroscopy, Chemometrics, protein-denaturation

Protein function depends on its secondary structure, emphasizing the need to monitor protein structure and denaturation in multiple industries including the pharmaceutical and food industries. Analytical techniques such as Raman spectroscopy and circular dichroism spectroscopy have been traditionally used to determine protein secondary structure and are used in end-of-line analytics and quality control. However, proteins are often used with other reagents, necessitating techniques that are sensitive to a wide range of substances and that are capable of continuous sensing.

Fourier transform infrared spectroscopy (FTIR) while being sensitive to secondary structure, has the drawback of limited path lengths due to the large absorbance of water in the amide-I region, which makes it cumbersome to employ for denaturation studies where clogging by protein aggregates is common. Laser-based mid-IR spectroscopy is a versatile technique that offers the benefits of traditional FTIR and overcomes its shortcomings by using high power light sources such as external cavity quantum cascade lasers (EC-QCL). When conjugated with chemometrics, it presents the ability to resolving complex mixtures, hence facilitating automation.

In this presentation we demonstrate the capability of EC-QCL-IR spectroscopy and chemometrics for the dynamic determination of protein secondary structure changes in continuous monitoring setups. We analyzed the response of proteins to two different stimuli: heat and chaotropic agents. Applied to the thermal denaturation of bovine serum albumin (BSA), QCL-IR and MCR-ALS show the concentration dependence of protein denaturation and reveal a second intermediate in the process of unfolding

When studying the chemical induced folding and unfolding of proteins by surfactants, we reduced the interference of media components in the protein spectra using a PLS based approach that determined the concentrations of multiple surfactants from the spectra and then calculated their spectral contributions. Once the baseline had been thus corrected, MCR-ALS was used to recover the pure spectra of protein-relevant components.

Laser-based mid-IR spectroscopy shows potential in the study of protein denaturation by multiple agents and promises a plethora of information when coupled to chemometrics. The ease of automation of the system makes it a very favourable analytical method for integration into industrial processes.

Dynamic Modeling for Enhanced Process Simulation and Optimization in Steel Production

Arleen V. Walk, Bernd Weiß, Walter Wukovits

The steel industry, known for its significant global impact on CO_2 emissions, demands continuous efforts to-wards sustainable and efficient practices. Process simulation has emerged as an essential tool in optimizing steel production, providing insights into complex unit operations. Traditionally, static models have been employed to expedite simulations, leveraging computational efficiency. However, recent advancements in computer capabilities have made the utilization of rigorous dynamic models both practical and feasible.

In the pursuit of enhancing process simulation, my research focused on the Blast Oxygen Furnace (BOF) unit operation. During my master thesis I successfully constructed and implemented a dynamic BOF model using gPROMS®, an advanced process simulation software by Siemens AG. This model was integrated into an existing static calculating model library, paving the way for a more comprehensive understanding of the dynamic aspects of the steel production process.

My simulation results for the BOF model demonstrate its versatility in simulating different converter sizes and operational procedures. The model accurately reproduces refining reactions of carbon, silicon, manganese, and phosphorus, showcasing excellent agreement with measured data. Furthermore, the dynamic BOF model captures physiochemical phenomena, including melting behavior and dissolution, along with ballistic droplet movement.

The focus of my ongoing doctoral research, is to further dive into the development of dynamic unit operations. My first mission: development and implementation of a sinter strand model. This model aims to depict the most influential reactions, including homogeneous gas-gas reactions and heterogeneous solid-gas reactions. By extending the capabilities of process simulation to encompass complex dynamic phenomena, this research contributes to the evolving landscape of steel production optimization.

For the 5th Scientific Workshop (FemChem) I would like to present:

- The impact of process simulation on sustainability and process optimization
- BOF:
    - The advancements accomplished in BOF modelling
    - Simulated phenomena and results
- The sinter strand model and its current capabilities as well as future plans

Photocatalytic generation of solar fuels and simultaneous oxidation of microplastics

Madeline Weisweiller, Alexey Cherevan, Dominik Eder

Keywords: microplastics, photoreforming, heterogeneous photocatalysis

A predominant issue of the 21st century is the employment of fossil fuels, for transport, energy and as feedstock for many important chemicals, which all lead to their detrimental impact on the environment. In addition, they are utilized for the production of everyday plastics, such as polypropylene (PP), polyethyleneterephthalate (PET) and (low density) polyethylene ((LD)PE). Their abatement is a further concern, as a majority is deposited onto landfills, slowly degrading to microplastics, which are particles constituting less than 5 mm in size. Their precarious impact on both the environment and health are yet to be fully established. In recent years, photoreforming, which describes the simultaneous generation of solar fuels, such as H2 and CH4, and the upcycling of plastics to high-value-added chemicals, has gained a lot of interest.

In this work, the concepts of photoreforming were studied by investigating the effect of temperature, substrate, irradiation source, presence of a co-catalyst on TiO_2, and atmospheric conditions on the process. Hereby, the focus was set on the comparison between room temperature (RT) and 70°C, UV irradiation and a broad-band Xe lamp, neat P25-TiO_2 and the one with Pt as co-catalyst examining PET, PP and LDPE as substrate. The reaction solution was either purged with He, for inert conditions and investigation of the gaseous products, or compressed air (CA), to expedite oxidation of the investigated substrate and analysis of products in the liquid phase. Furthermore, the feasibility for future industrial application was also of interest, thus experiments in an upscaled manner were additionally conducted.

My results demonstrate that all studied microplastic sources could be successfully processed by means of photocatalysis, resulting in a mixture of high-value products. In addition, the established methodology has provided reproducible results and a scaleup was achieved. Both exalted temperature and the employment of Pt resulted in the highest quantities of H$_2$ (1,42 µmol/h) and CH4 (0,09 µmol/h). Moreover, no beneficial impact of CA on the degradation of the substrates could be concluded, which shows that direct hole transfer is the predominant oxidation pathway for the investigated samples. When analysing liquid-phase products, oxalic acid (OA), acetic acid (AA) and ethylene glycol (EG) were found, with the highest conversion rates presented by AA (15,8%) and EG (9,5%). However, no direct correlation to the applied parameters of the respective samples could for now be established.