BOOK OF ABSTRACTS

http://eugsc4.iciq.es/
WELCOME TO EUGSC-4

It is our great pleasure to welcome you all to the 4th edition of the EUCheMS conference on Green and Sustainable Chemistry hosted in Tarragona at the Institute of Chemical Research of Catalonia (ICIQ) during 22-25 September 2019. This meeting follows previous successful editions held in Budapest (2013), Lisbon (2015) and York (2017) and continues to offer a platform for the communication of the latest advances in green and sustainable chemistry.

The leading topics of this conference are green/bio-polymers, photochemistry & catalysis, electrochemistry & catalysis, carbon dioxide valorization and biomass conversion. The program is divided over 4 days and counts with a joint session co-organized by the Division of Chemistry and the Environment (DCE) that focuses on water treatment. Further to this, two industrial sessions are organized with contributions from various representatives from larger and smaller companies, and start-ups discussing the role and impact of sustainable approaches in the commercial sector.

The program consists of 6 plenary, 10 keynote and 45 oral presentations and there are two poster sessions with over 50 contributions. We thank in advance all the invited speakers/ and those that kindly accepted to deliver talks and present posters. We also are grateful to all our sponsors, and in particular the RSEQ, its Catalan section, the Catalan Chemical Society and all companies for their generous support to EUGSC-4.

We hope you will enjoy the conference and Tarragona, known for its Mediterranean cuisine, hospitality, attractive climate, many ancient Roman sites and the UNESCO protected cathedral.

We wish you will have a great time with us here in Tarragona and at ICIQ, and thank you for making the EUGSC-4 a success.

On behalf of the organizing committee,

Arjan Kleij – chair of the EUGSC-4
SPEAKERS

**Plenary Speakers**

Walter Leitner – RWTH Aachen University  
Paul Dyson – Ecole Polytechnique Fédérale de Lausanne  
Roger Sheldon – Delft University  
David Cole-Hamilton – University of St. Andrews  
Javier Pérez-Ramírez – ETH Zürich  
Siegfried R. Waldvogel – Johannes Gutenberg-University Mainz

**Keynote Speakers**

Benjamin R. Buckley – Loughborough University  
Alessandra Quadrelli – Laboratoire de Chimie Organométallique de Surface, Lyon  
Michael Meier – Karlsruhe Institute of Technology  
Marcella Bonchio – University of Padova  
Sophie Guillaume – Université de Rennes 1  
François Jérôme – IC2MP – University of Poitiers  
Ioannis Katsoyiannis – Aristotle University of Thessaloniki  
Núria López – Institute of Chemical Research of Catalonia  
Steve Nolan – Ghent University  
Michael North – University of York

**Industrial Speakers**

Jordi Simón – BASF  
Andreas Taden – HENKEL  
Luca Giannini – PIRELLI  
Michael Mager – CLARIANT  
Esther Alza – ERT-FLOW  
Fátima Lucas – ZYMVOL
## Conference at a Glance

### Sunday, 22nd September

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<td>Registration</td>
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<td>17.00-18.00</td>
<td>Coffee/tea/refreshments</td>
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<td>Conference opening</td>
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<td>18.15-19.15</td>
<td>PL1: Coie-Hamilton</td>
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<td>19.15-20.30</td>
<td>Reception</td>
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<td>20.30</td>
<td>Free time</td>
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### Monday, 23rd September

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<tr>
<td>8.30-9.00</td>
<td>Official opening of EUGSC4 by Prof. Antonio Echavarren (RSEQ) and Prof. Arjan W. Kleij (chair of the EUGSC4)</td>
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<tr>
<td>9.00-10.00</td>
<td>PL2: Walter Leitner</td>
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<tr>
<th>Session: Catalysis for Synthesis</th>
<th>Session: Polymers</th>
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<tr>
<td>10.30-11.10 KN1: Nolan</td>
<td>KN3: Guillaume</td>
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<td>11.10-11.30 OC1: Licini</td>
<td>OC9: Ligadas</td>
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<td>11.30-11.50 OC2: Margalef</td>
<td>OC10: Pellis</td>
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<td>11.50-12.10 OC3: Claros</td>
<td>OC11: Pellecchia</td>
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<td>12.10-12.30 OC4: González</td>
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<th>Session: Sustainable Solvents</th>
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<tr>
<td>15.45-16.25 KN2: North</td>
<td>KN4: Buckley</td>
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<tr>
<td>16.25-16.45 OC5: Longeras</td>
<td>OC13: Capacchione</td>
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<td>16.45-17.05 OC6: Cruz</td>
<td>OC14: Maquilón</td>
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<td>17.05-17.25 OC7: Araújo</td>
<td>OC15: Lamb</td>
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<td>17.25-17.45 OC8: Pereiro</td>
<td>OC16: Fernández</td>
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<tr>
<td>17.50-18.50</td>
<td>PL3: Sheldon (ChemSusChem lecture)</td>
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<td>20.30</td>
<td>Free time &amp; Speakers Dinner</td>
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### Tuesday, 24th September

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<th>ICIQ Auditorium</th>
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<td>9.00-10.00</td>
<td>PL4: Pérez-Ramírez</td>
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<td>10.30-11.10</td>
<td>Session: Heterogeneous catalysis</td>
<td>Session: Biomass conversion</td>
<td>Session: Water purification &amp; Sustainable Synthesis</td>
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<td>11.10-11.30</td>
<td>KNS: López</td>
<td>KN7: Jerôme</td>
<td>KN8: Katsyiannis</td>
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<td>11.30-11.50</td>
<td>OC17: Kaiser</td>
<td>OC25: Raupp</td>
<td>OC29: Misra</td>
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<td>11.50-12.10</td>
<td>OC18: Romero</td>
<td>OC26: Deuss</td>
<td>OC30: Luna</td>
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<td>12.10-12.30</td>
<td>OC19: Díaz</td>
<td>OC27: Saengdee</td>
<td>OC31: Scaiano</td>
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<td>13.00-15.30</td>
<td>OC20: Puértolas</td>
<td>OC28: Smith (Wiley)</td>
<td>OC32: García</td>
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<td>13.00-15.30</td>
<td>Lunch &amp; Poster Session &amp; Exhibition</td>
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<td>15.45-16.25</td>
<td>Session: Biomass Conversion &amp; Upgrading</td>
<td>Industrial Session</td>
<td>Session: CO₂ conversion</td>
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<td>16.25-16.45</td>
<td>KN6: Meier</td>
<td>BASF: Jordi Simon</td>
<td>KN9: Quadrelli</td>
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<td>16.45-17.05</td>
<td>OC21: Aguiar</td>
<td>Pirelli: Luca Giannini</td>
<td>OC33: Papp</td>
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<td>17.05-17.25</td>
<td>OC22: Moreno</td>
<td>OC34: Ngassam</td>
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<td>17.25-17.45</td>
<td>OC23: Triantafyllidis</td>
<td>Clariant: Michael Mayer</td>
<td>OC35: Das</td>
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<td>17.50-18.50</td>
<td>OC24: Gaikwad</td>
<td>OC36: Milocco</td>
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<td>PL5: Waldvogel</td>
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<td>21.00</td>
<td>Conference dinner: Casa Joan Miret</td>
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### Wednesday, 25th September

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<td>9.00-10.00</td>
<td>PL6: Dyson (Green Chemistry lecture)</td>
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<td>10.30-11.10</td>
<td>Session: Photochemistry</td>
<td>Henkel: Andreas Taden</td>
<td>OC41: Sala</td>
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<td>10.50-11.10</td>
<td>KN10: Bonchio</td>
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<td>OC42: Sans</td>
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<td>11.30-11.50</td>
<td>OC38: Pascual</td>
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<td>OC44: Shi</td>
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<td>11.50-12.10</td>
<td>OC39: Sahoo</td>
<td>Ert-Flow: Esther Alza</td>
<td>OC45: Gao</td>
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<td>12.10-12.30</td>
<td>OC40: Moonshiram</td>
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<td>12.35-13.00</td>
<td>Closing Ceremony AUDITORIUM (Prof. Carles Bo, president of the Societat Catalana de Quimica &amp; Prof. Arjan W. Kleij, Chair)</td>
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PROGRAM

Sunday, 22nd September

ICIQ Auditorium

15:00 – 17:00 Registration

17:00 – 18:00 Coffee / Tea / Refreshments

18:00 – 18:15 Conference Opening

18:15 – 19:15 Plenary Lecture 1: David Cole-Hamilton
Effect Chemicals from Waste Bio - Oils

19:15 – 20:30 Reception

Monday, 23rd September

ICIQ Auditorium

08:30 – 09:00 Official Opening of EUGSC-4 by Prof. Antonio M. Echavarren (President of the RSEQ) and Prof. Arjan W. Kleij (chair of the EUGSC-4)

09:00 – 10:00 Plenary Lecture 2: Walter Leitner
Metal Nanoparticles on Supported Ionic Liquid Phase Catalysts (M@SILP): A Molecular Approach to Multifunctional Catalytic Systems

10:00 – 10:30 Coffee / Tea / Refreshments

Session: Catalysis for Synthesis – ICIQ Auditorium

10:30 – 11:10 Keynote Lecture 1: Steve Nolan
Easy Access to Metal-N-heterocyclic Carbene Catalysts

11:10 – 11:30 Oral Communication 1: Giulia Licini
Vanadium Catalyzed Aerobic Oxidative C-C Bond Cleavage

11:30 – 11:50 Oral Communication 2: Jèssica Margalef
Efficient and Readily Available Metal-Catalyst Libraries for the Presentation of High Value Chiral Compounds
11:50 – 12:10 Oral Communication 3: Miguel Claros  
Visible-Light Reductive Cyclization of Unactivated Alkyl Chlorides

12:10 – 12:30: Oral Communication 4: Nerea González-Gallardo  
Palladium Mesoionic Carbenes as General Precatalyst for Sustainable Cross-Coupling Reactions

Session: Polymers – ICIQ Library

10:30 – 11:10 Keynote Lecture 3: Sophie Guillaume  
Tailor-made PolyHydroxyAlkanoates by Stereocontrolled Ring-Opening Polymerization of Functional β-lactones.

11:10 – 11:30 Oral Communication 9: Gerard Lligadas  
Uncovering Opportunities for Sustainable Polymer Synthesis by SET-LRP

11:30 – 11:50 Oral Communication 10: Alessandro Pellis  
Enzymes: Powerful Catalysts for the Synthesis of Functional Polyesters

11:50 – 12:10 Oral Communication 11: Claudio Pellechia  
Alternating CO₂-Cyclohexene Oxide Copolymers and (Stereo)Block Copolymers of L-, D-, rac-Lactides and ε-Caprolactone by New Pyridylamidozinc(II) Catalysts

12:10 – 12:30: Oral Communication 12: Marta E. G. Mosquera  
Earth Abundant Metals Compounds as a Catalysts for the Production of Bioplastics

13:00 – 15:00 Lunch & Poster Session & Exhibition (outside, ICIQ terrace)

Session: Sustainable Solvents – ICIQ Auditorium

15:45 – 16:25 Keynote Lecture 2: Michael North  
Sustainable Solvents for Organic Synthesis

16:25 – 16:45 Oral Communication 5: Olympe Longeras  
Sustainable Deep Eutectic Solvent for CO₂ Capture Improvements

16:45 – 17:05 Oral Communication 6: Hugo Cruz  
Deep Eutectic Solvents as Sustainable Materials for Energy Applications
17:05 – 17:25 Oral Communication 7: João M. M. Araújo
Bioprivileged Ionic Liquids and Deep Eutectic Solvents: From Extraction/Purification to Drug Development

17:25 – 17:45: Oral Communication 8: Ana B. Pereiro
Fluorinated Ionic Liquids as Novel Task-Specific Materials

Session: Transformation of CO₂ – ICIQ Library

15:45 – 16:25 Keynote Lecture 4: Benjamin Buckley
Selective Anti-Markovnikov Hydrocarboxylation of Olefins: Formation of All-Carbon Quaternary Centres

16:25 – 16:45 Oral Communication 13: Carmine Capachione
Reaction of Carbon Dioxide with Epoxides Promoted by [OSSO]-type Iron(III) Complexes

16:45 – 17:05 Oral Communication 14: Cristina Maquilón
Stereo/Regio-Divergent Synthesis with CO₂

17:05 – 17:25 Oral Communication 15: Katie J. Lamb
Using Metal Salen and Salophen Complexes for the Green Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide

17:25 – 17:45: Oral Communication 16: Sergio Fernández
Identification of the Key Mechanistic Steps involved in the Cobalt-Catalyzed CO₂ Reduction

ICIQ Auditorium

Green Chemistry & Biocatalysis: Engineering a Sustainable Future

20:30: Speakers’ Dinner (on invitation only)

Tuesday, 24th September

ICIQ Auditorium

09:00 – 10:00 Plenary Lecture 4: Javier Pérez-Ramírez
Frontiers in Catalysis Engineering for Sustainable Technologies
10:00 – 10:30 Coffee / Tea / Refreshments

Session: Heterogeneous Catalysis – ICIQ Auditorium

10:30 – 11:10 Keynote Lecture 5: Núria López
A Modeling Perspective on Green and Sustainable Chemistry

11:10 – 11:30 Oral Communication 17: Selina K. Kaiser
Metal-Dependant Structure-Activity Relations in Acetylene Hydrochlorination

11:30 – 11:50 Oral Communication 18: Núria Romero
Ru Nanoparticles for Photocatalytic Hydrogen Evolution

11:50 – 12:10 Oral Communication 19: Miriam Diaz de los Bernardos
Facile Synthesis of NHC-Stabilized Metal Nanoparticles and their Catalytic Application in Selective Hydrogenations

12:10 – 12:30: Oral Communication 20: Begoña Puértolas
Mechanism of the Ceria-Catalyzed Phosgene-Free Synthesis of Polyurethane Precursors

Session: Biomass Conversion – ICIQ Library

10:30 – 11:10 Keynote Lecture 7: François Jérôme
Synthesis of Renewable Meta-Xylylenediamine and Alkyl Levulinate from Biomass-Derived Furfural

11:10 – 11:30 Oral Communication 25: Yasmin S. Raupp
Catalytic Aerobic Oxidation of Terpenes and Follow-up Chemistry towards Renewable Poly(hydroxyurethane)s

11:30 – 11:50 Oral Communication 26: Peter J. Deuss
Towards High Value Lignin; Reactive Fractionation and Modification

11:50 – 12:10 Oral Communication 27: Laksana Saengdee
Facile Preparation of Modified Natural Rubber by Both Epoxidation and Hydrogenation and its Properties

Challenges in Sustainable Chemistry Publishing
Session: Water Purification & Sustainable Synthesis – CTTI-URV

10:30 – 11:10 Keynote Lecture 8: Ioannis Katsoyiannis
Overview of Technologies used for Wastewater Reclamation and Reuse and Implementation Examples

11:10 – 11:30 Oral Communication 29: Archimista Misra
Magnetic Removal of Multiple Pollutants from Water by Polyoxometalate Supported Ionic Liquid Phases (POM-SILPs)

11:30 – 11:50 Oral Communication 30: Azahara Luna-Triguero
Record Capacity in Zr-based Metal-Organic Framework for Heat Pumps and Water Generator Applications

11:50 – 12:10 Oral Communication 31: Juan C. Scaiano
Design and Implementation of Novel Materials for Heterogeneous Photocatalysis

12:10 – 12:30: Oral Communication 32: Eduardo García-Verdugo
Polymer as non Innocent Vector to Develop Efficient Rose Bengal Supported Catalyst

13:00 – 15:00 Lunch & Poster Session & Exhibition (outside, ICIQ terrace)

Session: Biomass Conversion & Upgrading – ICIQ Auditorium

15:45 – 16:25 Keynote Lecture 6: Michael Meier
Renewability is not Enough: Sustainable Synthesis of Biomass-derived Monomers and Polymers

16:25 – 16:45 Oral Communication 21: Ana Aguiar-Ricardo
Comparison of Advanced Extraction Techniques for the Recovery of Interesting Compounds from Vineyard Pruning Waste

16:45 – 17:05 Oral Communication 22: Andrés Moreno
Use of Microwave Radiation Catalysis in the Treatment and Transformation of Lignocellulosic by-Products from Agrifood Industries

17:05 – 17:25 Oral Communication 23: Konstantinos Triantafyllidis
Catalytic Fast Pyrolysis of Birch and Spruce Organosolv Lignin with Conventional and Hierarchical ZSM-5 Zeolites for the Production of Alkylphenols and Aromatics
17:25 – 17:45: Oral Communication 24: Rohit Gaikwad
Biogas Conversion to Methanol via Steam Reforming in a Container Sized Module

Industrial Session – ICIQ Library

15:45 – 16:25 BASF: Jordi Simón
Biodegradables-Compostable Polymers as Key for Closing the Loop of Organic Matter

16:25 – 17:05 PIRELLI: Luca Giannini
Tackling the Challenge of Sustainability in the Tyre Industry

17:05 – 17:45 CLARIANT: Michael Mager
Perspectives on Sustainability in the Polymers Industry

Session: CO₂ Conversion – CTTI-URV

15:45 – 16:25 Keynote Lecture 9: Alessandra Quadrelli
CO₂ reduction: en route to renewable energies storage via MOFs and Porous Organic Polymers

16:25 – 16:45 Oral Communication 33: Gábor Papp
CO₂ Hydrogenation in Aqueous Solutions with Water Soluble Ir-Catalysts

16:45 – 17:05 Oral Communication 34: Charlene Ngassam
Dual Activation Catalysts for the Selective Conversion of CO₂ into Alkylidene Cyclic Carbonates and Oxoalkyl Carbonates

17:05 – 17:25 Oral Communication 35: Shoubhik Das
CO₂-Catalysed Oxidation and Dehydrogenation Reactions: Its Transition Metal-Free

17:25 – 17:45: Oral Communication 36: Francesca Milocco
Bifunctional Anionic Iron(II) Catalysts for the Conversion of CO₂ into Cyclic Carbonates

ICIQ Auditorium

17:50 – 18:50 Plenary Lecture 5: Siegfried Waldvogel
Concepts for Electrifying Organic Synthesis
21:00 Conference Dinner at the “Casa Joan Miret”

**Wednesday, 25th September**

**ICIQ Auditorium**

09:00 – 10:00 Plenary Lecture 6: Paul Dyson  
*Catalytic Transformations of Renewable Polymers*

10:00 – 10:30 Coffee / Tea / Refreshments

**Session: Photochemistry – ICIQ Auditorium**

10:30 – 11:10 Keynote Lecture 10: Marcella Bonchio  
*Bio-inspired Nano-Architectures for Artificial Photosynthesis*

11:10 – 11:30 Oral Communication 37: Julien Bonin  
*Solar Energy Storage in Chemical Bonds by Molecular Catalysis: from CO₂ to Fuels*

11:30 – 11:50 Oral Communication 38: David Pascual  
*Light-Driven Competitive Reduction of Aromatic Ketones vs Aromatic Olefins in Aqueous Media*

11:50 – 12:10 Oral Communication 39: Basudev Sahoo  
*Remote sp³ C-H Carboxylation Enabled by the Merger of Nickel and Photoredox Catalysis*

12:10 – 12:30 Oral Communication 40: Dooshaye Moonshiram  
*Tracking the Electronic and Structural Configurations of Water Splitting Catalysts for Artificial Photosynthesis*

**Industrial Session – ICIQ Library**

10:30 – 11:10 HENKEL: Andreas Taden  
*Bio-based Adhesives: Where Do We Come From and Where Do We Go?*

11:10 – 11:50 ZYMVOL: Fátima Lucas  
*Making in Silico Enzyme Evolution a Commodity for the Widespread use of Industrial Biocatalysts*
11:50 – 12:30 ERT-FLOW: Esther Alza
Efficient Reaction Technologies for Sustainable Chemistry

Session: Fuels – CTTI-URV

10:30 – 10:50 Oral Communication 41: Xavier Sala
Tunable Molecular-Material Hybrids at the Nanoscale for Catalytic Water Splitting

10:50 – 11:10 Oral Communication 42: Víctor Sans
Efficient Base-Free Selective CO2 Hydrogenation with Multifunctional Ionic Liquids

11:10 – 11:30 Oral Communication 43: Joaquín Soriano-López
Electrocatalytic Oxygen Evolution in Neutral Water by a Bioinspired Manganese-Oxo Cluster

11:30 – 11:50 Oral Communication 44: Haifeng Shi
Fabrication of 2D g-C3N4 Based Photocatalyst for Efficient Photocatalytic Degradation and CO2 Reduction

11:50 – 12:10: Oral Communication 45: Dandan Gao
Modular Design of Noble Metal-Free Mixed Metal Oxide Electrocatalysts for Complete Water Splitting

ICIQ Auditorium

12:35 – 13:00 Closing Ceremony of EUGSC-4 by Prof. Carles Bo (President of the SCQ) and Prof. Arjan W. Kleij (Chair of the EUGSC-4)
As oil supplies dwindle and the price increases, it is essential to find new ways of making the many chemicals on which the quality of our lives depends. One approach is to use renewable resources which can be grown but being aware of land use.

We shall show how homogeneous carbonylation, metathesis, and reductive amination can be used to make difunctional esters acids, alcohols, amines for polymer formation from unpurified natural oils containing oleate residues. We shall also describe the formation of N-heterocycles by hydrogenation of diesters in the presence of amines.

Cashew nut shell liquid contains interesting phenols meta substituted with an unsaturated C15 chain. We shall described how it can be used to synthesise the compounds in Figure 2.

References

Plenary Lecture Abstract 2
Walter Leitner

Metal Nanoparticles on Supported Ionic Liquid Phase Catalysts (M@SILP):
A Molecular Approach to Multifunctional Catalytic Systems

Walter Leitner*a,b
a) Max-Planck-Institut for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr
b) Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 2, 52074 Aachen
*leitner@cec.mpg.de

Metal nanoparticles are of major importance in catalysis and essential elements in multifunctional catalytic materials. Their controlled synthesis from organometallic precursors has emerged as a fruitful link between the traditional fields of “homogeneous” and “heterogeneous” catalysis. Whereas the ligands control the reactivity of isolated metal centers in coordination compounds, the stabilizing matrix (e.g. polymer, solvent, or support) becomes a critical control factor for the metal assemblies on a nanoscale.

In the present talk, we will discuss the potential of combining the stabilizing effect of ionic liquid (IL) type structures attached to silica surfaces as matrix for catalytic active metal nanoparticles (M@SILP-catalysts) [1]. This approach allows controlled introduction of additional molecular functionalities in the support matrix [2,3]. The generation from organometallic precursors provides the possibility to synthesize well-defined bimetallic nanoparticles in these matrices [4]. The systematic development of this molecular toolbox opens access to catalyst materials for very challenging hydrogenation/hydrogenolysis processes as required for example in selective biomass conversion [5,6].

References


Green Chemistry & Biocatalysis: Engineering a Sustainable Future

Roger A. Sheldon

The concepts of green chemistry and sustainable technology focus attention on the development of clean, catalytic technologies for waste minimization and the elimination of toxic/hazardous materials in chemicals manufacture. Biocatalysis has numerous environmental and economic benefits to offer in this context. Biocatalytic processes are generally more efficient in energy and raw materials and generate less waste than conventional routes and are conducted at ambient temperature and pressure. Enzymes are readily available from renewable resources and are biocompatible, biodegradable, non-hazardous and non-toxic.

In the last two decades advances in biotechnology, in particular in (meta)genome mining, gene synthesis and directed evolution have completely revolutionized biocatalysis. Moreover, the ongoing transition to a sustainable, bio-based economy is inspiring the development of efficient, cost effective biocatalytic processes for the conversion of renewable biomass to chemicals.

References

Heterogeneous catalysis is possibly the most relevant discipline in the chemical industry, spearheading the crusade to solve energy, resource, and environmental challenges of society. This vibrant field is confronting these threats head-on by becoming progressively design-driven, a shift facilitated by the availability of increasingly powerful tools to expand fundamental knowledge of catalyzed processes across all relevant time and length scales. In this talk, I will discuss recent examples from my laboratory that illustrate how this intellectual growth can kindle revolutionary technological advancements to tackle key sustainability targets. As a vector for transitioning from fossil to renewable feedstocks, this will embrace pioneering routes for the halogen-mediated functionalization of natural gas components where I will highlight the critical role of operando mechanistic studies to distinguish between surface and gas-phase processes.

Breaking barriers in the synthesis of alcohols from carbon dioxide, I will emphasize the importance of controlling nanostructures at the atomic level to design stable and selective catalysts. Complementing the detailed molecular-level understanding derived from experiments and modeling, I will move towards the implementation and design of a renewable-based process for methanol synthesis. Towards other environmental goals, I will address the avoidance of harmful selectivity enhances such as lead via the nanostructuring of noble metals in the form of defined ensembles. I will also show how the use of single-atoms can cross borders in catalyst design, enabling the replacement of homogeneous with heterogeneous systems for carbon-carbon coupling. Finally, I will address frontiers in the establishment of structure-performance relationships over low-nuclearity species and in bridging understanding to traditional nanoparticle-based formulations. In this second golden age of catalysis, with the development of a plethora of innovative catalytic technologies and ever-evolving toolbox, the most exciting and significant challenges are coming into our reach.
Plenary Lecture Abstract 5
Siegfried R. Waldvogel

Concepts for Electrifying Organic Synthesis

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The direct use of electrochemistry for the generation of reactive intermediates can have major advantages towards conventional synthetic strategies.[1] Less or no reagent waste is generated and new reaction pathways are accessible.[2] In order to exploit the electricity driven conversions for synthetic purposes and to install unique selectivity two modern approaches will be outlined:

1) Solvent-controlled selective dehydrogenative cross-coupling reactions: A key for this is the use of boron-doped diamond anodes and fluorinated alcohols within the electrolyte.[3] This methodology opened new pathways for innovative and scalable arylation reactions.[4]

2) New electrode systems for the anodic and cathodic conversion to value-added organic compounds. These systems are capable to go beyond common limits in electro-organic synthesis.

The working horse to identify suitable electrolytic conditions is the electrosynthetic screening approach. This strategy gives also rise to fast optimization and subsequent scale-up.[5]

References
Plenary Lecture Abstract 6
Paul J. Dyson

Catalytic Transformations of Renewable Polymers

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Interest in the transformation of waste materials into valuable products has intensified in recent years with a slow, but steady transition towards a circular economy. Over the last decade or so, we have worked on the development of catalysts that transform complex renewable (polymeric) feedstocks into fuels, platform chemicals or high-value chemicals [1-3]. In this lecture, I will describe the progression of our research from simple model compounds, through to purified and well-characterized biopolymers, i.e. cellulose and lignin, and eventually to highly complex heterogeneous biomass containing waste streams. The challenges we faced as we progressed from model compounds through to heterogeneous waste streams will be highlighted together with the solutions we developed to overcome the various hurdles encountered. In addition, I will demonstrate how the application of a mechanistic approach facilitated the delineation of the critical parameters needed to improve the performance of our catalysts.

References
We have reported on the use of an external weak base as an effective method to generate Au- and Cu-NHC complexes. In the course of our studies, an unusual intermediate was isolated, an “ate” complex, that could be easily observed within minutes of mixing the metal precursor, copper or gold and now palladium and further examples of transition metals, and the imidazolium salt in air. Action of a weak base upon this intermediate led to the well-defined M-NHC complex (M= Au, Cu and Pd) (Figure 1). We suspected that such “ate” complexes might be more prevalent than imagined in the context of the organometallic chemistry of M-NHC complexes and might even offer a uniquely simple, greener and more sustainable approach to catalyst synthesis and catalysis.

To test this hypothesis, synthetic studies have shown the route to be so far quite general and these studies and the reactivity of the M-NHC family of catalysts will be presented.

References

Sustainable solvents for organic synthesis

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Solvent typically accounts for at least 85% of the waste produced in the manufacture of fine chemicals and pharmaceuticals. Polar aprotic solvents are a particular concern as DMF and NMP are reprotoxic and are classified as substances of the highest concern under the EU REACH regulations. This presentation will summarise our results on the development of greener replacements for conventional polar aprotic solvents.

Proline catalysed aldol reactions have many green credentials: the catalyst is a natural product; reactions require no heating or cooling, are 100% atom economical and can establish multiple stereocentres with high stereoselectivities. However, these reactions are usually carried out in DMSO or DMF. We have shown that cyclic carbonates 1 and 2 (Figure 1) can be used as green solvents for proline catalysed aldol reactions, giving results which are as good as, or better than, those obtained in conventional solvents.

Peptide synthesis is also usually carried out in polar aprotic solvents and we have shown that propylene carbonate 2 can also be used as a green polar aprotic solvent for both solution and solid-phase peptide synthesis (SPPS). An issue in SPPS is the need for the solvent to swell the resin. As a result, when carrying out SPPS in propylene carbonate, it was necessary to use ChemMatrix resin rather than the more common Merrifield resin. This led us to study the interactions between green solvents and solid-phase resins in more detail and to the realisation that mixtures (both miscible and immiscible) of two green solvents could mimic the properties of conventional solvents for which no single-component green replacement was available. The viability of this approach was demonstrated by showing that appropriate mixtures of propylene carbonate 2 and 2,2,5,5-tetramethyloxolane 3 will swell Merrifield resin and permit its use as a support for SPPS without the need for any conventional polar aprotic or chlorinated solvents.

References
Poly(hydroxyalkanoate)s (PHAs) are a class of natural or synthetic aliphatic polyesters which feature the same three-carbon backbone structure, only differing by their substituent (R) in β-position. PHAs have attracted considerable interest as “green” engineering plastics. These biodegradable and biocompatible polymers represent a targeted choice for in particular packaging, and biomedical applications in tissue engineering and as drug delivery systems.

Recent highlights of research at Rennes University in the field of 1) tunable catalytic systems for the ring-opening (co)polymerization (ROP) of functional β-lactones (e.g. β-butyrolactone (BL), β-malolactonates (MLAOLS; R = CH;Ph (Bn), (CH);=CH; (All)), or 4-alkoxymethylene-β-propiolactones (BPLORS; R = Me, Allyl, Bn)) into their corresponding PHAs (poly(3-hydroxybutyrate) (PHB), poly(alkyl β-malolactonate) (PMLAso), poly(alkoxymethylene-β-propiolactone) (PBPLow), respectively), and 2) original sequence controlled PHAs featuring a high degree of control over molecular and microstructural characteristics, will be presented. Our most significant achievements in this endeavor include the development of strategies that enable the synthesis of alternated PHA-based copolymers, and the evidences of the relationship between the catalytic system, the chemical structure and the composition of the macromolecules.

References
Selective Anti-Markovnikov Hydrocarboxylation of Olefins: Formation of all-carbon quaternary centres

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Currently efficient chemical incorporation of CO$_2$ is in general limited to reactive substrates, such as epoxides or amines to produce cyclic carbonates and carbamates, respectively. We have recently embarked on a programme of research directed at carbon dioxide utilisation and have reported our initial efforts in this area. Although encouraging a major issue with this electrosynthetic system was the requirement for the use of a sacrificial anode.

The formation of a thermodynamically and kinetically stable C-C bond is one of the most desirable applications for CO$_2$ utilization. The stoichiometric hydrocarboxylation of alkenes was initially reported by Hoberg using low-valent Ni$^-$ or Fe$^-$alkene complexes to give carboxylic acids. Since then several groups have reported impressive metal and photo-catalysed routes to the hydrocarboxylation of terminal alkenes. Whilst these processes are appealing from a selectivity point of view they tend to be limited to aromatic terminal or di-substituted alkenes.

Here we will report a novel system for the selective carboxylation of terminal, di-, tri- and tetra-substituted olefins; see scheme below.

References

Keynote Lecture Abstract 5
Núria López

A Modeling Perspective on Green and Sustainable Chemistry

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In the talk I will review the most important aspects of sustainability from an atomistic point of view. I will address issues regarding raw metal efficiency, use of inactive feedstocks and waste with an special emphasis in the understanding of activation, selectivity and stability of the catalytic materials.
Renewability is not Enough: Sustainable Synthesis of Biomass-derived Monomers and Polymers

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In ages of depleting fossil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. In order to develop truly ‘green’ approaches, using renewable resources is insufficient.[1] The available feedstocks rather have to be used in a sustainable fashion by combining as many of the principles of green chemistry as possible and by accessing and comparing the sustainability of chemical transformations. Within this contribution, new approaches for the synthesis of monomers as well as polymers from plant oils,[2,3] lignin[4] and carbohydrates will be discussed, thereby highlighting developed sustainable (catalytic) modification strategies. The focus of this presentation will be on novel approaches towards the sustainable functionalization of cellulose[5] and lignin, including new solubilisation and catalysis concepts as well as the use of multicomponent reactions. For instance, a switchable ionic liquid, first introduced by Jerome[6] as well as Xie[7] for cellulose solubilisation, was studied and optimized[8] and later on applied for cellulose aerogel preparation.[9] The use and the advantages of this switchable solvent system for the preparation of various cellulose derivatives, for instance fatty acid cellulose esters (FACEs)[10] or cellulose succinylation with subsequent grafting via multicomponent reactions,[11] will be discussed in detail.

References
Keynote Lecture Abstract 7
François Jérôme

Synthesis of Renewable meta-xylylenediamine and alkyl levulinate from Biomass-Derived Furfural

Ivan Scodeller, Alban Chappaz, Jonathan Lai, Karine De Oliveira Vigier, Raphael Wischert, Stéphane Streiff, and François Jérôme,*

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The catalytic conversion of renewable feedstocks to fuels, fine or specialty chemicals is now the subject of intense research efforts. Although a myriad of reports published daily on this topic, the emergence of bio-based fuels and chemicals in our society is unfortunately facing important hurdles such as catalyst deactivation and high dilution, thus leading to low space time yields. As a case in point, we will discuss on the catalytic conversion of furfural to specialty chemicals, a cheap bio-based building block (1.0-2.0 €/kg) available in large scale from biomass (>300 kT/year). Two reactions will be discussed:

1. The catalytic conversion of furfuryl alcohol (FA) to alkyl levulinate (AL).
   In this part, we will focus on the design of catalytic systems (metal triflates) capable of selectively converting concentrated feed of FA to AL, with unprecedented space time yield as high as 182 kg/m$^3$/h. A comparison with the commercialized SFOS process is included to benchmark the catalytic systems.

2. The catalytic conversion of furfural to meta-xylylenediamine, an important aromatic target widely used in the polymer industry. The investigated pathway involves a Diels-Alder/aromatization sequence as a key step. Guided by DFT calculations, we will discuss that (1) the aromatization step could be catalyzed at low temperature by superbases instead of acids, thus avoiding the usually observed retro-Diels-Alder reaction, and (2) by playing with the rate of the reactions, it was possible to selectively drive the reaction to the meta aromatics only.

If time allows, we will then discuss how alternative technologies, such as ultrasound for instance, can promote the selective conversion of concentrated feed of biomass, without assistance of any catalyst.

References

Access to adequate supplies of water is central to a sustainable future and climate change is expected to exacerbate water scarcity problems in several European regions. Recycling of water is considered as an adaptation measure to save resources through reuse mainly for not-for-drinking uses, although in some countries such as in Singapore, recycled water is used for drinking water as well. Sources of water to be recycled include domestic water from baths, showers and sinks as well as treated wastewater. The presentation will analyse the problems that Europe is facing regarding water scarcity, it will show model predictions for the future of European and Mediterranean countries and will analyse the main technologies used for abating certain categories of pollutants, in order to provide reused water complying with the legislative requirements. The talk will also highlight the difficult process in balancing a precautionary approach and will illustrate operational challenges.
Partial replacement of fossil-fuel by renewable energy is a central approach toward global carbon footprint reduction. CO$_2$, N$_2$ and biomass can be key vector molecules to enable such renewable energy insertion in the value chain of process industry [1]. A frontier in catalysis connected with this challenge is the development robust and stable solid catalysts which can be integrated in 3D devices capable of harvesting renewable energy (be it a “green electron”[1b] or a photon) to perform the targeted reductions. Some recent research achievements around CO$_2$ catalytic reduction by single-atom catalytic centers developed by surface organometallic chemistry on MOFs [2] and porous organic polymers (POPs) will be presented here to yield, inter alia, uncommonly stable (96-hours) fully heterogeneous photocatalytic system. MOF can also be interesting mediators for the electroreduction of gas phase CO$_2$ at carbon based cathodes.[3]

References
Bio-inspired Nano-Architectures for Artificial Photosynthesis

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The perfect machinery of Natural Photosynthesis, powering our daily life with solar energy, is shaped by a modular network of photocomplexes, where molecular/nano-range order and distances are precisely tuned on membrane-bound compartments. Along these guidelines, the current frontier of Artificial Photosynthesis looks at a multi-component, interconnected system, where the cross-talk of photo-active and catalytic building blocks implements function and optimization/repair strategies. The expectation for man-made systems is to dissect the photosynthetic complexity and replicate its core-apparatus under a totally artificial environment, using cost-efficient synthetic strategies. In this scenario supramolecular strategies can play a crucial role to boost photo-assisted catalysis by a tailored interplay of non-covalent interactions, including hydrogen bonding, hydrophobic and electrostatic forces. Building on these concepts we report herein the functional characterization of photosynthetic nano-patterns emerging from the combination of water soluble photosensitizers with oxygenic polyoxometalates (POMs) known as the inorganic analogs of the natural PSII-OEC.

References

2. S. Piccinin, A. Sartorel, M. Bonchio, S. Fabris et. al. PNAS 2013, 110, 4917.
INDUSTRIAL SESSION
ABSTRACTS
Biodegradables Compostable Polymers as Key for Closing the Loop of Organic Matter

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Biodegradables-compostable polymers help to close the loop of the Organic Matter:

by the production of aliments: mulch, twines & clips
by the transportation, conservation: bags and packaging
by the use: coffee capsules
by the gestion of bio waste: bags in combination with vented kitchen caddy

All of these, help us to: produce fruits & vegetables (F&V) reducing soil contaminations; use the rest of harvest in green houses as raw material for composting; extend shelf life of F&V in the refrigerator (reducing food waste); avoid waste generation (coffee capsules dispose with biowaste together); help to increase quality of compost. Compost that will be use to improve the quality of soil, closing the loop of Organic.

Insert one graphic (Scheme or Figure, with reference in the text, preferred settings ChemDrawACS Document 1996).

References

Tackling the Challenge of Sustainability in the Tyre Industry

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Tyres are complex engineered products based on hundreds of raw materials and integrating different technologies. Tyre development is driven by the requests of vehicle manufacturers, legislation and market forces: Pirelli integrates the former inputs into an Open Innovation Model, involving collaborations with OE customers, selected suppliers and research institutes. Pirelli is strongly committed to the development of high performance products and to their continuous improvement in terms of safety and environmental impact, according to its “green performance” strategy “safe for People, safe for the Planet”. In 2018 Pirelli set ambitious objectives on product and raw materials:  
- Product - to improve noise by 15%, rolling resistance by 20%, and wet grip by 15% within 2020 (reference 2009 values)  
- Raw materials - for selected segments, Pirelli will double the share of renewable materials and reduce the fossil based materials by 30% within 2025 vs 2017.  

New Materials and Technologies are a fundamental part of Pirelli’s Innovation Strategy. Main developments in new materials are: i) New Polymers to resolve trade-offs between Rolling Resistance, Wet and Winter performances; ii) Chemicals from renewable feedstock with potential use as plasticisers, protective and curing agents iii) Nanofillers and biofillers to support lighter structures and further contribute to reduce the environmental impact of tyres, developing compound materials from renewable feedstocks (e.g. lignin and cellulose) and low environmental footprint minerals.
Perspectives on Sustainability in the Polymers Industry

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Perspectives on the future of sustainable polymers, existing barriers and selected examples of this emerging and fascinating field of chemistry are provided.

Polymers used as plastics or rubber are an essential part of modern life. In applications such as packaging, construction, automotive and medical equipment, coatings and functional materials, plastics play a crucial role in preserving food, efficient use of energy in housing and mobility (e.g. insulation, light weight parts), protecting goods (e.g. anti-corrosive coatings) and saving human lives (e.g. dialysis equipment). As part of many industrial and consumer products, (so-luble) polymers ensure performance in use (e.g. preservative-free paints), exploitation and preservation of natural resources (e.g. minerals, water) and con-tribute to basic human needs for hygiene (e.g. cleansing products) and well-being (e.g. cosmetics).

Inappropriate disposal of plastics, (potential) formation of micro-particles, finite fossil resources and the need to reduce green house gases will expand focus of the industry from established petro-chemical pathways more towards natural, renewable and bio-degradable polymers. Recycling strategies will allow efficient use of energy, materials or chemicals.

Renewable feedstocks have been the dominating source for chemical raw materials in the past (Figure 1), but were replaced by coal, gas and oil. Photosynthesis leads to natural polymers (e.g. cellulose) in amounts far beyond petro-chemical production, however, synthetic polymers vastly dominate most applications due to their superior cost/performance, ease of processing and variability of pro-perties. Sustainability needs might lead to a revival of natural polymers.

Renewable polymers can be obtained using structural analogues of current petro-chemical monomers, however, to be economically feasible, such monomers need to become available at acceptable quality, cost and scale. Renewable monomers, which will remain inaccessible for various reasons need to be functionally re-placed leading to the (re)emergence of (new) polymer classes.

Product life-cycle and more specifically end of life assessments will experience much more attention. For the latter, new chemical concepts for bio-degradation need to be developed complementing recycling strategies.

Figure 1. Raw materials used by the chemical industry in historical perspective a) renewable feedstocks; b) coal; c) natural gas, oil
References

Bio-based Adhesives: Where do we come from and where do we go?

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Bio-based adhesives have a long history - already 200,000 years ago birch pitch was used by Neanderthals, animal-based proteins were common glues in ancient Egypt and starch-based binders can be seen as the first truly industrial adhesives produced on larger scale. However, during the 20th century bio-based adhesives dramatically lost their importance, which is closely related to the scientific progress in synthetic polymer chemistry.

On the contrary, recent progress in biotechnology enables the green production of bio-renewable platform chemicals and specific design of functional proteins & peptides, which is expected to significantly impact adhesive development and create numerous new possibilities and applications (example given in Figure 1). In this context this contribution aims to discuss the requirements and perspective of bio-based, green and sustainable adhesives in our modern world.

Figure 1: Schematic representation of an adhesive peptide covalently bound to an adhesive binder based on classical synthetic polymer chemistry. This concept leads to adhesive bioconjugates that can combine specific interaction capabilities with strong mechanical performance.
Industrial Session Abstract 5
Fátima Lucas (ZYMVOL)

Making in Silico Enzyme Evolution a Commodity for the Widespread Use of Industrial Biocatalysts

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Computer simulations are already widely used to rationally engineer new enzymes with improved properties. But if we can accurately screen millions of enzyme variants in a computer, then we can move into a new generation of in silico enzyme evolution. At ZYMVOL we are able to produce, model and rank protein-substrate interactions (including full protein dynamics) for over 50,000 enzyme variants per day. We have accelerated physics-based simulations, and combined experimental data with quantum approaches to develop a highly predictive computational platform. Our ZYMEVOLVER software can effectively reduce experimental validation to a few hundred variants and enzyme optimization campaigns to less than 6 months.

In this talk, we will show how we moved from basic structure/function characterization studies to computer-guided enzyme optimization and finally to its application in multiple industries. Success stories will be shown and current challenges in in silico engineering discussed.
Efficient Reaction Technologies for Sustainable Chemistry

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Continuous flow chemistry presents many advantages compared to the traditional ‘batch’ processes.\textsuperscript{1} Flow techniques are slowly becoming mainstream practice. This involves that every day more and more labs, in academia and industry, possess a small collection of pumps and other related gadgets that a few years ago most chemists would have never dreamt of using.\textsuperscript{2} Despite this, expert pioneers able to guide the different sectors in the paradigm change from batch to flow approaches are needed, as well as the development of flow processes for an efficient utilization of energy and time, fundamentals of green chemistry.

ERTFLOW is a technology development unit and future spin-off from ICIQ, which aims the development of efficient processes in catalysis and continuous flow for sustainable chemistry.\textsuperscript{3} Key challenges in flow chemistry and applications performed with future industrial production will be discussed.

References
3. www.ertflow.com
Oxidative carbon-carbon bond cleavage of vicinal diols yielding carbonyl compounds is a fundamental reaction in organic synthesis[1] as well as in lignin-cellulose valorization and the general context of renewable feedstock transformation.[2] Here we will describe the aerobic oxidative C-C bond cleavage of vicinal diols catalyzed by vanadium amino triphenolates showing that that C-C bond cleavage can be performed in different solvents, under an air or oxygen atmosphere, with a large variety of glycols (cyclic or linear, with aromatic or aliphatic substituents) affording the corresponding carbonyl derivatives with high chemoselectivity. Reactions can be performed with as little as 10 ppm of catalyst reaching TON up to 81,000 and TOFs of up to 4150 h⁻¹. A reaction mechanism, rationalized by density functional theory calculations will be also proposed.

Furthermore, the application of the method to β-O-4 lignin models and lignin organosolv will be presented. The V(V) catalyst is effective and shows a significant amount of C-C bond cleavage selectivity (up to 25%).

References

Oral Communication Abstract 2
Jèssica Margalef

Efficient and Readily Available Metal-Catalyst Libraries for the Preparation of High Value Chiral Compounds
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Asymmetric hydrogenation (AH) of olefins is a sustainable and high efficient method for the synthesis of chiral valuable synthons. Most of the new catalysts are only tested in benchmark substrates, eluding challenging olefins that would yield to more appealing compounds. Here we present our recent finding in the design of improved M-P,N or M-P,S/Se catalyst libraries (M= Rh, Ir) for the elusive AH of tetrasubstituted olefins and cyclic β-enamides. These families of catalysts, with a modular architecture, have been synthesized in few steps from unexpensive starting materials and are solids and stable to air. The right choice of the ligand parameters gives for the frist time, ligands suitable for di-, tri- and tetrasubstituted olefins (70 examples). These catalysts not only exhibited an unprecedented high tolerance to the geometry and steric constrains of the olefin, but they also could tolerate different functional groups very well. Thus, a broad range of olefins containing both minimally coordinative groups (e.g. α,β-unsaturated carboxylic esters, enones, lactames, vinyl boronates and enol phosphinates) and coordinative groups (the challenging β-enamides) could be efficiently hydrogenated (ee’s up to 99%). Moreover, the excellent catalytic performance is maintained for a range of aryl and alkyl vinyl fluorides (dr’s > 99% and ee’s up to 98%), where two vicinal stereogenic centers are created. The effective hydrogenation of such a challenging olefins is of great importance since their reduced products can be found in many therapeutic agents and biologically active natural products (e.g. rotigotine, alnespirone,...).

References
Oral Communication Abstract 3
Miguel Claros

**Visible-Light Reductive Cyclization of Unactivated Alkyl Chlorides**

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Recent visible light metallaphotoredox methodologies have allowed the construction of a large variety of C-C and C-heteroatom bonds. Most of these novel photocatalytic protocols are limited to highly active aryl and alkyl iodides and bromides as coupling partners. Although alkyl chlorides are available, economic and bench-stable feedstocks, the chemical inertness of C\textsubscript{sp3}-Cl bonds hampers their use as electrophilic partners in most of catalytic methodologies, as showcased by the narrow number of transition metal-catalyzed reactions towards this endeavor.

In this work, we present a metallaphotoredox methodology to achieve the catalytic intramolecular reductive cyclization of unactivated alkyl chlorides with tethered alkenes. The cleavage of strong C\textsubscript{sp3}-Cl bonds is mediated by a highly nucleophilic low-valent cobalt or nickel intermediate generated via visible light photoredox reduction employing a copper photosensitizer. The high basicity and multidentate nature of the ligands are key to obtain efficient metal catalysts for the functionalization of unactivated alkyl chlorides.

**References**

Palladium Mesoionic Carbenes as General Precatalyst for Sustainable Cross-Coupling Reactions

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Carbon-carbon coupling reactions have an enormous importance in the field of Organic Chemistry, and they are the direct and efficient tool to form new bonds [1]. Most of them are performed under volatile organic compounds which are toxic, no biodegradable, etc [2]. Their replacement by safer and more sustainable ones is highly desired [3]. Recently, the use of deep eutectic mixtures has emerged as alternative to those solvents. In this communication the use of palladium strong σ-donor mesoionic carbene complex has been studied as pre-catalyst for all typical cross-coupling reactions (Scheme 1) employing DES.

References
Oral Communication Abstract 5
Olympe Longeras

Sustainable Deep Eutectic Solvent for CO₂ Capture Improvements

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To face the global warming, one solution is the use of Carbon Capture, Utilization and Sequestration (CCUS). One strategy is first to capture selectively the CO₂ in industrial fumes by use of absorbent solutions and then to valorize or to sequestrate it in secured sites. During capture process, a reversible acid-base reaction occurs between the absorbent solution and the CO₂. The process can be described in two steps: the first consists in a selective absorption of the CO₂ in the aqueous amine solvent, and the second in desorption of pure CO₂ by heating the solution. However, a significant energy is necessary to regenerate the solvent and released the pure CO₂, which induces a high cost for industrial uses.

In order to decrease the cost of the regeneration step, the use of solvents with Lower Critical Solution Temperature (LCST) is studied, especially aqueous solutions of demixing amines. The challenge is to find a system with a high CO₂ solubility, a convenient demixing temperature, and a low CO₂ concentration into the amine phase after separation [1]. The Deep Eutectic Solvent (DES) is a new solvent family which has emerged in last decade. A DES is a mixture of several compounds which present a melting temperature lower than the pure compounds. These solvents are attractive because of their easy preparation, their low cost and their specific properties [2].

The aim of this work is to combine a DES, which presents a LCST, with an aqueous amine solution for the CO₂ capture. The demixing temperature in such system was determined, the CO₂ solubility was measured and the volume of each phase was estimated. A new absorbent with promising properties for CO₂ capture has been evidenced.

Acknowledgements:
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References:
In the last decades, the development of stimuli-responsive materials gained much attention due to their ability to respond an external stimuli such as light (photochromic) and electricity (electrochromic) by changing their properties (e.g. optical properties) [1,2]. In this context, our group have been developed and tested different task-specific Ionic Liquids (ILs) or Deep Eutectic Solvents (DES) as efficient and reversible electrochromic Devices (ECD) [3-5]. DES as a new class of sustainable materials are formed by the suitable combination of hydrogen bonding donors (HBD) and acceptors (HBA). They can be applied as alternative electrolytes [6] as well as functional and efficient multi-colored ECDs [4,5].

Herein, we will present novel stimuli-responsive materials based on DES composed by polyoxometalates (electrochromism) or diarylethenes (photochromism) in combination with different HBD components. Also, the development of alternative electrolytes including metal and iodide salts as HBA will be reported. These new class of DES can open attractive applications for material science and energy devices (Figure 1).

**Figure 1**: General design of possible applications as energy devices

**References**


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Bioprivileged Ionic Liquids and Deep Eutectic Solvents: From Extraction/Purification to Drug Development

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Nowadays, sustainability challenges have advanced the research in unconventional solvents, extraction techniques and drug development. An emerging research field of interest is the use of ionic liquids (ILs) and deep eutectic solvents (DESs) in aqueous biphasic systems (ABS) and pharmaceutical applications. ILs have emerged as one of the most attractive solutes for ABS, with outstanding performance in the extraction of targeted biomolecules.[1] Recently, we have proposed a benign route for ABS containing cholinium-based ILs,[2] disclosed novel ABS composed of fluorinated ILs (FILs) [3] and demonstrated that FILs reduce the impact of the addition of water upon the IL’s H-bond acceptance ability,[4] which is a key factor to obtain functionalized materials to be used e.g. in the dissolution of biomolecules or extraction processes. Herein, bioprivileged ILs and DESs were implemented to develop more versatile and amenable to be tuned ABS. To understand the phase formation process and their potential as extractive platforms of biomolecules, the ternary phase diagrams, the polarity parameters of aqueous media in the coexisting phases, and the partition coefficients of biomolecules (e.g. tryptophan, lysozyme) were determined. Additionally, the standard batch was compared with flow-through processes (microfluidic devices), where the laminar regime and the low interfacial tension favour interface stabilization, a key requirement in ABS. Likewise, the development of ILs that are themselves APIs (API-ILs) [5] present many benefits, including the potential to modulate the water solubility and the membrane permeation properties of an API. The presented results clearly demonstrate that, within the green chemistry framework, a bioprivileged IL and DES platform constitutes a viable alternative for enhancing the bioavailability of poorly water-soluble APIs.

References
Fluorinated Ionic Liquids as Novel Task-Specific Materials

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Fluorinated Ionic Liquids (FILs) has been arisen as a greener biomaterial due to their unique and improved properties such as high surfactant power, chemical/biological inertness, easy recovery and recyclability, low surface tension, extreme surface activity, high gas solubility, negligible vapour pressure, large liquid range, null flammability and high thermal stability. This specific family of ionic liquids is characterized by having fluorine tags of at least four carbons which permits the formation of a new 3rd nanosegregated fluorinated domain, allowing the control of segregation capacity and converting FILs in 3-in-1-solvents with enhanced solubilisation power. Playing with the different types of interactions, size and type of domains (polar, hydrogenated/fluorinated apolar), surfactant behaviour and solubilization power, provide the ingredients to use FILs as biomaterials specially in separation processes and biomedical fields. The focus on these compounds has been boosted in areas where perfluorocarbons (PFCs) find relevant applications, allowing a cleaner and more sustainable chemistry increasing their interest also as an environmentally friendly biomaterial.

This work is focused on the possibility to develop and design FILs to replace, partially or totally, PCFs that are used in a wide range of industrial applications. FILs could be widely used in applications such as fire retardants, lubricants, insecticides, fluorocarbon gels, nanocompartmented supramolecular architectures and colloids, control and stabilization of emulsions, microbubbles, delivery of drugs and genes, artificial blood substitutes, liquid ventilation and intravenous formulations. To accomplish biomaterials based on FILs for these applications, characteristics like hydrophobicity, biodegradation, bioavailability, toxicity, surface properties, self-assembled structures and surfactant behaviour in aqueous solutions, thermophysical characterization and their solubilisation power have been investigated in this work. This will allow the designing and development of the best FILs with the most outstanding properties to be used in each specific application.
Oral Communication Abstract 9
Gerard Lligadas

Uncovering Opportunities for Sustainable Polymer Synthesis by SET-LRP

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Cu(0)–catalyzed single electron transfer-living radical polymerization (SET-LRP) represents a robust and versatile tool for the rapid synthesis of vinyl polymers with well-defined topology and chain end functionality.1 This LRP technique enables the ultrafast polymerization of a plethora of both hydrophobic/water-insoluble and hydrophilic/water-soluble monomers (e.g. (meth)acrylates, (meth)acrylamides and styrene). The disproportionation of the [Cu(I)(N-ligand)X] complex into Cu(0) aggregates and [Cu(II)(N-ligand)X]2 in solution is crucial for the occurrence of the SET-LRP mechanism. Nowadays, SET-LRP practitioners have a myriad of options on how to present the copper catalyst to the reaction mixture (e.g. Cu(0) powder or nanopowder, activated or nonactivated wire, Cu(0) generated “ex situ” or “in situ” by disproportionation,…) (Scheme 1).2

Scheme 1. General experimental procedures for two classical SET-LRP methodologies: (a) nonactivated Cu(0) wire-catalyzed SET-LRP in aqueous or organic media and (b) aqueous SET-LRP catalyzed by Cu(0) generated “in situ” by disproportionation of Cu(I)X. F-T-P: freeze-pump(-1 min)-thaw cycles that can be substituted by vigorous inert gas bubbling.

With the aim of providing inspiration to non-expert users, the different contemporary SET-LRP methodologies will be presented. Next, the simplest methodology, which uses Cu(0) wire wrapped around the stirring bar, will be applied to uncover opportunities for sustainable polymer synthesis by SET-LRP. Selected examples on the precise synthesis of vinylic polymers from biomass feedstock3 and the use of alternative reaction media to replace or reduce the use of traditional petroleum-derived solvents will be discussed to exemplify the potential of this LRP technique in providing sustainable technologies based on renewable resources.
Acknowledgements: Financial support from the National Science Foundation Grants DMR-1066116, DMR-1807127 and the P. Roy Vagelos Chair at the University of Pennsylvania (to VP) are gratefully acknowledged. We also thank Spanish Ministerio de Ciencia, Innovación y Universidades through project MAT2017-82669-R (to GL and JCR) and FPI grant BES-2015-072662 (to AM), the Serra Hunter Programme of the Government of Catalonia (to GL) and University Rovira i Virgili (DL003536 grant to NB).

References
Enzymes: Powerful Catalysts for the Synthesis of Functional Polyesters

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With the increase of society’s awareness of the significant problems caused by plastic pollution of oceans and rivers, governments and industry are combining efforts to reduce plastic-derived waste by implementing recycling and composting strategies and moving towards alternative bio-based plastics synthesized from renewable feedstocks.

In this work, a series of functional polyesters synthesized via environmentally friendly enzyme-catalyzed strategies are presented together with a series of polymers that are not easily obtainable using traditional metal-based catalysis.

In particular, the solvent-free synthesis of polymers using Candida antarctica lipase B as the biocatalyst were carried out for obtaining itaconate- and other unsaturated aliphatic polyesters that were post-functionalized via aza-Michael addition reactions.

Moreover, some novel lignin-derivable polyesters that aim to substitute terephthalic and furandicarboxylic acid-based polymers will also be introduced as potential alternatives to the currently used -and developed-polymers.

An in-depth characterization and discussion on the polymer’s properties and a comparison of the advantages and limitations of enzymatic vs chemocatalytic synthesis will be the illustrated showing how, in particular cases, enzyme catalysis is the way forward for the synthesis of linear polymers having lateral functionalities that are fully preserved and can be therefore used for further post-polymerization modifications.

References

Alternating CO₂-Cyclohexene Oxide Copolymers and (Stereo)Block Copolymers of L-, D-, rac-Lactides and ε-Caprolactone by New Pyridylamidozinc(II) Catalysts

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A family of three-coordinated Zn(II) complexes bearing chelating pyridylamido ligands with variable steric and electronic features has been tested for the alternating ring opening copolymerization (ROCOP) of CO₂ and cyclohexene oxide (CHO) and for the ring opening polymerization (ROP) of lactide (LA) and ε-caprolactone (CL) (see Figure 1).

The ROCOP of CO₂ and CHO affords polymers with carbonate linkages up to 99% and a slightly isotactic-enriched structure under a variety of reaction conditions, including 1 atm of CO₂ pressure, without any cocatalyst. Some experimental and theoretical evidence suggests that dimeric initiating species are involved in the catalytic cycle, as proposed for the (BDI)Zn catalysts. The title catalysts efficiently promote also the ROP of LA and CL, even at 25 °C. Owing to the catalysts living nature and high activity, precise stereodiblock poly(LLA-b-DLA)'s, which crystallize in the high melting stereocomplex phase, can be easily produced by one-pot sequential monomer addition in short reaction times. Various stereo-triblock and -tetra block copolymers of L-LA, D-LA and rac-LA, as well as diblock poly(CL-b-LA)'s, have been synthesized similarly and fully characterized by NMR, GPC, DSC, and MS analyses.

Reference


Acknowledgement

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Oral Communication Abstract 12
Marta E. G. Mosquera

Earth Abundant Metals Compounds as Catalysts for the Production of Bioplastics

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The access to polymers from renewable resources with good biodegradability and with properties that match the fuel-based polymers is of great interest. In this context, one type of polymers that have attracted a good deal of attention are polyesters derived from cyclic esters such as lactide or butyrolactone, since those monomers may be obtained from renewable sources and the polymers can be biodegradable, biocompatible and have a wide range of applications.1

One of our ongoing research areas is focused in the preparation of main group metal complexes as catalysts for the Ring Opening Polymerization (ROP) of cyclic esters. Within main group metals, aluminum stands out as the most abundant metal on Earth crust and also has well known catalytic properties, in fact recently aluminum is living a renascence as catalysts.2 As well alkali metals such as Li, Na and K are particularly attractive not only for their abundance but also due to their low toxicity.

We have prepared a series of aluminum and alkali metal complexes with phenoxy ligands that bear different substituents in the aromatic rings to assess their influence on the catalytic activity and on the microstructure of the final polymer.3 These compounds are very active in catalytic ROP processes of rac-lactide and ε-caprolactone and also in the ROP of a monomer quite reluctant to polymerize such as β-butyrolactone. Furthermore, to enlarge the family of polyesters from renewable feedstock a good strategy is to perform the copolymerization of anhydrides and cyclic ethers derived from renewable resources. In these processes our compounds have also proven very efficient.

References
Oral Communication Abstract 13
Carmine Capacchione

Reaction of Carbon Dioxide with Epoxides Promoted by [OSSO]-type Iron(III) Complexes

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Incorporation of CO$_2$ into fine chemicals represents a value-added utilization of this abundant and cost effective molecule. Among the possible targets, the selective and effective synthesis of cyclic carbonates (COCs) and aliphatic polycarbonates (APCs) under mild conditions, as well as the rationalization of metal-mediated processes, is still challenging and in the focus of interest for industrial and academic researchers. We have recently reported that a new group of [OSSO]-type iron(III) complexes be used as highly active catalysts for the reaction of carbon dioxide with epoxides under very mild conditions. Notably, these catalysts are able to promote both the formation of COCs and APCs depending on the type of epoxide employed. Supported by experimental and computational data, we have found that the real catalytic species is a ferrate complex formed by reaction of catalyst precursors and tetrabutylammonium bromide. This complex can be prepared and used as single component catalyst for the reaction of carbon dioxide with epoxides.

Figure 1. Reaction of CO$_2$ with epoxides by [OSSO]-Fe(III) complexes.

References
Oral Communication Abstract 14
Cristina Maquilón

Stereo/Regio-Divergent Synthesis with CO₂

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Carbon dioxide (CO₂) offers a cheap and renewable carbon feedstock for fine-chemical synthesis. However, it remains a huge challenge to prepare densely substituted/functionalized organic cyclic carbonate scaffolds. Stereoselective conversions represent a relatively new area in CO₂ valorization catalysis. In this respect, here the reactivity of the epoxy alcohols towards the stereocontrolled synthesis of cyclic carbonates has been studied employing bicyclic substrates (Figure 1). New stereo- and regio-divergent potential has been uncovered, allowing to convert a single substrate selectively into multiple products.

This project has so far resulted in the unexpected formation of various stereoisomers (i.e., of type 2) that cannot be formed via conventional pathways. Control experiments demonstrate a unique sequence of steps that depend on the stereochemical configuration of the epoxy alcohol substrate, and importantly on the presence of an alcohol fragment.

References

Oral Communication Abstract 15
Katie J. Lamb

Using Metal Salen and Salophen Complexes for the Green Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide
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There has been a recent paradigm shift towards promoting sustainable Carbon Dioxide Utilisation (CDU). One of the most studied CDU reaction is the conversion of carbon dioxide and epoxides into cyclic carbonates. Cyclic carbonates are commercially valuable products, used as electrolytes in lithium-ion batteries, alternative solvents and intermediates in the synthesis of pharmaceuticals. This reaction in the presence of Lewis acidic metal catalysts can proceed under ambient or mild conditions and with 100% atom efficiency, thus providing a green process for carbon dioxide valorisation.

Since 2007, researchers at the University of York have studied the use of metal salen and salophen complexes to promote CDU, by converting epoxides and carbon dioxide into cyclic carbonates (Figure 1).

Figure 1: Examples of salen and salophen catalysts used for the formation of cyclic carbonates from epoxides and carbon dioxide. These complexes include homogeneous monometallic chromium (Catalyst 1, Figure 1) and aluminium salophen catalysts, homogeneous dimetallic aluminium salen catalysts and heterogenous aluminium salen complexes (Catalyst 2, Figure 1). Many of these catalysts are extremely effective at ring-opening terminal epoxides under ambient conditions, to form cyclic carbonates with carbon dioxide. Some catalysts can even convert sterically hindered internal epoxides, more challenging substrates, under mild conditions.

This oral presentation will describe past, recent and currently on-going research into using salen and salophen complexes to promote green CDU. Research into using these catalysts for other reactions and other interesting finds will also be presented.
References
Oral Communication Abstract 16
Sergio Fernández

Identification of the Key Mechanistic Steps Involved in the Cobalt-Catalyzed CO2 Reduction

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Herein we report a mechanistic study in the electrochemical CO2 reduction process catalyzed by a molecular Co complex based on the PyMe2tn (Ln4) ligand.1) The combination of cyclic voltammetry and in-situ spectroelectrochemistry allowed for the detection of a [Ln4CoI-CO]+ (1)-(CO) intermediate at the CoII/I redox wave under CO2 atmosphere in anhydrous MeCN. The detection of this intermediate implies a first CO2 binding to CoI and a subsequent C-O bond cleavage at the same CoII redox potential. The computational modelling of the reaction mechanism confirmed that the formation of 1-(CO) is key in order to understand the activation of CO2 and the catalytic performance at more negative redox potentials. Finally, we propose the use of blue-light irradiation as strategy to recover the catalytically active species via light-induced metal carbonyl dissociation.2)

Figure 1. Proposed reaction mechanism.

References
Oral Communication Abstract 17
Selina K. Kaiser

**Metal-Dependant Structure-Activity Relations in Acetylene Hydrochlorination**

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The substitution of the toxic mercuric chloride catalyst in polyvinyl chloride production via acetylene hydrochlorination is an imperative step to reduce the environmental impact of this long-established industrial technology.\[1\] In this context, deriving structure-activity relations of promising metal-based catalysts (Au, Ru, Pt, Ir, and Rh) is key to guide the development of a more sustainable process. For this purpose, we derived a platform of these metal nanostructures, ranging from single atoms of tunable oxidation state to metallic nanoparticles. By combining advanced characterization techniques, steady-state experiments, density functional theory, and mechanistic studies we identify two main catalyst families: (i) Au, Pt and (ii) Ru, Ir, Rh-based systems which show fundamental differences regarding the structure of the active site (single atoms vs. nanoparticles Figure 1) and the prevailing deactivation mechanisms (single atom agglomeration and nanoparticle re-dispersion). With this understanding we developed system-oriented optimization strategies, including graphene encapsulation of nanoparticles and oxygen co-feeding, fostering the design of high-performance hydrochlorination catalysts.\[2\]

**References**

![Fig. 1: Single atoms vs. nanoparticles as the active site in acetylene hydrochlorination.](image)
The replacement of fossil fuels by a clean and renewable energy source is one of the most urgent and challenging issues in our society. A particularly attractive solution is the production of hydrogen from water splitting (WS) using sunlight as driving force.\(^1\) In this context, Ru nanocatalysts have demonstrated to be in some cases as efficient as the state-of-the-art Pt materials for the hydrogen evolution (HE) half reaction.\(^2\) The present work is focused on the visible-light induced generation of hydrogen at neutral pH by means of a Ru nanoparticulated catalyst\(^3\) deposited onto titanium dioxide (RuNPs/TiO\(_2\)), \([Ru(bpy)_2(4,4'(PO_3H_2)(bpy))Cl_2]\) and triethanolamine, as hydrogen-evolution catalyst, photosensitizer and sacrificial electron donor, respectively. The nanocatalysts were prepared by the organometallic approach followed by an impregnation step onto TiO\(_2\) (Figure 1). As observed through laser flash photolysis, the covalent bond formed between the photosensitizer and the TiO\(_2\) surface enables the electronic communication between the nanocatalyst and the photoabsorber through the semiconductor, thus dramatically improving the photocatalytic performance of the system. The nanomaterial shows long-term stability under catalytic conditions compared to other Ru HE photocatalysts.\(^4\)

References
One of the current challenges for industry is the development of environmentally sustainable processes. The use of heterogeneous catalysts offered a key tool to achieve suitable utilization of energy and chemicals. The selective semi-hydrogenation of alkynes into alkenes has been the object of particular attention for its relevance in the polymer and fine chemical industries, for which the development of chemo- and stereoselective catalysts is highly desirable to improve the productivity of the corresponding processes and prevent the overhydrogenation and/or oligomerisation of the substrates. In this context, metal nanoparticles (M-NPs) combine advantages of both homogeneous and heterogeneous catalysts, namely high activity/selectivity and facility for recycling and re-use. To enhance their catalytic performance, it is necessary to induce control on the physical and chemical properties of the M-NPs. Previously, we have demonstrated that strongly-coordinating ligands are able to efficiently induce this control.1

Here, a highly stereoselective akyne semihydrogenation with NHC-stabilized metal nanoparticles immobilized onto carbon nanotubes (CNTs) obtained through a new methodology involving the decarboxylation of a zwitterionic CO₂ adduct, have been developed under mild reaction conditions (50°C and 5 bar H₂ pressure). The corresponding alkenes can be isolated with high Z-selectivities and negligible overreduction to the alkene. The supported Ni nanocatalysts can be readily recovered and reuse at least 4 consecutive cycles without significant loss of its catalytic activity and selectivity. 2

References
Oral Communication Abstract 20
Begoña Puértolas

Mechanism of the Ceria-Catalyzed Phosgene-Free Synthesis of Polyurethane Precursors
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The alkoxy carbonylation of toluenediamines with dialkyl carbonates catalyzed by ceria attracts increasing attention as a sustainable route for the non-phosgene production of isocyanate precursors.\(^1\) Here, the mechanism of the alkoxy carbonylation of the industrially-relevant 2,4-diaminotoluene (2,4-TDA) with dimethyl carbonate (DMC) along with the evolution of the property-performance interplay upon consecutive cycles are rationalized \(\text{via}\) the assessment of the composition profile with the reaction time, characterization tools, and density functional theory (DFT) calculations. The reaction preferentially leads to the formation of the desired carbamates, part of which further react to form unique productive ureas that are subsequently transformed into carbamates. Their formation is accompanied by a number of side products that are identified by an unprecedented full product analysis and mostly comprise \(N\)-alkylated carbamates and ureas (\textbf{Figure 1a}). Evaluation in subsequent cycles evidences the catalyst deactivation, which is linked to the increasing amount of carbon deposits along with the DMC-induced partial surface restructuring into an oxygen-defective (100) facet after 6 cycles (\textbf{Figure 1b}).\(^2\) These findings are expected to be key for the rational design of heterogeneous catalysts for the production of polyurethane precursors.

\textbf{Figure 1.} a) Simplified reaction scheme of the process investigated. b) Schematic representation of the solvent-induced surface restructuring and catalyst deactivation.

\textbf{References}

Oral Communication Abstract 21
Ana Aguiar-Ricardo

Comparison of Advanced Extraction Techniques for the Recovery of Interesting Compounds from Vineyard Pruning Waste

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Especially in Mediterranean countries, where the wine industry is well developed, large amounts of vine pruning wastes are produced every year. Currently, these wastes have no commercial value and presents a management cost, but they have been proved to be a powerful source of phenolic compounds with antioxidant properties, cellulosic sugars and derivatives. This study reviews three different techniques, subcritical water extraction (SWE), ultrasound assisted extraction (UAE) and supercritical CO2 assisted extraction (SFE-CO2), for extracting phenolic compounds and sugars from the vineyard pruning wastes. The total phenolic content, the sugar content and the antioxidant activity of the extracts were analyzed and used to compare these methods. For each technique, the effect of extraction conditions, namely solvent nature, pressure, time and temperature of extraction, on the yield extracts was evaluated. Preliminary results showed that SWE (33.8±2.1 mg GAE/g dry sample) was more efficient technique and led to comparatively higher polyphenols content than SFE (0.032±0.003 mg GAE/g extract) and UAE (17.1±1.3 mg GAE/g dry sample). Furthermore, HPLC analysis is in progress to sugar content determination. These first results highlighted the potential of using Portuguese vine canes as a source of phenolic compounds for food and cosmetic applications and sugars to high value platform molecules for bioproducts and biopolymers.

Acknowledgements:
Use of Microwave Radiation Catalysis in the Treatment and Transformation of Lignocellulosic by-Products from Agrifood Industries


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Biomass waste is becoming increasingly recognised as a good feedstock and carbon source with different components and applications. Cellulose is the main component in lignocellulose waste, for this reason, the aim of this work is to study the catalytic conversion of cellulose into biofuels precursors such as 5-hidroxymethyl furfural (5-HMF) and levulinic acid (LA). One example of this type of feedstock is the agrofood wastes as sugarcane bagasse, melon rind and beer bagasse, which are considered in this work as potential bioresources with several applications.

Microwave radiation has been used as green energy source for the hydrolysis of biomass into these monosaccharides, and the process can be evolved into the obtainment of interesting compounds such as furfural, 5-HMF and levulinic acid.

In the work described here, a comparison of microwave and conventional heating is studied, as well as the use of sulfuric acid, p-toluensulphonic acid, Amberlyst and Montmorillonite KSF clay as catalysts. In conclusion, this approach highlights the opportunities of beer & sugarcane bagasse’s and melon rind carbohydrate fractions to be transformed in a source of biofuel precursors, in a clean and efficient manner.

References:

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Catalytic Fast Pyrolysis of Birch and Spruce Organosolv Lignin with Conventional and Hierarchical ZSM-5 Zeolites for the Production of Alkyl-Phenols and Aromatics

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Fast pyrolysis of lignin has been shown to provide a bio-oil with relatively homogeneous composition, i.e. compared to the parent biomass derived bio-oil, containing mainly alkoxy-phenols. The use of appropriate catalysts, such as ZSM-5 zeolites, may lead to partial or complete in situ deoxygenation of lignin bio-oil which consists of alkyl-phenols and/or mono-aromatics (BTX) and naphthalenes, as has been shown recently for softwood kraft lignin [1]. Organosolv lignins, being free of sulphur and other impurities can be ideal for catalytic fast pyrolysis. Recently, a hybrid organosolv – steam explosion method has been proposed that offers increased enzymatic digestibility of the obtained cellulose-rich biomass as well as a high purity isolated lignin [2]. In the present work, birch and spruce organosolv/steam explosion isolated lignins were studied as feedstock in the thermal (non-catalytic) and catalytic fast pyrolysis (CFP) using conventional, mesoporous and nanosized ZSM-5 zeolites, for the production of alkoxy- or alkyl-phenols and aromatics (BTX, naphthalenes).

Representative 2D HSQC NMR and fast pyrolysis results of the spruce derived lignin are shown in Figure 1. It is interesting to notice that the composition profile of spruce lignin as evidenced by NMR (i.e. comprising mainly of guaiacyl aromatic units) has been “transferred” to the thermal (non-catalytic) and catalytic fast pyrolysis (CFP) using conventional, mesoporous and nanosized ZSM-5 zeolites, for the production of alkoxy- or alkyl-phenols and aromatics (BTX, naphthalenes).

Similar trends and results have been obtained with the birch derived lignin.

Figure 1. 2D HSQC NMR spectra of aromatic structures in spruce organosolv lignin (left); composition of thermal and catalytic (micro- and mesoporous ZSM-5 zeolites) bio-oil produced by fast pyrolysis of spruce organosolv lignin
References

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Biogas conversion to methanol via steam reforming in a container sized module

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Biogas produced from biomass is a valuable renewable energy source. CH₄ and CO₂ are the main components of biogas. It can be used directly as a fuel or converted to hydrocarbons by converting it to syngas via steam reforming (SR), followed by Fischer-Tropsch or a methanol synthesis. Methanol is a C1 building block for synthesis of various chemicals and may also be used directly as a fuel [1]. Global warming and increasing fuel demands are some of the main driving forces for the development of efficient biogas to methanol synthesis processes. The present available methanol plants are normally only considered economical in connection with large-scale facilities. Therefore many farmers and small-scale biogas producers remain unexploited. Hence, a medium-sized reactor system for biogas to methanol conversion built in portable/movable ISO-sized container for these biogas producers is highly desirable and could potentially have great economical and environmental impact.

Our group is working extensively on developing such modular systems for biogas cleaning, upgrading and utilization. We have already successfully demonstrated an innovative waste-free gas cleaning system for sulphur removal and a biogas upgrading process converting CO₂ to methane. In the current work, we are utilizing biogas (both CH₄ and CO₂) to form syngas using a highly efficient Ni/Al₂O₃-based catalyst. The catalyst shows >90% conversion with zero coke formation and no deactivation up to 200 hours of labscale test. The syngas produced by SR has H₂/CO ratio >2, which will be directly fed to a methanol reactor targeting a methanol production of 2 litres per day.

Reference

Catalytic Aerobic Oxidation of Terpenes and Follow-up Chemistry towards Renewable Poly(hydroxyurethane)s

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The novel Mn-based mixed-linker metal-organic framework (MOF) MIXMIL-53-NH2(50)-Mal-Mn was successfully synthesized in a two-step post-synthetic modification reaction and investigated as catalytic material for the liquid-phase aerobic oxidation of α-pinene. Mn(III) acetate was furthermore used as homogeneous model catalyst. After investigating the influence of reaction time, solvent, temperature, oxidant flow rate and catalyst concentration on conversion, yield and selectivity for the model catalyst, optimized reaction conditions were transferred to the heterogeneous MOF-catalyst. The heterogeneous system showed very similar activity in a mixture of diethyl carbonate/dimethylformamide as solvent compared to the homogeneous catalyst, obtaining pinene oxide as main product along with small amounts of verbenol and verbenone. The heterogeneous MOF-catalyst was easily removed from the reaction mixture by filtration and could be reused for at least five catalytic cycles. Hot filtration tests showed that the catalysis mainly proceeds heterogeneously.

Figure 1 Catalytic oxidation of α-pinene by MIXMIL-53-NH2(50)-Mal-Mn resulting in pinene oxide, verbenone and verbenol.

Since the structure and reactivity of different terpenes is very specific, transferring the above presented oxidation method to other terpenes requires optimization of the reaction conditions. Oxidation of difunctional olefinic substrates like limonene, allows for the synthesis of diepoxides that can subsequently be used as monomers for renewable polymers. Limonene dioxide was further transformed into limonene dicarbonate by CO2 fixation. To utilize limonene dicarbonate (LC) for the synthesis of non-isocyanate polyurethanes, a second limonene-based diamine monomer was synthesized via thiol-ene addition of cysteamine hydrochloride to limonene. Catalyst- and solvent-free polymerization of LC and the amine-functionalized limonene monomer resulted in linear poly(hydroxy urethane) pre-polymers. By variation of the dicarbonate to diamine monomer ratio it was possible to obtain either telechelic carbonate or amine terminated pre-polymers as shown by NMR and FT-IR analyses. These pre-polymers can be further crosslinked to yield various NIPU thermosets.

References
Towards high value lignin; reactive fractionation and modification

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Biorefineries require the efficient use of all biomass components in order to be economically competitive and sustainable. However, currently, the major lignin fraction (10-30%) of lignocellulosic biomass is typically discarded as a low-value fuel. This, while as an aromatic biomolecule, it has significant potential as source for aromatic chemical products. The low value of lignin from current biomass fractionation processes arises from its structural degradation during extraction leading to highly recalcitrant “Technical lignins”. Recently, we have clearly demonstrated how lignin depolymerisation efficiency can be linked to the isolation conditions. Therefore, milder green fractionation processes that yield lignin of improved quality are highly desired in order to open up new pathways to specific chemicals or for use in materials. For this reason, we tailor existing fractionation methodologies such as organosolv extraction in order to find the appropriate balance between lignin yield and quality of the obtained structure. This includes using alternative solvents and different reactor setups. At the same time the actual lignin extraction process is investigated, revealing how the nature of the extracted lignin changes during the extraction process and how this can be utilized to allow for extraction of lignin with specific chemical motifs. These chemical motifs can subsequently be utilized for novel modification strategies as well as selective depolymerisation methods towards new aromatic monomers.

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Facile preparation of modified natural rubber by both epoxidation and hydrogenation and its properties

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Natural rubber (NR) is a renewable material obtained from Hevea Brasiliensis tree. It is the only commercial rubber from natural resource used in a wide variety of industrial product, as the vulcanized rubber possesses the excellent properties including high elasticity and high tensile strength. The chemical structure of NR is practically cis-1,4 polyisoprene which is a non-polar hydrocarbon resulting in poor solvent and oil resistance and it contains C=C bonds leading facile oxidative degradation. To extend the uses of NR, chemical modification of NR by simultaneous introduction polar epoxide groups using epoxidation and reduction of C=C bonds using hydrogenation were explored. In this study, epoxidation of NR latex using in-situ performic acid could be firstly achieved, followed hydrogenation using diimide hydrogenation without any purification between reactions (scheme.1). This process is facile, environmental friendly and economic benefit as it could be carried out in latex medium. Various conditions including rubber concentration, amount of reagents and reaction time were investigated and studied the properties. The chemical structure of the modified NR including the degree of modification was successfully analyzed by 1H-NMR. It was found that hydrogenated epoxidized NR (HENR) having 25 mol% degree of hydrogenation and 28 mol% degree of epoxidation after vulcanization had tensile strength of 23.67 MPa and elongation at break of 966%, which remains the outstanding mechanical properties of the rubber. Additionally, the lower change in mass (Δm100) of vulcanized HENR compared to NR vulcanizate after immersion in oil and solvent confirm the improvement of the oil/solvent resistance. Thermal stability of vulcanized HENR is superior to NR vulcanizate in which initial and final decomposition increase 15°C and 40°C, respectively. It clearly assures that the reduction of unsaturated hydrocarbon could enhance the thermal resistance of the natural rubber product.

Figure 1 Schematic diagram of epoxidation reaction followed by hydrogenation of natural rubber in latex stage

References
Challenges in Sustainable Chemistry Publishing

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Publishing is crucial to the advancement of sustainable chemistry and has a fundamental role in connecting scientists and providing them with a platform to share their findings with the appropriate audience. In this contribution, current developments and trends within sustainable chemistry publishing will be addressed and questions and concerns will be answered. Topics to be covered include open science, good publication practices, and future trends.[1]

References

Oral Communication Abstract 29
Archismita Misra

Magnetic Removal of Multiple Pollutants from Water by Polyoxometalate Supported Ionic Liquid Phases (POM-SILPs)

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A plethora of water filtration techniques aim at producing safe drinking water from contaminated surface or ground-water sources, especially when central water-purification facilities are unavailable, e.g. after industrial or environmental disasters.1 Many water resources in developing countries carry high concentrations of toxic organic, inorganic or microbial contaminants such as dyes, heavy metals and bacterial strains.2 Microplastic pollutants are one of the recently recognized threats to our aquatic life and human health upon entering the food chain.3 But intensive chemical treatment of wastewater can actually enhance the problems of contamination of freshwater sources. Therefore, fast and facile multifunctional filter systems that can simultaneously remove different classes of contaminants are a major research theme, particularly when tunable molecular components are envisaged which can be immobilized on a suitable reactive support material. Herrmann et al. developed a regular silica-based heterogeneous filter system composed of Polyoxometalate Ionic Liquids based Supported Ionic Liquid Phases (POM-SILPs) using water-immiscible room temperature POM-ILs having lacunary Keggin polyoxometalate anions with heavy-metal binding sites and antimicrobial alkylammonium cations. However, this system did not test microplastic and also used filtering columns which are inconvenient for large-scale filtration. This compelled us to design a microporous magnetic POM-SILP with iron oxide-cored silica support that facilitates the removal of the free-flowing powdery filter material using a permanent magnet once the contaminants are adsorbed by the filter. This presentation will showcase the synthesis of the magnetic POM-SILPs and their application in facile magnetic removal of organic dyes, heavy metals, microplastic and bacteria from polluted water (Fig 1). The pollutant removal is experimentally confirmed by UV-Vis, ICP-AES, DLS and antimicrobial assays. Electron microscopy and spectroscopic techniques support the adsorption of the contaminants on the SILP-surface. Future work will focus on investigating the SILP performance when exposed to a mixed solution of multiple contaminants under real-life conditions.

Fig 1: Water purification using magnetic polyoxometalate supported ionic liquid phases (magPOM-SILPs) based on water-immiscible POM-ILs supported on microporous magnetic Fe-oxide-silica.
References

Oral Communication Abstract 30
Azahara Luna-Triguero

Record Capacity in Zr-based Metal-Organic Framework for Heat Pumps and Water Generator Applications

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One third of the world energy consumption is generated in residential areas for heating and cooling purposes. It is crucial to find alternatives to supply the energy demand and to ensure the reduction of carbon dioxide emissions.1

Alternatives such as adsorption-based heat pumps (AHP) and desiccant cooling systems (DCS) are receiving much attention because of their moderate energy consumption.2 Here, we study the viability of zeolites HS-FAU and NaX, and water-stable Zr-based MOFs MOF-841, and ZJNU-30 for these applications.

The promising properties and the suitable behavior found for the studied adsorbents encourage us to study their transferability to adsorption water generator applications. Since the need of clean water is a current reality in deserted climates, the capture and release of fresh water is becoming an important topic.3

We performed experimental measurements of water adsorption-desorption, and we analyze the complete thermodynamic cycle of water-adsorbent working pair for DCS applications via molecular simulation.4

We showed that the composition of the structure strongly affects the water adsorption in FAU-topology zeolites controlling the hydrophobicity, an important property for these applications. HS-FAU improves the water capture and release in realistic desert conditions in comparison with NaX. Figure 1 shows the water capacity of the studied structures at realistic desert conditions. We found that a combination of properties of ZJNU-30 make this material a promising candidate for cooling applications and also for atmospheric water generator. ZJNU-30 exhibits records in water capacity (Figure 1), cooling capacity, and coefficient of performance for DCS.

References

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Design and implementation of novel materials for heterogeneous photocatalysis

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Heterogenous photocatalysts based on decorated titania or fiber glass have been developed with flow photocatalysis in mind. These materials find applications in organic chemistry such as in efficient carbon-carbon couplings, as well as environmental applications, from H₂ production to water remediation.¹ In the latter case, involving antimicrobial functions and degradation of organic matter, the use of flow is essential, and thus we develop fibrous materials that decontaminate water as it flows over the catalyst while exposed to light, absorbing as much as the solar spectrum as possible, with no catalyst leaching. Organic chemistry applications include Sonogashira and Ullmann couplings,² isomerization of alkenes and hydrogenation, including semihydrogenation of alkynes. While early decorated materials frequently involve Pd, Pt, Au and other expensive and low abundance elements, current efforts concentrate on earth-abundant elements that will enhance affordability and sustainability, while performing well in both the UVA and visible regions.³

Scheme 1: Examples of heterogeneous photocatalysis using fibrous catalysts

References

Oral Communication Abstract 32
Eduardo García-Verdugo

Polymer as Non Innocent Vector to Develop Efficient Rose Bengal Supported Catalyst.

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Rose Bengal (RB) has been widely applied as a photocatalyst in organic synthesis. Its key photophysical properties have enable the development of its synthetic applications in a wide variety of formation of C–C and C–X (N, O, S, P, Si, and Se) bonds.1

Here we report our efforts to immobilise RB onto different polymeric supports. The selection of the nature of the polymeric support and how the catalyst is immobilised are key factors for developing efficient polymeric supported catalysts.2 Thus, through the evaluation of different variables such: (i) the nature of the attachment of the catalytic sites to the support, (ii) the nature and length of the spacer between the catalytic sites and the polymeric network, (iii) the density of catalytic sites and their location along the polymeric network and (iv) the physicochemical nature of the polymeric backbone, we are able to tune the catalytic efficiency of the immobilised RB, especially in terms of activity and selectivity, in comparison with its behaviour under homogeneous conditions.3

References

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CO₂ Hydrogenation in Aqueous Solutions with Water Soluble Ir-Catalysts

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Distinction should be made between the use of formic acid (FA) as a replenishable fuel (H₂ source) and as a hydrogen storage material in a hydrogen battery. While in both devices H₂ is generated by dehydrogenation of FA, a hydrogen battery also requires hydrogenation of CO₂ back to formic acid in the same device. Presently available methods for additive-free hydrogenation of CO₂ to HCOOH are slow, and/or yield low HCOOH concentrations and/or require organic solvents. Here we present various water soluble Ir-catalysts for selective decomposition of FA₁ and CO₂-hydrogenation. Namely, the cis,mer-[IrH₂Cl(mtppms)] complex is an exceedingly active catalyst for decomposition of FA (TOF’s up to 298 000 h⁻¹ at 100°C) and it is also an active catalyst for the hydrogenation of carbon dioxide gas to FA in closed systems under mild conditions. The other water soluble Ir-NHC-phosphine catalyst (with a coordinated N-heterocyclic carbene ligand) shows good catalytic activity in the formate/hydrogencarbonate reversible hydrogen storage cycle in basic aqueous media. Here we present the activity of this catalyst in a similar hydrogen storage system under acidic conditions.

Acknowledgements
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References
Dual Activation Catalysts for the Selective Conversion of CO$_2$ into Alkylidene Cyclic Carbonates and Oxoalkyl Carbonates

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Carbon dioxide (CO$_2$) is a greenhouse gas responsible for global warming. In the last decades, efforts have been put towards the valorization of this abundant, nontoxic inexhaustible C1 source for the synthesis of useful commodity chemicals. The synthesis of cyclic carbonates is attracting much interest due to its 100% atom efficiency reaction and its large potential scope for the design of complex organic molecules or novel functional polymers (polycarbonates, polyurethanes, etc.). 5-membered cyclic carbonates can be obtained by the coupling of CO$_2$ with diols, epoxides and lastly, alkynols. The latter have the advantage of affording cyclic carbonates that are activated by the presence of an exocyclic vinylic bond, making them reactive towards alcohols and amines. In addition, their ring-opening is regio-selective affording E-oxo-carbonate by reaction with alcohols, β-oxo-urethanes with secondary amines or β-hydroxy-oxazolidones with primary amines.

Due to the inertness and high thermodynamic stability of CO$_2$, a catalyst is required to transform alkynols into alkylidene cyclic carbonates. Bases, ionic liquids, carbenes, metal salts, have been shown to promote the cyclisation of CO$_2$ with alkynols. Although full conversions are obtained in certain cases, the selectivity remains an issue. Also, harsh conditions and/or excessive amounts of base are often used.

In this work, we designed novel, cheap, highly efficient organocatalysts for the synthesis of α-alkylidene cyclic carbonates from CO$_2$ and alkynols. Several organocatalysts, based on ammonium cations and basic anions were screened, and kinetic studies were performed by Raman spectroscopy to identify the best anion/cation couple. We further optimized our catalytic system by developing cooperative catalysts providing conditions for the selective formation of α-alkylidene cyclic carbonates and oxoalkylcarbarnates under mild experimental conditions and short reaction times at low catalyst loading.

Scheme 1: synthesis of alkylidene cyclic carbonates from alkynols and CO$_2$ and their conversion into oxoalkyl carbonates

Oral Communication Abstract 35
Shoubhik Das

CO₂-Catalysed Oxidation and Dehydrogenation Reactions: Its Transition Metal-Free

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Carbon dioxide is a cheap, non-toxic, abundant chemical and has been widely utilized in organic syntheses. Many new strategies have been developed using CO₂ as a C1 building block. On the other hand, CO₂-catalysed or promoted reactions can also be important from the environmental point of view. These reactions avoid toxic chemicals, expensive catalysts and often occur under mild reaction conditions. Based on this, we have developed for the first time CO₂-catalysed transition metal-free catalytic oxidations of primary and secondary alcohols to the corresponding carbonyl compounds.1 This oxidation system operated under mild conditions, at atmospheric pressure, and replaced all the toxic reagents such as oxalyl chlorides, DCC etc. known for transition metal-free oxidation reactions such as in the Swern, Pfitzner-Moffatt type oxidation reactions. In fact, direct syntheses of anti-cancer drugs have also been achieved in g-scale using this protocol. Functional groups such as nitrile, nitro, aldehyde, ester, halogen, alkene, alkyne, ether, thioether, etc. have been tolerated in this oxidation reactions which clearly explained its high synthetic potential in natural products and pharmaceutical drug molecule syntheses. Additionally, we have developed dehydrogenation reactions of amines using the same principle under visible-light conditions.2 This reaction later have been applied for the synthesis of drug molecules. Detailed mechanistic studies revealed the role of CO₂ in these reactions.

References
Oral Communication Abstract 36
Francesca Milocco

Bifunctional Anionic Iron(II) Catalysts for the Conversion of CO$_2$ into Cyclic Carbonates

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From a sustainable perspective, using CO$_2$ as a feedstock for value-added chemicals is a key challenge, which is not trivial due to the high kinetic and thermodynamic stability of this molecule. The latter issue can be overcome by combining CO$_2$ with high free energy compounds, such as epoxides, which leads to either polycarbonates (PCs) or cyclic carbonates (CCs). Here, we present the first example of homogeneous formazanate iron catalysts for CO$_2$ conversion. The monoformazanate ferrate(II) dihalides, [LFeX$_2$]$^-$, are active catalysts for the reaction between CO$_2$ and epoxides to yield CCs under solvent-free conditions (Figure 1). While most catalyst systems reported to date require an additional nucleophilic co-catalyst (e.g., ammonium halides) to initiate epoxide ring-opening, the system reported here can act as bifunctional catalyst because it contains a labile halide (X$^-$), allowing catalytic reactivity also in the absence of a co-catalyst. A range of terminal and internal epoxides were selectively converted into CCs in the absence of added nucleophile, even in the case of cyclohexane-type substrates that are prone to polymerization.

![Figure 1. Catalytic conversion of CO$_2$ by ferrate(II) dihalide complexes.](image)

References

Facing the current environmental and energy issues, the activation of small molecules such as water, oxygen and carbon dioxide represents a main research challenge. In particular, the utilization of solar energy combined to catalysts made of abundant and non-toxic materials to generate energy vectors such as hydrogen, methanol or methane, is a strategic, even at long term, objective.

To efficiently convert sunlight into electrons and then into chemical energy stored in molecular bonds, either by electrochemical or photochemical ways, chemical processes require a selective and robust catalysis with desired properties, which necessitates the intimate understanding at the molecular scale.

In this presentation, I will give an overview of both fundamental and applied studies recently developed at LEM on the use of molecular homogeneous catalysts based on fourth-period transition metals (Fe, Co, Ni), and in particular iron porphyrins,\textsuperscript{1,2} in mild conditions including in aqueous environments,\textsuperscript{3,4} to efficiently use solar light to catalyze the photochemically induced reduction of CO\textsubscript{2} into CO\textsubscript{2}, and beyond.\textsuperscript{5,6}

References

Oral Communication Abstract 38
David Pascual

Light-Driven Competitive Reduction of Aromatic Ketones vs Aromatic Olefins in Aqueous Media

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A prerequisite for a sustainable society is to develop new efficient, cheap and greener synthetic methods. The use of sun light as a source of energy is one of the most sustainable approaches.1 Herein we present a catalytic system based on earth abundant-elements that selectively reduces aryl ketones in front of aryl olefins, using visible light as driving-force and H2O/amine as source of hydride. The catalytic system involves a robust and well-defined Co complex with an aminopyridine ligand2 and a Cu photoredox catalyst.3

Based on our mechanistic understanding, we envisioned that selectivity in the reduction of aromatic ketones versus aromatic olefins could be predictably tuned upon optimization of the catalytic conditions (scheme). Therefore, other photosensitizers and conditions were evaluated, reaching to a dual Co/Ir system capable of reducing all the aryl ketone with 100% selectivity before reacting with the aryl olefin. We envision that further optimization can lead to the inverse selectivity.

References
Remote sp³ C-H Carboxylation Enabled by the Merger of Nickel and Photoredox Catalysis

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Owing to its abundance, lack of toxicity and synthetic potential as renewable chemical feedstock, carbon dioxide has recently been employed in catalytic endeavors as a means to access carboxylic acids, privileged motifs in a myriad of pharmaceuticals, cosmetics, agrochemicals or polymers, among others.[1] In recent years, our group has shown a variety of metal-catalyzed reductive carboxylation protocols of organic matter with CO₂; despite the advances realized, however, these methods typically remain confined to the utilization of stoichiometric amounts of metal reductants, thus reinforcing a change in strategy.[1]

Promoted by the propensity of photoredox catalysis to trigger less-invasive outer-sphere single electron-transfer, it comes as no surprise that visible light photoredox catalysis has been employed within the context of carboxylation reactions.[2,3] However, all these protocols require prefunctionalization at the targeted reaction site. Herein, we outline a site-selective carboxylation of alkyl halides that occur at remote and previously unfunctionalized sp³ C-H reaction sites. This transformation occurs by the merger of nickel and photoredox catalysis and by a fine-tuning of the ligand backbone, allowing to promote the carboxylation event at either benzylic or less-activated remote primary sp³ C-H sites (Figure 1).[4]

Figure 1. Site-selective carboxylation of alkyl halides with CO₂.

References
Replacing fossil fuels with renewable energy sources is one of the most promising research fields that can provide a solution towards solving the global energy crisis. Although today’s technology has achieved progress in producing electricity using solar, tidal, and hydroelectric power sources, these intermittent sources will find limited applications without proper energy storage. One means of storing solar energy is through chemical energy conversion via fuel forming reactions inspired by natural photosynthesis.

Although active synthetic efforts have been invested in developing efficient water splitting complexes, the majority of the reported work is based on noble metals which demonstrate instability over long periods of time. Moreover, there is no clear understanding between their performance to their structures and ligand geometries. In this context, time-resolved X-ray absorption and emission spectroscopy are powerful tools for visualizing the “real-time” electronic and geometric changes involved in a photocatalytic system. This talk will demonstrate the reaction pathways of novel earth-abundant copper\(^1\), nickel\(^2\), and iron-based water splitting catalysts, examined in unprecedented detail with picosecond time resolution all the way towards the hydrogen and oxygen evolution reaction. Results shown will enable rational designs of molecular catalysts that can perform beyond the current microsecond time scale, and suggest ways in which the ligand structures can be adjusted to facilitate protonation and catalytic efficiency.

References

Molecular hydrogen is a promising candidate for replacing fossil fuels as energy sources. However, its renewable and clean generation is still a great challenge. A particularly attractive solution is the production of this gas from water splitting (WS) by sunlight. However, the practical development of this technology is still hampered by the lack of efficient and durable catalysts able to speed up the two redox half-reactions involved, namely oxygen evolution and hydrogen evolution reactions (OER and HER, respectively). Both molecular and metal/metal-oxide species are plausible candidates for efficiently catalyze these processes. If durability is the main challenge for molecular HER/OER catalysts, slow reaction rates are common when their heterogeneous or colloidal counterparts are employed. The lack of both mechanistic and surface chemistry information prevents the rational development of faster nanomaterials for these transformations.

This contribution deals with the work carried out in our laboratories to unravel the key factors able to change this last general trend by means of tunable molecular-material hybrid nanocatalysts (see Figure 1 for an example HER).

![Figure 1. RuPP NPs (PP is 4-phenylpyridine) as HER electrocatalysts](image)

This strategy allowed obtaining stable and efficient OER photocatalysts based on 1s-row transition metal oxide species and fast and rugged Ru-based cathodes that are competitive or even superior to the state-of-the-art Pt/C for the HER (Figure 1).

References

Oral Communication Abstract 42
Víctor Sans

Efficient Base-Free Selective CO₂ Hydrogenation with Multifunctional Ionic Liquids

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Formic acid (FA) is a primary product of the chemical industry with a production capacity of 600,000 tons per year and a projected annual increase of 22%. Currently the synthesis consists of multiple steps, e.g. methanol carbonylation followed by hydrolysis of the formate ester. Alternatively, formic acid could be directly generated from the one-step hydrogenation of CO₂, thus avoiding resource intensive purification steps. This would also represent an environmentally benign method, so long as the hydrogen is generated from renewable sources. Unfortunately, this reaction is highly challenging as CO₂ is inherently thermodynamically stable and kinetically inert. Here, we describe our recent efforts in developing sustainable routes to synthesise formic acid in the absence of bases, thus enabling subsequent syntheses (e.g. formaldehyde, MeOH) and the reversible use of formic acid as a hydrogen storage vector. This work is based on our current research showing that the use of basic ionic liquids can not only kinetically accelerate the reaction by forming intermediate carbonate species, but also shift the equilibrium, avoiding the formation of formate adducts and protecting the catalyst from deactivation by buffering of the reaction media. This enables us to use a simple and commercially available Ru cluster [Ru₃(CO)₁₂] as a catalyst. Furthermore, we show that formic acid can be easily separated when using an immobilised IL and that the reaction proceeds even when under just 6 bar total pressure. An in-depth study of the catalytic reaction cycle enables the design of the next generation base-free CO₂ hydrogenation catalysts.

References
Electrocatalytic Oxygen Evolution in Neutral Water by a Bioinspired Manganese-Oxo Cluster

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The complexity and energy demand of the H₂O oxidation half-reaction represents the bottleneck for the development of sustainable, environmentally-friendly H₂ economies using H₂O as energy feedstock.¹ In Nature, photosynthetic H₂O oxidation processes occur in photosystem-II (PS-II) and are facilitated by the Oxygen Evolving Complex (OEC), a manganese-oxo cluster {Mn₆CaO₅} with cubane-like topology.² In addition to its unique structural and electronic characteristics, one of the pivotal features of this complex is associated with self-healing processes that re-constitute the structure every 30 minutes avoiding deactivation under the harsh, prevailing oxidative conditions.³ In recent years, the use of manganese-based H₂O oxidation catalysts has attracted significant scientific attention, not only to mimic and understand the naturally occurring processes, but also due to the low toxicity and high abundance of Mn in the Earth’s crust. However, Mn-oxo clusters typically suffer from stability issues under the harsh working conditions, resulting in either the in-situ formation of active, heterogeneous manganese oxides (MnOₓ), or fast catalytic decay due to catalyst deactivation.⁴ Therefore, the correct catalyst assignment is not trivial, and strict speciation protocols are required to identify the O₂ evolving species.

Here we report the electrocatalytic water oxidation activity at neutral pH of a bio-inspired, high-nuclearity Mn-oxo cluster containing non-innocent redox active ligands (Figure 1). This Mn-oxo cluster electrocatalyst achieves satisfactory current densities at low overpotentials meeting the benchmarking values required for the use of photoanodes for direct ‘solar-to-fuel’ technologies.⁵

Figure 1: Bio-inspired Mn-oxo cluster catalytically active towards the water oxidation reaction.

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Oral Communication Abstract 44
Haifeng Shi

Fabrication of 2D g-C₃N₄ based photocatalyst for efficient photocatalytic degradation and CO₂ reduction

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As a typical two-dimensional semiconductor photocatalyst, graphitic-phase carbon nitride (g-C₃N₄) has been extensively studied in photocatalytic hydrogen evolution, environmental remediation, CO₂ reduction as well as N₂ fixation over the last few years. However, single g-C₃N₄ cannot satisfy the practical requirements, the layer structure and the suitable band structure of g-C₃N₄ can hybridize with other semiconductors effectively and serve as a promising supporting material. Recently, our researches show that designing g-C₃N₄-based catalysts have a great potential in enhancing the photocatalytic activities since the constructed heterojunctions and unique nanostructures of g-C₃N₄-based composites can effectively promote the separation of photo-induced electron-hole pairs and enlarge the absorption range of visible light. In recent years, we have successfully fabricated g-C₃N₄-based composite photocatalysts including g-C₃N₄/NaNbO₃, g-C₃N₄/AgVO₃, g-C₃N₄/KNbO₃, 2D/2D g-C₃N₄/Au/Bi₂WO₆, 2D/2D g-C₃N₄/BiVO₄, which have good performances in the efficient photocatalytic activities, especially in organic pollutants degradation and CO₂ conversion. These g-C₃N₄-based composites remarkably improved the interfacial charge transfer efficiency, promoted the separation of charge carriers, and effectively suppressed the photo-excited electron-hole pairs, enhancing the photocatalytic performance. For instance, the photocatalytic activity of the g-C₃N₄/NaNbO₃ heterojunction for the CO₂ reduction was almost 8 times higher than that of individual g-C₃N₄ under visible light irradiation (fig. 1). Such a remarkable enhancement of photocatalytic activity was mainly attributed to the improved separation and transfer of photogenerated electron-hole pairs at the intimate interface of g-C₃N₄/NaNbO₃ heterojunctions. In summary, the suitable construction of g-C₃N₄-based photocatalysts will provide an insight into interface design of hybrid photocatalysts and offer new strategies for exploring new type advanced catalyst design towards photocatalytic field.

Fig. 1. the CH₄ evolution rates over Pt loaded NaNbO₃, g-C₃N₄, and g-C₃N₄/NaNbO₃ composite photocatalysts and the BET surface areas.
References

Oral Communication Abstract 45
Dandan Gao

Modular Design of Noble Metal-Free Mixed Metal Oxide Electrocatalysts for Complete Water Splitting

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Transition-metal oxides, especially nickel, copper and cobalt oxides, are widely believed to be potential candidates for robust water splitting electrocatalysts as they are valence-tunable, earth-abundant, cost-efficient and stock-available.\cite{1,2} The anchoring of these catalysts to electrode surfaces is a key challenge to enable long-term stable water splitting performance.\cite{3} Here, we explore the in-situ growth of bifunctional electrocatalysts with outstanding electrocatalytic activity in the full water splitting reaction. The materials reported show high electrical conductivity, chemical tunability, nanostructured morphologies together with excellent long-term stability.

Recently, metal foam electrodes have received wide attention as high surface area supports for electrochemically active materials.\cite{3,4,5} Here, we explore how macroporous Cu foam can be used as a 3D framework for the in-situ growth and anchoring of cobalt tungsten oxide catalyst. Deposition of catalyst nanowires on the Cu electrode is achieved using the hydrothermal deposition of a molecular metal oxide precursor on the electrode surface. Electrocatalytic studies show that the material obtained is a high-performance catalyst for the hydrogen evolution as well as the water oxidation reaction. In consequence, an electrochemical water splitting cell was designed using the identical catalyst composite for both anode and cathode. Initial mechanistic insights, electrochemical performance analyses and stability studies are reported and an initial growth model for the formation of the high-surface area nanowires is described.

References:
POSTERS
ABSTRACTS
Cyrene® as a Novel Green Solvent for the Preparation of Coating and Filtration Membranes

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The Green Chemistry Centre of Excellence, York has developed in conjunction with Circa Group, a new bio-based polar aprotic solvent from cellulose waste. Cyrene can be used as a safer alternative to traditional polar aprotic solvents such as NMP and DMF, which are currently under pressure worldwide due to their toxicity and following dozens of accidental deaths. Cyrene® has received ECHA level 7 certification and is currently being scaled up towards commercial scale production.

Applications of Cyrene include graffiti removal and the production of poly (amide-imide) resins (PAI), showcased in a Patent from Huntsmann. Nowadays, graffiti is removed with cleaning products, solvents and even lasers, which can be very expensive, followed by hot water pressure washer and/or mechanical abrasion.

In this presentation we will review:

- Dissolution of acrylic and nitrocellulose graffiti in different solvents, including Cyrene®
- Cyrene applied to PAI resins, providing a more solvent resistant coating, more flexible and abrasion resistant than the one where the traditional NMP was used.
- The use of Hansen Solubility Parameters to predict Cyrene’s ability to dissolve polymers

References
Poster Abstract 2

Mª Angeles Corcuera

Synthesis and characterization of biopolyurethanes from biomass derived precursors

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Biomass, as a kind of environmentally friendly, renewable and abundant source, represents a promising alternative for obtaining precursors for the synthesis of polymers, and among them, for the synthesis of polyurethanes. Between the biomass sources, lignocellulosic biomass (cellulose, hemicellulose and lignin) is considered an ideal source of organic building blocks. Polyurethanes are polymers constituted of two blocks, one composed by a macrodiol and the other by an isocyanate and a chain extender, which usually is a low molecular weight diol. The main objective of this work was to synthesize polyurethanes using biomass derived precursors (1). Isosorbide (IS) (2) derived from cellulose was used for the synthesis of bis(6,6-isocyanatohexane) carbamate) (IS-HDI), used as diisocyanate, and 2,3-butanediol (BDO), obtained by fermentation of glucose, as chain extender. Poly(ε-caprolactone)diol (PCL), which is a biodegradable polymer, was used as macrodiol. The synthesis was carried out by a two step polymerization procedure without catalyst and using anhydrous N,N-dimethylformamide (DMF) as solvent. Polyurethane films were prepared by casting the polyurethane solutions on leveled Teflon molds and removing the solvent in a vacuum oven at 100 °C at 900, 600 and 200 mbar during 48, 24 and 24 h, respectively. The molar ratio of biobased presursors was varied in order to analyze its effect on the polyurethane final properties. The synthesized polyurethanes were characterized by means of Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis and mechanical tests. It was seen that biobased polyurethanes presented competitive properties with those synthesized with precursors derived from fossil sources.

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References

Gold nanoparticles (AuNPs) have been found as active, selective and recyclable heterogeneous catalyst in a wide range of organic reactions. Hydroamination of alkynes is a 100% atom-economical efficient process which allows the direct formation of new carbon-nitrogen bonds; this reaction needs to be efficiently catalysed in order to overcome the high activation barrier due to the repulsion between the nitrogen lone pair and alkyne π-orbitals. Homogeneous gold catalysts based on (Ph3P)Au(I)X (X= Me, Cl) were reported as effective in the one pot hydroamination of alkynes/asymmetric transfer hydrogenation of 2-(2-propynyl) anilines into tetrahydroquinolines, giving the desired products in high yields (87-99%) and good enantioselectivity (82-99%) in 16h in the presence of chiral Brønsted acid and Hantzsch ester.

We found that e.g. the intramolecular hydroamination of 1 (Scheme 1) catalysed by AuNPs followed by asymmetric transfer hydrogenation gives 2 in 3h with good yields, regioselectivity and high enantioselectivity. The catalyst is recyclable and active in green solvents.

The performances of the homogeneous and heterogeneous gold catalysts have been compared and discussed.

References
Real-time Fluorescence Imaging of Heterogeneously Catalyzed Suzuki-Miyaura Reaction

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Among C-C cross-couplings the Suzuki-Miyaura palladium-catalyzed reaction is among the most important ones, yet, the heterogeneous version of this reaction remains poorly understood, in particular the role and necessity of including a base in the reaction mixture. Today’s single molecule spectroscopy techniques allow an unprecedented level of understanding of intimate reaction details, in particular, in the case of heterogeneous catalysis involving nanometric catalysts. Our work involves a Pd-catalyzed Suzuki coupling leading to a highly fluorescent BODIPY dye (Scheme 1) and combines bench scale reactions, single molecule spectroscopy and plane-wave DFT calculations, and demonstrates that the C-C coupling is a truly heterogeneous process, with on-times ($t_{on}$) of 0.47 ± 0.02 s in the presence of K$_2$CO$_3$ and 1.28 ± 0.27 s in the absence of base. From this we have been able to establish for the first time that the base plays a crucial role in assisting product departure from the catalytic site, thus enabling the next reaction cycle. Our experimental results are corroborated by DFT calculations predicting that even a single molecule of base can increase the electron density on [111] facet of Pd nanoparticle, thus reducing the affinity between the metal surface and the product.

References

Poster Abstract 5
Fabio Salafia

Apocarotenoids Characterization in Human Blood Samples by Using online Supercritical Fluid Extraction-Supercritical Fluid Chromatography-Tandem Mass Spectrometry

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Apocarotenoids are cleavage products of C40 isoprenoid pigments, named carotenoids, synthesized exclusively by plants and microorganisms. Apocarotenoids are generated upon enzymatic and nonenzymatic cleavage of the parent compounds both in plants and in the tissues of mammals that have ingested carotenoid-containing foods. In addition to the well-known biological actions of vitamin A, it is becoming apparent that nonretinoid apocarotenoids also have the potential to regulate a broad spectrum of critical cellular functions, thus influencing mammalian health. Relatively few studies are available in the literature on the apocarotenoids detection in human blood samples, and those available studies were focused on the apocarotenoids detection in either serum, plasma or red blood cell, mainly by liquid chromatographic approaches. The detection of compounds present in very low amounts like the carotenoids and apocarotenoids in human blood samples, that could be used as biomarkers in large clinical or epidemiological studies, needs the development of very sensitive methodologies; therefore, the development of an analytical platform like the SFE-SFC-QqQ/MS one, could be considered as a rapid and sensitive single evaluation tool for a reliable qualitative profiling of carotenoids and apocarotenoids in human blood samples and also in other biological fluids. With these aims we have developed an automated online SFE-SFC-APCI(\pm)/QqQ/MS methodology that has shown to be a very powerful analytical tool for a possible rapid screening of potentially bioactive molecules in human blood samples. In this study we report on the detection and quantification of $\beta$-Apo-8'-carotenal, $\beta$-citrurin and Apo-8'-lycopenalin in human blood, using calibration curves obtained with multiple reaction monitoring (MRM). Analyzes were carried out on intact blood samples, immediately after collection, without any preliminary treatment, extraction and chromatographic separation were carried out with supercritical CO\textsubscript{2} and MeOH as modifier, and the overall analysis time was 25 minutes.
The Effect of using different acids to catalyse the prehydrolysis stage on the organosolv delignification of beech wood in two-stage process.

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Biorefineries produce chemical and fuels in a sustainable and renewable way from lignocellulosic biomass. The feedstock has to be fractionated into its main components; lignin, cellulose and hemicellulose before any further treatments or processes. In spite of the high efficiency of currently used pulping processes, like sulphide and kraft, they have many drawbacks like releasing sulphide containing compounds and other volatile sulphur compounds, which cause the stinky air emissions. Compared with the sulphide and kraft processes, organosolv pulping can be understood as an environmentally friendly and low cost chemical process for the fractionation of lignocellulosic biomass; in which delignification is achieved, using organic solvents (generally ethanol) mixed with water with or without using catalysts. Hemicellulose degradation may occur during the organosolv process, because organosolv process operates at higher temperatures (130 - 200˚C). For this reason, pretreatment methods prior to organosolv, like prehydrolysis and autohydrolysis is suggested. Prehydrolysis followed by organosolv delignification is a promising and low energy consumption process. In the current work, the effect of using different acids to reinforce prehydrolysis process is studied. Prehydrolysis of beech wood chips conducted at 175˚C in a 1L rotating autoclave. In the experiments, water free of catalysts or acidic conditions like 0.2% H2SO4, 0.2% H3PO4 and 2% oxalic acid were applied. The sequential organosolv process was conducted at mild conditions (155˚C, 1% H2SO4 for 160min). The main result is that using acids to catalyse the prehydrolysis has a negative effect on the delignification of beech wood. The yield of lignin decreased compared to a single organosolv process and uncatenlased prehydrolysis followed by organosolv process. In addition, the catalysed prehydrolysis stage succeed in hemicellulose removal with the formation of very low amounts of degradation compounds. On the other hand, the extracted lignin has a high purity compared with lignin extracted from a single organosolv process or uncatalysed prehydrolysis followed by organosolv process. The lignin has a low molecular weight, low carbohydrate content and includes low amounts of degradation compounds.
Figure 1: General schematic for the two-stage fractionation process that followed in this study.

References

B-PLAS DEMO Project: Using Biodiesel and Lipophilic Amines as Liquid Membrane for Volatile Fatty Acids Pertraction

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B-PLAS DEMO project (funded by EIT-climate KIC) aims at exploiting the chemical potential of wastewater treatment (WWT) sludge for producing polyhydroxyalkanoates (PHAs). B-PLAS DEMO project approach the issue by applying an initial hydrothermal carbonization (HTC) of WWT sludge, followed by a sequence of biochemical processes: i) acidogenic fermentation of HTC products for volatile fatty acids (VFA) production, ii) pertraction of VFA, and iii) aerobic conversion of VFA into polyhydroxyalkanoates (PHAs) through microbial mixed cultures. Therefore, VFA pertraction from anaerobic diluted fermentation broths to a slightly alkaline aerobic medium becomes a crucial step to develop a closed loop concept in which VFAs are used for PHAs production. New liquid membranes (LMs) based on lipophilic amines and biodiesel/biodiesel mixtures were proposed for this purpose. The performance of each LM was tested through a VFA distribution coefficient test and pertraction kinetic experiments. The transfer of VFAs from LM to receiving solution was the main limiting step of the process and the best LM was the one with 10wt% of trioctylamine. The biocompatibility of developed LM towards anaerobic bacteria was confirmed through a 15-d acidogenic fermentation test. Trioctylamine-biodiesel LM was finally tested in a specifically-designed module for achieving continuous VFA pertraction (Figure 1), from acidogenic broth, coming from HTC fermentation, to aerobic bacteria for PHAs production.

![Figure 1. Schematic representation of the pertractor system](image)

References:

SET-LRP of Bio- and Petroleum-Sourced Methacrylates in Aqueous Alcoholic Mixtures

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Single electron transfer-living radical polymerization (SET-LRP) represents a robust and efficient radical polymerization methodology to access to a large variety of materials and complex macromolecular architectures. SET-LRP mechanism and fundamentals are well established.\textsuperscript{[1]} Briefly, the initiation step is proposed to be mediated by a SET from the Cu(0) electron donor to the electron acceptor, usually an alkyl halide. The crucial step is the disproportionation of the in situ generated Cu(I)X into extremely active Cu(0) species and Cu(II)X\textsubscript{2}. This special type of redox reaction takes place only in the presence of polar solvents (e.g., water, DMSO, MeOH) and suitable \textit{N}-containing ligands (e.g., TREN, Me\textsubscript{6}-TREN) being the selection of the solvent a crucial decision. Recently our laboratory developed an approach coined “programmed” biphasic systems which is based in the use of organic solvent/water mixtures. This approach is sustained in the fast and almost quantitative disproportionation of Cu(I)X in water which makes secondary the role of organic solvent during the key disproportionation step and therefore allows the use of classically discriminated solvents (e.g., ACN, toluene…).

Herein, we report our efforts to expand the monomer scope for the “programmed” biphasic systems by targeting methacrylic monomers and polymers. Aqueous alcoholic mixtures were chosen as an environmentally friendly polymerization media in combination with the inexpensive and easy handle Cu(0) wire catalyst. Tris(2-dimethylaminomethyl)amine (Me\textsubscript{6}-TREN) as ligand and \textit{p}-toluenesulfonyl chloride (Ts-Cl) as initiator were used to deliver well-defined polymethacrylates from methyl methacrylate (MMA), butyl methacrylate (BMA) and other monomers derived from biomass feedstock (e.g., lactic acid, isosorbide, furfural, and lauric acid) (Scheme 1). The principle features for these systems such as the effect of water during the SET-LRP, reaction rate and control of the polymerization have been studied. Methacrylic polymers of different targeted molar mass as well as quasi-block AB copolymers by “in situ” chain extension at high conversion were obtained. The results obtained highlight the capabilities of SET-LRP to provide sustainable solutions based on renewable resources.
Scheme 1. Cu(0) wire/Me6-TREN-catalyzed SET-LRP of bio- and petroleum-sourced methacrylates in aqueous alcoholic mixtures initiated with p-toluenesulfonyl chloride (Ts-Cl). Color code: green refers to products that are derived from biomass and black refers to petroleum-sourced products.

References


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Poster Abstract 9

Andreu Ruiz de la Oliva

Development of an ECO-friendly PROTECTion for Aerospace Aluminium Parts

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The objective of the project is focused on the development of an eco-friendly chemical and electrochemical coating process of aluminium building parts for the aerospace industry. The goal of ECO-PROTECT, approved in the Eurostars competitive industrial call, is to develop and characterise Cr(VI)-free surface treatments to protect aluminium alloys used in the aerospace industry. The project aims to validate and improve the coatings (including the pre-treatment) that can replace the currently very toxic Cr(VI)-based surface treatments for protection of aerospace Al alloys (for example, Al2024).2,3 As a unique solution does not exist to cover different geometries and uses, considering the two following options: anaphoretic process for complex geometry parts and spray-based method for big parts. Both options should meet aerospace requirements, mainly for external building parts. Also, such eco-coating technology is aimed to expand its range of applications in catalysis and nanotechnology for the industrial sector.

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CO₂ Activation by HBD Organocatalysts Immobilized onto Supported Ionic Liquid-like Phases (SILLPs)

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Keywords: Organocatalyst ● Supported Ionic liquid ● CO₂ capture ● Continuous flow

The utilization of CO₂ as a building block for the synthesis of chemical products has the potential to fulfill many of the “Twelve Principles of Green Chemistry”. CO₂ is a renewable, inexpensive and abundant C1 feedstock, which is globally generated as a waste product. Finding efficient and durable catalysts for the activation and selective conversion of CO₂ is an important pursuit. The reaction between carbon dioxide and epoxides is an attractive pathway to provide added value products from CO₂ utilisation. The efficient activation of carbon dioxide by heterogeneous catalysts has been achieved through the design of organocatalysts with hydrogen bond donor capacity (HBD). Here, we present our efforts to fine tune the catalytic behaviour of HBD units immobilised onto supported ionic liquid-like Phases (SILLPs) by changing the cation substitution, the nature of anion, the loading of the IL-like units and the nature of the polymeric backbone used as support. The optimised catalyst provided high TON and TOF values even at atmospheric pressure.

Scheme 1. Flow system for the selective conversion of CO₂.

The properties of SILLPs have also allowed working under continuous flow conditions (scheme 1) implementing advanced catalytic platforms.

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Pollen: a Natural and Versatile Source of Reproducibles and Chemically Tunable Microcapsules.

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Pollen grains are 3D microstructures that can act as scaffolds or templates and can be exploited for applications in different fields including drug delivery [1]. To this aim, their structural component sporopollenin must be isolated. Recently, some of us reported a novel procedure for the separation of sporopollenin from the other pollen components, using room temperature ionic liquids (ILs) [2]. The resulting microcapsules can be functionalized taking advantage from the presence of several alcoholic groups on their surface [3]. Among the several possibilities an example is to use these structures to support chiral ionic liquids. Other functionalization protocols will be presented.

References
Poster Abstract 12
Ana Aguiar-Ricardo

**N-methyl-D-glucamine Functionalized Chitosan Beads and Membranes for Boron Removal from Water**

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Chitosan is a bio-based polysaccharide extensively used in a wide range of application fields, such as pharmaceutical devices, food industry and water treatment systems \cite{1,2}. N-methyl-D-glucamine (NMG) is a derivative of glucose possessing five hydroxyl groups that confer the molecule chelating properties and high affinity towards toxic elements such as boron. Therefore it is widely used in water treatment systems. However, commercial resins containing NMG moieties possess slow kinetics of sorption for boron \cite{3}. Chitosan functionalised with NMG devices were already synthesized but the procedure involved many steps and resulted expensive \cite{3,4}.

In this study, chitosan hydrogel beads were prepared using a co-axial air flow beads generator. Subsequently the beads were crosslinked and functionalized with NMG. Chitosan membranes were prepared using \textit{scCO}_2-assisted phase inversion process \cite{5}, followed by NMG functionalization. The sorption performance of the beads and membranes was evaluated by static and dynamic sorption tests which have shown the high potential of using these materials in the removal of boron from aqueous model solutions.

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Supramolecular coordination complexes attract increasing attention due to their ability to build more complex structures taking into account shapes, sizes and cavities for future applications in catalysis and molecular recognition. The presence of the pyrene in this complex molecules significantly enhance binding abilities through π-π stacking and by forming excimer upon excitation may also give information about energy transport within complex molecule scaffolds. Taking into account discussed above we introduce a new approach as a multipart ligand design to control the reactivity and enantioselectivity in light-driven H–E umpolung catalytic reactions developed recently in our group with Co(II). The control of enantioselectivity could be achieved by the use of the second coordination sphere of the catalyst and its attaching on polycarbon surface such as nanotubes or gráfe. For this purpose, the multipart ligand in addition to the metal-coordination side should possess a spacer part and polycromatic moiety to interact with polycromatic carbons through π-π stacking. With this idea in mind we developed a new synthetic route that allowed us to combine all three relevant parts of a new multipart ligand in only 5 steps. These ligands have been fully characterized in solution and solid state by polynuclear NMR spectroscopy, mass spectrometry and photophysical studies. We observed the appearance of a new band at 480 nm in the emission spectrum, that indicates the aggregation of pyrene units. In addition 4 new cobalt (II) complexes have been synthetized and the structure of one of them has been established by X-ray analysis. The initial tests of the catalytic activity of new complexes for hydrogen evolution gave promising results.

References
Poster Abstract 14
Rongji Liu

Atomically Dispersed Mo-Oxides for the Electrocatalytic Oxygen Reduction Reaction

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The near-atomic dispersion of noble-metal-free catalyst particles on electrode surfaces allows maximum exposure of catalytic sites and has led to breakthroughs in electrochemical energy conversion and storage. Here, we report a novel redox-cycling process which enables the facile, scalable fabrication of sub-nanometer metal oxide clusters on high surface-area mesoporous carbon. In the first step, the Bronsted-acidic polyoxometalate [H$_3$PMo$_{12}$O$_{40}$] ($= \{\text{PMo}_{12}\}$) catalyses the carbonization of organic precursors and is simultaneously reduced to give crystalline MoO$_2$ particles deposited on a mesoporous carbon matrix. Subsequent re-oxidation of the composite leads to a redox-driven fragmentation of the MoO$_2$ particles into single Mo(VI) sites (~ 38 %) and sub-nanometer (MoO)$_n$ clusters (~62 %, n = 2-20). The resulting metal oxide / carbon composite catalyst shows outstanding, stable catalytic performance for the electrochemical oxygen reduction reaction with catalyst characteristics superior to commercial Pt/C. The study demonstrates how noble-metal electrocatalysts could in future be replaced by earth-abundant composites accessible by a straight-forward fabrication route starting with tunable molecular precursors.

References
Effect of Ni NP morphology on catalyst performance in non-thermal plasma-promoted dry reforming of methane

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In an age of fossil fuel shortage and climate change crisis the issues of reducing and recycling greenhouse gases, and the production of economically viable synthetic fuels are both of huge importance. Dry reforming of methane (DRM) is a well known process, first reported in 1928 by Fischer and Tropsch [1]. The conversion of CO₂ and CH₄ into synthesis gas (CO + H₂) not only allows greenhouse gas utilisation but produces a valuable feedstock for the synthesis of liquid fuels and chemicals. Presently the process is energy intensive, requiring temperatures of up to 1000 °C, typically over critical noble metal catalysts [2]. The use of non-thermal plasma not only lowers the energy requirement of the reaction but also allows high efficiency conversion.

In this work a range of Al₂O₃ supported Ni catalysts with differing nanoparticle morphology and metal loadings were synthesised via hydrothermal and wet impregnation methods. The materials were characterised using XRD, SEM/EDX, TEM and FTIR, UV-Vis and Raman spectroscopies. Their catalytic activity was then analysed in the dry reforming of methane (DRM) reaction within a non-thermal plasma. Post-reaction characterisation of the materials (DFTIR, TGA/MS, SEM) was carried out to identify any changes to the materials.

The figure shows the typical transient conversion of CO₂ and CH₄ (and production of CO and H₂) following the application of a non-thermal plasma over a typical Ni/Al₂O₃ catalyst held under a DRM flow.

References

Assessing the Organic Fraction of Municipal Solid Waste as Carbon Source for Poly(3-hydroxybutyrate) Production

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In recent years not only has increased the plastics consume, but also the concern for its influence in the environment [1]. For that reason, the replacement of petroleum derived plastics with biodegradable plastics is gaining major attention. Within all types of bio-plastics, polyhydroxyalkanoates stand out from the rest for their good properties [2].

In this work the organic fraction of municipal solid waste (OFMSW) was studied for its potential as feedstock for the production of poly(3-hydroxybutyrate) (P(3HB)). To release the sugars, a diluted acid pre-treatment followed by an enzymatic hydrolysis was applied. A conversion of 49% was achieved using a pre-treated waste at a concentration of 135 g·L⁻¹ and an enzyme cocktail of Pentopan 500 BG and Celluclast BG with an enzyme load of 90 mg·g⁻¹ and 150 mg·g⁻¹, respectively. The addition of Glucoamylase NS 22035 (108 mg·g⁻¹) improved the hydrolysis rate. The sugar composition of the hydrolysate was (in g·L⁻¹): 21 glucose, 4 xylose and 0.6 arabinose. The hydrolysate was used as culture medium to produce P(3HB) by Burkholderia sacchari DSM 17165. Assays at shaking flask scale showed that the hydrolysate was an excellent substrate, but it was necessary to supplement it with extra glucose in order to increase the C/N ratio and thus achieve P(3HB) production. Also, to overcome the nutritional deficiencies of the hydrolysate, a mineral solution was added. Finally, the accumulation of P(3HB) was 58% (P(3HB))/g and the yield (YP/S) was 0.13 g/g.

In conclusion, the present study indicates that it is possible to produce P(3HB) from the OFMSW and, at the same time, alleviate the amount of waste in the environment.

References

New Covalent-Organic Frameworks Immobilized on Electrodes promotes the Electrocatalytic CO₂ Conversion

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Effective large-scale CO₂ conversion to fuels or value-added chemicals using renewable energies is critical to reduce our environmental impact [1]. To this end, better understanding of the CO₂ mechanism is needed to develop efficient and selective catalysts that operates in water. Covalent Organic Frameworks (COFs) are reticular materials, which can be used to combine the advantages of the well-defined molecular catalysts and the heterogeneous ones [2]. In this work, we present the first COF based on tricarbonyl Mn units, that by π-π stacking is attached to MWCNTs to form electrocatalytic electrodes active for CO₂ reduction in neutral water. The activity of this catalyst was evaluated by electrochemical techniques. With these materials we have integrated the classical Mn(bpy)CO₃Br catalyst into a heterogeneous material which clearly enhances its catalytic activity (FE~50%) at low overpotentials (~450 mV) in pure water. COF/MWCNTs/Nafion leads higher faradaic efficiency than molecular system and the encapsulation of tricarbonyl Mn active sites with a reticular covalent organic structure plays an important role by favouring the electrocatalytic CO₂ reduction over competitive H₂ evolution reaction. UV-vis and IR SEC were employed to obtain structural information on the catalytically relevant states of the immobilized COF with different solvents. The CO stretching vibrations, ν(CO), were monitored and the spectroelectrochemical studies evidence the formation of five-coordinate species in the catalytic cycle for CO formation.

References

Catalytic Aerobic Oxidation of Terpenes and Follow-up Chemistry towards Renewable Poly(hydroxyurethane)s

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The novel Mn-based mixed-linker metal-organic framework (MOF) MIXMIL-53-NH2(50)-Mal-Mn was successfully synthesized in a two-step post-synthetic modification reaction and investigated as catalytic material for the liquid-phase aerobic oxidation of α-pinene.1 Mn(III) acetate was furthermore used as homogeneous model catalyst. After investigating the influence of reaction time, solvent, temperature, oxidant flow rate and catalyst concentration on conversion, yield and selectivity for the model catalyst, optimized reaction conditions were transferred to the heterogeneous MOF-catalyst. The heterogeneous system showed very similar activity in a mixture of diethyl carbonate/dimethylformamide as solvent compared to the homogeneous catalyst, obtaining pinene oxide as main product along with small amounts of verbenol and verbenone. The heterogeneous MOF-catalyst was easily removed from the reaction mixture by filtration and could be reused for at least five catalytic cycles. Hot filtration tests showed that the catalysis mainly proceeds heterogeneously.

Figure 1 Catalytic oxidation of α-pinene by MIXMIL-53-NH2(50)-Mal-Mn resulting in pinene oxide, verbenone and verbenol.

Since the structure and reactivity of different terpenes is very specific, transferring the above presented oxidation method to other terpenes requires optimization of the reaction conditions. Oxidation of difunctional olefinic substrates like limonene, allows for the synthesis of diepoxides that can subsequently be used as monomers for renewable polymers. Limonene dioxide was further transformed into limonene dicarbonate by CO2 fixation.2 To utilize limonene dicarbonate (LC) for the synthesis of non-isocyanate polyurethanes, a second limonene-based diamine monomer was synthesized via thiol-ene addition of cysteamine hydrochloride to limonene.3 Catalyst- and solvent-free polymerization of LC and the amine-functionalized limonene monomer resulted in linear poly(hydroxy urethane) pre-polymers. By variation of the dicarbonate to diamine monomer ratio it was possible to obtain either telechelic carbonate or amine terminated pre-polymers as shown by NMR and FT-IR analyses. These pre-polymers can be further crosslinked to yield various NIPU thermosets.

References
A Series of Salen–Al/Triphenylamine Dyads: Systematic Controls of Intramolecular Energy Transfer

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Organometallic luminophores have drawn growing research interest regarding their capability to exhibit intriguing optical properties. Among them, triphenylamine (TPA)-based transition metal complexes have received much attention in the field of optoelectronics. The TPA molecule is an important building unit for both small-molecule and polymeric-optoelectronic materials because of their desirable electronic and charge-transport properties, as well as their high thermal stability. Recently, a number of π-extended conjugated systems based on transition metal complexes bearing TPA derivatives have been developed. In this manuscript, we first describes a series of Al/TPA-based dyads with intriguing optical properties via intramolecular energy transfer (IET) process. These dyads presented interesting dual-emission features via the IET from the TPA group to the salen–Al moiety in solution. Interestingly, such an IET feature was observed more clearly in the film state (5 wt% doped in poly(methyl methacrylate) (PMMA)) than in solution. Importantly, the IET process of the dyads was systematically tuned by varying of the substituents. The detailed synthetic procedures, characterization, and optical properties of these dyads in conjunction with theoretical calculations will be presented.

Figure 2

References
Rh-Catalysed Asymmetric Carbylonylation of 1,1-Disubstituted Olefins.

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The use of carbon monoxide as building block via metal catalyzed carbonylation processes has revealed an efficient tool for the functionalization of organic molecules; moreover, the atom-economy nature of this type of reactions has increased the interest for both academy and industry. For instance, the production of acetic acid through methanol carbonylation, and the production of aldehydes by hydroformylation of propene are the two main homogeneous processes currently applied in industry.

The enantioselective carbonylation of olefins is of particular interest since such processes can provide relevant compounds for the pharmaceutical sector since many drugs and molecules of biological importance contain a carbonyl group in close proximity to a chiral centre.

In this work, we report the rhodium catalysed asymmetric carbonylation of 1,1-disubstituted olefins employing a series of novel 1,3-phosphite-phosphoramidite ligands based on a sugar backbone. The products were prepared with high yields and excellent enantioselectivities (up to 99% ee) for a range of substrates. A mechanistic study using High-Pressure NMR is also described providing information on the coordination mode of the ligands at the Rh centre.

References
Pseudopeptidic Macrocyclic Compounds as Active Organocatalysts for CO\textsubscript{2} Conversion

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The concept of anthropogenic CO\textsubscript{2} capture, activation and conversion, in combination with other simple molecules, into added-value chemical products that can compensate for the energetic and economic costs of its capture is currently receiving increasing attention [1]. Hence, designing and developing efficient catalysts for the activation as well as selective conversion of CO\textsubscript{2} is an important current challenge among different research fields [2]. In this work, we present the highly selective synthesis of a pseudopeptidic macrocycle has been achieved. The main driving force of the macrocyclization is the optimal preorganization of the reagents, based on intramolecular non-covalent interactions and its applications in the former field.

Figure 1. General structure of the macrocyclic organocatalyst

Previous results show that some pseudopeptidic compounds can be used as minimalistic chiral enzymatic mimics to act as active, selective, and stable catalysts to activate and convert CO\textsubscript{2} into added-value materials under mild conditions [3]. The experiments presented here reveal that the new macrocyclic systems developed in our group can efficiently and selectively activate CO\textsubscript{2} to be converted in cyclic carbamates in the presence of the corresponding epoxide [4].

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Poster Abstract 22
Laura Mallón

Supported Cobalt-based Nanoparticles on Carbon Fibers as Water Splitting Catalysts

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The huge growth of world population during the last century\textsuperscript{1} and the accumulation of CO\textsubscript{2} in the atmosphere\textsuperscript{2} due to the increasing consumption of fossil fuels to fulfil the high energy demand have put forward the urgent need for a cheap, clean and carbon free energy source. One of the most attractive and feasible solutions to this challenge is the production of H\textsubscript{2} by sunlight photo-activated water splitting, mimicking green plants, algae and cyanobacteria, in a process called artificial photosynthesis.\textsuperscript{3} In this redox process, water is oxidized to dioxygen in the anode (Eq. A), constituting the source of electrons to reduce protons to dihydrogen in the cathode (Eq. B) (Scheme 1).

\begin{align}
\text{2H}_2\text{O} & \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad \text{(A)} \\
\text{2H}^+ + 2e^- & \rightarrow \text{H}_2 \quad \text{(B)}
\end{align}

Given their proved stability and high surface per volume ratio, nanoparticulate metal oxides are the chosen catalysts in this work. From an engineering point of view, supported catalysts that can act themselves as electrode materials are interesting systems. Therefore, the integration of metal-oxide electrocatalysts with conductive carbon-based supports such as graphene, carbon nanotubes (CNTs) or carbon fibers (CFs) is of current interest, being also a way to improve their typically low conductivity.

The synthesis of CoNPs onto CFs has been performed by two different methods based on the organometallic approaches: by the decomposition of an organometallic cobalt precursor under H\textsubscript{2} in the presence of a CFs brush (\textit{in-situ} method) or by impregnation of a CFs brush with pre-synthesized colloidal CoNPs (\textit{ex-situ} method). The obtained nanomaterials are characterized by complementary techniques including TEM, ICP-OES, XPS and electrochemical analyses.

\textbf{Scheme 1.} Schematic representation of an electrochemical cell for Water Splitting.

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Coordinative Alignment of an Organocatalyst in a Metal-Organic Framework for the Development of Visible-Light Photoredox Strategies

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Recently, the progress of cost-effective and less toxic organic dyes as photoredox catalysts has been encouraged in the catalysis field. However, these dyes are used as homogeneous catalysts that cannot be easily separated from the reaction mixture and recovered for further use. Therefore, to facilitate recovery/reuse of catalysts, new heterogeneous catalysts have been developed by immobilizing the homogeneous photocatalysts into solid-state materials including porous zeolites, polymers, and metal–organic frameworks (MOFs).

Herein we present the coordinative alignment of an organic photocatalyst, i.e., perylene-1-carboxylic acid (P) into MOF-520, named MOF-520-P. We can directly envision a well-defined arrangement of perylene molecules inside the crystal structure of MOF-520, enhancing the understanding of its photophysical properties. Using 1% loading of MOF-520-P as a noble and re-doxx active metal free organophotoredox catalyst, we perform the reductive dimerization of aromatic aldehydes and ketones under mild reaction conditions, with broad functional groups and stereoselectivity. Under light illumination with the MOF as heterogeneous catalyst, we carried out the chemical transformation in flow process for manufacturing large quantities of a product under steady-state conditions and less effort. This work provides a new approach for construction of precious metal free heterogeneous MOFs catalyst.

References
Valorization of Organic Hazardous Wastes via Pyrolysis

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The management of hazardous organic solid wastes has become one of the most crucial environmental problems in modern societies. Nowadays, incineration is one of the most applied methods [1], but there has been quite a controversy concerning its negative environmental aspects [2]. On the other hand, pyrolysis may offer a more sustainable solution. Within this context, the objective of this work was to study the pyrolysis of certain hazardous organic wastes, such as petroleum-based sludges and sediments, residual acrylic-based paints/topcoats left on used/scrap metal packaging and treated wood waste that has been impregnated with creosote, as preservative. The experiments were carried out on a fixed bed reactor, at 600°C, with N₂ flow of 100 cm³/min, with or without a catalyst. The obtained pyrolysis oils were analyzed by GC/MS and the identified compounds were categorized in different groups. Representative results (Figure 1) showed that the use of an acidic ZSM-5 zeolite catalyst induced increased concentration of mono-aromatics and PAHs (mostly naphthalenes), when compared to the composition of thermal pyrolysis oils. However, the pyrolysis oil yield was lower when ZSM-5 was employed, due to over-cracking effects, which led to increased gaseous product yields, including the high added value ethylene and propylene (data not shown).

Figure 1. Composition of the pyrolysis oils from waste paint and creosote treated wood, at 600°C (a) Thermal pyrolysis, (b) Catalytic pyrolysis with ZSM-5 (Si/Al=40); cat/waste = 1.

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We report for the first time the precise synthesis of polymers derived from alkyl lactate ester acrylates. Kinetic experiments were conducted to demonstrate that alcoholic Cu(0) wire-catalyzed single electron transfer-living radical polymerization (SET-LRP) provides a green methodology for the controlled polymerization of such forgotten class of bio-based monomers at 25 °C. The acrylic derivative of ethyl lactate (ELA) was polymerized with excellent control over molecular weight and molecular weight distribution ($M_w/M_n \approx 1.20$) (Figure 1a). However, aqueous ethyl lactate mixtures were found to be most suitable than pure ethyl lactate solvent to mediate a LRP process. Pushing the envelope of the ethanolic SET-LRP, we further investigated its potential in delivering well-defined poly(ethyl lactate acrylate) across a broad range of molecular weight. SET-LRP provided excellent control over molecular weight, polydispersity and chain end functionality (Figure 1b,c). These results establish the basis for the synthesis of a large diversity of more complex biobased polymer architectures based on alkyl lactate ester acrylates and other bio-based monomers. As a proof of concept, poly(ELA) soft blocks have been shown suitable for the preparation of block copolymers with phase-separated morphology using pinene-derived polyacrylate as model hard block. Indeed, a block copolymer of poly(ELA)-b-poly(glycerol acrylate) was shown to form micellar assemblies in water with chiral lactic acid-derived block forming micellar core as confirmed by pyrene-probe-based fluorescence technique. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) measurements revealed nanosize spherical morphology for these bio-based aggregates.
Figure 1. Cu(0)-catalyzed SET-LRP of ELA in EtOH initiated with ethyl α-bromoobutyrate (EBiB) in the presence of tris[2-(dimethylamino)ethyl]amine (Mes-TREN). (a) Monomer conversion, kinetics plots and evolution of experimental $M_n$ (GPC) and $M_w/M_n$ based on the calibration by PMMA standards, versus theoretical $M$(th), (b) GPC traces at various targeted degrees of polymerization and (c) representative MALDI-TOF analysis of low molecular weight poly(ELA).

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References
Poster Abstract 26
Giorgio Tofani

Study on the Hydrogen Peroxide Consumption in Paper Fibre Bleaching: Model Construction and Verification

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Paper industry is one of the main industrial activities in Europe. Moreover, paper recycling becomes more and more important to preserve forests. In Europe, around 57 million tons of paper were collected in 2017. In most cases, the paper waste needs to be bleached before it can be reused for e.g. magazines. At this moment, the applied technology consists of a single bleaching step with hydrogen peroxide. However, waste paper is a complex material, composed of different fibres with a diverse reactivity to the peroxide bleaching. The fibre types are chemical (wood pulped using chemicals such as sodium sulphide), mechanical (wood pulped using rotating discs at high temperature and/or pressures) and semi-mechanical (wood pulped using a combination of the previous processes). Moreover, the relative quantities of the fibres in waste paper are not constant in time. These problems make the industrial bleaching difficult as variable amounts of bleaching agents will be necessary to reach the same level of brightness influencing cost and process death time.

The target of this study is to evaluate the bleaching of pulp model mixtures composed of known fibre types. In the first part of the study, the same total peroxide amount was added to reference non-recycled fibre samples, but over a different number of additions, showing that small peroxide additions over a longer time are more effective than one big peroxide injection at the start (Figure 1). In the second part, the most effective bleaching sequence was applied on the models. The 100% chemical fibre samples showed the largest increase of brightness. Moreover, the presence of mechanical fibres reduces significantly the bleachability. The results of this study still need to be implemented on pilot-scale conditions. However, they will allow to design a better peroxide bleaching once the fibre composition of real life samples is known.

Figure 1: ISO brightness obtained after bleaching of Kraft (chemical fibres) fibres; P50 = hydrogen peroxide addition, 50% w/w on dry fibres, P10x5: hydrogen peroxide addition, 10% w/w on dry fibres for five times

References
Poster Abstract 27
Clarinda Costa

**Supercritical CO$_2$- Assisted Spray-Drying: A Greener and Sustainable Process Towards Lung Diseased Treatment**


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Lung diseases represent the third main cause of worldwide mortality. In 2017, the World Health Organization estimates that chronic obstructive pulmonary disease (COPD) affects over 65 million people [1]. Dry powder formulations are promising in the pharmaceutical landscape due to increased storage stability, minimize infection risk enabling an easier availability and higher patient compliance. However, the pharmacokinetic profile for inhaled agents may vary due to poor aqueous solubility of bioactive agent or specific physico-chemical properties of the formulations, posing delivery challenges [2]. Supercritical carbon dioxide (scCO$_2$) is a non-toxic, non-inflammable, with a mild critical temperature and is a cheap solvent. In that way, supercritical CO$_2$- assisted spray drying represents an alternative and sustainable process, where organic solvents are avoided, constituting a greener approach [3]. In this work, we applied the supercritical CO$_2$ to perform dry powder formulations for fusidic acid delivery. Fusidic acid is an antimicrobial agent with a bacteriostatic action in bacterial conjunctivitis, colitis, cystic fibrosis and respiratory infections [4]. However, fusidic acid has a low bioavailability as consequence of its low water solubility. So, here fusidic acid was conjugated to two different polymer (polyethylene glycol and polyoxazoline). In order to acquire suitable aerodynamic properties, those conjugated compounds were encapsulated in trehalose using the supercritical CO$_2$- assisted spray drying. The chemical, physical and antimicrobial characteristics of formulations were studied by diverse techniques as NMR, LC-MS, Karl-Fisher, FTIR-ATR, Andersen Cascade Impactor and Morphologi G3 and minimum inhibitory concentration (MIC) assays assays for Staphylococcus aureus.

**References**


**Acknowledgments**

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Readily Available Carbene/Phosphinite/Phosphite-Thioether Ligands for the Ir-Catalyzed Asymmetric Hydrogenation of Unfunctionalized Alkenes

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Asymmetric hydrogenation (AH) is a sustainable tool for preparing chiral compounds due its low catalyst loadings and perfect atom economy. Whereas ligands for AH of functionalized olefins are available, the AH of unfunctionalized olefins is less developed. 1 Ir-PHOX catalysts reported by Pfaltz, was a breakthrough in the catalyst design for the AH of unfunctionalized olefins. 1 Since then, several modifications in the ligand structure have been developed. 1 Recently, N-heterocyclic carbenes (NHCs) have emerged as powerful ligands for catalysis. Owing to their strong σ donor ability and air stability NHCs have been considered as practical alternatives to the most used phosphines. In 2001, Burgess et al. reported carbene-oxazoline ligands for AH of unfunctionalized olefins with enantioselectivities up to 98%. 2 Since then, a few more carbene-N ligands have been applied in this process but with less success. 2 To further explore the potential of carbene-based ligands in this process, we here present the synthesis of simple thioether-carbene ligands, that combines the advantages of thioether and carbene moieties. We also compare their effectiveness with their related thioether-phosphinite/phosphite.

References

A New Family of Tetradentated N-based Ni/Co Complexes for Visible-Light Photocatalytic Cleavage of Strong σ-Bonds

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Recent photoredox catalytic methodologies based on the visible-light-induced generation of highly reactive radicals have allowed the construction of a large variety of selective C-C and C-heteroatom bonds.1,2 The inertness of chloroalkanes has precluded them as prevailing coupling partners in both conventional and photocatalytic cross-coupling reactions.

We have achieved the activation of unactivated Csp3-Cl bonds by means of a dual metal catalytic system based on earth-abundant metals (Cu, Co/Ni) and using visible-light as a source of energy. This bimetallic system has been employed to develop sustainable intramolecular reductive cyclization reactions of chloroalkanes with tethered alkenes/alkynes.3

Herein we disclose the synthesis of a family of tetradentate N-based Co and Ni complexes. The electronic properties of the metal center are modulated by the introduction of several electron-withdrawing and electron-donor substituents at the β- and γ- positions of the pyridine framework. Moreover, we bring to light the catalytic activity of this family of complexes in the aforementioned reactions. The ultimate goal of this project is to obtain the structure/activity relationship and understand the intermediates in the catalytic cycle in order to develop highly robust and efficient metal catalysts for the cleavage of strong σ-bonds.

References

New Aluminum-based Catalysts for CO₂/Epoxide Coupling Reaction at Ambient Temperature and Pressure

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We have designed and synthesized aluminium-based catalysts capable of effectively coupling of carbon dioxide and epoxide at ambient temperature and atmospheric CO₂ pressure to afford cyclic carbonates. Logically designed dimeric aluminium compounds with heterocyclic pendant group attached to nitrogen of bidentate ligands were used as catalysts. Their catalytic activities were compared with those of aluminium complexes with N-functionalized pendants or with non-heterocyclic pendants. Among several aluminium-based complexes, aluminum complex with pyridine pendant group showed the best catalytic activity. In this poster presentation, we will look at the effect of substituents on the activity of the coupling reaction at ambient temperature and atmospheric CO₂ pressure. In addition, we will show the broad epoxide scope using new catalytic system.

Figure 1. Single crystal X-ray structure for dimeric aluminium complex with N-thiophenemethyl substituent.
Poster Abstract 31
Tamás Hergert

**Pyrroloindolones as a Versatile Building Block: A Synthetic Study and Application**

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Pyrroloindolones and their derivatives are important building blocks of biologically active substances. Conventional synthetic methods to produce these targets usually afford moderated yields, therefore close attention is still paid to the development of enhanced methods. The aim of our research was to develop effective and generally applicable strategies for the synthesis of pyrroloindolones, then utilize them to form organic dyes for dye-sensitized solar cell and as heterocyclic scaffolds for the synthesis of drugs (Figure 1).

![Diagram](image)

**Figure 1**

**References**

A Combined Use of Deep Eutectic Solvents (DESs) and Ionic Liquids (ILs) for the Valorization of Biomass Wastes

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Ionic liquids (ILs) and deep eutectic solvents (DESs) are considered promising alternative media for addressing the challenge of biomass waste valorization. In this study, biomass wastes from different sources (i.e. chestnut shells, olive pomace and apple pomace) have been investigated for the development of a sustainable process (Figure 1). This is based on two consecutive steps, namely the extraction of polyphenols (high added value compounds with antioxidant, anti-carcinogenic, anti-inflammatory and antibacterial activity) employing DESs, followed by the fractionation of the lignocellulosic residue exploiting ILs. The composition of the extracts, which was determined by HPLC analysis, changed by using different DESs. The nature of the cellulose- and lignin-enriched fractions was ascertained by infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA), while the micromorphology was investigated by scanning electron microscopy (SEM).

Figure 1. Schematic biomass waste valorization process.

References
Poster Abstract 33
Joan Saltó

**DFT-Guided Synthesis of a Readily Available Family of P,S-Ligands for Pd-Allylic Asymmetric Substitution**

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Allylic substitution is a valuable tool for organic synthetic chemistry. Nevertheless, most of the reported studies have shown low reaction rates, high substrate specificity and a really short nucleophile scope. To overcome those limitations, the introduction of ligands containing a phosphite-biaryl moiety have shown to be advantageous.

On the field of allylic substitution, P-thioether ligands use have been dismissed since high enantioselectivities have been achieved only by using the standard substrates.

We here give a new push to the potential of P-thioether ligands for this process. The P-S ligand library was synthesized in three steps from inexpensive indene (Figure 1). DFT calculations allowed the optimization of the ligand parameters. We were able to apply them to a wide range of C-, N- and O-nucleophiles (up to 40 compounds) with a very high enantioselectivities. The results were maintained using the propylene carbonate as green solvent. We also used tandem reactions to show the versatility of this synthetic methodology to prepare a variety of chiral hetero- and carbocycles.

**Figure 1.** Application of P-S ligands to allylic substitution.

**References**


Due to the increase in the concentration of carbon dioxide (CO$_2$) in the atmosphere and the concern over global climate change, there has been an ever-increasing interest in carbon dioxide sequestration (Bachu, 2000; Oeklers and Schott, 2005; Daval et al., 2009; Dufaud et al., 2009). Mineral carbonation appears to be one of the plausible methods for the practical removal of carbon dioxide. The preeminent advantage of carbon sequestration by mineral carbonation is the permanent disposal of CO$_2$ in an environmentally benign and geologically stable form. Carbon consumption and sequestration by carbonation reactions containing alkaline earth metals such as calcium (Ca) and magnesium (Mg) were developed. Suitable feedstock for mineral CO$_2$ sequestration are Ca/Mg-silicates such as wollastonite (CaSiO$_3$) and olivine ([Ca, Fe, Mg]$_2$SiO$_4$), and alkaline solid residues such as steel slag. Magnesium silicate minerals such as lizardite [Mg$_3$Si$_2$O$_5$(OH)$_4$] have a high potential for the sequestration of CO$_2$; thus, their reactivity toward dissolution under CO$_2$-free and CO$_2$-containing conditions in acidic solvents is a critical process with respect to their carbonation reactions (Ryu, 2016). To examine the carbonation efficiency and dissolution mechanism of lizardite, hydrothermal treatment was performed to the starting material via a modified direct aqueous carbonation process at 100 and 150 °C. The lizardite dissolution experiments were conducted in H$_2$SO$_4$ solution with concentration range of 0.3–1 M and at a CO$_2$ partial pressure of 3 MPa. The pH was increased to 10 for carbonation by the addition of NaOH (OCI, extra pure) directly into the vessel via a liquid pump without any filtering process. The leaching rate under CO$_2$-containing conditions was higher than that under CO$_2$-free conditions. This suggests that shows the presence of CO$_2$ affects the Mg extraction. The carbonation efficiencies at 150°C in 1 M H$_2$SO$_4$ solution under CO$_2$-containing conditions were 84%. The dissolution rate of Mg was higher than that of Si, such that the Mg : Si ratio of the reacted lizardite decreased from the inner part (approximately 1.5) to the outer part (less than 0.1). The resultant silica-rich layer of the reaction product ultimately changed through the Mg-depleted skeletal phase and the pseudo-lizardite phase to the amorphous silica phase. A passivating silica layer was not observed on the outer surface of the reacted lizardite.

Key words : lizardite, carbon dioxide, carbonation, dissolution rate, magnesite
Figure. Carbonation rate in the presence of various concentrations of sulfuric acid at (a) 100°C and (b) 150°C under CO$_2$-bearing and CO$_2$-free conditions.

References

Poster Abstract 35
Youngjo Kim

**Halide-free and Neutral Chromium Catalysts for the Synthesis of Cyclic Carbonates from CO₂ and Epoxides**

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As shown in Figure 1, catalysts for the coupling reaction of CO₂ with epoxides can be roughly classified into three categories. They are binary systems consisting of a metal–based catalyst in conjunction with a halide additive, bifunctional one-component catalytic systems, and halide-free dimeric systems. Apart from the three systems shown in Figure 1, another promising catalytic system is halide-free and bifunctional one-component catalysts. We hypothesized that catalysts of this new concept could be achieved if the ligand molecule has both a binding site and a Lewis basic site, and at the same time, the Lewis acidic metal center remains coordinatively unsaturated to allow epoxide coordination. Thus, we chose LnM(CO)₄ (M = Cr, Mo, and W; Ln = bidentate diamine ligands) as model catalysts for the halide-free and bifunctional one-component systems. In this poster presentation, we will report here the first use of group VI metal (0) tetracarbonyls containing four kinds of tertiary diamines as neutral catalytic systems without any cocatalyst for coupling reaction of CO₂ with epoxides.

![Figure 1. Schematic representation of catalytic systems for the synthesis of cyclic carbonates.](image)

**References**

Understanding the Self-Assembly Process of Imine Cages

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Porous organic cage materials (POCMs) are materials derived from organic molecules with an accessible intrinsic pore. Porous crystals of these compounds tend to present high gas storage capacity with the advantage of being molecular solids, allowing also applications as membranes. Within these POCMs the Imine cage family of compounds has a modular design based on a monomer with aldehyde groups and a monomer with primary amine groups that generally follows a one-pot synthesis. Whereas some experimental work has attempted to understand the kinetics of this self-assembly process there is much to learn yet. To do so we are using computational techniques to study the synthesis of the CC1 imine cage and build a reaction network that connects the monomers with the cage. Scheme 1 shows the different parts studied of the reaction network that has allowed to draw interesting conclusions.

References
Poster Abstract 37
Moreshwar Chaudhari

Sustainable C-H Peroxidation of Carbonyl Compounds Using Batch/Continuous Flow Process and their Molecular Rearrangement

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In the realm of science, peroxide bond (C-O-O) is a key pharmacophore due to its omnipresence in a variety of biologically active anticancer, anti-HIV, anthelmintics, and antimalarial, etc. pharmaceuticals, natural products, and drugs. To synthesize peroxylated compounds; cheap and readily available peroxide donors, such as hydrogen peroxide (H₂O₂) and tert-Butyl hydroperoxide (TBHP) are commonly employed. On a large scale, handling of peroxides turns out to be a big problem in the industry due to its explosive nature. To minimize the explosive hazards of peroxides we envisaged to develop an efficient and practical method for C-H peroxidation on a large scale using earth-abundant Iron; since the salts of iron are inexpensive, nontoxic, bench stable and easily available.

To this context, we have established the sustainable continuous-flow process for the C-H peroxidation, which is operationally simple, and mild than traditional batch reactions. The use of a continuous-flow reactor is rational because it allows accessing greater process windows, more efficiency, environmentally benign properties, better safety, and superior mass transfer feature than traditional batch reactions. In an extension, the Lewis or Brønsted-acid-mediated, biomimetic and novel rearrangement of peroxides has been developed by us. In this presentation, I will discuss the notable details of our novel approach for C-H peroxidation using homogeneous as well as heterogeneous catalysis in continuous-flow reactor and the rearrangement of peroxo compounds using metal triflates.

References
CO₂-Based Monomers: a Detailed Investigation of the Carbonation Reaction over Diols for the Synthesis of (a)Cyclic Carbonates Promoted by Organic Dual Systems

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The present research aims at investigating in details the reaction between carbon dioxide and a diol to afford cyclic and acyclic carbonates in moderate to good yields. Thanks to its chemical structure, CO₂ has been identified as a promising reagent for the synthesis of organic carbonates as it is non-toxic, cheap and an abundant C1 renewable feedstock, and could potentially replace phosgene based carbonates produced industrially. Prior research has been focused on the epoxide/CO₂ coupling to afford cyclic carbonates in good yields. Yet, this coupling suffers from limitations such as restricted substrates and exclusive synthesis of 5-membered cyclic carbonates. In order to extend the products availability through Carbon Dioxide Utilization, more recent research has been carried out with new substrates such as the use of diols. Thus, efforts are still needed to identify cheaper and more efficient protocols for the selective synthesis of cyclic and acyclic carbonates from the coupling of CO₂ with diols. In this context, the use of organic bases/alkylating agent dual system as promoters and low pressure and temperature conditions (P<1MPa, r.t) seem to be a good alternative to afford organic carbonates. The general strategy is presented in Scheme 1.

Scheme 1: One pot/one step strategy to afford cyclic carbonates under mild conditions.

Thanks to an in-situ ATR-IR spectroscopy monitoring, a detailed understanding of the synthesis of propylene carbonate from propylene glycol and CO₂ promoted by organic bases and the addition of co-reagents is proposed. Reaction intermediates are identified, and kinetic profiles determined for various parameters (pressure, temperature, solvent…). Two dual systems, one combining DBU and an alkyl halide (e.g. Bromoethane), and another one with TEA and TsCl were compared. Different substrates were also tested such as 1, x diols (2 ≤ x ≤ 4) and Isosorbide. The selectivity toward the cyclic carbonate or the side products is discussed.
Density Functional Theory (DFT) was also performed in this work to understand and validate the reaction pathways proposed via ATR-IR monitoring. Structures of transition states were optimized and comparisons between several reagents and/or paths were calculated, giving capital information about further enhancement of the CO2-diol conversion into carbonates.

References
Poster Abstract 39
Aarón Pérez

ABA TRIMETHYLENE CARBONATE/FURFURYL METHACRYLATE COPOLYMERS AS THERMOPLASTIC ELASTOMERS

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Thermoplastic elastomers (TPEs) combine the properties of crosslinked elastomers and melt processing properties of thermoplastics, showing the ability of recycling and reprocessing, thus being beneficial for environmental protection. TPEs often comprise linear ABA triblock copolymers with a soft middle block and hard minority end blocks. The most common TPEs triblock ABA copolymers are polyurethane and polydiene-based copolymers and one of the drawbacks of these materials is that they are derived from fossil resources and are not degradable. Shifting towards innovative sustainable and environmentally compatible alternatives presents enormous interest. The aim of this work is the development of poly(furfuryl methacrylate)-b-poly(trimethylene carbonate)-b-poly(furfuryl methacrylate) (PFMA-PTMC-PFMA) ABA triblock copolymers as a new class of renewable and degradable TPEs.

The soft rubbery middle block is constituted by the aliphatic polycarbonate obtained by ring opening polymerization (ROP) of trimethylene carbonate (TMC). This six-membered cyclic carbonate, an interesting sustainable precursor from 1,3-propanediol and CO₂, has been polymerized at room temperature by organocatalytic ring opening polymerization. Moreover, TMC is a degradable material that yields CO₂ and alcohols upon hydrolitic degradation.

Polycarbonate hydroxyl end-groups have been derivatized to obtain a macroinitiator and the hard blocks of the triblock copolymer have been obtained by atom transfer radical polymerization (ATRP) using fufuryl methacrylate. This monomer can be obtained from carbohydrates as renewable source and can be used further for Diels-Alder (DA) reactions, thus broadening the TPEs applications. The block copolymers PFMA-PTMC-PFMA have been characterized by NMR spectroscopy and SEC. Good control of polymer molecular weight as well as of the end group structure was achieved. The thermal and mechanical properties of the ABA triblock copolymers have been investigated by differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and dynamical mechanical analysis (DMA).

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References
Poster Abstract 40
Pia S. Löser

Synthesis of cleavable bio-based monomers: Towards recyclable thermosets

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Replacing commercial petro-based polymers with bio-based alternatives is an important topic of green chemistry. Lignin is a valuable source of renewable aromatic compounds.\textsuperscript{[1]} Especially vanillin constitutes a versatile building block for polymer science. In addition to the nature of the feedstock, the end of life of the material also has to be considered, which is problematic for chemically cross-linked and therefore non-degradable thermosetting polymers. Therefore, herein, the synthesis of bio-based monomers featuring a degradable linkage was investigated. Vanillic alcohol was selectively allylated on the aromatic hydroxyl group, using catalytic amounts of palladium nanoparticles in water\textsuperscript{[2]} and subsequently coupled with different molecules to form dimeric compounds exhibiting a cleavable linker with different degradation conditions (Figure 3).

![Figure 3](image)

Figure 3 Target molecules for the replacement of DGEBA.

First, the diallylated monomers were polymerized by thiol-ene reaction with a bio-based dithiol. The obtained linear polymers were used as a model system to investigate the degradability of the different linker groups.

In the next step, these monomers will be epoxidized in order to mimic and substitute the commercial diglycidyl ether of bisphenol A (DGEBA).

In parallel, the synthesis of diamines from terpenes is developed. With this approach, fully bio-based epoxy networks will be synthesized and degraded into smaller polyols, that can be reused for the synthesis of another material such as polyurethane.

References


Poster Abstract 41
Ana V. M. Nunes

**Organic Carbonates from Renewable-Derived Diols and CO₂ Using Ionic Liquids as Alternative Solvents**

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CO₂ has been widely explored as feedstock for the production of cyclic carbonates (CC) [1,2]. The importance of this topic has grown significantly due to the belief that being a versatile molecule, CC, may become a platform to introduce CO₂ as a C1 building block into the chemical, pharmaceutical and energy sector. Most straightforward route to CC production comprises a cycloaddition reaction between CO₂ and epoxides. The possibility of extending the range of substrates to diols would significantly increase the number of usable substrates, namely bio-based ones [3]. This latter reaction is equilibrium limited and the resulting water has to be removed from the process to achieve reasonable conversions (Fig. 1).  

![Fig.1 Cyclic carbonates formation from diols and CO₂](image)

In this preliminary work, a high pressure CO₂ process was explored to continuously remove the water from the reaction mixture liquid phase. In order to overcome the low water solubility in CO₂, highly hydrophobic ILs were used to push the water into the gaseous flowing phase. The strategy was applied using different ionic liquids, e.g. fluoroalkylphosphate- and tetracyanoborate-based ionic liquids. Resulting cyclic carbonates were quantitatively analysed by 1H-NMR spectroscopy.

**References**


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Poster Abstract 42
Jordi Faiges

**Ir-CATALYZED WATER OXIDATION AND HYDROGEN TRANSFER REACTIONS: APPLICATION OF NEW HETERODONOR C,N WITH MESOIONIC CARBENES**

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The use of metal catalysts modified with heterodonor ligands containing a carbene group has become highly adventitious for hydrogen transfer reactions (both oxidations and reductions) as well as for water oxidation. In this respect they have shown to be extremely efficient in the protonation/deprotonation of reactants and in redox catalysis, in particular in the oxidation of water and alcohols (Figure 1).[1]

![Figure 1](image_url)

**Figure 1.** Examples of Ir-catalysts developed for alcohol and water oxidation

In this communication we will present the application of iridium(I) and iridium(III) complexes with triazolylidene ligands that contain pendant benzoazole, thiazole, and methyl ether groups as potentially chelating donor sites in the transfer hydrogenation of both carbonyl compounds and olefins, in the base-free dehydrogenation of alcohols and in water oxidation.

**References**

Poster Abstract 43
Junshan Lai

**Immobilization of cis-4-Hydroxydiphenylprolinol Silyl Ethers onto Polystyrene. Application in the Catalytic Enantioselective Synthesis of 5-Hydroxyisoxazolidines in Batch and Flow**

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A new family of polystyrene-supported cis-4-hydroxydiphenyl-prolinol silyl ethers has been prepared, and the resulting polymers have been evaluated as organocatalysts to promote the tandem reaction between N-protected hydroxylamines and α,β-unsaturated aldehydes in batch and flow. Immobilized diarylprolinol 1c, has afforded the best results while proving remarkably stable under the reaction conditions. This has allowed to run ten consecutive cycles of the same reaction, providing the same enantioselectivity and without significant loss of yield. In addition, eleven flow experiments involving nine different substrates have been carried out over a period of 2 months with the same packed column. The new PS-supported catalysts compare favorably with well-established immobilized Jørgensen-Hayashi catalysts, affording 5-hydroxy-isoxazolidines as single diastereoisomers with high enantioselectivities and good yields (up to 83% yield, up to 99% ee).

References

Poster Abstract 44
Martina Vagnoni

Deep Eutectic Solvents as Catalysts for Cyclic Carbonates Synthesis from Epoxides

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Cyclic carbonates find many applications as building blocks, especially for the production of important polymers. They can be produced by a coupling reaction starting from epoxides and CO2 in various studied conditions. In fact this 100% atom economy reaction turns out to be a valid green alternative for the production of cyclic carbonates both because it uses CO2 as carbon feedstock and it represents a greener and safer alternative to the conventional synthesis of cyclic carbonates from diols and toxic phosgene.

DES (Deep eutectic Solvents) are a new generation ionic liquids, consisting of 2-3 components (H-bond donor and H-bond acceptor) able to associate through H-bonds to form an eutectic mixture. They respect all the requirement to be defined “green solvents”, they are biodegradable, non-toxic, bio-based, non-flammable, non-volatile, inexpensive and easy to synthesize.

In recent studies, the capacities of some DES (especially those containing choline chloride) for CO2 reversible absorption had been investigated and demonstrated. Meanwhile some derivatives of choline and betaines have shown an activity in the synthesis of cyclic carbonates from epoxide, in common organic solvents and at high pressure of CO2. Since both choline and betaine are components of most common DES, in this work we present some results about the use of some DES as catalysts for synthesis of cyclic carbonates from various epoxide in mild and low-pressure conditions.

References:
Poster Abstract 45
Raúl Porcar

Synthesys and application of Alcohol dehydrogenases (ADHs) immobilised onto Suported Ionic Liquid Like Phases.

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Here we present the great potential of supported IL-like phases (SILLPs) as “solid solvents” for the direct immobilization and stabilization of alcohol dehydrogenases (ADHs). The efficiency of the resulting biocatalysts, in terms of both activity and specific activity, for the reduction of prochiral ketones, is affected by several factors, as are the nature and morphology of the polymeric material, the loading of IL-like moieties, the loading of the enzyme and the chemical structure of the IL-like fragments, in particular the nature of the anion (which is essential to define the hydrophilic/hydrophobic balance of the corresponding material). All those parameters can be easily adjusted and optimised.1,2 The use of a crosslinked resin facilitates the preparation of biocatalytic minireactors for continuous-flow applications.

Figure 1

References


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Building carbon-carbon bond from CO$_2$ with malic enzyme and viologen derivative

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The reduction in CO$_2$ emissions is an important global objective. Hence, CO$_2$ utilization technologies have been received much attention. To use CO$_2$ as a C1 feedstock for chemical production, effective catalyst for C-C bond formation with CO$_2$ is necessary. Malic enzyme (ME), a biocatalyst, catalyzes introducing CO$_2$ to pyruvate (C3) to form malate (C4) via oxaloacetate (C3). Recently, we reported that double-electron reduced diphenylviologen (PV$_0$) derivative involved in the reaction of introducing CO$_2$ to pyruvate. However, the reaction mechanism of introducing CO$_2$ into pyruvate by ME and PV$_0$ have not been clarified yet. Therefore, in this study, we investigated the reaction of introducing CO$_2$ using ME and PV$_0$ derivative by enzymatic kinetic analysis.

Water-soluble PV derivative, 1,1’-bis(p-carboxyphenyl)-4,4’-bipyridinium dichloride (PCV) was synthesized. The sample solution consisted of pyruvate, bicarbonate, Mg$^{2+}$, double-electron reduced PCV (PCV$_0$) and ME. The initial rate of oxaloacetate production increased with increasing the concentration of PCV$_0$ (Fig. 1). This indicated that the reaction of introducing CO$_2$ was followed Michaelis-Menten equation. Kinetic parameters for oxaloacetate production from CO$_2$ and pyruvate were determined by enzymatic kinetic analysis. In addition, reaction mechanism was suggested. In this oxaloacetate production, PCV$_0$ acted as a base and promoted enolization of pyruvate. Enolate of pyruvate was carboxylated by CO$_2$ with ME and PCV$_0$.

These findings help to improve the catalytic activity of ME for building C-C bond from CO$_2$ by developing novel viologen derivatives.

References

Deep eutectic solvents (DESs) are novel media with properties analogous to those of ionic liquids (ILs). The additional advantages of DESs are their lower cost, easy synthesis, and little environmental impact. The primary goal of the presented work is to present a force field model (FFM) to indirectly account for polarization effects in DES in the framework of classical molecular dynamics (MD) simulations. Here, we illustrate its successful operation on the example of a DES propeline, composed by choline chloride (Fig. 1a) and propylene glycol (Fig. 1b) with molar ratio of 1:2. Several FFMs, available in literature for all components of the studied mixture, were tested and the most promising were then chosen for further refinement. The initial electrostatic charges on all cation’s and anion’s interaction sites were reduced according to the charge distributions derived from ab initio MD simulations of the bulk propeline system [1], as it is described in our previous work [2].

The potential was carefully validated against various experimental properties, such as density, self-diffusion and viscosity, among others, in a wide temperature range (from 298.15 up to 373.15 K). The structural properties of propeline at a molecular level are discussed in terms of atom-atom and center-of-mass radial and spatial distribution functions and hydrogen bonding analysis.

Fig. 1. Geometries of (a) choline chloride, and (b) propylene glycol along with the atom types, used throughout this work. Nitrogen, carbon, oxygen, hydrogen, and chlorine atoms are represented by blue, black, red, white, and green spheres, respectively.

References

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PS-Supported C2-Chiral Triamines and Their Application in Asymmetric Organocatalysis

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In the last two decades there has been an increasing interest in the field of organocatalysis as showed by the increasing number of publications. However there is still the need of continuing the research in this field and new methodologies have to be developed to overcome the gap between organometallic and metal-free catalysis.

Recently our group reported the development of a family of C2-symmetric chiral bifunctional triamines (C2-CBT) as organocatalysts for different asymmetric transformations as the aldol condensation between ketones and isatins.

In this work we propose the immobilization of the C2-CBT organocatalysts onto a polystyrene resin. The performance of the most successful candidates will be evaluated for the development of user-friendly sustainable continuous flow applications.

Scheme 1: Asymmetric aldol reaction catalysed by PS-supported C2-CBT.

References

More

Fluorinated greenhouse gases (F-gases) are used primarily in refrigeration, air conditioning and heat pump equipment. They are often used as substitutes for ozone-depleting substances because they do not damage the atmospheric ozone layer. However, F-gases are powerful greenhouse gases with a global warming effect up to 23,000 times greater than carbon dioxide.[1] In European Union (EU), F-gases emissions have increased up to 60% since 1990, in contrast to all other greenhouse gases whose emissions have been reduced.[1]

Ionic liquids (ILs) are recognized as greener media due to their properties, such as almost null volatility, high tuneability and recyclability. Furthermore, fluorinated ionic liquids (FILs) present 3 nanosegregated domains (fluorinated, polar and hydrogenated) [2,3] and can be used as “3 in 1” solvents. Playing with the interactions and the size of the different domains, one can design specific solvents for the separation of F-gases.[4]

The objective of this work, within the framework of the KET4F-Gas project (SOE2/P1/P0823), is to develop climate-friendly processes based on FILs to recover and recycle F-gases. The F-gases that are usually used in air conditioning and commercial refrigeration equipment, such as R-134a (1,1,1,2-tetrafluoroethane), R-32 (difluoromethane) and R-125 (pentafluoroethane) will be studied. In order to evaluate the performance of FILs in this application, sorption equilibrium isotherm will be measured using an high-pressure magnetic-suspension microbalance. Neat FILs and FILs composites (using supported porous materials) will be studied, as a first attempt to deliver both fundamental understanding of the behaviour of these new alternative solvents and the skills to manipulate their behaviour to process development and scale-up.

References
It is impossible to imagine a life without plastics, on a daily basis we all come in contact with for instance polyethylene terephthalate (PET – plastic bottles). Apart from the fact that this is a fossil fuel derived plastic, we can all see the outcome of PET’s high stability, as it accumulates in the environment. As a result the polymer sector is currently shifting towards biosourced and/or biodegradable plastics. Previously we developed a method to produce polyesters from the peel of citrus fruits such a lemons and oranges, effectively transforming waste into polymeric materials with possible applications in textile and packaging (Figure 1). Based on this proces we now plan to generate a family of different polyesters via copolymerization reactions of bioaccessible monomers (limonene and other terpene oxides). This will allow us to identify a polyester that combines both biorenewable and biodegradable character with the material properties required to compete with existing petrol-based plastics.

Figure 1. Polyesters using lemons as starting material and a possible final product (polyester fiber).

References


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Electro-catalytic Reduction of CO₂ Using Supported Au, Pd Nanoparticles

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Carbon dioxide, the potential industrial & anthropogenic waste, is a fast upcoming feedstock for fuels, chemicals, polymers, and other value added materials. CO₂ can be converted into these products either via chemically or biologically. Electro-reduction is one among the many chemical methods to valorize CO₂ into useful products like CO, CH₃OH, HCOOH etc (1-3). Electro-reduction of CO₂ using single crystal catalysts have been widely studied by the academic fraternity. But they are still model catalysts and not ready for real world applications. Hence there is a serious need to develop real catalytic materials to mitigate CO₂ efficiently and selectively to desired products. In ‘real’ catalyst front, size & shape controlled metal nanoparticles prepared via colloidal methods are the promising upcoming catalytic materials for CO₂ electro-reduction.

With colloidal methods, the metal precursor (Mₙ⁺) is electronically reduced to metallic state (M₀) by galaxies of reducing agents and maintained in its nanoparticle size or specific geometrical shape by stabilizer polymers. These nanoparticles are further immobilized on stable solid supports, in order to have ideal heterogeneous catalysts, which are further fabricated on the working electrode surface. These modified working electrodes are used in an electrochemical cell saturated with reactant CO₂, to catalyze the electro-reduction of CO₂ when the working potential is applied. We at University of Turku, working out on such a material and modified electrode as shown in Fig. 1. We believe that these Au, Pd nanoparticles can turn promising candidates for recycling CO₂ to chemicals/fuels, if they are developed diligently by keeping their size, geometrical shapes, surface exposed atoms in account. Thus, greenhouse gas like CO₂ can be made ‘a threat no-longer’.

![Figure 1: Electro-catalytic reduction of CO₂ using supported Au, Pd metal nanoparticles](image-url)
References