

BOOK OF ABSTRACTS

ICIQ RedINTECAT School

September 25-27, 2019

ICIQ Auditorium, Tarragona

<http://iciqschool.iciq.es>

WELCOME

It is our great pleasure to welcome you all to the **ICIQ-RedINTECAT School** (September 25-27, 2019) that this year will focus on “*Technologies for Carbon Dioxide Conversion and Valorization*”. The event will take place in the Auditorium of the Institute of Chemical Research of Catalonia (ICIQ). Tarragona is located 100 km South of Barcelona at the heart of the Costa Dorada, where some of the most attractive beaches in Spain can be found. Tarragona, designated by UNESCO as a Humankind Heritage Site, also enjoys some of the best preserved Roman ruins in the Iberian Peninsula.

The **ICIQ-RedINTECAT School** will bring expertise from a range of national and international top-researchers working in the area of CO₂ (photo)catalysis and conversion active in power-to-X, fine-chemical synthesis and biopolymer development. We strongly encourage young scientists, particularly graduate students and postdoctoral fellows, to actively participate in this event. The meeting will offer an excellent opportunity to meet prestigious speakers that cover a broad range of topics at the frontier of CO₂ research. The scientific program of this symposium will include 7 plenary lectures and various short communications.

The **ICIQ-RedINTECAT School** is co-funded by the AEI/Ministerio de Ciencia, Innovación y Universidades through the project CTQ2016-81923-REDC/AEI.

We look forward to welcome you to this exciting event,

Julio Lloret (ICIQ Group Leader)

Arjan W. Kleij (ICIQ Group Leader)

SPEAKERS

Etsuko Fujita

Brookhaven National Laboratory, USA

Andreas Greiner

Universität Bayreuth, Bavarian Polymer Institute, Germany

Jürgen Klankermayer

RWTH Aachen Universität, Germany

Burkhard König

Universität Regensburg, Germany

Víctor de la Peña

IMDEA, Spain

Cristina Sáenz de Pipaón

Orchestra Scientific, Spain

Atsushi Urakawa

Technische Universiteit Delft, The Netherlands

CONFERENCE AT A GLANCE

25	26	27
	9:00-10:00 Klankermayer	9:00-10:00 Greiner
	10:00-10:15 Questions	10:00-10:15 Questions
	10:15-10:35 05: Duan	10:15-10:35 O12: Rintjema
	10:35-11:05 Coffee Break	10:35-11:05 Coffee Break
	11:05-11:25 O6: Della Monica	11:05-11:25 O13: Fernández
	11:30-11:45 07: Gu	11:25-11:45 O14: Gonell
	11:45-12:05 O8: Guzmán	11:45-12:45 Fujita
	12:05-13:05 König	12:45-13:00 Questions
	13:05-13:20 Questions	13:00-13:15 Closure
	13:20-15:00 Lunch	
15:00-16:00 Registration	15:00-16:00 Urakawa	
16:00-17:00 de la Peña	16:00-16:15 Questions	
17:00-17:15 Questions	16:15-16:45 Coffee Break	
17:15-17:45 Coffee Break	16:45-17:05 O9: Garcia-Muelas	
17:45-18:05 O1: Dubed	17:05-17:25 O10: Ventosa	
18:05-18:25 O2: Vereschchuk	17:25-17:45 O11: Dattila	
18:25-18:45 O3: Prsjla	17:45-18:45 Saenz	
18:45-19:05 O4: van den Bosch	18:45-19:00 Questions	
21:00 Dinner (on invitation)	21:00 Dinner - Barquet	

PROGRAM

Wednesday, 25th September

15:00 – 16:00 Registration

16:00 – 17:00 Plenary Lecture 1: Víctor de la Peña

Solar Fuels Production by Artificial Photosynthesis: From Inorganic to Hybrid Multifunctional Materials

17:00 – 17:15 Questions

17:15 – 17:45 Coffee Break

17:45 – 18:05 Oral Communication 1: Geyla C. Dubed

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

18:05 – 18:25 Oral Communication 2: Nataliia Vereshchuk

Rational Desig of New Efficient and Robust Ru Based Molecular Water Oxidation Catalysts

18:25 – 18:45 Oral Communication 3: Paulina Prslja

CO₂ Reduction Towards CO with MNC-like Catalysis

18:45– 19:05 Oral Communication 4: Bart van den Bosch

Electrochemical Reduction of CO₂ to CO Paired with Biomass Oxidation

21:00 Speaker's Dinner (on invitation)

Thursday, 26th September

09:00 – 10:00 Plenary Lecture 2: Jürgen Klankermayer

*E = m*CO₂: Translational Molecular Catalysis at the Interface of Energy and Chemistry*

10:00 – 10:15 Questions

10:15 – 10:35 Oral Communication 5: Yaya Duan

Site-selective Dicarbofunctionalization of Vinylboronates with Organic Halides

10:35 – 11:05 Coffee Break

11:05 – 11:25 Oral Communication 6: Francesco Della Monica
[OSSO]-Fe(III) Catalysts for the CO₂/Epoxides Reaction

11:30 – 11:45 Oral Communication 7: Yiting Gu
Base-Catalyzed 1,1-Silaboration of Terminal Alkynes

11:45 – 12:05 Oral Communication 8: Jefferson Guzmán
Influence of Silicon Substituents on the Performance of Iridium-NSiR Catalyzed CO₂ Hydrosilylation

12:05 – 13:05 Plenary Lecture 3: Burkhard König
Chemical Photocatalysis: Organic Synthesis with Light and Carbon Dioxide

13:05 – 13:20 Questions

13:20 – 15:00 Lunch

15:00 – 16:00 Plenary Lecture 4: Atsushi Urakawa
Playing with Thermodynamics and Kinetics: Efficient Conversion of CO₂ to Chemical Energy Carriers

16:00 – 16:15 Questions

16:15 – 16:45 Coffee Break

16:45 – 17:05 Oral Communication 9: Rodrigo García-Muelas
Atomic-Scale Promotion of Indium Oxide for CO₂ Hydrogenation to Methanol

17:05 – 17:25 Oral Communication 10: Marta Ventosa
Solar-Driven Water Splitting: from Molecular Catalysts to Photoelectrochemical Cells

17:25 – 17:45 Oral Communication 11: Federico Dattila
Basicity-Driven Selectivity to Formate for Carbon Dioxide Reduction on Chalcogen Modified Copper

17:45 – 18:45 Plenary Lecture 5: Cristina Sáenz de Pipaón
Orchestra Scientific: Developing an Economically Affordable Technology for CO₂ Separation

18:45 – 19:00 Questions

21:00 ICIQ-RedINTECAT School Dinner

Friday, 27th September

09:00 – 10:00 Plenary Lecture 6: Andreas Greiner

New Biobased Polycarbonates – Candidates for a Novel Class of Sustainable Engineering Plastics?

10:00 – 10:15 Questions

10:15 – 10:35 Oral Communication 12: Jeroen Rintjema

From Lemons to Polymers

10:35 – 11:05 Coffee Break

11:05 – 11:25 Oral Communication 13: Sergio Fernández

An Experimental and Computational Study of the Cobalt-Catalyzed CO₂ Reduction Mechanism

11:25 – 11:45 Oral Communication 14: Sergio Gonell

Mechanistic Studies on Carbene-Supported Complexes for Electrocatalytic CO₂ Reduction

11:45 – 12:45 Plenary Lecture 7: Etsuko Fujita

Carbon Dioxide Reduction and Hydrogenation by Molecular Catalysts Involving Second-Coordination-Sphere Interactions

12:45 – 13:00 Questions

13:00 – 13:15 Closure

PLENARY LECTURES ABSTRACTS

Plenary Lecture Abstract 1

Víctor de la Peña

Solar Fuels Production by Artificial Photosynthesis: From Inorganic to Hybrid Multifunctional Materials

Víctor A. de la Peña O'Shea

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Photocatalytic conversion of CO₂ and H₂O is an interesting route to produce fuels and chemicals; this process is also known as Artificial Photosynthesis (AP). In last years, extensive efforts have been made to develop efficient catalytic systems capable of harvesting light absorption and reducing CO₂ especially when using water as the electron donor.

Herein, we report different strategies and modifications of photocatalysts to increase process performance. Among them, an interesting approach to improve charge separation in photocatalytic systems is the use of heterojunctions. In this line, the combination of different semiconductors with noble metal nanoparticles or organic semiconducting polymers leads to a separation of the photogenerated charge carriers to increasing their life time, facilitating charge transfer to adsorbed molecules.

The main products, using bare TiO₂, were CO and H₂, with low concentrations of CH₄. The deposition of surface plasmon nanoparticles (SP-NPs) leads to changes in the selectivity to higher electron-demanding products, such as CH₄. TAS measurements confirm that this behaviour is due to the electron scavenging ability of SP-NPs [2].

Organo-inorganic hybrid materials show a dramatic reactivity improvement in CO₂ photoreduction, enhancing methane selectivity. To explain this behaviour a combination of in-situ NAP-XPS, FTIR, TAS spectroscopies and theoretical tools has been used, showing a more efficient light absorption and charge transfer in the hybrid photocatalyst compared with bare materials.

References

- [1] V. A. de la Peña O'Shea, D. P. Serrano, J. M. Coronado, "Current challenges of CO₂ photocatalytic reduction over semiconductors using sunlight", in *Molecules to Materials—Pathway to Artificial Photosynthesis*, (Eds. E. Rozhkova, K. Ariga) Springer, London, **2015**. 171-191
- [2] L. Collado, A. Reynal, F. Fresno, M. Barawi, V. Perez Dieste, C. Escudero, J. M. Coronado, D. Serrano, J. Durrant, V. A. de la Peña O'Shea. *Nat. Commun.* **2018**, 9 (1), 4986..

Plenary Lecture Abstract 2

Jürgen Klankermayer

E = m*CO₂: Translational Molecular Catalysis at the Interface of Energy and Chemistry

Jürgen Klankermayer

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The utilization of carbon dioxide (CO₂) as a raw material for chemical synthesis has intrigued chemists ever since it was recognized that nature capitalizes on this molecule to harness the energy of the sun for production of organic matter through photosynthesis. Especially in the last two decades, the utilization of renewable resources as chemical building block, solvent, or additive has emerged as vital research area for the development of sustainable chemical processes. In this respect, CO₂ is an important, but challenging renewable C₁ resource, which is already used as raw material for the production of industrial chemicals in certain cases and intensively researched for novel transformations.^[1] Whereas current approaches largely focus on the combined usage of CO₂ and molecular hydrogen towards C₁-synthons and e-fuels, a novel methodology enables to synthesize complex molecular structures with the additional direct integration of bio-based platform molecules or plastic waste. Thus, the concept of “bio-hybrid” transformations was introduced, envisioning the integration of biomass or waste material and CO₂ utilization.

Herein, the challenges and opportunities using CO₂ as a C₁ synthon in catalytic reactions and processes are presented. The general aspects will be illustrated with current research from our laboratories concerning the development, application, and mechanistic understanding of molecular catalysts and catalytic systems.^[2]

References

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Plenary Lecture Abstract 3

Burkhard König

Chemical Photocatalysis: Organic Synthesis with Light and Carbon Dioxide

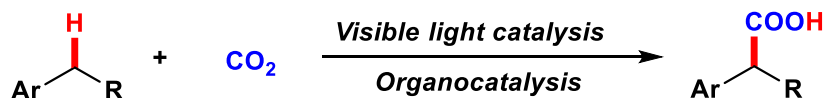
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Light is a fantastic reagent for chemical conversions: It provides energy, can be used in excess and leaves no trace. Its application in chemistry has a long history, but the last 15 years have seen a fast progress in the development of light-driven synthetic organic transformations.

We start with a short review on the key principles of photocatalytic reactions¹ and discuss strategies how to accumulate the energy of several photons for one chemical step.² We look at light-driven C-H activations and possibilities to generate carbanions³ with photocatalysis. This arsenal of recently developed methods will then be applied to utilize carbon dioxide as a C1 building block in organic synthesis.⁴⁻⁶



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Plenary Lecture Abstract 4

Atushi Urakawa

Playing with Thermodynamics and Kinetics: Efficient Conversion of CO₂ to Chemical Energy Carriers

Atsushi Urakawa

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The amount of captured CO₂ from the flue gas released by various industry is expected to be on the order of a few gigatons in a decade globally. This enormous amount clearly points out that, besides actively demonstrated CO₂ sequestration technologies, we need to urgently develop highly efficient CO₂ conversion technologies to close the carbon cycle by recycling the carbon contained in CO₂ into a usable form. One of the most promising paths to transform a vast amount of captured CO₂ into useful forms is its catalytic conversion to largely demanded chemicals like fuels. However, general challenges are its efficient activation and selective conversion to desired products. Numerous catalysts are developed to date; however, the efficiencies are often hindered by the high thermodynamic stability of CO₂ as well as by unfavoured reaction kinetics and thermodynamics.

In this talk, engineering and chemical strategies for efficient catalytic conversion of CO₂ to chemical energy carriers are presented. Impacts of high-pressure conditions and chemical traps in combination with innovative catalysts on creating highly reactive environment will be presented for the synthesis of methanol, dimethyl ether, dimethyl carbonate, formic acid and methyl formate. Furthermore, unique characteristics of unsteady-state operation to combine CO₂ capture and conversion in one process to produce syngas (CO+H₂) and methane are explained, highlighting the importance of *operando* methodologies to rationally develop and optimise catalytic materials and processes.

Plenary Lecture Abstract 5

Cristina Sáenz de Pipaón

Orchestra Scientific: Developing an Economically Affordable Technology for CO₂ Separation.

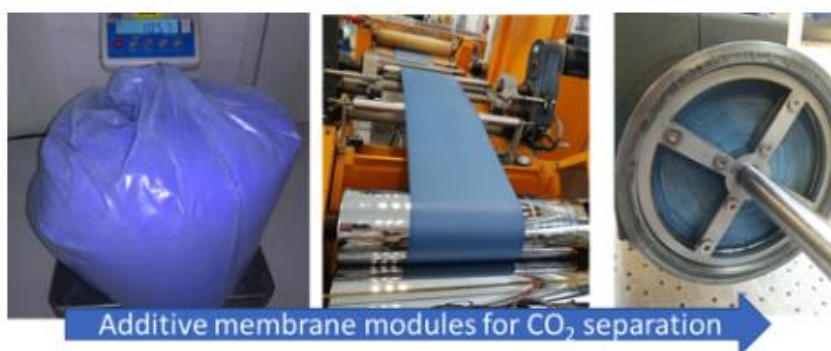
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There is a wide number of CO₂ capture and separation technologies: Amine solutions, Pressure swing adsorption, cryogenic technologies... and all of them present their advantages and drawbacks. For instance, amine solutions it the widest used technology, in spite of its only-large-scale-profitability and the inconvenient caused by the residues.

What the industry is looking for? What are the requirements that a CO₂ separation should meet to be adopted by the industry? Low maintenance, easy operations, low space requirements, high selectivity and of course low installation and operation cost. Several industries could benefit for such a technology: CO₂ emissions capture, biogas upgrading, gas natural sweetening...

Orchestra Scientific, the first spin-off from ICIQ, it is developing highly selective CO₂ membranes modules. From a new patented chemical compound, TAMOF, an industrial development leads to additive membranes that keep all the advantaged of this CO₂ separation technology while reducing their main drawback: the low selectivity. By increasing the selectivity, the operation pressure can be reduced and hence the operation costs.

A successful technological transfer and industrial development leads Orchestra from milligrams produced in the ICIQ labs to an industrial trial this September, along with agreements with several companies and economic investment to reach the market.



Plenary Lecture Abstract 6

Andreas Greiner

New Biobased Polycarbonates – Candidates for a Novel Class of Sustainable Engineering Plastics?

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Biobased polymers are promising alternatives for fossil based polymers. We have materialized the biobased (non-food resource) polylimonene carbonate (PLimC) as highly promising engineering plastic with a unique combination of physical and chemical properties.¹ PLimC is prepared by copolymerization of limonene oxide and CO₂. Limonene oxide is prepared from limonene which is available in plenty. PLimC is highly transparent (Figure 1), has a glass transition temperature of 135°C is scratch resistant, and shows good selectivity in gas permeation. Most interestingly, the lateral double bond in each repeating unit of PLimC makes it a perfect platform for functional polymers.² The double bonds can be utilized for a wide variety of polymer analogous chemical modifications of PLimC which result in polymers with a wide variety of novel combination of properties like antimicrobial, elasticity, and wettability. Novel block copolymers PLimC and their morphology³ will be discussed in this contribution as well as the potential of PLimC for novel applications, e. g. as membrane material.⁴



Figure 1. Photograph of a PLimC film in front of a mandarin tree.

References

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Plenary Lecture Abstract 7

Etsuko Fujita

Carbon Dioxide Reduction and Hydrogenation by Molecular Catalysts Involving Second-Coordination-Sphere Interactions

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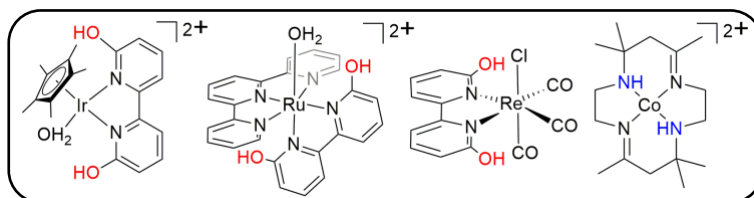
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The concentration of CO₂ in the atmosphere has reached unprecedented levels and continues to increase owing to an escalating rate of fossil fuel combustion. In view of the inevitable depletion of fossil fuels, it is important to pursue the recycling of CO₂ to fuels and chemicals under mild conditions, which can be achieved with: (i) so-called artificial photosynthesis using photoinduced electrons; (ii) bulk electrolysis using electricity produced by photovoltaics; and (iii) CO₂ hydrogenation using solar-produced H₂. At this meeting, we will present our research on CO₂ reduction and hydrogenation using molecular catalysts focusing on catalysts bearing pyridinol- or tetraazacyclo- tetradecadiene-type ligands that provide second-coordination-sphere effects.¹⁻⁴

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ORAL COMMUNICATIONS ABSTRACTS

Oral Communication Abstract 1

Geyla C. Dubed

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

G.C. Dubed,^{a*} S. S. Mondal,^a F. Franco,^a A. Bucci,^a V. Martin-Diaconescu,^a M. Ortuño,^a A. Shafir,^b N. López,^a J. Lloret.^{a,b}

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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

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a,

Oral Communication Abstract 2

Nataliia Vereshchuk

Rational Desig of New Efficient and Robust Ru Based Molecular Water Oxidation Catalysts

Nataliia Vereshchuk^{a,b}, Roc Matheu^{a,b}, Jordi Benet-Buchholz^a, Muriel Pipelier^c, Jacques Lebreton^c, Didier Dubreuil^c, Arnaud Tessier^c, Carolina Gimbert-Suriñach^a, Mehmed Z. Ertem^d and Antoni Llobet^{a,e}

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Developing a sustainable and global energy currency is the major challenge of our time. Solar fuels and related technologies are promising alternatives to fossil fuels since they are renewable, carbon free and abundant.^{1,2}

Since most of the current renewable technologies today are intermittent and difficult to store, the ideal solution will be to store them into reduced chemicals. This is actually what nature is doing via a process known as photosynthesis. Water splitting with sunlight is a process with many similarities as in Photosynthesis and that is regarded today as one of the potentially available solutions to replace fossil by solar fuels. In this process one of the main challenges is the water oxidation reaction that involves the removal of four electrons and four protons from water and the formation of an O-O bond to generate molecular oxygen. This process is not only energetically demanding, but kinetically very complex. Thus to overcome these problems, efficient water oxidation catalysts need to be developed. The most efficient WOCs known today are based on the Flexible Adaptative Multidentate Equatorial (FAME) ligands containing polypyridyl carboxylate groups such as H₂tda and H₂bda.^{3,4,5} In this work, we present a new Ru-based catalyst, which is coordinated to a terpyridyl diphosphonate ligand with additional auxiliary ligands completing the Ru coordination sphere. Our initial catalytic studies show the exceptional behavior of these new catalysts towards the water oxidation reaction.

References

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Oral Communication Abstract 3

Paulina Prslja

CO₂ Reduction Towards CO with MNC-like Catalysis

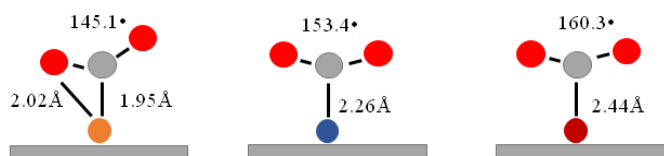
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The development of efficient electrochemical carbon dioxide reduction (eCO₂RR) catalyst still remains a challenge. Metal-nitrogen-carbon (MNC), where the single metal atom (M = Mn, Fe, Co, Ni and Cu) is coordinated with four pyridinic nitrogen atoms, is a promising new material for achieving high activity and selectivity towards CO. The unique structure of carbon based catalyst makes it good compressor of competing HER, because the single site of MNC-like structure requires an ontop binding of hydrogen [1].

The aim of our work was to establish experimental and theoretical correlations between physicochemical and catalytic properties for the eCO₂RR of MN₄C centres. Detailed DFT was performed to investigate coordination of different (no ligand, H₂O, OH, O) ligands around the metal to resemble a coordination complex. The models represent ex situ and operando characterization of metal oxidation states and coordination number, at the rest and during the reaction. Experimental results showed that Co and Mn did not change oxidation states during the reaction, while Fe and Ni were partially reduced. Furthermore, regarding selectivity, FeNC, NiNC and MnNC had Faradaic efficiency for CO around 80%. We discovered volcano-trend between their activity toward CO formation and the nature of the transition metal in MN_x sites, where depending on the electrochemical potential, Fe and/or Co were at the top of the volcano. In our study we explored different configuration of *CO₂- intermediate. While Fe presented an η²-C,O hapticity with an Fe-O contact, this was absent for Co or Ni that preferred the η¹-C configuration (Fig: Schematic representation of CO₂ coordination to Fe(II)N₄(H₂O), Co(II)N₄(H₂O) and Ni(I)N₄, in the order from the left to the right).



References

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Oral Communication Abstract 4

Bart van den Bosch

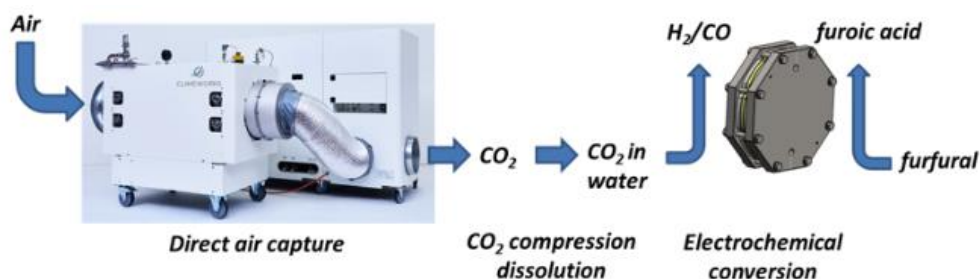
Electrochemical Reduction of CO₂ to CO Paired with Biomass Oxidation

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We present the development of an integrated process in which CO₂ is captured from air and electrocatalytically converted to syn gas. This electrochemical reduction reaction is coupled with the oxidation of furfural to furoic acid. The coupling of valuable oxidation and reduction reactions in a single electrochemical reactor can dramatically reduce costs associated with electrocatalysis. The work presented is performed with the EU H2020 Celbicon project. A goal of this project to demonstrate the technical feasibility of this process at a technology readiness level 5.

The focus of the presentation is on the development of the electrochemical processes. The reduction of CO₂ is performed on silver nanoparticles, which are immobilized on graphitic carbon nitride. The oxidation of furfural is performed on nickel-based anodes. The importance of the catalyst material and morphology for the anode and cathode is highlighted. An electrochemical cell is customly engineered to couple both reactions in a single cell. We will present the optimal conditions for the anodic and cathodic processes, and the requirements of the automated setup to be able to continuously run both reactions in parallel.



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Oral Communication Abstract 5

Yaya Duan

Site-selective Dicarbofunctionalization of Vinylboronates with Organic Halides

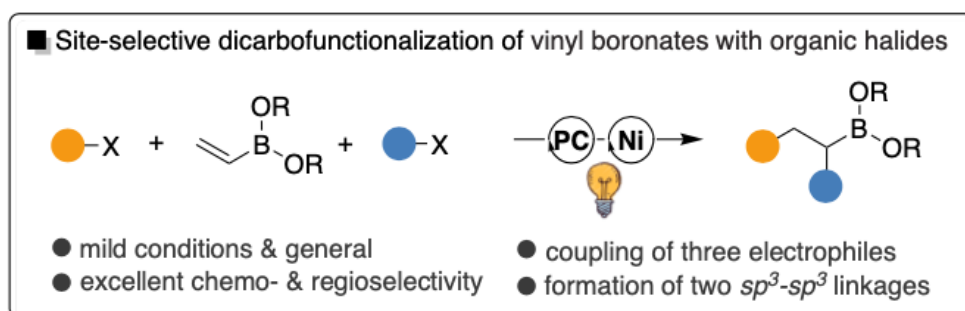
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Organoboron compounds rank amongst the most versatile organometallic reagents to build up molecular complexity.¹ Despite the recent advances realized for their synthesis, the design of a complementary platform that allows to access the organoboron core with improved flexibility and modularity still constitutes a worthwhile endeavour for chemical invention.²⁻⁵ Herein, we describe a new site-selective catalytic protocol that enables the access to functionalized alkyl boron reagents by combining three different electrophilic partners (alkyl halides, aryl halides and vinyl boronates) by merging photoredox and nickel catalysis. The transformation occurs under mild conditions and with an excellent chemo- and regioselectivity profile.



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Oral Communication Abstract 6

Francesco Della Monica

[OSSO]-Fe(III) Catalysts for the CO₂/Epoxides Reaction

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Chemical transformations of CO₂ play a prominent role in the concretization of circular economy. Among the others, the synthesis of cyclic organic carbonates (COCs) and polycarbonates (PCs) from CO₂ and epoxides is one of the most appealing. Numerous homogeneous catalysts has been reported for this reaction, usually based on Al, Mg, Cr, Co and Zn.¹ Only few of them are based on Fe,² despite large abundance and low toxicity of this metal. The behaviour of a catalytic systems, based on [OSSO]-Fe(III) complexes, is described in this contribution. In details, beside to proven efficiency at low temperature and pressure, mechanistic investigations gave information for the development of a single component catalytic system.³

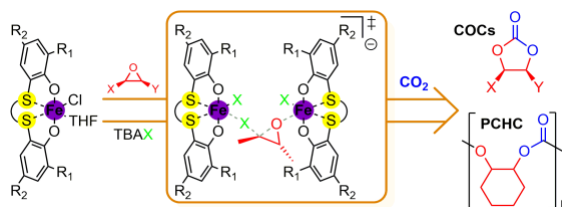


Figure 1. CO₂/epoxides reaction toward cyclic organic carbonates (COCs) and poly(cyclohexene carbonate) (PCHC), catalysed by [OSSO]-Fe(III) complexes.

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Oral Communication Abstract 7

Yiting Gu

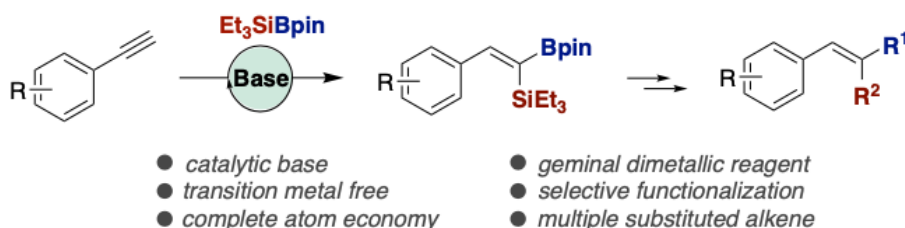
Base-Catalyzed 1,1-Silaboration of Terminal Alkynes

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Alkynes rank amongst the most basic functional groups in organic synthesis.¹ Indeed, the recent years have witnessed a wide number of transformations that make use of alkynes as synthons to build up molecular complexity. Despite the advances realized, difunctionalization reactions remain predominantly confined to 1,2-difunctionalization events² whereas a limited knowledge has been acquired in technologies aimed at accessing 1,1-difunctionalization compounds, particularly in the absence of transition metal complexes.³ As part of our interest in difunctionalization reactions of π -components, we have recently discovered a base-catalyzed protocol that enables a site-selective 1,1-silaboration of terminal alkynes (Scheme 1). This protocol is characterized by its mild conditions and high stereoselectivity, thus allowing to access versatile geminal silylboronates in an atom and step-economical manner from simple and readily available precursors.



Scheme 1. Site-selective 1,1-silaboration of terminal alkyne

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Oral Communication Abstract 8

Jefferson Guzmán

Influence of Silicon Substituents on the Performance of Iridium-NSiR Catalyzed CO₂ Hydrosilylation

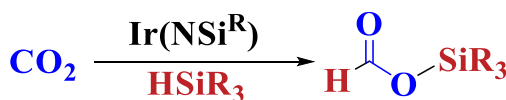
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The activity of Iridium(III)-NSiR (NSiR= 4-methylpyridin-2-yloxydialkylsilane; with Me, *i*Pr and *t*Bu as alkyl groups)₁ complexes as CO₂ hydrosilylation catalysts has been studied. The nature of the substituent at the silicon atom influences the structure of the catalyst precursors. Thus in the case of R = *t*Bu only one NSiR ligand can enter into the coordination sphere of the metal; however when R = *i*Pr or Me, the complexes with only one ligand NSiR are not stable, but instead two NSiR ligands are incorporated into the metal. In addition, complexes with R = Me tends to dimerize, while those with R = *i*Pr are monomeric. Moreover, it has been found that the alkyl groups at the silicon center also exert key role on the catalytic performance of these systems.



Scheme 1. Ir-NSiR-catalyzed CO₂ Hydrosilylation

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Oral Communication Abstract 9

Rodrigo García-Muelas

Atomic-Scale Promotion of Indium Oxide for CO₂ Hydrogenation to Methanol

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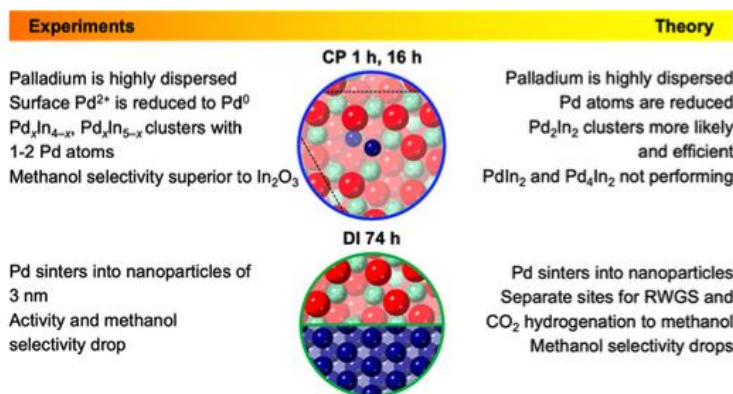
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Recently, it was found that In₂O₃ catalyzes the hydrogenation of CO₂ to methanol with high selectivity, stability, and activity.[1] The activity can be promoted with palladium, which is an efficient H₂-splitter.[2] However, palladium nanoparticles mediate the parasitic reverse water-gas shift reaction and sinter or alloy with indium, thus limiting the selectivity and stability. This limitation can be overcome by controlled co-precipitating Pd with In. Following this synthetic protocol, we have found that only two Pd atoms go to the active ensemble on In₂O₃ without further synthering under reaction conditions (CP 1h, 16h, see Figure), thus producing a stable, selective, and active catalyst for the CO₂ hydrogenation to methanol.[2]



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Oral Communication Abstract 10

Marta Ventosa

Solar-Driven Water Splitting: From Molecular Catalysts to Photoelectrochemical Cells

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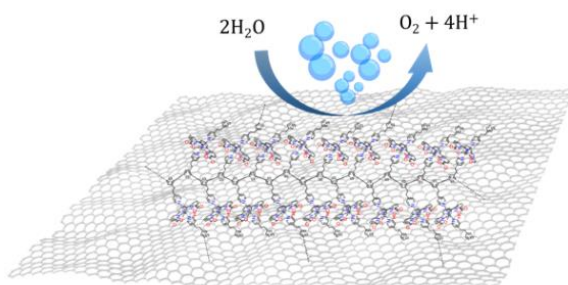
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Water reduction and water oxidation catalysts are the core of light-induced water-splitting devices. Current designs are based on heterogeneous catalysts such as metals -Pt or Ni- for the hydrogen evolution reaction (HER) and metal oxides for the oxygen evolution reaction (OER).¹ However, the field of molecular catalysts for HER and OER have grown in the recent years due to a thorough understanding of the mechanisms of the catalytic reactions, that has allowed to reach turnover frequencies orders of magnitude higher than related oxides.² Moreover, molecular catalysts have the potential to tune their activity and selectivity by modifying the ligands in the first and second coordination sphere.

The heterogenization of molecular water oxidation catalysts into conductive or semiconductive solid surfaces allows to generate molecular electroanodes or photoanodes that can later on be incorporated into practical devices for solar fuels generation. In addition, the heterogenization of molecular catalyst can improve its long term stability by avoiding bimolecular catalyst-catalyst deactivation pathways.³

The present work attempts to bridge the fields of heterogeneous and molecular catalysis by polymerization of a water oxidation molecular catalyst, modified with thiophene groups. The new molecular material combines the robustness of heterogeneous polymers and the efficiency and selectivity of the well-known active sites. This is the first step towards an applicable solar-driven water splitting device.



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Oral Communication Abstract 11

Federicco Dattila

Basicity-Driven Selectivity to Formate for Carbon Dioxide Reduction on Chalcogen Modified Copper

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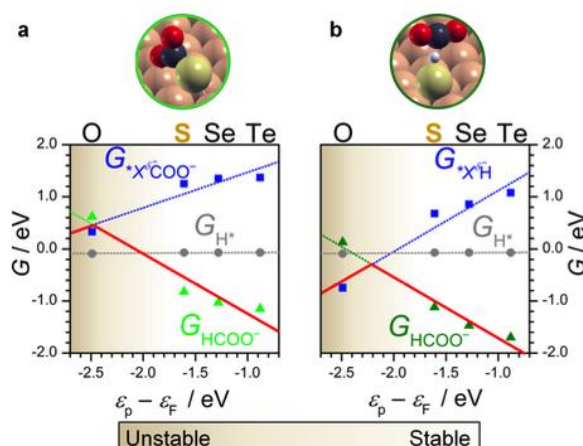
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CO₂ reduction (CO₂R) toward fuels and chemicals is expected to provide a sustainable alternative to fossil fuels exploitation. Among carbon products (C_x), formate / formic acid presents a relevant market price, whilst its production via electrochemical reduction requires low energy.¹ Copper has been proved to be an inexpensive catalyst for CO₂R toward C₁ or C₂ products, though presenting low selectivity.²⁻⁴ Thus, surface modifiers have been successfully employed to improve its catalytic performance.^{5,6}

Chalcogen modified copper surfaces (Cu-X) show higher selectivity than clean copper for the electrochemical reduction of CO₂ toward formate at mild overpotentials (−0.6/−0.8 V vs RHE) since the formation of any other product is inhibited.⁷ Among the chalcogens, sulfur modified copper presents the best selectivity. We rationalize the selectivity switch toward formate by means of Density Functional Theory, developing a model extended over the chalcogen series (X = O, S, Se, Te).⁸

Chalcogen sites, modeled as adatoms on copper surfaces, provide two direct reaction paths toward formate, whilst inhibiting CO₂ adsorption on unselective neighbor copper sites. More specifically, the negatively charged chalcogen adatoms can adsorb either **a**) a CO₂ or **b**) a hydride intermediate, leading to formate production respectively via a transition state (from C-X to C-H bond) or a Heyrovsky-like mechanism (from CO_{2(aq)} to *XHCO₂[−]). The selectivity switch is driven by chalcogen basicity ($\epsilon_p - \epsilon_F$ as its proxy). Sulfur sites exhibit the best compromise in effectively tethering the relevant intermediates (CO₂ / hydride, blue squares), though still presenting an exergonic formate production (green triangles). Hydrogen adsorption (gray circles) is instead independent of chalcogen basicity, thus H₂ production is not promoted.

Based on our model, chemical properties of modifiers actively influence the catalytic performance of the resulting system, being able to promote desired reaction pathways and inhibit undesired ones.



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Oral Communication Abstract 12

Jeroen Rintjema

From Lemons to Polymers

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It is difficult to imagine a world free from plastics, but what we can do is make them environmentally friendlier. Previously we developed a method to produce polycarbonates from the peel of citrus fruits such as lemons and oranges, effectively transforming waste into polymeric materials with possible applications in textile and packaging (Figure 1).¹

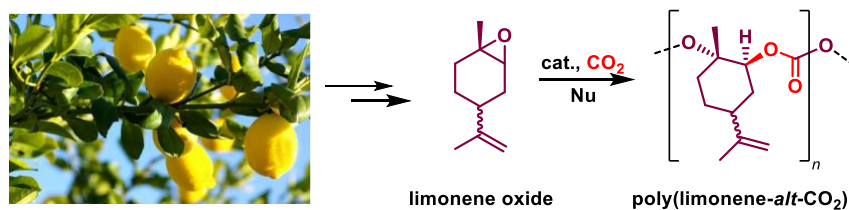


Figure 1: Co-polymerization of CO₂ and limonene oxide

We performed reaction optimization and scale-up of this process to explore the industrial feasibility with external partners. The reaction depicted in figure 1 has been carried out successfully at about 0.5 kg scale obtaining good molecular weights and PDI. Interestingly, the unreacted monomer after the reaction can be recovered and reused in a subsequent polymerization batch. In addition the polycarbonate can be reverted to limonene oxide quantitatively and allows for recycling of the product. Meanwhile we are investigating important polymer properties such as crystallinity, water permeability and biodegradability.

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Oral Communication Abstract 13

Sergio Fernández

An Experimental and Computational Study of the Cobalt-Catalyzed CO₂ Reduction Mechanism

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In this work, we report a mechanistic study in the electrochemical CO₂ reduction process catalyzed by a molecular Co complex based on the PyMe₂tacn (LN4) ligand.^[1] The combination of cyclic voltammetry and *in-situ* spectroelectrochemistry allowed for the detection of a [LN₄CoI-CO]⁺ (**1(n)-CO**) intermediate at the Co^{III/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 Co^{III/I} redox potential. The computational modelling of the reaction mechanism confirmed that the formation of **1(n)-CO** is key in order to understand the activation of CO₂ and the catalytic performance at more negative redox potentials. Finally, we employ blue-light irradiation as strategy to recover the catalytically active species *via* light-induced metal carbonyl dissociation.^[2]

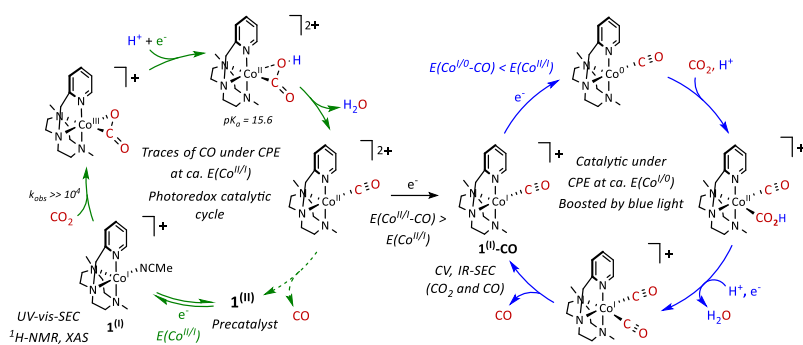


Figure 1. Proposed reaction mechanism.

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Oral Communication Abstract 14

Sergio Gonell

Mechanistic Studies on Carbene-Supported Complexes for Electrocatalytic CO₂ Reduction

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The electrochemical reduction of CO₂ is a challenging reaction of interest from a fundamental perspective and as a candidate for converting an environmentally harmful gas into a valuable fuel.¹ Ruthenium complexes bearing a 2,2':6,2''-terpyridine paired with a bidentate ligand containing mixed pyridine-N-heterocyclic carbene (Figure 1) are well established electrocatalysts for CO₂ reduction to CO.² The asymmetry of the bidentate chelating ligand raises the possibility of reaching two geometrical isomers with completely different properties.³ In this contribution, our efforts to unravel the role of each isomer in the mechanism of electrochemical CO₂ reduction will be discussed. A combination of NMR spectroscopy, cyclic voltammetry, and spectroelectrochemical infrared spectroscopy have established the influence of the isomers in the different steps of the catalytic cycle. Special attention will be paid to the effect of the bite angle of the bidentate ligand, the identity of the ligand in the precatalyst that occupies the eventual CO₂ binding site, and the nature of the metal center used.

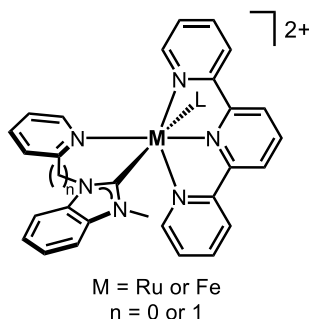


Figure 1

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