



ACCADEMIA NAZIONALE DEI LINCEI E FONDAZIONE «GUIDO DONEGANI»

CONVEGNO IN MEMORIA DI RENATO UGO

# FROM HOMOGENEOUS CATALYSIS TO SURFACE ORGANOMETALLIC CHEMISTRY AND SINGLE ATOM CATALYSTS

30-31 MAGGIO 2024

## A B S T R A C T

Comitato Ordinatore: Silvio AIME (Linceo, Università di Torino), Roberto ANTONELLI (Presidente dell'Accademia Nazionale dei Lincei), Vincenzo AQUILANTI (Linceo, Università di Perugia), Sergio CARRÀ (Linceo, Politecnico di Milano), Marta CATELLANI (Linceo, Università di Parma), Gaetano GUERRA (Linceo, Università di Salerno), Gennaro MARINO (Linceo, Università di Napoli "Federico II"), Gianfranco PACCHIONI (Linceo, Università degli Studi di Milano-Bicocca), Giorgio PARISI (Presidente della Classe di Scienze Fisiche e Naturali), Maurizio PRATO (Linceo, Università di Trieste), Alberto QUADRIO CURZIO (Presidente Emerito Lincei), Antonio SGAMELLOTTI (Linceo, Università di Perugia), Adriano ZECCHINA (Linceo, Università di Torino).

## PROGRAMMA

Il convegno vuole commemorare la figura di Renato Ugo e i suoi fondamentali contributi alla chimica italiana sia sul piano della ricerca accademica che soprattutto su quello delle relazioni tra Università e impresa e della ricerca industriale. Il convegno scientifico è dedicato alle relazioni tra catalisi omogenea, chimica organometallica di superficie e catalizzatori eterogenei ad atomo singolo, un tema di grande attualità in cui i lavori pionieristici di Renato Ugo hanno fatto da apripista.

### Giovedì 30 maggio

10.00 Vincenzo AQUILANTI (Linceo, Università di Perugia): *Indirizzi di saluto*

### RENATO UGO CHIMICO

10.05 Giorgio PARISI (Presidente della Classe di Scienze Fisiche e Naturali)

10.10 Sergio CARRÀ (Linceo, Politecnico di Milano)

10.30 Alberto QUADRIO CURZIO (Presidente Emerito Lincei)

10.50 Coffee break

11.20 Fulvio UGGERI (Bracco Imaging Spa)

11.40 Rinaldo PSARO (FAST Federazione delle Associazioni Scientifiche e Tecniche, Milano)

12.00 Luigi NICOLAIS (Università di Napoli Federico II)

12.20 Andrea BAIRATI (AIRI - Associazione Italiana Ricerca Industriale)

**Chair: Gianluca FARINOLA (President, Società Chimica Italiana, Università di Bari)**

- 14.30 Christophe COPÉRET (ETH Zürich, Svizzera): *Bridging Gaps*
- 15.05 Paolo FORNASIERO (Università di Trieste, Italia): *Carbon structures with "more or less" active metals*
- 15.40 Marcella BONCHIO (Università di Padova, Italia): *Hybrid Organic-Inorganic Interfaces for Supramolecular Photosynthesis: The Quantasome Vision*
- 16.15 Coffee break
- 16.30 Invited oral poster presentations
- 17.30 Poster session

**Venerdì 31 maggio**

**Chair: Filippo DE ANGELIS (Università di Perugia)**

- 9.30 Gareth S. PARKINSON (Technische Universität Wien): *Single-atom catalysis: an atomic scale view*
- 10.05 Gianvito VILÈ (Politecnico di Milano): *New perspectives on the structure, characterization, and reactivity of single-atom catalysts*
- 10.40 Coffee break
- 10.55 Silvia BORDIGA (Lincea, Università di Torino): *From molecules to materials and from materials to molecules in the landscape of copper-based catalysts*
- 11.30 Rinaldo PSARO (Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", CNR): *A journey into the world of catalysis with Renato Ugo*
- 12.05 Concluding remarks

**POSTERS**

1. Elena BASSAN (Institut Català d'Investigació Química, Tarragona, Spagna): *Selective ethanol oxidation to ethyl acetate by an immobilized tetra-ruthenium polyoxometalate*
2. Elisa BORFECCHIA (Università di Torino): *Synchrotron-based X-ray spectroscopy to understand methane conversion over Cu-zeolites*
3. Filippo BOSSOLA (SCITEC, CNR Milano): *Tuning small metal nanoparticles and surface chemistry for enhanced hydrogen production*
4. Giovanni DI LIBERTO (Università di Milano-Bicocca): *Modelling single-atom catalysis: role of stability and coordination chemistry*
5. Giacomo FILIPPINI (Università di Trieste): *Tailored nitrogen-doped carbon dots as nano-organocatalysts in aqueous media*
6. Andrea MARTINI (Fritz Haber Institut, Berlin): *Tracking the evolution of Ni-based single atom catalysts for the CO<sub>2</sub> electroreduction reaction: an operando X-ray Absorption and Emission study assisted by machine learning techniques*
7. Lorenzo MINO (Università di Torino): *Catalysts for photo-driven H<sub>2</sub> production: from nanoparticles to single atoms*
8. Matteo MONAI (University of Utrecht): *Anchoring atoms on defective supports for small molecule activation*

9. Chiara NEGRI (Politecnico di Milano): *Quantitative kinetic insights from operando UV-Vis: an application to Cu ions redox cycle during NH<sub>3</sub>-SCR*
10. Alessandro PIOVANO (Politecnico di Torino): *Evolution of silica-supported metallocene catalysts upon ethylene polymerization: from the active sites to particles morphology*
11. Matteo SIGNORILE (Università di Torino): *MOFs as platforms for single-site catalysis*
12. Marta STUCCHI (Università di Milano): *Disclosing the role of catalyst-substrate interaction and surface dynamics in liquid-phase heterogeneous catalysis*
13. Giulia TUCI (ICCOM, CNR Pisa): *An open gate for atomically dispersed Cl-FeN<sub>4</sub> sites for oxygen reduction reaction*

*Il convegno è organizzato con il contributo della Fondazione Bracco, della Fondazione Edison e dell'AIRI*

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L'attestato di partecipazione al convegno viene rilasciato esclusivamente a seguito di partecipazione in presenza fisica e deve essere richiesto al personale preposto in anticamera nello stesso giorno di svolgimento del convegno  
The certificate of participation in the conference will be issued only following on attendance in presence and must be requested to the staff in charge on the same day of the conference.

## Bridging Gaps

Christophe COPÉRET (ETH Zürich, Switzerland)

Industrial processes, in particular large-scale ones, mostly rely on heterogeneous catalysts. The search for more sustainable processes and the changes in environmental policies impose the continuous development of improved catalyst performances and catalytic processes, as well as the exploration of alternative routes. However, due to their inherent complexity, heterogeneous catalysts are mostly developed empirically rather than through detailed structure – activity relationships as the nature of the active sites are rarely known.

In this context, our group has been interested in understanding and controlling chemistry on surfaces, with the ultimate goal to generate isolated metal sites with defined chemical environment.[1] This approach has been used to develop highly active and selective single-site catalysts that can overperform their homogeneous counterparts, but it can also provide useful information to understand and further develop industrial catalysts[2] or to study much more complex systems such as supported nanoparticles, where support effects, interfaces, alloying... remain complex to understand at the molecular level.

This lecture will be developed around these themes and will show that a careful characterization of surface sites on a molecular level is key to develop high performance catalysts and to bridge the gap between fundamental and applied catalysis.[3]

### References:

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- <sup>3</sup> a) C. Copéret Single-Sites and Nanoparticles at Tailored Interfaces Prepared via Surface Organometallic Chemistry from Thermolytic Molecular Precursors. *Acc. Chem. Res.* **2019**, *52*, 1697-1708. DOI: 10.1021/acs.accounts.9b001388. b) Deciphering Metal-Oxide and Metal-Metal Interplay via Surface Organometallic Chemistry: A Case Study with CO<sub>2</sub> Hydrogenation to Methanol. S. R. Docherty, C. Copéret *J. Am. Chem. Soc.* **2021**, *143*, 6767-6780. DOI: 10.1021/jacs.1c02555. c) Heterogeneous Alkane Dehydrogenation Catalysts Investigated via a Surface Organometallic Chemistry Approach. S. R. Docherty, L. Rochlitz, P.-A. Payard, C. Copéret *Chem. Soc. Rev.* **2021**, *50*, 5806 – 5822. DOI: 10.1039/d0cs01424a.

### Sustainable processes: Producing better and more with less

Paolo FORNASIERO (Università di Trieste)

Heterogeneous catalysis using readily available, well-defined, single atom or metal-free catalysts is of great interest in view of the increasing pressure on industry to move towards sustainable schemes of chemical production. In the energy sector, innovative materials have been shown to be able to efficiently convert biomass to diesel [1], liquid hydrogen carriers [2], hydrogen [3-4] also coupled with organic synthesis [5]. With the focus on sustainability in photocatalyst design, graphitic carbon nitride (g-CN) is becoming a very versatile semiconductor nanomaterial, well known for many applications. We have recently highlighted the key role that g-CN could play in the realm of photocatalytic organic

synthesis, [6] and showed that tailoring the structure of g-CN by means of minimally invasive post-synthetic protocols could be the solution to tackle challenging coupling reactions with great efficiency. [7-9] Photothermal catalysts, including TiN [10], have received increasing attention even though correct temperature measurements remain difficult under those conditions [11]. All these emerging catalysts are expected to go beyond fundamental research, and will propel industrial interests toward the establishment of green organic synthesis, renewable energy conversion, pollution prevention and control [12], which represent the real challenges of modern society and the focus of the present talk.

## References

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## Acknowledgements

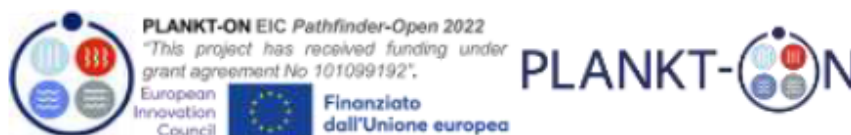
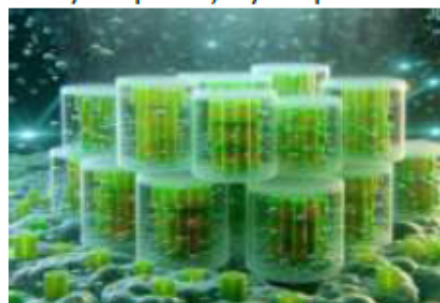
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# Hybrid Organic-Inorganic Interfaces for Supramolecular Photosynthesis: The Qantasome Vision

Marcella Bonchio

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Photosystem II (PSII) organization in natural thylakoids sets key guidelines to rethink the molecular design of innovative artificial photo-electrolysers. Building on the early “qantasome” hypothesis (Science 1964, 144, 1009-1011), PSII mimicry can be pared down to essentials by shaping a photocatalytic ensemble (from the Greek term “soma”= body) where light-quanta trigger a water oxidation. We have recently reported on PSII-inspired nanodimensional qantasomes (QS) that readily self-assemble into hierarchical photosynthetic nano-stacks, made of bis-cationic perylenebisimides as chromophores and deca-anionic tetraruthenate polyoxometalates (Ru4POM) as water oxidation catalysts (Nature Chem. 2019, 11, 146–153). A combined supramolecular and click-chemistry strategy allows to interlock the multi-lamellar architecture emerging from the perylene aromatic stacking in water, while installing tetraethylene glycol (TEG) cross-linkers thus enhancing water harvesting and transport in proximity of the oxygen evolving center (J. Am. Chem. Soc. 2022, 144,14021-14025). The resulting nanostacks evolve oxygen using low energy green photons ( $\lambda > 450$  nm, FEO<sub>2</sub> > 95 %). Action spectra, mass-activity, light-management, photoelectrochemical impedance spectroscopy (PEIS) together with Raman mapping of hydration shells, point to a key role of the supramolecular nano-arrays, where the interplay of hydrophilic, hydrophobic domains is reminiscent of PSII-rich natural thylakoids.



Plankton-Like Protocells for Artificial Photosynthesis Targeting Carbon-Neutral Energy Vectors, *Pathfinder-Open 2022, grant agreement n. 101099192*

Marcella Bonchio is Full Professor of Organic Chemistry and Delegate Director and Scientific Coordinator of National Council of Research, Institute of Membrane Technology, (ITM-CNR), section of PADOVA at the Department of Chemical Sciences, University of Padova. She has published more than 160 papers on international peer reviewed journals. Research awards include the prestigious “Lombardia è Ricerca” 1ME prize for breakthrough strategies in Artificial Photosynthesis applied to renewable energy.

<http://www.chimica.unipd.it/NanoMolCat/>



## **“Single-Atom” Catalysis: A Surface-Science Perspective**

Gareth S. PARKINSON (Technische Universität Wien)

The ability to coordinate multiple reactants at the same active site is important for the wide-spread applicability of single-atom catalysis. Model catalysts are ideal to investigate the link between active site geometry and reactant binding, because the structure of single-crystal surfaces can be precisely determined, the adsorbates imaged by scanning tunneling microscopy (STM), and direct comparisons made to density functional theory [1]. In this talk [2], we follow the evolution of Rh<sub>1</sub> adatoms and minority Rh<sub>2</sub> dimers on Fe<sub>3</sub>O<sub>4</sub>(001) during exposure to CO using time-lapse STM at room temperature. CO adsorption at Rh<sub>1</sub> sites results exclusively in stable Rh<sub>1</sub>CO monocarbonyls, because the Rh atom adapts its coordination to create a stable pseudo-square planar environment. Rh<sub>1</sub>(CO)<sub>2</sub> gem-dicarbonyl species are also observed, but these form exclusively through the breakup of Rh<sub>2</sub> dimers via an unstable Rh<sub>2</sub>(CO)<sub>3</sub> intermediate. The results illustrate how minority species invisible to area-averaging spectra can play an important role in catalytic systems, and show that the decomposition of dimers or small clusters can be an avenue to produce reactive, metastable configurations in single-atom catalysis. In the second part of the presentation, I will focus on our recent studies of Rh and Pt atoms on Fe<sub>2</sub>O<sub>3</sub>, and show that stability is achieved through a distortion of the support lattice. The reactivity of the resulting species to small molecules will be discussed.

### **References**

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### **A journey into the world of catalysis with Renato Ugo**

Rinaldo PSARO (Istituto di Scienze e Tecnologie Chimiche “Giulio Natta”, CNR)

In the field of Homogeneous Catalysis, since 1967 Renato has been one of the first scientists promoting academic studies with complexes of the transition metals as catalysts. This activity granted him many international honors, it is worth mentioning 12 papers on catalysis with palladium salts, 7 papers on catalysis with cobalt carbonyl complexes and 7 papers on catalysis with transition metal complexes.

He was a pioneer in the field of *Relation between Homogeneous and Heterogeneous Catalysis*. His first works date back to 1967-1968. The plenary lecture given on this subject in 1972 at IV International Catalysis Congress is highly significant. An important review article was published in the *Catalysis Review* in 1975, where the molecular metal cluster concept as a model of a surface or of a metal particle was discussed for the first time. Renato contributed in outlining the molecular approach to the interpretation of catalysis by metals and in general of surface processes of heterogeneous catalysis.

The subject *Surface Organometallic Chemistry* is related to the previous field of research as its logic conclusion. It is based on the study of the interaction of metal carbonyl clusters with inorganic oxide surfaces like silica, alumina and magnesia. In 1977, Renato in a pioneering work together with the group headed by Jean-Marie Basset of CNRS at Lyon,

interpreted and developed such field of surface chemistry. It has become clear that the surface of an inorganic oxide was behaving not only as a ligand but also as an electron donor, whose properties were related to acidic or basic nature of the surface oxygen or hydroxyl groups.

Renato also studied the synthesis, characterization and reactivity of complexes with silanol ligands that mimic the surface of silica. These are models of the molecular interaction between an organometallic compound and the silica surface and their reactivity allows a better understanding of the mechanisms of aggregation to form metallic nanoparticles.

However, no comment on the achievements and work of Renato would be complete without a word about his magic way of teaching and his ability to guide, inspire and encourage his student to develop their own ideas.

J.M. Basset, R. Psaro, D. Roberto and R. Ugo eds *Modern Surface Organometallic Chemistry*, 2009, WILEY-VCH