

## Biomimetic oxidation catalysis

### Foreword

I have accepted with pleasure an invitation from Prof. Pierre Braunstein, the Editor-in-Chief of the *Comptes Rendus Chimie*, the chemistry journal of the French Academy of Sciences, to act as a Guest Editor for the current special issue, dealing with *Biomimetic Oxidation Catalysis*.

We had planned for research articles, with a majority of the ‘account character’ describing (mainly) own research results in a short review. As can be seen from the current issue, we have managed to keep this aim well; the thematic issue of the journal is largely focused on homogeneous biomimetic oxidation catalysis, dealing with a variety of metals. The cover picture deals with the active site of catechol oxidase, a dinuclear Cu enzyme, responsible for many everyday oxidation processes. The artist’s impression displays it on a background of a famous Van Gogh painting, *Irisés*, acknowledged in the first paper of the issue (Belle et al.).

The present issue in fact deals with 14 contributions from groups that are all actively involved in oxidation catalysis. The several contributions to this issue come from a variety of countries and regions from the world, from academic institutes and industries.

Oxidations occur everywhere in nature and in industry, and on large scales. Nature has developed, during the evolution, smart systems (enzymes) that can perform highly selective oxidation reactions, in efficient catalytic processes. Mankind has tried to find inspiration from nature to make synthetic catalytic systems that mimic (at least), or compete with (the ultimate aim), enzymatic catalysis. The fastest enzymatic reaction, i.e. that of the enzyme superoxide dismutase (1 billion turnovers per second), is still a far-away goal. The second best catalyst system in nature makes a turnover of 1 million, and is also not yet in reach from model systems.

Each of the papers in this thematic issue covers an example of such biomimetic and bio-inspired systems, of course without the intention to be complete. Nature

primarily uses the transition metals V, Mn, Fe, Cu, Mo and W for oxidations, in some cases assisted by radical groups on the protein side chains, or by prosthetic groups, like hemes. Not all these topics can of course be treated in a single issue of the journal, and we had chosen to focus on porphyrins and copper, and give relatively little attention to molybdenum, non-heme iron, and manganese. We also decided to give proper attention to applications in industry for catalysis and for materials, as is seen from a number of papers.

The issue as a whole covers a variety of themes, but all directly related to biomimetic oxidation catalysis and all based on metal coordination complexes. In several contributions, the selective conversion of hydrocarbons with H<sub>2</sub>O<sub>2</sub> using biomimetic non-heme iron and manganese oxidation catalysis is addressed. The catalytic processes covered include alkane hydroxylation, cis-dihydroxylation, aromatic hydroxylation and olefin epoxidation.

We have included a few contributions where the porphyrins play a crucial role in oxidations. Daniel Mansuy (Paris) provides an excellent, brief history of the contribution of metalloporphyrin models to cytochrome P450 chemistry and oxidation catalysis. If hemes are immobilized, they can be important biomimetic electrocatalytic reduction species for nitric oxide, as illustrated in detail by Matheus T. de Groot, Maarten Merx, Marc M. Koper (Leiden and Eindhoven).

Stefania Nicolis, Luigi Casella, Raffaella Roncone, Corrado Dallacosta, Enrico Monzani (Pavia, Milan) give a detailed overview of heme–peptide complexes for use as peroxidase models. They successfully link a peptide residue to hemin, to introduce substrate selectivity and stereoselectivity in the catalytic activity; the axial ligands play a crucial role in this process. By using microperoxidases, they can prepare complexes with high activity and substrate selectivity.

Non-heme iron is discussed by Mallayan Palaniandavar and Ramasamy Mayilmurugan, who show that mononuclear non-heme iron(III) complexes can

be very good functional models for the intradiol-cleaving catechol dioxygenases and protocatechuate 3,4-dioxygenases. The mononuclear, octahedral cis-facially coordinated complexes of iron(III) with phenolate and non-phenolate ligands efficiently catalyze the intradiol cleavage of 3,5-di-*tert*-butylcatechol.

A number of contributions deal with copper chemistry. In the opening article, Catherine Belle, Katalin Selmecezi, Stéphane Torelli, and Jean-Louis Pierre (Grenoble) give a detailed overview of the chemical tools used in the mechanistic studies on catechol oxidase activity. Patrick Gamez, Sunita Gupta, and Jan Reedijk (Leiden) discuss the copper-catalyzed oxidative coupling of 2,6-dimethylphenol and address the question whether this is a radical-based or an ionic polymerization. The structure–activity correlations in highly pre-organized dicopper catechol oxidase model systems are discussed in a full paper by Jens Ackermann, Silke Buchler, and Franc Meyer (Heidelberg).

Chika Nozaki Kato and Wasuke Mori (Japan) discuss the oxidation catalysis of microporous metal carboxylate complexes, with a focus on dinuclear copper(II) building bricks, but also dinuclear mixed-valence Ru compounds have been studied. Chemical models relevant to the enzyme nitroalkane-dioxygenase, a rare Fe enzyme, are discussed by Eva Balogh-Hergovich, Jozsef Kaizer, Gabor Speier (Veszprem, Hungary). Applications of biomimetic Fe- and Cu-mediated reactions and complexes, and their use as functional models in oxygenations of 2-nitropropane are presented.

An important industrial contribution deals with design and application of transition metal catalysts for laundry bleach, and is present from Henkel industries by Torsten Wieprecht, Menno Hazenkamp, Hauke Rohwer, Gunther Schlingloff, and Juntao Xia. It appears that manganese is very important here, as well as iron. Detailed attention is given to well-chosen ligand variations.

Manganese in oxidation catalysis is also discussed in detail by Johannes W. de Boer, Wesley R. Browne, Ben L. Feringa, and Ronald Hage (Groningen and Unilever). A focus is put on carboxylate-bridged dinuclear manganese systems, in field varying from catalases to oxidation catalysis.

The report of Chandan Mukherjee, Thomas Weyhermüller, Eberhard Bothe, and Phalguni Chaudhuri deals

with a manganese(IV)-monoradical complex, mimicking the function of amine oxidases and phenoxazinone synthase. This Mn(IV)-radical complex catalyzes the oxidation of primary amines with aerial dioxygen as the sole oxidant to afford aldehydes under mild conditions.

A special topic is highlighted by Craig L. Hill, Laurent Delannoy, Dean C. Duncan, Ira A. Weinstock, Roman F. Renneke, Richard S. Reiner, Rajai H. Atalla, Jong Woo Han, Daniel A. Hillsheim, Rui Cao, Travis M. Anderson, Nelya M. Okun, Djameladdin G. Musaev, and Yurii V. Geletii (Emory, Atlanta), who discuss a variety of complex catalyst systems. In fact, a number of interrelated catalysis research results are presented: (1) catalytic photochemical functionalization of unactivated C–H bonds by polyoxometalates; (2) self-repairing catalytic systems; (3) catalysts for air-based oxidations under ambient conditions; (4) terminal oxide complexes of the late transition-metal elements and their use in oxidations.

The final chapter by Martin Jarenmark, Håkan Carlsson, and Ebbe Nordlander deals with asymmetric dinuclear metal complexes as models for active sites in hydrolases and redox enzymes; the authors elegantly show that Nature not only had used (asymmetric) dinuclear metal sites for oxidations, but in some cases also for other important reactions, like hydrolases. The analogy is striking, and the similarities and differences are discussed in detail by the authors.

All senior authors and their co-authors in this special issue are gratefully acknowledged for their efficient collaboration and efforts made to closely meet the set deadlines for the production of this issue. The Editor-in-Chief and I believe that these 14 contributions cover important advances in inorganic and bioinorganic chemistry, in particular in the field of biomimetic oxidation catalysis. It is to be expected that this area will prove to be of fundamental interest to a variety of environmental, biological and industrial processes. I trust that the general readership of this journal will also benefit from this thematic issue.

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