

# CONFERENCE REPORT

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## Modern Aspects of Catalysis The Spring Meeting of the Swiss Chemical Society, University of Geneva, March 9<sup>th</sup> 2007

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**Abstract:** The 2007 Spring meeting of the Swiss Chemical Society was held at the University of Geneva on Friday March 9<sup>th</sup>. The general theme was catalysis and the different speakers covered various aspects of the field. Karl Anker Jørgensen discussed organic catalysis, and Robert Schlögl heterogeneous catalysis. Martyn Poliakoff presented the use of supercritical solvents in catalysis and Richard Schrock discussed the homogeneous catalytic reduction of nitrogen to ammonia. Finally Sir John Meurig Thomas illustrated the many ways in which catalysis contributes to modern life.

**Keywords:** Catalysis · Enantioselective catalysis · Nitrogen reduction · Supercritical solvents

The Spring meeting of the Swiss Chemical Society was held on March 9<sup>th</sup> 2007 at the University of Geneva. The theme uniting the lectures by the five invited speakers was catalysis, in all its forms, and its successes and future challenges.



Karl Anker Jørgensen

The first speaker, **Karl Anker Jørgensen** (University of Aarhus, Denmark) illustrated the theme of catalysis by organic molecules. He illustrated how nonracemic organic amines more or less closely related to proline could be used to form chiral enamines or enaminones, and allow high yielding enantioselective functionalisation in positions  $\alpha$ -,  $\beta$ -,  $\gamma$ - to aldehyde carbonyls with a wide variety of functional groups. Emphasis was laid on using a general purpose amine rather than seeking a different amine for each reaction. Combining several activations in one step, domino reactions, led to diastereoselective syntheses of cyclic molecules with up to three stereogenic centres controlled by the catalyst. The lecture concluded with the use of cinchona alkaloids as phase transfer catalysts to prepare chiral alkenes. Apart from the impressive synthetic results, his talk showed the power of modern molecular chemistry, with DFT calculations of reaction pathways to explain transition states and stereoselectivity and crystal structures of models intermediates.

The second speaker, **Robert Schlögl** (Fritz Haber Institut, Berlin) discussed heterogeneous catalysis, and emphasised the difference between the well characterised catalysts of



Prof. Robert Schlögl

the previous talk and the often poorly characterised but highly efficient heterogeneous systems. *In situ* study of these catalysts is essential if their mode of action is to be understood, and the active sites are often very different from what might be imagined upon extrapolation from a simple single crystal surface. Thus electron microscopy of a vanadium pentoxide on titania catalyst shows not only different zones of  $V_2O_5$  but also different zones of both rutile and anatase. Studies on the hydrogenation of pentynes by palladium metal show that complete hydro-

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generation occurs initially, but a carbonaceous layer builds up below the surface, restricting the diffusion of hydrogen from the bulk of the metal and resulting in a catalyst active for partial hydrogenation only. Here electron microscopy and lattice imaging can be used to establish the incorporation of carbon in the palladium lattice. The oxidation of butane to maleic anhydride catalysed by vanadium oxide requires initial activation of the precatalyst to give an active species with small oxide crystals, but if the crystals grow the catalyst loses activity. The study of a complex oxide catalyst based on Mo, V, Nb and Te showed a strong dependence of properties on the temperature. Catalytic activity is concentrated at the disordered ends of crystals, and X-ray spectroscopy shows that partial reduction of molybdenum is required for catalytic activity. If the talk emphasised the complexity of heterogeneous catalysis, it also showed how modern physical methods can gradually unravel the complexities.



Sir John Meurig Thomas (left) and Martyn Poliakoff (right)

After a pause for lunch and the annual general meeting of the Swiss Chemical Society, the afternoon session began with the award of the Sandmeyer prize to a research team from Ciba Speciality Chemicals and the ETH Zürich for the development of a new synthetic method for acylphosphaneoxide photoinitiators. The third lecture by **Martyn Poliakoff** (University of Nottingham, United Kingdom) gave a new look at the solvents used for catalytic reactions. Supercritical fluids offer a number of interesting properties in comparison with more traditional solvents: the two most popular, carbon dioxide and water are environmentally friendly, and the solubilities of non-polar gases such as hydrogen and oxygen are greatly enhanced in these solvents. It has been possible to develop continuous flow reactors which can effect hydrogenation and hydroformylation in essentially quantitative yield. The elimination of purification steps can compensate for the extra investment needed for the supercritical fluid, and reactors capable of production of up to a thousand tonnes per year are now available. Oxygen in supercritical

water is a sufficiently powerful oxidant to be used for recycling precious metals in catalyst recovery. The speaker discussed some of the objectives of green chemistry, emphasising that any technology which helps to achieve these should be considered, with particular attention to large-scale processes which give low yields or large amounts of unwanted side products such as the 4 kg of ammonium sulphate produced for each kilo of caprolactam used for polymer synthesis. The final part of the lecture considered more exotic solvents such as fluorosolvents which may be switched from biphasic to homogeneous by controlling the temperature, and the use of fluorosoluble surfactants to dissolve enzymes in supercritical CO<sub>2</sub> or fluorosolvents.



Prof. Richard Schrock

The fourth lecture was given by **Richard Schrock** (MIT, Cambridge, USA) and focussed on a challenge which catalysis has yet to solve, the reduction of dinitrogen to ammonia. In terms of number of molecules, this is probably the most important industrial process in chemistry, with world production of the order of 100 million tonnes per annum. The Haber-Bosch process has been improved over the years, but still requires high temperature and pressure, while biology can carry out the same reaction at ambient temperature and pressure. It may at first sight seem remarkable that this simple diatomic molecule cannot yet be activated, but the transformation of a nitrogen molecule to two ammonium ions requires addition of six electrons and eight protons, and thus fourteen elementary steps, comparable with many natural product syntheses. After describing the enzyme nitrogenase, the speaker presented his system based on a single molybdenum ion complexed by a sterically hindered tripod ligand. A mechanistic scheme was proposed in which the nitrogen is progressively reduced and protonated, with the molybdenum shuttling between oxidation states III, IV, V, and VI to provide the most favourable coordination environment for the nitrogen at any given state of reduction. Many of the intermediates have been isolated and characterised. A major problem is that the potential of the reductant and the

pK of the proton source must be tuned both to the requirements of nitrogen, and to avoid the reduction of the proton by the reductant – it is a slight consolation to know that biology also has this problem, since nitrogenase also shows hydrogenase activity. The system can turn over and gives about 60% yield of ammonia compared to the enzyme's yield of 80%. Hydrogen is also generated, but significantly no hydrazine, a strong point in comparison with Shilov's system (the only other reasonably effective model) which generated more hydrazine than ammonia.

The final talk of the day by **Sir John Meurig Thomas** (University of Cambridge, UK) was destined equally for the general public and covered the importance of catalysis in everyday life. He pointed out that catalysis is involved in about 80% of chemical manufacturing processes. The phenomenon was recognised by the Greeks, and acid catalysis was used by Arabic alchemists for the preparation of ether. Catalysis plays a vital role in the elimination of waste, avoids the use of dangerous reagents, and will play an increasing role in energy production. He illustrated these ideas with a wealth of examples from different areas including the unwanted catalytic destruction of the ozone layer, olefin metathesis (illustrated by dancing Hungarians), and ammonia production. Biological catalysts were illustrated by the use of carbonic anhydrase to allow rapid incorporation of <sup>15</sup>CO<sub>2</sub> into blood for positron emission tomography, and the structure of lysozyme. Catalysis for energy was exemplified by the fuel cell (first invented in the nineteenth century by his fellow Welshman Sir William Robert Grove) and the three-way catalyst developed for automobile exhausts. Frequent reference was made to aspects discussed by previous speakers of the day.



The very high level of the talks attracted a large and enthusiastic audience from industry and academia

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