

Organometallic Chemistry and Applied Catalysis

A REVIEW OF THE FOURTH ANGLO-DUTCH SYMPOSIUM

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The Anglo-Dutch Symposium on organometallic chemistry and applied catalysis was held at the University of Utrecht, The Netherlands, on the 26th and 27th October 2000. The fourth in this series of meetings (1) attracted over 100 delegates with 42 posters and 18 talks covering a wide range of projects related to catalysis. In particular, a number of highlights relevant to platinum group metals chemistry were described.

Homogeneous Catalysis

Professor J. M. Brown (University of Oxford) gave an elegant presentation dealing with the detection of rhodium-based intermediates during the hydrogenation of enamide substrates. When the hydrogenation of an enamide by $[\text{Rh}(\text{PHANEPHOS})(\text{MeOH})_2]^+$ was examined using parahydrogen-based sensitisation of the NMR experiment, a new intermediate was detected. This intermediate contained both rhodium hydride and agostic hydrogen units with the latter interacting strongly with the α -carbon of the enamide substrate. The intermediate corresponds to the direct precursor of the essential alkyl hydride and serves to illustrate the continuing opportunities offered by the parahydrogen technique. Several other talks served to illustrate how varying the ligand environment around a metal can control reactivity. For example, G. P. F. van Strijdonck (University of Amsterdam) described how palladium-catalysed C-C and C-N bond formations could be facilitated by bisphosphine ligand systems – in conjunction with secondary sulfur and oxygen donors (the xantphos family). Details of the kinetics associated with the cross-coupling of PhBr and aminoarenes were shown to vary, depending on whether halide abstraction from $\text{Pd}(\text{P-P})(\text{Ar})\text{Br}$ was achieved rapidly, via the addition of AgOTf ,

or naturally, via an initial pre-equilibrium step. Both routes, however, involved $[\text{Pd}(\text{P-P})(\text{Ar})]^+$ as the key species.

Professor J. M. J. Williams (University of Bath) demonstrated how reversible acetal or cyanohydrin formation can be used to facilitate what would otherwise be unsuccessful hydrogenation reactions. This was explained by reference to the palladium-catalysed hydrogenation of a vinyl aldehyde via initial conversion to the acetal in acidified methanol (MeOH). After hydrogenation, subsequent MeOH elimination leads to the rapid formation of the required aldehyde. An impressive summary by Professor K. Vrieze (University of Amsterdam) detailed how the successful synthesis of nitrogen diimine ligands and their subsequent attachment to palladium allowed CO insertion reactions to be achieved.

High Throughput Screening

Other notable developments reported were based around the session on high throughput screening and parallel synthesis in catalysis. This started with an overview by Professor G.-J. M. Gruter (Eindhoven University of Technology-Avantium Technologies B.V.), before M. L. Turner (University of Sheffield) and Professor J. N. H. Reek (University of Amsterdam) illustrated the benefits of rapid screening. Turner described how rapid parallel screening using a multi-channel reactor developed at Sheffield allowed the heterogeneous conversion of CO to ethanol to be optimised. An elegant analysis based on parent-daughter methods with crossover and mutation effects was used to rapidly deduce an optimised catalyst composition – without the need to complete runs for all possibilities. Reek focused on the solid-phase synthesis and rapid screening of

ruthenium catalysts for asymmetric hydrogen transfer reactions, such as the conversion of acetophenone to 1-phenylethanol by IR spectroscopy. A silica-immobilised catalyst was shown to exhibit good selectivity.

Earlier in the programme Professor D. Vogt (Eindhoven University of Technology), in a related talk, illustrated how the immobilisation of catalysts via carbosilane dendrimer supports, in conjunction with ceramic membranes, can remove the problem of separating products from a catalyst. In one example a palladium catalyst had been used to achieve the asymmetric hydrovinylation of styrene. The dendrimer-supported system was shown to achieve high local catalyst concentrations with site isolation overcoming deactivation.

Developments in Novel Media

Continuing with this theme, B.-J. Deelman (University of Utrecht-ATOFINA Vlissingen B.V.) talked about fluororous biphasic catalysis and A. J. Carmichael (University of Warwick) detailed opportunities offered by ionic liquids. Both presentations suggested methods for separating the catalyst from the products.

In the final presentation, Professor D. J. Cole-Hamilton (University of St Andrews) described work performed in supercritical fluids. Notable achievements included the illustration that tri-alkylphosphine complexes readily dissolve in the

supercritical fluid, have good activity for hydroformylation of alkenes and yield better selectivity for the desired straight-chain aldehyde than normal organic solvents. Furthermore, the construction of a flow reactor for supercritical fluid catalysis allowed the use of a biphasic approach involving ionic liquids in conjunction with supercritical CO₂. While the catalyst remained firmly dissolved in the ionic liquid, the aldehydes generated during catalysis were readily soluble in supercritical CO₂ and easily separated.

In summary, the symposium clearly illustrated the strengths and depth of organometallic chemistry and catalysis in the United Kingdom and The Netherlands. It will be interesting to see what new developments will be reported at the fifth meeting in this series, which is scheduled to take place in the U.K. in Sheffield in early 2002. Details of the next Symposium can be found by contacting Dr Michael Turner or Dr Anthony Haynes at the University of Sheffield.

References

- 1 B.-J. Deelman, *Platinum Metals Rev.*, 1999, 43, (3), 105; A. F. Chiffey, *ibid.*, 1998, 42, (1), 25; P. R. Ellis, *ibid.*, 1997, 41, (1), 8

The Author

Simon Duckett is a Senior Lecturer in Inorganic Chemistry at the University of York. He is interested in the study of catalytic reactions by NMR spectroscopy, applications of the parahydrogen effect, and binuclear catalysis.

Chemical Fluid Deposition of Conformal Palladium Films

Thin films of palladium (Pd) and Pd alloys have many industrial applications, such as in catalysis, gas sensors and microelectronics, where Pd film is used as contacts in integrated circuits and as seed layers for electroless plating. Pd film is presently prepared by vacuum sputtering and electroplating, but for complex topographies consistent coverage is problematic.

High-purity, contour-following conformal Pd film may be prepared by chemical vapour deposition (CVD), but at temperatures > 200°C. A drawback to this is that low deposition temperatures are needed by microelectronics to suppress mechanical stress during device fabrication and to minimise interdiffusion and reactions between adjacent layers. The thickness of CVD-produced film also varies, giving inconsistent coverage for high-aspect ratio features.

Researchers at The University of Massachusetts, U.S.A., have now succeeded in depositing highly pure, conformal Pd films onto silicon wafers and polyimide at low temperature using chemical fluid deposition (J. M. Blackburn, D. P. Long and J. J. Watkins, *Chem. Mater.*, 2000, 12, (9), 2625–2631). This involves the chemical reduction of soluble organopalladium compounds in supercritical carbon dioxide (CO₂) at 40–80°C and 100–140 bar pressure.

Deposition by hydrogenolysis of π -2-methylallyl-(cyclopentadienyl)palladium(II) in CO₂ was completed in less than 2 minutes at 60°C, yielding pure, continuous, 100–200 nm thick, reflective Pd films free from ligand-derived contamination. Conformal coverage was observed on a patterned silicon wafer with features as small as 0.1 μ m wide \times 1 μ m deep.