

Catalyst Life Cycle Conference

By Stephen Poulston and Stephen Pollington

Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, U.K.

The Catalyst Life Cycle conference, held at the University of Bath on 16–17th September, 2002, was a joint meeting of the U.K.'s Royal Society of Chemistry and Institution of Chemical Engineers under their subject groups of SURCAT, Process Technology and Applied Catalysis. This is a bi-annual thematic meeting, with a previous one in Edinburgh being on kinetics and *in situ* methods in heterogeneous catalysis. Approximately 75 participants, mostly from U.K. universities and industry, attended the conference. There were 16 oral presentations – half of which were concerned with the platinum group metals (pgms) – and a number of poster presentations. As expected from the sponsoring groups, the talks provided an interesting combination of applied catalysis and more fundamental catalytic chemistry on the microreactor scale. With the conference subtitle of 'Preparation, Activation, Deactivation and Regeneration', most talks focused on catalyst deactivation/regeneration and covered such diverse areas as large scale industrial reactions (for example, catalytic combustion and partial oxidation), automotive catalysis, fuel cells and fine chemical synthesis.

The opening invited lecture by John Birtill (consultant, U.K.) was entitled 'But will it last until the shutdown?'. This presentation introduced techniques for interpreting and predicting the effects of catalyst decay in industrial process catalysis. Kinetic expressions for describing catalyst decay and possible approaches for determining the mechanism of decay were discussed.

From the industrial plant scale the talks moved to the nanoscale with Mike Bowker (University of Reading, U.K.) describing scanning tunnelling microscopy studies of model supported-catalysts. Atomic scale processes can be observed for pgms (Rh and Pd) deposited *in situ* on TiO₂ single crystals in ultra high vacuum conditions. Effects such as spillover of chemisorbed oxygen, encapsulation under oxidising conditions and compound forma-

tion between metal and the reduced support were demonstrated.

The second invited lecture, given by Pierre Gallezot (CNRS, Villeurbanne, France), was on the stability of platinum metal catalysts in the liquid phase hydrogenation and oxidation of organic compounds. He began by outlining the main causes of catalyst deactivation: sintering, leaching and poisoning by strongly adsorbed species. One example he described was the hydrogenation of glucose to sorbitol which is used in the food and pharmaceutical industries. This reaction is usually performed with a Raney Ni catalyst which deactivates by leaching of the metal promoter. An alternative catalyst that can be used is ruthenium (Ru) on activated carbon. This has higher activity, especially when platinum (Pt) is added, and gives extremely high conversion/selectivity and higher stability than the Ni catalyst. A second example described was the total oxidation of organic pollutants in water. This uses a Ru/TiO₂ catalyst which provides advantages over homogeneous catalyst alternatives such as Cu salts, which are efficient but have issues associated with catalyst recovery.

The third and final invited lecture was by Malcolm Green (University of Oxford, U.K.) who discussed new catalysts for the conversion of methane (CH₄) to liquid hydrocarbons. Besides looking at catalysts for syngas production from CH₄, he demonstrated the performance of a new Co-based catalyst for Fischer Tropsch synthesis suggesting that gas to liquid technology would become increasingly important in the near future as oil reserves are depleted.

David Jackson (University of Glasgow, U.K.) presented work on butane dehydrogenation over a Pt/Al₂O₃ catalyst using a pulsed flow microreactor. Changes in product formation and carbonaceous residue were observed for sequential pulses of butane for different catalyst pretreatments. The first pulse produced no butene but only CH₄ and

carbonaceous residue. With subsequent pulses of butane the build up of the carbonaceous deposit increased and the selectivity to butene also increased.

Jenny Jones (University of Leeds, U.K.) presented work on sulfur poisoning of CH₄ combustion catalysed by Pt, Pd and Rh. Sulfur compounds, such as mercaptans, are used as odorants in domestic supplies of natural gas, so the effects of a range of sulfur compounds on catalyst deactivation were studied. Catalysts used were 2 wt.% Pd, Pt and Rh on alumina with a gas feed of 4% CH₄ in air. Activity was found to increase in the order: Pt < Rh < Pd. TEM helped to distinguish between sulfur-induced agglomeration and simple site blocking effects in catalyst deactivation.

Automotive Catalysis

The final session contained three presentations on automotive catalysis. The first two were concerned with NO_x storage/reduction (NSR) catalysts for NO_x control in lean-burn engines. These catalysts consist of a Pt/Ba component which stores NO_x as nitrate during lean engine operation. The engine periodically runs rich and under this condition the nitrate is decomposed and the released NO_x is reduced with the help of a Rh component in the catalyst. David James (University of Reading, U.K.) presented pulsed flow microreactor work on the effect of Pt loading on the decomposition of Ba(NO₃)₂ and the difference between using H₂ or CO as the reductant. Pt was shown to promote nitrate decomposition with the extent of the promotion increasing with Pt loading. H₂ was shown to be superior to CO in NO_x reduction.

The second presentation on NSR catalysts was by Stephen Poulston (Johnson Matthey) who described the effects of gas composition on the regeneration of nitrated or sulfated model NO_x storage catalysts consisting of Pt/Ba. Again the advantage of H₂ over CO as a reductant was highlighted. The influence of CO₂ in the simulated gas feed was also described. CO₂ is often omitted from synthetic exhaust feed compositions but has an effect on catalyst regeneration by lowering the temperature of Ba nitrate and sulfate decomposition.

The final talk by James Anderson (University of Dundee, U.K.) was on the use of an oxychlorination treatment to regenerate engine-aged three-way catalysts. Oxychlorination partially recovered catalyst activity and, in the case of Pd-based catalysts, also the oxygen storage capacity; there was some evidence for redispersion of Pt but not of Rh.

Conclusions

This short highly-directed conference provided an insight into many of the current themes of interest to catalyst scientists. Selected papers will be published in a special issue of *Catalysis Today*.

The next conference is expected to be a meeting to mark the retirement of Professor Geoff Webb on 16–18th July, 2003, at the University of Glasgow (http://www.chem.gla.ac.uk/colloquia/catalyst/Catalysis_Symposium.html). For further information visit the websites at www.rsc.org and www.icheme.org.

The Authors

Stephen Poulston is a Senior Scientist at the Johnson Matthey Technology Centre. His interests lie in automotive catalyst technology.

Steve Pollington is a Senior Scientist at the Johnson Matthey Technology Centre. He is interested in process catalysis and automotive catalyst technology.

Rhodium Dendrimer Catalysts

Rhodium (Rh) complexes have high reactivity and selectivity and could be used in the hydroformylation of long chain alkenes to form aldehydes – an important industrial process. However, due to their difficult and costly recovery this particular use of Rh has been restricted.

Now, researchers at the University of St. Andrews, Scotland, have successfully used diphenylphosphine functionalised polyhedral oligomeric silsesquioxane (POSS) dendrimers (with 16 or 48 diphenylphosphine end groups) as ligands for the Rh catalysed hydroformylation of oct-1-ene (L. Ropartz, K. J. Haxton, D. F. Foster, R. E. Morris, A. M. Z. Slawin and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 2002, (23), 4323–4334).

Unexpectedly high regioselectivity to the linear aldehyde (86%) was obtained with a POSS dendritic ligand (with a spacer of five atoms between the P atoms, and C-Si linkage). Small molecule analogues and other dendritic ligands had lower selectivity.