Institution: University of Bath

Unit of Assessment:8: Chemistry

Title of case study:
Replacement of Heavy Metal Catalysts in the Plastics Industry

1. Summary of the impact

Catalysis is a major UK industry strength and wealth generator for the UK economy. Research carried out in the group of Professor Matthew Davidson in the Department of Chemistry at the University of Bath resulted in the development of titanium and zirconium alkoxide catalysts for use in three industrial polymerisation processes and patented by the UK companies ICI Synetix and Johnson Matthey. Patents have recently also been acquired by the Indian multinational Dorf Ketal and filed by the Dutch multinational Corbion Purac. The research has resulted in the adoption of new catalysts in industry leading to increased turnover, onward dissemination and implementation of the Bath intellectual property. It has also generated £4.6M from sale of intellectual property and an increase in generated sales of new, sustainable titanium catalysts that replace heavy metals such as tin, antimony and mercury in major industrial processes. The intellectual property and process developments have been implemented globally in the poly(ethylene terephthalate) (PET) and poly(urethane) (PU) plastics markets, worth $23B and $33B, respectively, in 2010.

2. Underpinning research

The research group of Professor Matthew Davidson in the Department of Chemistry at the University of Bath has been exploring the rich chemistry of a range of ligands and their use in the stabilisation of highly reactive Lewis acidic metal centres since 1999-2000. This work has focused on the use of more environmentally friendly metals such as titanium as replacements for heavy metals such as tin, antimony and mercury in areas such as catalysis. The research is aligned to the Catalysis and Sustainable Chemical Technologies research themes within Bath Chemistry.

The development of new and increasingly active homogeneous catalysts has been one of the main driving forces behind recent advances in modern organometallic chemistry. One such area has been the need to develop new Lewis acid catalysts to mediate industrial polymerisation processes such as PET and PU manufacture, as well as for the ring-opening polymerisation (ROP) of cyclic esters. The chemistry is motivated by a drive for the use of more sustainable metals in these high-volume manufacturing processes and also by the introduction of a new generation of commercially viable, sustainable degradable plastics available from renewable resources.

Chelating N- and O-containing ligands, which are capable of providing a range of stable steric and electronic environments for catalytically active metal centres, have been the subject of considerable research for some time, not least for their ability to bind active metal centres in well-defined environments [1, 2]. This has attracted huge industrial interest, since the area of new catalyst development is highly competitive and requires a continuous process of innovation and materials development, to facilitate both new processes and new target products.

The important breakthrough resulting from this underpinning metallo-organic coordination chemistry was the discovery in 2001-2002, during Davidson's time as a Royal Society Industry Fellow with Johnson Matthey (1999-2003), that well-defined molecular titanium-based complexes being developed at Bath were highly effective in replacing the heavier and more toxic metals that were used in PET and PU polymerisation processes, notably tin, antimony and mercury. This initial discovery immediately led to follow-on industrial funding, a detailed understanding of structure-activity relationships for titanium complexes with commercially viable ligands, and the protection of the chemistry though patents led by the industrial partners as detailed below. Subsequent development in Davidson's group and at Johnson Matthey refined the molecular chemistry and processes, leading to functional catalysts that could be implemented in relevant industrial contexts. For example, this work included the synthesis and structural characterisation of a series of Group 4 metal complexes and assessment of their potential as Lewis acid catalysts for polyester synthesis. In this work, a series of ligands were prepared and their Group 4 metal complexes studied, allowing isolation of well-defined titanium and zirconium complexes which were shown to be active catalysts for the ROP of cyclic esters such as ε-caprolactone and lactide with excellent levels of conversion and control [3]. This work was subsequently developed further with industrial collaborators and funding [4, 5], exerting influence over the development of the entire Johnson Matthey metal alkoxide catalyst portfolio.

Key Researchers

Professor Matthew Davidson (Whorrod Professor of Sustainable Chemical Technologies, lead academic; at Bath since 1999)

Dr A L Johnson (PDRA, now Lecturer, at Bath 2000-), Dr M D Jones (PDRA, now Senior Lecturer; at Bath 2004-), Dr C J Chuck (Industrial PhD and PDRA, now Whorrod Fellow; at Bath 2004-)

Dr E Gullo (Industrial PDRA, 2004-2007); G F Eade (2001-2004), C L Doherty (2004-2007), A L Chmura (2006-2009) (PhD students in Davidson group); M D Lunn (2001-2005), L Paches (2004-2008) (Industrial PhD students in Davidson group)

3. References to the research

[1] M.G. Davidson, C.L. Doherty, A.L. Johnson and M.F. Mahon, Chem. Commun., **2003**, 1832-1833. *Isolation and characterisation of transition and main group metal complexes supported by hydrogen-bonded zwitterionic polyphenolic ligands*. [DOI: 10.1039/b303618a]

[2] A.L. Johnson, M. G. Davidson, M. D. Lunn, M.F. Mahon, Eur. J. Inorg. Chem., **2006**, 3088-3098 (with industrial co-authors, Johnson Matthey). *Synthesis, Isolation and Structural Investigation of Schiff-Base Alkoxytitanium Complexes: Steric Limitations of Ligand Coordination.* [DOI: 10.1002/ejic.200600113]

[3] A.J. Chmura, M.G. Davidson, M.D. Jones, M.D. Lunn, M.F. Mahon, Dalton Trans., **2006**, *7*, 887-889 (with industrial co-authors, Johnson Matthey). *Group 4 complexes of amine bis(phenolate)s and their application for the ring opening polymerisation of cyclic esters.* [DOI: 10.1039/b513345a]

[4] A.J. Chmura, M.G.Davidson, M.D. Jones, M.D. Lunn, M.F. Mahon, A.F. Johnson, P. Khunkamchoo, S.L. Roberts and S.S.F. Wong, Macromolecules, **2006**, *39*, 7250-7257 (with Johnson Matthey co-authors). *Group 4 complexes with aminebisphenolate ligands and their application for the ring-opening polymerization of cyclic esters.* [DOI: 10.1021/ma061028j]

[5] Direct industrial / translation funding
Total of £954k including: Royal Society Industry Fellowship (M G Davidson) 1999-2003 (£250k); Industrial PDRA (ICI Synetix, now Johnson Matthey) 2002-2004 (£134k); EPSRC/TSB Link Project (with ICI Synetix, now Johnson Matthey) 2004-2007 (£200k); Knowledge Transfer Account Award and Industrial co-funding (with Purac, now Corbion Purac) 2010-2013 (£270k); Industrially-funded PhD (M Lunn, L Paches), 2001-2008 (£100k).

4. Details of the impact

Impacts from this work: Adoption of new products and processes, wealth generation from Intellectual Property transfer and environmental benefits

- The performance of an existing business has been improved through the introduction of new products, processes or services – **Plastics manufacturing**
- A sector has adopted a new or significantly changed technology or process, including through acquisition and/or joint venture – **Intellectual Property transferred (raising £4.6M) and implemented**
- Highly skilled people having taken up specialist roles that draw on their research – **PhD Researchers** from the programme of work underpinning this Case Study joined **IBM, Johnson Matthey, Cyton Biosciences, EPSRC** and **Pfizer**
- The environment has been improved through the introduction of new product(s), process(es) – **Elimination of heavy metals in industrial catalysts and enhancement of processes for manufacture of degradable materials from renewable resources**

The Catalyst Industry

Catalysis is a major UK industry strength and wealth generator for the economy, and a key component of cleaner, more sustainable manufacturing processes for a wide range of products. The development of new catalysts can lead to more efficient, sustainable, cost-effective processes; those developed in Bath have been translated rapidly and effectively into industrial processes. This direct reach into major players in the global plastics industry underpins the impact of this work.

The Bath chemistry, the intellectual property pathway and product development

Three classes of titanium and zirconium catalysts for plastics manufacture have been developed at Bath and patented, covering manufacturing processes for the important polymers poly(ethylene terephthalate) (PET), poly(urethane) (PU) (with plastics markets worth $23B and $33B, respectively, in 2010) and, more recently, towards use in improved processes for poly(lactic acid) (PLA). Crucially, these catalysts are based on titanium and zirconium rather than tin, antimony or mercury, thus ***eliminating the environmentally unfriendly heavy metals*** from the catalysts used in these large-scale industrial polymerisation processes.

Demonstrating the impact of this work involves a detailed following of the original Bath-invented intellectual property but also derivative patents and processes advanced by the partner industries and their successors (ICI Synetix, Johnson Matthey; [A]). The impact outlined here focuses on PET and PU. Developing commercial applications of the third strand of Bath Group 4 catalysts (for PLA manufacture) is more recent, with patent applications in 2006 (Johnson Matthey; [A]) and a recent collaboration with Corbion Purac leading to implementation of Bath-developed benign tin-replacement catalysis for pilot scale PLA manufacture and patent filing in 2013 [A].

A critical element of the Bath research is not only the specific catalysts developed in the published work but the fact that these innovations, and the sharing of the intellectual property with Johnson Matthey, through extensive collaboration and a Royal Society Industry Fellowship for Davidson, resulted in the methodology from Bath heralding a new, more sophisticated molecular approach to catalyst design in the PET and PU areas, ***thereby influencing the development of the whole metal alkoxide Johnson Matthey catalyst portfolio***. The Bath-developed materials have been described as “first in class”, and have also resulted in the establishment of rigorous molecular design process in the industrial environment [B]:

> *“In addition to the specific catalysts and IP …, the methodology from Bath influenced the whole JM Ti- and Zr alkoxide catalyst portfolio, including establishing the rigorous molecular design of these families of materials, and the Bath Chemistry and materials are acknowledged as being “first in class” in this area. … there is thus no doubt that many of these developments including the whole Vertec^{TM} and Snapcure^{TM} portfolio can be linked directly to the Bath research.”*

In March 2011 ***Dorf Ketal****, an Indian Chemicals company who are one of the largest in the world, purchased PET and PU catalyst intellectual property from Johnson Matthey in a* ***£4.6M*** *transaction* [C]*; this income can be* **directly attributable to the Bath research** [B]. Due to the high value of the product portfolio, the sale of the order book was blocked by the UK Office of Fair Trading [D]. The intellectual property covered titanium citrate-based Vertec catalysts first characterised by Bath that are used in PET manufacture and the titanium alkoxide 'Snapcure' catalysts developed from Bath chemistry and used in PU manufacture. Dorf Ketal rebranded these products as part of their Unilink range and they are now manufactured at their new Mundra plant in India:

> *From Dorf Ketal release* [E]*: ”the plant will produce up to 10,000 metric tons of the industry's broadest portfolio of titanates annually, making it the largest facility of its kind in the world. The Mundra plant joins the company's recently expanded Dadra plant in shipping TYZOR®, and VERTEC™ organic titanates worldwide…In April 2011, the company acquired the patents, trademarks and related intellectual property for VERTEC™ polyester catalysts and SNAPCURE™ polyurethane catalysts”.*

Implementation in Industrial Processes

The titanium citrate-based catalysts first characterised in Bath have successfully replaced antimony in PET fibre and film applications, with initial impact in bottle resin (PET is the main material used in drinks bottles) with significant environmental and process benefits. In addition, the price of antimony catalysts has recently escalated rapidly due to mining restrictions in China such that there is now an additional significant upsurge in take-up of titanium-based catalysts from a cost basis. Large-scale manufacturers have made substantial process improvements in PET manufacture that allow good quality titanium-based PET; Dorf Ketal are supplying to this market. For example, a new ThyssenKrupp Uhde (Germany) process makes PET through a route in which Vertec titanium-based catalysts are the best on the market by far at matching antimony catalyst performance. These PET catalysts are part of the portfolio taken on by Dorf Ketal, to supply some of the largest PET resin plants in the world (>600 tonnes per day currently with up to 1500 tpd planned) [B]; conversion in these plants results in substantial reduction in antimony usage.

The Snapcure (now Unilink) solution has also been implemented widely for PU [F], with significant trials run with a number of large mercury catalyst users including full scale trials. This new process, based on the molecular design principles introduced by Bath, is increasingly relevant due to the onset of REACH regulations, which are, increasingly, severely restricting the use of mercury.

These new Bath-developed catalysts have thus had impact through their adoption in manufacturing processes, as a replacement for undesirable heavy metal catalysts (notably antimony and more recently mercury). In addition to their adoption in manufacturing plants, aspects of these catalysts and associated processes have been sold on internationally, providing evidence that this chemistry is of ongoing value and impact.

Key Impacts Timeline

2008 – Snapcure range of products launched by Johnson Matthey
2008-2010 – Pilot scale developments of process for various polymerisation products
2010 – Large scale implementation of Snapcure catalysis solution for polyurethane
2011 – VERTEC portfolio of PET and PU catalyst IP acquired and used by Dorf Ketal, generating £4.6M income from IP sale alone
2011 – Dorf Ketal implementing Ti catalysts in PET plant – branded Unilink, and manufactured at new Mundra plant in India demonstrating increasing global reach and uptake
2011-2013 – Molecular design principles applied to new Group 4 metal PLA catalysts trialled with Corbion Purac and patent application filed

5. Sources to corroborate the impact

[A] *Patents*

- WO2005035622 (Johnson Matthey PLC, 2005). *Catalyst for the Manufacture of Esters*, Partridge, McIntosh, Hanratty; Group 4 metal hydroxyacid complexes as **PET** catalysts. http://www.google.com/patents/WO2005035622A1
  Led directly from the molecular characterization of the ammonium titanium citrate complex described by Davidson & Partridge, *Chem. Br.* **2002**, *38(7)*, 26 (article can be accessed through http://opus.bath.ac.uk/37761/).
- WO2003018662 (Johnson Matthey PLC, 2003). *Catalysts and Curable Compositions*, Davidson, Lunn, Johnson, Stengel; Group 4 metal alkoxide complexes as **PU** catalysts http://www.google.com/patents/WO2003018662A1
- WO2004052980 (Johnson Matthey PLC, 2006). *Polymerisation Reaction and Catalyst Therefor*; Partridge, Davidson, Eade; covers a range of Group 4 metal alkoxide complexes as ring-opening polymerization catalysts for lactones and lactides. http://www.google.com/patents/WO2004052980A1

All JM intellectual property in this area sold on to Dorf Ketal as part of the IP acquisition [C]

- EP13166273.6 (Purac Biochem, 2013). *Method to Manufacture **PLA** Using a New Polymerization Catalyst*, Chuck, Davidson, Gobius du Sart; filed in May 2013.

[B] Letter of evidence of impact, R&D Director, Johnson Matthey Process Technologies

[C] *Purchase of Intellectual Property by Dorf Ketal*, *18 April 2011*
http://www.reuters.com/article/2011/04/18/idUS125100+18-Apr-2011+PRN20110418
“Dorf Ketal Purchases VERTEC™ Patents and Intellectual Property”

[D] *UK Office of Fair Trading press release on the proposed sale of business outright to Dorf Ketal*, *November/December 2010*
http://www.oft.gov.uk/shared_oft/mergers_ea02/2010/Dorf-Ketal.pdf

[E] *Dorf Ketal Announces Full Production at World's Largest Organic Titanate Plant*,
4 May 2011 http://www.prnewswire.com/news-releases/dorf-ketal-announces-full-production-at-worlds-largest-organic-titanate-plant-121228969.html

[F] *Johnson Matthey Product Case Study*
SNAPCURE – Replacing Mercury with Titanium in Catalysts for Polyurethane Elastomers
http://www.matthey.com/Sustainability2009/case-studies/products_cs_24.html