ELSEVIER

Coordination Chemistry Reviews
154 (1996) 179-192

COORDINATION
CHEMISTRY
REVIEWS

Some basic research in coordination chemistry and catalysis, related to applications for industry [1]

David T. Thompson

Consulting Chemist and Adviser on University/Industry Research Collaboration, Reading, UK

Received 22 November 1995

Contents

Abstract . . . 179
1. Introduction . . . 180
2. Investigations of the interaction of metals with olefins . . . 180
3. Early NMR studies on transition metal complexes . . . 184
4. Dinuclear metal carbonyls and related catalyst systems . . . 184
5. Some examples of liquid phase heterogeneous catalysts . . . 186
6. Some examples of gas phase heterogeneous catalysis . . . 187
7. Links between universities and industry in the area of inorganic chemistry and catalysis . . . 189
Acknowledgements . . . 191
References . . . 191

Abstract

Working with Joseph Chatt for one year, in 1962, seemed far too short a time, especially when this brief collaboration came to an abrupt end in early 1963, but this experience seeded many thoughts which have led to research activities in a wide range of basic and applied research topics relevant to defining new products and processes for industrial organizations. These include the interactions of transition metals with unsaturated hydrocarbons, the important potential of di- and polynuclear mixed metal systems in both homogeneous and heterogeneous catalysis, and many other facets, some of the most significant of which are summarized in this review.

---

[1] Dedicated to Joseph Chatt, FRS who first stimulated my enthusiasm for innovative inorganic chemistry research relevant to commercial applications.

PII S0010-8545(96)01282-9

Keywords: Transition metal/unsaturated hydrocarbon interaction; Industry; Dinuclear mixed metal system; Polynuclear mixed metal system; Homogeneous catalysis; Heterogeneous catalysis

---

1. Introduction

At the beginning of 1962 when I joined Chatt's group at the ICI Akers Research Laboratories at The Frythe in Hertfordshire there were investigations, and into the interaction of platinum group metal systems with unsaturated hydrocarbons, and studies on transition metal hydrides and other basic research topics which might give rise to ideas for useful applications. To me, as an organic chemist trained at Imperial College, with postdoctoral experience in synthetic and mechanistic studies at the University of California (UCLA), this was an eye opening experience into the potential of the new aspects of inorganic chemistry which were emerging rapidly, and contrasting strongly with the more classical inorganic chemistry I had been taught in my undergraduate days in the early 1950s.

2. Investigations of the interaction of metals with olefins

The palladium-catalyzed Wacker process had been developed in Germany in the 1950s [1] and had demonstrated for the first time an effective economic use for a platinum group metal catalyst system in solution in large scale chemical processing. Reaction (1), as originally reported in 1894, was stoichiometric:

$$C_2H_4 + PdCl_2 + H_2O \rightarrow CH_3CHO + Pd + 2HCl \qquad (1)$$

The Wacker workers had demonstrated that the reaction could be made catalytic by reoxidizing the palladium with cupric chloride and in turn reoxidizing the reduced cuprous ion with oxygen:

$$\begin{array}{l} Pd + CuCl_2 \rightarrow PdCl_2 + 2CuCl \\ \underline{2CuCl + \frac{1}{2}O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O} \\ \text{(overall) } C_2H_4 + \frac{1}{2}O_2 \rightarrow CH_3CHO \end{array}$$

In 1962, members of the development department at ICI Heavy Organic Chemicals Division were investigating the possible similar use of soluble Pd catalysts for the manufacture of vinyl acetate [2].

$$CH_2{=}CH_2 + CH_3CO_2H + \frac{1}{2}O_2 \rightarrow CH_2{=}CH.CO.OCH_3 + H_2O \qquad (2)$$

The research group working at Teesside were seeking the advice and experience of Chatt and members of his group. There were numerous interactive discussions at the Frythe and on Teesside on this topic, and eventually a new process was developed by the Teesside research group. The research was initially inspired by the discovery in 1960 that vinyl acetate could be formed by passing ethylene into palladium chloride contained in a solution of sodium acetate in acetic acid. Within a few years, further research developments resulted in the emergence of two quite separate processes. One was a liquid phase process developed primarily by ICI in the UK, although Hoechst also had patents in the same area. Eventually, however, corrosion problems proved to be too severe and the process was abandoned [2] A gas-phase process based on use of a supported palladium on alumina catalyst was developed subsequently and used to produce vinyl acetate. A reaction mixture of ethylene, oxygen and acetic acid is supplied to the reactors at 5–10 atm and conversions of 10–15% ethylene, 15–30% acetic acid and 60–90% oxygen are achieved at selectivities of 91–94% based on ethylene or 98–99% based on acetic acid.

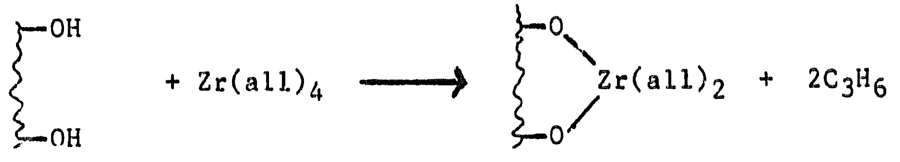
In the Akers Laboratory in 1962 we were studying chemistry related to these processes. One of my first assignments was to investigate the reversible reaction between olefins and platinum hydrides [3]. Deuterium labelling showed that the action of heat upon *trans*-$Pt(C_2H_5)Br(PEt_3)_2$ gives ethylene and *trans*-$PtHBr(PEt_3)_2$ in which the hydridic hydrogen originates from both the α and β carbon atoms of the ethyl group:

$$trans\text{-}[Pt(C_2H_5)Br(PEt_3)_2] \rightarrow trans\text{-}[PtHBr(PEt_3)_2] + C_2H_4 \quad (3)$$

The position of equilibrium in the reversible reaction between olefins and platinum hydrides depends both upon the nature of the olefin and the group trans to the hydride. In the reactions of higher olefins with *trans*-$[PtHCl(PEt_3)_2]$ and of alkyl Grignard reagents with *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$, *n*-alkyl-platinum derivatives are formed more readily than isoalkyl.

Later, during a period of secondment to ICI Plastics Division, Welwyn Garden City, the polymerization of propylene was investigated using zirconium tetraallyl systems [4] and comparing the process and the polymers produced with those obtained using the well developed Ziegler Natta titanium aluminium systems. Later work at Corporate Laboratory, Runcorn produced some exciting results for formation of polyethylene from ethylene on the surface of glass fibres immediately after their production on the spinning threadline or on organic fibres [5].

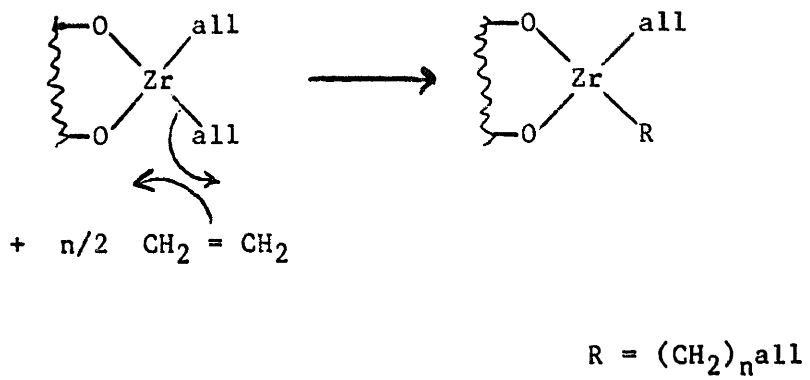
Transition-metal hydrocarbyls catalyse the polymerization of vinyl monomers [4] and these catalysts become much more effective (with respect to both activity and quality of polymer produced if supported on alumina or silica by reaction with the surface hydroxyl groups:



(4)

where all = C_3H_5.

The supported zirconium allyl species then acts as a catalyst via the usual insertion mechanism:



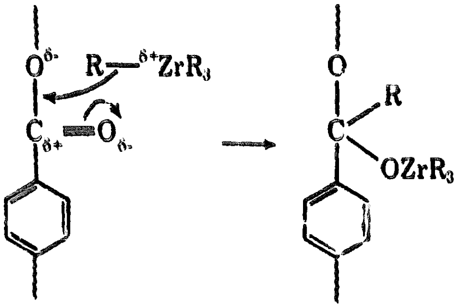
(5)

where $R = (CH_2)_n$all

Using $Zr(benzyl)_4$ on alumina, catalyst activities of the order of 10^4 g polymer (mmol catalyst)$^{-1}$ MPa^{-1} h^{-1} can be achieved over several hours, thus providing an effective means of preparing polymers having a low non-corrosive ash content.

Subsequently it was shown that much higher catalyst activities could be observed in the first few milliseconds when freshly spun glass fibres were treated with catalyst and taken through an ethylene atmosphere [6]. These activities would have corresponded to ca 10^7 g polymer (mmol catalyst)$^{-1}$ MPa^{-1} h^{-1} if they could have been maintained for a whole hour, but owing to limited access of monomer to catalyst sites (when the polymerization was carried out batchwise on chopped fibre) the activity died to zero in a few minutes. The glass fibre thus gains a protective layer of polythene, although this is very thin in the 'on-line' situation since the residence time in the ethylene chamber is very short due to the high wind-up speed of the filaments (about 1–20 m s^{-1}).

When dried, finish-free, nylon 66 or poly(ethylene terephthalate) (PET) yarn was treated with zirconium hydrocarbyl catalyst in toluene solution it was found that effectively instantaneous surface reactions took place; the catalyst solutions were decolorized, and the surface of the fibres became slightly coloured. Infrared studies demonstrated that the hydrocarbyl species reacts with the carbonyl groups of the polyester by 1,2-addition across the >C=O bond:



(6)

where R = π-allyl or benzyl.

Batch experiments demonstrated that the supported zirconium catalysts could be used to polymerize a sheath of polythene around the fibres. For example, zirconium tetrabenzyl on PET gave rise to a 30% (w/w) growth of polyethylene on the fibre (at 80°C, 2.0 MPa pressure of ethylene, 2 h in an autoclave). The morphology of the polymer on the PET was reminiscent of the worm-like growth of polyethylene produced previously on glass fibre [6], again being consistent with the polymer chains growing via repeated insertion of the ethylene molecule into a $-\mathrm{Zr}-\mathrm{R}$ bond to give $-\mathrm{Zr(CH_2)_nR}$ polymeric chains in an analogous manner to that depicted in Eq. (5).

In later work on ethylene oligomerization it was shown that the addition of alkylchloroaluminium derivatives to $\mathrm{ZrR_4}$ (R = allyl or benzyl) produces active catalysts for the preparation of $\mathrm{C_4}$–$\mathrm{C_{20}}$ α-olefins [7].

A wide range of aspects of homogeneous catalysis had been considered whilst at ICI, starting with the Wacker selective oxidations and moving on to homogeneous hydrogenations and isomerizations of unsaturated hydrocarbons, as well as polymerization and carbonylation reactions [8–13].

Homogeneous hydroformylation of olefins using rhodium catalyst systems was a principal area of interest in the Catalyst Department at Johnson Matthey (JM), which I joined in 1974. The reaction under study was the hydroformylation of propylene:

$$\mathrm{CH_3.CH{=}CH_2 + CO + H_2 \rightarrow CH_3.CH_2.CH_2.CHO + CH_3.CH(CH_3).CHO} \quad (7)$$

This investigation had been initiated following the discovery by Professor Sir Geoffrey Wilkinson (see Section 7) that the use of rhodium catalyst systems rather than the more traditional cobalt systems enabled milder conditions to be used and much higher *n*/iso ratios to be achieved. The *n*-product is much more desirable commercially since the aldol condensation reaction gives 2-ethylhexanol, the plasticizer used in the manufacture of PVC:

$$\mathrm{2CH_3.CH_2.CH_2.CHO \rightarrow CH_3.(CH_2)_3.CH(CH_2CH_3).CH_2OH} \quad (8)$$

Collaborative work between JM, Union Carbide and Davy McKee had led to the design of a low-pressure phosphine-modified rhodium process for the hydroformylation of propylene. The mechanism of this reaction involves $\mathrm{HRh(CO)_{1,2}(PPh_3)_{3,2}}$ species. The alkene coordinates to rhodium and then inserts into a Rh–H bond to give a metal alkyl. Insertion of CO into the rhodium–alkyl bond gives metal–acyl which upon hydrogenolysis gives the aldehyde with regeneration of the rhodium hydride catalyst.

Advantages of the rhodium-based process [14] are flexibility (*n*/iso ratios can be controlled from 8:1 to 16:1), lower plant capital cost, lower running costs and production of a simpler mix containing no $\mathrm{C_4}$ alcohols. The process is operated at 100°C, 7–13 atm and gives high selectivity to the aldehyde product. At the time I joined JM, the research and development work for this process was well advanced. JM's role was to provide the catalyst technology and maintain the supplies of rhodium. We now initiated a substantial research project looking at the possibility of supporting the catalyst on polymer to enable its more ready separation for the purposes of recovery and recirculation. These approaches were not included in the technology used, however, partly because the homogeneous catalyst proved to have an acceptably long lifetime (more than 1 year), and partly due to the now well known disadvantage of polymer-supported systems, i.e. metal catalyst leaching from the support.

3. Early NMR studies on transition metal complexes

The principal initial reason for my employment at the ICI Akers Laboratory was familiarity with nuclear magnetic resonance (NMR) spectroscopy, since my organic chemical research had involved studies on the use of NMR to characterize organic molecules. The use of NMR as a powerful diagnostic tool to determine the structure of molecules in solution was still at a comparatively early stage of development, but I had collaborated with Lloyd Jackman to use this new technique to good effect on both polycyclic and linear aliphatic molecules. In 1962 Chatt was keen to apply the technique to his inorganic systems, and a 60 MHz analytical NMR spectrometer was installed at The Frythe and was used for this and other purposes.

The following examples will serve to illustrate the effective use of NMR to give valuable structural information about the systems being investigated by Chatt's group.

The proton magnetic resonance spectra of complexes of hydroxyalkylacetylenes with Pt(II) were clearly consistent with intramolecular hydrogen bonding via the hydroxy groups, and it could be demonstrated that this bonding was to the chloro atoms rather than the metal atom itself — there were no high field lines characteristic of hydrides attached to Pt [15].

The second example is the establishment of a rhenium hydride structure via quantitative measure of the size of the high field hydride peaks. Treatment of the complexes $[ReX_4(PR_3)_2]$ (X = halogen, $X_4 = OCl_3$ or $O(OR')Cl_2$; R = alkyl or aryl groups) with lithium aluminium hydride gave three classes of hydride complex of general formulae $[ReH_7(PR_3)_2]$, $[\{ReH_x(PR_3)_2\}_2]$ ($x < 7$) and $[ReH_5(PR_3)_3]$ according to the actual phosphine used and the experimental conditions [16]. The observation of high field peaks which integrated for up to seven hydrides per rhenium was an unexpected result when obtained in 1962, but this assignment of structure was made very precisely using the quantitative aspects of NMR spectroscopy. Similar structural investigations on iridium hydrides are reported elsewhere [17].

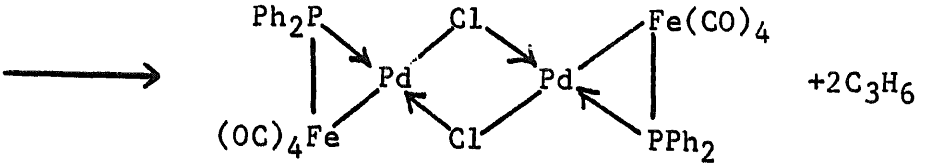
During a study of square planar platinum alkyls, *trans*-$[CH_3XPt(PEt_3)_2]$ (X = Br, CN), the Pt–H coupling constants for the methyl group depended on the group present in the trans position. When CN is substituted by Br, the central triplet for the methyl group protons moves upfield from 9.03 to 9.19, and the J_{PtH} coupling constant increases from 48 to 71 Hz, i.e. the coupling constant was increasing as the trans-effect of the trans-substituent increased [18].

4. Dinuclear metal carbonyls and related catalyst systems

This work was started at the Frythe and continued after the move to ICI Petrochemical and Polymer Laboratory (later renamed ICI Corporate Laboratory), Runcorn, Cheshire. A series of dinuclear metal carbonyls had been prepared by Chatt and Thornton [19], and the range of phosphorus-bridged dinuclear compounds was extended and the reactivity of some of the new systems studied [20,21]. A dinuclear iron compound having both a sulphur and a phosphorus bridge was also prepared and characterized [22]. When solutions of dinuclear iron or molybdenum phosphorus-bridged carbonyls were irradiated with visible light in the presence of trialkyl-, or triarylphosphines, carbonyl groups situated in positions trans to metal–metal bonds were replaced by the phosphine but carbonyl groups trans to phosphines or other carbonyl groups were not attacked. Meanwhile, an improved method for the synthesis of dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, had led to a study of its reactivity, some aspects of which turned out to be different from the reactivity of $Fe_3(CO)_{12}$ [23].

Some very interesting results were obtained with a mixed metal Pd–Fe compound, prepared in high yield by reaction between allyl palladium chloride and diphenylphosphineiron tetracarbonyl in toluene solution [24]:

$2(OC)_4FePPh_2H + [(\pi\text{-}C_3H_5)PdCl]_2$



(9)

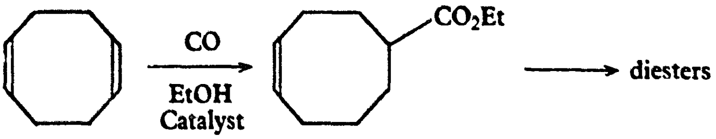
This palladium–iron compound is a good selective hydrogenation catalyst (175°C, 100 atm, 1 h) for the hydrogenation of hex-1-yne in the presence of hex-1-ene. Under test conditions (10 ppm moles metal/mole substrate), 93% of a sample of hex-1-yne in benzene was reduced to hexene and only 3% to hexane. This selectivity was unexpected since palladium is normally an excellent catalyst for the hydrogenation of olefins [25]. The effect probably arises from easier formation of a palladium–acetylene coordinate bond than a palladium–olefin bond. The rate of hydrogenation of the olefin on its own is in fact faster than the acetylene on its own. The effect is analogous to those found with supported palladium catalysts (5%Pd–$BaSO_4$) and described as 'molecular queuing.'

The carbonylation of oct-1-ene was studied under mild conditions (4% HCl, EtOH) and the activity of the palladium–iron complex compared with that of $PdCl_2(PPh_3)_2$. At 75°C and 50 atm, the total yield of esters was ten times greater for the mixed metal catalyst than for $PdCl_2(PPh_3)_2$. The threshold temperature for the reaction was about 30°C lower in the palladium–iron case than in the palladium. The isomer distribution of products was, however, about 1:1 in both cases, with a tendency for the iso to predominate:

$$CH_3(CH_2)_5CH{=}CH_2 \rightarrow CH_3(CH_2)_5CH(CH_3)CO_2Et + CH_3(CH_2)_7CO_2Et \qquad (10)$$

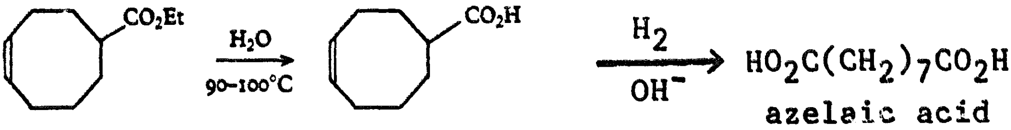
Because the 50:50 *n*/iso ratio obtained with linear olefins had comparatively little commercial potential, we next investigated the carbonylation of 1,5-cyclooctadiene

(1,5-COD):



(11)

If this reaction could be stopped selectively at the first stage, then this ester could be converted in 80% overall yield into azelaic acid via two hydrolysis steps:



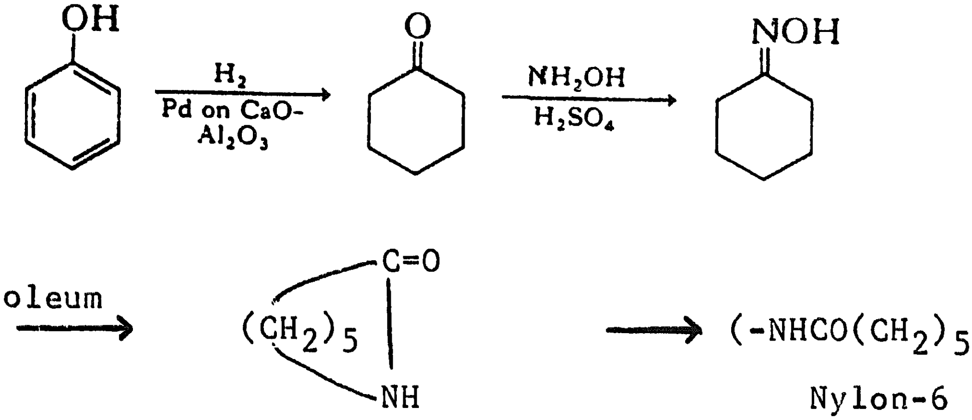
(12)

Azelaic acid is an intermediate for the manufacture of nylon-6,9, a hard nylon used for example in the manufacture of brushes. Using $PdCl_2(PPh_3)_2$ as catalyst, the optimum temperature for producing the monoester, with no diester by-product, was found to be 110°C (at 100 atm), and optimization studies [26] showed that yields of up to 7000 moles ester/g atom Pd could be obtained using anhydrous ethanol (rather than methanol), PPh_3 (rather than PBu_3), and a Lewis acid such as $FeCl_3$, $TiCl_4$ or $NbCl_5$. Under these conditions no 1,5-COD isomerized to 1,3-COD and unchanged starting material could be recycled. The Pd–Fe complex described above (see Eq. (9)) was also an effective catalyst but not as good as $PdCl_2(PPh_3)_2$–$FeCl_3$, which may give rise to $[PdCl(PPh_3)_2]^+[FeCl_4]^-$. The two hydrolysis stages give very high yields of almost pure azelaic acid, and the three stage reaction from 1,5-COD to product represents a very selective route to the synthesis of azelaic acid compared with the traditional route from castor oil which can give up to 8% impurities (e.g. other carbon number dicarboxylic acids) in the product.

New methodologies for the use of platinum group metal homogeneous catalyst systems have recently been reviewed [27]. These include a ligand-enhanced biphasic rhodium catalyst system, and the use of glass micro-beads with a chiral ruthenium catalyst. In this latter example the new heterogeneous system is basically the same as for the homogeneous system from which it derives, leading to only a small reduction in activity while retaining high enantioselectivity, an important factor in synthesis of pharmaceuticals. Further links between homogeneous and heterogeneous catalysis were considered in a 1992 review [28].

5. Some examples of liquid phase heterogeneous catalysis

Supported palladium catalysts have been investigated for a whole range of liquid phase hydrogenation reactions of commercial interest. These include the possible use of palladium on carbon catalysts in fat hardening reactions as a replacement for or alternative to the use of supported nickel catalysts; and the well established hydrogenation of phenol to cyclohexanone, the important nylon-6 intermediate [14], i.e. in the first stage of the reaction sequence indicated below the hydrogenation reaction is catalysed by Pd on CaO–Al_2O_3:



(13)

Studies on palladium solubility and hydrogen availability are discussed in an article published in 1980 [29]. Solubility of palladium from heterogeneous catalysts during hydrogenation can be a problem, particularly when nitroaromatics are reduced to aromatic amines. Palladium can be leached from the support when employing either reduced (metallic palladium) or unreduced (palladium oxide) catalysts. The palladium becomes insoluble, however, if it is converted into palladium hydride with either gaseous hydrogen or a compound which decomposes on the catalyst to give hydrogen. We can therefore conclude that palladium can be rendered insoluble if the metal can be maintained as a hydride during the catalytic reaction. This can only occur if the rate of hydrogen arrival at the metal surface is greater than the rate of consumption, i.e. the reaction must be controlled by surface kinetics and not by a parameter of mass transport.

Traditionally, liquid phase powder catalysts were manufactured with the metal located within the pore structure. This was thought to confer poison resistance on the catalyst; but work on edible oil hydrogenation suggests that palladium located on the exterior of the carbon is quite resistant to poisoning. Older catalyst manufacturing technologies gave rise to the metal being located within the pore structure. However, technology now exists to locate the metal on the catalyst particle where it will be most effective from an activity/selectivity point of view. Thus, metal can be located on the 'exterior' of the charcoal, i.e. on the outside surface and within pores greater than 1000 Å; or metal can be located exponentially from the outside of the catalyst particle to the interior; or metal can be located uniformly throughout the pore structure.

6. Some examples of gas phase heterogeneous catalysis

In 1974, when I joined the catalysis group at JM, new autocatalyst systems were in advanced stages of research, development and manufacture in order to meet the legislative requirements for the 1975 model year in the US. These systems were developed in liaison with vehicle manufacturers and based on mixed platinum group metal catalysts supported on alumina and containing other components. Early catalysts were designed to meet the legislative requirements for hydrocarbon and CO oxidation but there were even more sophisticated demands in the pipeline for the design of three-way catalysts, which also catalyse the reduction of nitrogen oxides, thus reducing NO_x emissions [30].

Both ceramic and metallic monoliths were used to support catalyst systems under investigation for use in the exhaust systems of motor vehicles. Although ceramic supported systems were chosen for production, metal supported technology continued to be utilized in research projects, and such a system was used for a very interesting investigation into catalytic combustion in gas turbines [31].

The metal monoliths used for the supported platinum catalyst systems were specially developed for this study and fitted into the combustion chamber of the turbine. The system had the advantages of low pressure drop, high temperature stability, and high surface to volume ratios [32]. The research demonstrated that efficient power generation, combined with minimum noxious emissions could be achieved in this way.

Thus the catalytic combustion system could be used to generate power from a Rover 60/65 BHP gas turbine engine. This was confirmed by running the engine at full power for a period of 60 h. The use of catalytic combustion in gas turbines in this way reduces considerably the level of carbon monoxide, hydrocarbons and nitrogen oxides emissions compared with those produced during conventional flame fired combustion. This is a result of the lower temperature of combustion, which is not sufficiently high to generate appreciable reaction between atmospheric nitrogen and oxygen to give nitrogen oxides, and the surface-catalysed free radical chain mechanism for the combustion, which lowers the levels of all the pollutants.

Metal-supported catalyst systems were also used for studies on the catalytic methanation of synthesis gas:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{14}$$

A patent was filed [33] to cover the use of ruthenium and other metal and mixed metal catalyst systems for this reaction. Selectivity to methane was in the range 61–74%. Although nickel is the metal usually used for this process, ruthenium is more active and gives high selectivity to methane at high temperatures and low pressures [14].

In a collaborative investigation at Potchefstroom University in South Africa, 0.5% ruthenium on alumina catalysts were evaluated for whether they could produce economically viable ranges of gasoline and diesel oils from the synthesis gas obtained by coal gasification [34]. Simultaneous use of ruthenium with an intermediate pore zeolite produces a high octane gasoline. Some aspects of the ruthenium process compared favourably with the established system based on iron catalyst. Ruthenium is intrinsically more expensive than iron or cobalt but it may be recovered from spent catalysts and recycled in the form of fresh catalyst, thus reducing the overall catalyst inventory. Examples of reactions taking place during Fischer Tropsch synthesis are:

$$\begin{aligned}&(n+1)H_2+2nCO \rightarrow C_nH_{2n+2}+nCO_2\\&(2n+1)H_2+nCO \rightarrow C_nH_{2n+2}+nH_2O\end{aligned} \qquad (15)$$

7. Links between universities and industry in the area of inorganic chemistry and catalysis

Chatt had insight into how basic research performed at universities or in industry can give rise to ideas upon which commercial processes might be based, and believed in devising mechanisms for stimulating dialogues between basic researchers and industrial development departments.

A mechanism used effectively by JM is the precious metals Loans Scheme for universities. This secures an initial contact with a university investigator, and can be regarded as a stimulus for such dialogues. The Loans Scheme [35] has been operative since at least the early days of this century, and there is also evidence of earlier loans. This willingness to provide innovative university investigators with precious metals and metal compounds has assisted the discovery and development of a number of notable new products and processes for JM.

The JM-Davy McKee-Union Carbide process based on the rhodium-catalyzed hydroformylation of propylene was derived from an initial discovery by Professor Sir Geoffrey Wilkinson's group at Imperial College (see Section 2) who observed the very high activity and selectivities obtainable using rhodium rather than cobalt catalysts, the rhodium having been provided under the Loans Scheme. The development of the anti-cancer drugs exemplified by cisplatin and carboplatin has had significant inputs from university and hospital research, some of it assisted by metal loans and more substantial funding from JM. Valuable insights into the formation and catalytic action of autocatalyst systems for pollution control from motor vehicles has also received valuable assistance from university research laboratories, some of the work being funded by JM in addition to providing metal loans. The Loans Scheme can therefore turn out to be an effective catalyst in that once a link with a university had been established in this way, more substantial funding is an option.

Some good examples of university/industry collaboration are described in a recently published book in which significant applications of inorganic chemistry research are described [36]. Written by both academic and industrial researchers, it gives accounts of how chemical knowledge translates to manufacturing and the market place. The wide variety of topics includes heterogeneous and homogeneous catalysts for chemical processing, catalysts for stereospecific synthesis and solar energy conversion, catalytic systems for pollution control; together with discussions of refining methods, inorganic pharmaceuticals, materials with electrical and magnetic properties, superconductors, inorganic colours, ceramics, glasses, and hard metals, corrosion inhibitors, and inorganic chemicals in water purification and the nuclear industry. it is hoped that the content of this multidisciplinary publication will stimulate constructive thoughts on directions for future research in these areas.

The principles of effective collaboration between the two types of establishment are discussed in 'Universities and Industrial Research' [37], and it may be useful to outline a few of the carefully considered conclusions reached. We must first appreciate the differences between academic research and industrial R&D, and that it is these differences that are the very source of the industrial researchers' interest in the output of academic research. Universities and Industry consist of two different cultures but each needs the other and mutual understanding and stimulating interaction is essential if the community as a whole is to derive maximum benefit. Ideas from university can stimulate new product and process lines for industry, and the wealth created by industry is necessary in order to provide funds for university teaching and research.

A principal objective within academia is to advance knowledge of the physical world; the equivalent in industry is to advance company business against competition. Though academic research topics tend to be sequential based on experience, in industry there must be a match between company needs and individual experience. In university the predominant expertise is in understanding phenomena and developing techniques, but in industry the predominant expertise is in products and processes of interest to the company. The completeness of research investigations is important in academia, but in industry timeliness is often more important than completeness. Publication of results is an important facet of university life and is usual, but publication is only encouraged in industry when the information is not valuable to competitors. In universities the advance of the subject, new ideas, and intrinsic value of the work are highly valued, whereas the equivalent in industry is new tested ideas which make an impact on the business.

Basic research can have direct industrial relevance whether performed in academia, industry or research institutes, and can give serendipitous pointers to entirely new technologies. Whilst it is possible to identify broad groups of topics that are relevant to established industries, it is much more difficult to anticipate which of a bunch of research proposals are most likely to produce results that will stimulate new ideas and new technology for industry. The principal hazard in the effective use of the funding available for innovative research is excessive and unrealistic control of what is done, and evaluation committees drawn from the university and industry spheres must realize that they cannot guarantee selection of the best areas for study based on the merits of research proposals. Funding bodies should therefore be encouraged to devise monitoring methods aimed at identifying academics who have a good track record for innovative research so that further financial support can be offered to them for new work of a relevant nature. Special arrangements are needed to identify and encourage innovative young scientists. For the most efficient generation and development of ideas it is essential for industrialists to keep in close touch with bench scientists both at university and in industry, and ensure multidisciplinary input into projects, as appropriate.

Many discoveries of industrial importance have been made by bright researchers in both university and industrial laboratories recognizing the implications and potential of scientific observations. Researchers in industry as well as university should have the freedom to follow up unexpected research discoveries which may have potential for applications.

Acknowledgements

I would like to thank all my co-workers, many of whom are cited in the list of references, for making major contributions to the success of the work described in this review.

References

[1] J. Smidt, Chem. Ind., (1962) 54.

[2] W.R. Patterson, Selective hydrocarbon oxidation, in R. Pearce and W.R. Patterson (Eds.), Catalysis and Chemical Processes, Leonard Hill, Blackie, Glasgow, 1981, pp. 251–303.

[3] J. Chatt, R.S. Coffey, A. Gough and D.T. Thompson, The reversible reaction between olefins and platinum hydrides, J. Chem. Soc. A, (1968) 190.

[4] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter and H. Zimmermann, Angew. Chem. Int. Ed. Engl., 5 (1966) 151.

[5] B. Dobbs, R. Jackson, J.N. Gaitskell, R.F. Gray, G. Lynch, D.T. Thompson and R. Whyman, Modification of poly(ethylene terephthalate) and nylon 66 surfaces by using organometallic polymerization catalysts, J. Polym. Sci., 14 (1976) 1429.

[6] B.W. Cook, J.D. Emmerson, K. Jones, R. Jackson, A.J. Margetts, S. Morris and D.T. Thompson, German Patent 2305203, 1972.

[7] C.J. Attridge, R. Jackson, S.J. Maddock and D.T. Thompson, Ethylene oligomerization with zirconium arylalkyls and alkenyls, J. Chem. Soc. Chem. Commun., (1973) 132.

[8] D.T. Thompson, Homogeneous catalysis by transition metals, Chem. Ind., (1970) 74.

[9] D.T. Thompson, Homogeneous catalysis in industry, Ind. Chim. Belge, 75 (1970) 1085.

[10] J.P. Candlin, K.A. Taylor and D.T. Thompson, Reactions of Transition Metal Complexes, Elsevier, Amsterdam, 1968, pp. 1–483.

[11] C.H. Bamford and D.T. Thompson, Polymerization process, British Patent 1 0865 066, 1967.

[12] P.J. Davidson, R.R. Hignett and D.T. Thompson, Homogeneous catalysis involving carbon monoxide, Chem. Soc. Spec. Per. Rep. Catal., 1 (1977) 369.

[13] D.T. Thompson, Carbon–carbon bond formation—carbonylation, in R. Pearce and W.R. Patterson (Eds.), Catalysis and Chemical Processes, Blackie, Glasgow, 1981, pp. 164–193.

[14] D.T. Thompson, Platinum group metal catalysts in industrial organic synthesis, Chem. Brit., (1984) 333.

[15] J. Chatt, R.G. Guy, L.A. Duncanson and D.T. Thompson, Complexes of acetylenes with platinum(II), J. Chem. Soc., (1963) 5170.

[16] J. Chatt and R.S. Coffey, Hydrido-complexes of rhenium-containing tertiary phosphines, J. Chem. Soc. A, (1969) 1963.

[17] J. Chatt, R.S. Coffey and B.L. Shaw, Hydrido complexes of iridium(III) stabilized by tertiary phosphines and arsines, J. Chem. Soc., (1965) 7391.

[18] D.T. Thompson, Spectra of platinum alkyls, MELLONMR Newsletters, September 1963.

[19] J. Chatt and D.A. Thornton, Dinuclear phosphorus and arsenic bridged carbonyl compounds. Part I, J. Chem. Soc., (1964) 105.

[20] J. Chatt and D.T. Thompson, Dinuclear phosphorus and arsenic bridged carbonyl compounds. Part II, J. Chem. Soc., (1964) 2713.

[21] D.T. Thompson, Dinuclear phosphorus and arsenic bridged carbonyl compounds. Part III Photochemical reactions with phosphines, J. Organomet. Chem., 4 (1965) 74.

[22] B.E. Job, R.A.N. McLean and D.T. Thompson, Binuclear metal carbonyls having both phosphorus and sulfur bridges, J. Chem. Soc. Chem. Commun., (1966) 895.

[23] J.P. Candlin, K.K. Joshi and D.T. Thompson, Reactivity of dodecacarbonyltriruthenium, Chem. Ind., (1966) 1960.

[24] B.C. Benson, R. Jackson, K.K. Joshi and D.T. Thompson, A new method for the preparation of mixed metal complexes, J. Chem. Soc. Chem. Commun., (1968) 1506.

[25] D.T. Thompson, Mixed metal catalysts for the synthesis of azelaic acid, Platinum Met. Rev., 19 (1975) 88.

[26] R. Jackson and D.T. Thompson, British Patent 1340873, 1973; US Patent 3952034, 1976.

[27] D.T. Thompson, Recent developments in methodologies using platinum group metal catalysts, Platinum Met. Rev., 39 (1995) 108.

[28] D.T. Thompson, The noble metals, Annu. Rep. Prog. Chem. (1992), Sect. A, Inorg. Chem., (December 1993) 209.

[29] A.J. Bird and D.T. Thompson, Palladium solubility and hydrogen availability, in Catalysis in Organic Synthesis, Academic Press, 1980, pp. 61-106.

[30] M. Bowker and R.W. Joyner, Automobile catalysts, in D.T Thompson (Ed.), Insights into Speciality Inorganic Chemicals, Royal Society of Chemistry, Cambridge, UK, 1995, pp. 145-167.

[31] B.E. Enga and D.T. Thompson, Catalytic combustion applied to gas turbine technology, Platinum Met. Rev., 23 (1979) 134.

[32] B.E. Enga and A.S. Pratt, German Patent 2809407, 1978.

[33] D.T. Thompson and M. Wyatt, Improvements in and relating to the catalytic methanation of synthesis gas, British Patent 1603101, 1977.

[34] R.C. Everson and D.T. Thompson, Liquid fuels from coal — developments in the use of ruthenium catalysts for the Fischer-Tropsch reaction, Platinum Met. Rev., 25 (1981) 50.

[35] D.T. Thompson, Johnson Matthey metals loans scheme, a continuing commitment to innovation, Platinum Met. Rev., 31 (1987) 171.

[36] D.T. Thompson (Ed.), Insights into Speciality Inorganic Chemicals, Royal Society of Chemistry, Cambridge, UK, 1995, pp. 1-505.

[37] E. Konecny, C.P. Quinn, K. Sachs and D.T. Thompson, Universities and Industrial Research, Royal Society of Chemistry, Cambridge, UK, 1995, pp. 1-181.