A quarterly journal of research on the science and technology of the platinum group metals and developments in their application in industry
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Catalysis in the Service of Green Chemistry: Nobel Prize-Winning Palladium-Catalysed Cross-Couplings, Run in Water at Room Temperature

Heck, Suzuki-Miyaura and Negishi reactions carried out in the absence of organic solvents, enabled by micellar catalysis

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Palladium-catalysed cross-couplings, in particular Heck, Suzuki-Miyaura and Negishi reactions developed over three decades ago, are routinely carried out in organic solvents. However, alternative media are currently of considerable interest given an increasing emphasis on making organic processes ‘greener’, for example, by minimising organic waste in the form of organic solvents. Water is the obvious leading candidate in this regard. Hence, this review focuses on the application of micellar catalysis, in which a ‘designer’ surfactant enables these award-winning coupling reactions to be run in water at room temperature.

1. Introduction

Decades ago, before palladium-catalysed cross-couplings arrived, copper was the transition metal of choice for mediating carbon–carbon bond formation, regardless of which organometallic complex was used as the precursor to arrive at various Cu(I) reagents. However, palladium eventually gained in popularity, and in 2010 with the recognition of Heck, Suzuki and Negishi as Nobel Prize recipients (1), the importance of Pd-catalysed carbon-carbon bond-forming reactions in organic synthesis was confirmed.

Each modern organic synthetic reaction was developed along traditional lines; that is, the chemistry was matched, not surprisingly, to an organic solvent in which the coupling best took place (Scheme 1). And while the presence of varying percentages of water is not an issue for Heck reactions that lead (2–4) to products such as cinnamates, and Suzuki-Miyaura reactions that afford (5–7), for example, arylated aromatics, the far more basic nature of organozinc halides (RZnX, R = alkyl) (8–11) in Negishi couplings (12, 13) that give products such as alkylated aromatics
None of these would typically be thought of as amenable to use in pure water especially at ambient temperatures, pKₐ issues aside, if for no other reason than that organic substrates are not normally soluble in water.

The world is paying increased attention to organic waste produced by the chemical enterprise, and organic solvents play a considerable role in this regard (14). ‘Sustainability’ is becoming a guiding principle in many areas of science and engineering (15), and the concept of ‘green chemistry’ is gaining in importance (16–21). Much emphasis, therefore, is being directed towards ‘alternative media’ (22, 23) in which synthetic chemistry can be conducted. In this way, our dependence on organic solvents, whether derived from petroleum reserves or otherwise, is minimised.

It should be appreciated that green chemistry is an all-inclusive term, and an evaluation of the full cycle (a full life cycle assessment (LCA)) of all components associated with a given process should be considered in order to fully evaluate the ‘greenness’ of that process (24–26). Clearly, reductions in major factors such as the number of steps, the number of changes in solvent(s), and the number of product isolations can play a huge role in controlling the generation of organic waste. Notwithstanding the many virtues of water as a medium, its use could be costly in terms of its downstream handling and processing, and if heating is required either during a reaction or for its eventual evaporation. But it is also acknowledged that total LCAs can be both challenging to produce, and expensive, while on the other hand, solvents, whether organic or otherwise, are well known entities that can be readily assessed, quantified, and analysed in terms of their use in manufacturing and waste disposal.

Therefore this review considers solvents alone with regard to ‘greener’ processes.

The most likely alternative among the various choices available (for example, ionic liquids (27–30), supercritical carbon dioxide (31–37) etc.), in terms of potential generality is water (38–41). To get around the substrate solubility issue, the leading candidate technology appears to be micellar catalysis, in which reactants can be ‘solubilised’ within the surrounding aqueous phase by the addition of surfactants (42, 43). Although this approach to mixing ‘oil and water’ is decades old, the nature of the surfactants available to the organic chemist through normal commercial channels is actually very modest; a handful of each type (ionic, nonionic and zwitterionic) is all that is normally seen in the literature. It seems odd, given the importance of solvent effects in organic chemistry (24–26), that the choice of amphiphile supplying the organic medium in which the chemistry is to take place would be so limited. Moreover, most common surfactants were created for use in the manufacture of paint, cosmetics, oil, cleaning fluids, leather, etc. rather than for their use in organic synthesis.

To be able to run Heck, Suzuki-Miyaura and Negishi cross-couplings in water at room temperature, thereby totally bypassing organic solvents as the reaction medium, as well as to derive energy savings by avoiding any need for either heating or cooling reaction mixtures, the requirements are: (a) identification of an existing, or possibly newly designed and synthesised surfactant that leads to results that are as good as or better than those in organic media; and (b) assurance that any amphiphile chosen is fully compliant with ‘The 12 Principles of Green Chemistry’ (44).

2. The Amphiphile TPGS-750-M

Unlike many surfactants that contain lipophilic, usually hydrocarbon fragments that have been ‘PEGylated’ (PEG = polyethylene glycol), the newly designed amphiphile DL-α-tocopherol methoxypolyethylene glycol succinate (TPGS-750-M) (1, Figure 1) has three components (45): non-natural α-tocopherol (vitamin E), a succinic acid linker, and methoxy polyethylene glycol (‘MPEG-750’). This latter, hydrophilic portion is monomethylated at one terminus and contains on average 17 oxyethyl units (750 divided by 44). The ‘TPGS’ nomenclature derives originally from Kodak’s ‘TPGS’, which by analogy is TPGS-1000, and contains the same α-tocopherol (albeit in its natural, nonracemic form) and succinic acid linker, while the PEG is PEG-1000 (which has ca. 23 oxyethanyl units.
and a free hydroxyl residue at its terminus) (46). These look very similar on paper, but their chemistry is very different, allowing opportunities to fine-tune the nanoreactors formed during micellar catalysis that serve as an organic solvent-like medium for homogeneous cross-coupling reactions in water.

In designing TPGS-750-M (45), it was anticipated that the economics of its synthesis would be quite favourable, since it is based on racemic vitamin E, succinic anhydride, and a commercially available MPEG. It can be prepared in >90% overall yield using a simple two-step procedure (45). Couplings within its larger nanomicellar interior should be as fast or faster than those in other surfactants that form smaller particles in water, since both size and shape appear to be significant (for example, TPGS-1000 forms ca. 13 nm spherical micelles, while TPGS-750-M forms ca. 60 nm particles). An important implication was that a Pd catalyst would be found for each reaction type that would function well under the high concentrations typically found in micelles. However, it was far from obvious whether the ‘rules’ of modern homogeneous catalysis, in which each process and catalyst is precisely matched with a particular organic solvent, would apply to homogeneous catalysis taking place at much higher concentrations within nanomicelles. Therefore, a wide range of Pd catalysts, obtained from Johnson Matthey, were screened for applicability to transition metal-catalysed couplings under the influence of the hydrophobic effect.

3. Heck Reactions

Cinnamate-forming reactions between aryl bromides and acrylates take place very smoothly at room temperature within the nanomicellar environment of TPGS-750-M (5 wt%) (45, 47), akin to those seen earlier in the first generation surfactant polyoxyethylenyl \( \alpha \)-tocopheryl sebacate PTS (PTS-600; Figure 2) (48, 49). The keys to success in this type of coupling are the use of 3 M sodium chloride solutions in
place of water alone, and either of the electron-rich Johnson Matthey catalysts bis(tri-tert-butylphosphine)-palladium(0) (Pd(tBu3P)2) or dichloro[1,1'-bis(di-tert-butylphosphino)]ferrocene palladium(II) (PdCl2(dtbpf)) (Figure 2). Other catalysts, such as those derived from various Pd(II) salts (for example palladium(II) acetate (Pd(OAc)2), palladium(II) chloride (PdCl2), or tris(dibenzylideneacetone)dipalladium(0) (Pd2(dba)3)) as Pd(0) precursors in the presence of various bidentate phosphine ligands were all less effective. The ‘salting out’ effect (50) of the NaCl leads to a complete alteration from spherical to worm-like micellar arrays (as seen by cryogenic transmission electron microscopy (cryo-TEM) analysis) (49) with presumably greater binding constants of substrates within the particles and hence, faster rates of reactions. Triethylamine appears to be the common base for these Heck couplings. Representative examples, in general, of (E)-favoured arylated products are shown in Scheme II.

Likewise, (E)-stilbenes constructed from aryl halides and styrene derivatives can be readily fashioned under similar micellar conditions (Scheme III) (45, 47). Reactions with aryl iodides and styrene derivatives can be performed at room temperature in aqueous micellar solutions using either deionised water or 3 M NaCl and typically are complete in less than four hours (global concentration = 0.50 M). The product stilbenes are obtained in excellent yields with >8:1 E:Z selectivity, and often precipitate directly from the reaction mixture. As with the case of acrylates (Scheme II), 3 M NaCl can be used to enhance the rates of otherwise sluggish reactions.

4. Suzuki-Miyaura Cross-Couplings

Biaryl-forming reactions of arylboronic acids and aryl or heteroaryl bromides can be efficiently catalysed by PdCl2(dtbpf) at room temperature in aqueous solutions of either PTS or TPGS-750-M. Three representative cases are illustrated in Scheme IV, including the cross-coupling of a relatively hindered 2,4,6-trisopropyl-substituted bromide.

The air stable complex, PdCl2(dtbpf), has seen less extensive use in organic solvents for Suzuki-Miyaura chemistry than its diphenyl analogue, dichloro-[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) (PdCl2(dppf)). Nonetheless, early reports from Johnson Matthey suggested far greater activity
of PdCl$_2$(dtbpf) in promoting cross-couplings of aryl chlorides over its more established relative (51). However, under micellar conditions, with challenging aryl chlorides, PdCl$_2$(dtbpf) appears not to be the catalyst of choice (Scheme V). The Pd(0) catalyst Pd($t$Bu$_3$P)$_2$ showed little improvement, despite the $t$Bu$_3$P ligand’s effectiveness at promoting Suzuki-Miyaura couplings at room temperature in tetrahydrofuran (THF) (52). And while dichlorobis($p$-methylaminophenyl-di-$t$-butylphosphine)palladium(II) (PdCl$_2$(Amphos)$_2$) showed a marked improvement, the $N$-heterocyclic carbene (NHC) bound catalyst phenylallylchloro[1,3-bis(diisopropylphenyl)imidazole-2-ylidene]palladium(II) ([IPrPd(cinnamyl)Cl] or Neolyst CX31), which has been shown to be highly efficient in an organic solvent (53), was the most effective for these reactions being carried out in nanomicelles.

Interestingly, the scope of Suzuki-Miyaura couplings in surfactant-water catalysed by this NHC-ligated catalyst proved to be rather narrow, as PdCl$_2$(Amphos)$_2$ generally provided superior results with heteroaryl chlorides (Scheme VI). More surprisingly, a large number of aryl bromide combinations for which PdCl$_2$(dtbpf) had previously proven effective (Scheme VII) failed to reach completion under catalysis with the NHC complex, despite this catalyst’s demonstrated competence with these substrate types in organic solvents (53). The effectiveness of PdCl$_2$(Amphos)$_2$ with heteroaryl coupling partners was not unexpected given early reports by Amgen researchers of its high efficiency with educts of this type in Suzuki-Miyaura reactions (54, 55). trans-Dichlorobis(tricyclohexylphosphine)palladium(II) (PdCl$_2$(Cy$_3$P)$_2$) notably led to very low conversions with heteroaromatic chlorides under PTS-water conditions, in spite of previous reports of the Cy$_3$P ligand’s effectiveness in this role for reactions in dioxane/water (albeit at elevated temperatures) (56). While an extensive study comparing specific catalysts’ efficacy in water vs. organic solvent has not been undertaken, and notwithstanding the corresponding change of other parameters (most notably the choice of base), catalysts PdCl$_2$(dtbpf) and PdCl$_2$(Amphos)$_2$ clearly do seem especially well-suited to use in water relative to organic solvents.

5. Negishi-Like Couplings in Water

Negishi couplings today have come to imply a Group 10 metal-catalysed cross-coupling between an organozinc reagent and an $sp^2$-hybridised electrophilic partner (12, 13). In fact, there were several other organometallics
Scheme III. Representative Heck couplings to form stilbenes using PdCl₂(dtbpf) in water at room temperature

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-I + Ar to form stilbene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PdCl₂(dtbpf) (2 mol%)</td>
<td>Et₃N (3 equiv.)</td>
<td>PTS or TPGS-750-M (5 wt%)</td>
</tr>
<tr>
<td>(R-O8n-N=N-N-octyl)</td>
<td>95%</td>
<td>95%</td>
</tr>
<tr>
<td>(R-N=N-BnO)</td>
<td>94%</td>
<td>94%</td>
</tr>
<tr>
<td>(R-Cl)</td>
<td>95%</td>
<td>95%</td>
</tr>
<tr>
<td>(R=NC)</td>
<td>93% (2 h)</td>
<td>(TPGS-750-M)</td>
</tr>
</tbody>
</table>

Scheme IV. Representative Suzuki-Miyaura couplings in water at room temperature

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArBr + Ar'B(OH)₂</td>
<td>ArAr'</td>
<td></td>
</tr>
<tr>
<td>PdCl₂(dtbpf) (2 mol%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surfactant-H₂O (2 wt%)</td>
<td>Et₃N (3.0 equiv.), RT</td>
<td></td>
</tr>
<tr>
<td>(TPGS-750-M)</td>
<td>93% (2 h)</td>
<td>88% (24 h)</td>
</tr>
<tr>
<td>(PTS)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

that were utilised by the Negishi school before zinc (for example, aluminium, zirconium and boron) (57–61). The synthetic potential of zinc reagents, RZnX, however, is undeniable, as they possess a suitable level of nucleophilicity to participate in a transmetalation step to a Pd(II) intermediate, while being especially
tolerant of most functionality (62). Unfortunately, however, they are definitely not tolerant of water (12, 13). Nonetheless, Negishi couplings can be, and have been, conducted in pure water (63–65). The secret to success in this unlikely methodology is avoidance of the traditional up-front use of stoichiometric Zn reagents; this is achieved by generating a zinc reagent over time on the surface of the metal, surrounded by the hydrophobic pocket of a nanomicelle. The catalyst must: (a) be readily available while tolerating exposure to water; and (b) respond favourably to the hydrophobic effect associated with micellar catalysis. One species has been identified to date that meets these criteria: PdCl$_2$(Amphos)$_2$ (54, 55) (Figure 3). Other species, including the parent bis-desamino system PdCl$_2$(tBu$_3$P)$_2$ (Figure 3), were screened, but the rates of conversion were too low to make the reaction synthetically viable. Interestingly, among the

Scheme V. Comparison of catalysts for Suzuki-Miyaura couplings of aryl chlorides in water at room temperature

Scheme VI. Comparison of NHC-containing catalysts with phosphine-ligand containing catalysts
catalysts shown in Figure 3 are selected cases that are well known to mediate Negishi couplings in THF (66, 67). Clearly, in a nanomicelle, they are not the preferred species.

There is a third essential component: the ‘gatekeeper’, without which there is no coupling whatsoever: tetramethylethylenediamine (TMEDA). TMEDA likely plays several important roles in these couplings: (i) to clean the metal surface for subsequent electron transfer; (ii) to chelate and thereby stabilise the newly formed RZnX; and (iii) to enhance the transfer of RZnX into the nanomicellar interior.

When an alkyl halide (iodide or bromide), an aryl bromide, excess TMEDA, and PdCl$_2$(Amphos)$_2$ are mixed together in water containing 2 wt% TPGS-750-M (or PTS), nanomicelles are formed containing high concentrations of these species. Upon addition of either Zn powder or dust, chemistry takes place in water at room temperature. The selective insertion of Zn into the sp$^3$-carbon-halogen bond via successive electron transfer steps is presumed to form RZnX on the metal surface, protected momentarily by the surrounding micelle. The newly formed organozinc halide, thought to be chelated by TMEDA, then enters the hydrophobic interior where a coupling partner and associated reagents are located.

As illustrated in Scheme VIII, C–C bond formation takes place smoothly with aryl bromides, including coupling with a secondary alkylzinc reagent to give product 3 in good yield (45, 63). It is especially worthy of note that traditional Negishi couplings with aryl bromides in THF do not typically occur at room temperature (Scheme IX; C) (12, 13); heating at reflux is common, especially for non-activated substrates. A control experiment using RZnX (prepared in THF) in an aqueous surfactant environment gave the expected low level of conversion due to quenching of the organozinc halide (A in Scheme IX). Thus, the hydrophobic effect adds yet another benefit to these reactions (B in Scheme IX).

Several heteroaromatic halides have also been studied under micellar catalysis conditions (Scheme X) (64). Here again, PdCl$_2$(Amphos)$_2$, used in catalytic amounts (2 mol%), is crucial for success. Bromides located on each position on a substituted pyridyl ring lead to good yields of alkylated products, although the parent 2-, 3- or 4-bromopyridines gave...
only traces of substitution. Heteroaromatics including thiophenes, benzothiophenes, indoles and quinolines appear to be amenable. As expected for organozinc reagents, excellent tolerance to functionality in either partner is observed. Noteworthy is the case of indole derivative 4, where a secondary centre can be directly inserted onto the ring in high yield.

In addition to aryl bromides, cross-couplings involving alkanyl halides are also amenable using catalyst PdCl₂(Amphos)₂, although in these cases the added feature of olefin geometry is present (Scheme XI) (65). As anticipated, (E)-alkenyl halides, whether iodides or bromides, retain their original geometry in the coupled products. Likewise, (Z)-alkenyl halides maintain their stereochemical integrity (45) which was unexpectedly found not to be the case for the corresponding reactions under traditional Negishi coupling conditions in THF (66, 67). The positive stereochemical outcome for these reactions in water is a fortunate occurrence, since the choice of ligands that help mediate these couplings (as noted above), at least to date, is not broad.
Scheme VIII. Representative Negishi-like couplings between two halides, in water at room temperature

\[ \text{R–X} + \text{Br} \rightarrow \text{R–R'} \]

(R = primary or secondary alkyl)

\[ \text{PdCl}_2(\text{Amphos})_2 \text{ (0.5 mol%) TMEDA (3–5 equiv.) Zn dust (3 equiv.) Surfactant-H}_2\text{O (2 wt%), RT}} \]

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reaction Conditions</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTS; X = I</td>
<td>82%</td>
<td></td>
</tr>
<tr>
<td>TPGS-750-M; X = Br</td>
<td>71%</td>
<td></td>
</tr>
<tr>
<td>TPGS-750-M; X = Br</td>
<td>75%</td>
<td></td>
</tr>
<tr>
<td>TPGS-750-M; X = Br</td>
<td>93%</td>
<td></td>
</tr>
<tr>
<td>TPGS-750-M; X = Br</td>
<td>74%</td>
<td></td>
</tr>
</tbody>
</table>

MOM = methoxymethyl

Scheme IX. Comparison reactions: traditional Negishi coupling conditions vs. micellar conditions

A. n-C\textsubscript{7}H\textsubscript{15}ZnI in THF
2 mol% catalyst 2
2% PTS-H\textsubscript{2}O, RT, 12 h

Conversion = 30%

B. n-C\textsubscript{7}H\textsubscript{15}I, Zn, TMEDA
2 mol% catalyst 2
2% PTS-H\textsubscript{2}O, RT, 12 h

Isolated yield = 90%

C. n-C\textsubscript{7}H\textsubscript{15}ZnI or n-C\textsubscript{7}H\textsubscript{15}I, Zn
2 mol% catalyst 2
THF, RT, 12 h

Conversion < 20%
**Scheme X. Cross-couplings of heteroaromatic and alkyl halides using catalyst PdCl$_2$(Amphos)$_2$ in water at room temperature**

FG = functional group

<table>
<thead>
<tr>
<th>Heteroaromatic (FG)</th>
<th>Alkyl (FG')</th>
<th>Heteroaromatic-alkyl (FG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{N}]OTBS</td>
<td>Ph</td>
<td>[\text{N}]OTBS</td>
</tr>
<tr>
<td>86%</td>
<td>71%</td>
<td>74%</td>
</tr>
<tr>
<td>[\text{OTBS}]</td>
<td>Cl</td>
<td>[\text{OTBS}]</td>
</tr>
<tr>
<td>82%</td>
<td>89%</td>
<td>4, 97%</td>
</tr>
</tbody>
</table>

**Scheme XI. Representative cross-couplings of alkenyl and alkyl halides, in water at room temperature**

<table>
<thead>
<tr>
<th>Alkenyl halides</th>
<th>Alkyl halides</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{BnO} ]</td>
<td>[\text{n-C}<em>7\text{H}</em>{15}]</td>
</tr>
<tr>
<td>85% (from the iodide; PTS)</td>
<td>87% (from the bromide; TPGS-750-M)</td>
</tr>
<tr>
<td>[\text{Boc}]</td>
<td>[\text{CO}_2\text{Et}]</td>
</tr>
<tr>
<td>91% (from the bromide; PTS)</td>
<td>91% (from the bromide; PTS)</td>
</tr>
</tbody>
</table>

6. Conclusions

The Nobel Prize awarded for the Heck, Negishi and Suzuki cross-coupling reactions is further recognition of the importance of the role that catalysis, in particular by Pd, plays in society. But catalysis is also a key component of green chemistry, and this requires ligands on the metal that adjust catalyst reactivity and selectivity. Catalysts that work well in traditional organic solvents at modest concentrations (usually 0.1 to 1 M in substrate) may not be the species of choice under far higher concentrations in an alternative medium such as nanomicelles in water. A completely new set of factors that control catalyst motion in and out of micelles and result in greater time spent within nanoreactors (greater binding constants) may require alternative or even newly devised ligands for Pd-catalysed cross-couplings. Thus, as an outgrowth of the hydrophobic effect, some rules for catalysis may change, giving rise to both new discoveries and opportunities for new catalysts.
Acknowledgements

Financial support provided by the National Institutes of Health (GM86485) is warmly acknowledged. We are indebted to Johnson Matthey for generously providing the catalysts and ligands that were successfully applied to the cross-coupling chemistry discussed herein.

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The Authors

Bruce Lipshutz began his career at University of California (UC) Santa Barbara, USA, in 1979, where today he is Professor of Chemistry. His programme has recently shifted towards green chemistry, with the specific goal of getting organic solvents out of organic reactions. For this, ‘designer’ surfactants have been introduced that allow for transition metal-catalyzed cross-couplings to be carried out in water at room temperature.

Ben Taft received his BS in Chemistry at California State University, Chico, in 2004. He took a PhD from UC Santa Barbara in 2008 with Bruce H. Lipshutz. He then moved to Stanford as an NIH postdoctoral fellow under Barry Trost. He began at Novartis, in Emeryville, in 2011, where he works in the oncology discovery group.

Alexander Abela carried out his graduate work in the Lipshutz group at UC Santa Barbara, focusing on transition metal-catalyzed Suzuki-Miyaura cross-coupling reactions in water and C–H activation chemistry. Following completion of his PhD, he joined the Guerrero group at UC San Diego in 2012 to continue his studies as a postdoctoral scholar.

Subir Ghorai took his PhD in 2005 from the Indian Institute of Chemical Biology. After a year of research at UC Riverside, he joined the Lipshutz group at UC Santa Barbara. Currently, he is in the Catalysis and Organometallics group at Sigma-Aldrich in Wisconsin, USA. His research interests are focused on catalysis, organometallics, and green chemistry.

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The annual SAE Congress is the vehicle industry’s largest conference and covers all aspects of automotive engineering. The 2011 World Congress was held in Detroit, USA, from 12th–14th April 2011. There were upwards of a dozen sessions focused on vehicle emissions technology, with most of them on diesel emissions. About 60 papers were presented on the topic. In addition, there was one session on gasoline engine emissions control with about six papers presented.

This review focuses on key developments related to the platinum group metals (pgms) for both diesel and gasoline engine emissions control from the conference. Papers can be purchased and downloaded from the SAE website (1). As in earlier years, the diesel sessions were opened with a review paper of key developments in diesel emissions and their control from 2010 (2).

**Lean NOx Traps**

Joseph Theis (Ford Motor Co, USA) reported (3) on an interesting study in which they alternated lean NOx trap (LNT) and selective catalytic reduction (SCR) slices in one can to check the effect of NOx, ammonia and hydrocarbon (HC) distribution on deNOx performance. The total volume of the LNT and SCR was constant as was the pgm loading on the LNT, at about 3.0 g l⁻¹. The system performance improved as the number of alternating slices of the LNT and SCR increased. As shown in Figure 1, deNOx efficiency for the eight segment system (four pairs of LNT and SCR catalysts) was 81% in a reference test at 275°C, vs. 78% for four segments and 60% for two segments. The reference single LNT with no SCR catalyst had only 30% deNOx efficiency. The authors estimate that the pgm loading on the LNT-only system would need to double to reach the performance of the four- or eight-segment system. The authors also show reduced nitrous oxide (N₂O), ammonia, HC and carbon monoxide (CO) emissions with the segmented systems. Various dynamics are operative, but the segmented systems tend to better match the nitric oxide (NO) and ammonia concentrations in the
SCR, and alternating SCR slices better adsorb HCs for enhanced utility.

Ford also reported vehicle and laboratory testing on a second generation LNT + SCR system (4). The diesel oxidation catalyst (DOC) (2.2 l, 7 g pgm) + LNT (3.6 l, 10.8 g pgm) + SCR (4.9 l) + diesel particulate filter (DPF) (6.6 l, 1.2 g pgm) system was installed on a prototype Ford F-150 pick-up truck (2610 kg, 4.4 litre V8, turbo-diesel). The aged system (64 h, 750ºC) reduced NOx by 96% to 13.5 mg mile–1, and HC emissions were 14 mg mile –1 (reduced by 99%), bringing the vehicle to within the emerging California third generation Low Emission Vehicle (LEV III) programme limit values (30 mg mile–1 HC + NOx) on the standard certification test cycle. The laboratory work focused on HC reductions from the system. The SCR component reduced HCs by about 75%, mainly by adsorption under rich conditions and oxidation under lean conditions.

Low load (low temperature) NOx exhaust emissions control is difficult using urea-SCR because urea cannot be properly evaporated and decomposed to form ammonia at low temperatures. Hiroshi Hirabayashi (Hino Motors, Ltd, Japan) reported on a new HC-SCR approach using a platinum catalyst on a front DOC, and palladium/platinum catalysts on the DPF and

![Figure 1: LNT + SCR system performance improves if the catalysts are applied in alternating segments (3). Solid lines show net NOx conversion for each catalyst system; dotted lines show N2O production.](image)
rear DOC, in addition to an undisclosed HC-adsorbant material (5). Fuel is dosed ahead of the front DOC to provide reductant. The combination system has a peak deNOx efficiency at 200ºC of about 70%, but it rapidly decreases to 20% at 275ºC. The system achieved 37% deNOx efficiency on the Japanese 2005 emission standards ('JE05') heavy-duty transient certification test cycle. Engine methods are used at higher temperatures to reduce NOx.

**Diesel Particulate Filters**

Papers at the 2011 Congress were offered on DPF regeneration, and several papers were presented on next generation DPF substrates.

More than ten years ago, in the first wide-scale application of DPFs for particulate control on light-duty diesels, Peugeot chose a ceria-based fuel borne catalyst (FBC) to facilitate the regeneration of the DPF. Researchers at Rhodia and Lubrizol described a new generation of FBC based on iron that improves DPF regeneration characteristics with or without pgms on the DPF (6). Compared to the original which contained 30 ppm cerium and 10 ppm Ce/Fe, the new formulation uses only 5 ppm Fe and gives similar performance, resulting in half the ash load on the DPF. The new FBC lowered the DPF regenerating start temperature of a stock pgm-catalysed DPF (also known as a catalysed soot filter (CSF)) from 410ºC to 360ºC, and increased the total soot burn from 12% in the baseline ramp-up test (to 500ºC) to 75% with the FBC-CSF combination. The improved regeneration efficiency and decreased temperature will reduce thermal exposure of the SCR catalyst in Euro 6 systems, as well as reducing the DPF regeneration fuel penalty when the SCR system is located upstream of the DPF.

Shingo Iwasaki (NGK Insulators, Ltd, Japan) updated the field on their development of inorganic DPF membranes to enhance filtration and reduce back pressure (7). The membrane is added to the inlet cells of the DPF and keeps the soot from entering the wall, preventing rapid back pressure build up in the early stages of filtration. In vehicle testing, pressure drop was reduced by 30%−40% depending on speed and soot load, relative to the same filter without a membrane. This membrane benefit was also demonstrated on SCR-coated DPFs in engine dynamometer testing. Alternatively, in engine tests the investigators demonstrated that the membrane can be used to increase the soot mass limit of a cordierite DPF by about 2 g l⁻¹ without a back pressure penalty by applying it to a lower porosity substrate.

Thorsten Boger (Corning Inc, USA) and his team took a different approach to reducing back pressure in DPFs (8). They tightened the pore size distribution and decreased porosity in the next generation aluminium titanate filter to provide either a 2–3 g l⁻¹ increase in soot mass limit, or a 20%−25% reduction in back pressure, depending on cell geometry. Catalysed samples of the low-pressure-drop version had 20%−30% lower back pressure with no soot on the filter and 15%−20% lower back pressure with 6 g l⁻¹ soot loading shown in Figure 2. The soot mass limit

![Figure 2](http://dx.doi.org/10.1595/147106712X630615)

**Fig. 2.** Pressure drop comparisons for the next generation aluminium titanate filter (DEV AT), in the low-pressure-drop thin wall version. 300/10 refers to 300 cells per square inch with 10 mm wall thickness. Two different catalyst coatings and two soot loadings are shown at the left. Both asymmetrical cell technology (ACT) and ‘Octosquare’ have the entry cell larger than the exit cell to add ash storage capacity and lower pressure drop (8)
was similar to that of a silicon carbide (SiC) filter with the same cell geometry, but the SiC version had 50% higher back pressure. As a result of lower thermal conductivity, the regeneration efficiency of the new filter in a standard drop-to-idle test at 575°C was 6% higher than the earlier version and 16% higher than the SiC comparison.

Taking advantage of improvements in SCR technology, future heavy-duty diesel engines will be calibrated to produce higher NOx and lower particulate matter (PM) in order to save fuel. This will result in favourable conditions for passive oxidation of soot by NO2 and will dramatically decrease the need for active regeneration of the DPF at high soot loadings. Less thermal mass will be needed in the DPF to provide a buffer against uncontrolled active regenerations. Boger and his colleagues gave a paper on their next generation thin wall cordierite filter to address this trend (9). Relative to the current offering, the pore size distribution was tightened and made nominally smaller, and the porosity was increased to ~55%. Wall thickness was reduced by 33% in the 200 cells per square inch (cpsi) geometry. To enable this, the inherent strength of the cordierite was increased. As with membrane technology, this redesigned porosity allows little, if any, soot penetration into the wall that causes rapid build-up of back pressure. Also, there is little difference between the back pressures of coated and uncoated filters. The result is that soot-laden filters have 40%–50% lower back pressure than their 2010 predecessors under a variety of conditions. Interestingly, because of the reduced thermal mass, skin temperatures are higher but centreline temperatures are the same during active regeneration, reducing the thermal stress in the part. Although the authors made no mention of soot mass limit impacts, the filter survived worst case drop-to-idle testing at 3.5 g l−1 soot. In the presentation, the authors added that the lower thermal mass of the DPF will provide a buffer against uncontrolled active regenerations. Boger and his colleagues gave a paper on their next generation thin wall cordierite filter to address this trend (9). Relative to the current offering, the pore size distribution was tightened and made nominally smaller, and the porosity was increased to ~55%. Wall thickness was reduced by 33% in the 200 cells per square inch (cpsi) geometry. To enable this, the inherent strength of the cordierite was increased. As with membrane technology, this redesigned porosity allows little, if any, soot penetration into the wall that causes rapid build-up of back pressure. Also, there is little difference between the back pressures of coated and uncoated filters. The result is that soot-laden filters have 40%–50% lower back pressure than their 2010 predecessors under a variety of conditions. Interestingly, because of the reduced thermal mass, skin temperatures are higher but centreline temperatures are the same during active regeneration, reducing the thermal stress in the part. Although the authors made no mention of soot mass limit impacts, the filter survived worst case drop-to-idle testing at 3.5 g l−1 soot. In the presentation, the authors added that the lower thermal mass of the DPF allowed faster heat-up of a downstream SCR catalyst, resulting in 10% more time for urea injection in the US certification test cycle. This can result in 15% lower cumulative NOx emissions in the cold-start test (10).

The impact of catalyst washcoat on DPF performance will become more important as more functionality is added to the DPF. Koji Tsuneyoshi and Osamu Takagi (TYK Corp, Japan) and Kazuhiro Yamamoto (Nagoya University, Japan) showed how washcoat loading can affect back pressure and filtration efficiency (11). They tested γ-alumina washcoats on SiC filters with 16.5 μm average pore size and 47% porosity. Doubling the washcoat loading from an undisclosed reference decreased the time to achieve 90% particle number filtration efficiency by 50%, to 20 seconds. The time to reach 99% efficiency dropped by 40%, to 60 seconds. Back pressure increased by 28%.

**Diesel Oxidation Catalysts**

DOCs play two primary roles in commercial emissions control systems: (a) to oxidise HCs and CO, either to reduce emissions coming from the engine, or to create exothermic reactions used to regenerate a DPF; and (b) to oxidise NO to NO2, which is used for continuously oxidising soot on a DPF, and/or for enhancing the SCR deNOx reactions, particularly at low temperatures. Cary Henry et al. (Cummins Inc, USA) and Mario Castagnola et al. (Johnson Matthey Inc, USA) used a series of iterative reaction decoupling experiments to explain interactions between HC and NO oxidation (12). They showed that inhibition of NO oxidation in the presence of HCs on Pt/Pd is due to the reduction of NO2 during HC oxidation. Long chain alkanes had a more adverse effect than short chain alkenes due to their slower oxidation rate with oxygen. Decreasing space velocity was shown to help NO2 formation in the presence of HCs. Pre-storing HCs on the DOC improved NO oxidation performance up to 300°C. At higher temperatures, coke formation from propylene, for example, inhibited NO oxidation, but stored non-coking HCs, like dodecane, maintained a positive impact at the higher temperatures. It is hypothesised that the stored HCs prevent over-oxidation of the Pt surface, thus enabling more NO adsorption and oxidation.

Researchers have been substituting Pd for Pt in DOCs for several years. However, there have been few published systematic studies on the effects of varying the Pt:Pd ratio on DOC HC and NO oxidation and durability under different conditions. Chang Hwan Kim et al. (General Motors Co, USA) and Michelle Schmid (Optimal, Inc, USA) investigated (13) the relationship between the Pt:Pd ratio and catalyst activity and stability by evaluating a series of catalysts with various Pt:Pd ratios (1:0, 7:1, 2:1, 1:2, 1:5 and 0:1). All bimetallic Pt-Pd catalysts showed better HC light-off activity and thermal stability than the Pt-only catalyst. Small amounts of Pd (Pt:Pd = 7:1) reduced the propylene light-off temperature from 205°C to 155°C, but no further improvements were observed at higher Pd levels. However, too much Pd (more than Pt:Pd = 1:5) caused light-off to deteriorate. Hydrothermal stability improves with even small Pd additions, but further additions have minimal additional impact. NO oxidation to NO2 was found to depend directly on Pt content, with better NO oxidation at
higher Pt loadings. Similar durability trends were observed as with HCs. Figure 3 shows a schematic representation of these findings. High propylene concentration (1190 ppm vs. 260 ppm) increased light-off temperatures by 20°C independently of the Pd level, but higher HC concentrations had only a small impact on the NO_2 yield. The presence of CO promoted HC oxidation, with increasing impact as Pd levels increased. There was little or no impact of CO on NO oxidation. At 300°C, high concentrations (5000 ppm) of either light or heavy HCs (propylene or n-dodecane and m-xylene) increased HC light-off temperature by 20°C, although there was increasing deterioration with increasing Pd content, especially for the heavy HCs. HC type or levels had no impact on NO oxidation, confirming that Pt content is the only driver for NO oxidation found in this study.

The use of biodiesel in place of petroleum-based fuel is mandated in the US and Europe for the coming years. The transesterification step of the vegetable oil, animal fat, or cooking oil feedstocks with methanol involves the use of an alkali catalyst, which can result in sodium and potassium ash in the fuel. Potential adverse effects of this ash on diesel emissions control components was described by a large collaborative research group led by Aaron Williams (National Renewable Energy Laboratory, USA) (14). Using an accelerated fuel ash loading method, with alkali components added at the maximum specification, combined with extensive dynamometer testing and chemical and physical analyses, the group reported that, after a simulated 150,000 miles of durability testing, HC slip increased nominally by 20%–25% over the range of temperatures in steady-state tests (240–390°C) as a result of alkali exposure from the biodiesel ash. NO_2 formation declined from 35% to 20%. In addition, the thermal shock parameter of the DPF, as indicated by mechanical property measurements, declined by 69% after simulated exposure of 435,000 miles, again due to alkali attack of the cordierite substrate. NOx emissions from the SCR increased by about 50%, but more work was needed to determine whether this was due to alkali attack of the zeolite catalyst. The group concluded that operating with fuel at the maximum alkali ash specification will significantly deteriorate emissions control system performance.

Gasoline Emissions Control
In the last year or two, the automotive industry has become increasingly interested in gasoline emissions control technology. This is driven by two regulatory developments. The first is the proposed tightening of criteria pollutant tailpipe regulations in California via the LEV III programme. Beginning in 2015 with the aim of being fully phased-in by 2025, the formal proposal is to tighten non-methane HCs (NMHCs) and NOx limits by 70% (to 30 mg mile\(^{-1}\) NMHCs + NOx) from the current LEV II standards, which are already the tightest in the world. Improved three-way catalyst (TWC) technology is the main approach to meeting these standards. The second regulatory development is the introduction of a particle number (PN) standard for Euro 6 gasoline engines beginning in 2014. Auto companies are moving towards direct injection gasoline engines to meet tightening CO2 standards, but these engines have higher PN emissions than multi-port injection engines. As such, gasoline particulate filters (GPFs) are emerging as a possible solution to meet this regulation.

Yuki Aoki et al. (Toyota Motor Corp, Japan) and Shingo Sakagami and Masaaki Kawai (Cataler Corp, Japan) reported on complex TWC coating architectures as a way of improving performance and reducing pgm loadings (15). They showed that HC light-off time is reduced by 50% if all the Pd is concentrated in the front 20% of the catalyst substrate. Conversely, because rhodium is poisoned by phosphorus (from lubricant oil ash), the Rh should be concentrated in the back 20% of the substrate. They also show that ceria-zirconia washcoats can be formulated for different properties and distributed on the substrate accordingly. Zirconia-rich recipes (0 to 0.40 ceria:zirconia mole ratio) release oxygen fastest, and therefore should be in the front half of the catalyst, while ceria-rich formulations (0.8 to 1.2) store more oxygen, and are best located in the back half. To wrap up the study, they showed that an

**Fig. 3. Conceptual impact of substituting platinum with palladium in DOCs, according to General Motors Co and Optimal, Inc (13). Moderate substitutions improve durability and HC oxidation, without significant deterioration of NO oxidation.**
alumina addition can prevent zirconia sintering and allow better Rh dispersion, and niobia can prevent grain growth of the Rh catalyst. Figure 4 shows the improved performance of the new technologies relative to a baseline catalyst.

Douglas Ball, Carlos Buitrago (Umicore Autocat USA Inc) and Michael Zammit and Jeffery Wuttke (Chrysler Group LLC, USA) (16) reported on meeting the LEV III challenge more efficiently by moving the under body catalyst to a position directly behind the close-coupled catalyst. HC and NOx emissions were cut by 25%. They also looked at optimising pgm loadings with the new design. Six formulations reduced pgm loading by up to 25% from the previous partial zero emission vehicle (PZEV) design, while meeting a 20 mg mile\(^{-1}\) NMHC + NOx limit on the federal test procedure (FTP) light-duty transient cycle. This is low enough to meet the lowest certification level in the proposed LEV III regulation.

In another contribution, Douglas Ball showed why low-sulfur gasoline is an important enabler for modern catalysts to meet the LEV III regulations (17). Figure 5 shows the results. If the fuel contains 33 ppm sulfur, the poison builds up on the catalyst in back-to-back tests (T1–T3, first set of data). If a hot US06 high-load test cycle is run, some of the sulfur is purged, dropping NOx emissions by 30% (second set of bars). Alternatively, and quite pertinent to urban low-load operation, if the fuel sulfur is dropped to 3 ppm, the NOx emissions are cut by 40% without the need for a high-load purge.

Lean burn direct injection engines are emerging to meet the current and upcoming CO\(_2\) regulations in the major world automotive markets. LNTs can in some cases be used to meet the NOx regulations, but Chang Hwan Kim \textit{et al.} and Orgun \textit{et al.} (General Motors Co, USA) showed in two papers an alternative design (18, 19). They describe a TWC+SCR approach wherein ammonia generated from the TWC during rich tip-ins in normal operation is stored and utilised in a downstream SCR catalyst for use during lean operation. The first paper (18) shows that ammonia production in the TWC is enhanced with Pd-only formulations. Rh, although beneficial for CO oxidation and stoichiometric NOx reduction, contributes little to ammonia generation. An oxygen storage catalyst (OSC) detracts from ammonia generation, but is beneficial for CO and HC oxidation. However, CO and HC oxidation can be promoted with higher Pd loadings (200 g ft\(^{-3}\) vs. 60 g ft\(^{-3}\) in the base formulation). The authors conclude that the system might be suitable for European applications, where the NOx regulations are not as tight, but more research is needed on optimising pgm and washcoat formulations, and improving the SCR catalyst durability and performance. In the second paper (19), the researchers used the TWC+SCR system in a stoichiometric direct injection engine adapted for lean idle and aggressive deceleration fuel cutoff (DFCO), saving 11% on fuel consumption. DFCO sends air through the system, cooling the catalyst and

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{New TWC coating architecture decreases stoichiometric gasoline emissions relative to a conventional double-layer catalyst. The new designs can be used to decrease the rhodium loading by 45%, while still delivering a 20% NOx reduction (‘Developed Catalyst 2’), or can reduce emissions by 30 to 45% at the same pgm loadings (15)\footnote{Fig. 4. New TWC coating architecture decreases stoichiometric gasoline emissions relative to a conventional double-layer catalyst. The new designs can be used to decrease the rhodium loading by 45%, while still delivering a 20% NOx reduction (‘Developed Catalyst 2’), or can reduce emissions by 30 to 45% at the same pgm loadings (15)}}
\end{figure}
saturating the OSC with oxygen, adversely impacting stoichiometric deNOx functionality. The combination aftertreatment system lowers NOx levels by 95% with this engine strategy compared to a TWC only system.

Conclusions
To meet tightening of criteria pollutant emissions regulations and new fuel efficiency demands, much effort is being placed on decreasing emissions on lean burn engines with less or better utility of pgm. Lean NOx trap – SCR systems are being optimised and are now moving onto much more vehicle testing. Ammonia generation from the LNT and finding optimum system configurations are at the forefront. Lean burn engines have high particulate emissions, and new filter designs (gasoline and diesel) are improving performance. DOCs have complex functionality, and even though they are decades old, work is continuing to decrease pgm costs and understand fundamental behaviour. Finally, studies on meeting the next round of tailpipe emissions tightening on stoichiometric gasoline engines show impressive pgm utilisation gains, and the adverse effects of fuel sulfur in advanced systems.

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The Reviewer

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Palladium nanoparticles are of great importance as catalytic materials, as well as for a number of other applications such as hydrogen storage and sensing. Their synthesis has been widely studied and interest in their properties is growing. Here the synthesis of palladium nanoparticles by chemical and electrochemical methods using a variety of stabilisers including organic ligands, salts/surfactants, polymers and dendrimers is reviewed and their potential benefits in catalytic applications are introduced.

1. Introduction
Nanotechnology represents one of the major breakthroughs of modern science, enabling materials of distinctive size, structure and composition to be formed. Such nanodimensional materials (in the 1–100 nm size domain) are seen as a bridge between atomic and bulk materials and have been shown to exhibit a variety of unique chemical, physical and electronic properties (1). The study of these properties has become an increasingly important area in chemistry, physics, biology, medicine, and material sciences. However, reliable preparations of the nanomaterials are required for their exploitation, and this remains an area of active research.

Whilst much research has focussed on nanomaterials of the coinage metals (especially those of gold) (2), interest in the properties of other transition metal nanomaterials is also considerable and growing (3). The high surface-area-to-volume ratio makes nanomaterials highly desirable for use as potential catalysts. Given that palladium is one of the most efficient metals in catalysis (4, 5), the study of palladium-based materials is hugely important and valuable. As a consequence, nanoparticles of palladium have been heavily studied in a wide range of catalytic applications including hydrogenations (6, 7), oxidations (8, 9), carbon–carbon bond formation (10, 11), and electrochemical reactions in fuel cells (12). However, it should be noted that...
the applications of palladium go beyond catalysis. For example, the propensity of palladium to adsorb hydrogen has also led to palladium nanoparticles being utilised in hydrogen storage (13, 14) and sensing applications (15, 16).

In the present article, the synthesis of palladium nanoparticles prepared via chemical and electrochemical routes is reviewed. The preparation of palladium nanoparticles with well-controlled particle sizes and shapes (17, 18) of a high monodispersity is a key technology in producing materials that are more effective and efficient than the current state of the art. For example, particle size can play a critical role in a catalytic process and a monodispersed particle with an optimal size enables the most efficient use of the valuable metal and the highest selectivity in the subsequent reaction.

2. Types of Stabilisation

As nanoparticles are essentially finely divided bulk materials, they are typically thermodynamically unstable with respect to agglomeration. Consequently, they need to be kinetically stabilised and this is typically done using a protective stabiliser. The stabilisation is achieved by electrostatic or steric forces or a combination of the two (electrosteric forces). The stabiliser is typically introduced during the formation of the nanoparticles, and this is achieved via the chemical or electrochemical reduction or thermal decomposition of metallic precursors. The subsequent interaction between the stabiliser and the surface of the nanoparticle is a highly dynamic one, with its strength and nature often controlling the long-term stability of a dispersion of the nanoparticles. This interaction can take many forms, such as a strong covalent linkage (as in the case of a thiol), a chemisorbed atom (for example via a lone pair of a heteroatom in a polymer) or an electrostatic interaction with a layer of anions (within a double layer structure of a surfactant).

The formation of palladium nanoparticles stabilised by the most common stabilisers (organic ligands, surfactants, polymers and dendrimers) (Figure 1) are discussed below.

3. Ligands

One of the most frequent methods of stabilising palladium nanoparticles is by the addition of an organic ligand that typically contains a heteroelement bearing an accessible lone pair. The organic chain of the ligand prevents agglomeration, whilst the heteroatom binds strongly to the surface of the metal.

3.1 Sulfur-Based Ligands

The strong interaction between the platinum group metals and soft sulfur-based donors make sulfur-containing ligands highly efficient stabilisers for nanoparticles. In the 1990s, Brust demonstrated that thiols made excellent stabilisers in the two-phase preparation of gold nanoparticles (19). The 1–3 nm diameter nanoparticles were stabilised by a monolayer of thiolate ligands and were readily isolable as dry powders and, subsequently, redispersable into non-polar solvents. This methodology has been used to prepare nanoparticles containing a wide range of precious metals including palladium. In general, it is the use of thiol and thioether ligands that

![Fig. 1. Schematic representing the stabilisation of palladium nanoparticles using different protecting groups: (a) surfactants; (b) polymers; and (c) ligands](image-url)
dominates the literature due to the high stability of the nanostructures that they can generate.

The use of sulfur-based ligands to stabilise palladium nanoparticles usually restricts their use as potential catalysts due to the poisoning effect of sulfur (20). However, this effect is not universal. For example, dodecylthiolate-stabilised palladium nanoparticles have been shown to be active catalysts for the formation of carbon nanotubes (21). Furthermore, they have been demonstrated to be a stable and recyclable catalyst in the Suzuki-Miyaura C–C coupling reaction of halogenoarenes and phenylboronic acid (Figure 2) (22), while thiolated β-cyclodextrin (HS-β-CD)-stabilised palladium nanoparticles have shown good activity in the hydrogenation of allylamine (Figure 2) (23).

### 3.1.1 Thiol Ligands

Alkanethiol-protected palladium nanoparticles can be directly prepared via the two-phase Brust methodology (Figure 3) (24). Typically, a tetrachloropalladate salt is initially phase transferred from aqueous to organic solution (in solvents such as dichloromethane or toluene) by the addition of a long-chain ammonium salt (for example, tetra-n-octylammonium bromide or Aliquat 336®). The stabilising ligand is then added to the organic phase prior to reduction with an aqueous solution of sodium borohydride. The ligand is usually introduced as a long-chain thiol molecule; however, the in situ reduction of an alkylsulfate (such as S-dodecylthiosulfate (25)) has been demonstrated to be an effective alternative strategy.

The size and morphology of the resulting palladium nanoparticles are sensitive to a number of different reaction conditions (26). These include the surfactant used (27), the reducing agent employed, the reaction time, the nature of the stabilising ligand (28), and the ratio of the palladium precursor to the other reagents (29). In general, to prepare small nanoparticles it is beneficial to use a large excess of long thiols with an excess of reducing agent (26).

The Brust route has proved to be an excellent preparative technique for the formation of nanoparticles stabilised by simple lipophilic

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**Fig. 3. Scheme illustrating the synthesis of thiol-stabilised palladium nanoparticles using the modified Brust method (24)**

**Fig. 2. Reported catalytic transformations using thiol-stabilised palladium nanoparticles (NPs): (a) Suzuki-Miyaura carbon–carbon coupling reaction of halogenoarenes and phenylboronic acid (22); and (b) hydrogenation of allylamine (23)**
n-alkanethiols (24). The use of a two-phase system also allows the organically soluble nanoparticles to be simply separated from the aqueous byproducts. However, when more polar ligands are used, the purification is less facile. There have been several variations that have enabled the fabrication of complementary nanoparticles that are soluble in aqueous or polar solvent systems.

An alternative synthetic approach allowing a wider variety of ligands to be used was achieved by Ulman and coworkers, who employed Super-Hydride® (lithium triethylborohydride, LiEt3BH) as a reductant (30). The combination of palladium(II) acetate with octylthiol resulted in a soluble metal-thiolate complex in tetrahydrofuran (THF). Addition of Super-Hydride® solution to this resulted in stable nanoparticles being formed with an average diameter of 2.3 nm.

Whilst the Super-Hydride® route allows stabilisers (such as hydroxyl-terminated alkylthiols) to be used that cannot be used in the two-phase reaction, and also avoids the use of phase transfer surfactants, there are limited solvent systems that can be used and the reductant is less easy to handle than sodium borohydride.

An alternative strategy for preparing palladium nanoparticles that are soluble in aqueous systems has been the use of 6-substituted thiol ligands (those terminated with a charged functional group, such as ammonium or carboxylate salts). Indeed, the one-phase sodium borohydride reduction of potassium tetrachloropalladate(II) in the presence of the chloride salt of the N,Ntrimethyl(undecylmercapto)ammonium ligand yielded water-soluble palladium nanoparticles with an average diameter of 2.7 nm (± 1.1 nm) (31).

Similarly, the functionalisation of watersoluble hosts with thiol groups enables the preparation of ligands that can stabilise the formation of palladium nanoparticles in aqueous solvent systems. Cyclodextrins are highly functionalised watersoluble hosts that can easily be synthetically modified (32). The sodium borohydride reduction of a dimethyl sulfoxide-water solution of the per-6-thio-β-cyclodextrin and sodium tetrachloropalladate(II) produces a colloidal dispersion (Figure 4) (23). The nanoparticles were shown to be active in hydrogenation reactions and could also be easily recovered by precipitation with ethanol.

For many precious metal nanoparticles, a successful way to introduce functionality to preformed nanoparticles is via ligand exchange (33, 34). Typically, the addition of a second ligand can statistically displace those bound to the surface of the particle without destroying the size of the metallic core. For example, the addition of a thiol ligand containing electrochemically active ferrocene derivatives could displace hexanethiol- and dodecanethiol-stabilising molecules (35), thus providing additional functionality to the nanomaterial. In addition, the replacement of one ligand by another may be desirable in order to alter the solubility of the nanoparticles (for example, from organic to aqueous solvent systems (36)) or

Fig. 4. Structure of thiol functionalised beta-cyclodextrin per-6-thio-β-cyclodextrin (HS-β-CD) (23)
to improve their solubility by introducing a better stabilising group (26,37).

3.1.2 Other Sulfur-Based Ligands
Given that there is much literature on the stabilisation of palladium nanoparticles by thiol ligands and that there is a strong interaction between palladium and sulfur, there are surprisingly few other sulfur-based ligands that have been reported as stabilisers. Two such examples are the thioether (38) and thioester (39) functional groups. The interaction between these groups and the metal surface is weaker than for thiols as the ligand is unable to form anionic species via the same mechanism by which thiols readily form thiolates. However, this can lead to advantages, with greater surface accessibility in applications such as catalysis and facile post-synthetic modifications via ligand displacement reactions (40).

The use of thioethers has enabled stabilised palladium nanoparticles to be prepared on a gram scale by heating palladium(II) acetate in the presence of an excess of the ligand (38). It was found that thioether chains greater than six carbons in length were required to form stable dispersions with a narrow particle size distribution, with longer chain lengths giving rise to smaller particle sizes. Furthermore, n-dodecylsulfide stabilised palladium nanoparticles were shown to be active hydrogenation catalysts for a range of olefins when used either unsupported or following deposition onto silica. This illustrates the accessibility of the surface when such ligands are employed and their potential benefits in catalytic applications.

3.2 Phosphorus-Based Ligands
The use of phosphorus-containing compounds in the formation of nanosystems dates back to the 19th century, when Faraday prepared gold nanoparticles by reducing tetrachloroaurate salts with phosphorus vapours (41). It is therefore not surprising that they have subsequently been exploited in the stabilisation of precious metal nanoparticles and subsequent catalytic transformations (42,43).

The use of phosphine ligands has been reported by several authors for the preparation of monodisperse palladium nanoparticles. Hyeon and coworkers reported how the thermolysis of a preformed palladium-trioctlyphosphine (TOP) complex yielded such nanoparticles (44). The mean size could be varied depending on the reaction conditions. For example, 3.5 nm nanoparticles were formed when Pd(acac)$_2$ (acac = acetylacetonate) and TOP were heated to 300°C under an argon atmosphere. When TOP was used in combination with oleylamine as a stabiliser and solvent, larger monodispersed nanoparticles up to 7.5 nm could be formed.

A further benefit of phosphine ligands is the presence of a nuclear magnetic resonance (NMR) active nucleus in close proximity to the metal surface. Examination of $^{31}$P NMR spectra has given insights into the coordination of phosphorus-based ligands to metal surfaces (45). The coordination of the phosphine ligand to a palladium nanoparticle typically results in a downfield shift in the $^{31}$P NMR peaks compared to that of the free ligand, such that it resembles that of a Pd(0)-phosphine coordination complex. While this is the case for triphenylphosphine-stabilised palladium nanoparticles, the bond to the surface is weaker in TOP and, consequently, the shift is not as great. It is thought that strong van der Waals interactions between the alkyl chains in the different TOP ligands hinder the effective adsorption of TOP ligands onto the surface of the palladium nanoparticles.

In addition to the direct preparation of phosphine-stabilised nanoparticles, indirect ligand exchange reactions can also be successfully undertaken. These reactions are particularly effective when TOP-stabilised palladium nanoparticles are used, as the weak binding of the ligand on the surface allows easy displacement. Son et al. demonstrated that a wide variety of monodentate and bi-dentate phosphines could be used to exchange with TOP (Figure 5) (45). The methodology was also used to introduce hydrophilic phosphines, which were able to solubilise the resulting nanoparticles in aqueous solvent systems. All of the exchange reactions were achieved while maintaining the monodispersity and particle size of the initial nanoparticles.

The preparation of phosphine-stabilised palladium nanoparticles has also been undertaken by Fujihara and coworkers using a two-phase process. They adapted an existing route for preparing analogous gold nanoparticles (46) by phase transferring potassium tetrachloropalladate(II) into dichloromethane using tetroctylammonium bromide before sodium borohydride reduction in the presence of optically active bidentate BINAP (2,2’-bis(diphenylphosphino)-1,1’-binaphthyl) ligands (Figure 6) (47).

The use of chiral (R)- and (S)-BINAP gave rise to the corresponding chiral palladium nanoparticles, for which circular dichroism spectra showed positive and negative Cotton effects, respectively. The nanoparticles were also effective as a catalyst in the hydroisilylation
of styrene with trichlorosilane, leading to the formation of an asymmetric product. Subsequent oxidation using hydrogen peroxide retained the chiral centre and yielded optically active 1-phenylethanol in an enantiomeric excess of 75%. This revealed the active role of the chiral ligand surrounding the palladium nanoparticles as both a promoter and an asymmetric induction reagent.

Palladium nanoparticles stabilised by BINAP-thioether-derivatives have also been used in the (quasi)homogeneous C–C coupling reactions (Figure 7) (48). The presence of the chelating diphosphine ligand provided remarkable stability to the nanoparticles,
preventing their aggregation throughout the process. Furthermore, the nanoparticles could be subsequently isolated and reused without any loss of catalytic activity.

3.3 Nitrogen-Based Ligands

The use of electron-rich nitrogen-containing ligands has been extensively used to stabilise precious metal nanoparticles. The lone pair of the nitrogen species (such as long-chain primary amines) is able to strongly chemically adsorb onto the surface of the metal, with the alkyl group preventing agglomeration via steric stabilisation.

Mazumder and Sun prepared monodispersed palladium nanoparticles by reducing Pd(acac)₂ in oleylamine with boron tributylamine (BTB) at 90°C (Figure 8) (49). The oleylamine served as a solvent, stabilising ligand and reductant, with BTB as a coreductant. When oleylamine alone was used as a stabiliser/solvent, higher reaction temperatures were required and, subsequently, transmission electron microscopy (TEM) showed that larger and more polydispersed nanoparticles were formed (44).

A wide range of alternate primary amines can also be employed in this one-phase reaction. However, using the saturated analogue dodecylamine did not provide such high quality nanoparticles, suggesting that the double bond present in oleylamine plays a crucial role in particle stabilisation and the control of the growth process. Furthermore, the palladium precursor used was also observed to have a significant effect on the nanoparticles formed. The acac salt gave more monodispersed distributions than the corresponding nitrate or chloride salts. It is possible that the carbon monoxide molecules generated in situ from the decomposition of the acac ligand also play a key role in controlling the particle growth process (44).

Primary amines have also been employed in two-phase reactions. Choi and coworkers demonstrated that particle size could be altered by varying the initial ratio of palladium(II) chloride to amine and the length of the alkyl chain (50). The particle size decreased

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Fig. 7. (Quasi)-homogeneous carbon–carbon coupling reactions undertaken by BINAP thioether-derivatised palladium nanoparticles (48)

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with increasing chain length, which corresponded to superior catalytic performance in the electrochemical oxidation of methane.

This demonstrates that, despite the presence of amine groups, palladium is still able to act effectively as a catalyst, largely due to the resulting accessibility of the metal surface. The surface accessibility has been examined by \(^1\)H NMR studies, which show that fast exchange occurs between free and uncoordinated amine ligands at the surface of the palladium nanoparticles (51). In contrast, polyphosphine ligands do not display fast exchange, with the ligands firmly coordinated on the surface of the nanoparticles. The weaker binding of the amino ligands makes them more attractive for use in catalytic processes. Furthermore, the presence of the ligand on the surface may even provide additional protection to the palladium nanoparticle when corrosive solvent systems are employed.

In addition to aliphatic amines, several other nitrogen-containing molecules have been used to stabilise palladium nanoparticles. These include aromatic amines (52), porphyrins (53), pyryl groups (54) and imidazole derivatives (55).

The readily available 4-dimethylaminopyridine (DMAP) ligand has been widely explored as a stabiliser for metal nanoparticles. Of these, palladium-based systems have been used as catalytic microcapsules, exploiting the non-bulky nature of the ligand, thereby allowing access to the particle surface by organic reactants (56).

Although the synthesis of DMAP-stabilised palladium nanoparticles has been undertaken via the reduction of sodium tetrachloropalladate(II) using sodium borohydride in aqueous conditions (57), its use has been better documented in a ligand exchange reaction (54). Gittins and Caruso prepared tetralkylammonium bromide-stabilised palladium nanoparticles in a two-phase (toluene/water) reaction (Figure 9) (54). Addition of an aqueous solution of DMAP gave rise to rapid and complete transfer of the nanoparticles into the aqueous phase. This not only offers a simple and effective method of transferring nanoparticles into aqueous media, but also allows the particle size of the initial palladium nanoparticle to be maintained.

Recently, Serpell et al. have demonstrated that imidazole derivatives can also be used as effective stabilisers for palladium nanoparticles and the subsequent deposition of these onto activated carbon gives rise to an active catalyst for hydrogenation reactions (55). Furthermore, the addition of hydrogen bond donors into the aliphatic chain of the imidazole derivative has proved efficient in preparing core-shell nanoparticle structures. For example, an appended amide group is able to bind an anionic metallic salt in close proximity to the surface of the nanoparticle and its subsequent reduction generates the desired core-shell structure (Figure 10). When gold is added to a preformed palladium nanoparticle in this way, the selectivity of the resulting catalyst in the catalytic hydrogenation of 2-chloronitrobenzene to 2-chloroaniline is dramatically enhanced by the core-shell system.

### 3.4 Other Ligands

In general, ligands containing heteroatoms stabilise precious metal nanoparticles by forming strong bonds with the surface. However, recently there have been examples of nanoparticles being stabilised with carbon-based ligands (58, 59). Palladium has been extensively used as the contact metal of choice in the fabrication of carbon nanotube-based nanoelectronic devices and circuitries because of its low contact resistance (60, 61), and so it is not unexpected that carbon can be used to stabilise nanoparticles. In fact, the bonding energy for a Pd–C single bond is 436 kJ mol\(^{-1}\), even larger than that of the Pd–S linkage (380 kJ mol\(^{-1}\)) (62).

Stable palladium nanoparticles have been prepared by passivating the metal cores with Pd–C covalent linkages by using diazonium derivatives as precursors (62). The addition of Super-Hydride\(^{\circledR}\) to palladium(II) chloride resulted in the generation of nanoparticles. Simultaneously, aliphatic radicals generated by the reduction of diazonium ligands formed the strong Pd–C linkages. A range of
Fig. 9. Partitioning of palladium nanoparticles from organic to aqueous solvent systems via the addition of DMAP to tetraalkylammonium bromide-stabilised nanoparticles. Inset shows the resonance structures of DMAP illustrating the high electron density present on the donor nitrogen.

Fig. 10. (a) Preparation of imidazole-stabilised palladium-based nanoparticles. The use of an anion binding group on the backbone of the ligand enables well-defined core-shell nanoparticles to be prepared. Aberration-corrected high angle annular dark field STEM images clearly show the formation of the (core@shell) materials; (b) Au@Pd; and (c) Pd@Au nanoparticles (55).
spectroscopic and microscopic measurements were consistent with the formation of carbon-stabilised palladium nanoparticles (Figure 11).

4. Surfactants
The use of salts/surfactants is a popular route to stabilising metal nanoparticles. Frequently, tetra-$N$-alkylammonium halide salts are chosen for this purpose, although other analogous materials (such as imidazolium-based ionic liquids (63–65)) can act as stabilisers using the same mechanism. Here the stabiliser is able to prevent irreversible agglomeration of the metal via a combination of electrostatic and steric effects (66). It is thought that surfactant-stabilised nanoparticles strongly adsorb a layer of anions to the surface of the metal, which in turn are surrounded by a layer of countercations, in order to retain electroneutrality (Figure 12) (4, 67, 68). Both elements of the surfactant play a key role in protecting the metal from agglomeration. Varying the nature of the cationic component allows the nanoparticles to be dispersed in either organic or aqueous media. Furthermore, surfactants such as cetyltrimethylammonium bromide (CTAB) enable the generation of anisotropic particle shapes (69).

Bönneman demonstrated that the choice of metal salt used was also vitally important (70). For example, the hydrogen reduction of [(octyl)$_4N]$PdCl$_4$ only gave a metallic precipitate, whereas the reduction of [(octyl)$_4N]$PdBr$_4$ by hydrogen does not occur, even at 50 bar H$_2$. In contrast, the hydrogen reduction of [(octyl)$_4N]$PdCl$_2$Br$_2$ in THF yields 4 nm nanoparticles, albeit after fourteen days.

Many routes have been employed for the synthesis of surfactant-stabilised palladium nanoparticles. Gittins and Caruso prepared tetra-$n$-octylammonium bromide (TOAB) stabilised palladium nanoparticles in a two-phase (toluene/water) reaction (54). This is a modification of the Brust route, which used thiol ligands. In the modified method, the ammonium salt acts as both a quantitative phase transfer agent and a stabiliser. Subsequent work has illustrated that the two key parameters to obtain small nanoparticles with a narrow size distribution

![Fig. 11. $^1$H NMR spectra of Pd nanoparticles stabilised by metal-carbon bonds: (a) Pd–BP; (b) biphenyldiazonium (BP); (c) Pd–DP; and (d) decylphenyldiazonium (DP). The samples were all prepared in CDCl$_3$ (62) (Copyright © 2008, Royal Society of Chemistry. Reproduced with permission)](http://dx.doi.org/10.1595/147106712X632415 • Platinum Metals Rev., 2012, 56, (2)•)
were the concentration of the capping agent and the stirring rate used upon addition of the reductant (71). The latter can be explained by considering that the reduction of Pd(II) to Pd(0) occurs at the phase boundary (organic to aqueous). Therefore, controlling the size of the water droplets formed in the toluene/water mixture has a dramatic effect on the subsequent particle size.

A similar approach was adopted by Bönneman and coworkers (72), who combined the stabilising agent (NR₄⁺) with the reducing agent to allow a high local concentration of the stabiliser to build up at the reduction centre (entropic stabilisation factor), which reduces the need to add an excess of the capping agent or reductant. However, this has the disadvantage that a stoichiometric ratio of the two is always maintained and an additional cost of preparing the reducing agent is present (Figure 13) (72).

Reetz also employed surfactants as stabilisers for palladium nanoparticles, but using an electrochemical synthetic procedure (Figure 14) (3). By using an electrochemical cell with a sacrificial palladium anode as the metal source, and with the supporting electrolyte also acting as a source of stabilising surfactant, stable nanoparticles can be formed (73). Varying the current density influences the particle size, with higher current densities giving rise to smaller nanoparticles. The synthesised nanoparticles precipitate out of the initial acetonitrile/THF solvent system, but are subsequently redispersible. Altering the surfactant can dramatically alter the solubility of the nanoparticles – for example, using tetraoctadecylammonium bromide gives nanoparticles that are soluble in organic solvents; whereas using sulfobetaine 3-(N,N-dimethyldodecylammonio)propanesulfonate gives nanoparticles that are soluble in aqueous solvent systems.

One of the major advantages of using surfactants as protecting agents for nanoparticles is that their relatively weak and poorly defined interactions with the metal surface give reagents a high degree of accessibility to the surface of the nanoparticles. This feature has been exploited in ligand exchange reactions (where the surfactant can be displaced by a stronger binding ligand (54)) as well as in catalysis. For example, tetra-n-alkylammonium halide-stabilised palladium nanoparticles have demonstrated good catalytic activity in liquid phase hydrogenation reactions. However, as alluded to earlier, over time the nanoparticles precipitate out of solution under a hydrogen atmosphere and are therefore ineffective as semi-homogeneous catalysts. However, once immobilised onto a solid support, the nanoparticles remain active and the heterogeneous catalyst can undergo numerous turnovers (74).

5. Steric Stabilisation (Polymers and Dendrimers)
The stabilisation of nanosystems can also be achieved by incorporating them within an organic matrix, which can be either a flexible polymer or a more preorganised dendritic structure. The steric bulk of this class of stabilising agents prevents agglomeration of the nanoparticles to bulk metal (75, 76).
5.1 Polymers
Polymers, such as poly(N-vinyl-2-pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA), are widely used to protect nanoparticles because of their commercial availability at relatively low cost and their solubility in a range of solvents, including water (Figure 15) (77, 78). The use of polymers is often associated with the ‘polyol method’, in which a metal precursor is dissolved and reduced at high temperatures by an alcohol (typically ethylene glycol) (78, 79). The standard procedure requires several hours of reflux to fully reduce the precursors to their metallic state, although the process can be hastened by irradiating the sample with microwaves (80, 81). The use of alcohols as reducing agents offers the advantage that any byproducts are simple organic compounds, unlike the residues of other reducing agents, such as borane derivatives (82).

In particular, PVP, poly(N,N-dialkylcarbodiimide) and polyurea-stabilised palladium nanoparticles give highly efficient catalysts for Suzuki-Miyamura reactions (83, 84). In addition, palladium-catalysed Suzuki and Stille cross-couplings of aryl bromides and chlorides were carried out under mild conditions and with the recycling of the catalyst (84).

5.2 Dendrimers
Dendrimers are macromolecules that, unlike polymers, are perfectly defined on the molecular level (85, 86). Their internal cavities behave as molecular boxes that can entrap and stabilise metal nanoparticles, especially if there are heteroatoms present in the interior of the dendrimer. Two families of dendrimer have been extensively studied and are commercially available: poly(amidoamine) (PAMAM) and poly(propylene imine) (PPI) (Figure 16). Both of these have been employed in the synthesis of numerous metallic nanoparticles (87, 88).

In order to prepare palladium-encapsulated nanoparticles, metal ions are generally sorbed into the interior of the dendrimer. Subsequent reduction yields nanoparticles that remain encapsulated within the structure of the macromolecule, which prevents agglomeration to bulk metal (89). The size of the nanoparticles is primarily determined by the number of palladium(II) species preloaded into the dendritic structure and the generation of the dendrimer limits the particle size and maximum metal loading that is possible. Typically, nearly monodispersed nanoparticles in the range of 1–3 nm with a high proportion of accessible metal sites are prepared by this route (90). Whilst the interior of the dendrimer can be tuned to control the metal nanoparticles, the periphery of the dendrimer can also be modified to allow solubility in either organic (91), aqueous (92), supercritical carbon dioxide (93), or fluorous media (87).

There has been considerable research into using dendrimer-stabilised nanoparticles for applications such as catalysis (94, 95). The cavities of the dendrimer are sufficiently porous to allow the passage of substrates and products to and from the reaction media and the surface of the metal. Furthermore, adjusting the ‘mesh’ of the dendrimer allows control over the rate of reaction and the selectivity of the catalytic process (Figure 17) (94, 96).

Dendrimer-encapsulated nanoparticles can also be used in quasi-homogeneous reactions, with the advantage that the process can be controlled due to the well-defined dendritic structure. For instance, the catalytic activity toward the hydrogenation of allyl alcohol and N-isopropylacrylamide by hydroxyl-terminated PAMAM dendrimer containing palladium nanoparticles has been shown to be strongly affected by the structure of the stabiliser. In particular, catalysts based on high-generation dendrimers have been found to be selective towards linear substrates, because of their low porosity (96, 97).
5.3 Other Bulky Ligands

Recently, the use of sterically bulky biomolecules (such as proteins, polypeptides and DNA) has attracted attention for controlling the growth of water-soluble metal nanoparticles (98–101). Furthermore, the functionalised nanoparticles offer a range of bio-related applications, including the assembly of hybrid structures, and biodetection (102). Varying the amino acid sequence in stabilising peptide chains has been shown to have a significant effect on particle size, as a peptide can act not only as a stabiliser but also as a mild reducing agent. Huang and coworkers demonstrated that increasing the proportion of tryptophan in the peptide resulted in reduction of sodium tetrachloropalladate(II) and tight binding to the palladium surface (103).

The adoption of green chemistry techniques by the use of naturally occurring products as stabilisers for nanomaterials is also an area of huge potential. For example, Varma has used tea and coffee extract...
to stabilise nanoparticles of palladium and other precious metals (104). The polyphenols present in the caffeine act as an effective reducing and capping agent. The environmentally benign nature of the caffeine (its high water solubility, low toxicity and biodegradability) make this route highly desirable.

The use of stabilising agents with considerable steric bulk in order to prevent agglomeration has also been applied to resorcinarenes (105) and non-functionalised cyclodextrins (106). Analysis of palladium nanoparticles stabilised with 2-hydroxypropyl-β-cyclodextrin found that the cyclic oligosaccharide was only physisorbed onto the surface via hydrophobic interactions. This weak interaction resulted in the nanoparticles showing good yields and selectivities in Suzuki, Heck and Sonogashira reactions in neat water under low palladium loadings.

6. Conclusions
The utilisation of nanodimensional materials offers significant benefits in a range of different applications. In order to maximise their usefulness, reliable syntheses are required that can generate well-defined nanoparticles with a high degree of monodispersity. This aim is being achieved in the synthesis of palladium nanoparticles by using organic ligands, surfactants and sterically bulky molecules to control the synthesis. This enables properties such as the size, shape, solubility and surface functionality of the resulting nanoparticles to be carefully tuned. Such materials are being explored for many different applications, especially in catalysis, where palladium can effectively catalyse a range of different transformations.

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The third meeting on “Challenges in Catalysis for Pharmaceuticals and Fine Chemicals” took place on 2nd November 2011. Around ninety delegates, evenly spread across academia and industry, attended the event in London, which was organised jointly by the Society of Chemical Industry (SCI) Fine Chemicals Group and the Royal Society of Chemistry (RSC) Applied Catalysis Group. Following the first two meetings of the series in 2007 (1) and 2009 (2), the themes focused on the practical aspects of applied catalysis including scale-up, flow chemistry and one-pot multi-step procedures. Four of the seven oral presentations and a third of the poster presentations featured work on platinum group metals (pgms). The following brief review brings together the pgm aspects of the work presented.

Optimising Scalable Catalysis

The scale on which reactions are performed varies across different areas of the chemical industry. Many organisations employ separate groups of chemists to work at different scales, from milligrams for screening and assays to tonnes for the industrial production of fine chemicals.

Rocco Paciello (BASF, Ludwigshafen, Germany) leads the homogeneous catalysis group at BASF, working across many scales from the initial chemical idea through to the laboratory, miniplant, pilot plant and finally the production plant. His group deal with all aspects of homogeneous catalysis from computer assisted design, synthesis and high throughput screening to the technology necessary for the recovery and recycling of catalysts.

L-Menthol is the world’s top selling aroma chemical and thousands of tonnes are manufactured each year. BASF produce around 40,000 tonnes per year of citral at their plant in Ludwigshafen from which they sought to develop a new enantioselective synthesis of menthol. The most important step in this process is the rhodium-catalysed chemo- and enantioselective reduction of cis-citral (Scheme 1). Identifying the optimal process involved screening the Rh source, chiral ligand, hydrogen pressure, temperature
and reaction time on 1.5 ml scale. After extensive mechanistic studies, a new catalyst system, Rh(acac)(CO)$_2$/Chiraphos/syngas, was developed which gave good yields and selectivities and can be efficiently recycled (3). Syngas is required in order to form the active precatalyst from the ‘resting states’ which can then enter the catalytic cycle (Scheme II) (4).

The homogeneous catalysis group at BASF makes considerable use of density functional theory (DFT) calculations in their work. This has been of great importance in aiding understanding of a process and optimising lead structures once a ligand has been found but has not yet been successful in predicting an optimal catalyst system.

**Practical Flow Chemistry**

Flow chemistry has been the focus of much research but is still regarded by some as an interesting curiosity rather than a useful industrial tool. Matthew Yates (Eli Lilly, Indianapolis, USA) spoke of the advantages of applying flow chemistry to catalytic processes in the pharmaceutical industry. He highlighted three cases in which the use of reactive gases (oxygen, hydrogen or syngas) in conjunction with pgms is simplified by using a continuous flow process. Increased pressures can be applied within the reduced volume of a flow reactor without the concomitant safety problems and plant equipment required for a batch process.

The most atom efficient method for oxidations uses molecular O$_2$ however, this can present safety issues. Use of flow chemistry for the oxidation of alcohols allowed shorter reaction times, lower loading of the homogeneous Pd(OAc)$_2$/pyridine catalyst and increased pressures while exposing only a small portion of the entire reaction mixture to oxygen at any one time. The optimised flow process used 8% O$_2$ in nitrogen, thus avoiding operating within the organic/ O$_2$ explosion limits. Moreover the process is scalable, providing yields up to 99% on a kilogram scale (5).

Hydroformylation chemistry is widely used in the bulk preparation of aldehydes. A pulsed flow system for hydroformylation of methyl methacrylate provided significant benefits over a batch process allowing 1000 psi of syngas to be used with a Rh catalyst such as RhH(CO)(PPh$_3$)$_3$. 13 kg per day of purified product could be generated in this way, reducing byproduct formation and the volume of waste.

In the arena of hydrogenations, safety and scalability benefits are again evident. The use of a continuous flow system allowed 1000 psi of H$_2$ to be used, while ensuring that the concentration of H$_2$ present at any given time was far below the explosive limit even if the entire system released at once.

The presented work demonstrated that flow chemistry can usefully be applied to pgm-catalysed processes on multi-kilogram scales. These methods have the potential to increase yields and enantioselectivities by adjusting reactor residence times and pressures while lowering associated risks through reducing the volume of hazardous mixtures. Flow chemistry is now more than a laboratory curiosity and has a significant role to play in the future of the pharmaceutical industry.

**One-Pot Reactions**

Although processes can be optimised individually for manufacturing, it is equally important to have efficient methods for the expedient synthesis of diverse structures for discovery chemistry. This can be achieved through multi-step, one-pot procedures.

The use of boronates as coupling partners in metal-catalysed carbon-carbon bond forming reactions remains a favoured choice in synthesis. Todd Marder (Durham University, UK; now University of Würzburg, Germany) presented his and Patrick Steel’s groups’ research into borylation reactions, including how to combine borylations with Suzuki-Miyaura cross-coupling reactions in a one-pot process.
The challenge until now has been that iridium-catalysed borylation processes work best in non-coordinating solvents such as hexane. Unfortunately Suzuki-Miyaura cross-couplings, which use a Pd catalyst, are most effective when performed in polar solvents such as dimethylformamide (DMF), ethanol or dioxane. Previously this meant carrying out separate steps, hence two solvents, two work-ups and often two purifications. Using an optimised protocol with methyl tert-butyl ether (MTBE) as solvent, the entire process could be performed sequentially in one pot. Yields of 87%–94% of biaryls were achieved with low catalyst loadings in a total reaction time of 9 hours under thermal conditions (6). Microwave heating (µW) significantly accelerated the borylation reactions while giving comparable yields. This allowed the one-pot tandem C–H borylation/Suzuki-Miyaura sequence to proceed in 95%+ yields on a range of aryl and heteroaryl substrates with reaction times of under an hour and in some cases as short as ten minutes (7).

The tandem one-pot principle has been extended to a borylation/1,4-conjugate addition. A Rh catalyst promotes conjugate addition, and microwave heating accelerated both steps, reducing total reaction time to minutes rather than hours. Choice of solvent proved vital to the outcome of the reaction. After the borylation step in MTBE, addition of the Rh catalyst and enone in MTBE gave the 1,4-conjugate addition product in 30%–69% yield. If iso-propanol (IPA) was used as the solvent, reduction of the ketone via transfer hydrogenation occurred providing the secondary alcohol product (a three-step process) (8). The chemistry has been shown to be suitable for array synthesis and the production of compound libraries (Scheme III).

Borylation of C–H bonds as a means to further functionalisation has been a major research theme for many years (9) and John Hartwig (University of California, Berkeley, USA) presented some of his group’s contributions to this important area. Crude reaction mixtures from the Ir-catalysed formation of pinacol boronate esters can be used directly in the synthesis of boronic acids, trifluoroborates, halides, nitriles, ethers and amines. A series of mechanistic studies on the borylation reaction identified that the rate determining step in catalytic turnover is oxidative addition of the aryl C–H to the catalyst (10). Creating
a more electron-rich Ir centre by careful tuning of the ligand gave rise to a more active catalyst. Switching from the usual 4,4′-di-tert-butylbipyridine (dtbpy) ligand to a substituted phenanthroline resulted in a catalyst which allowed a practical borylation of octane catalysed by the same starting Ir complex.

As a complementary approach, intramolecular silylation of aromatic C–H bonds can provide a useful chemoselective handle for further functionalisation of arenes (Scheme IV). Acetophenones can readily be converted to the corresponding benzosiloxanes without any intermediate purification and careful choice of base allowed sequential Suzuki-Miyaura and Hiyama couplings to be performed (11). This practical approach to building molecular complexity in two one-pot procedures not only provides rapid accessibility to diverse structures, but also reduces the number of manipulations required and waste produced in the sequence.

**Poster Presentations**

The award for best student poster went to Paul Colbon (University of Liverpool, UK) who presented a method for the direct acylation of aryl halides with alkyl aldehydes. A palladium-amine cooperative catalysis approach was successful in generating alkyl aryl ketones from aryl chlorides using a bulky, electron-rich monophosphine ligand (13). Condensation of the amine with the aldehyde produces an enamine which undergoes a Heck-type arylation. Reductive elimination of Pd reforms the enamine which hydrolyses to give the ketone product and turns over the amine. In keeping with a major theme of the meeting, this method can be extended to a one-pot process where the aldehyde is formed in situ by arylation and isomerisation of allyl alcohol. Addition of pyrrolidine and a second aryl bromide to the reaction mixture results in acylation (14).

Selectivity in heterogeneous catalysis can be achieved by modifying the formation of Pd nanoparticles. James Cookson (Johnson Matthey, UK) showed how nanoparticles formed in the presence of a simple amine or amino acid could be used in selective reductions. Alkynes were reduced exclusively to alkenes and nitro chloro arenes could be reduced to the corresponding amine without any dehalogenation (15).

Probing the exact nature of pgm catalysts and the changes they undergo during a catalytic process is not easy. Anna Kroner (Diamond Lightsource, UK) gave an overview of the techniques available at the
UK synchrotron science facility which could be useful for the study of such processes. X-ray scattering and X-ray absorption spectroscopy are already available at Diamond and a new dispersive extended X-ray absorption fine structure (EXAFS) beamline should come online in the near future to allow time resolved studies at the microsecond level.

Concluding Remarks

Improving the efficiency and practicality of catalytic processes can be achieved in a number of ways. Finding optimal conditions through a directed screening approach is one successful strategy, but other factors play an important role. Achieving multiple transformations in one-pot or taking advantage of technologies such as flow chemistry can have a dramatic impact on safety, waste management, cost and hence the overall practicality of a chemical process. In both industry and academia much progress has been made in improving and widening the scope of pgm methods, but significant challenges remain and many processes are still far from perfect. What is certain is that the scientific community is actively addressing these "Challenges in Catalysis for Pharmaceuticals and Fine Chemicals".

The next meeting in the series is expected to take place towards the end of 2013 and will be announced by the SCI and RSC in due course.

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The Reviewer

John Brazier is a Research Associate in the Department of Chemistry at Imperial College, London, UK. A background in mechanistic catalysis led him to his current position working on various aspects of both homogeneous and heterogeneous palladium catalysis with particular interest in the roles which solvents play in these reactions.
Both heterogeneous and homogeneous platinum group metal (pgm) catalysts have remarkable properties: invariably they have outstanding activities, longevity, and often particularly attractive selectivities so they are used in many demanding situations. Therefore perhaps it is not surprising that the discovery of heterogeneous catalysis involved platinum. In 1817 Humphry Davy discovered catalytic combustion by placing a heated coiled platinum wire into a town gas/air mixture that became and stayed white hot as it sustained combustion (1, 2). This illustrated the exceptional activity of platinum since the wire had a very low surface area, and soon there were a number of reports concerning catalysis by platinum, including selective oxidations such as the oxidation of ethanol to acetaldehyde or acetic acid (3). The interest in catalysis continued to grow but the introduction of a successful large scale industrial heterogeneous catalytic process did not take place until Oswald’s work (4) culminated in the introduction of the high-temperature selective oxidation of ammonia to nitric oxide over platinum/rhodium en route to nitric acid at the beginning of the 20th century (5). Now heterogeneous pgm catalysts are at the heart of many industrial processes, and also in environmental areas where platinum, rhodium and palladium catalysts control exhaust emissions from vehicles to keep urban air clean (6). In these solid heterogeneous catalysts the reaction takes place on surface atoms, often via mechanisms that have yet to be completely elucidated.

In contrast, homogeneous soluble pgm catalysts have the advantage of being discrete molecular compounds that can be characterised in the solid state and in solution by techniques used in organic chemistry. The mechanisms of reactions catalysed by them can be probed in this way, and as a result of intense work over more than three decades much is
understood about the intimate mechanistic details of homogeneously catalysed reactions. These include hydrogenations, hydroformylations, carbonylations, and especially carbon–carbon bond forming processes that often provide elegant routes to desirable organic compounds that are not easily accessed by other means. The importance of this work has been recognised by several Nobel Prizes, most recently for C–C bond forming Heck-type coupling reactions (7). Initially rhodium homogeneous catalysts were the most significant of the pgms, and now palladium has this position, but platinum and rhodium as well as ruthenium and iridium catalysts are important in some areas.

During the catalytic cycle the metal centre in these homogeneous reactions usually moves between two oxidation states differing by two units, with the lower oxidation state being stabilised by soft ligands like mono- and polydentate phosphines.

These catalysts can be remarkably selective. For example, in suitable situations when chiral ligands are present chiral products can be obtained. The facile oxidation state interchange is key for catalytic activity, and for rhodium it is rhodium(III) and rhodium(I) that are usually involved (and similarly for iridium), while for platinum and palladium it is the 0 and +II oxidation states. For instance, oxidative addition of a R–X compound to a palladium(0) centre affords a palladium(II) species, which after suitable transformations, undergoes a reductive elimination process to complete the catalytic cycle and reform palladium(0) and an organic product.

Less well investigated are two oxidation state interchanges at higher oxidation state levels in organopalladium and organoplatinum compounds. Almost two decades ago Allan Canty reviewed the evidence for the possible presence of the +IV oxidation state in homogeneous reactions catalysed by organopalladium species (8). A lot of work has been done in this area since then, and the role of palladium(IV) has been firmly established in some important processes. The present monograph, edited and partially written by Allan Canty, is concerned with the ability of platinum and palladium species to access these higher oxidation states, and their involvement in stoichiometric and catalytic reactions. It is becoming increasingly apparent that this chemistry may be important in a variety of situations including oxidative reactions. The book covers both basic chemistries and applications in seven chapters written by authors eminent in their fields of specialisation.

**Higher Oxidation State Platinum Species**

The first chapter, by Kyle Grice, Margaret Scheuermann and Karen Goldberg (University of Washington, Seattle, USA), is concerned with five-coordinate organometallic platinum(IV) complexes. Based on kinetic studies it has long been believed that the slow first order reactions of octahedral low-spin $d^6$ platinum(IV) coordination complexes are dissociative in nature and involve reactive five-coordinate intermediates (9). Five-coordinate platinum(IV) intermediates are required as the preliminary step in some ‘organometallic’ insertion reactions like C–C, C–X and C–H reductive eliminations, and in $\beta$-hydride eliminations. Although isoelectronic rhodium(III) and iridium(III) five-coordinate complexes have long been known, it is only in recent years that five-coordinate platinum(IV) complexes have been isolated and characterised and their reactivity directly observed. The first was reported some ten years ago and is shown in **Structure 1**. This is an almost perfect square pyramidal compound, while the second one to be isolated, **Structure 2**, is a distorted square pyramid in which the metal is not in the plane of the base.

![Structure 1](image1.png)

![Structure 2](image2.png)

Clearly steric effects are important stabilising factors in moderating their reactivity which enable them to be characterised by nuclear magnetic resonance (NMR) spectroscopy in solution and by X-ray diffraction in the solid state. Notwithstanding this, processes involving the addition of small molecules such as dioxygen and carbon monoxide that can access the metal centre have been observed, and study of several of these compounds is shedding valuable light on the chemistries of five-coordinate platinum(IV) complexes.

The next chapter, by Jay Labinger and John Bercaw (California Institute of Technology, USA), is about higher oxidation platinum species in C–H alkane activation. For many years low-temperature ‘methane activation’ has been a major goal of catalysis. At high
temperatures deuterium exchange takes place over heterogeneous nickel catalysts (and others), and the industrially important methane steam reforming reaction takes place also over a nickel catalyst with a similar activation energy. Under much milder conditions unsaturated hydrocarbons and arenes undergo deuterium exchange in solution (10) while remarkably methane does so in the presence of [PtCl₄]²⁻ in solution (11). Therefore alkane activation per se is not necessarily the major difficulty in producing useful chemical products directly from methane. The need is to intercept short lived, highly reactive intermediate species to give desired products more rapidly than, for instance, reaction with hydrogen (or deuterium) which gives no overall meaningful reaction.

The Shilov system remarkably directly produces methanol from methane at low temperature! Originally an aqueous mixture of platinum(II) and platinum(IV) chloroplatinates was used, and modified systems were subsequently developed. The original reports (12, 13) of this amazing chemistry were published in the Russian literature during the late 1960s and early 1970s, and the overall oxidation of methane by [PtCl₆]²⁻ is shown in Equation (i).

$$\text{CH}_4 + [\text{PtCl}_6]^{2-} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + [\text{PtCl}_4]^{2-} + 2\text{HCl}$$  (i)

The key step in this process is the initial reaction of alkane with [PtCl₄]²⁻ which is rapidly followed by oxidation of the thus formed alkyl complex with [PtCl₆]²⁻, presumably via a chloride bridge, which is a unique oxidant because it cannot destroy platinum(II), whereas to be effective alternative oxidants must oxidise the alkyl complex while not oxidising the platinum(II). Copper in conjunction with molecular oxygen appears to be the most effective alternative oxidant system (copper alone is ineffective so the presence of oxygen is not simply to re-oxidise the copper), and it is pertinent to compare this process with the Wacker reaction where palladium is also re-oxidised by oxygen in the presence of copper (14). The practical difficulties with the powerfully oxidising platinum(IV) Shilov system are reproducibility and shortened life caused by erratic precipitation of platinum metal. It is mainly because of this that the highly appealing and intriguing reaction has not been commercialised, although the mechanistic understanding that has been gained shows the direction in which further development needs to go.

### Reactions of Palladium(IV) Complexes and Their Mechanisms

The next chapter, by Joy Racowski and Melanie Sanford (University of Michigan, USA), deals with the formation of C–heteroatom bonds by reductive elimination reactions from palladium(IV) complexes. It is a comprehensive review covering published material from 1986 to 2010. Transient palladium(IV) intermediates have been proposed as the product release stage in a number of important transformations including arene and alkane functionalisations, allylic acetoxyations, alkene borylations etc. And indeed palladium(IV) compounds such as Pd(bipy)(CH₃)₃I (formed by oxidative addition of CH₃I to Pd(bipy)(CH₃)₂) undergo facile reductive elimination to give ethane. Since this reaction was reported (15), the area has expanded considerably with examples of C–S, C–Se, C–O, C–I, C–Br and C–Cl bond forming reactions, and each of these are covered in some detail, including the considerable amount of work that is being done to confirm the mechanisms of these processes. Very importantly C–F bonds can be formed using XeF₂ as a fluorine source (16), and although this area is still in its infancy it may be expected to be developed as a route to important fluoro-compounds that are otherwise difficult to access.

'Palladium(IV) Complexes as Intermediates in Catalytic and Stoichiometric Cascade Sequences Providing Complex Carbocycles and Heterocycles' is the title of the next chapter, by Helena Malinakova (University of Kansas, USA). This deals with the capability of some palladium compounds to mediate sequential functionalisation of one substrate to create multiple C–C or C–heteroatom bonds in a single operation, for example in multicomponent annulation reactions in which palladium(IV) complexes are implicated as intermediates. Studies on isolatable palladium(IV) compounds have been used to obtain evidence for the participation of such intermediates, and stoichiometric reactions in palladium provide routes to 1,3-dienes, norbornene derivatives, benzoxepines, benzoypyrans and benzofurans that are discussed in detail, as is the spectroscopic and crystallographic characterisation of the relatively rare palladium(IV) intermediates. Further work on moderately stable palladium(IV) compounds is likely
to clarify whether they can participate in fundamental processes other than reductive eliminations.

**Organic Reactions Mediated by Palladium and Platinum Complexes**

The fifth chapter is by Allan Canty and Manab Sharma (University of Tasmania, Australia) and is concerned with higher oxidation state palladium and platinum \( \eta^1 \)-alkynyls. That is, species in which the metal in an oxidation state greater than +II is bonded to alkynyl ligands, which can be prepared by oxidation of alkylnylmetal(II) complexes and reactions of organometal(II) complexes with alkynyl(aryl) iodine(III) reagents. The metal(IV) compounds obtained are octahedral, and only platinum compounds have been characterised in the solid state by X-ray crystallography. Some of these compounds decompose via reductive elimination, generating C–C bonds (diacetylenes) (17). Stoichiometric reactions of the palladium(II) and platinum(II) complexes suggest that the higher oxidation state complexes are feasible (undetected) intermediates in some organic synthetic procedures. Interesting metal–metal bonded systems that can be seen as Pt(III)–Pt(III) or Pt(II)–Pt(IV) species have been characterised as intermediates in the oxidation of Pt(II) to Pt(IV) compounds, and the potential implications for mechanisms of organic reactions mediated by higher oxidation metal centres are discussed. Clearly this is a very fertile area for much future research.

There then follows a chapter on palladium(III) species in synthetic and catalytic reactions by David Powers and Tobias Ritter (Harvard University, USA). Unlike platinum(III) coordination complexes their palladium(III) counterparts are very rare, and for example, \( \text{Pd} \text{F}_3 \) is better described as the Pd(II) salt of the Pd(IV) complex anion \( \text{[PdF}_6\text{]}^{2−} \). As previously noted, few organometallic palladium(III) compounds have been isolated and characterised – examples of these are given in the book. There is however growing evidence that such species might be important in a variety of known palladium-catalysed reactions. For instance, silver(I) is often used as a beneficial additive in practical palladium-catalysed oxidative C–H coupling reactions, and one-electron oxidation of \( [(\text{bipy})\text{Pd(Me)}_2] \) with \( \text{AgPF}_6 \) affords a moderate yield of ethane via a suggested mechanism involving disproportionation of the first formed palladium(III) complex \( [(\text{bipy})\text{Pd(Me)}_2]^{2+} \) to \( [(\text{bipy})\text{Pd(Me)}(\text{solvent})]^{+} \) and \( [(\text{bipy})\text{Pd(Me)}_2]^{-} \), followed by elimination of ethane from the Pd(IV) compound – this mechanism nicely explains the 50% yield of ethane. The possible involvement of methyl radicals was discounted because radical traps had no effect on the reaction. However, the addition of isopropyl iodide to Kumada and Negishi coupling reactions results in remarkable accelerations in reaction rates that were attributed to a radical pathway with transient palladium(I) intermediates and isopropyl radicals with palladium(II) and palladium(III) chain carriers. Palladium(III) has also been proposed in dioxygen insertion reactions into Pd(II)–methyl bonds, consistent with a radical process that is light sensitive, and addition of a radical inhibitor was needed to obtain consistent reaction rates. Photolysis of isolated palladium(III) complexes made by electrolysis gave products that were inhibited by radical scavengers, consistent with photoinduced homolytic Pd–C cleavage as the pathway to the observed organic products, although other routes are possible. It might be thought that palladium(III) forms dimers, and oxidation of dinuclear palladium(II) complexes can result in diamagnetic dinuclear palladium(III) complexes with a metal–metal σ-bond that is shorter than that in a comparable palladium(II) complex (18). There is also evidence that such species are present as intermediates in some catalytic reactions. Thus well defined palladium(III) complexes participate in productive organometallic reactions, and their presence in better studied processes seems likely, processes that previously were thought to proceed via traditional two-electron monometallic palladium redox cycles. This area is likely to yield many intriguing results in the near future that may substantially change the mechanistic view of some established reactions!

The final chapter is entitled ‘Organometallic Platinum(II) and Palladium(II) Complexes as Donor Ligands for Lewis-Acidic \( d^{10} \) and \( s^2 \) Centers’, by Marc-Etienne Moret (ETH Zurich, Switzerland, and California Institute of Technology, USA). The filled axial orbitals of square planar palladium and platinum complexes enable them to be ‘metalloligands’ for Lewis-acidic metal centres, and a wide range of such donor-acceptor metal–metal bonded species have been reported. This nucleophilic reactivity is key in the oxidative addition of alkyl halides to organopalladium(II) and organoplatinum(II) complexes via an \( S_2\text{2} \) process, and electron-rich complexes can be protonated on the metal to give metal(IV) hydrides, which is the first step in the protonolysis of many Pt–C bonds. The early examples of isolated metal(II) square planar adducts with metal–metal bonds date from the early 1980s and have Pt–Hg or Pt–Ag bonds, and since then a wide
variety of related compounds have been prepared. There are several bonding patterns, some involving interactions with ligands bound to the central metal, but all have M–M interaction. Again methyl complexes undergo some particularly interesting reactions, as illustrated for instance in Equation (ii), which takes place in solution at low temperature.

\[(\text{bipy})\text{Pt}(	ext{CH}_3)_2 + \text{AgBF}_4 \rightarrow (\text{bipy})(\text{CH}_3)_2\text{Pt–Ag–Pt(\text{CH}_3)_2(bipy)}^+ + \text{BF}_4^- \] (ii)

This compound is not stable but the presence of metal–metal bonding in solution at low temperature was confirmed by NMR coupling constants. The palladium counterparts are less stable and have a reduced tendency to form donor-acceptor metal–metal bonds. More recently exotic complexes have been prepared in which a central metal, for example copper(I), is coordinated to two pyridine nitrogen atoms and two Pt(CH$_3$)$_2$ moieties forming part of a macrocycle, as shown in Structure 3.

Thallium forms stable palladium–thallium bonds, and a remarkable complex cation has a linear chain of four Pd(II)–Tl(I) bonds. This tendency of thallium(I) to be involved in extended structures is expanded upon later. The chapter then details a bewildering array of increasingly complex structures, mostly containing metal–metal bonds that include alkynyl complexes, diphosphine-bridged complexes and carbene complexes, before examining electron transfer, ligand migration and hydrocarbyl transmetallation reactions. The reactions of the polymetallic compounds of the type discussed in this chapter provide further chemical insight into why adding copper(I) and silver(I) salts to palladium and platinum-based catalytic systems can enhance reaction rates. This may happen via more facile alternative mechanisms involving donor-acceptor metal–metal bonded species and understanding here may lead to more productive catalytic systems.

Concluding Remarks

Overall this is a nice up to date book that provides a very readable account of highlights in a topical and exciting area of developing chemistry. All the contributors and the editor, as well as the publishers, are to be congratulated for making available such a well produced and interesting monograph. The accepted mechanistic pathways of many established catalytic reactions are being questioned as increasing amounts of evidence suggest that alternative mechanisms involving higher oxidation state species are possible and may well take place. For example, where metal centres are in higher oxidation states they are likely to form reactive free radicals more readily than in lower oxidation state processes. This monograph will be of value to all those who are working in the area, and it should be in libraries wishing to keep up to date in these chemical areas that have so much potential.

Notes and References

1 H. Davy, Phil. Trans. R. Soc. Lond., 1817, 107, 77. The term catalysis was not introduced until 1836 when J. J. Berzelius first used it to describe the effect that some reactions are accelerated by the presence of a material that is unchanged after the reaction.


4 The key Ostwald patents on ammonia oxidation over platinum included: W. Ostwald, “Improvements in the Manufacture of Nitric Acid and Nitrogen Oxides”, British Patent 698, 1902; W. Ostwald, “Improvements In and Relating to the Manufacture of Nitric Acid and Oxides of Nitrogen’, British Patent 8300, 1902; with others in France, America and Switzerland. In Germany much earlier prior art by Kuhlmann prevented granting of patents so the process was developed secretly in that country.

5 For a review of the early history of catalytic ammonia oxidation over platinum catalysts see: S. J. Green, “Industrial Catalysis”, Ernest Benn Ltd, London, UK, 1928, pp. 130–146. The first plants used corrugated platinum foil, platinum-based gauzes were introduced later.
Martyn Twigg retired as the Chief Scientist of Johnson Matthey in 2010. Dr Twigg was previously European Technology Director for the Environmental Catalysts and Technologies Division of Johnson Matthey in Royston, UK. He has authored or co-authored many research papers, written numerous chapters in encyclopaedic works, and edited and contributed to several books. He edits the book series ‘Fundamental and Applied Catalysis’, and a series on the kinetics and mechanisms of inorganic and organometallic reactions. He is on the editorial board of several journals, and maintains active associations with universities in the UK and elsewhere, with honorary positions at some.
Commercial Development of Palladium(0) Catalysts for Highly Selective Cross-Coupling Reactions

New preformed L₂Pd(0) (L = tertiary phosphine) catalysts now available

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Palladium-catalysed cross-coupling has huge importance for the synthesis of many organic molecules at both laboratory and industrial scale. A range of commercially available preformed (R₃P)₂Pd(0) catalysts have now been developed and are available from Johnson Matthey. Some unique and highly selective applications of these palladium catalysts for various cross-coupling reactions, including novel reactions such as carbohalogenation reactions, Negishi coupling of aryl chlorides and copper-free Sonogashira coupling, are highlighted in this review.

Introduction
Palladium-catalysed cross-coupling has become one of the most powerful synthetic methods in organic and organometallic chemistry. It has found numerous applications (1–6) in the laboratory, in addition to the commercial production of pharmaceuticals, agrochemicals and electronic materials. The importance of the method was recognised by the awarding of the 2010 Nobel Prize in Chemistry to the original pioneers: Professors Heck, Negishi and Suzuki (7). For a historical perspective of Pd catalysed cross-coupling contextual to the Nobel Prize see the recent review (8).

It is now commonly accepted that LₙPd(0) (n = number of ligands) is the active catalytic species to facilitate a cross-coupling transformation. However, until recently there were not many commercially available examples of preformed (R₃P)₂Pd(0) catalysts. Recently, we reported our development of a novel, general and practical synthetic route to a variety of preformed L₂Pd(0) catalysts (see Scheme 1). This process produced catalysts in excellent yield, specifically using the bulky, electron-rich tertiary phosphine ligands tBu₃P, Cy₃P, (o-tol)₂P, tBu₂(Ph)P, tBu₂(p-Me₂N-C₆H₄)P, (C₅H₄FeC₅Ph₅)(tBu)₂P (Q-Phos) and tBu₂(Np)P (see Table 1). These L₂Pd(0)
catalysts are now commercially available at scales ranging from gram to multi-kilogram quantities (9, 10). An example of the crystal structure of one of the complexes is given in Figure 1 (11).

Although these L₂Pd(0) complexes with the exception of Pd(tBu₃P)₂ have only recently been made available commercially (Table I), several have shown some unique and interesting applications as summarised below. A detailed review on the applications of these catalysts as well as the newly developed LPd based catalysts is underway (12).

Selected Applications of Pd(tBu₃P)₂
Of the various catalysts listed in Table I, Pd(tBu₃P)₂, the potential of which was originally identified by Fu (2, 6) in the early 2000s, is one of the best new generation catalysts. Pd(tBu₃P)₂ has been shown to be superior in many applications when compared to the classical Pd(Ph₃P)₂. Selected examples of aryl chloride couplings using Pd(tBu₃P)₂ are shown in Scheme II (13–16).

Selectivities of Pd(Cy₃P)₂ and Pd(tBu₃P)₂
Laboratory studies using preformed catalysts and literature reports of in situ systems (17) have shown that Pd(Cy₃P)₂ is a unique catalyst which
Enamine followed by Heck coupling of Ar–Cl (13)

\[
\begin{align*}
R^1 & \quad \text{NH} \\
R^2 & \quad \text{O} \\
R^3 & \quad \text{R}^4 \\
\end{align*}
\]

Suzuki coupling of Ar–Cl (14)

\[
\text{PhB(OH)_2} + \quad \text{Cl} \\
\text{SO}_2\text{Me} \\
\text{F}_3\text{C} \\
\text{Ph} \\
\text{SO}_2\text{Me} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{Ot}
\]

Negishi coupling of Ar–Cl (15)

\[
\text{Cl} \\
\text{OMe} \\
\text{Ph} \\
\text{Br} \\
\text{MeO} \\
\text{Me}
\]

C–H activation (16)

\[
\text{Scheme II. Selected reactions of Pd(}^\text{tBu}_3\text{P)}_2
\]

\[
\text{Scheme III. Selectivity of Pd(Cy}_3\text{P)}_2 \text{ vs. Pd(}^\text{tBu}_3\text{P)}_2 \text{ in Ar-Cl coupling (18)}
\]
can selectively carry out aryl triflate coupling in the presence of a chloride. Interestingly, Pd(\(\text{tBu}_3\text{P}\))\(_2\) shows the reverse selectivity (Scheme III) (18).

**Unique Selectivity of Pd(Q-Phos)\(_2\)**

Among the many L\(_2\)Pd(0) catalysts selected from **Table I** or generated *in situ* using commercially available ligands, Pd(Q-Phos)\(_2\) has recently been identified as a unique catalyst for effective carboiodination, a new type of carbon-carbon bond forming reaction reported by Lautens (Scheme IV) (19). In this case the Heck reaction is inhibited, and it is thought that the reductive elimination of the halide might be taking place after oxidative addition.

Recently the same group modified the reaction conditions to make the iodide in 95% yield (Scheme V) from the corresponding bromide by iodide exchange (20).

**Pd(\(\text{tBu}_2(\text{o-Me}_2\text{N-C}_6\text{H}_4)\text{P}\))\(_2\) for Sonogashira and Negishi Coupling**

Preliminary studies indicate that Pd(\(\text{tBu}_2(\text{o-Me}_2\text{N-C}_6\text{H}_4)\text{P}\))\(_2\) is a very good catalyst for the Sonogashira coupling of heteroaryl chlorides or activated aryl chlorides in the absence of copper (Scheme VI) (9). More detailed work will be published later (21).

Lipshutz recently identified Pd(\(\text{tBu}_2(\text{o-Me}_2\text{N-C}_6\text{H}_4)\text{P}\))\(_2\) as a very useful catalyst for the aryl bromide Negishi coupling of alkyl zinc iodides very effectively with excellent regioselectivity (Scheme VII) (22, 23).

**Pd((o-tolyl)\(_3\text{P}\))\(_2\) for Monoarylation of Ammonia and Primary Amines**

Hartwig utilised Pd((o-tolyl)\(_3\text{P}\))\(_2\) as a unique amination catalyst, in the presence of the hindered Josiphos ligand CyPF\(_2\text{Bu}\), for the monoarylation of primary amines using challenging aryl tosylate substrates under very low Pd loadings (Scheme VIII) (24). Hartwig believes that the rigidity of the chelated ring might be one of the factors favouring this selectivity.

This chemistry has also been extended to monoarylation of ammonia with aryl and heteroaryl chloride substrates, with selectivities for primary aryl amines, A, up to 98% in good yield (Scheme IX) (25).

![Scheme IV. Pd(Q-Phos)\(_2\) catalysed carboiodination (19)](image1)

![Scheme V. Carbobromination followed by iodide exchange (20)](image2)
Scheme VI. Cu-free Sonogashira coupling of aryl and heteroaryl chlorides

Scheme VII. Pd(tBu2(p-Me2N-C6H4)P)2-catalysed sp2-sp3 Negishi coupling at milder temperatures

Scheme VIII. Monoarylation of primary amine with aryl tosylate
Conclusion
A highly effective method for the synthesis of highly active precatalysts of general formula \( L_2Pd(0) \) has been developed, which is pivotal for the availability of these catalysts in commercial quantities. These tertiary phosphine (L) based \( L_2Pd(0) \) complexes show very promising applications with excellent selectivity in cross-coupling. The complexes discussed in this article are described in Table I, with a summary of their specific applications.

The difference in selectivity for each catalyst for a particular reaction is quite fascinating. Many more new applications of these catalysts are yet to come.

For more applications of precatalysts developed beyond the 2010 Nobel Prize, see the recent review (12).

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Introduction

For some years Italian groups have been at the forefront of research into membranes for hydrogen separation, with thin film palladium-based alloy membranes being a particular area of specialisation. The slower-than-predicted growth in the hydrogen economy has meant that the fruits of their research have yet to make a major impact in commercial terms but the quality of the research is well-recognised within the global membrane fraternity. Two recent books have been published (1, 2), which complement other recent chapters, reviews, presentations and articles, and highlight some of their work in the areas of membrane manufacture and utilisation within catalytic reactors, demanding applications in which marrying the performance requirements of the membranes with those of the catalysts has led many to suggest that neither technology is best served by the combination.

“Membrane Reactors for Hydrogen Production Processes”

This book (1) provides a consolidation of the results from a collaborative project, ‘Hydrogen Production from Light Multi-Fuels and Storage in Porous Materials’, started in 2006 by Italian academic and industrial groups to translate laboratory scale membrane reactors to pilot scale. Supported by the Italian Research Ministry under the Fondo Integrativo Speciale per la Ricerca (FISR) programme and managed by the University of L’Aquila, the success of the programme is demonstrated by the construction of a 20 Nm³ h⁻¹ pilot plant at the Tecnimont KT SpA facility in Chieti Scalo, about 200 km north-east of Rome, in which pre-commercial membranes from four suppliers (ECN, MRT, Acktar and ‘a Japanese company’) were evaluated. Initially describing the general case for membrane reactors, for most of the book the authors have concentrated primarily on aspects of H₂ separation through dense Pd alloy membranes, with each chapter providing a stand-alone account of the topic it addresses.

The first chapter discusses the thermodynamic and kinetic aspects of the integration of selective membranes into chemical processes, utilising the ability to remove one of the product gases as a means of overcoming equilibrium constraints. The authors clearly lay out the equations governing the performance of membrane reactors, discussing formats in which the membrane is either in proximity with the catalyst or separated in order to optimise performance. Highlighting the enormous potential of membrane reactors, they acknowledge that commercial applications have been slow to be adopted, due in the main to a number of practical issues such as membrane stability, mass transfer limitations and high production costs.

These issues are ably discussed in Chapters 2 and 3, which cover the current ‘state of the art’ and economic requirements of small-scale Pd alloy membrane manufacture. Anyone who has worked in the area of H₂ separation will be aware of the rapid increase in publications associated with membrane fabrication and use in reactor systems. The lists of references for the two chapters, providing a good selection from groups around the world, bear testament to the large amount of money and time devoted to this area in the last two decades. Primary interest has been in thin film palladium-silver and palladium-copper alloy membranes, with as much time devoted to substrate preparation as to developing methods for forming the alloy foils to be supported. Most workers have concentrated on tubular geometries, as highlighted by three of the four suppliers to the programme. Only one, Membrane Reactor Technologies Ltd (MRT), from Canada, produces flat foil systems for these alloys, although this geometry has been more favoured by developers of the base metal alloy membranes. Notable absences among the membrane suppliers are some of the US groups, for example, Worcester Polytechnic Institute and Colorado School of Mines, who have long been fabricating systems capable of extended performance.
Integrated Modules and Reactor-Membrane Combinations

For the integrated membrane reactor modules, a large amount of work must go into the module design. To operate at maximum efficiency, the membrane must rapidly remove the product $H_2$ from the reaction zone. However, poor design can mean that, if the product $H_2$ is removed too quickly, its partial pressure in the reaction gas drops and segments of the membrane perform no function, adding needless cost to the module. Conversely, if the $H_2$ is removed too slowly, the desired equilibrium shift is not achieved. The additional requirements of the operational and maintenance aspects of the fully integrated membrane reactor, albeit having the advantage of in-reactor $H_2$ removal, mean that some workers have chosen to concentrate on staged membrane reactors, in which catalyst bed and gas separation functions are separated. Modelling of integrated and separated reactors is a critical function, highlighted in Chapter 4. With good membrane and catalyst performance data, coupled with algorithms capable of describing the radial and axial mixing, inter- and intra-particle diffusion and interfacial gradients between solid and fluid phases, modellers are able to accurately predict the performance of their membrane reactor designs.

Chapters 5–9 deal with the application of separation membranes to example chemical processes, either as integrated catalyst-membrane reactor units or as separated reactor–membrane combinations, offering the opportunity to run both at their optimum conditions. Chapter 5 looks at natural gas steam reforming (NGSR), modelling the performance benefits that could be obtained by switching from the traditional reactors to membrane reactor designs. Whilst benefits can be found, the limitations imposed by forcing together two functions not running optimally lead the authors to the conclusion that separated reactor membrane combinations are necessary until membranes durable at NGSR conditions can be manufactured.

Autothermal Reforming and Water Gas Shift

Autothermal reforming (ATR) is considered in the next chapter. In this application, not only are the temperatures high but there are large thermal gradients present within the reactor. In the preamble, the authors point to references in which other groups have considered use of higher operating temperature ceramic membranes, both oxygen- and hydrogen-transporting versions, as means of improving efficiency of $H_2$ production. Within the study reported here, the group used a microporous alumina membrane (10 cm long × 1 cm diameter) with annular rings of foam-supported catalyst around the membrane. Reforming of methane was attempted, with some separation of the product $H_2$ observed. However, the authors rightly point out that, whilst this study shows encouraging results, there are many materials problems that need to be addressed before larger scale integrated ATR membrane reactors can be successfully constructed.

The water gas shift reaction is much more amenable to study within membrane reactors, due to its moderate temperatures, moderate exothermicity and pressure independence, meaning that operators can increase reactor pressures to drive separation membranes without adversely affecting conversion. Most investigators have constructed reactors based around either dense Pd or silica $H_2$ separation membranes, employed in different reactor-membrane configurations and with base metal and noble metal catalysts. The authors provide a good overview of the status of work at the time of writing, with a number of groups focusing upon the application within integrated gasification combined cycle (IGCC) power plants, where separation of $H_2$ from carbon dioxide streams would provide large commercial benefits. As with other candidate processes outlined in this book, workers are considering both integrated and staged reactor-membrane systems but the greatest gains are to be had with the integrated systems. In addition to managing the thermal issues, however, the coal-derived syngas will contain an array of contaminants that will rapidly poison Pd alloy membranes, with the result that workers must either develop efficient gas cleaning technologies or produce microporous membranes having high selectivity on a large scale.

Hydrogen Sulfide Cracking and Alkane Dehydrogenation

Membrane reactor enthusiasts are willing to trial many reactions in attempts to commercialise their technology, but few applications can be more demanding than the catalytic cracking of hydrogen sulfide. Having very limited industrial use, $H_2S$ is generally viewed as a pollutant. Currently separated from hydrocarbon gas streams by amine adsorption, concentrated streams are treated by the barely economical Claus Process. However, the authors point out that, if $H_2S$ could be decomposed to sulfur and hydrogen, this would yield valuable products that could offset the high costs associated with the decomposition process. Straightforward thermal decomposition requires temperatures...
well in excess of 1000ºC to achieve any level of commercial conversion and other potential decomposition technologies have not progressed beyond laboratory scale. Researchers have suggested, however, that the combination of two reactors separated by a microporous ceramic membrane unit could, with a great deal of process engineering, catalyst development and membrane scale-up, provide a commercial alternative for H2S decomposition. To give an idea of the engineering requirement, the authors suggest that a 200 tonne/day plant would require a microporous membrane area of around 1800 m², somewhat beyond the fabrication capabilities of current manufacturers.

Alkane dehydrogenation reactions have been widely studied within membrane reactor modules, since removal of the formed H₂ should provide a useful product gas stream as well as conversions beyond those limited by equilibrium conditions. Chapter 9 begins with an overview of typical dehydrogenation processes, the catalysts used, typically alumina-supported chromium oxide and alumina-supported platinum, both with various promoters, and, more importantly, the drawbacks associated with the reactions. Thermodynamic restrictions, endothermicity, side reactions like cracking and isomerisation, rapid coke formation at excessive reaction temperatures and the need for low pressure operation are factors that combine to complicate the incorporation of dehydrogenation reactions into membrane reactors. Pd membranes have high selectivity; but their fragility means that many researchers have turned to the more durable microporous silica and zeolite membranes, although these are hampered by having low H₂ selectivities and generally show minimal impact upon the conversions achieved. The chapter gives an honest assessment of the status of membrane reactors for these processes, but points to some encouraging recent performance data suggesting that the technology may be developed in the future.

Pilot Plant and Commercialisation

The penultimate chapter discusses the design, successful construction and current status of the 20 Nm³ h⁻¹ pilot plant at the Tecnimont KT SpA facility in Chieti Scalo, Italy (Figure 1), using natural gas steam reforming (SR) as the studied process. Design was based on the preliminary work described in Chapter 5. Typically, SR processes are run at 850–900ºC, too hot for incorporation of a Pd alloy membrane. Research has been carried out, using both base metal and platinum...
group metal (pgm) catalysts, to reduce the reaction temperature to 550–650°C. However, this is still above the working temperatures for Pd alloy membranes, so

Feeding desulphurised natural gas into the process, the operational parameters of the reformers were characterised in order to control the feedgas to the membrane units. The results presented are those from the first preliminary experiments. That the membranes are having an effect is clear, but the conclusions section makes the claim that ‘four types of Pd-based H₂ selective membranes are tested and compared’, which is perhaps slightly misleading. No comparative data is shown for the membrane modules and only limited performance data for two of them. More testing was planned at the time of writing, so better assessment of the modules should now be possible.

The final chapter draws together the key points from the previous chapters and examines the prospects for membrane reactors, forecasting a very positive future for the Pd systems. Clearly, there are several key obstacles to their widespread use:

- fabrication costs, although this is less the cost of the Pd and more the labour intensive routes to produce the membranes;
- membrane stability under poisoning and process conditions, necessitating the use of staged reactors for some processes;
- a current lack of industry-produced, commercial scale units;
- no acceptable accelerated ageing tests, without which longevity can only be assessed by actually carrying out thousands of hours of testing.

However, the authors cite the recent advances in substrate development, Pd layer deposition, module modelling and design and the beneficial efficiencies that successful commercialisation would bring as demonstrating the need for development to continue.

Overall, the book provides a very good summary of both the field of Pd membrane reactors and, specifically, the recent work carried out by primarily European groups, culminating in the successful construction and operation of the pilot plant in Chieti Scalo. The reviewer may not quite share the long-term optimism of the authors but their commitment is undeniable and progress to date has been impressive. We await future developments with great interest.

“Preparation of Thin Film Pd Membranes for H₂ Separation from Synthesis Gas and Detailed Design of a Permeability Testing Unit”

The experience of the Italian research groups is further highlighted by the second book (2), predating the first and concentrating on the manufacture and testing of Pd-only membranes on porous steel supports by the group at the University of Pisa. This study was also financed (in part) by the Italian Research Ministry under the FISR programme.

Constructed in the format of a doctoral thesis or extended journal publication, the 74-page book begins with a discussion around the overall area of H₂ generation and subsequent applications, before highlighting various membrane types available for gas separation: dense metallic and ceramic, polymeric, microporous ceramic and composite.

The second chapter summarises the specific properties that give rise to the use of Pd membranes and some of the methods used to fabricate the thin-walled, supported films desirable for large-scale, cost-efficient separation. As with other membrane reviews in recent years, the authors highlight the large number of journal articles and patents associated with Pd membrane development. The reader, and probably several funding bodies, may be left to ponder just how much more work and how many more research dollars will be needed before the technology is viable for long-term, large-scale operation.

Manufacture of Thin Palladium Films

The manufacturing route and equipment used for the thin Pd films on discs and tubes – cleaning, surface oxidation, preactivation and electroless plating – is similar to that used by other groups, for example, Ma’s group at the Worcester Polytechnic Institute, USA. Many groups have now moved beyond the simple oxidation of the steel surface to incorporate a diffusion barrier, such as alumina or nitrides, to minimise the risk of Pd migration into the steel substrate. Observations during the preparation are noted in Chapter 4 and here the reviewer must applaud the authors. Too often authors gloss over the minor experimental details, leaving out key points which may seem obvious at the time. Whilst everyone appreciates the importance of ‘trade secrets’, the time may be approaching when funding will begin to decline if the promised growth in commercial applications fails to materialise, and sharing ‘minor’ details among the membrane community may go some way to minimise wasted time.
Membrane thicknesses of between 10–17 μm were produced, with higher plating efficiencies noted for the disc-based membranes. This was reasonably ascribed to loss of Pd by plating out on the walls of the recirculating equipment used for the tubular versions. Leak testing of tubular membranes at ambient temperature, using nitrogen pressurisation testing and immersion in water for bubble formation, showed that, unsurprisingly, leaks decreased with Pd thickness. The principal area for leaks to occur was around the welded join between the porous steel support and the dense end attached for sealing, suggesting that further work is required to avoid irregular Pd deposition and delamination in that area. For the future, the authors might consider leak testing with helium, which will pinpoint holes more readily than nitrogen.

The experimental setup for testing the H2 separation capabilities of the membranes, described in Chapter 5, is quite thorough. It includes not only the usual capability to test in pure H2 and model syngas streams, but also can introduce poisons such as sulfur, ammonia and hydrocarbons. Frustratingly, the book ends without test data being presented and no indication of when or where such data may be found, requiring the interested reader to search the usual literature sources. Although the title specifies the preparation and design aspects, it is unclear why the book was published without giving the reader a flavour of the membrane performance under application conditions.

A search did uncover some details of testing carried out on a range of tubular membranes, having a surface area of 19 cm², supported on porous stainless steel supports and prepared by varying deposition parameters (3). Testing at elevated temperatures and pressures was carried out in pure H2, N2 and CO2, with the H2 selectivity being calculated and no deterioration seen over 500 hours of testing. The permeation data was subsequently used to model the performance of a 3 m long membrane having 50% H2:50% CO2 feedgas. Despite having the gases available, it appears that they did not use that mixed feedgas during their experimental campaign, which would have supported their calculated selectivities and modelling results. Perhaps that information will form the basis of new reports.

Conclusion

Looking at the details of the FISR programme, it is clear that the Italian government is committed to investing in a hydrogen capability and infrastructure and in renewable energy sources. The construction of the Chieti Scalo plant shows that the years of experience in laboratory-scale membranes and reactors can be translated to pilot-scale, with encouraging early results. Membrane researchers worldwide will look forward to future developments.

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References

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Dr Hugh Hamilton has worked at the Johnson Matthey Technology Centre, Sonning Common, UK, for nearly 24 years, during which time he has researched in a range of areas including autocatalysts, palladium membranes, fuel-cell membrane electrode assembly manufacture and hydrogen storage. His current role includes sorbent development for mercury from syngas, titanium powder metal injection moulding process development and modified atmosphere packaging development.
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Marcello De Falco received a master’s degree in Chemical Engineering from the University of Rome “La Sapienza”, Italy, in 2004. He was awarded a PhD in ‘Industrial Chemical Processes’ in 2008, with the thesis ‘Pd-Based Membrane Reactor: A New Technology for the Improvement of Methane Steam Reforming Process’. He has been a researcher in the Faculty of Engineering at University Campus Bio-Medico in Rome since 2010. His research activity is mainly focused on mathematical modelling of chemical reactors, hydrogen production processes, solar technologies, and the design of cogeneration plants. He is the author of 34 scientific papers (including 20 papers in international journals and 14 in conference proceedings) and 3 book chapters about selective membrane technology and applications.

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Gaetano Iaquaniello is a Vice President of Technology and Business Development at Tecnimont KT SpA, a process and engineering company based in Rome, Italy. He received his MSc in Chemical Engineering from the University of Rome in 1975, a doctorate from the University of Limoges, France, in 1984 and an MSc degree in Management from the London Business School, University of London, in 1997. He has more than 35 years of experience in designing and operating chemical plants, particularly for syngas manufacturing. After being a technical director, he is now head of research and development activities at Tecnimont and coordinates several national and European projects. He has authored and co-authored numerous papers and patents on syngas production and, more recently, on membrane reactors.

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EuropaCat X

Highlights of platinum group metal catalysis from biennial congress

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Introduction
Held under the auspices of European Federation of Catalysis Societies (EFCATS) the 10th EuropaCat Congress was held in Glasgow, UK, from 28th August to 2nd September, 2011 (1). EuropaCat is a highly regarded biennial congress which brings together researchers from across Europe and further afield for scientific dissemination in catalysis. EuropaCat X was a truly international congress with approximately 1200 delegates attending, representing some 44 countries. The theme of the Congress was ‘catalysis across the disciplines’ with an aim of delivering a unified conference covering all aspects of catalysis. The setting for the conference was the Glasgow University main building, a fine example of Gothic revival architecture and a prominent local landmark.

The programme included six plenary and 21 keynote lectures. The plenaries were presented by international leaders from a wide range of disciplines. In total over 210 oral presentations were given, representing the latest in scientific advances and successful commercial applications. Each day was split into five parallel sessions covering the following topics: Catalyst Preparation, Catalyst Characterisation, Kinetics and Mechanism, Theory and Modelling, Homogeneous Catalysis, Industrial Application, Catalyst Deactivation and Environmental Catalysis. In addition there were three poster sessions with approximately 900 posters. A parallel workshop on Selective Oxidation (ISO 2011, X European Workshop on Selective Oxidation) was organised independently with 17 oral presentations and 97 posters.

There was an excellent attendance from industrial attendees who accounted for approximately 15% of the delegates, representing over 90 companies. The exhibition space, with 24 companies represented, was also well attended throughout the conference.

A full social programme was organised for the attendees with a range of day trips available showcasing the best of Scotland. The conference dinner was held in the magnificent Kelvingrove Art Gallery and Museum and the final night’s Céilidh was a popular and energetic event!

In terms of its original aims EuropaCat X was a huge success in delivering a unified conference covering all aspects of catalysis and highlighting the huge
breadth and depth of science and technology that is encompassed in the field. In terms of the impact of platinum group metals (pgms) in the conference, over 30% of the oral papers presented involved the use of pgms. A more detailed analysis shows the following split between the pgms: 32 platinum, 22 palladium, 13 ruthenium, 12 rhodium and 2 iridium papers respectively. The industrial applications sessions included 11 papers that incorporated pgms.

With such a range of oral presentations and parallel sessions to choose from, this conference review can only discuss a few highlights. Therefore, in this review only papers which made significant use of pgms have been included.

Fischer-Tropsch Synthesis
The influence of pgm promoters on cobalt-supported Fischer-Tropsch catalysts continues to be an area of interest. Eric Marceau (Université Pierre et Marie Curie/ Centre National de la Recherche Scientifique (CNRS), France) presented a keynote paper characterising the impact of sorbitol and Ru promotion in the structure and performance of silica-supported cobalt catalysts. Addition of sorbitol to the impregnating solution was found to lead to a decrease in the size of the cobalt(II)(III) oxide (Co₃O₄) crystallites formed from 11 nm to 7 nm. Sorbitol was shown, by a combination of in situ quick-scanning X-ray absorption spectroscopy (Q-XAS), in situ UV-visible spectroscopy and thermal analysis to retard the decomposition of the cobalt precursor into Co₂O₃. In situ Q-XAS and temperature-programmed reduction (TPR) showed that the Co₂O₃ particles first reduced to cobalt(II) oxide (CoO). The reducibility of the Co-sorbitol/SiO₂ catalyst was quite low due to the formation of cobalt silicate (2). The presence of Ru greatly enhanced the reducibility of the catalysts. Transmission electron microscopy (TEM) images of reduced catalysts demonstrate the homogeneous distribution of cobalt particles in the catalyst prepared with sorbitol (Figure 1).

Ru in its own right can, of course, be used as a Fischer-Tropsch catalyst. Although cobalt and iron are preferred for industrial application due to cost considerations, Ru continues to draw scientific interest due to its ability to produce high molecular weight hydrocarbons. Xian-Yang Quek (Schuit Institute of Catalysis, Eindhoven University, The Netherlands) presented a very interesting paper demonstrating unprecedented oxygenate selectivity during Fischer-Tropsch synthesis over Ru nanoparticles. The Ru nanoparticles, encapsulated and stabilised in polyvinylpyrrolidone (PVP), were prepared in a size range of between 1.3 and 3.3 nm. The product distribution formed depended strongly on temperature. An aldehyde selectivity as high as 70% was obtained over 2.2 nm Ru nanoparticles at 125°C. With increasing temperature the total oxygenate selectivity decreased and the amount of hydrocarbon produced was increased. Mechanistic consideration of the product chain lengths suggested that the hydrocarbons and the oxygenates were formed on different sites.

Michael Claeyes (University of Cape Town, South Africa) presented an in situ magnetometer study on

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**The 2011 Michel Boudart Award for Advances in Catalysis**
This was awarded to **Professor James Dumesic** (University of Wisconsin-Madison, USA), who presented a plenary lecture on ‘Routes for Production of Liquid Transport Fuels by Liquid-Phase Catalytic Processing’.
the formation and stability of cobalt carbide during Fischer-Tropsch synthesis. Novel methods that yield different attributes of a catalytic system within the same measurement are both information rich and valuable from a research and development efficiency perspective. The application of magnetometry can reveal structural features of Co crystallites under authentic gas-to-liquid (GTL) process conditions. This study concentrated upon the formation and role of cobalt carbides during time on line of a simple Co-Pt/ alumina catalyst operated under varying conditions typical of Fischer-Tropsch processes. The experimental approach made use of a fixed-bed reactor placed within the field supplied by a magnetometer, from which it was possible to infer the state of magnetisation of the catalyst at different times and subject to the influence of reaction condition changes. Changes in magnetisation could be correlated with the extent of carbide formation, as confirmed by ex situ X-ray diffraction (XRD) measurements, and with the degree of reduction when the catalyst was treated under TPR conditions. Detailed analysis of magnetisation hysteresis allows modelling of Co crystallite size and some insight into active site mobility under reaction conditions.

When tested under Fischer-Tropsch conditions (230°C, 14 bar, H₂:CO = 2:1) a pre-carbided catalyst showed an increase of magnetisation during time on line, which is indicative of carbide decomposition to form the metallic state. However, this carbide decomposition took place slowly and remained incomplete even after an extended period of testing, suggesting that once carbides are formed, they will not decompose completely under typical Fischer-Tropsch conditions. The pre-carbided catalyst also displayed inferior Fischer-Tropsch performance (activity and methane selectivity) compared to a non-carbided catalyst. This performance was regained after hydrogen treatment, which also lead to completely restored magnetisation (Figure 2).
Biomass Conversion

One of the Industrial Application sessions was devoted to the conversion of biomass into liquid fuels. In this session it was clear that the use of pgms was key in many of the processes described.

Two papers were presented on the use of supported Ru catalysts to convert cellulose to sugar alcohols. The first of these from Kameh Tajvidi (Max-Planck-Institut für Kohlenforschung, Germany) investigated alternatives to sulfuric acid in conjunction with a 5 wt% Ru/C catalyst for the hydrolytic hydrogenation of cellulose. Reactions in the presence of silicotungstic acid achieved almost full conversion of cellulose and a sugar alcohol yield of up to 80%. The concept was successfully transferred to the direct conversion of spruce wood fibres as a real feedstock again with an almost full conversion of cellulose and hemicellulose content to sugar alcohols. An alternative approach, presented by Weiping Deng (Xiamen University, China), was to adsorb Ru nanoparticles onto caesium salts of tungstophosphate. This bifunctional catalyst contained both the acidity and hydrogenation activity required for the conversion of cellulose. A Ru/Cs3PW12O40 material was stable in repeated use and sorbitol yields of ~75% could be sustained after five recycling uses. The sorbitol yield increased with decreasing mean size of Ru particles from 10.8 to 1.6 nm.

Alexey Kirilin (Åbo Akademi University, Finland) investigated the use of a 5 wt% Pt/Al2O3 catalyst for the aqueous phase reforming (APR) of erythritol, xylitol and sorbitol as a means of producing hydrogen and components of liquid fuels. Sorbitol and xylitol were viewed as the most promising raw materials for the APR process due to the possibility of obtaining transportation fuel components (hexane etc.). No catalyst deactivation was observed after more than 140 h on line. Hydrogen yields for erythritol, xylitol and sorbitol under the same operating conditions were 48%, 28% and 22% respectively (Figure 3).

A series of supported 2 wt% Ru catalysts (Ru, ruthenium(IV) oxide, ruthenium(IV) sulfide) were investigated by Marcelo Kaufman-Rechulski (Paul Scherrer Institut, Villigen, Switzerland) as an alternative to the cold scrubbers that are currently used to remove tars and organic sulfur compounds during biomass gasification. The Ru catalysts were tested against commercially available NiMoS and CoMoS materials. The RuS2 catalyst was active for all three of the reactions under investigation (sour water gas shift, sulfur...
resistant hydrogenation and hydrodesulfurisation of thiophene) and appeared to be more stable under real process conditions.

Chuan Wang (Institute of Materials Science and Engineering, Singapore) presented an interesting paper on low-temperature hydrogenation of furfural on Pt catalysts supported on a multiwall carbon nanotube (MWCNT) support. A 5 wt% Pt/MWCNT catalyst at 150ºC and 20 bar H₂ achieved a furfural conversion of >95%. Both of the products formed, furfuryl alcohol (~90% selectivity) and 2-methylfuran, are more chemically stable than furfural, thereby facilitating further bio-oil upgrading at high temperature.

Aldehydes such as furfural are present in significant amounts in bio-oils obtained from the fast pyrolysis of biomass. Under typical conditions for bio-oil upgrading, these reactive aldehyde compounds can form tar-like black solids. This work demonstrated that a mild hydrogenation treatment can be used to remove reactive compounds in bio-oils, facilitating their storage and further high-temperature upgrading.

**Methanol Reforming**

Karin Föttinger (Vienna University of Technology, Austria) presented a paper investigating the use of in situ X-ray and vibrational spectroscopic studies on palladium/zinc(II) oxide and palladium/gallium(III) oxide as potential methanol steam reforming (MSR) catalysts. The localised generation of hydrogen as a fuel for proton exchange membrane (PEM) assemblies, is key to the successful design and deployment of fuel cells intended to support initiatives for sustainable means of transportation. The paper sought to address, with some success, the issue of current steam reforming catalysts in which the conversion of methanol generally results in the co-production of carbon monoxide – a potent catalyst poison. Pd supported on ZnO and Ga₂O₃ had shown excellent activity and selectivity to the steam reforming reaction, yielding only H₂ and CO₂ (3). Experiments undertaken at the Swiss Light Source (superXAS beamline), made use of a catalytic reaction cell from which it was possible to study the system by extended X-ray absorption fine structure (EXAFS) and infrared (IR) techniques, along with gas chromatography-mass spectrometry (GC-MS) analysis of catalyst performance. Using time-resolved EXAFS, it was possible to follow, in situ, the formation of the active Pd-Zn alloy phase of a Pd/ZnO MSR catalyst, via spillover and reduction of the ZnO by H₂ generated in the reaction. With time-on-stream, the degree of alloying was observed to steadily increase and, in parallel, the reactivity changed from methanol decomposition (CO/H₂) to MSR (CO₂/H₂), confirming that the Pd-Zn alloy is the selective phase for MSR. Pd-Zn alloying was found to be reversible on contact with O₂, producing Pd metal and ZnO with a corresponding reversion of selectivity to CO/H₂. The corresponding surface state and available adsorption sites were studied by FTIR spectroscopy of CO adsorption. Pd-Zn alloy formation led to the disappearance of bridge-bonded CO and a shift of the on-top CO band from 2080 cm⁻¹ to 2070 cm⁻¹. Upon O₂ treatment the bands assigned to unalloyed
metallic Pd reappeared but at a lower intensity which may be explained by a partial decoration of the Pd by patches of ZnO.

The theme of this paper was continued in a subsequent presentation from the same group, given by Christian Weilach, who extended the range of spectroscopic methods to expose more detail of the surface transformations associated with alloy formation and the change in the selectivity pattern observed during MSR (Figure 4).

**Characterisation**

Gary Attard (Cardiff Catalysis Institute, UK) gave a thought-provoking lecture on electrochemical perspectives on catalysis. This addressed the challenges of specifically identifying those surface topographies and two-dimensional morphologies that are associated with selective catalytic transformations. The presentation concentrated upon the application of cyclic voltammetry (CV) as a means of characterising surface states – including the existence of defects. Typical CV data collected from a series of palladium-gold alloys supported on graphite (0.4%–3% total metal loading) spanning the whole range of alloy composition were presented. Referring to one set of voltammograms, it was shown that the number of Pd surface sites is signified by the area of the CV peaks between 0 and 0.3 V associated with hydrogen electrosorption. The oxide stripping peaks also provide a measure of the available Pd and Au surface area (for example, the Au oxide stripping peak area at 1.1 V). More interestingly, the extent to which the surface is alloyed is given by a systematic shift in the potential of the Pd oxide peak to more positive potentials as surface Au composition increases. Similar studies using single crystal electrodes allow for direct comparison between supported metal catalysts and shape-controlled nanoparticle behaviour in catalytic and electrocatalytic reactions, since it can be demonstrated that the electrosorption charge between 0 and 0.3 V acts as a 'finger-print' analytical technique for the presence of particular step, terrace and kink sites (Figure 5).

**Concluding Remarks**

The study and use of pgms continues to be an essential component of catalyst research, both to extend fundamental understanding and to allow industrial exploitation. The three application areas reviewed in this article: Fischer-Tropsch, biomass conversion and methanol reforming, are linked by the challenge of meeting the world’s future energy demands and requirements. The pgms find use in a wide range of chemical reactions as demonstrated by this conference, and their use is also essential in several exciting new areas of research not reviewed here (for example, NOx storage and reduction for lean-burn gasoline and diesel vehicles and the direct synthesis of hydrogen peroxide from H2 and O2). The versatility of the pgms and the reaction selectivity they impart will make them an integral part of many future catalytic processes.

![Fig. 4. Illustration of the suggested structural changes of Pd/ZnO in various environments (Reprinted with permission from (4) © 2011 American Chemical Society)](http://dx.doi.org/10.1595/147106712X634080 • Platinum Metals Rev., 2012, 56, (2) •)
Fig. 5. Systematic changes in the CV response for a series of PdAu catalysts supported on graphite. Sweep rate = 50 mV s⁻¹ in 0.5 M aqueous sulfuric acid. The reference electrode was a saturated Pd/H electrode in contact with the electrolyte (Courtesy of Gary Attard, Cardiff Catalysis Institute, UK)

References
1 EuropaCat X: 10th European Congress on Catalysis: http://www.europacat.co.uk (Accessed on 28th February 2012)

The Reviewers
Gordon Kelly joined Johnson Matthey in 1994 following a Chemistry degree and PhD in Catalysis at Glasgow University, UK. He has worked in various research roles in areas such as solid base catalysis, hydrogenation, methanol synthesis, low-temperature shift and Fischer-Tropsch catalysis. He has over 40 catalysis publications including eight patents. Currently he is the Johnson Matthey Fischer-Tropsch Development Manager.

Steve Bailey has a PhD and over 20 years’ experience working in the fields of catalyst development and characterisation. He began his catalysis career at ICI where his principal roles were to apply surface characterisation methods to assist the understanding of catalyst performance across a broad range of industrial processes. He then moved into the roles of catalyst development and project management, focusing upon selective hydrogenation and gas purification, and more recently, has led the growth of catalyst characterisation capabilities within Johnson Matthey’s Process Technologies R&D centre.
In 1995, a review in Chinese was published to introduce the importance and the current state of the art of chiral technology. The National Natural Science Foundation of China started to actively support research in this area. From 2000, the Ministry of Science and Technology also started to support such research. Chinese researchers have been making notable achievements in this area by developing alternative effective new chiral ligands for established enantioselective transformations, as well as new catalytic enantioselective reactions with known or new ligands. Chinese chemists were invited to write an account on their own contribution in this area by briefly touching on the background for the contribution from chemists outside China.

“Dendrimers: Towards Catalytic, Material and Biomedical Uses”


This book covers the properties and uses of dendrimers and dendrons. The aim of this book is to be the reference book about dendrimers applications. It is divided in four main parts: Part 1: Generalities, Syntheses, Characterizations and Properties; Part 2: Applications in Catalysis; Part 3: Applications for the Elaboration or Modification of Materials; and Part 4: Applications in Biology/Medicine. Platinum group metal complexes are involved in catalytic applications, biological sensors, chemical sensors and luminescent dendrimers.

“Electrochemical Science and Technology: Fundamentals and Applications”

By K. B. Oldham and J. C. Myland (Trent University, Canada) and A. M. Bond (Monash University, Australia), John Wiley & Sons, Chichester, UK, 2012, 424 pages, ISBN: 978-0-470-71084-5 (paperback), £44.95, €54.00, US$65.00

This book addresses the scientific principles underlying electrochemistry. It could serve as a text for a course in electrochemistry at a university or college. To keep the size and cost of the book reasonable, much of the more tangential material is available as ‘Webs’: documents devoted to a single topic that are freely accessible from the publisher’s Student Companion Site at: http://www.wiley.com/go/EST. Topics include fuel cells, electrodes, corrosion protection and pollution control, among many others.

“Interfacial Phenomena in Electrocatalysis”


This is claimed to be the first and only volume to cover interfacial electrochemistry, as opposed to other facets of interfacial science. Contributors are international leaders in their area of expertise. Topics include:
(a) Temperature Effects on Platinum Single-Crystal/Aqueous Solution Interphases. Combining Gibbs Thermodynamics with Laser-Pulsed Experiments;
(b) Surface Thermodynamics of Metal/Solution Interface: the Untapped Resources;
(c) XAS Investigations of PEM Fuel Cells;
(d) Palladium-Based Electrocatalysts for Alcohol Oxidation in Direct Alcohol Fuel Cells;
(e) Structure and Reactivity of Transition Metal Chalcogenides Toward the Molecular Oxygen Reduction Reaction;
(f) Materials, Proton Conductivity and Electrocatalysis in High-Temperature PEM Fuel Cells.
“Supported Metals in Catalysis”, 2nd Edition
The second edition of “Supported Metals in Catalysis” has new and updated chapters containing summaries of research in this rapidly evolving field. Chapters of interest include: ‘Supported Metal Catalysts for Fine Chemicals Synthesis’, ‘Supported Metals in the Production of Hydrogen’, ‘Supported Metals for Application in Fuel Cells’ and ‘Supported Metals in Vehicle Emission Control’.

JOURNALS
ChemistryOpen
Editors: K. Hindson and H. Ross; Deputy Editor: N. Ortúzar; Wiley-VCH and ChemPubSoc Europe; E-ISSN: 2191-1363
Wiley-VCH and ChemPubSoc Europe, an association of sixteen chemical societies, have launched ChemistryOpen, the first open access chemical society journal. ChemistryOpen will publish peer-reviewed primary research in all areas of chemistry, and will thus satisfy funding organisations and institutes which require that the research funded by them should be accessible to all. As an additional feature, short summaries of PhD theses with a link to the full version will be published. This Thesis Treasury will make PhD theses in chemistry readily accessible while linking them through CrossRef to all cited journal articles in the programme.

ChemPlusChem
Editor: N. A. Compton; Deputy Editor: M. Spiniello; Wiley-VCH and ChemPubSoc Europe; E-ISSN: 2192-6506
Wiley-VCH and ChemPubSoc Europe have launched ChemPlusChem. Original papers published will cover at least two different aspects (subfields) of chemistry or one of chemistry and one of another scientific discipline. ChemPlusChem succeeded the Collection of Czechoslovak Chemical Communications which ceased publication at the end of 2011. Editorial Board Co-Chairman Michal Holec explained: “Research in chemical and molecular sciences is becoming more and more complex and inter- and multidisciplinary and also its impact in physical, biological and material sciences is rapidly growing. Typically nowadays projects involve synthesis of compounds, catalysis, spectroscopy, crystallography, biological evaluations, physical measurements, and/or material studies”.

Integrating Materials and Manufacturing Innovation
Editor: C. Ward; The Minerals, Metals & Materials Society (TMS) and Springer; ISSN: 2193-9764; e-ISSN: 2193-9772
Integrating Materials and Manufacturing Innovation (IMMI) is a new open access journal supporting the discovery, development, and application of materials, materials systems, and materials processes for practical use in manufacturing. IMMI covers innovations from the discovery of materials to their deployment.

Special Issue: Celebrating the 150th Anniversary of the Department of Chemistry, The University of Tokyo
The Department of Chemistry of The University of Tokyo, Japan, celebrated its 150th anniversary in 2011. To commemorate this occasion and to honour the department’s tradition of excellence, this special issue featuring contributions from international scientists closely linked with the department was dedicated to this anniversary. The cover picture, provided by the issue co-organisers, Professors Shu Kobayashi and Eiichi Nakamura, captures the history and the many faces of the department. Items of interest include: ‘New Design Tactics in OLEDs Using Functionalized 2-Phenylpyridine-Type Cyclometalates of Iridium(III) and Platinum(II)’, ‘One-Pot Nitrile Aldolization/Hydration Operation Giving β-Hydroxy Carboxamides’ and ‘Platinum-Acetylide Polymers with Higher Dimensionality for Organic Solar Cells’.
Themed Issue: Heterogeneous Catalysis for Fine Chemicals

Mario Pagliaro (Istituto per lo studio dei materiali nanostrutturati, CNR, Palermo, Italy) and Graham Hutchings (Cardiff University, UK) introduce this themed issue. Today, in addition to the original rhodium homogeneous catalysts, there are a number of commercial fine chemicals production processes using highly efficient and selective solid catalysts. To celebrate the contribution of Professor Michele Rossi to this field on the occasion of his 70th birthday, this themed issue aims to “grasp the current momentum in heterogeneous catalytic chemistry for fine chemicals”. Palladium with interstitial carbon atoms is shown to be an ultraselective hydrogenation catalyst. Other contributions demonstrate how to discriminate between homogeneous or heterogeneous nano-catalysis in the conjugate addition of arylboronic acids mediated by palladium(II) complexes; how the selective hydrogenation of functionalised nitroarenes can be carried out under ultra-mild conditions; and how ruthenium-modification of gold catalysts enhances the selective oxidation of aliphatic alcohols.

ON THE WEB

CatApp
CatApp is a web application, from SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park and Department of Chemical Engineering, Stanford University, California, USA, for looking up calculated reaction and activation energies for elementary reactions occurring on metal surfaces. The database includes reaction energies for all surface reactions that involve C–C, C–H, C–O, O–O, N–N, C–N, O–N, N–H splitting for molecules with up to three C, N, or O atoms on close-packed fcc(111), hcp(0001), and bcc(110) surfaces, as well as stepped fcc and hcp surfaces. The metals included in the database are Ag, Au, Co, Cu, Fe, Ir, Mo, Ni, Pd, Pt, Re, Rh, Ru, Sc and V.

Find this at: http://suncat.stanford.edu/catapp/

Materials Project

Researchers from the Department of Energy’s Lawrence Berkeley National Laboratory and the Massachusetts Institute of Technology, USA, jointly launched the Materials Project, which is a search engine for material properties. With the Materials Project, researchers can use supercomputers to characterise properties of inorganic compounds, including their stability, voltage, capacity and oxidation state, which had previously not been possible. The results are then organised into a database.

Find this at: http://www.materialsproject.org/
Abstracts

CATALYSIS – INDUSTRIAL PROCESS

Kilogram-Scale Asymmetric Ruthenium-Catalyzed Hydrogenation of a Tetrasubstituted Fluoroamide


Ru-catalysed asymmetric homogeneous hydrogenation (AHH) was used as the key step of a multi-kg scale synthesis of an enantiomeric fluoropiperidine. The AHH of a tetrasubstituted β-fluoroamide was carried out under mild conditions using a Ru/Josiphos catalyst with an ee of 98%.

CATALYSIS – REACTIONS

Hydrodeoxygenation of Waste Fat for Diesel Production: Study on Model Feed with Pt/Alumina Catalyst


Hydrodeoxygenation of a model feed mixture has been investigated. Oleic acid and tripalmitin in molar ratio 1:3 were hydrotreated at 325ºC with 20 bars H₂ in a stirred batch autoclave with 5 wt% Pt/γ-Al₂O₃. Hydrogenation of both reactants was limited and decarboxylation or decarbonylation of the ester and carboxylic acid functionalities were highly favoured, giving C chain lengths of odd numbers. Pd/γ-Al₂O₃ was found to be slightly more active than Pt/γ-Al₂O₃ and had a higher ratio of decarboxylation and decarbonylation to hydrogenation, while Ni/γ-Al₂O₃ was substantially less active. The conversion of oleic acid increased from 6% to 100% when the temperature was increased from 250ºC to 325ºC.

Selective Hydrogenation of Sunflower Oil over Noble Metal Catalysts


Pd and Pt supported on Al₂O₃, ZrO₂ and TiO₂ were screened as heterogeneous catalysts for the selective hydrogenation of sunflower oil in a batch reactor under different operating conditions. Metal dispersions between 6–69% and loadings between 0.3–3.9% were studied for promotion of selectivity in cis C₁₈:₁. Pd catalysts were found to be much more active than a conventional Ni catalyst. The Pt catalyst was not as active as the Pd catalysts but produced lower *trans* fatty acids. The level of *trans* could be further reduced by increasing the operating pressure to 10 bar and reducing the reaction temperature to 100ºC especially with the Pt catalyst.

The Conversion of 1,8-Cineole Sourced from Renewable Eucalyptus Oil to *p*-Cymene over a Palladium Doped γ-Al₂O₃ Catalyst


The conversion of the title 1,8-cineole over a Pd-doped γ-Al₂O₃ catalyst was studied. Both Pd and γ-Al₂O₃ were found to be bifunctional catalysts but the Pd-doped system showed very high activity and selectivity, yielding >99% *p*-cymene, while producing large amounts of H₂ at a bed temperature of ~250ºC. The reaction mechanism is suggested to involve C–O bond fission in cineole, followed by dehydrogenation/isomerisation to give *p*-cymene.

Asymmetric Synthesis of 2-Alkyl-3-phosphonopropanoic Acid Derivatives via Rh-Catalyzed Asymmetric Hydrogenation


The ferrocene-based diphosphine ligand (S₃c,S₃Fc)-TaniaPhos was shown to be highly efficient in the Rh-catalysed asymmetric hydrogenation of 3-aryl-2-(phosphonomethyl)propenates. Excellent enantioselectivity (90–98% ee) and high catalytic activity (S/C up to 1000) were exhibited.
α,β-Unsaturated Imines via Ru-Catalyzed Coupling of Allylic Alcohols and Amines

α,β-Unsaturated imines were synthesised using only an allylic alcohol, an amine and a Ru catalyst. The use of large excesses of oxidants or dehydrating reagents and the purification of sensitive intermediates were not required. The reaction was most effective with trisubstituted allylic alcohols. The reaction conditions are mild enough to preserve other unsaturated functional groups from reduction. The ability of Milstein’s PNN Ru catalyst to catalyse the efficient redox isomerisation of secondary allylic alcohols to the corresponding ketones was also demonstrated for the first time.

FUEL CELLS
Products of SO2 Adsorption on Fuel Cell Electrocatalysts by Combination of Sulfur K-Edge XANES and Electrochemistry

SO2 adsorption products on Pt/Vulcan C catalyst coated membranes (CCMs) were investigated at different electrode potentials using a combination of in situ S K-edge XANES spectroscopy and electrochemical techniques. SO2 was adsorbed from a SO2/N2 gas mixture with the Pt/Vulcan C electrode potential held at 0.1, 0.5, 0.7 or 0.9 V vs RHE. S0 adatoms were identified as the SO2 adsorption products at 0.1 V; mixtures of S0, SO2 and sulfate/bisulfate ((bi)sulfate) ions at 0.5 and 0.7 V; and (bi)sulfate ions at 0.9 V.

Effect of Deactivation and Reactivation of Palladium Anode Catalyst on Performance of Direct Formic Acid Fuel Cell (DFAFC)
S. M. Baik, J. Han, J. Kim and Y. Kwon, Int. J. Hydrogen Energy, 2011, 36, (22), 14719–14724

Pd and Pt were used as anode and cathode DFAFC catalysts, respectively, and were applied to a Nafion membrane by CCM spraying. As multiple repeated DFAFC operations were performed, the cell performance of DFAFC steadily degraded. This is attributed to the electrooxidation of Pd into Pd–OH, which occurs between 0.1 and 0.55 V. In CV experiments where the voltage was higher than 0.9 V vs DHE, cell performance was reactivated due to redox reactions of Pd–OH into Pd–O and Pd–O into Pd.

Development of a Catalytic Hollow Fibre Membrane Microreactor as a Microreformer Unit for Automotive Application

A catalytic hollow fibre membrane microreactor (CHFMMR) was prepared by electroleless plating of a uniform, defect-free Pd/Ag membrane with a total thickness of 5.0 μm onto the outer layer of a YSZ hollow fibre substrate. A thin layer of a 10 wt% NiO/MgO–CeO2 ethanol steam reforming (ESR) catalyst (max. 1.3 wt%) with a high surface area was impregnated into the YSZ hollow fibres using the sol–gel Pechini method. ESR was carried out and high purity H2 was obtained outside the shell with a yield of <53% of the total H2 produced in the ESR. This CHFMMR can be used in the development of on-board H2 generation using EtOH as a fuel for PEMFCs in vehicular applications.

APPARATUS AND TECHNIQUE
Brittle Failure Analysis of PtRh10 – Pt Thermocouple Wire

The brittle failure of PtRh10–Pt thermocouples in reducing atmospheres was investigated. Electron probe microanalysis indicated that the formation of the low melting point eutectic, Pt5Si2, is the main cause of brittle failure.

Electrospun Carbon Nano-Felt Surface-Attached with Pd Nanoparticles for Hydrogen Sensing Application

A C nano-felt with Pd NPs attached at the surface was prepared from electrospun polycrylonitrilene nano-felt surface-functionalised with amidoxime groups. The material consisted of relatively uniform and randomly overlaid C nanofibres with diameters of ~300 nm. The electrospun C nano-felt was mechanically flexible and resilient, and its resistance varied on exposure to H2 at room temperature. This material could therefore be used for the fabrication of gas- or biosensors.
ELECTRICALS AND ELECTRONICS

Injection of Synthesized FePt Nanoparticles in Hole-Patterns for Bit Patterned Media

T. Hachisu, W. Sato, S. Ishizuka, A. Sugiyama, J. Mizuno and T. Osaka,

Previously, the immobilisation of FePt NPs on a thermal oxide Si substrate was carried out by utilising the Pt–S bonding between the -SH in (3-mercaptopropyl)trimethoxysilane (MPTMS) and Pt in FePt NPs. In this study, attempts were made to control the distortion of the arrangement of FePt NPs using an MPTMS layer modified with a silane coupling reaction and a geometrical structure prepared by UV nanoimprint lithography. The hole-patterns used for the geometrical structure on Si(1 0 0) were 200 nm wide, 40 nm deep, and had a 500 nm pitch. The 5.6 nm FePt NPs were used to coat the hole-patterns by using a picolitre pipette.

REFINING AND RECOVERY

Recovery of Platinum from Spent Catalysts by Sintering-Leaching

M. Wang, X. Dai, J. Wu, B. Zhang, Y. Wu and T. Chen,
*Precious Met. (Chin.)*, 2011, **32**, (4), 6–10

The sintering-leaching method was used to treat the Al₂O₃ in spent catalysts. Pt was then recovered from the residues after the enriching process. The residual C was 0.54% with a high decoking rate of 92.66%, after roasting the spent catalysts at 600°C for 1 h. The Pt was enriched 17.87 times by the sintering-leaching process. The ‘cinder’ was mixed with NaOH and then sintered at 800°C for 2 h. The ‘clinker’ was leached at 95°C for 10 min.

PHOTOCONVERSION

Photodegradation of 2,4-D over PdO/Al₂O₃–Nd₂O₃ Photocatalysts Prepared by the Sol–Gel Method

A. Barrera, F. Tzompantzi, V. Lara and R. Gómez,

The photocatalytic activity of 1.0 wt% PdO/Al₂O₃–Nd₂O₃ was studied in the photodegradation of 2,4-dichlorophenoxyacetic acid (2,4-D). PdO/γ-Al₂O₃ photodegraded 2,4-D; however, the addition of Nd₂O₃ to γ-Al₂O₃ improves the photocatalytic activity. As the concentration of Nd₂O₃ was increased from 2 to 10 wt%, the photodegradation of 2,4-D was enhanced.

Surface oxide films formed on the Pd were found to be relatively insoluble in neutral conditions and in the absence of Cl⁻, where dissolution was limited by the solubility of Pd²⁺. In HCl the greater solubility of PdCl₂ allowed the oxide film to dissolve completely.
Patents

**CATALYSIS – APPLIED AND PHYSICAL ASPECTS**

**Core-Shell Catalyst Particle**
Toyota Jidosha Kabushiki Kaisha, US Appl. 2012/0,010,069

A core-shell catalyst particle is produced by preparing a core particle containing a first core metal (selected from Pd, Ag, Rh, Os or Ir) which has a standard electrode potential of at least 0.6 V and a second core metal (selected from Co, Cu, Fe or Ni) with a lower electrode potential. The second core metal is eluted by adjusting the pH (2 to 4) and the potential (−2 V to 1 V) of the core particle and the shell portion is coated on the core particle by displacement plating to replace a Cu monoatomic layer deposited by underpotential deposition. The shell portion includes a metal selected from Pt, Ir and Au. The average diameter of the core particle is 4–40 nm.

**Mixed Bed Polymeric Catalyst**
Dow Global Technologies LLC, Chinese Appl. 102,309,989; 2012

A mixed bed polymeric catalyst consists of 10–90 wt% of a first catalyst having ion exchange resin loaded with zerovalent metal selected from Pt, Pd, Rh, Ir, Ru, Cu, Au or Ag and 10–90 wt% of a second catalyst which has a strong acidic ion exchange resin without metal, this comprises of a styrenic strong acid cationic resin with a moisture hold capacity from 10–90% and a volume capacity from 0.5–7 meq l−1. The first and second catalysts both have a particle size of 100 μm to 2 mm. The metal is uniformly distributed throughout the mixed bed. This catalyst is used for the hydrogenation of alkenes, alkenes, aldehydes, ketones, alcohols, nitriles, amines and nitro groups.

**CATALYSIS – REACTIONS**

**Producing Olefin Oxide**
Sumitomo Chem. Co., Ltd, World Appl. 2012/005,824

A method for producing an olefin oxide e.g. propylene oxide involves reacting an olefin (propylene) with O₂ at 100–350°C in the presence of a catalyst consisting of CuO, OsO₂, an alkali metal or alkaline earth metal and a halogen component. This catalyst is obtained by impregnating a porous support (selected from Al₂O₃, SiO₂, TiO₂ or ZrO₂) with a solution containing Cu⁺⁺ ions, Os³⁺ ions, alkali metal or alkaline earth metal ions and halogen ions, followed by calcining the composition. The molar ratio of Cu:Os in the catalyst is 1:99 to 99:1.

**EMISSIONS CONTROL**

**Two Layers in an Exhaust Gas Purifying Catalyst**
Johnson Matthey Plc, US Appl. 2012/0,031,085

An exhaust gas purifying catalyst comprises two catalyst layers, each containing different compositions of fire resistant inorganic compound (this is a powder selected from Al₂O₃, SiO₂-Al₂O₃, zeolite, TiO₂, SiO₂, CeO₂ and ZrO₂ or a mixture and has an average particle diameter of 2–10 μm). The first catalyst layer is selected from Pt, Pd, Rh or Pt/Pd and the second catalyst layer is selected from Pt, Pd, Rh, Rh/Pt and Rh/Pd, with both layers extending a length of ≥40% to <100% of the total passage length. The first layer is extended from the exhaust gas introduction port side to the discharge port side and the second layer is extended from the exhaust gas discharge port side to the introduction port side so that both layers are partly overlapped.

**Treatment of Nitrogen Oxides and/or Particulate Matter in Lean Gas**
Johnson Matthey Plc, British Appl. 2,481,057; 2011

A method for treating NOx and PM or both comprises of: (a) a NO conversion catalyst (for converting NO to NO₂) supported on a substrate monolith, the catalyst contains a Mn oxide and one or more of Pt, Pd and Rh in a loading of 1–240 g ft⁻³; (b) a SCR catalyst (for selectively catalysing the reduction of NOx to N₂) supported on a flow-through substrate monolith and located downstream from the NO conversion catalyst; and optionally (c) a catalysed filter substrate for removing PM to combust it in NO₂.

**FUEL CELLS**

**Platinum Alloy Catalyst**
Johnson Matthey Plc, World Appl. 2012/017,226

A Pt alloy catalyst, PtXY, where X = Ni, Co, Cr, Cu, Ti or Mn and Y = Ta or Nb (which is less leachable than X in an acidic environment) with (in at%): 20.5–40 Pt; 40.5–78.5 X; and 1–19.5 Y is utilised for PAFC and PEMFC. This catalyst is supported on a conductive support material and is used at the fuel cell cathode.
METALLURGY AND MATERIALS

Palladium-Containing Alloy for Jewellery Ware
Pasquale Bruni Spa, World Appl. 2012/017,299
An alloy consists of (in wt%): 4–4.5 Au; 35–68 Ag; 8–30 Pd; and one or more elements selected from Ir, Cu, Zn, Ni and Si in a total amount from 18–32 wt% or In in a total amount from 25–32 wt%. This alloy can be used for goldware or jewellery.

Platinum Jewellery Alloy
Krastsvetmet, Russian Patent 2,439,180; 2012
An alloy comprising of (in wt%): 99–99.5 Pt; 0.1–0.7 Ir; 0.1–0.5 Co; and the balance Ga. This alloy is suitable for manufacturing jewellery, especially chains, using investment microcasting or plastic deformation.

APPARATUS AND TECHNIQUE

Palladium in Heating Circuit
A planar device consists of a heater circuit which is formed by first depositing a heater precursor material consisting of Pd, optionally alloyed with Rh to reduce its tendency to oxidise, in a predetermined pattern on the surface of a first unfired ceramic substrate. This is then laminated to a second unfired ceramic substrate where Pd is in contact with the second substrate to form a laminated combination, this is then fired in an oxidising atmosphere at 400–850°C sufficiently slowly to prevent the formation of voids in the final structure. The line widths of the heater circuit are 0.1–0.25 mm in the area which reaches the highest temperature.

MEDICAL AND DENTAL

Stent Delivery Catheter
Kaneka Corp, Japanese Appl. 2012-000,328
A stent delivery catheter has a multilayer shaft tube comprising of an outer layer, a reinforcement layer and an inner layer. A tubular member (e.g. PtIr) is formed between the outer layer and reinforcement layer on the shaft tube end.

PHOTOCONVERSION

Reflective Electrode for Light-Emitting Diode
LG Innotek Co, Ltd, European Appl. 2,410,583; 2012
The structure of a LED comprises of two conductive semiconductor layers and an active layer. An electrode is disposed on the first semiconductor layer and a reflective electrode (surrounded by a channel layer selected from Pt, Pd, Rh, Ir, Ti, Ni and W and connected to a support substrate through an adhesive layer) is disposed on the second semiconductor layer which also has an ohmic layer disposed on the current blocking layer.

Solar Cells with Multiple Dyes
Bangor Univ., British Appl. 2,481,035; 2011
A method for the preparation of dyes-sensitised solar cells with multiple dyes consists of: (a) preparing the first electrode from an electroconducting substrate, which is a glass or polymer plate coated with a transparent conducting oxide, preferably SnO2 which has been preferably doped with F; (b) applying ≥1 layers of a paste of TiO2 NPs on the conducting side of the substrate; (c) subjecting the coated substrate to a thermal treatment from 300–600°C for 1 h; (d) preparing a second electrode in the same way as the first electrode and additionally coating it with Pt; (e) optionally predyeing the first coated electrode with a solution containing ≥1 dyes; (f) piercing two perforations in the first and/or second electrode and sealing these together with glue or a thermoplastic polymer; (g) injecting or pumping ≥2 solutions containing ≥1 different dyes under vacuum to covalently bind the dye(s) to the surface of the metal oxide; (h) injecting or pumping the electrolyte (selected from a liquid nitrile solvent containing a redox couple selected from Ru bipyridil complexes, Ru terpyridin complexes, coumarins, phthalocyanines, squaraines, indolines or triarylamine dyes) through the holes in the electrodes; (i) sealing the holes in the electrodes with glue or a thermoplastic polymer; and (j) providing an external connection between the two electrodes for electron transport. The dyeing between the sealed electrodes takes place from 10–70°C and the electrolyte is added <10 min after the dye, therefore, the dyeing is completed in 10 min.
Platinum in Dye-Sensitised Solar Cell
Toyo Aluminium Ltd, Japanese Appl. 2011-171,133
A cathode for a dye-sensitised solar cell contains an Al substrate. The surface of the substrate is laminated by sputtering with at least one metal selected from Pt, Au or Ag. The Al substrate is 7–200 μm thick and the Pt, Au or Ag layer is 1–50 nm thick. The cathode is suitable for a dye-sensitised solar cell using an ionic liquid free from iodine or iodide.

REFINING AND RECOVERY
Recovery of Platinum Group Metals
Wintermute Metals Pty Ltd, World Appl. 2011/140,593
A method for extracting pgms from a pgm-containing material, especially spent automotive catalysts, is claimed. This involves mixing the pgm-containing material with a chloride leaching solution which consists of 10–20 wt% HCl and ≥1 trivalent metal chloride salt selected from AlCl3, FeCl3, CrCl3, or lanthanide chloride salts. This process occurs in an overpressure of Cl2 gas of ~1–2 atm at ~55–90ºC for ~120 min. The leachate solution may be recycled for use as the chloride leaching solution. The recovery of pgms in the leachate solution involves subjecting this solution to electrowinning, cementation, solvent extraction, gas-reduction or adsorption.

SURFACE COATING
Coating for Gas Turbine Engine Component
General Electric Co, US Patent, 8,084,094; 2011
A coating system is applied to the surface of a substrate (formed from a Ni-base alloy e.g. Ni3Al) to prevent the formation of a secondary reaction zone. This system involves plating a stabilising layer (selected from the pgms: Pt, Pd, Rh or Ir) on the surface of the substrate then heat treating at ~900–1120ºC for ~1–8 h prior to depositing an Al-containing overlay coating which has also been coated with a ceramic coating. The stabilising layer consists of ~75 at% pgm and optionally Ni, Co, Cr, Al and/or Ru in a combined amount of up to 25 at%. This layer has a thickness of ~3–12 μm.

Leaching with 15% HCl and Cl2 gas at 90ºC for 5 min

SURFACE COATING
Coating for Gas Turbine Engine Component
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A coating system is applied to the surface of a substrate (formed from a Ni-base alloy e.g. Ni3Al) to prevent the formation of a secondary reaction zone. This system involves plating a stabilising layer (selected from the pgms: Pt, Pd, Rh or Ir) on the surface of the substrate then heat treating at ~900–1120ºC for ~1–8 h prior to depositing an Al-containing overlay coating which has also been coated with a ceramic coating. The stabilising layer consists of ~75 at% pgm and optionally Ni, Co, Cr, Al and/or Ru in a combined amount of up to 25 at%. This layer has a thickness of ~3–12 μm.
A common question asked by process chemists is "Do I use a biocatalyst or one based on a transition metal?". The choice can be an important part of route scouting (1). Unlike many articles that leave the reader waiting to the end, here is the answer: "It depends".

The advantages of using a catalyst rather than a stoichiometric reagent can be summed up by the concepts of ‘green’ chemistry (2), but the simple way to look at the catalytic approach is that less of a catalyst is used compared to a stoichiometric reagent, so the cost of the material and its removal is reduced.

In the past, processes were designed by chemists who had little familiarity with biotransformations and enzymes. Thus, the use of an enzyme was a means of last resort (3). Now, many companies have process groups which include members who are familiar with enzymes and biotransformations. Indeed, to those who are familiar with biological systems, they seem to be the solution to most problems!

Background Knowledge
One of the criteria for the choice between bio- and chemical catalysis is background knowledge. Our understanding of chemistry is far from complete. However, there is a wealth of information available and the key parameters to control the reaction outcome are known for a wide range of transformations. This knowledge has often been gained by trial and error. As our knowledge has increased, better and more selective catalysts have been developed. Even if we still cannot design the ultimate catalyst from first principles, we can use prior knowledge to obtain a workable catalyst.

For biological systems, trial and error has again been used, but often there are subtle differences between very similar enzymes so that interpretation of the results can be difficult. Examples of this are provided by baker's yeast reductions and pig liver esterase. More recently, our understanding of active sites and how to manipulate them either in a controlled or random way has allowed for the expansion of biomethods to make useful compounds.

Modern screening methods make it almost as easy to determine whether a chemical or a biocatalyst is capable of the desired transformation. However, chemical approaches will often require a more involved analysis, such as high-performance liquid chromatography (HPLC). Although biocatalysts may also need this type of analytical method, much faster methods have been developed and even the survival of the strain can be used.

An Exclusive Approach
Closely related to this consideration is the ability of one system to perform a transformation that is very difficult for the other to accomplish. Examples are the hydrolysis of a meso-diester and the coupling of aryl groups. In the first case, chemical catalysts have been developed to hydrolyse just one ester group of a diester to provide a chiral monoester. In contrast, there is a wealth of information on enzymatic examples and for some, as with pig liver esterase, a mnemonic has been developed to predict whether the reaction can be performed with 'wild-type' enzyme and what the stereochemical outcome will be (4).

In the example of aryl couplings, there are many examples and variations of palladium-catalysed Heck and Suzuki reactions (5, 6), to name but two of these types of reaction; these approaches are the methods of choice in most cases. There are very few examples of enzymatic aryl couplings and, thus, this will only be used when alternative chemical methods are not applicable.

Solvent Choice
Another criterion used to decide what type of catalyst is used is that the process must include isolation of the product in acceptable yield and purity. Although significant advances have been made for the use of enzymes in the presence of organic solvents and with substrates that are poorly soluble in aqueous media, problems can still exist. Conversely, if the product is very water soluble, isolation of the desired material can present a significant challenge. Chemical transformations usually have the advantage of a
number of solvent systems being available to perform the transformation and subsequent isolation.

Scaling Up
The scale-up of chemical catalytic reactions is usually an exercise in normal process chemistry. Synthesis of the ligands and transition metal catalyst usually present few problems, as the amounts are much lower than for the reaction itself. However, to improve specificity and efficiency new catalysts have to be prepared and tried. This can be a time-consuming exercise. On the biocatalytic side, modifications to the original enzyme can be made by genetic modifications and rapid screening. This allows selectivity, stability and other issues to be addressed. On the other hand, these studies can be time-consuming and may require more resources than just making a new ligand.

Cost and Speed
The criteria of cost and speed also contribute to the choice of catalyst system. In the early stages of development of a drug candidate, speed is of the essence but cost is still important. Precedence and the availability of the catalyst will be key factors. For larger scale work, the pendulum may swing from a chemical method to a biocatalytic one. For commercial production, biological routes are often cost effective. However, it must be remembered that the catalytic step is usually part of a synthetic sequence. The substrate for the catalytic step has to be prepared and the product converted to the final target molecule.

As an example, consider the synthesis of (S)-2,3-dihydro-1H-indole-2-carboxylic acid. It was necessary to replace an inefficient route that used a late stage resolution. Many alternatives were considered but the most efficient used a copper-catalysed cyclisation to form the product. To prepare the substrate for this reaction, three enzymatic approaches were identified (Figure 1). When the alternative methods were compared in terms of costs and efficiencies (including the number of steps), the ammonia lyase approach was the route of choice as the starting material is readily available (7, 8). Although there are a number of approaches to ortho-halocinnamic acid (8), the Heck reaction provides an efficient synthesis. Without the use of this palladium-catalysed reaction, the remainder of the sequence would not be efficient. Thus, the overall sequence shows that biocatalysts and chemical catalysts are required to effect an efficient, sustainable process.

Conclusion
In summary the choice between a chemical and a biological catalyst depends on many factors. The background literature plays an important role, as

![Fig. 1. Some routes to (S)-2,3-dihydro-1H-indole-2-carboxylic acid](image-url)
does cost and speed to implement the process. There are some transformations where both types of catalysts excel. Chemical catalysts can work well with a specific and well documented range of substrates, and in particular palladium finds wide use in essential reactions such as Heck coupling. Enzymatic approaches can have a broader application but may be less well understood. In the end, both transition metal catalysts and biocatalysts may be required to produce an efficient process.

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References

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