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Molecular Design for Long-Range Electronic Communication between Metals

POLYNYNE AND ETHYNYLATED AROMATIC SYSTEMS AS MOLECULAR WIRES
IN BINUCLEAR RUTHENIUM β-DIKETONE COMPLEXES

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To construct molecular devices it is necessary to use mixed-valence metal complexes which have a large metal-metal separation distance and which exhibit strong coupling between the metals, so that errors which might arise from electrostatic interaction between the metal ions are prevented. Bridges, or spacers, are needed between two metal terminal sites to operate as effective molecular wires when one metal terminal site is in the excited state, and/or when both the terminal components are in the ground state. Binuclear ruthenium complexes, consisting of tris(β-diketonato)ruthenium(III) units, which are suitable as the terminal redox sites, can be used to evaluate how well the bridges function as molecular wires in the ground state. This is because their Ru(III)-Ru(II) and Ru(IV)-Ru(III) mixed-valence states are accessible for experimental use. In this article, a polyynyl system and an ethynylated aromatic system are evaluated as molecular wires, using the binuclear (β-diketonato)ruthenium(III) complexes containing these systems as the bridges. In the Ru(IV)-Ru(III) mixed-valence state, the ruthenium complexes show relatively strong electronic interactions between the metal centres. This is interpreted by a superexchange (through-bond) hole transfer mechanism via the highest occupied molecular orbitals of the bridge. Molecular orbital calculations provide a guide to the molecular design of bridging ligands for long-range electronic coupling.

Mixed-valence binuclear complexes have been actively studied since 1969 when Creutz and Taube reported the fascinating mixed-valence ion, \([\text{NH}_3)_5\text{Ru}(\mu-\text{pz})\text{Ru(NH}_3)_5]^+\) (pz = pyrazine), the so called ‘Creutz-Taube ion’ (1). Studies on mixed-valence complexes are closely related to the kinetics of electron transfer reactions, and provide valuable information on the degree of interaction between two metal sites. In such studies, three classes of symmetrical binuclear systems may be distinguished, depending on the degree of the electronic coupling between the two metal ions (2, 3).

In the Class I system, the electronic coupling is so weak that the mixed-valence complex exhibits only the properties of the isolated mononuclear complexes. The Class II system has electronic coupling to some extent, so the mixed-valence complex exhibits slightly perturbed mononuclear characteristics but also has obvious properties not associated with the isolated units. This system remains ‘valence trapped’ or charge localised. In the Class III system, the coupling is so large that the properties of the isolated mononuclear complexes are absent and only new properties are discerned. This is the delocalised case.

We can estimate the extent of the metal-metal interactions by the stability of the binuclear complex formed in a ‘comproportionation’ (reverse of disproportionation) reaction, in which the oxidation numbers of the metals mix. The comproportionation reaction for the Class II system is:

\[
M(Z+1)-M(Z+1) + M(Z)-M(Z)
\]

\[
K_c = \frac{2M(Z+1)-M(Z)}{M(Z+1)-M(Z+1) + M(Z)-M(Z)}
\]

where M represents the metal and Z the oxidation number. The comproportionation constant (equilibrium constant of Equation (i)), \(K_c\), and the free energy change for the comproportionation, \(\Delta G_c\), are calculated from the difference in the reversible
half-wave potentials between the two reduction potentials $\Delta E_{1/2} = (E_{1/2}(1) - E_{1/2}(2))$.

$$
\begin{align*}
M(Z+1) - M(Z+1) + e^- &= M(Z+1) - M(Z) \quad E_{1/2}(1) \\
M(Z+1) - M(Z) + e^- &= M(Z) - M(Z) \quad E_{1/2}(2)
\end{align*}
$$

(K)

$$K_c = \exp(\Delta E_{1/2} F/RT) \quad (iv)$$

$$\Delta G_c = -\Delta E_{1/2} F \quad (v)$$

The free energy change of the comproportionation, $\Delta G_c$, is expressed by the Equation:

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r \quad (vi)$$

where $\Delta G_s$ is an entropy factor, $\Delta G_e$ is an electrostatic factor arising from the repulsion of the two similarly charged metal centres, $\Delta G_i$ is an inductive factor dealing with the competitive coordination by metal ions for the bridging ligand, and $\Delta G_r$ is the free energy of resonance exchange which represents the actual metal-metal coupling (3, 4).

For a strongly coupled system with a large metal-metal distance ($d(M-M) > ~1.5$ nm), the resonance exchange term ($\Delta G_r$) dominates $\Delta G_c$, because the electrostatic factor ($\Delta G_e$) exponentially decreases with the increasing charge separation, the entropy factor ($\Delta G_s$) has a constant value of $-RT\ln 4$, and the contribution of the inductive factor ($\Delta G_i$) is generally small. In such a system the degree of the metal-metal coupling can be estimated by the $K_c$ value.

Thus the value of the comproportionation constant $K_c$ is important for the design of bridging ligands. Studying mixed-valence systems with large metal-metal distances which show strong metal-metal coupling is needed to gather information about electron transfer in inorganic and biological systems and to aid construction of molecular devices. In constructing molecular devices the through-space distance between the donor and acceptor should be big (not the through-bond distance) in order to prevent errors arising from any electrostatic interaction. Mixed-valence ruthenium complexes have been reported, which despite having a metal-metal distance $d(M-M) > 1.0$ nm, have relatively strong metal-metal coupling, that is, large comproportionation constants ($K_c > 10^3$) (4b, 5).

However, to the author's knowledge, large $K_c$ values have never been reported for any binuclear complex (not an organometallic compound) with a metal-metal distance $d(M-M) > 2.0$ nm.

One of the aims of our research, therefore, is to produce a guide that can be used in the design of molecular bridging ligands which will be able to achieve good metal-to-metal communications over a long metal-metal distance.

**Spacers between the Metal Terminal Sites**

The polyyne system is one of the most effective spacers for potential long-range electronic communication between two redox centres. In fact, butadiyne ($C_4$ spacer) and octatetrayne ($C_8$ spacer)-bridged diiron organometallic compounds, where the polyynes directly connect to the metal
centre, exhibit quite large $K_q$ values: $1.60 \times 10^{12}$ for the C₄ spacer and $2 \times 10^7$ for the C₈ spacer (6). Furthermore, the C₁₂ and C₁₆ μ-polynediyl dirhenium complexes exhibit two one-electron oxidation steps in their cyclic voltammograms: for the C₁₂ spacer $\Delta E_{1/2}$ is 0.19 V, and for the C₁₆ spacer $\Delta E_{1/2}$ is 0.09 V (7). However, ethynyl and butadiynyl bridges actively promote long-range electronic coupling between remote cationic units when illuminated with visible light (8).

It has not been proved that the polyyne system in the ground state of mixed-valence systems, where polyynes indirectly connect to the metal centre, operate as molecular wires between the redox metal sites; the $K_q$ values of the diruthenium complex bridged by bis(4-pyridyl)acetylene (9) and of the ruthenium and osmium polypyridyl complexes linked by bridging polyynes (10) are very small.

The functioning of the polyyne system as molecular wires in the ground state of mixed-valence complexes depends on the characteristics of the connecting moiety between the bridges and the metal centres, see Figure 1. To evaluate the polyyne system β-diketonate was chosen as the connecting moiety because the β-diketonate chelate has aromaticity and a π molecular system, which can interact with the dπ orbitals of a metal centre. The distance between a metal and a terminal carbon of the polyyne bridge (at the γ-position of a β-diketonate ring) is shorter than any involving pyridine rings used previously (except at carbons adjacent to ligating nitrogen atoms). Thus, we chose tris(β-diketonato)ruthenium(III) units as the redox sites. These can be electrochemically oxidised and reduced to give ruthenium(IV) and ruthenium(II) species (11). Therefore, the degree of interactions between two redox sites bridged by a polyyne system and an ethynylated aromatic system in two kinds of mixed-valence states, Ru(IV)-Ru(III) and Ru(III)-Ru(II), can be found.

**Syntheses of Binuclear Ruthenium Complexes**

Because of the quasi-aromatic reactivity of the γ-methine of a β-diketonate chelate ring, it should be possible to introduce an alkyne group at the γ-position. No such synthesis has yet been described,
although a wide variety of γ-substitution reactions are known, for example, halogenation, nitration and acetylation (12). We have successfully introduced an ethynyl group into this γ-position, using Sonogashira reaction-type palladium catalysts (13). Ethynyl links can be elongated by oxidative coupling (14), see Scheme I, (15). Binuclear complexes, including ethynylated thiophene-bridged (S) and anthracene-bridged (An) complexes, can be prepared by similar coupling reactions, see Scheme II, (16). These complexes have been characterised by 1H NMR and IR spectroscopies and by mass spectrometry (13, 16). The 1H NMR spectra of these binuclear complexes show paramagnetic shift because of an unpaired electron in the Ru metal centre, and do not contradict the spectra derived from the expected structure.

The IR spectra show the characteristic C=C stretching vibrations in the region from 2100 to 2200 cm⁻¹. In their FAB mass spectra, the observed parent peaks correspond to the molecular weight of these binuclear complexes. Preparing single crystals of these complexes has often been attempted, but insufficient crystals for X-ray structure analysis have been obtained.

Electrochemical Properties

A typical cyclic voltammogram of a binuclear ruthenium complex (RuAnRu) is shown in Figure 2. The two pairs of peaks on the positive side of the voltammogram correspond to two consecutive, Nernstian, one-electron oxidation steps (one pair of peaks (A and D) corresponds to the Ru²⁺/Ru³⁺ couple, and the other pair of peaks (E and C) correspond to the Ru³⁺/Ru⁴⁺ couple, and the other pair of peaks (B and C) correspond to the RuAN/Ru⁴⁺/Ru⁴⁺-Ru³⁺ couple). The pair of peaks (E and F) on the negative side can be assigned to two overlapping one-electron reduction processes. The reduction steps of RuAnRu and RuSRu can be assigned to the reduction of the metal centres, while the oxidation steps correspond to metal-based oxidation and not to ligand-based oxidation (16). Values for the reversible half-wave potentials (E₁/₂), Kc and for the estimated metal-metal distances in the complexes are given in Table I (13, 15, 16).
Five oxidation states, including the original oxidation state of these binuclear complexes, are electrochemically accessible as expected: Ru(II)-Ru(II), Ru(II)-Ru(II), Ru(III)-Ru(II), Ru(IV)-Ru(III) and Ru(IV)-Ru(IV). The bridging ligands containing the polyene and the ethynylated aromatic groups can now be evaluated as molecular wires in the two mixed-valence states, Ru(IV)-Ru(III) and Ru(III)-Ru(II).

**K_\text{c}** Values for the (III, II) and (IV, III) States

The **K_\text{c}(III, II)** values are significantly smaller than the **K_\text{c}(IV, III)** values; **K_\text{c}(III, II)** values of Ru3Ru and Ru4Ru in particular are close to the statistical limit (**K_\text{c} = 4**). This indicates that the free energy change of the comproportionation, \(\Delta G(III, II)_c\), which is the stabilisation of the Ru(III)-Ru(II) mixed-valence system, is small, and also that the electron resonance exchange term, \(\Delta G(III, II)_e\) is only a minor factor contributing to \(\Delta G(III, II)_c\), see Equation (vi). On the other hand, \(\Delta G(IV, III)_e\) is a major factor contributing to the \(\Delta G(IV, III)_c\) of the Ru(IV)-Ru(III) system. Therefore the degree of the electronic coupling between the metal centres in the Ru(IV)-Ru(III) state is much larger than that in the Ru(III)-Ru(II) state.

In the present systems, see Figure 3, it is energetically favourable for a hole to move from the

![Fig. 2 The cyclic voltammogram for RuAnRu in 0.1 mol dm^{-3} of (C,H)_3NBF_4-CH_2Cl_2 on a platinum disk electrode at 25°C. The sweep rate was 0.1 V s^{-1}](image)

### Table I

<table>
<thead>
<tr>
<th>Complex</th>
<th><strong>\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}</strong></th>
<th><strong>K_\text{c}(IV, III)</strong></th>
<th><strong>\text{Ru}^{\text{IV}}/\text{Ru}^{\text{II}}</strong></th>
<th><strong>K_\text{c}(III, II)</strong></th>
<th><strong>d(M-M)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>RuAnRu</td>
<td>0.280, 0.463</td>
<td>183</td>
<td>1200</td>
<td>-1.344, -1.424</td>
<td>80</td>
</tr>
<tr>
<td>RuSRu</td>
<td>0.383, 0.558</td>
<td>175</td>
<td>900</td>
<td>-1.334, -1.414</td>
<td>80</td>
</tr>
<tr>
<td>Ru2Ru</td>
<td>0.396, 0.621</td>
<td>225</td>
<td>6360</td>
<td>-1.361, -1.472</td>
<td>111</td>
</tr>
<tr>
<td>Ru3Ru</td>
<td>0.465, 0.589</td>
<td>124</td>
<td>125</td>
<td>-1.319, -1.372</td>
<td>53</td>
</tr>
<tr>
<td>Ru4Ru</td>
<td>0.516, 0.602</td>
<td>86</td>
<td>28</td>
<td>-1.260, -1.315</td>
<td>55</td>
</tr>
</tbody>
</table>
$d\pi$ orbital of the ruthenium(IV) site to one of the ruthenium(III) sites via the highest occupied molecular orbitals (HOMOs) of the bridge is favourable. Such a 'through-bond' mechanism is called a 'superexchange' mechanism (17).

The large difference between the $\Delta G_r$(IV, III) and $\Delta G_r$(III, II) indicates the large difference between the degree of electronic coupling for the hole transfer and for the electron transfer. This large difference between hole and electron transfer can be interpreted by the difference in character of HOMOs and LUMOs of the bridging ligands, as mentioned below.

Recently, we have prepared the following:

(a) a new metal coordination polymer of ruthenium(III) β-diketone units linked by a butadiyne bridge;

(b) a mononuclear complex [Ru$^{III}$(mEma)$_3$] (mEma$^-$ = 3-ethynyl-2,4-pentanedionate ion) as the starting material for the polymerisation (18) and (c) their electrochemically reduced products, poly-[Ru$^{III}$(mEma)$_3$]$^{2+}$ and [Ru$^{III}$(mEma)$_3$]$^{3+}$.

To our surprise, spectroelectrochemical measurements showed that the visible spectra for the poly-[Ru$^{III}$(mEma)$_3$]$^{2+}$ (new band at 499 nm) and the [Ru$^{III}$(mEma)$_3$]$^{3+}$ (new band at 497 nm) are approximately the same. The new band of [Ru$^{III}$(mEma)$_3$]$^{2+}$ is assigned to metal-to-ligand charge transfer (MLCT) – a transition from the metal $d\pi$ level to the ligand mEma$^-\pi^*$ orbitals, while the new band of poly-[Ru$^{III}$(mEma)$_3$]$^{2+}$ comes from the combination of two of the MLCT bands; one band corresponds to transitions from the $d\pi$ levels to the terminal mEma$^-\pi^*$ orbitals and the other is transitions from the $d\pi$ levels to the bridging ligand, the tahdy$^{\pi^*}$ $\pi^*$ orbitals (tahdy$^{\pi^*} = 1,1,6,6$-tetraacetyl-2,4-hexadiynate dianion). In spite of the combination, the shape of the absorption bands of poly-[Ru$^{III}$(mEma)$_3$]$^{2+}$ are consistent with those of [Ru$^{III}$(mEma)$_3$]$^{2+}$: both bands have a shoulder near 460 nm. With this observation, it is possible to predict that the energy levels of the tahdy$^{\pi^*}$ $\pi^*$ orbitals are approximately equal to those of the mEma$^-\pi^*$ orbitals.
To confirm this prediction, extended Hückel molecular orbital (EHMO) calculations were carried out for \([\text{Na}_2\text{(mEma)}]\) and \([\text{Na}_2\text{(tahdy)}]\) as model compounds for \([\text{Ru}(\text{mEma})_3]\) and poly-
\([\text{Ru}(\text{mEma})_5]\), respectively (18). The calculations show that the LUMO energy level of \([\text{Na}_2\text{(tahdy)}]\) is approximately equal to that of \([\text{Na}_2\text{(mEma)}]\). Both of the LUMOs have a node on the 3-position carbon atom of the \(\beta\)-diketone ring, see Figure 4, so that there is no wavefunction on the ethynyl carbons of \([\text{Na}_2\text{(mEma)}]\) or on the butadiynyl carbons of \([\text{Na}_2\text{(tahdy)}]\). Therefore, the LUMO of \([\text{Na}_2\text{(tahdy)}]\) is essentially the same as that of \([\text{Na}_2\text{(mEma)}]\). On the other hand, the \(\pi\)-conjugated system in the second highest occupied molecular orbital (SHOMO) of \([\text{Na}_2\text{(tahdy)}]\) is extended through the entire bridging ligand (18).

Consequently, the atomic orbitals of the ethynyl bridge do not contribute to the LUMO of the tahdy\(^2\) bridging ligand. The LUMOs of the other analogous tetraketonate bridging ligands in this study should have a node, so the superexchange would not operate for electron transfer via LUMOs of the bridge in the ground state of the Ru(III)-Ru(II) systems.

**Fig. 4  Schematic of the lowest unoccupied molecular orbitals (LUMOs) of [Na(mEma)] and [Na(tahdy)]**

Metal-to-Metal Communication in the Ru(IV)-Ru(III) State

According to the Marcus-Hush theory (19) (which links the rate of electron transfer of electrons from one molecule to another, or from part of a molecule to another, in terms of structural changes in the molecule. For a large molecular rearrangement the rate of electron transfer will be slow, while for small molecular rearrangements the rate will be fast) and superexchange theory (8c, 20):

\[
\Delta G_T = 2H_{ab}^2/\lambda \\
H_{ab} = (H_{ab})_o \exp[-\beta R/2] \\
H_{ab} = \xi_a \cdot \xi_b / \delta E
\]

Here, \(\Delta G_T\) depends on the electronic coupling matrix element, \(H_{ab}\), where \((H_{ab})_o\) is the matrix element when donor and acceptor orbitals are in contact, and \(\lambda\) is the reorganisation parameter; \(\beta\) reflects the efficacy of the medium during donor-acceptor coupling and \(R\) is the length of the bridge; \(\xi_a\) is the atomic orbital coefficient for the coupling between the donor and the bridge, and \(\xi_b\) is the atomic orbital coefficient for the coupling between bridge and acceptor; \(\delta E\) represents the energy gap between the appropriate orbitals on the donor(acceptor) and the bridge.

For the homologous series of Ru\(_n\)Ru (n = the number of ethynyl groups = 2, 3, and 4), the \(K_c(\text{IV}, \text{III})\) values decrease exponentially with the increasing number of ethynyl bridges; in particular, the \(K_c(\text{IV}, \text{III})\) value for Ru4Ru is close to the corresponding \(K_c(\text{III}, \text{II})\) value (15). This result is in accord with the distance, \(R\), dependence of \(H_{ab}\) (Equation (viii)) (21). Thus, strong electronic coupling is not expected for the Ru\(_n\)Ru system when \(n > 4\) with polyyne as the bridge and the \(\beta\)-diketonate chelate as the connecting moiety. Therefore, an increase in the \(K_c(\text{IV}, \text{III})\) value with decreasing \(\delta E\) was planned by inserting another conjugated moiety with electron-donor ability, that is thiophene and anthracene units, into the ethynyl bridges (16).

In fact, although the \(d(M-M)\) of RuAnRu (1.71 nm) and RuSRu (1.67 nm) are both longer than...
Table II
Values of the SHOMO Energy ($E_h$), the Sum of Squared Extended Hückel MO Coefficients at the Terminal Carbons (C(1)) of the Triple Bond in Tetraketones, $\Sigma C_i^2$, and Square Roots of the Natural Logarithms of the Comproportionation Constants ($K_c$) of Various Binuclear Ruthenium Complexes

| H$_2$BL (X)* | $E_h$, eV | $\Sigma C_i^2$ | Complex | $|\ln K_c(IV, III)|^{1/2}$ |
|--------------|-----------|----------------|---------|---------------------------|
| H$_2$An (C$_4$H$_8$) | -10.60 | 0.196 | RuAnRu | 2.67 |
| H$_2$S (C$_2$H$_4$S) | -10.83 | 0.185 | RuSRu | 2.61 |
| H$_2$ (none) | -11.22 | 0.198 | Ru2Ru | 2.96 |
| H$_3$ (C$_3$) | -11.22 | 0.158 | Ru3Ru | 2.20 |
| H$_4$ (C$_4$) | -11.22 | 0.138 | Ru4Ru | 1.83 |

*BL denotes bridging ligand

that of Ru3Ru (1.56 nm), the $K_c(IV, III)$ values for RuSRu and RuAnRu are larger than that for Ru3Ru by a factor of about 10. This indicates that metal-to-metal communication in the Ru(IV)-Ru(III) mixed-valence state, that is, the electronic coupling, is amplified by inserting other conjugated moieties with electron-donor ability into the two ethynyl groups. This amplification seems to be caused by decreased $\delta E$, due to the presence of the electron-donor groups in the bridge. This can be confirmed by EHMO calculations for a series of tetraketones, H$_2$BL, whose dianions are net bridging ligands (BL). The SHOMO energies ($E_h$), which correspond to the $\pi\pi$ HOMO energies of the bridging ligands in the complexes, are given in Table II (22). The $\pi$-conjugated system in the SHOMO of H$_2$S is extended through the entire bridging ligand, see Figure 5. The SHOMO energy levels of H$_2$An and H$_2$S are higher than that of H$_3$. From these calculations we can foresee that the energy gap between the $d\pi$ orbitals of the metal centres and the $\pi\pi$ HOMO of the bridging ligands in RuAnRu and RuSRu becomes smaller compared with that in Ru3Ru.

On the other hand, the SHOMO energies ($E_h$) of the H$_n$ system, see Table II, are in good agreement with each other ($\approx -11.22$ eV) and are constant. This result predicts that the energy gap

Fig. 5 Schematic of the second highest occupied molecular orbital (SHOMO) of H$_2$S. The $\pi$-conjugated system in the SHOMO of H$_2$S is extended through the entire bridging ligand.
Fig. 6 The linear relationship between the square root of \( \ln K_{c(IV, III)} \) values, for various binuclear ruthenium complexes, and the sum of the squared extended Hückel MO coefficients \( \Sigma \epsilon_i^2 \) in SHOMO at the terminal carbons (C(1)) of the triple bond in tetraketones. This relationship can thus be used as a guide for the molecular design of mixed-valence (tetraketonato)diruthenium complexes with long-range hole transfer.

Conclusions

The evaluation of a polyyne system and an ethynylated aromatic system as molecular wires using binuclear ruthenium \( \beta \)-diketone complexes has been discussed. Binuclear species based on tris(\( \beta \)-diketonato)ruthenium(III) units can be used to evaluate bridges as molecular wires as their Ru(III)-Ru(II) and Ru(IV)-Ru(III) states are experimentally accessible within the potential window of common supporting electrolyte solutions. The binuclear complexes are also useful for investigating the superexchange mechanism, as the absence of wavefunctions on the bridge in the LUMOs of the bridging ligands simplifies the mechanism into a single pathway – a hole transfer process. In fact, the mixed-valent properties of dimeric ruthenium(II) complexes containing sulfur-substituted bridging \( \beta \)-diketonate rings are currently under investigation by Professor Shimizu’s research group (23).

Molecular orbital calculations performed on bridging ligands containing a connecting moiety between a bridge and a metal centre provide a linear relationship between the square root of \( \ln K_c \), substituted for the electronic coupling, and the sum of the squared extended Hückel MO coefficients, \( \Sigma \epsilon_i^2 \), substituted for the product of atomic orbital coefficients (Equations (iv), (v), (vii) and (ix)): 

\[
\{ \ln K_c(IV, III) \}^{1/2} \propto \epsilon_a \epsilon_\beta
\]

(8)

Here, \( \epsilon_a \) (or \( \epsilon_\beta \)), which describes the coupling between the donor (or acceptor) and the bridge, can be considered as the orbital coefficient at the terminal atom of the bridge, because the magnitude of the coupling firstly depends on the probability density of finding the electron at the terminal atom.

Figure 6 shows the linear relationship between values of square roots of \( \ln K_c(IV, III) \) and \( \Sigma \epsilon_i^2 \), the sum of the squared extended Hückel MO coefficients, see Table II, for SHOMO at the terminal carbons (C(1)) of the triple bond in the tetraketones. This relationship can thus be used as a guide for the molecular design of mixed-valence (tetraketonato)diruthenium complexes with long-range hole transfer.

Acknowledgements

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References

21 A distance required by Hush theory is the effective donor-acceptor separation distance (\(\alpha\)), assumed to be related to dipole moment expectation values by 
\[ r = |\mu_1 - \mu_2| / n , \]
where \(\mu_1\) and \(\mu_2\) are the dipole moments of the localised initial and final states in a mixed-valence system, respectively, and where \(n\) is the number of electrons in the system. On the other hand, \(R\) in Equation (vii) derived by the superexchange mechanism may be defined in terms of the actual bond lengths for the through-bond sequence pertinent to the pathway being modelled (20c). The Ru-Ru separation (\(d(MM)\)) approximately reflects the length of the bridge in the present systems. In Class II binuclear metal complexes, when the metal-metal coupling is not very strong (probably \(K < 10^7\)), the metal-metal separation is usually used instead of the dipole moment length (24).

22 Y. Hoshino, H. Umeda and Y. Kano, Abstracts of papers at the 44th Symp. on Coordination Chemistry of Japan, Yokohama, 1994, p. 178


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Yoshimasa Hoshino is an Associate Professor in the Department of Chemistry, Faculty of Education, Nagasaki University, Japan. His main interests are in the molecular design of binuclear and polynuclear metal complexes with strong metal-to-metal communication and of rotaxane and polyrotaxane metal complexes for molecular switches.

Rapid Synthesis of Colloidal Clusters
Scientists from PCLCC, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China, have synthesised uniform and stable polymer-stabilised colloidal clusters of platinum, iridium, rhodium, palladium, ruthenium and gold by microwave irradiation (W. Tu and H. Liu, J. Mater. Chem., 2000, 10, 9), 2207-2211. As microwave heating has uniform and fast heating characteristics only a short irradiation time was needed. The colloidal clusters formed have small average diameters and narrow size distributions. Stable colloidal ruthenium clusters without boron were prepared using ethylene glycol as the reductant.
On 12th October 2000, Johnson Matthey opened a new plant at its site in Royston, Hertfordshire, to manufacture the latest generations of supported catalysts, including platinum group metals catalysts, for chemical processes. The new facility, which uses state-of-the-art production technology, has the capacity and flexibility to produce several hundred tons of catalyst per year for a wide range of applications.

This Johnson Matthey plant has been designed initially to manufacture special catalysts for two new processes belonging to BP Chemicals. The first of these, known as LEAP™, uses fluid bed technology to produce vinyl acetate monomer (VAM), a key intermediate for polymer manufacture. The process, based on a radical new fluid-bed reactor and new catalyst design, rather than the traditional fixed-bed system, offers large savings in capital and downstream process costs. Johnson Matthey has worked in close partnership with BP Chemicals to optimise the performance of the catalyst and to scale-up its production. LEAP™ is the first fluid-bed process to use a supported precious metal catalyst. For its work in helping to develop the new catalyst, Johnson Matthey was given a BP Amoco Chemicals Breakthrough Award in 1999.

The second BP Chemicals process is known as AVADA™, and is to be used for the single-step manufacture of ethyl acetate. The new AVADA™ plant is based on BP Chemicals 'direct addition' method for the manufacture of ethyl acetate from ethylene and acetic acid. The process is simpler and cleaner than other routes and is suited to locations where feedstocks, such as the ethanol needed for these current processes, are not competitively available. Johnson Matthey has again worked with BP Chemicals to develop a manufacturing route for the catalyst used here.

While the new facility is now being used to produce these two catalysts, the plant is highly versatile and is designed to manufacture a wide range of supported catalysts, including platinum group metals catalysts, for the fine and specialty chemicals industries.

Brian Harrison is the Technology Director for the Johnson Matthey Chemicals Business at Royston. His interests are in homogeneous and heterogeneous catalyst development and in platinum group metals-based fine chemicals and platinum group metals refining.
Organometallic Chemistry and Applied Catalysis
A REVIEW OF THE FOURTH ANGLO-DUTCH SYMPOSIUM

By Simon Duckett
Department of Chemistry, University of York, England

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

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

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

High Throughput Screening
Other notable developments reported were based around the session on high throughput screening and parallel synthesis in catalysis. This started with an overview by Professor G.-J. M. Gruter (Eindhoven University of Technology-Avantium Technologies B.V.), before M. L. Turner (University of Sheffield) and Professor J. N. H. Reek (University of Amsterdam) illustrated the benefits of rapid screening. Turner described how rapid parallel screening using a multi-channel reactor developed at Sheffield allowed the heterogeneous conversion of CO to ethanol to be optimised. An elegant analysis based on parent-daughter methods with crossover and mutation effects was used to rapidly deduce an optimised catalyst composition – without the need to complete runs for all possibilities. Reek focused on the solid-phase synthesis and rapid screening of...
ruthenium catalysts for asymmetric hydrogen transfer reactions, such as the conversion of acetophenone to 1-phenylethanol by IR spectroscopy. A silica-immobilised catalyst was shown to exhibit good selectivity.

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

Developments in Novel Media

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

In the final presentation, Professor D. J. Cole-Hamilton (University of St Andrews) described work performed in supercritical fluids. Notable achievements included the illustration that trialkylphosphine complexes readily dissolve in the supercritical fluid, have good activity for hydroformylation of alkenes and yield better selectivity for the desired straight-chain aldehyde than normal organic solvents. Furthermore, the construction of a flow reactor for supercritical fluid catalysis allowed the use of a biphasic approach involving ionic liquids in conjunction with supercritical CO2. While the catalyst remained firmly dissolved in the ionic liquid, the aldehydes generated during catalysis were readily soluble in supercritical CO2 and easily separated.

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

References


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

Chemical Fluid Deposition of Conformal Palladium Films

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

High-purity, contour-following conformal Pd film may be prepared by chemical vapour deposition (CVD), but at temperatures > 200°C. A drawback to this is that low deposition temperatures are needed by microelectronics to suppress mechanical stress during device fabrication and to minimise interdiffusion and reactions between adjacent layers. The thickness of CVD-produced film also varies, giving inconsistent coverage for high-aspect ratio features. Researchers at The University of Massachusetts, U.S.A., have now succeeded in depositing highly pure, conformal Pd films onto silicon wafers and polyimide at low temperature using chemical fluid deposition (J. M. Blackburn, D. P. Long and J. J. Watkins, Chem. Mater., 2000, 12, (9), 2625–2631). This involves the chemical reduction of soluble organopalladium compounds in supercritical carbon dioxide (CO2) at 40–80°C and 100–140 bar pressure.

Deposition by hydrogenolysis of trans-2-methylallyl-(cyclopentadienyl)palladium(II) in CO2 was completed in less than 2 minutes at 60°C, yielding pure, continuous, 100–200 nm thick, reflective Pd films free from ligand-derived contamination. Conformal coverage was observed on a patterned silicon wafer with features as small as 0.1 μm wide × 1 μm deep.
The combination of RuCl₃(PP₃)$_3$ and 2,2',6,6'-tetramethylpiperidine N-oxyl (TEMPO) affords an efficient catalytic system for the aerobic oxidation of a variety of primary and secondary alcohols, giving the corresponding aldehydes and ketones, in > 99 per cent selectivity in all cases. This interesting catalytic system is probably based on a hydridometal mechanism, involving a 'RuH₂(PP₃)$_3$' species as the active catalyst. TEMPO acts as a hydrogen transfer mediator and is regenerated by oxygen.

The catalytic conversion of primary alcohols into aldehydes and of secondary alcohols into ketones is essential for the preparation of many key synthetic intermediates in organic chemistry (1). Traditional methods for performing such transformations generally involve the use of stoichiometric quantities of inorganic oxidants, notably chromium(VI) reagents (2), and generate copious quantities of inorganic waste. Hence, the quest for effective catalytic systems that use clean inexpensive oxidants such as oxygen and hydrogen peroxide - a 'green method' - to convert alcohols to carbonyl products on an industrial scale remains an important challenge.

Most examples of aerobic oxidation of alcohols, both homogeneous and heterogeneous, involve the use of Group VIII metal complexes as catalysts (3). In particular, ruthenium compounds, which are widely used as catalysts in organic synthesis have been thoroughly investigated (4). For example, tetrapropylammonium perruthenate (TPAP), either as such (5), or supported on an ion exchange resin (6) or MCM-41 (a mesoporous molecular sieve) (7), and ruthenium hydrotalcites (8) are capable of aerobically oxidising a variety of alcohols to carbonyl compounds. However, all the reported metal systems require relatively large quantities of catalyst (5–10 mol%) and/or additives, that is cocatalyst (10–20 mol%) and drying agent (2 equiv.), to achieve their activity.

In addition to metal complexes, stable nitroxyl radicals, such as 2,2',6,6'-tetramethylpiperidine N-oxyl (TEMPO), have been used as catalysts for the oxidation of alcohols to aldehydes, ketones and carboxylic acids (9). Typically, these transformations employ 1 mol% of the nitroxyl radical and a stoichiometric amount of a terminal oxidant, such as sodium hypochlorite (10), trichloroisocyanuric acid (11), $m$-chloroperbenzoic acid (12), sodium bromite (13), sodium chlorite (14) and Oxone® (15). In these systems, an oxoammonium cation is generated and acts as the active oxidant, see Reaction (i).

Alternatively, the use of TEMPO in combination with copper salts and oxygen as the primary oxidant was reported by Semmelhack (16). However, this system was effective only with easily oxidised benzylic and allylic alcohols.

**Ruthenium/TEMPO Catalyst System**

Based on the catalytic systems described above, we reasoned that the combination of ruthenium and TEMPO would likely lead to an efficient catalytic system for the aerobic oxidation of alcohols. For our initial experiments, we selected octan-2-ol...
Ruthenium/TEMPO-Catalysed Aerobic Oxidation of Various Alcohols

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Substrate/Catalyst ratio</th>
<th>Time, h</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>octan-2-ol</td>
<td>octan-2-one</td>
<td>100</td>
<td>7</td>
<td>98 (90)</td>
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<tr>
<td>2c</td>
<td>octan-1-ol</td>
<td>octanal</td>
<td>50</td>
<td>7</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>benzylalcohol</td>
<td>benzaldehyde</td>
<td>200</td>
<td>2.5</td>
<td>&gt; 99 (90)</td>
</tr>
<tr>
<td>4</td>
<td>p-nitrobenzylalcohol</td>
<td>p-nitrobenzaldehyde</td>
<td>200</td>
<td>6</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>1-phenylethanol</td>
<td>acetophenone</td>
<td>100</td>
<td>4</td>
<td>&gt; 99 (93)</td>
</tr>
<tr>
<td>6c</td>
<td>geraniol</td>
<td>geranial</td>
<td>67</td>
<td>7</td>
<td>91</td>
</tr>
<tr>
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<td>3-methyl-2-butenal</td>
<td>67</td>
<td>7</td>
<td>96</td>
</tr>
<tr>
<td>8</td>
<td>cyclooctanol</td>
<td>cyclooctanone</td>
<td>100</td>
<td>7</td>
<td>92</td>
</tr>
<tr>
<td>9c</td>
<td>octan-2-ol/octan-1-ol</td>
<td>octan-2-one/octanal</td>
<td>50</td>
<td>7</td>
<td>10/80</td>
</tr>
<tr>
<td>10</td>
<td>benzylalcohol/1-phenylethanol</td>
<td>benzaldehyde/acetophenone</td>
<td>200</td>
<td>3</td>
<td>90/5</td>
</tr>
</tbody>
</table>

Reaction conditions: 15 mmol substrate, ratio of RuCl₂(PPh₃)₃:TEMPO = 1:3, 30 ml chlorobenzene, 10 ml min⁻¹ O₂: N₂ (8:92; v/v), p (total pressure) = 10 bar, T = 100°C. Conversions based on GC results (selectivity > 99% in all cases) using n-hexadecane as internal standard. The numbers in parenthesis are isolated yields (21).

as a test substrate and allowed it to react in chlorobenzene with catalytic quantities of a ruthenium complex in the presence of TEMPO and oxygen. The best results were obtained when using 1.0 mol% of RuCl₂(PPh₃)₃ (17) and 3.0 mol% of TEMPO (18), see Reaction (ii). In this case, the turnover frequency (TOF) was 14 h⁻¹, which is superior to the most active aerobic ruthenium system described in the literature, that is TPAP (5), which in our hands gave a TOF of 5.5 h⁻¹ for octan-2-ol (19).

The use of RuCl₂(PPh₃)₃/TEMPO as catalyst for the aerobic oxidation of alcohols was then applied to a range of representative alcohols. As can be seen from the Table, octan-1-ol is oxidised selectively into octanal (Entry 2). TEMPO not only accelerates the oxidation of octan-1-ol, but also completely suppresses the over-oxidation of octanal to octanoic acid (19). Attempted oxidation of octanal under the same reaction conditions, in the presence of TEMPO, gave no reaction in one week. On the other hand, without TEMPO octanal was converted completely to octanoic acid within 1 hour. The ability to suppress over-oxidation is due to the well known anti-oxidant activity of TEMPO. This stable nitroxyl radical efficiently scavenges free radical intermediates during autoxidation and thereby terminates free radical chains.

Allylic alcohols were selectively converted into the corresponding unsaturated aldehydes in high yields without intramolecular hydrogen transfer (Entries 5 and 6). Some ruthenium(II) phosphine complexes are known to catalyse intramolecular hydrogen transfer reactions of allylic alcohols to saturated ketones (20), which obviously is not occurring in the present system. Besides aliphatic and allylic alcohols, cyclic and benzylic alcohols were also smoothly oxidised into the corresponding ketones and aldehydes (Entries 3, 4 and 7). In these cases lower catalyst loadings were required (substrate/catalyst > 100).

A problem in the present aerobic Ru/TEMPO catalysed oxidation of alcohols is the deactivation of both ruthenium and TEMPO during catalysis. Attempts to use heterogeneous TEMPO systems, such as PIP0 (polymer immobilised TEMPO) (22) or MCM-41 and silica-supported TEMPO (23), lead to inactive systems (24). This is probably due to coordination of ruthenium to the amine moiety in PIP0 and absorption of ruthenium on the MCM-41 and silica surfaces. The latter was
proven by performing the Ru/TEMPO catalysed aerobic oxidation of octan-2-ol in the presence of silica. In this case, only minor formation of octan-2-one was observed as well as a brightening of the reaction mixture from dark brown to slightly orange. Because of the results with heterogeneous TEMPO systems and the fact that ruthenium is much more expensive than TEMPO, we refocused our aim and are currently working on the heterogenisation of ruthenium.

Mechanistic Aspects

Although in separate experiments secondary alcohols are oxidised faster than primary ones, in competitive experiments, the Ru/TEMPO system displayed a preference for primary versus secondary alcohols (Entries 8 and 9). Since these reactions are generally believed to involve the intermediate formation of an alkoxo-ruthenium complex (25), we interpret this result as an indication that the ruthenium preferentially complexes with primary alcohols, leading to selective oxidation of the latter even though the rate-determining dehydrogenation step is faster with secondary alcohols.

When the effect of the TEMPO concentration on the oxidation rate was investigated, an almost linear increase was observed, with respect to the TEMPO concentration in the range 0–4 mol%, for the oxidation of octan-2-ol, see Figure 1. Above 4 mol% the increase starts to level out, and further addition of TEMPO led to only a minor increase in the yield obtained after 1 hour. The same ‘mediator’ dependency was observed with a ruthenium/benzoquinone/MnO2 system, reported by Bäckvall and coworkers (26), and we propose a similar mechanism, see Figure 2. The result can be explained in terms of a change in the rate-limiting step. At low concentrations of TEMPO, reoxidation of the ‘ruthenium hydride’-species may be the slowest step, whereas at high concentrations of TEMPO, dehydrogenation is probably rate limiting.

Under an inert atmosphere, no regeneration of TEMPOH should take place and RuCl3(PPh3)3 catalyses the stoichiometric reaction of TEMPO and octan-2-ol.
RuH₂(PPh₃)₄ in chlorobenzene, under an inert atmosphere, also resulted in the formation of TEMPH.

Based on the results presented above, we propose the following catalytic cycle to explain the aerobic RuCl₃(PPh₃)₃/TEMPO-catalysed aerobic oxidation of alcohols, see Figure 3. The reaction of 'RUH~(PP~)~' with TEMPO, followed by the insertion of an alcohol to form a ruthenium alkoxide species, is currently under investigation (using in situ IR spectroscopy and electron-spray mass spectrometry) and probably proceeds via complex (a). The formed ruthenium alkoxide species (b) undergoes normal β-hydrogen elimination to produce the ketone/aldehyde and the active ruthenium dihydride species.

Concluding Remarks

We have discovered that the combination of catalytic amounts of RuCl₃(PPh₃)₃ (< 2 mol%) and TEMPO (< 5 mol%) affords an efficient catalytic system for the aerobic oxidation of a broad range

Fig. 3 Proposed mechanism for the Ru/TEMPO-catalysed aerobic oxidation of alcohols
of primary and secondary alcohols, giving the corresponding aldehydes and ketones, in > 99 per cent selectivity in all cases. Most probably, this interesting catalytic system is based on a hydridometal mechanism, involving a \( \text{RuH}_2(\text{PPH}_3) \cdot \) intermediate. TEMPO acts as a hydrogen transfer mediator and is easily regenerated by oxygen. We are presently investigating methods for heterogenising the ruthenium catalyst.

Acknowledgement

We gratefully acknowledge IOP Catalysis (Innovation-Oriented Research Program on Catalysis), Ministry of Economic Affairs, The Netherlands, for financial support and Johnson Matthey for their donation of RuCl₃ hydrate.

References


17. RuCl₃(PPH₃)₂ was prepared according to: R. Holm, Inorg. Synth., 1970, 12, 238.

18. Typical procedure for the aerobic oxidation of octan-2-ol: octan-2-ol (15.0 mmol; 1.96 g), n-hexadecane (internal standard; 3.0 mmol; 0.69 g), RuCl₃(PPH₃)₂ (0.225 mmol; 216 mg) and TEMPO (0.675 mmol; 106 mg) were dissolved in 30 ml of chlorobenzene, heated in a high-pressure reactor (10 bar) to 100°C under a continuous stream (10 ml min⁻¹) of an oxygen-nitrogen mixture (8:92; v/v) and stirred for 7 hours. Octan-2-ol conversion and octan-2-one selectivity were determined using GC-analysis (50 m × 0.53 mm CP-Wax 52 CB column).


21. Typical procedure for isolating the product: the reaction mixture was diluted with n-hexane (to remove ruthenium) and dried over MgSO₄. The resulting mixture was filtered and the solvent removed in vacuo. The product was separated from chlorobenzene using Kugelrohr distillation.


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Techniques for Catalyst Manufacture

REVIEW OF A ROYAL SOCIETY OF CHEMISTRY MEETING ON APPLIED CATALYSIS

The Industrial Affairs Division of the RSC (Applied Catalysis Group) held a meeting on “Techniques of Catalyst Manufacture” at the Advantica (formerly BG Technology) Research and Technology Centre, in Loughborough, U.K., on 8th November 2000. Delegates were introduced to Advantica’s activities in a diverse range of areas, which included the development of natural gas powered vehicles, high-temperature solid oxide fuel cells (SOFCs) and molten carbonate fuel cells as well as catalytic technologies for the functionalisation of methane through partial oxidation, steam reforming and Fischer-Tropsch synthesis.

Industrial Catalyst Preparations

This introduction provided the background for the presentation by Andrew Dicks (Advantica, Loughborough) on the preparation of industrially relevant catalysts by coprecipitation, especially for the activation of methane. Much effort has been directed at the preparation of Al2O3-supported nickel catalysts by coprecipitation, for reactions such as steam reforming and catalytic partial oxidation (CPO). Latterly, supported platinum group metals catalysts, such as Al2O3-supported palladium and platinum in addition to TiO2-supported rhodium, have found favour for CPO due to their enhanced rates of reaction and resistance to coke formation. The technique of homogeneous coprecipitation, where hydrolysis of urea at 120°C results in uniform release of OH− groups throughout the catalyst precursor slurry, has been employed to produce a supported-ruthenium (Ru/ZnO-Al2O3) Fischer-Tropsch catalyst. The BET surface area of the final material was shown to be strongly dependent on the ZnO:Al2O3 ratio. The greatest surface area was obtained with the highest Al2O3 content.

These preparation techniques have formed the basis for the catalyst which is used to internally reform CH4 in a SOFC. More recently, the anode exhaust from a SOFC has been converted by means of shift reactors and a final preferential oxidation (PROX) unit to provide a hydrogen-rich feed to a proton exchange membrane (PEM) fuel cell. A SOFC-PEM hybrid system of this type with an electrical output of 500 kW was claimed to be 61 per cent efficient.

Metal Precursors and Catalyst Carriers

Very convincing evidence highlighting the pitfalls associated with deposition of metal precursors on preformed supports was given by Robert Terorde (Engelhard, The Netherlands). While his presentation dealt exclusively with the introduction of iron into a preformed SiO2 support, it is clear that the lessons learnt would be applicable to the deposition of other metals onto other supports and it would be possible to extend this work to help optimise platinum group metal distributions. He claimed that the final distribution of the metal oxide throughout the support was influenced by properties of the metal precursor, such as its interaction with the support surface, its crystallisation behaviour and the viscosity of the salt solution. The speed of the drying process was also found to be critical. Egg-shell distributions of the metal salts were formed when solutions of strongly crystallising salts, which do not become viscous during the drying step, for example K3Fe(CN)6, were used in the initial impregnation. The microscopic effect of an egg-shell distribution was shown to be the growth of large metal particles.

Andrew Holt (Catal International, Sheffield)
explained the equipment required and process variables associated with producing catalyst carriers in high volume by the cost-effective technique of extrusion. Extruder designs and therefore the shape of the extrudates depend on the material to be extruded. Catalyst supports used for reactions such as hydrotreating are produced using a twin contra-rotating screw. The wet metal oxide pastes, used to make the supports, are normally very abrasive and possess poor flow characteristics. However, in the extrusion process the precursor paste ('dough') needs to possess sufficient plasticity, lubricity and particulate cohesion to pass through a small orifice. In order to achieve this the support powder, for example Al₂O₃, is normally treated with dilute HNO₃ to help peptisation. The pH of this peptisation step has a large influence on the pore size distribution of the final material. At low pH (< 2) microporous materials could be produced. The plasticity and particulate cohesion of the 'dough' can be controlled by the introduction of one or more of a range of organic modifiers from wood flour to methyl cellulose. Addition of wood flour has the effect producing large voids in the extrudate upon calcination. This can lead to improved gas flow characteristics. Lubricity additives, such as graphite or stearates, can also be introduced.

Progress in Techniques for Catalyst Manufacture

Professor Friedrich Schmidt (Sud-Chemie, Germany) reviewed recent progress in techniques for catalyst manufacture. Large scale catalyst preparation is strongly driven by cost. It is, therefore, necessary to demonstrate a very significant performance benefit before it is viable for industry to make the investment to adopt a new technique for manufacture of a particular catalyst.

If organic solvents or organometallic precursors are to be used in precipitation or sol-gel preparations, significant plant modifications will be required. Such modifications, dictated by safety, environmental and engineering considerations, have prevented large-scale adaptation of these techniques for industrial catalyst manufacture. Exceptions include the manufacture of titanium silicalite (TS-1) and the Condea process for the manufacture of high purity Al₂O₃ from aluminium alkoxides. Sol-gel preparations are not restricted to stoichiometric compositions and can result in better control of the porosity of the final material. Professor Schmidt also suggested that use of supercritical CO₂ has the potential to greatly simplify solvent removal.

The conference organiser Barry Nay (BP Chemicals, Sunbury-on-Thames) thanked all the participants at the well-attended meeting and suggested that the next meeting of the RSC Applied Catalysis Group may take place outside Britain. Further information on events organised by the RSC Industrial Affairs Division, Applied Catalysis Group are obtainable from nayb@bp.com.

The Authors

P. J. Collier, M. R. Feaviour and M. J. Hayes

Heterogenised Rhodium Catalyst

The search for a clean benign replacement for the industrial synthesis of amines (N-(phenyl-N'-iso-propyl)-p-phenyldiamine and N,N'-di(1,4-dimethylpentyl)-p-phenyldiamine) used as antioxidants in vulcanising rubber, additives in biomimetic sensors and anticorrosive agents, has resulted in a one-pot synthesis using a platinum/carbon-based catalyst. However, this synthesis is not reproducible.

Now researchers at the Universitat Rovira i Virgili, Spain, have developed a reproducible one-pot synthesis to convert a primary amine into a secondary amine by imine intermediate formation (R. Margalef-Català, C. Claver, P. Salagre and E. Fernández, Tetrahedron Lett., 2000, 41, (34), 6583-6588). The catalyst was prepared by immobilising preformed [Rh(COD)(PPh₃)₂]BF₄, and its iridium analogue on montmorillonite K10. The rhodium catalyst had the higher activity. The reaction is mild and solvent-free and the catalyst can be easily recovered and reused.
Ferrocenyl Phosphine Complexes of the Platinum Metals in Non-Chiral Catalysis
THEIR APPLICATIONS IN CARBON-CARBON AND CARBON-HETEROATOM COUPLING REACTIONS

By Thomas J. Colacot
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The C2 symmetric ligand, 1,1'-bis(diphenylphosphino)ferrocene, discovered about three decades ago, has opened up a new area of chiral and non-chiral ligands. This ligand is a relatively air- and moisture-stable solid and has a large phosphorus-metal-phosphorus bite angle in its metal complexes. These types of ligands have demonstrated numerous applications in metal-catalysed organic transformations, such as coupling reactions, asymmetric hydrogenation, hydrogen transfer, hydrosilation and allylic alkylation. In this brief review, some recent applications, particularly using platinum metals, will be discussed.

Ferrocenyl phosphines, such as the C2 symmetric 1,1'-bis(diphenylphosphino)ferrocene, dppf, have emerged as a new class of ligands, with a wide range of unique applications, since their first discovery and use in 1965 (1). The literature describing this includes, for example, the first two chapters of the book, “Ferrocenes”, edited by Togni and Hayashi. In this book they give a detailed account of the syntheses and catalytic applications of dppf (2) and chiral ferrocenyl phosphines (3) up to the year 1995. Recently, Hartwig has emphasised the applications of dppf and related ligands in carbon-heteroatom coupling reactions (4). Hayashi (5), Richards (6), Togni (7), Knochel (8), Kagan (9) and Ito (10) have also reviewed the syntheses of chiral ferrocenyl phosphate ligands which have applications in asymmetric syntheses.

Aspects of this work, related to the platinum group metals, is updated here. In particular this review covers some recent applications of non-chiral ferrocenyl phosphines, coordinated to platinum group metals, in homogeneous catalysis. Emphasis is placed on Kumada-Hayashi, Suzuki, Heck and Buchwald-Hartwig coupling reactions.

Types of Ligands
Ferrocenyl ligands are classified into two types: chiral and non-chiral. The best known example of a non-chiral phosphine is dppf which has C2 symmetry (2). Monodentate (11) and bidentate alkyl or aryl (12) substituted phosphines are known in the literature, and their applications in difficult coupling reactions are currently being explored. A few examples of unsymmetrical ferrocenyl phosphines have also been reported (13), although their catalytic applications have not been investigated in detail. Different research groups have utilised the planar chirality of the ferrocene molecule in designing novel chiral phosphines — because of their inherent resistance to racemisation. As a result the area of chiral ferrocenyl phosphines has outgrown that of non-chiral ferrocenyl phosphines (3, 5-10).

Synthesis of 1,1'-Bis(diphenylphosphino)ferrocene and Related Ligands
The first example of a ferrocene-based phosphine ligand, 1,1'-bis(diphenylphosphino)ferrocene, dppf, was synthesised in 1965 by reacting the dilithium salt of ferrocene with Ph2PCl (1). Subsequent process improvements from academic (12) and industrial laboratories (14) led to the commercialisation of dppf in multi kilogram quantities. Examples of Cp2Fe(PR2)2, where R is an aliphatic group such as t-Bu or i-Pr are also known (12-14). Seyferth (11) and Cullen (13) demonstrated an elegant way to make a few examples of unsymmetrical ferrocenyl phosphate ligands, where the dilithium salt of ferrocene is reacted initially with RPCl2 to produce a C-P-C bridged species. This bridge is
later opened with \( \text{RLi} \), followed by the subsequent coupling reaction with \( \text{R'}_2\text{PCI} \) to produce \( (\text{C}_6\text{H}_5\text{PR}_2)\text{Fe}(\text{C}_6\text{H}_5\text{PR}'_2) \). There are also reports of the synthesis of monosubstituted ferrocenyl phosphines (11). Although monosubstituted electron-rich ferrocenyl ligands are useful for aryl chloride coupling reactions, their syntheses are tricky, tedious and the products are very often contaminated with disubstituted byproducts – as the mono lithium salt is not easy to isolate in pure form (15). General routes for the syntheses of various non-chiral ferrocenyl phosphines are summarised in Scheme I.

Applications of Ferrocenyl Phosphines

Numerous patents and publications have appeared during the past decade describing the applications of ferrocenyl phosphines in metal-catalysed organic reactions. Recently, increasing numbers of pharmaceutical and chemical companies have become interested in palladium-catalysed carbon-carbon and carbon-nitrogen coupling reactions. The special advantages of using ferrocenyl phosphines in such coupling reactions are reported here.

Carbon-Carbon Coupling

**Kumada-Hayashi Coupling**

Kumada and Hayashi were the first group to demonstrate the extraordinary ability of \( \text{PdCl}_2\text{dpdf} \), in difficult C-C coupling reactions involving Grignard reagents and organic bromides. In 1984 Hayashi, Kumada, Higuchi and their coworkers (16) studied the reaction of organic bromides with alkyl magnesium or zinc reagents in the presence of various catalysts, such as \( \text{PdCl}_2(\text{PPh}_3)_2 \), \( \text{Pd}(\text{PPh}_3)_4 \), \( \text{PdCl}_2\text{dppe} \), \( \text{PdCl}_2\text{dppp} \).
and PdCl₂dppe, where dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane and dpbb = 1,4-bis(diphenylphosphino)butane, respectively. In particular see Scheme II for PdCl₂dpf.

The PdCl₂dpf catalyst gave excellent selectivity with nearly quantitative yield of the desired, coupled product, see the Table. They attributed the remarkable success of this catalyst to its larger bite angle and a flexible bite size. Gan and Horr called PdCl₂dpf a 'magic catalyst' as its behaviour was far superior to that of the classical monodentate PPh₃-based catalysts or even to that of the conventional diphenylphosphinoalkane-based bidentate ligands (2). Until recently it was believed that the larger P-Pd-P angle and longer P-Pd bond distance promoted the facile reductive elimination (that is, coupling), thereby minimising the β-hydride elimination. However Hayashi’s recent work with bis(diphenylphosphino)biphenyl, dpbp, seems to suggest that the smaller Cl-Pd-Cl angle more strongly influences the reactivity than does the larger P-Pd-P bite angle, see the Table, (17).

Further work is needed to correlate the reactivity/selectivity with the X-P-X bond angles (X = halogen or leaving group).

**Suzuki Coupling**

Another interesting application of dpf in C-C coupling was demonstrated by Suzuki and coworkers on reacting aryl boronic acids with more challenging aryl and vinyl triflates in the presence of PdCl₂dpf (18). The coupling becomes more difficult with inherently less reactive and less expensive aryl mesylates and sulfonates. By changing from PdCl₂dpf to NiCl₂dpf/Zn, Percec obtained 81 per cent yield of 4-methoxybiphenyl by the Suzuki coupling reaction of phenyl mesylate with 4-methoxyboronic acid (19). Miyaura later extended this work to other examples of aryl...
mesylates and even more challenging aryl chlorides, and achieved yields of over 90 per cent by using Ni(0)-dpff catalysts, see Scheme III, (20). In all these cases dpff as ligand is far superior to other biphosphines, such as dppp, dppe and dppb or monophosphines, such as PCy₃ and PPh₃.

Interestingly, it was observed by Pandgen that there was no coupling reaction between chiral fluorosulphonates and aryl boronic acids in the presence of NiCl₂dpff, while PdCl₂dpff gave over 98 per cent yield of the coupled product, 1,3-diaryl indene, without any racemisation (21). These compounds are precursors to SmithKline Beecham’s: SB 209670 and SB 217242 (code numbers of future drug candidates). Water soluble Ph₃P(m-NaOS-C₄H₄)PdCl₂ and [P(o-tolyl)_3]PdCl₂ are equally effective, but they are either more expensive or not readily available.

A C-C coupling of aldehydes with a ‘Suzuki reagent’ (organic boronic acid) in the presence of rhodium catalysts was also successfully demonstrated recently by Miyaura, see Scheme IV, (22).

In this case, with dpff as ligand, 99 per cent conversion was obtained. The other bidentate ligands gave only modest to moderate conversions. Although the results generally correlate with the P-Rh-P bite angles, dppb stands out as an exception: giving only 17 per cent conversion despite its relatively large bite angle. This seems to suggest that Hayashi’s recent observation has to be taken seriously (17), and there may be factors other than the bite angle which decide the reactivity in the coupling reactions.

Heck Coupling:

Only a small number of reports are available on applications of ferrocenyl phosphines in Heck coupling, although the importance of dpff in such chemistry is documented with several examples (23).

Butler (24), one of the early workers in this area with Cullen (13), recently demonstrated that reactions using P(i-Pr)₂ substituted ferrocenyl phosphine provided very high yields of coupled trans products (Scheme V) (1b: R, R' = i-Pr). The monosubstituted derivative (2a: R = i-Pr) also gave very high yields, whereas dpff (1a: R, R' = Ph) and its alkyl-aryl mixed derivative,
Fe(η₅-C₅H₅PPh₂)η₅-C₅H₅P(i-Pr)₂ (3a: R = Ph, R' = i-Pr) gave only modest and moderate yields, respectively, indicating the importance of aliphatic phosphine moieties in Heck chemistry.

Subsequently Hartwig's high throughput screening studies (25) using 45 structurally different phosphines indicated that P(t-Bu), and di(t-butylphosphino)ferrocene, 1c, are the two most active systems to date for the Heck olefination of unactivated aryl bromides, and that di(t-butylphosphino)ferrocene is the most efficient ligand for olefination of aryl chlorides.

Fu's successful work on palladium-catalysed Heck, as well as Suzuki and Stille couplings, using P(t-Bu), needs to be mentioned here (26), as it has rekindled the interest in these difficult aryl chloride coupling reactions. However pharmaceutical companies tend to avoid using P(t-Bu), as it is extremely air-sensitive and undergoes oxidation if proper care is not taken.

Stille Coupling

Stille also observed that PdCl₂(dppf) behaves in a unique way in C-C coupling reactions. Of several palladium phosphine catalysts tried in the study it was the only one which gave consistently higher yields of the Stille coupled products when aryl triflates were coupled with organostannanes (27).

Carbon-Heteroatom Coupling

C-N Coupling Using dppf

The most prominent reaction in this area is carbon-nitrogen bond formation, commonly referred to as Buchwald-Hartwig coupling (4, 28). Buchwald's work (29) in this area indicated that the ligand BINAP (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, existing in racemic and chiral forms) in combination with Pd₂dba₃ (tris(dibenzylideneacetone)dipalladium(O)) is capable of catalysing the aryl amination process involving a primary amine (Scheme VI). Use of the conventional bidentate ligand, dppe or monodentate P(o-tolyl), gave unsatisfactory results.

Concurrently, Hartwig (30) identified palladium complexes of dppf (that is PdCl₂(dppf), Pd(OAc)₂/dppf or Pd(dba)₂/dppf) as second generation catalysts for similar couplings. These complexes are capable of producing high yields of coupled products with aryl halides and various aniline derivatives, see Scheme VII. Electron-rich,
electron-poor, hindered or unhindered aryl bromides or iodides all performed well in this chemistry. Hartwig’s attempt to use other bidentate ligands, such as bis(diphenylphosphino)propane or bis(diphenylphosphino)benzene, in these types of coupling reactions were not successful in terms of producing high yields of the desired coupling products (31).

This chemistry has also been extended to the amination of aryl triflates with anilines to give excellent yields, see Scheme VIII, (32). However, electron-poor aryl triflates were susceptible to cleavage under basic conditions. This problem has been overcome by the slow addition of triflates (32) or by the use of the base Cs₂CO₃ (33).

The unique nature of dppf or BINAP could be associated with their steric bulkiness, which may be responsible for the slow rate of Β-hydride elimination in comparison with the reductive elimination process. This would also prevent the formation of Pd-diamine complexes.

Although there may be a few exceptions where BINAP behaves better than dppf, Hartwig found that dppf is effective in many coupling reactions (4, 30). Buchwald in his recent review states “while optically active BINAP is expensive, the finding that (±)-BINAP is usually a suitable surrogate has led to its commercial availability” (34). However, dppf is less expensive than racemic BINAP and is much easier to synthesise and purify.

Limitations of dppf
Neither dppf nor BINAP were effective for the amination of aryl bromides, such as 4-<i>t</i>-butylbromobenzene with di-<i>n</i>-butylamine and have provided only 8 to 9 per cent yield of the desired product (although 43 per cent product could be obtained by using 5 mol% PdCl₂dppf and 15 mol% of dppf (34)). This limitation was overcome by Buchwald using another ferrocenyl phosphine ligand, (±)-PPF-OMe, 4, which provided a yield of ~ 95 per cent, see Scheme IX, (28, 34-35).

Couplings of aryl chlorides with cyclic and acyclic secondary amines were also difficult with dppf and BINAP. The use of palladacycle 5 in the coupling of CF₃C₆H₄Cl with an acyclic amine proceeded in reasonable yield (60 per cent). When the cyclic amine, piperidine, was used the yield increased to 98 per cent (36). Reddy and Tanaka (37) used the electron-rich phosphine, PCy₃, to couple chlorobenzene with a secondary cyclic amine, N-methyl piperazine. Hartwig also performed the same type of chemistry very successfully with several substrates by using di(<i>t</i>-butylphosphino)ferrocene, 1c, (38), while Buchwald followed a similar approach by using the bulky PCy₂ substituted biphenyl ligand, 6, (39).

Interestingly, ligand 6 has been useful even for coupling electron-rich aryl chlorides. Subsequently 2-di(<i>t</i>-butylphosphino)biphenyl was found to be a
good ligand by the same group. Hartwig has also used the ferrocene-based chelating aliphatic phosphines, 7 and 8 originally prepared by Cullen (12a) and Butler (13), to couple an electron-rich aryl chloride, MeC₆H₄Cl, with amines, including a primary amine, π-BuNH₂ (38). All these studies suggest that bulky electron-rich ligands in combination with palladium or nickel are extremely useful for difficult aryl chloride (ArCl) coupling. In this regard, Nolan’s original work with the nucleophilic carbene ligand 9 is worth mentioning as he demonstrated a very efficient coupling of ArCl with a wide variety of aliphatic cyclic and acyclic secondary amines, and aliphatic and aromatic primary amines (40).

C-O, C-S and C-P Coupling

Intramolecular C-O bond formation leading to the formation of heterocycles containing O atoms was reported by Buchwald using Tol-BINAP (Tol = tolyl) or dppf in the presence of Pd(OAc)₂ (41). Hartwig reported the first intermolecular C-O coupling of aryl halides, leading to the formation of ethers, using dppf in the presence of Pd(dba)₂ (42). For the latter reaction, the yields were greater than 90 per cent. Ni(COD)₂ in the presence of dppf or Tol-BINAP, gave more or less identical yields (68 to 98 per cent) for the formation of t-butyl, methyl and silyl aryl ethers (43). More details on C-O and C-S coupling using dppf ligands have been reviewed recently (4).

Hartwig’s group (44) has recently identified the in situ formation of an interesting ligand Ph₅FeP(t-Bu)₃, 10, by the palladium-catalysed perarylation of the cyclopentadienyl group in PF₆(t-Bu)₃, 2b, (45). This ligand is very useful for room temperature aromatic C-O bond formation with yields of up to 99 per cent (44).

About five years ago, a group reported a convenient and efficient synthesis of BINAP by a C-P coupling involving the ditriflate of binaphthol with Ph₂PH or Ph₂P(O)H in the presence of a phosphine complex of NiCl₂ (46). Although dppf is a good ligand for the same reaction, the authors did not mention any special advantage of dppf over other phosphines. A recent non-catalytic study suggests that PdCl₂dppf, in the presence of Pd(dba)₂, is capable of forming C-P bonds by reductive elimination (47). However, this is an area, which needs further exploration.

Conclusion

The importance of dppf and related ligands in late transition-metal catalysed organic reactions are fairly significant, especially in coupling reactions. The steric bulkiness, large bite angles (for chelating ligands) and relative stability of the aliphatic substituted ferroceny phosphines, in comparison to P(t-Bu)₃, are some of the special advantages of these types of ligands which give facile reductive elimination without any undesired isomerisation (β-hydrogen elimination) leading to byproducts. Many of the ligands such as dppf or its P(η-Pr)₃ or P(η-Bu)₃ substituted analogs are commercially available, and their air and moisture stabilities increase further when they are complexed with palladium.

Ni(0) complexes also appear to be useful for certain difficult coupling reactions. However, these complexes are fairly difficult to make in large quantities, and nickel is not a very environmentally friendly metal for pharmaceutical processes.

The other C-heteroatom coupling reactions are also important in the chemical and pharmaceutical industries. A fuller review, where chiral applications will be discussed in greater detail, is planned for publication during 2001 (48).
Acknowledgements

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The 2000 MacRobert Award for the Platinum CRT™

The MacRobert Award is the premier prize for engineering innovation in the U.K. and is awarded annually by the Royal Academy of Engineering to a team responsible for a world-leading engineering development demonstrating technological achievement, successful commercial exploitation and benefit to the community.

In 2000 the MacRobert Award was won for the second time by Johnson Matthey, this time for engineering innovation in the U.K. and is awarded by the Royal Academy of Engineering development demonstrating technological achievement, successful commercial exploitation and benefit to the community.

The breakthrough occurred in the early 1990s when Sweden introduced low-sulfur fuel in response to environmental concerns. Low sulfur fuel and the CRT™ are now sold across Europe, in the U.S.A. and in Japan.

The MacRobert Award coincided with the fifth anniversary of the commercial launch of CRT™, first described in this Journal in a paper by Pelham Hawker (2). Hawker is a member of the winning team, along with Pär Jones and the co-inventors of CRT™, Barry Cooper and Jim Thoss. Barry Cooper was also in the team which won the MacRobert Award in 1980 and so becomes the first person to win the Award twice. To celebrate the Award, Johnson Matthey has produced a special commemorative report, “CRT5: Fifth Anniversary Publication”. Copies of this may be requested from: Ms Vanessa Bystry, Johnson Matthey CSD, Orchard Road, Royston, Herts SG8 5HE, U.K; Fax: +44 1763 253 475 or E-mail: bystrv@matthey.com.

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References

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Robert Evans is the Marketing Manager for the Johnson Matthey Catalytic Systems Division. His interests lie in vehicle emissions control systems, particularly retrofit applications.
21st Century Emissions Technology
REVIEW OF AN INSTITUTION OF MECHANICAL ENGINEERS CONFERENCE ON EMISSION CONTROL

The Combustion Engines Group of the Institution of Mechanical Engineers (IMechE) held a conference on '21st Century Emissions Technology' at their London headquarters on the 4th and 5th December 2000. Nearly 100 participants from the U.S.A., Japan and most European countries gathered to hear 23 excellent talks and to discuss engine and aftertreatment technologies.

The major theme of the conference was the need for ongoing research in emissions reduction strategies and technologies for both on-highway transport and off-road mobile machinery. The conference was thus a forum for the leading experts from motor manufacturers, oil companies, vehicle testing houses and universities to discuss the reduction of particulate matter and nitrogen oxides, NOx, in order to meet the forthcoming stringent European and U.S. federal emissions legislation. Vehicle emissions can form a large part of the measured pollutant levels in ambient air, thus, this review examines the role that catalyst systems, based on platinum group metals (PGMs) play in ensuring the continual global lowering of vehicle emissions.

Emissions Control Technology for 2000–2010

Robert Searles (AECC, Belgium) addressed the challenges to and opportunities for catalyst technology in the 21st century. He highlighted the need for cleaner fuels, with lowered sulfur levels, which enhance and make possible the use of more sophisticated catalyst systems, such as NOx traps and particulate filters. He mentioned the launch of the new Peugeot 607 diesel passenger car, which is an industry first for a European diesel passenger car to have a particulate filter system. There was speculation about whether a strategy of using non-continuous regeneration with a fuel-borne catalyst, and an appropriate conventional platinum-based catalytic converter would be a realistic way forward for all classes of passenger cars. He reported growing interest in the selective catalytic reduction (SCR) of NOx for use in the aftertreatment of heavy-duty diesel emissions. Searles also summarised work on hydrocarbon-absorbers, electrically heated catalysts, and on active and passive NOx.

The technologies currently available for passenger cars and larger vehicles were reviewed by Timothy Johnson (Corning, U.S.A.). He discussed developments in various catalyst supports (made of cordierite) and trends, such as:

- advanced integration of catalyst and engine management
- lower ammonia emissions from gasoline vehicles
- better cold start response
- hybrid (or layered) catalysts and
- PGM flexibility.

Johnson noted that flexibility in using the PGMs is an important new concept for major automobile manufacturers. This will help to ease cost volatility by substitution of one metal for an equally active one, where possible. This might lead to a need for certification of multiple catalyst systems at the initial design phase and production testing of vehicles, and would ultimately result in cost savings for most parties.

The costs of various SCR systems were assessed by James Warren (The Open University, U.K.) for Euro 5 heavy-duty diesel trucks. It was shown that most long-haul transportation trucks can 'pay back' the complete cost of the catalyst system within one to two years if fuel savings of 3 to 5 per cent are achieved, by tuning the engine for higher, raw (precatalyst) NOx emissions, and then choosing an appropriate catalyst and control system.

A possible way of reducing NOx via engine method alone was presented by Patrick Flynn (Cummins Engines, U.S.A.). He described work on exhaust gas recycling (EGR) which clearly indicates that combustion chemistry is the limiting factor in determining the minimum NOx produced in both gasoline and diesel engines (heavy duty, cylinders > 1 litre). The minimum levels of NOx achievable are listed in the Table, along with the proposed European and U.S. federal limits. His
One route to lowered NOx levels is offered by the non-thermal plasma (NTP) technique. Hermann Breitbach (Delphi, Luxembourg) showed that a potential NTP system, coupled with a zeolite-based catalyst, can reduce emissions from passenger cars. Currently, when running the NTP system on a car, ~300 W (~1 kW at peak condition) is required to generate good dielectric behaviour. This results in a fuel penalty of ~3 per cent. However, with the future 42 V electrical systems, coupled with integrated starter motors, NTP in cars will be much easier to integrate and to supply with power.

Diesel Particulate

Diesel particulate and its measurement – down to aerodynamic particle diameters of ~7 nm – remains of strong interest to engine manufacturers and, indeed, to the public at large. The use of CRT™ (Continuously Regenerating Trap) systems, containing a platinum-based catalyst and particulate filter, is well established for particulate reductions.

The characterisation of particles from heavy-duty diesel (HDD) and light-duty diesel (passenger cars) was examined by Barbara Wedekind (Ricardo Consulting Engineers, U.K.). She also discussed the effects of a CRT™ on a Euro 2 HDD, as well as the effects of diesel particulate filters on a selection of passenger cars. Work on the Peugeot 607, VW Golf and Peugeot 406, all fitted with a variety of oxidation catalysts and filters, showed that vehicles fitted with these devices were capable of achieving very low particulate mass emissions. Under all conditions tested, the CRT™ consistently reduces particulate mass. However, further work on the characterisation and measurement of particulate is required both to establish the origin of any particulate observed after filtration, and to find a standard set of measurement conditions on which all test houses can agree, for possible future legislation and correlation.

The post-catalyst exhaust gases from gasoline-powered vehicles (aiming at SULEV (super ultra low emission vehicle) emissions) are so clean as to be almost immeasurable with some of today’s devices. Indeed, in some instances the exhaust gas has been cleaner than the intake ambient air. This illustrates the need for more advanced quantitative methods for measuring evaporative hydrocarbons, particulates and other pollutants.

Future Trends in Engines

Compressed natural gas (CNG) and controlled auto-ignition (CAI) were among other engine/fuel powertrains described. Both promise potentially lower NOx emissions. While gaseous fuels are currently relatively inexpensive, the potential emission of methane from such engines will need to be addressed catalytically. CAI gives NOx values as low as 10 ppm, but system control is extremely difficult, and CAI has not yet been fully demonstrated in a running vehicle.

Paul Kapus (AVL, Austria) reviewed work on the ‘G90’ vehicle. The ‘G90’ is a modified GM/Vauxhall/Opel Corsa with a typical fuel consumption of 5.7 litres/100 km (as purchased). After modifications to body shape (for superior aerodynamic drag) and transmission, and the addition of variable valve actuation, along with partial downsizing, the fuel consumption was reduced to 3.9 litres/100 km and CO₂ emissions were lowered from 137 to 90 g km⁻¹. This shows that the way forward to enable engines to meet CO₂ limits will be a smart combination of technologies.

The views of Toyota on hybrid powertrains, were presented by Tokuta Inoue (Toyota and Genesis Research Institute, Japan). He described
the Prius, Toyota's hybrid electric vehicle (HEV). Currently, the Prius (second generation coupled to a gasoline internal combustion engine) contains a new rectangular battery module (21 kW) coupled to a 33 kW gasoline engine. This delivers 3.4 litres/100 km under the Japanese driving test. When compared to a pure electric vehicle, this HEV has a longer driving range, good fuel economy and good drivability without the need for recharging. The year 2001 Prius meets the Japanese and U.S. SULEV emissions, as well as the Euro 4 regulations. The Prius is the first Toyota vehicle, and perhaps one of the first-ever production vehicles, to use a catalyst support of 900 cells inch$^{-2}$, wall thickness 0.5 mm, carrying a palladium and rhodium catalyst. The increase in highly active geometric surface area has optimised together with an $\sim 19$ per cent lower total catalyst volume than prior systems. It contains a hydrocarbon absorbing component to assist hydrocarbon capture at low temperatures with subsequent oxidation after light-off is complete.

**Future Vehicles and Technologies**

It is expected that future vehicles will include more models with direct injection (gasoline and CNG) with advanced variable valve timing. Powertrains will be based more on combinations of technologies, such as turbo-charged CNG, CAI with direct injection, and CNG with direct injection. The market will become segmented with some sectors finding unique solutions (HDD vehicles will remain for trucks/transport of goods). In other areas multiple solutions are possible, with fuel cells and hydrogen-based fuels expected to eventually gain a large part of the market share. Hybridisation and hybrid vehicles will begin to play a prominent part in powertrains, with electric/fuel combinations being prominent. Clearly, the variety of powertrain combinations will have an effect on the catalyst systems they use. Future developments will need to take all component into consideration (filters, catalysts, monitors, sensors, fuels, etc.) and to maximise any synergistic effects to achieve the lowest overall emissions, and the lowest possible CO$_2$ levels for their class. Vehicle designers and component suppliers will probably work together closely to achieve cost-effective solutions. In general, consumers will increasingly demand comfort, safety, cost reductions, good driving performance, enhanced durability, reliability and low emissions. However, the catalytic converter will clearly remain the main pollution control device for the next generation of vehicles, although, 15 years from now, it may not be recognisable in its present form.

The papers presented at this conference will be published in Spring 2001 in the IMechE Seminar publication series. Information can be found at: http://www.imeche.org.uk.

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**Palladium Cross-Coupling Reaction for Brain Tracers**

Brain imaging via positron emission tomography (PET) using the short-lived $^{11}$C positron emitter (half-life $\sim 20$ minutes) requires a fast chemical reaction to incorporate the small amounts of $^{11}$C into a carrier (tracer) which delivers it to the tissue under examination.

Researchers in Japan and Sweden have now developed a new rapid, efficient Stille methylation of arylstannanes which produces a structure system that can deliver sufficient quantities of $^{11}$C to prostaglandin receptors (IP$_2$) in the brain (M. Suzuki, H. Doi, K. Kato, M. Björkman, B. Långström, Y. Watanabe and R. Noyori, Tetrahedron, 2000, 56, (42), 8263–8273). The Stille methylation involves a palladium-promoted cross-coupling reaction of methyl iodide and tributyltin derivatives of tolylisocarbyclins (TICs); the TIC binds to the IP$_2$ receptors. In one methylation, which is a novel stepwise operation, an initial methylpalladium complex is produced and is then mixed with other materials for the cross-coupling. The Pd promoter is a Pd(0) complex generated from Pd$_2$(dba)$_3$ and P(o-CH$_3$C$_6$H$_4$I)$_2$ in the presence of CuCl and K$_2$CO$_3$. The synthesis is highly reproducible, and with $^{11}$C incorporated, results in a $^{[11]}$C-labelled PET tracer with radioactivity of several GBq, which can be injected intravenously.
Improved Start-Up for the Ammonia Oxidation Reaction

ELECTRICAL HEATING DEVICE FOR PLATINUM-RHODIUM GAUZE CATALYSTS AND NEW PROCEDURE REDUCES EXPLOSIVE HAZARDS AND PLATINUM LOSSES AT START-UP

By V. I. Chernyshev and S. V. Zjuzin

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The start-up operation in a nitric acid plant is one of the most important stages, from the viewpoint of safety and platinum loss, in the entire ammonia oxidation process. Usually, flame burners using hydrogen or hydrogen-containing gas preheat the platinum alloy gauze catalyst to the operating temperature. However, there are disadvantages and peculiarities in this method of initiating the start-up reaction. These are discussed here and a new electrical heating device and a new technique are described for preheating the platinum alloy gauze catalyst. The device and technique are free of these disadvantages, and together they reduce the explosive hazard and platinum losses during start-up. Results from their commercial utilisation over a 12-year period at various nitric acid plants are described.

The ammonia oxidation process has been used in nitric acid production since the start of the twentieth century. As early as 1902 it was shown that the most promising catalysts for this process were platinum alloys (1) and the optimal form for the catalyst was found to be gauze, fabricated from wires of diameter 0.06-0.09 mm, and placed in stacks (2). Today, knitted or woven platinum alloy gauze is used as the catalyst for the production of nitric acid and prussic acid, and also to produce hydroxylamine sulfate.

The initial stage of the ammonia oxidation process for nitric acid production begins when an ammonia:air mixture (AAM) at a temperature of 80–200°C is input into a reactor in which platinum alloy gauzes are installed. The catalyst must be preheated to 250°C prior to the start of the ammonia oxidation in order to change this process into a high-temperature diffusional regime (3). Various techniques are used to preheat the catalyst. In commercial nitric acid plants one of the most applied techniques is to use the heat from burning hydrogen or hydrogen-containing gases. The burners used are in the form of perforated tubes mounted in the reactors near to the gauzes. These burners can either be fixed or rotating. Only 'technological air' (air pumped from a compressor) is fed into the reactor, as it has been preheated by the combustion gases. When the temperature reaches 600°C (visible red glow) ammonia is mixed with the technological air (4). Hydrogen combustion is continued until the ammonia oxidation process is observed to start. This apparently simple start-up operation will be looked at in detail.

Hydrogen Oxidation by Oxygen Using Burners

The homogeneous oxidation of hydrogen using oxygen which takes place during start-up in an ammonia oxidation reactor has been studied for a long time (5) and can be described by a number of chain reactions which take place in the free space above the gauzes in the reactor, as well as on the catalyst surface. The main reactions can be described as follows:

\[ ^1H + O_2 \rightarrow ^1OH + ^1O \] (i)
\[ ^1O + H_2 \rightarrow ^1OH + ^1H \] (ii)
\[ ^1OH + H_2 \rightarrow H_2O + ^1H \] (iii)

The outcome of reactions (i), (ii) and (iii) is an increase in the concentration of free hydrogen atoms which occurs as a geometric progression. The free atoms 'H, 'O and the 'OH radicals are active intermediate products of the chain reactions.
and easily recombine either in the volume or at the
surface of the catalyst to eventually become the
stable molecules: H₂O, O₂ and H₂O₂. However,
for the hydrogen oxidation process the recombi-
nation reactions of 'H atoms are of main interest:

\[ 'H + O₂ + M \rightarrow 'HO₂ + M \]

(iv)

where M is an arbitrary particle. It follows from
Equation (iv) that chain breakage of reactions (i)
and (ii) in the volume does not result in the for-
mation of a stable molecule. A new type of
peroxide radical is formed which contains exces-
sive chemical energy and is a long-lived
intermediate product. This 'HO₂ radical undergoes
recombination reactions:

\[ 'HO₂ + H₂O \rightarrow H₂O₂ + 'OH \]

(v)

\[ 'HO₂ + H₂O₂ \rightarrow H₂O + O₂ + 'OH \]

(vi)

Reactions (v) and (vi) describe processes which
occur at the surface of the gauze and produce con-
siderable amounts of heat.

At the same time as the above processes are
occurring, the heterogeneous oxidation of the
hydrogen – which did not react according to
Equations (ii) and (iii) – is taking place on the plat-
inum alloy gauze surface:

\[ 2H₂ + O₂ \rightarrow 2H₂O \]

(vii)

When the temperature of the platinum alloy
gauze exceeds 250°C, ammonia oxidation begins
(6):

\[ 4NH₃ + 5O₂ \rightarrow 4NO + 6H₂O \]

(viii)

\[ 4NH₃ + 3O₂ \rightarrow 2N₂ + 6H₂O \]

(ix)

\[ 4NH₃ + 4O₂ \rightarrow 2N₂O + 6H₂O \]

(x)

These reactions have different thermal effects
which eventually define the temperature of the
platinum alloy gauze catalyst.

**Drawbacks of Flame Burners for
Start-Up of Ammonia Conversion**

Some conclusions can be drawn from the
above simplified analysis. During the start-up peri-
od in a commercial ammonia oxidation reactor
when the activity of the platinum alloy catalyst is
not high enough, the use of flame burners masks
the progress of the process towards increased
activity to the desired reaction (viii). This
phenomenon bears testimony to an idea that the
recombination reactions of atoms and radicals
produced by the hydrogen flame on the catalyst
surface (Equations (iv) – (vi)) are the dominant
reactions in preheating the catalyst. However,
these reactions also disable the active centres of
the catalyst which are common and not dependent
on the chemical character of the combustible gas
(in this case hydrogen or ammonia).

Even though Equation (vii) is a promotor reac-
tion with respect to Equation (viii) (7) and
although during preheating the surface of the plat-
inum alloy catalyst has a uniform glow, dark spots
are often observed on the catalyst surface after the
hydrogen to the burners is switched off. Such
spots are due to side reactions (Equations (iv) –
(vii)) when atoms and radicals from the hydrogen
flame recombine. This well-known negative effect
increases considerably if the catalyst contains
impurities and poisons.

During the start-up period, which sometimes
lasts for 10 or more minutes, ammonia passes
through unactivated areas of the catalyst surface
without being oxidised, while at the active surface
areas of the catalyst it is oxidised into nitrogen
oxides in the usual manner. On the downflow side
of the catalyst this unreacted ammonia reacts with
the nitrogen oxides to form nitrite-nitrate com-
pounds of ammonia which tend to collect in
stagnant areas of the equipment and can form a
hazardous explosive situation. Such explosions
have caused breakdowns in nitric acid plants
resulting in prolonged downtime. Fatal accidents
are also known to have occurred. Using hydrogen
as the combustion gas to start-up the ammonia
oxidation is also an explosive hazard and this too
has caused accidents and breakdown in equip-
ment.

Another considerable disadvantage of flame
burners is the so-called 'heat wear' of the platinum
alloy catalyst which can result in a burn-out of
local areas of platinum alloy gauze during the start-
up period. This causes additional platinum losses.
Such heat wear of the platinum alloy catalyst, espe-
cially in the upper gauze, is induced mainly by local
overheating to temperatures above the boiling
points of the platinum materials, due to recombination reactions of atoms and radicals in the hydrogen flame, which have a high thermal effect (Equations (iv), (v) and (vi)). Overheating in localised areas of the platinum alloy catalyst is probably also due to the non-uniform distribution of the hydrogen flame over the gauze catalyst surface, for example, because of imperfect burners and the design of the AAM flow distributors.

An analysis of 50 Russian nitric acid plants has shown that unrecoverable platinum losses occur only during the start-up, due to using hydrogen flame burners. The platinum losses total 0.001 to 0.0015 per cent by weight or, with respect to the productivity of all the plants in Russia, 10 to 12 kg annually (the average daily expected output of each plant analysed is 355 tonnes of nitric acid).

There are other disadvantages when using flame burners for initiating the ammonia oxidation reaction. One is the possibility of ammonia pre-catalysis which can take place on the exterior surfaces of the burners, which receive additional heat as radiation from the hot platinum alloy gauzes. Last, but not least, the start-up reaction requires a source of pressurised hydrogen, if the ammonia synthesis plant does not provide hydrogen-containing gas from one of its intermediate stages.

New Procedure and Electrical Device for Start-Up of Ammonia Conversion

All the above circumstances defined the research that was devised, directed and participated in at GIAP (8). The main aim of the research lay in finding new engineering solutions which could help towards avoiding the use of hydrogen flame burners in commercial ammonia conversion reactors. The investigations enabled us to create a unique method and devices for electrically heating isolated areas of platinum alloy gauzes, stacked in packs, to initiate the ammonia conversion reaction over the whole surface of the catalyst in the shortest possible time (9, 10).

This new electrical ignition device (EID) uses linear heating elements arranged in a unique manner on the surface of the platinum alloy catalyst which needs to be ignited. The positioning of the heating elements on the surface depends on the
Reactors Performance Data from a Reactor at the JSC Kirovo-Chepetsky Chemical Company

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAM consumption (STP)</td>
<td>66,000 m³ h⁻¹</td>
</tr>
<tr>
<td>AAM temperature at start-up</td>
<td>130°C</td>
</tr>
<tr>
<td>AAM temperature during stationary periods of operation</td>
<td>200°C</td>
</tr>
<tr>
<td>Ammonia concentration</td>
<td>11 vol.%</td>
</tr>
<tr>
<td>Number of gauzes in pack</td>
<td>12</td>
</tr>
<tr>
<td>Total weight of gauzes in pack</td>
<td>24 kg</td>
</tr>
<tr>
<td>Gauze pack operating diameter</td>
<td>1650 mm</td>
</tr>
</tbody>
</table>

The ammonia conversion reaction was started up with values for the current and voltage of 31 A and 180 V, respectively. The time taken for the spread of the reaction from the initial local areas to the all the catalyst surface was about 1 minute which was somewhat longer than the calculated 25 seconds. This emphasised the point that effective work using EIDs requires very pure platinum alloy catalyst. Hence, subsequent start-up operations were preceded by special activation of the platinum alloy gauzes, using a technique devised by the authors (11). After such activation the time taken for the initiated localised reaction areas to spread over all the catalyst surface was 20 to 25 seconds. This technique was also successfully applied to activate the fouled gauzes.

Over a two year period, 15 starts-up were performed using the EID. The state of the electrical insulation of the EID and the state of the catalyst surface were inspected each time the plant was shut down. The experience gained was used as the basis for designing commercial EIDs which have two ways of inputting electrical power to the heating elements: through either the upper or lower parts of the reactor, see Figures 3 and 4, respectively.

For the UKL-7-type nitric acid plant, inputting power via the lower part of the reactor is more convenient both for assembly and operation, as there is no need to assemble and dismantle the electric power input device (assembly 2 in Figures 3 and 4) when opening the reactor to replace spent platinum alloy gauzes. This method of assembly also achieves safe electrical insulation and prevents AAM leakage during reactor operation.

Commercial implementation of EIDs then began simultaneously at three UKL-7-type nitric acid plants: at JSC ‘Dorogobouzh’, Dorogobouzh, Smolenskaya obl., Russia; JSC ‘Achema’, Jonava, Lithuania and at Nitrogenmuvek Rt., Varpalota, Hungary.

During a 6-year period the Hungarian enterprise successfully used EIDs, specially designed for a Sumitomo-designed concentrated nitric acid reactor (0.8 MPa pressure), see Figure 3. The operating diameter of the gauze pack was 1.9 m. Even though the catalyst surface in this Sumitomo reactor is 40
Fig. 2 A view of the four parallel heating elements of an electrical ignition device installed in a UKL-7 ammonia oxidation reactor. The elements are ~ 500 mm apart. The UKL-7 is a Russian-designed non-concentrated nitric acid plant and this particular one belongs to JSC ‘Achema’ in Jonava, Lithuania.

Performance characteristics of the reactor and on the design of the catalyst pack, see Figures 1 and 2. The heating elements are made from high electrical resistance metal alloy, in wt.%: C < 0.12, Cr = 27, Al = 5, Ti < 1, Fe remainder. They are catalytically inactive and encased in porcelain tubes for electrical insulation. The external diameter of an element is less than 5 mm.

The elements are heated electrically (for example, 220 V at 50 Hz) and monitored throughout. When in use, the EID starts up reactions (viii), (ix), and (x) only on the catalyst surface. The technique we devised for initiating the ammonia conversion reaction, incorporates the following:

- a value for the electric power which evolves per unit length of the electric heating element
- a number of EID switches in the electric circuit
- periods of time when the switches are on, and
- local areas of the catalyst surface which can be served by a single heating element of the EID.

The values of these intervals are determined by the parameters of the actual process of ammonia conversion, catalyst composition and gauze design. Using this new technique gives:

- a reduction to 10 to 60 seconds in the initiation period for the ammonia conversion reaction over the whole catalyst surface, the upper value being for large reactors using platinum alloy gauze catalysts with diameters exceeding 2.5 m, and
- a reduction in the risk of explosions – by cutting down the amount of non-reacted ammonia passing through the gauzes. This reduction is achieved by decreasing the initiation period and preventing the undesirable recombination reactions of the \(^{1}H\) and \(^{1}O\) atoms and the \(^{1}OH\) and \(^{1}HO_{2}\) radicals, as well as \(^{2}H_{2}\) oxidation. These block the active centres of the catalyst which are meant to be converting ammonia to NO.

- An increase in the yield of NO, due to preventing ammonia precatalysis (precatalysis usually takes place on the exterior surfaces of the burners);
- an increase in the service life of the catalyst gauzes by preventing damage caused by heat and by preventing the gauze being fouled by oil and ferrous oxides in the hydrogen-containing gases used in the burners, and
- freedom from using hydrogen-containing gas as a method of starting up the reactor.

Results of Commercial Operations

The first test of commercial EIDs was carried out in 1987 at JSC Kirovo-Chepetsky Chemical Company’s mineral fertiliser works (in Russia) using a single-pressure (0.716 MPa) nitric acid plant with a daily output of 355 tonnes of nitric acid. EIDs were installed into a reactor.

The electrical heating components included four linear heating elements arranged at intervals of 400 mm on the catalyst surface. For the first test an autotransformer was provided in the monitoring system to control the power. Data from the
Fig. 4 Schematic of an ammonia oxidation reactor with electrical input through the lower part of its shell. The plant is a 0.716 MPa (UKL-7) single-pressure nitric acid plant being operated in Russia. 

1 - lower flange of the shell of the reactor  
2 - electric input device  
3 - heating wire  
4 - insulating tubes  
5 - Pt-Rh gauze pack

per cent larger than the catalyst surface in the Russian UKL-7 reactor, the initiation period for both reactors is almost the same. The start-up operation for the Sumitomo plant occurs under following conditions:

- AAM consumption: 56,000 m³ h⁻¹  
- AAM temperature: 200°C  
- Ammonia concentration: 8 vol.%

Commercial EID implementation was found to give more advantages to woven gauze than to knitted gauze.

A new commercial EID design has been used in an ammonia conversion reactor at the Grande Paroisse nitric acid plant belonging to Chemical Industries of Northern Greece, in Thessaloniki. This single-pressure plant (0.4 MPa pressure) uses platinum alloy gauze catalyst of operating diameter 2.7 m. The EID for this reactor consisted of four linear parallel heating elements spaced 500 mm apart, as is also shown in Figure 2. Start-up was performed under the following conditions:

- AAM temperature: 170°C  
- Ammonia concentration: 5 vol.%

The time for initiating the reaction did not exceed 60 seconds.

The methods and devices described here have been used successfully at nitric acid plants in Russia, Lithuania, Hungary and Greece for over 12 years. Figures 5 and 6 show some results from industrial tests performed at the Russian UKL-7...
nitric acid plant. The power evolved per unit length of heating element versus the number of gauzes in the catalyst pack is shown in Figure 5, while the power versus linear velocity of the AAM is shown in Figure 6.

Conclusions

The experience gained from implementing commercial EID has produced data which have been used for the design of devices for ammonia conversion reactors working under a wide range of technical parameters. The structure of the catalyst gauze, its size and geometric design are now taken into consideration when simulating an ammonia oxidation reaction spreading over the whole surface. Technical characteristics of the ammonia oxidation process, gauze composition and geometric characteristics of the platinum alloy gauze are also taken into account.

As a result of this research, it may be expected that this new, simple, explosion-free technique for starting-up ammonia oxidation reactors to produce nitric acid, prussic acid and hydroxylamine sulfate will find wide application in the near future.

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Ammonia Reactions on Ruthenium

Studying ammonia (NH3) decomposition helps in understanding the kinetics of NH3 synthesis and contributes towards cleaning up NH3 emissions from sewage and activated sludge. For nearly a century iron catalysts have been used to synthesise NH3 from hydrogen (H2) and nitrogen (N2). However, ruthenium (Ru) materials are now replacing them. The major drawback of Ru catalysts is H2 poisoning, as H2 retards the dissociative adsorption of N2, which is the rate determining step in NH3 synthesis. As cerium oxide (CeO2) can stabilise noble metal dispersion and improve H2 poisoning, it has been used as a catalytic support to promote N2 activation or NH3 synthesis.

Scientists from Osaka Municipal Technical Research Institute, Japan, have now used Ru and CeO2 to prepare a catalyst which decomposes NH3 with high activity (K. Hashimoto and N. Toukai, *J. Mol. Catal.: A Chem.*, 2000, 161, (1-2), 171-178). The catalyst consists of Ru-CeO2 highly dispersed in Y-form zeolite (YZ). Ru-CeO2/YZ works at conditions where YZ and CeO2 are inactive.

The catalyst contained (in wt. %): 64.0 SiO2, 19.5 Al2O3, 10.2 CeO2 and 1.9 Ru. The decomposition rate was first order in NH3. The Ru particles loaded on CeO2/YZ reduce inhibition of the decomposition rate by H2.

IR spectra for the catalyst showed that NH3 decomposition at 300°C proceeded via formation of intermediate species, such as Ru-NH3, Ru-N2, Ru-N2 and Ru-H on the Ru surface.

Glass Conference in Veliky Novgorod

On 4th to 8th June 2001, the first international conference on 'Markets of Glass Fiber Materials, High-Quality Glasses, Monocrystals and Precious-Metal Equipment for Their Production' is to be held in Veliky Novgorod, Russia. Other topics likely to be discussed include the science and technology of glass and glass fibre, production and applications, manufacture of silicate products and the use of platinum metals equipment. The working languages will be Russian and English.

Further information may be obtained from NPK 'Supermetal', Ozerkovskaya nab., d. 22/24, korp. 2, Moscow, 113184, Russia; Fax: +007 (095) 5334453; E-mail: supermetal@cityline.ru.
ABSTRACTS of current literature on the platinum metals and their alloys

PROPERTIES

A New Approach for Atomistic Modeling of Pd/Cu(110) Surface Alloy Formation


The formation of Pd/Cu(110) surface alloys was investigated using the Bozzolo-Ferrante-Smith method for alloys. A straightforward modelling approach was introduced, ranging from the deposition of one single-Pd atom to the formation of Pd/Cu surface alloy. The approach gave information on the exchange mechanism between adatoms and substrate atoms, the formation of Pd-Cu chains and the formation of Cu islands.

Deuterium Solubility and Electrical Resistance of Palladium-Rhodium Alloys


Pd-5.0 and 10.0 at.% Rh alloys were investigated at different temperatures by a gas phase method. A decrease in low pressure D solubilities and increase in plateau pressures with increasing Rh content were observed. The miscibility gap decreased with increasing Rh content. Higher D solubility was attained for lower Rh content alloy at the maximum exerting pressure. The α_{max} resistance values gradually decreased with increasing Rh content and increased with increasing temperature.

Preparation of Pd Cluster/Polymer Composites Using Bis(acetylacetonato)palladium(II) Vapor


Pd cluster/polymer composites (I) were prepared using bis(acetylacetonato)Pd(II) vapor. (1) with Pd concentrations > 20% or in which the Pd clusters are locally distributed were achievable. Nylon 6 and poly(ethylene terephthalate) were applicable to the preparation of (1). Composites containing Pt clusters were also obtained using the Pt acetylacetonate.

Low Temperature Specific Heat of CeRu4Si4 at the Field Induced Metamagnetic Instability


Specific heat measurements are reported at 0.06–20 K on CeRu4Si4 in magnetic fields applied parallel to the c-direction around the critical field B_{c1}, where the metamagnetic transition from the itinerant to the localised state takes place. In the critical field B_{c1} = 7.8 T a distinct deviation from the usual Fermi-liquid behaviour was found down to the lowest temperature. Below 1.8 K C/T = (1 – aT), while for 1.8 K < T < 20 K a power law T^(-\lambda) with \lambda = 0.66 was found.

CHEMICAL COMPOUNDS

A Novel N-Heterocyclic Carbene of Platinum(II):

Synthesis in Ionic Liquids and Crystal Structure


cis-(C_4H_4)(1-Ethyl-3-methylimidazol-2-ylidene)PtCl_2 was obtained by reacting a mixture of PtCl_2 and PtCl_4 with C_4H_4 (50 atm) in the basic [EMIM][AlCl_4] (1:3:1) ionic liquid ([EMIM]^+ = 1-ethyl-3-methylimidazolium) at 200°C. PtCl_2 assists the reaction by enhancing the formation of PtCl_4^2-.

Cationic Unsymmetrical 1,4-Diazabutadiene Complexes of Platinum(II)

P. J. ALBIEZ, K. YANG, R. J. LACHICOTTE and R. EISENBERG, Organometallics, 2000, 19, (19), 3543–3555

Glyoxal-bis((2-α-trisopropylsiloxymethyl)-6-methylphenyl)diimine (TIPS-6-MPD) (1) and glyoxal-bis((2-α-trisopropylsiloxymethyl)-4-methylphenyl)diimine (TIPS-4-MPD) (2) were reacted with trans-Pr(SMe_2)(Me)Cl to give (TIPS-6-MPD)Pt(Me)Cl (3) and (TIPS-4-MPD)Pt(Me)Cl (4), respectively. Cationic complexes [(N,N-chelate)Pt(Me)(L)]BF_4 (L = solvent/olefin; N,N-chelate = (1) and (2)) were generated by reaction of (3) and (4) with AgBF_4 in L.

Hydrogen Bonding in Transition Metal Complexes: Synthesis, Dynamics, and Reactivity of Platinum Hydride Bifluoride Complexes


trans-[Pt(PR_2)_2]HFHF] (R = Cy, Pt) (HFHF = bifluoride) complexes (1) were synthesised by the reaction of the corresponding trans-dihydride complex (2) with NMe_2(3)(HF) in THF. (1) were also formed in C-F activation reactions of (2) with CF_3 in the presence of MeCN. The NMR and IR spectra show that the bifluoride ligand (3) involves a H bond Pt-C–H–F. (3) is easily replaced by anionic ligands such as OTf- or neutral ligands such as PPh_3 or py.

The Preparation of the First Examples of Sulfinylimine Complexes of Platinum; the X-Ray Crystal Structure of [Pt(PPh_3)SnH_2]Cl_2


Solutions of PPh_3SnH (1) and [PtCl_2(PMe_2Pb)] exhibited an equilibrium between the starting materials and cis-[PtCl_2(PMe_2Pb)](PMe_2Pb)Cl. The addition of [NH_3][BF_4] gave cis-[PtCl_2(PMe_2Pb)](PMe_2Pb)BF_4. Four equiv. of (1) reacted with [PPh_3][PtCl_4] over a week to give crystalline [Pt(PPh_3)SnH_2]Cl_2 which has square planar geometry with significant H-bonding interactions between the cation and the chlorides.

PHOTOCONVERSION

Characterization by Resonance Raman Spectroscopy of Sol–Gel TiO2 Films Sensitized by the Ru(PPh3)2(decbipy)Cl2 Complex for Solar Cells

Application


Ru(PPh3)2(decbipy)Cl2 (1) (decbipy = 2,2’-bipyridyl-4,4’-dicarboxylate) was tested as a TiO2 sensitizer in a wet regenerative photoelectrochemical cell. Very intense Raman bands due to PPh3 and decbipy were observed for (1) on TiO2, when characterised by Raman spectroscopy. Altering the potential applied to the TiO2 electrode for a given laser excitation energy can selectively enhance the PPh3 vibrational modes. A reversible shift of decbipy Raman lines was observed.

ELECTRODEPOSITION AND SURFACE COATINGS

Catalytic Activity of Sputtered Palladium Films for Electroless Nickel Plating Studied Using a Quartz Crystal Microbalance


The catalytic activity of Pd film (1) sputtered on a quartz resonator was studied using a Ni plating bath and a quartz crystal microbalance. The adhesive interface between (1) and the quartz surface influenced activity. A Cr underlayer (2) suppressed the catalytic activity of (1), but a Au underlayer (3) did not. (1) sputtered on (3) is usable as an active anode for monitoring electroless plating. The catalytic activity of (1) on (2) was enhanced by cathodic treatment in HCl.

Electrosynthesis and Characterisation of Nanostructured Palladium–Polypyrrole Composites


Electroactive Pd-polypyrrole composite thin films were obtained using three different bottom-up procedures. The procedures all comprised electrochemical synthesis of Pd nanoparticles which are subsequently potentiostatically deposited or embedded into electrochemically grown polypyrrole thin film. The metallic Pd inclusions have a mean diameter of ~5 nm with a homogeneous size distribution.

APPARATUS AND TECHNIQUE

Organoplatinum Crystals for Gas-Triggered Switches


Non-porous crystalline materials consisting of [PtCl(NCN-OH)] (NCN-OH = C6H2(CH3NM3)2-2,6-OH-4) (1) undergo a controlled and fully reversible crystalline-state reaction with gaseous SO2. (1) dramatically changes colour from colourless to deep orange due to the formation of the corresponding adduct [PtCl(NCN-OH)(SO2)]. Similarly, the reverse reaction in a SO2-free environment leads to the complete regeneration of (1). (1) has potential for gas storage devices and optoelectronic switches.

A Fiber-Optic Evanescent-Wave Hydrogen Sensor Using Palladium-Supported Tungsten Oxide


Pt or Pd supported on WO3 were used as H2 sensing media in an optical-fibre H2 sensor (1). Two types of clad fibre were fabricated: (a) Pd/WO3 containing silicone resin as the clad and (b) a sol-gel Pt/WO3 or Pd/WO3 thin clad. In the presence of H2, strong evanescent wave absorption was observed as a result of W bronze formation. (1) formed from (b) gave improved response time compared to (a). The properties of (1) are controlled by the amount of catalyst.

Lifetime-Based pH Sensor System Based on a Polymer-Supported Ruthenium(II) Complex


A luminescence pH sensor system is based on [Ru(phen)2(DCBpy)]+ dye (DCBpy = 4,4’-dicarboxy-2,2’-bipyridine) immobilised in a mixed domain network copolymer utilising hydrophobic regions in a hydrophilic, H2O-swallowable, poly(ethylene oxide) (PEO) matrix. The Ru dye is modulated reversibly to the hydrophobic domains leaving pH-sensing COOH groups projecting into a H2O-rich PEO region. The lifetime of the immobilised Ru dye has increased 3–4 fold. The sensor provides a usable pH range of ~3–5.

Sol–Gel Immobilised Ruthenium(II) Polymeric Complexes as Chemical Transducers for Optical pH Sensing


Protonable Ru(II) polymeric complexes (1) have been evaluated for use as the chemical transducer component in optical pH sensor devices. The immobilisation of (1) in a microporous sol–gel glass matrix resulted in a similar modulation of fluorescence emission with changing pH as is shown by (1) in solution. The matrix provided a highly stable support that widened the working pH sensitive range to pH 3–9 with only minimal sensitivity to O2.
HETEROGENEOUS CATALYSIS
Effects of the Radial Distribution of Platinum in Spherical Alumina Catalysts on the Oxidation of CO in Air
Pt/Al2O3 catalysts with a shell (1) and a homogeneous distribution (2) of Pt were prepared. Co-impregnation of chloroplatinic acid (3) and citric acid was used to prepare (2), resulting in a lower Pt dispersion than the traditional impregnation method with (3) which was used to prepare (1). Compared to (1), the conversion of CO started at lower temperatures when using (2), but higher temperatures were needed for total conversion.

The Role of Pt/SiO2 in the Catalytic Denitration by HCO2H in HNO2 Concentrated Media
Pt/SiO2 catalysts (1) are used together with HCO2H in chemical denitration to reduce nuclear tures when

Y. S. CUENAIS-LANGMIS, C. BOUYER, J.-C. BROUDIC and B. COQ, The Role of Pt/SiO2 in the Catalytic Denitration by B. ANDERSSON, CO in Air

Spherical Alumina Catalysts on the Oxidation of HC02H in chemical denitration to reduce nuclear tures when

B. ANDERSSON, HETEROGENEOUS CATALYSIS
New Highly Active Chiral Phosphapalladacycle Catalysts. First Isolation and Characterization of a Pd(IV) Intermediate
A new active Pt-chiral phosphapalladacycle (1) was synthesised from the chiral s-tolylidiazaphospholidine ligand and Pd(OAc)2 in refluxing toluene. (1) was successfully used in the asymmetric hydroarylation of norbornene at 120°C in DMSO, with turnover numbers ≤ 105. An intermediate Pd(IV) complex was fully characterised by X-ray structure analysis.

Wacker Reaction in Supercritical Carbon Dioxide
The Wacker reaction of alkenes such as oct-1-ene, styrene and cyclohexene was carried out smoothly in sc-CO2 or ROH/sc-CO2 (R = Me, Et). PdCl2 and CuCl2 were the catalysts with O2 as oxidant. Both sc-CO2 and co-solvent affect the selectivity towards methyl ketone and the presence of ROH accelerates the reaction. The presence of a small amount of H2O reduces the reaction rate although selectivity is retained. It is suggested that the reaction is homogeneous since Pd and substrates may form organo-Pd complexes in the oxidative process.

Novel Carbon–Carbon Bond Formation through Mizoroki–Heck Type Reaction of Silanols and Organotin Compounds
Aryl- or alkenylsilanols and aryl-Sn compounds react with various olefins in the presence of the stoichiometric amount of Pd(OAc)2 or by a combination of 0.1 molar amount of Pd(OAc)2 and Cu(OAc)2/ LiOAc (molar ratio 3:2) to give aryl- or alkenyl-substituted olefins. Aryl-Sn compounds show reactivity superior to silanols, although the Sn reagents sometimes induce undesirable homocoupling. Arylsilanols and aryl-Sn compounds react with C2H4 to give styrene derivatives without formation of stilbenes.

Palladium-Catalyzed C–C Coupling under Thermomorphic Conditions
Poly(N-isopropylacrylamide) (PNIPAM)-bound phosphine ligands with a Pd(0) catalyst are shown to be efficient catalysts in Heck, Suzuki, and sp–sp2 cross-coupling reactions under thermomorphic conditions. Air-stable tridentate S-C-S-Pd(II) catalysts bound to soluble polymer supports of PNIPAM or poly(ethylene glycol) are also described. The use of a thermomorphic solvent system in conjunction with the selectively soluble polymer support, allowed for facile product isolation and catalyst recycling.
Rhodium-Catalyzed Copolymerization of Norbornadienes and Norbornenes with Carbon Monoxide
Alternate copolymerization of norbornadienes and norbornenes with CO is catalysed by Rh(Cl)(CO)\textsubscript{16} under water gas shift reaction conditions selectively to give the corresponding polyketones in high yields. A possible mechanism based on the structure of the oligomeric products is discussed.

Practical Synthesis of (S)-1-(3-Trifluoromethyl-phenyl)ethanol via Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation
(S)-1-(3-Trifluoromethylphenyl)ethanol was prepared from the corresponding acetophenone by phenyl)ethanol via Ruthenium(II)-Catalyzed Transfer Hydrogenation. This route gives high ee, low catalyst cost, and safe operation. When sec-alcohols were used as the H source, the chiral catalyst (S,J)-N-(arylsulfonyl)-1,2-diphenylethylenediamine. With formic acid as the H source, the chiral catalyst (S,J)-N-p-tosyl-1,2-diphenylethylene-1,2-diamine–Ru was used.

FUEL CELLS
Platinum-Tin Alloy Electrodes for Direct Methanol Fuel Cells
Pt electrodes, modified by partial galvanostatic or potentiostatic Sn electrodeposition, were used as anodes for the catalytic electro-oxidation of MeOH in acid medium. Cyclic voltammetry was used to study MeOH electro-oxidation. From the MeOH peak current densities, Pt-Sn electrodes are claimed to be superior to pure Pt electrodes. Sn also improved the performance of anode stability over repeated cycles.

ELECTRICAL AND ELECTRONIC ENGINEERING
X-Ray Study of Co/Ni and Co/PT/Ni/PT Multilayers
Ultra thin Co/Ni magnetic multilayers, deposited by dual electron beam evaporation, grow with poor interface quality, which destroys the superlattice structure after a few bilayers. However, the quality of the superlattice in Co/PT/Ni/PT magnetic multilayers (1) was substantially better, mostly due to the lower mutual diffusion of Pt and Co, and Pt and Ni. For (1), X-ray reflectivity measurements yielded information on thickness and interface roughness of individual layers. These were compared with thickness and interface roughness obtained from XRD.

PdGe-Based Ohmic Contact on n-GaAs with Highly and Poorly Doped Layers
The ohmic contact formation mechanism for a low contact resistance PdGe-based system on GaAs containing highly and poorly doped layers annealed at 380–450°C is reported. The lowest average specific contact resistance of the Pd/Ge/Ti/Pt ohmic contact was $2.4 \times 10^{-4} \Omega \text{cm}^2$ after annealing at 400°C.

Investigation of the Electrical Properties of Tantalum-Ruthenium Dioxide as a Diffusion Barrier for High Dielectric Capacitors
The effects of RuO\textsubscript{2} addition on the electrical properties of the Ta-RuO\textsubscript{2} diffusion barriers of capacitor bottom electrodes as a function of the Ta/RuO\textsubscript{2} ratio and contact size, at 650–800°C in air, were studied. For both the Ta + RuO\textsubscript{2}/n\textsuperscript{++}-poly-SiSiO\textsubscript{2}/Si and the Pt/Ta + RuO\textsubscript{2}/n\textsuperscript{+}-poly-SiSiO\textsubscript{2}/Si contact systems, a conductive RuO\textsubscript{2} crystalline phase was formed after annealing. Surface oxidation of the diffusion barrier was prevented and the bottom electrode structure was retained at $< 800°C$.

MEDICAL USES
The antitumour properties of [(tir-Pt(NH\textsubscript{3})\textsubscript{2})(\mu-OH)(\mu-1,2,3-ta)][NO\textsubscript{3}]/2, [(Pt(R,R-dach)(\mu-OH))(\mu-pz){Pt(S,S'-dach)}][NO\textsubscript{3}], (2) and [(Pt(R,R-dach)) (\mu-1,2,3-ta){Pt(S,S'-dach)}][NO\textsubscript{3}]/2, (3) were tested after preparation. (1) and the parent compound [(tir-Pt(NH\textsubscript{3})\textsubscript{2})(\mu-OH)(\mu-pz)][NO\textsubscript{3}]/2 showed higher cytotoxicity than cisplatin, while (2) was shown to be moderately active and (3) was only marginally cytotoxic.

Synthesis, Spectroscopic, Electrochemical and Antibacterial Studies of New Ru(II) 1,10-Phenanthroline Complexes Containing Aryldiazopentane-2,4-dione as Co-ligand
Mono- and dinuclear Ru(II) complexes of 1,10-phenanthroline containing aryldiazopentane-2,4-diones as co-ligands were prepared. Complexes having 1,10-phenanthroline as terminal ligand showed better bacterial inhibition than those bearing 2,2'-bipyridine as terminal ligand. The 1,10-phenanthroline system already bound with DNA showed poorer activity than the unbound system.
NEW PATENTS

**ELECTROCHEMISTRY**

**Manufacturing Active-Hydrogen Water**

*Sun Eng. K.K.*  
*Japanese Appl. 2000/192,272*

A method to manufacture active-hydrogen (AH) H₂O uses Pd or a Pd alloy as the cathode for H₂O electrolysis. H₂ (as AH) is occluded into the cathode. The cathode is then put into H₂O containing an alkali electrolyte. This releases the AH in the Pd which attaches to the alkali ions. The AH-alkali-ion H₂O obtained is stable and can be preserved for long periods by freezing. As the AH has high reactivity it may be used as a H source in liquid phase hydrogenation.

**Cathode for Electrolysis**

*Permelec Electrode Ltd.*  
*German Appl. 1/00/06,449*

A cathode (1) for electrolysis of a H-containing material consists of a first layer of Pd or Pd alloy (2) deposited on the reaction chamber side of a membrane and a second layer of Pt black or Pt-Au porous catalyst deposited on (2). An electrolysis cell is divided by (1) into a reaction chamber and an electrolysis chamber, and is used for reduction or hydration of a reactant in the reaction chamber. (1) also contains an ion exchange membrane or a porous membrane.

**ELECTRODEPOSITION AND SURFACE COATINGS**

**Improving Performance of Electroplating Bath**

*SPECIALTY CHEM. SYSTEMS INC.*  
*World Appl. 00/56,952*

The plating performance of aqueous sulfate (1), sulfonic acid, fluoroborate and halide electroplating baths is improved by the addition of an alloy and/or alkanol sulfonic salt. (1) comprises: a source of sulfate ions; soluble Rh, Ru, Sn, Ni, Cu, Cr, Cd, Fe, Zn, Pb and/or In metal salts; and a salt of an alkyl and/or alkanol sulfonic acid. The additives give a wider range of useful current densities and improved appearance.

**Metal Component for Turbine Blade**

*Ishikawajima Harima Heavy Ind.*  
*Japanese Appl. 2000/178,763*

A metal component for a turbine blade used in a gas turbine engine of an aircraft, has an antioxidant film (1) comprising an upper Al coating layer, an intermediate Ir layer and a lower Pt layer formed on the surface of a base material. (1) has improved strength and oxidation resistant ability.

**Electroless Rhodium Plating of Ceramics and Metals**

*Robert Bosch G.m.b.h.*  
*German Appl. 1/99/09,678*

A Rh plating bath comprises H₂O and a readily H₂O-soluble Rh compound selected from ammonium Rh(III) di(pyridine-2,6-dicarboxylate), Rh amine complexes: RhClₓ(NH₃)ₙ × where x = 0–3, Rh acetate and Rh chloride triethylenetetramine or diethylenetri-amine complexes. Rh precipitation is minimal, so plating efficiencies of ≥ 90% can be obtained.

**APPARATUS AND TECHNIQUE**

**Tunable Optic Filter for Filtering Light**

*MCNC*  
*World Appl. 00/45,202*

A tunable optic filter (1), for filtering UV light in windows, comprises sets of alternating layers of dielectric material with different refractive indexes separated by an intermediate layer (2), of PLZT, PZT, BaTiO₃, etc., the refractive index of which changes with the intensity of an applied electric field. Two further electrically conductive layers: of ITO, SnO₂, In₂O₃, ZnO and RuO₂, provide an electric field across (2). (1) has faster reaction time, requires no motor-driven mechanism to tune it, and is adaptable to different shapes without any energy increase.

**Detection of Methyl Methacrylate**

*Opi Prod. Inc.*  
*U.S. Patent 6,100,097*

Methyl methacrylate (1) is identified quickly from other methacrylates in a liquid monomer by the formation of a blue coloured methacrylate-Pd molybdate complex after Pd molybdate is added to the monomer, followed by other treatment. (1) is detected in the liquid part of liquid/powder systems used for forming artificial nails.

**Limiting-Current Type Oxygen Sensor**

*Hitachi Chem. Co. Ltd.*  
*Japanese Appl. 2000/146,904*

A limiting-current type O₂ sensor (1) comprises a solid electrolyte adhered to an inner wall of a ceramic columnar body by heat resistant material. The surface is permeable to air. Electrodes are formed on either side of the electrolyte. A Pt wire is fixed to the electrolyte. (1) is used in gas supply apparatus. It has excellent heat resistance, is dependable and can withstand heat shock. It can also be mass produced.

**Filter for Removal of Tobacco Odour**

*Kobe Steel Ltd.*  
*Japanese Appl. 2000/210,373*

A deodorant placed in a deodorising filter, for efficient removal of tobacco odour, has a porous support containing 0.1–10 wt.% Pd and Cl with Pd:Cl molar ratio ≥ 2.5. The deodorant can also efficiently remove chemical agents such as alkali and acid and other odorous components.

**Spin Valve Magnetoresistive Sensor**

*Ridaiito Smi K.K.*  
*Japanese Appls. 2000/251,225–256*

A spin valve type magnetoresistive sensor (1) for a magnetic recording device, includes an antiferromagnetic alloy layer containing either (in at.%): 45–55 Cr, 2–10 Mn and remainder Pt; or (in wt.%): 2–10 Pd, 45–55 Mn, 20–35 Cr and remainder Pt. The alloy layer is heat treated at 250–300°C. (1) suppresses rotation of the thin magnetic layer by the bias magnetic field of the magnetic head, hence improving the thermal magnetic stability. A high magnetoresistive variation rate and high linear response result in a high recording density and a reliable magnetic head.
HETEROGENEOUS CATALYSIS

Hydrogenation of Epoxidised Cyclohydrocarbons

UBE IND. LTD.  European Appl. 1,018,498

Epoxidised 6C–12C cyclohydrocarbons are efficiently hydrogenated in a single-step process by contacting the hydrocarbons with H₂ at a pressure of 0.1–5.4 MPa and a temperature of 100–280°C in the presence of Ru, Rh, Pd, Os, Ir and/or Pt catalysts supported on activated C, Al₂O₃, SiO₂, SiO₂-Al₂O₃, TiO₂, zeolites and spinel. Total yields of cycloalkane and cycloalkanol of 93% were obtained. These are intermediates for the production of lactams, lactones, etc., for use in synthetic resins and fibres.

Hydrodesulfurisation-Isomerisation Catalyst

COSMO OIL CO. LTD.  World Appl. 00/35,581

A catalyst for simultaneous hydrodesulfurisation and isomerisation of light hydrocarbons comprises a support of Zr oxide or Zr hydroxide and a sulfate radical, impregnated with (in mass%) either: 0.05–10 Pd; 0.05–10 Pd and 0.05–10 Pt; or 0.05–10 Ni. After heat stabilisation at 550–800°C the specific surface area is 50–150 m² g⁻¹. Manufacture of the catalyst is also claimed. The catalyst has high activity, high S resistance, and reduced running costs.

Production of Alkylhydrogenohalosilanes

RHODIA CHIM.  World Appl. 00/39,132

Alkylhydrogenohalosilanes (1) are produced by the catalytic hydrogenation of alkylsilanes (2) using a bimetallic Ru-Sn catalyst. The process is especially useful for vaporising excess (2), especially Me₂SiCl₃, formed as byproduct during the Rochow-Müller synthesis (direct reaction of metallic Si with CH₃Cl). This reaction gives monomers used to produce silicone resins. Under industrial conditions in the presence of the Ru-Sn catalyst, (2) can be easily converted into (1) with a high degree of specificity.

Steam Reforming Hydrocarbons

IMPERIAL CHEM. IND. PLC.  World Appl. 00/43,121

A catalyst for steam reform hydrocarbons, such as CH₄, naphtha, LPG, etc., and to treat coal gasification gases comprises 0.1–2.5 wt.% Ru and/or Ru oxide, impregnated on a preformed porous carrier with oxides of Ni, La and Al. Hydrocarbon feedstock and/or steam are passed over the cylindrical catalyst heated at 600–850°C. Ru and/or Ru oxide improve resistance to C deposition and give high catalytic activity.

Catalyst for Vinyl Acetate Synthesis

CELANESE CHIM. EURO. G.m.b.H.  World Appl. 00/44,496

A catalyst for gas-phase production of vinyl acetate from ethylene, acetic acid and O₂ contains Pd, Cd and/or their compounds and alkali metal(s) on a moulded porous support. The support is based on pyrogenic SiO₂ and contains Mg. It has a hollow cylindrical configuration with facet edges. Activity and selectivity are increased by using this support, which gives a totally impregnated or shell catalyst.

Removal of Methanol from Off-Gases

GENERAL ELECTRIC CO.  World Appl. 00/47,309

MeOH impurities in off-gases generated during isopropylbenzene oxidation are oxidised to CO₂ and H₂O at low temperature by contacting the off-gases with a Pt/zeolite catalyst. Granulated HZSM-5 zeolite is impregnated with H₂PtCl₆ solution, followed by drying and calcining to decompose the acid to give ≥ 0.1% Pt content. The resulting discharge stream contains MeOH at concentrations of ≤ 20 ppm.

Manufacture of Acetic Acid

SHOWA DENKO K.K.  World Appl. 00/51,725

A catalyst for the manufacture of acetic acid by reacting ethylene and O₂ in the gas phase, comprises Pd metal, Au metal and heteropoly acids and/or their salts on a support. The Pd:Au weight ratio is 1.01–5.0. The manufacture of the catalyst is claimed. Space-time yield, compared to prior art is high, and selectivity to CO₂ is low. Catalyst deterioration is low while acetic acid production is high.

Purification of Gas for High Purity Uses

AIR PROD. & CHEM. INC.  U.S. Patent 6,093,379

Purified gas is produced by removal of CO₂, H₂O, CO and H₂ from a gas stream by adsorbing H₂O and CO₂ on a solid adsorbent, such as Al₂O₃ or zeolite, and oxidising CO to CO₂ over a Pt group metal catalyst on a support which has zpc (zero point charge) of > 8.0. The CO₂ formed is adsorbed, and any H₂ is chemisorbed on the catalyst, such as Pd/Al₂O₃. This method can purify air by removing CO and H₂ before or after cryogenic distillation for generation of N₂ and/or O₂ for electronic and high purity applications. Enhanced efficiency, simple energy-efficient regeneration for continuous use and reduction of costs are obtained.

Fischer-Tropsch Synthesis

ENERGY INT. CORP.  U.S. Patent 6,100,304

Pd-promoted Co/γ-Al₂O₃ catalysts provide significantly enhanced activity for Fischer-Tropsch synthesis in a continuous reaction system, particularly in a slurry bubble column reactor. The catalyst contains (parts by weight): 10–65 Co and 0.25–7 Pd per 100 of γ-Al₂O₃ support. The catalyst is formed by total aqueous co-impregnation so that the Co and Pd form a dispersed catalytic phase and are in intimate contact. The process is rate and cost efficient, has higher selectivity, and is environmentally friendly.

Treating Diesel Engine Exhaust Gases

FORD GLOBAL TECHNOLOGY INC.  U.S. Patent 6,103,207

A catalyst for treating diesel engine exhaust gases contains a mixture of 25–65 wt.% particles of a Mn and Zr bimetallic oxide and a supported Pt group metal, for example 0.25 wt.% Pt/Al₂O₃. The atomic ratio of Mn:Zr is 3:1–1:3. The catalyst reduces NOx in an oxidising atmosphere during diesel engine operation. A wider NOx conversion window in the low temperature region is obtained.
Manufacture of Polyalkylene Glycol 1-Alkenyl Ethers

SHOWA DENKO K.K. Japanese Appl. 2000/143,567

Highly pure polyalkylene glycol 1-alkenyl ethers are manufactured at a high selection rate and in high yield by inhibiting the formation of byproduct. The reaction comprises isomerisation at 30–200°C of a polyalkylene glycol 2-alkenyl ether using at least one type of a catalyst carrying 0.05–10 wt.% of a noble metal(s), such as Pd/carrier. The product ethers are useful as resin materials and reaction diluents.

Production of High Purity Sugar Alcohols

ROQUETTE FRERES S.A. French Appl. 2,789,683

Production of sugar alcohols comprises hydrogenating the corresponding sugar in a series of trickle-flow reactors comprising a first reactor containing a fixed bed of a Ru catalyst and a second reactor containing a fixed bed of a promoted Ru catalyst. The process can convert D-glucose into high purity sorbitol (≥ 98.5% for sorbitol) at high conversions (≥ 99.85%) and with high selectivities (≥ 99%).

Epoxidised Olefin Production

BAYER A.G. German Appl. 1/98/57,137

Epoxidised olefins (1) are produced by reacting olefins with H₂O₂ solution in the presence of a synthetic Ti-containing zeolite, followed by separation of (1) and recycling the H₂O₂ solution. The H₂O₂ solution, which is dilute alcoholic or aqueous-alcoholic, optionally contains a stabiliser and is prepared by continuous reaction of H₂ and O₂ on a Group VIII metal catalyst. The process gives high selectivities (> 85% for propylene oxide) despite using the dilute H₂O₂ solution directly, without any intermediate purification.

Homogeneous Catalysis

Production of Oligocarbonates

BAYER A.G. European Appl. 1,013,634

Oligocarbonates are produced by reacting an aromatic dihydric compound with CO and O₂ in the presence of a Pt metal catalyst, a cocatalyst, a base, an inert organic solvent and, optionally, a quaternary salt. The solvent forms an azeotrope with the H₂O byproduct and is removed from the reaction mixture. The catalytic system has increased activity. The oligocarbonates have low residual H₂O content.

Preparation of Mono- and Di-arylphosphines

CYTEC TECHNOLOGY CORP. World Appl. 00/32,613

Mono- (1) and di-arylphosphines (2) are prepared by reacting an aryl compound with phosphine in the presence of a Group VIII metal catalyst, for example, an adduct of a Pd(II) compound and a triarylphosphine. The aryl compound has a leaving group attached to a C atom of the aromatic ring. The process avoids or alleviates corrosion and can be carried out on a large scale. (1) and (2) are obtained in good yield along with relatively small amounts of tertiary phosphate.

Production of Aldehydes

MITSUBISHI CHEM. CORP. Japanese Appl. 2000/159,719

An aldehyde is produced by reacting an olefinic compound, such as propylene or 1-butene, with H₂ and CO in a solution containing a Rh complex catalyst which has an organophosphite ligand, such as diphenyl-(2,4-diteriarybutylphosphine), at 15–150°C and pressures of atmospheric to 200 kg cm⁻². Ni (1–10³ ppm) is added to the solution to reduce catalyst decomposition and inhibit deactivation, so that the catalyst can be circulated and reused.

Biphenyl Tetracarboxylic Acid Ester

UBE IND. LTD. Japanese Appl. 2000/186,063

Manufacture of 3,3',4,4'-biphenyl tetracarboxylic acid ester involves the dimerisation of p-phthalic acid diester in the presence of sequentially added catalyst (powdered Pd salt of specific surface area ≥ 0.5 m² g⁻¹) and a basic bidentate ligand. The adherence of Pd metal precipitate to the reaction vessel is inhibited.

Preparation of Benzoic Amides

CENTRAL GLASS CO. LTD. Japanese Appl. 2000/191,612

Benzoic amides (1) are prepared in a single step by reacting aromatic compounds, Ar-X (Ar = optionally substituted aromatic group, X = halogen, trifluoromethanesulfonate, 1-4C alkylosulfonate, etc.), CO and NH₃ in the presence of a catalyst of Pd and phosphines. Benzoic acid is produced which is separated from the reaction system. The recovered Pd-phosphine complex is then used as a catalyst. (1) are useful intermediates for pharmaceuticals and agrochemicals.

Production of Alkyl 3-Alkenoates

BASF A.G. German Appl. 1/99/04,200

Alkyl 3-alenoates are produced by adding formates to dienes in the presence of CO (at a partial pressure ≥ 1 MPa) and a catalyst containing a Pd compound and metal chloride(s) MCl₅ (M is an alkaline earth metal when n = 2, or a metal ion of sub-Group IV when n = 4, or a metal ion of sub-Group VI when n = 3, 5 or 6). Organic base containing P or N is not present. The process is more selective and operates at lower pressures than existing processes. It can be carried out without solvent or with the educts as solvent, so HCl acid need not be added.

Fuel Cells

Electrode Structure for Fuel Cells

JOHNSON MATTHEY PLC. World Appl. 00/35,037

A piston-tolerant anode structure, for use in membrane electrode assemblies and PEMFCs, has two catalytic components. The first is Pt-Y, where Y is a bronze forming element, (Ti; V; Nb, Ta, etc.) with an optional third metal X (X = Ru, Rh, Ti, Cr, Mn, Fe, Co, Ni, Cu, Ga, Zr, Hf or Sn, especially Ru, Rh, Mn, Co and Nb). The second catalyst is Pt-M (M = one of the above metals, especially Ru or Rh). The anode has improved tolerance to CO and CO₂ poisons while maintaining high activity.
Catalyst Ink and MEAs for Fuel Cells

A catalyst ink for DMFCs comprises catalytic material, such as Pt or Pt and Ru, and poly(vinylidene fluoride). The catalyst ink improves interfacial bonding characteristics between deposited electrocatalytic layers and the proton conducting moieties of MEA structures. Electrical performance is improved and impedance reduced. MeOH crossover in a fuel cell stack is reduced.

Fuel Cell Catalyst for PAFC and DMFC

A ternary Pt-Ru-Pd catalyst for use in electrochemical reactor devices, especially as fuel cell electrodes, comprises (in at%): 20–60 Pt, 20–60 Ru and 5–45 Pd. The atomic ratio of Pt:Ru is 0.6–1.8. The fuel cells, for instance PAFCs or DMFCs, electrochemically convert a hydrocarbon-based fuel and O₂ to H₂O, CO₂ and electricity. The catalysts give improved fuel cell efficiency while allowing a decrease in the size of the cell and the costs.

Hydrogen Refiner for Fuel Batteries

A H₂ refiner which produces H₂ as a fuel for fuel batteries, comprises a feedzone for a modified gas and a reaction chamber downstream of the feedzone. The reaction chamber contains a catalyst which removes CO from the gas. The CO transforming catalyst is Pt, Ru, Rh and/or Pd. The gas may also contain H₂ and H₂O. The refiner has a shorter startup time and problems caused by O₂ are prevented. The refiner operates stably for longer times.

ELECTRICAL AND ELECTRONIC ENGINEERING

Conductive Barrier Layers in Electronic Capacitors

A temperature stable conductive barrier layer, for IC ferroelectric capacitors used in FRAMs, comprises a first barrier layer containing Ta on a substrate, with a film of Ir or Ir-Ta-O. The film of Ir-Ta-O remains conductive after annealing at high temperature in an O₂ ambient atmosphere. Adhesion, conductance, hillock and peeling problems are minimised, as the Ir does not interact with the substrate.

Integrated Circuits

An integrated circuit for non-ferroelectric or ferroelectric devices with high dielectric constant has a diffusion barrier layer of Ir oxide which is located between a thin film of layered superlattice material and a local interconnect. The Ir oxide inhibits diffusion of chemical species from the local interconnect to (1) and is thus effective for preventing diffusion of metals, Si, and other chemical species.

Horizontal Magnetic Recording Medium

A horizontal magnetic recording medium (1) has a magnetic layer of granular film with grains of chemically ordered FePt or FePtX alloy (or CoPt or CoPtX) (X = Cr, Cu, Ag, Ta, etc.). It also has an etched seed layer of nonmagnetic Pt, Pd, Cr, CrV, etc., on a substrate. The magnetic properties are controlled by grain size and distribution, degree of chemical ordering, and the nonmagnetic materials. (1) has low-noise, high density and the high magnetic stability.

Ferroelectric-Based Capacitor

A ferroelectric-based capacitor used in memory systems has: a bottom electrode consisting of a Pt layer in contact with a layer of ohmic material; a dielectric of Pb-Zr titanate doped with an element having an oxidation state > +4; and a top electrode consisting of a second ohmic material layer in contact with a second Pt layer. The capacitor exhibits low fatigue, low imprint and is used in memory systems.

Production of Printed Circuit

Circuit board is produced by forming a thin film of a polysilane (1), containing a C functional silane, on a substrate and contacting it with a Pd salt to form a colloidal Pd layer. A photosensitive resin layer is light to form a patterned groove. An electroless plating solution is applied to form a conductive metal layer in the groove. The circuit substrate has superior heat resistance and fineness of pattern.

Semiconductor Devices such as FRAM

A reliable semiconductor device, such as FRAM, with good fatigue resistant characteristics contains an electrode which carries a metal oxide (Pt, Ir, Ru, Ni, Ti, Zr and Ce) film on which a metal film is formed. A ferroelectric film (1) is formed on the electrode and on this is formed an electrode containing a perovskite. By repeated polarisation inversion, O vacancies in (1) are supplemented by O from the perovskite film. Capacitors which operate at low voltage can use the material.

Circuit Electrode of Laminate Structure

A laminated electrode structure for use on a printed circuit board has a Pd corrosion-resistant film over a Ni plated film formed on the circuit pattern of the substrate. A Au film is formed on the Pd film surface. Contact adherence strength between each film layer in the laminate is improved as it is surface flatness. Bonding and ball shear strength are also increased.