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Editorial

Johnson Matthey and Advanced Functional Materials

Readers of this journal and its predecessor title, *Platinum Metals Review*, will be well aware of Johnson Matthey’s long-standing expertise in platinum group metals (pgms) science and technology. The company has been active in this area for most of its long history, starting in 1817. Fast forward to the 21st century and many of Johnson Matthey’s products and research and development (R&D) activities revolve around the development and applications of a range of advanced materials, not just pgm. These materials take many forms, from powdered or coated catalysts and coated components to fully functional devices.

The design of functional materials requires deep understanding of the science. As well as its knowledge of pgm chemistry, Johnson Matthey has over the years gained much experience in surface science and it is these together with other specialised expertise that allows new products to be designed, optimised, characterised and scaled up to solve real-life problems. Some 89% of Johnson Matthey’s sales are currently from products with sustainability benefits (1).

This issue of the *Johnson Matthey Technology Review* deals with the theme of Advanced Functional Materials with a particular focus on zeolites and nanoparticles. These two classes of materials can be applied in a range of areas from process catalysis and emissions control to environmental clean-up.

Insights into nanoparticle synthesis and assembly are provided in a conference review (2), while another conference review discusses the role of materials chemistry in establishing connections between structure, properties, processability and performance of molecular materials, with emphasis on the contribution of pgms in areas such as artificial photosynthesis and the possible generation of a fuel via the photochemical dissociation of water (3). These particles, which are usually titania or zinc oxide coated with a noble metal, are also the subject of an extensive review on their preparation by spray pyrolysis processes (4).

As was promised in a previous Editorial (5) we also present Professor Edward Rosenberg’s critical review of the use of ion exchange and sorption methods for the remediation of uranium in industrial and surface waters (6), an essential read for anyone involved in this area. Zeolites exist in a variety of forms (7) and they may be used in a wide variety of applications including biomass conversion, catalysis for industrial and fine chemicals, photocatalysis and electrocatalysis. Two of Johnson Matthey’s scientists review a recent event from the point of view of vehicle emissions control where zeolite based catalysis sees significant applications (8). The vital significance of characterisation techniques in the development of new functional materials is also highlighted in another conference review (9).

In the Archive

Zeolites have long been used in catalysis and emissions control. Previous papers in this journal have included conference reviews (10, 11) and articles (12). Zeolites loaded with pgms have also made an appearance (13, 14). Just some of Johnson Matthey’s innovations involving zeolites have included programmes aimed at creating new applications via collaborations with academic groups (15), a product for preserving the freshness of fruits, vegetables and flowers which is now in commercial production under the brand name (and company) It’s Fresh! (16) and also work has been carried out into alternatives to zeolites, for example involving a novel preparation of pgm on carbon (17).

Flame technology is a scalable, continuous and well-established method for production of nanoparticles in large quantities, and Johnson Matthey’s development-scale Flame Spray Pyrolysis Facility, housed at the company’s main UK technology centre, offers a unique facility for the production of a wide array of nanopowders from single metal oxides such as alumina to more complex mixed oxides, metals and...
catalysts. The technique was first developed by the research group of Sotiris E. Pratsinis at ETH Zurich, Switzerland (18). Applications of materials prepared by this technique include catalysis, sensors, biomaterials and microelectronics (19). The photocatalytic activities of titanium dioxide (TiO₂) nanoparticles have also been investigated (20).

It is to be hoped that the continuing efforts of many research groups around the world will advance the knowledge and understanding of functional materials such as those discussed here, and develop their application towards a sustainable future.

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References

The First Year of the Johnson Matthey Technology Review

Thanks to the high quality of submissions to the journal it has been a successful first full year of publication for the renamed journal, Johnson Matthey Technology Review. The top two cited articles of 2015 so far are reviews on the subjects of platinum investment casting (21) and lithium-ion battery anodes (22).

The last full Impact Factor for the predecessor title, Platinum Metals Review, was announced in mid-2015 and was a respectable 1.924 (2014). The year 2016 will see the announcement of that title’s last partial Impact Factor plus the first partial Impact Factor of the Johnson Matthey Technology Review. The first full Impact Factor for the new journal, covering data for its first two full years of publication to 2016, will be expected in mid-2017. These numbers will be reported via our website in due course.

Coverage in various library, database and indexing services is progressing. The journal was accepted into Thomson Reuters’ Science Citation Index, the basis for the annual Impact Factor, in mid-2014. The assessment by Elsevier’s Scopus database is complete and the journal is due to be listed by February 2016.

As always we welcome enquiries or submissions of articles, features and reviews in any of the topics listed in our Editorial Policy. If in doubt contact the Editorial Team for further information.
Selected Electrical Resistivity Values for the Platinum Group of Metals Part II: Rhodium and Iridium

Improved values obtained for liquid phases of rhodium and iridium

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Electrical resistivity values for both the solid and liquid phases of the platinum group metals (pgms) rhodium and iridium are evaluated. In particular improved values are obtained for the liquid phases of these metals.

1. Introduction

A previous review on electrical resistivity was given in Part I for palladium and platinum (1).

The elements rhodium and iridium are both superconducting with transition temperatures of 325 μK for rhodium (2) and 0.1125 ± 0.001 K for iridium (3). Both metals have a face-centred cubic structure and their melting point are secondary fixed points on the International Temperature Scale of 1990 (ITS-90) at 2236 ± 3 K and 2719 ± 6 K respectively (4).

2. Rhodium

2.1 Solid

As given in Table I the measurement of Powell and Tye (5) is assumed to be superseded by the later measurements of Powell et al. (8, 9) and the measurement of White and Woods (6) by the later measurement of White and Woods (7). The measurement of Powell et al. (8) is not considered to be superseded by the later measurements of Powell et al. (9) since it is at a specific temperature whereas the later measurements are obtained from an interpolation. The selected value is an average of the last four determinations.

Values up to 273.15 K are based on the measurements of White and Woods (7) (20–295 K) after correction to the selected value at 273.15 K using the ratio 4.35/4.36. At 100 K and above the data was fitted to Equation (i) which has an overall accuracy as a standard deviation of ±0.02 μΩ cm.

The measurements of White and Woods (7) are considered to exceed their earlier measurements (6) (15–295 K). Measurements of Powell and Tye (5) (86–282 K) vary from initially 2.5% high to 4.3% high at 97 K and 1.3% low at 214 K then converge towards the selected values whilst those of Kemp et al. (10) (4.2–292 K) above 50 K can be considered as trending from 2.6% high to 7.1% high. After correction for residual resistivity the value of Natarajan and Chari (11) at 4 K and 0.014 μΩ cm is notably higher than the value obtained by White and Woods (7) at 0.0018 μΩ cm at 20 K.

In the high temperature region the combined measurements of Sorokin et al. (12) (1250–2050 K) and of Filippov and Yurchak (13, 14) (1300–2000 K) showed a distinct change in slope at 1750 K...
allowing a linear extrapolation to the melting point of 53.8 \( \mu \Omega \) cm which is notably lower than the value of 60.7 \( \mu \Omega \) cm determined by Hüpf et al. (15) (1950–2236 K in the solid region). The measurements of Milošević (16) (300–2200 K) are intermediate extrapolating to a value of 57.4 \( \mu \Omega \) cm at the melting point. The values of Milošević compared to those of Sorokin et al. and Filippov and Yurchak trend from initially 5.3% low at 1250 K to 4.0% low at 1700 K and then to 5.5% low at 2050 K. The measurements of Hüpf et al. trend from 3.6% high to 5.6% high. Measurements of Jain et al. (17) (1180–1573 K) trend from 0.9% lower to 8.9% higher than the measurements of Milošević.

Because of these large discrepancies and in order to obtain a consistent set of values for solid rhodium it is noted for the cubic pgms that at the melting points the ratio of the resistivities of the liquid phase \((\rho_l)\) and of the solid phase \((\rho_s)\) can be considered in terms of the entropy of fusion \((\Delta S_M)\) by using a modified version of the Mott equation (18): \(\ln \left(\frac{\rho_l}{\rho_s}\right) = A \Delta S_M + B\) where \(A\) and \(B\) are constants. Using selected values of \(\rho_l/\rho_s\) of 1.738 for palladium (1), 1.610 for platinum (1) and 1.391 for iridium (see below) and values of \(\Delta S_M\) of 8.80 J mol\(^{-1}\) K\(^{-1}\) for palladium (19), 10.83 J mol\(^{-1}\) K\(^{-1}\) for platinum (20) and 15.20 J mol\(^{-1}\) K\(^{-1}\) for iridium (21) leads to the equation \(\ln \left(\frac{\rho_l}{\rho_s}\right) = 0.85387 - 3.4535 \times 10^{-2} \Delta S_M\) with the degree of correlation indicated by the fact that the standard deviation was only \(\pm 0.008\). Substituting in the entropy value of \(\Delta S_M = 12.21\) J mol\(^{-1}\) K\(^{-1}\) for rhodium (22) then \(\rho_l/\rho_s = 1.541\) and based on the selected value of \(\rho_l = 89.2 \mu \Omega\) cm then \(\rho_s = 57.9 \mu \Omega\) cm which is very close to the extrapolated experimental value of Milošević which is therefore selected after taking into account possible systematic errors in the entropies of fusion and the liquid electrical resistivity measurements. However although the measurements of Milošević were given preference it is noted that the equation given by Milošević extrapolates to a value at 273.15 K which is 13% higher than the selected value and in order to achieve compatibility only the measurements of Milošević at 1000 K and above could be considered. However these were used to produce Equation (ii) which is assumed to represent the electrical resistivity from 273.15 K to the melting point. The measurements of Binkele and Brunen (23) (273–1373 K) gave a value at 273.15 K which was 6.0% higher than the selected value and therefore these measurements could not be considered below 700 K but above this temperature bias only 0.5% low which, based on very large differences between the various sets of other measurements, is considered as confirming the selection procedure. Therefore above 100 K Equations (i) and (ii) were used to generate the selected values for the solid in Table II where values at 600 K and above were given to four significant figures only for interpolation purposes. Three sets of measurements of resistivity ratios were corrected for thermal expansion using values selected by the present author (24) and then values above 273.15 K were compared with the selected curve (Figure 1). The measurements of Holborn (25) (81–773 K) were given as \(R_T/R_{273.15 K}\) and on this basis trended to 4.0% low at 773 K. Mimeault and Hansen (26) (100–700 K) gave measurements as the ratio \(R_T/R_{295}\) and after correcting to \(R_T/R_{273.15 K}\) trended to 12.5% low whilst the measurements of García and Löfler (27) (295–1000 K) which were also corrected from \(R_T/R_{295}\) to \(R_T/R_{273.15 K}\) trended to 13.5% low.

For comparison purposes as given in Figure 2 the resistivity ratios are reconsidered as being electrical resistivity values. At the melting point the measurement of Savvatimskii (28) is 6.2% high and that of Martynyuk and Tsapkov (29) is 2.7% high. The electrical resistivity measurements of Glazkov (30) (800–2000 K) are given

<table>
<thead>
<tr>
<th>Authors</th>
<th>Ref.</th>
<th>(\rho_p) (\mu\Omega) cm</th>
<th>Temperature of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powell and Tye</td>
<td>5</td>
<td>4.34</td>
<td>Interpolated 213.8–281.6 K</td>
</tr>
<tr>
<td>White and Woods</td>
<td>6</td>
<td>4.38</td>
<td>At 273.15 K</td>
</tr>
<tr>
<td>White and Woods</td>
<td>7</td>
<td>4.36</td>
<td>At 273.15 K</td>
</tr>
<tr>
<td>Powell et al.</td>
<td>8</td>
<td>4.31</td>
<td>At 273.15 K. Corrected for (\rho_0 0.024 \mu\Omega) cm</td>
</tr>
<tr>
<td>Powell et al.</td>
<td>9</td>
<td>4.33, 4.38</td>
<td>First sample. Interpolated 200–400 K. Corrected for (\rho_0 0.024 \mu\Omega) cm</td>
</tr>
</tbody>
</table>

Selected \(4.35 \pm 0.04\) \(\mu\Omega\) cm at 273.15 K
Table II Intrinsic Electrical Resistivity of Rhodium

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<thead>
<tr>
<th>Temperature, K</th>
<th>$\rho_i$, $\mu\Omega$ cm</th>
<th>Temperature, K</th>
<th>$\rho_i$, $\mu\Omega$ cm</th>
<th>Temperature, K</th>
<th>$\rho_i$, $\mu\Omega$ cm</th>
</tr>
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<td>Solid</td>
<td></td>
<td>Solid</td>
<td></td>
<td>Solid</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.0018</td>
<td>180</td>
<td>2.52</td>
<td>700</td>
<td>13.74</td>
</tr>
<tr>
<td>25</td>
<td>0.0049</td>
<td>190</td>
<td>2.72</td>
<td>800</td>
<td>16.22</td>
</tr>
<tr>
<td>30</td>
<td>0.011</td>
<td>200</td>
<td>2.92</td>
<td>900</td>
<td>18.77</td>
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<tr>
<td>40</td>
<td>0.043</td>
<td>210</td>
<td>3.12</td>
<td>1000</td>
<td>21.39</td>
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<tr>
<td>50</td>
<td>0.10</td>
<td>220</td>
<td>3.32</td>
<td>1100</td>
<td>24.08</td>
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<tr>
<td>60</td>
<td>0.20</td>
<td>230</td>
<td>3.51</td>
<td>1200</td>
<td>26.81</td>
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<tr>
<td>70</td>
<td>0.34</td>
<td>240</td>
<td>3.71</td>
<td>1300</td>
<td>29.59</td>
</tr>
<tr>
<td>80</td>
<td>0.51</td>
<td>250</td>
<td>3.90</td>
<td>1400</td>
<td>32.41</td>
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<tr>
<td>90</td>
<td>0.69</td>
<td>260</td>
<td>4.10</td>
<td>1500</td>
<td>35.27</td>
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<tr>
<td>100</td>
<td>0.88</td>
<td>270</td>
<td>4.29</td>
<td>1600</td>
<td>38.17</td>
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<tr>
<td>110</td>
<td>1.09</td>
<td>273.15</td>
<td>4.35</td>
<td>1700</td>
<td>41.10</td>
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<tr>
<td>120</td>
<td>1.30</td>
<td>280</td>
<td>4.48</td>
<td>1800</td>
<td>44.07</td>
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<tr>
<td>130</td>
<td>1.51</td>
<td>290</td>
<td>4.68</td>
<td>1900</td>
<td>47.07</td>
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<tr>
<td>140</td>
<td>1.71</td>
<td>300</td>
<td>4.87</td>
<td>2000</td>
<td>50.10</td>
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<tr>
<td>150</td>
<td>1.92</td>
<td>400</td>
<td>6.91</td>
<td>2100</td>
<td>53.18</td>
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<tr>
<td>160</td>
<td>2.12</td>
<td>500</td>
<td>9.08</td>
<td>2200</td>
<td>56.30</td>
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<tr>
<td>170</td>
<td>2.32</td>
<td>600</td>
<td>11.36</td>
<td>2236</td>
<td>57.44</td>
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<td>Liquid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2236</td>
<td>89.2</td>
<td>2500</td>
<td>93.6</td>
<td>2900</td>
<td>100.3</td>
</tr>
<tr>
<td>2250</td>
<td>89.4</td>
<td>2600</td>
<td>95.3</td>
<td>3000</td>
<td>102.0</td>
</tr>
<tr>
<td>2300</td>
<td>90.2</td>
<td>2700</td>
<td>97.0</td>
<td>3100</td>
<td>103.7</td>
</tr>
<tr>
<td>2400</td>
<td>91.9</td>
<td>2800</td>
<td>98.6</td>
<td>3150</td>
<td>104.5</td>
</tr>
</tbody>
</table>

Fig. 1. Solid rhodium – percentage deviations from selected curve

Fig. 2. Solid rhodium – percentage deviations from selected curve
only as a temperature coefficient of electrical resistivity which over the given temperature range decreases from 0.021 to 0.019 \( \mu \Omega \text{cm K}^{-1} \), differing from the present evaluation which suggests a rise from 0.025 to 0.031 \( \mu \Omega \text{cm K}^{-1} \) over the same temperature range.

2.2 Liquid

Measured electrical resistivity values for rhodium at the melting point are given in Table III. In the liquid region electrical resistivity measurements of Hüpf et al. (15) (2236–3150 K) were accepted and are given by Equation (iii) and are also included in Table II.

Table III Differences Between the Solid and Liquid Electrical Resistivity of Rhodium at the Melting Point

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reference</th>
<th>( \rho_S ), ( \mu \Omega \text{cm} )</th>
<th>( \rho_L ), ( \mu \Omega \text{cm} )</th>
<th>( \rho_L/\rho_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Savvatimskii</td>
<td>28</td>
<td>61.0</td>
<td>85.5</td>
<td>1.402</td>
</tr>
<tr>
<td>Martynyuk and Tsapkov</td>
<td>29</td>
<td>59.0</td>
<td>92.5</td>
<td>1.568</td>
</tr>
<tr>
<td>Hüpf et al.</td>
<td>15</td>
<td>60.7</td>
<td>89.2</td>
<td>1.470</td>
</tr>
<tr>
<td>Present assessment</td>
<td>–</td>
<td>57.44</td>
<td>89.2</td>
<td>1.553</td>
</tr>
</tbody>
</table>

3. Iridium

3.1 Solid

As given in Table IV the measurement of Powell and Tye (5) is assumed to be superseded by the later measurements of Powell et al. (8, 9) and the measurements of White and Woods (6) by the later measurement of White and Woods (7). The measurement of Powell et al. (8) is not considered to be superseded by the later measurements of Powell et al. (9) since it is at a specific temperature whereas the later measurements are obtained from an interpolation. The selected value is an average of the last three determinations.

Values up to 273.15 K are based on the measurements of White and Woods (7) (20–295 K) after correction to the selected value at 273.15 K using the ratio 4.67/4.65. At 100 K and above, but less than 220 K, the data was fitted to Equation (iv) which has an overall accuracy as a standard deviation of \( \pm 0.01 \mu \Omega \text{cm} \).

The measurements of White and Woods (7) are considered as superseding their earlier measurements (6) (15–295 K). Measurements of Volkenshtein et al. (32) (0.4–70 K) are only shown graphically whilst measurements of Volkenshtein et al. (33) (4.2–300 K) are also shown graphically except at 25 K and below. These are given in the form of an equation which appears to lead to electrical resistivity values about half those of White and Woods (7). Measurements of Powell and Tye (5) (83–289 K) are initially 2.8% high drifting to 5.6% high at 90 K to 0.6% high at 191 K and then to an average of 1.6% high at 278 K and above.

Table IV Electrical Resistivity of Iridium at 273.15 K

<table>
<thead>
<tr>
<th>Authors</th>
<th>Reference</th>
<th>( \rho_i ), ( \mu \Omega \text{cm} )</th>
<th>Temperature of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powell and Tye</td>
<td>5</td>
<td>4.75</td>
<td>Extrapolated 277.5–289.3 K</td>
</tr>
<tr>
<td>Wimber and Halvorson</td>
<td>31</td>
<td>5.29</td>
<td>Extrapolated from equation 295–2275 K</td>
</tr>
<tr>
<td>Garcia and Löffler</td>
<td>27</td>
<td>8.47</td>
<td>Extrapolated from 295–850 K</td>
</tr>
<tr>
<td>White and Woods</td>
<td>6</td>
<td>4.63</td>
<td>At 273.15 K</td>
</tr>
<tr>
<td>White and Woods</td>
<td>7</td>
<td>4.65</td>
<td>At 273.15 K</td>
</tr>
<tr>
<td>Powell et al.</td>
<td>8</td>
<td>4.65</td>
<td>At 273.15 K. Corrected for ( \rho_0 ) 0.055 ( \mu \Omega \text{cm} )</td>
</tr>
<tr>
<td>Powell et al.</td>
<td>9</td>
<td>4.72</td>
<td>Interpolated 200–400 K. Corrected for ( \rho_0 ) 0.056 ( \mu \Omega \text{cm} )</td>
</tr>
<tr>
<td>Selected</td>
<td></td>
<td>4.67 ± 0.05</td>
<td>At 273.15 K</td>
</tr>
</tbody>
</table>
In the high-temperature region measurements of Trukhanova and Filippov (34) (1300–2500 K) and of Filippov and Yurchak (13, 14) (1500–2500 K) over the full range at 100 K intervals, Pottlacher (35) (2000–2719 K in the solid range) at 50 K intervals from 2000 to 2700 K and Wimber and Halvorson (31) (293–2300 K) at 100 K intervals from 700 to 1900 K, after correcting the latter for thermal expansion using values selected by the present author (36), were combined with the selected value at 273.15 K and fitted to Equation (v) with an overall accuracy as a standard deviation of ±0.33 \( \mu \Omega \) cm. Therefore above 100 K Equations (iv) and (v) were used to generate a selected value for the solid in Table V where values at 600 K and above were given to four significant figures only for interpolation purposes. Deviations of the input values from this equation are shown in Figure 3 except for the measurements of Wimber and Halvorson at 300 K and 400 K which are respectively 10.2% and 7.3% higher than the selected values.

Measurements of Binkele and Brunen (23) (273–1373 K) combined from four runs trend from initially 16% high to 1.4% high whilst measurements of Gathers et al. (37) (2000–2720 K in the solid range) trend from 2.7% high to 6.4% high and those of L’vov et al. (38) (100–1700 K) above 273.15 K scatter 5.8%

### Table V Intrinsic Electrical Resistivity of Iridium

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>( \rho_i ), ( \mu \Omega ) cm</th>
<th>Temperature, K</th>
<th>( \rho_i ), ( \mu \Omega ) cm</th>
<th>Temperature, K</th>
<th>( \rho_i ), ( \mu \Omega ) cm</th>
</tr>
</thead>
<tbody>
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<td>Solid</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>15</td>
<td>0.0013</td>
<td>190</td>
<td>3.01</td>
<td>1000</td>
<td>21.19</td>
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low to 4.6% high. At the melting point the value of electrical resistivity determined by Lebedev et al. (39) is 1.6% high whilst that determined by Martynuk and Tsapkov (29) is 4.8% low.

Values determined as resistivity ratios were corrected for thermal expansion (36) and from RT/R295 K to RT/R273.15 K. Measurements of Mimeault and Hansen (26) (100–700 K) on this basis trend to 18% low above 273.15 K whilst the measurements of García and Löfler (27) (295–1100 K) trend to 30% low. Measurements of Gugnin et al. (40) (473–1973 K) were only shown in the form of a small graph. Deviations of these measurements from Equation (v) above 300 K are shown in Figure 4 where values of Mimeault and Hansen and of García and Löfler were reconsidered as electrical resistivity values based on the selected value at 273.15 K.

### 3.2 Liquid

Electrical resistivity values for iridium at the melting point are given in Table VI. The variation of electrical resistivity with temperature as given by Pottlacher (35) (2719–3550 K) are accepted and are given as Equation (vi) and included in Table V. Over the common temperature range of 2719 to 3550 K the measurements of Gathers et al. (37) (2719–4250 K in the liquid range) trend from 3.8% high to 1.3% high.

<table>
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<th>Authors</th>
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<th>$\rho_S$, $\mu\Omega$ cm</th>
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Low Temperature Intrinsic Resistivity of Solid Rhodium (100 to 273.15 K)
\[ \rho_i (\mu\Omega \text{ cm}) = 2.37925 \times 10^{-2} T - 1.49605 \times 10^{-5} T^2 + 1.66098 \times 10^{-8} T^3 - 1.37121 \] (i)

High Temperature Intrinsic Resistivity of Solid Rhodium (273.15 to 2236 K)
\[ \rho_i (\mu\Omega \text{ cm}) = 1.45031 \times 10^{-2} T + 1.00331 \times 10^{-5} T^2 - 3.35384 \times 10^{-6} T^3 + 5.05588 \times 10^{-13} T^4 - 0.294564 \] (ii)

Intrinsic Resistivity of Liquid Rhodium (2236 to 3150 K)
\[ \rho_i (\mu\Omega \text{ cm}) = 1.680 \times 10^{-2} T + 51.6 \] (iii)

Low Temperature Intrinsic Resistivity of Solid Iridium (100 to 273.15 K)
\[ \rho_i (\mu\Omega \text{ cm}) = 2.47088 \times 10^{-2} T - 1.58538 \times 10^{-5} T^2 + 1.58062 \times 10^{-8} T^3 - 1.21847 \] (iv)

High Temperature Intrinsic Resistivity of Solid Iridium (273.15 to 2719 K)
\[ \rho_i (\mu\Omega \text{ cm}) = 1.66688 \times 10^{-2} T + 5.70656 \times 10^{-6} T^2 - 8.95612 \times 10^{-10} T^3 - 0.290595 \] (v)

Intrinsic Resistivity of Liquid Iridium (2719 to 3550 K)
\[ \rho_i (\mu\Omega \text{ cm}) = 1.316 \times 10^{-2} T + 60.5 \] (vi)

References
Applied Phys., 1972, 5, (1), 155

The Author

John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.
Faraday Discussion: Nanoparticle Synthesis and Assembly

Recent advancements in nanoparticle research

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Introduction

Faraday Discussions are unique international meetings that focus on miscellaneous areas of chemistry and have been held for over 100 years. The format of these meetings is distinctive because delegates submit their papers in advance and these are distributed to all the participants prior to the meeting. During the meeting, the presenting authors are given five minutes to summarise the key points of their work and the remaining time is devoted to discussing the papers. The conference was held at Argonne National Laboratory, USA, from 20th to 22nd April 2015 and was jointly organised by the Royal Society of Chemistry, UK, the Department of Physics, Kansas State University, USA, and Argonne National Laboratory. There were approximately 130 delegates representing 23 countries. The programme consisted of 10 invited talks, 14 paper presentations, 72 poster presentations and 12 lightning poster presentations upon invitation by the scientific committee. The themes that were covered include:

- Nanoparticle synthesis – physical chemistry of nanoparticle shape and ligand control
- Theoretical insights into nanoparticle synthesis and nanoparticle assembly
- Nanoparticle self-assembly
- Nanoparticle directed assembly.

The purpose of this conference was to bring together scientists from a variety of backgrounds to discuss recent advancements in nanoparticle synthesis and assembly, and to enable collaborations. Due to the specified topic of the conference, the majority of the talks focused on these two aspects of nanoscience. Therefore, in this review, examples of these two areas will be presented to give an overview of the discussions that took place.

Further information about the event can be found on the conference website (1).

Nanoparticle Synthesis

Nanoparticles are used in many applications and therefore research in this field is often application driven. However, one of the sessions was focused on research into the fundamental principles behind nanoparticle synthesis. The importance of the synthetic strategies and the phenomena that govern nanoparticle synthesis were explained and the correlation of the synthetic route and of the final properties of the nanoparticles were emphasised.

The challenge to control both the shape and composition of platinum nanoparticles and platinum-based alloys using wet chemistry was highlighted by Christophe Petit (Université Pierre et Marie Curie, France) (2). Petit and colleagues examined the effect of the order of adding the capping agent during the
synthesis, as well as the effect of the dissolved gases on the structure of the final nanoparticles. They showed that in the synthesis of monometallic Pt nanoparticles, irrespective of the presence of H₂, when the capping agent (an alkylamine) is added to the reaction mixture prior to the chemical reduction of the metal salt, the outcome of the reaction is mostly spherical particles. When the alkylamine is added after the reduction step in the presence of H₂, Pt nanocubes were obtained as the main product whereas in the absence of H₂, spherical and wormlike particles are observed. The schematic illustration presented in Figure 1 shows the protocols of synthesis that were followed during their experiments.

Their work showed that the different adsorption abilities of the amine-containing capping agent and the dissolved H₂ on the crystal facets of the growing particles may affect the outcome of the reaction. In the case of Pt-based alloyed systems, the authors explained the difficulties of controlling the composition of CoₓPt₁₋ₓ or PdₓPt₁₋ₓ particles using liquid-liquid synthesis. They attributed the large discrepancies in the composition of the particles to the different reduction kinetics when one of the metal precursors is in the aqueous phase and the second in the organic phase. Additionally, they suggested that better control over the final metal composition can be achieved when the two precursors have similar reduction potentials and are well dissolved in the same media.

Of particular interest was the paper presented by Ger Koper (TU Delft, The Netherlands) (3) that proposed a robust preparation method to obtain ultrafine Au and Pt nanoparticles by bicontinuous microemulsion. The importance of their work lies in the fact that the reactant concentration can be increased, while the size of the particles remains the same. In their experiments, the particle size is controlled by the surfactant size and not by the composition of the microemulsion. A range of surfactants with different charges were used to validate their observations. This could be of particular relevance to industrial processes since a large production of nanoparticles is often required, however increased amounts of the reactants used often lead to undesirable larger particles.

### Nanoparticle Assembly

As the main focus of the conference was nanoparticle assembly, a large number of presented papers were devoted to this aspect of nanoscience.

An exceptional paper was presented by Rafal Klajn (Weizmann Institute of Science, Israel) (4), titled 'Magnetic Field-induced Self-assembly of Iron Oxide Nanocubes'. They examine how the shape of the iron oxide nanocrystals and their surface chemistry affect their self-assembly properties. Several experimental parameters were evaluated and they identified the conditions under which the particles can form superstructures including one-dimensional filaments and helices, as well as carbon-shaped assemblies (Figure 2).

These superstructures were reported for the first time and the optical and mechanical properties of each assembly were analysed.
The experimental conditions were found to be crucial for the final shape of the assembly nanoparticles; by changing the particle density or the direction of the applied magnetic field the organisation of the final assembly can be controlled. However, parameters such as particle size, shape, composition and surface chemistry cannot be overlooked and the interplay between all those factors should be considered. Finally, the authors performed Monte Carlo simulations to further investigate the mechanisms of self-assembly of these superstructures.

On the same topic, outstanding work was presented by Mathias Brust and his group (University of Liverpool) (5), by monitoring for the first time in situ pattern formation of drying and wetting dispersions of gold nanoparticles, using an environmental scanning electron microscope (ESEM). This allows direct monitoring of the particle assembly in the nanoscale and offers real time information of how the entire process occurs. This type of investigation offers the possibility to explore further this phenomenon that is as yet poorly understood, and perhaps will provide some information on the mechanistic details that govern this process. The gold nanoparticles that were used were functionalised with hydrophilic thiol ligands since the only dispersant that could be used was water.

During the experiments, significant interactions were revealed between the gold nanoparticles and the substrate, and surprisingly, once the pattern was formed it would either stick on the substrate or could be lifted. Redispersion of the pattern in condensed water droplets was found to be difficult.
Conclusions

It is essential to understand nanoparticle synthesis and the effects of experimental conditions on the properties of the final nanoparticles in order to design optimised materials for high-performance applications. Research in this field is ongoing and many aspects in nanoparticle synthesis and assembly are yet to be fully understood. In particular, the much larger number of presentations devoted to nanoparticle assembly – far more than could be described in this brief review – indicates the high level of interest in this area of nanoparticle preparation. This Faraday Discussion meeting provided a good overview of the advances of nanoscience on these topics and the overall content of the presentations and the discussions that took place were very insightful and informative.

References


The Reviewer

Anastasia Mantalidi graduated with a BSc in Chemistry from the University of Crete, Greece, in 2011, and a MSc degree in Chemical Research from University College London, UK, in 2012. Currently, she is in the last year of her PhD project that is jointly sponsored by the Chemistry Department at UCL and Johnson Matthey. Her project is heavily involved with nanoparticle synthesis employing solution phase protocols and monitoring in situ the decomposition of the metal precursors and the subsequent particle formation using synchrotron based techniques.
24th North American Catalysis Society Meeting

Highlights in emission control and zeolites from the biennial US event

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Introduction

The 24th North American Meeting of the Catalysis Society (NAM) was held from 14th to 19th June 2015 at the David L. Lawrence Convention Center in Pittsburgh, Pennsylvania, USA, with the Pittsburgh-Cleveland Catalysis Society as hosts (1). This biennial meeting is recognised as the premier conference about the science and applications of catalysis and catalytic processes and as a forum to explore their boundaries and shared concepts with homogeneous catalysis, electrocatalysis and photocatalysis.

There were approximately 1300 delegates from academia and a range of industries such as Chevron, BASF, Exxon Mobil, Synfuels China, Zeolyst, Dow, Sabic, Albemarle, Clariant, Haldor Topsee, DuPont, BP, GM, Cummins and Velocys. It included three plenary lectures, presented by the recipients of the Michel Boudart, Eugene Houdry and Paul H. Emmett awards; 20 keynote addresses presented by the foremost leaders in the field; more than 400 oral presentations distributed along six parallel sessions; and about 600 posters on three of the days.

A wide range of topics were covered: Biomass Conversion; Catalysis for Fossil Energy; Coal, Petroleum, and Natural Gas; Catalyst Characterisation; Catalyst Design and Synthesis; Catalyst Modelling and Simulation; Environmental Catalysis; Fundamentals of Catalysis; Industrial and Fine Chemicals; Photocatalysis and Electro catalysis; and Reaction Engineering. This selective review will focus on some highlights from Environmental Catalysis. There was not a specific programme for zeolites; however, there were various sessions dealing with zeolites.

Copper Zeolite Selective Catalytic Reduction

There were a large number of talks focusing on different aspects of Cu zeolite selective catalytic reduction (SCR) technology. A presentation by Feng Gao (Pacific Northwest National Laboratory (PNNL), USA) on 'Effects of Si/Al Ratios and Alkali Cocations on Cu/SSZ-13 NH3-SCR Catalysts: Active Cu Species, Roles of Brønsted Acidity, and Hydrothermal Stabilities' claimed that with dehydrated Cu/SSZ-13, at low Cu loading, Cu was present in the D6Rs, while at higher loadings, Cu was present in both D6Rs and 8R. However, on hydration, all the Cu²⁺ is fully hydrated and less bound to the framework. It was shown that Cu-SSZ13 does not dehydrate until 200°C in flowing dry air. With a silica-to-alumina molar ratio (SAR) of 70, there was some evidence of Cu dimers, while at SAR 24, there was no evidence of Cu dimers. The presence of Brønsted acidity was shown to be essential for Cu location and it was proposed that
H\(^+\) was involved in the Cu redox process. Analysis of activity data indicated that although monodispersed Cu was best for SCR, it was poorer for NO oxidation, with dimers being more active.

In his presentation ‘Molecular Elucidation of the Cu Redox Cycle Underlying NOx Selective Catalytic Reduction in Cu-SSZ-13’ Christopher Paolucci (University of Notre Dame, USA) described the use of modelling and extended X-ray absorption fine structure (EXAFS) analysis to show the state of the Cu under reaction conditions. Reduction to Cu\(^+\) is observed in the absence of molecular oxygen by 400ºC and under SCR conditions a mixture of both Cu\(^{2+}\) and Cu\(^+\) is observed (2). With ammonia, modelling predicts that Cu\(^+\) will form a linear dimer (H\(_3\)N-Cu-NH\(_3\))\(^+\), while Cu\(^{2+}\) will form a four-coordinated species with two framework oxygens and two ammines. It was also claimed that the turn over frequency (TOF) for SCR is the same for Cu-chabazite (CHA) and beta polymorph A (BEA).

Atish Parekh (Purdue University, USA) presented ‘Cu(I)-Cu(II) Redox Chemistry on Isolated Cu Ions for Ammonia Standard SCR’, an X-ray absorption near edge structure (XANES) study on the effect of SCR feed components on Cu oxidation state. This was a complementary study to Paolucci’s presentation. Using a nitric oxide, ammonia, oxygen, water and carbon dioxide feed, increasing the NO concentration led to an increase in Cu\(^+\) to a maximum of 50%. Removing the NH\(_3\) led to only Cu\(^{2+}\) present and removing O\(_2\) led to only Cu\(^+\).

Jean-Sabin McEwen (Washington State University, USA) gave a detailed study of XANES spectra through modelling in his talk ‘Spectroscopic Properties of Cu-SSZ-13 in the SCR of NOx: Computational IR and XANES Study’. He was able to show that the partial density of states (PDOS) is sensitive to the Cu location (dehydrated) and may be resolvable in XANES spectra. With hydrated spectra for both Cu\(^+\) and Cu\(^{2+}\), an increase in the XANES peak is expected due to the Cu having a higher symmetry as it is not bound to the framework. With NH\(_3\), a change in the XANES peak is expected due to NH\(_3\) coordination rather than Cu\(^{2+}\) reduction. This group has also studied Cu-silico-alumino-phosphate (SAPO)-34.

Peter Vennestøm (Haldor Topsøe A/S Research & Development Kgs, Denmark) presented ‘Solid-State Ion-Exchange of Cu into Zeolites by Ammonia at Low Temperatures’. Building on the observation that a mixture of copper(II) oxide and H-MFI zeolite under SCR conditions at 250ºC gives active SCR catalysts, the work was extended to CHA and BEA, although 450ºC was required for CHA to get good activity. In situ X-ray diffraction (XRD) showed that under NO+NH\(_3\) and NH\(_3\)-only feeds, copper(I) oxide was formed. The presenter proposed that [Cu(NH\(_3\))[\_]\(^+\) is the active migration species. The catalyst showed similar SCR activity to ion-exchanged Cu-CHA with a solid state exchanged sample, but needed much higher amounts of Cu, suggesting the process is not 100% efficient.

**Other SCR Systems**

János Szanyi (PNNL, USA) discussed ion exchange of ammonium-CHA with iron sulfate under nitrogen to give Fe-SSZ-13 in his talk ‘Kinetic and Spectroscopic Characterization of Fe-SSZ-13 NH\(_3\) SCR Catalysts’. Ultraviolet-visible (UV-vis) spectroscopy shows that even fresh catalysts have FeO\(_x\) clusters and iron (III) oxide in addition to well-dispersed Fe. SCR activity is poorer than Cu-CHA with a full gas mix. This appears to be due to H\(_2\)O inhibition, with suppression of both NO and NH\(_3\) oxidation by H\(_2\)O. On hydrothermal ageing, an increase in Fe oxide species is observed. Use of NO diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) shows formation of Fe\(^{2+}\)–NO species, although initial vacuum treatment appears to reduce the Fe. The Fe is present in both D6R and 8R sites but only the Fe in 8Rs sites is able to take part in the redox cycle.

Erisa Saraci (Universität Leipzig Institute of Chemical Technology, Germany) presented ‘SCR-DeNOx on Mesoporous and Hierarchically Structured V\(_2\)O\(_5\)/TiO\(_2\) Mixed Oxide Catalysts’. This covered the preparation of vanadium-titania catalyst by sol-gel with the inclusion of polyethylene glycol (PEG) to generate 1 \(\mu\)m macropores as well as normal 4 nm mesopores. The presenters found a 200% increase in SCR activity with added macropores overcoming significant mass transport issues in the non-PEG material.

Stanislaw Dzwigaj (Sorbonne University, France), in his presentation ‘The Promotion of Co-BEA Zeolites by Copper for SCR of CO with NH\(_3\)’, aimed to isomorphously substitute cobalt and Cu into BEA, by dealumination of aluminium-BEA to give SAR 1500 and then adding Co or Cu nitrates. He showed substitution by loss of silicon hydroxide nests and UV-vis showed no cobalt oxide species until 3.5 wt% Co loading. Hydrogen temperature-programmed reduction (H\(_2\)-TPR) showed very stable Co species not reducing until 1120 K. Pure Co-BEA only showed NH\(_3\)-SCR activity over 450 K with a peak at around 600 K. Addition of Cu brought this down to approximately...
500 K. It was not clear whether this provides any advantage over standard ion-exchanged Cu BEA.

The presentation by Shijian Yang (Nanjing University of Science and Technology, China) titled ‘Origination of N₂O from NO Reduction by NH₃ over MnOₓ-CeO₂: Mechanism and Effect Factors’ showed the MnOₓ-CeO₂ system suffers from poor sulfur dioxide tolerance and low N₂ selectivity. N₂O formation appears to come from NH₃ oxidation rather than directly from the SCR reaction. H₂O inhibits the SCR at low temperature but improves N₂ selectivity.

There were also a number of hydrocarbon-SCR presentations generally concerned with silver-alumina catalysts.

NOₓ Storage and Reduction

Laura Righini (Politecnico di Milano, Italy) presented ‘The Role of Pt/Ba Interaction on the NOₓ Storage and Reduction Processes over PtBa/Al₂O₃ LNT Catalysts’. It is commonly accepted that during the lean phase nitrogen oxides (NOₓ) are stored in the form of nitrates and nitrates over the platinum-barium on alumina lean NOₓ trap (LNT) catalyst. Nitrite and nitrate routes were reviewed and it was proposed that the reduction of stored NOₓ is not initiated by thermal decomposition but instead proceeds through a Pt catalysed pathway. When H₂ is used as reductant, it is activated by forming Pt-H species. Then the reductant spills from Pt to Ba, where stored NOₓ are converted to N₂ and other by products. Alternatively, a reverse spillover of stored NOₓ from Ba to reduced Pt sites may also occur. In these processes, a major role of the Pt/Ba proximity is expected. Fourier transform infrared (FT-IR) spectroscopy and transient reactivity experiments were carried out to gain information on the surface and gas phase species to be able to understand the relevance of the Pt/Ba interaction on both the adsorption and reduction pathways.

Other DeNOₓ Systems

Joseph Theis (Ford Motor Company, USA) highlighted disadvantages of the current LNT formulation based on alumina, ceria and high Pt loading in his talk: ‘Assessment of Low Temperature NOₓ Adsorbers for Cold-Start NOₓ Control on Diesel Engines’. These formulations rely on the oxidation of NO to NO₂ and storage of the NO₂ as nitrates, which would be difficult to purge completely at low temperatures. A ‘new’ formulation was presented based on palladium on ceria to store and release NO directly and this was compared to model catalysts Pt/CeO₂, Pt/Al₂O₃ and Pd/Al₂O₃. Data on Pd on ceria-zirconia demonstrated 38% NOₓ trapping efficiency. Effects of H₂O and hydrocarbons (C₂H₄) on the NOₓ storage were assessed. It was found that higher concentration of C₂H₄ improves the storage at lower temperatures (90°C–160°C) with 59% efficiency and shifts the release temperature to higher values. No N₂O was formed during the test, therefore HC-SCR reaction was ruled out. The formation of alkyl nitrates/nitrites was proposed. When H₂O was present during the test, a reduction in efficiency of 11% occurred and this was likely to be related to competition for storage sites at low temperature. If the storage temperature during the test was increased, H₂O did not show any effect. The effect of the rich purge was also presented. The catalyst was purged at 300°C and cooled down under ‘neutral’ conditions. The catalyst was completely deactivated due to a change in oxidation state. Additional data comparing to model catalysts was also presented. The mechanism of storage for Pt/Al₂O₃ is based on the oxidation of NO to NO₂. It showed good NOₓ storage above 200 seconds in the Federal Test Procedure (FTP) cycle, but is not suitable for low temperature applications. High N₂O formation due to HC-SCR reaction also occurred. The Pd/Al₂O₃ catalyst had poor storage performance, suggesting that ceria is important.

Jason Loiland (University of Delaware, USA) gave a talk titled ‘NO Oxidation Reaction Mechanisms over Microporous Materials’. The NO oxidation reaction was studied over CHA, MFI and BEA zeolites, looking at the effect of the SAR and the extra framework cation (H⁺, Na⁺ and siliceous) on NO oxidation rates. Infrared experiments were performed to monitor NₓO_y surface species formed on the catalysts. The authors demonstrated that NO⁺ species are coordinated to framework aluminium sites. These species are directly involved in the catalysis at temperatures above 423 K, explaining the catalytic activity improvement.

Joon-Hwan Choi (Korea Institute of Materials Science, South Korea) presented a new catalyst coating technique with very strong adhesion strength to metal substrate and higher porosity in ‘De-NOₓ SCR Catalyst Coating with Strong Adhesion to Metal Honeycomb Substrate’. The technique is based on aerosol deposition and no binder is needed.
Methane Oxidation

James B. Miller (Carnegie Mellon University, USA) discussed ‘Support Roles in Pd Catalysts for Total Methane Oxidation’. In this kinetic study of Pd supported on Al₂O₃, CeZrOₓ and CeO₂ for methane oxidation, dynamic light-off data were used to generate pseudo-Arrhenius plots and determine activation energies. Hysteresis and activation effects were investigated with repeated ramps up and down in temperature. It was found that Al₂O₃-supported catalysts showed good initial activity followed by slow deactivation, CeZrOₓ-supported catalysts showed poor initial activity and slow activations and CeO₂-supported catalysts showed poor activity and little activation. A Mars-van Kevelen mechanism requiring both neighbouring reduced and oxidised Pd sites was proposed.

Henrik Grönbeck (Chalmers University of Technology, Sweden), in his talk ‘Methane Oxidation over Palladium Oxide from First Principles’, showed that taking a Pd metallic surface and applying O₂ led to the formation of Pd-O species by 167ºC and a full PdO surface by 333ºC. On passing CH₄, CO₂ formation was observed at 333ºC which corresponded to a relatively thick film of PdO (ordered PdO (101)) (3) (Figure 1). Formation of an ordered PdO (111) film was unstable with CH₄ and loss of activity was observed. Density functional theory (DFT) calculations suggested that CH₄ adsorption on a one-layer PdO (101) surface is unfavourable, but becomes favourable over a two-layer PdO (101) surface. It was proposed that surface Pd sites needed a sub-surface O to bind CH₃. A detailed micro-kinetic model of 80 reaction steps was shown.

Zeolites

Toshiyuki Yokoi (Tokyo Institute of Technology, Japan) discussed ‘Improvement of Catalytic Activity in the MTO Reaction by Control of Location of Al Atoms in the Pores of ZSM-5’. Different structure-directing agents (SDAs) were used to control Al location in ZSM-5, for example the use of tetrapropylammonium (TPA) should only give Al at intersections. HC cracking (constraint index) was used to probe Al locations combined with 27Al nuclear magnetic resonance (NMR) spectroscopy as differences in AlO₄ positions were observed.

Andrei Khodakov (Université Lille, France) presented a talk titled ‘Influence of Zeolite Crystallite Size on the Activity and Stability of Hybrid Copper-Zeolite Catalysts for Direct Synthesis of Diethyl Ether’, in which lutidine adsorption was used as a method to measure external zeolite acidity.

Trees de Baerdemaeker (KU Leuven Centre for Surface Chemistry and Catalysis (COK), Belgium) presented ‘Introducing Catalytic Function in Zeolites Derived from Layered Precursors’. RUB-36, a ferrierite (FER)-like layer structure (SAR = 200–∞), was used to introduce functionality and metal species. Addition of Fe via iron (III) chloride gave only isolated Fe species, which appear quite stable to reaction (benzylation of toluene). The crystals are dense, so mesoporosity can be introduced by base treatment, although this was shown be quite damaging.

Manjesh Kumar (University of Houston, USA) gave a talk about the evolution of crystalline structure in zeolite gels, entitled ‘Tailoring the Physicochemical Properties of Zeolite Crystals through Molecular Design’. With CHA, small amorphous particles are observed at short synthesis times, followed by aggregation, then crystallisation and conversion of small crystallites into large crystallites. It was shown that use of macromolecules could control crystal sizes, giving CHA crystals of 100 nm to 20 μm.

Jeffrey Rimer (University of Houston, Texas, USA) presented ‘Time-Resolved in situ Imaging of Zeolite Surface Growth Reveals the Mechanism of Crystallization’, a companion talk to the above. In situ solvothermal atomic force microscopy (AFM) was used to observe zeolite crystallisation and growth. Both molecular and nanoparticle deposition were observed on growing planes, with particle size being highly sensitive to the pH.

Michiel Dusselier (California Institute of Technology (Caltech), USA), in ‘The Synthesis of SSZ-39 Using
Mixtures of Isomeric, Organic Structure Directing Agents’, found SSZ-39 difficult to prepare at high yield and with the target SAR (for example 16 instead of 60). Also mordenite (MOR) and gismondine (GIS) impurities were found. A high SAR is desirable for methanol to olefins use as too many H⁺ sites lead to coking, but this was unsuccessful by direct synthesis.

**Base Metal Catalysts for Emission Control Reactions**

Masatoshi Sakai (Toyota Central R&D Laboratories, Aichi, Japan) presented ‘Catalytic NO Reduction over Cu/CeO₂: Characterisation of Copper-Ceria Interface Active Sites’. Cu-CeO₂ catalysts prepared by Cu(OAc)₂ impregnation onto CeO₂ were studied in simple carbon monoxide-nitric oxide gas feeds. The onset of CO-NO reaction was observed at lower temperatures than over rhodium on ceria but full conversion did not occur until higher temperatures. There was no evidence of Cu incorporation into the CeO₂ lattice, although electron paramagnetic resonance (EPR) showed isolated Cu²⁺ at 0.5%, with formation of CuO clusters by 6%. TPR showed that isolated Cu²⁺ was stabilised towards reduction compared to CuO clusters and CO-NO light-off correlated with TPR reduction temperature. Small Cu(O) clusters formed by reduction of Cu²⁺ and local migration that ‘wet’ the CeO₂ were proposed as the most active Cu species (4) (**Figure 2**). At high Cu loading, pre-formed CuO particles are less active, possibly due to less interface sites.

Charles A. Roberts (Toyota Motor Engineering & Manufacturing North America, Inc, USA) presented a study of Fe-CeO₂ catalysts to see if they can mimic isolated Fe sites in zeolites with simple CO-NO reaction feeds in his presentation ‘In Situ Spectroscopic Characterization of Highly Dispersed Fe-Oxide Catalysts for NOx Reduction’. Catalysts were prepared by sodium-iron-ethylenediaminetetraacetic acid (EDTA) impregnation onto CeO₂ and compared to Fe(NO₃)₃ + NaHCO₃. The EDTA based catalyst showed higher activity (although still modest compared to the above Cu example). DFT, XANES and NO DRIFTS were applied to study the systems but no real conclusions were drawn, with suggestions that the system can be significantly improved.

Stephen Golden (Clean Diesel Technologies Inc (CDTi), USA) gave a presentation on the development of the CDTi technology, entitled ‘Spinel Mixed Metal Oxide with Enhanced Oxygen Storage Capacity for Zero-PGM Three Way Catalyst’. Initial targets have been to develop low platinum group metal (pgm) spinel catalysts with an ambition to move to zero-pgm. Also, there was an initial focus on underfloor applications, but this has now moved to close-coupled. Only the CuMn₂O₄ spinel system was mentioned. High oxygen storage capacity (OSC) was claimed for this material, but there was significant loss with ageing temperature. The use of ternary compositions improved fresh OSC further, but these still showed degradation on ageing. Good NOx reduction under rich conditions was also claimed, but no lean NOx reduction just above stoichiometric.

Andrew Binder (Oak Ridge National Laboratory (ORNL), USA) presented a talk entitled ‘CuO-Co₃O₄-CeO₂ Ternary Oxide Catalyst with High CO Oxidation Capability Shows no Inhibition by Propene’. A Cu:Co:Ce (1:5:5) catalyst was investigated for diesel oxidation. For simple CO oxidation, T₉₀ was observed at 150°C with little inhibition by C₃H₆ in the feed (no SO₂ present). The ternary composition was more active than binaries. Characterisation suggests that Cu is dispersed over a Co₃O₄-CeO₂ composite.

**Characterisation Techniques**

Yuriy Roman (Massachusetts Institute of Technology (MIT), USA) presented ‘Hyperpolarization NMR Methods for the Characterization of Isolated Lewis Acid Sites in Zeolites’. Dynamic nuclear polarisation-solid-state nuclear magnetic resonance (DNP-SSNMR) was used to characterise metal framework substituted zeolites with difficult NMR parameters. Most examples were with ¹¹⁹Sn and a chemical shift correlation plot with ¹⁵N pyridine adsorption was developed. Then ¹⁵N pyridine adsorption was used with quadrupole nuclei such as zirconium and hafnium to map onto the plot.
Korneel Cats (Utrecht University, The Netherlands) presented ‘Active Phase Distribution Changes within a Catalyst Particle during Fischer-Tropsch as Revealed by Multi-Scale Microscopy’ describing the use of hard X-ray transmission X-ray microscopy (TXM) (50 nm resolution, 3D), soft X-ray scanning transmission X-ray microscopy (STXM) (30 nm resolution, 2D) and scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS) (0.5 nm, 2D) to characterise a 15% Co/TiO2 catalyst fresh and after testing. There was evidence that Co redistributes during reaction to give a 1–2 nm Co layer around the TiO2 particles, together with carbon.

Libor Kovarik (PNLNL, USA) presented ‘Gamma-Alumina Platelets: Characterization and Comparative Study As a Model Catalyst Support’. Bulk and surface structures of transition aluminas are poorly understood due to low crystallinity, small particle sizes and the presence of multiple phases. In this presentation, the authors focused on δ-Al2O3 as a model system for fundamental studies of surface and structural properties. The morphological characteristics and surface properties were analysed by high-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM), XRD and NMR. The structure was found to be highly complex and no clear conclusions were given at the end of the talk.

Ruiang Wang (Youngstown State University, USA) discussed ‘Atomic-Level Interfacial Structure and Chemistry of Low-Temperature Active Metal-CeO2 Nanocatalysts’. The CO oxidation activity over metal nanoparticle catalysts (Pt, Au, Ni, Cu, Ag) can be promoted, especially at low temperature, when using CeO2 as support due to higher oxygen mobility via a redox reaction. The role of CeO2 is believed to involve the adsorption and interaction of CO at the metal/CeO2 interface. However, the interfacial structure and chemistry in metal-CeO2 catalysts for CO oxidation is not well understood. Different shapes (nanorods, nanotubes or nanocubes) and reactive faces on the crystal surface were explored in the presentation by using high-resolution transmission electron microscopy (HR-TEM) and EELS. Nanorods and nanocubes possess higher OSC properties. Incorporation of Cu or Ni into ceria nanorods enhances the oxygen transfer between the metal and CeO2. The interfacial structure and the surface area play a key role in the low temperature activity.

Patrick Wolf (Swiss Federal Institute of Technology (ETH) Zürich, Switzerland) presented ‘Towards the Understanding of the Active Site-Distribution in Sn-Beta’. This work gave fundamental insights into the nature of the active sites in tin-Beta zeolites. Sn-Beta zeolites were prepared according to different procedures. Several issues were found during in situ preparations; therefore a commercial Beta zeolite was used instead. Silanol nests were generated by acid treatments (HNO3 at high temperature) and Sn was incorporated afterwards on the silanol nests. The structure of the material and the different types of active sites were determined by looking at the chemical shift in NMR (5).

Timothy D. Courtney (University of Delaware, USA) discussed ‘Effect of Water Treatment on Sn-BEA Zeolite: Origin of 960 cm-1 FTIR Peak’. It is known that conditions during calcination influence the concentration of open vs. closed sites in a metal-zeolite. In Sn-BEA the closed sites are the Sn species in tetrahedral coordination whereas open sites are related to Sn and Si bonds. IR spectroscopy was used to determine if the metal is incorporated into the zeolite framework. Typically, the 960 cm-1 IR absorption band observed in Sn-BEA is associated with the incorporation of Sn in the zeolite framework. This is supported by the fact that by increasing the Sn loading the mentioned band displays a more significant perturbation. However, water can affect this band as well. IR and NMR spectra of calcined and water treated zeolites combined with first principles calculations indicate that the 960 cm-1 band is not a vibration involving Sn but a result of isolated internal silanol groups. Thermogravimetric analysis and temperature-programmed desorption showed the silanol groups condense to form water at temperatures between 400°C and 700°C. Further water uptake experiments helped to elucidate the presence of sites that can be hydroxylated at relatively low temperatures and dehydrated at temperatures typically used for zeolite calcination.

In the presentation by Dmitry Doronkin (Karlsruhe Institute of Technology (KIT), Germany), ‘Operando Spatially- and Time-Resolved XAS and Valence-to-Core-Xes to Study the Mechanism of the NH3-SCR over Fe- and Cu-Zeolites’, operando X-ray absorption spectroscopy (XAS) was applied under realistic reaction conditions to gain information such as oxidation state, coordination geometry, type and number of nearest neighbours or structural changes due to interaction with reactants. Changes occurring in the pre-edge and edge were monitored. Additionally, valence-to-core (V2C) X-ray emission spectroscopy (XES), allowed also to distinguish between atoms with close atomic numbers, like O and N. Brunauer, Emmett and Teller (BET)
surface area, atomic absorption spectrometry (AAS) and UV-vis spectroscopy were also applied to gain more information on the materials under study. Strong gradients of Fe and Cu oxidation state and a decrease of coordination number of the studied metal atom were observed along the catalyst bed for processes involving NOx and NH3. Re-oxidation of metal sites by oxygen is suggested to be the rate limiting step of the NH3-SCR which is strongly inhibited by NH3 at lower temperatures for Fe-zeolites (in contrast to Cu-zeolites). It was also observed that water inhibits the SCR reaction by coordination to the Fe-active centre. This was further supported by application of V2C-XES. The methodology applied provides evidence of the adsorption of NH3 and NO in the presence of water and in combination with DFT calculations allowed the identification of potential reaction intermediates for the SCR process on metal-zeolite.

Daniel E. Resasco (University of Oklahoma, USA) presented ‘Role of the Density of Zeolite Defects in the Instability of Zeolites in Hot Liquid Water’. The understanding of the susceptibility of different zeolites to hot liquid water allows the design of catalysts based on zeolites with higher stability and activity, for example for reactions of great importance in bio-oil refining such as fluid catalytic cracking (FCC), hydrocracking and alkylation. The thermal susceptibility of zeolites in liquid water is different from that in steam. While a pre-steamed zeolite can sustain treatments in the presence of steam at temperatures above 500°C, its crystal structure is completely destroyed after a few hours in liquid water at 200°C. It is believed that the susceptibility of the zeolite to hot liquid water depends on the structure and SAR, although this is still under discussion. Here it was presented that the susceptibility of the zeolite to hot liquid water is related to the density of zeolite defects rather than to the SAR (6) (Figure 3).

The role of zeolite structure, SAR, density defects, cation type, presence of mesoporosity and preparation parameters were analysed.

Jeffrey Rimer (University of Houston, USA) returned to give a presentation entitled ‘Time-Resolved in situ Imaging of Zeolite Surface Growth Reveals the Mechanism of Crystallization’. Knowledge of zeolite growth mechanisms is helpful to design improved catalysts with physicochemical properties that can be determined a priori. In situ characterisation of zeolite crystal growth at length scale was presented. A dual mechanism is proposed, involving classical and non-classical mechanisms.

**Single Site Catalysis**

Preparation and characterisation of (non-zeolite) single-site catalysts appears to be a big topic in US catalysis at present and there were a number of interesting talks on this.

Aidan Mouat (Northwestern University, USA) discussed ‘Highly Dispersed SiOx/Al2O3 Materials: Catalytic Relevance of Isolated Silanol Active Sites’. Single mild acid sites are required on Al2O3 for aromatic dihydroxylation chemistry (biomass conversion). Atomic layer deposition (ALD) was used to deposit tetraethoxysilane (TEOS) onto γ-Al2O3 at a silicon loading below saturation of Al reactive sites (3.2 Si nm–2). Characterisation by X-ray photoelectron spectroscopy (XPS) (reduced binding energy compared to SiO2) and 29Si DNP-enhanced cross polarisation-magic angle

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Fig. 3. The main characteristic of the zeolite that determines its susceptibility to hot liquid water is the density of silanol-terminated defects (Reprinted with permission from (6). Copyright 2015 American Chemical Society)
spinning (CP-MAS) NMR. NH$_3$ DRIFTS can be used to detect surface Si-OH and under-coordinated Al sites. Testing of samples for cyclohexane dehydrogenation gave lower TOFs compared to 5% Si-Al$_2$O$_3$ but with much higher selectivity.

Luan Nguyen (University of Kansas, USA), in his presentation ‘Catalysis on Singly Dispersed Bimetallic Sites’, proposed that very small metal clusters will show higher selectivity for certain reactions. RhCo$_3$ clusters on CoO$_x$ were prepared by first reducing Co$_3$O$_4$ and then adding Rh using deposition-precipitation. EXAFS shows the presence of Rh-Co metallic bonds and a coordination number ~1. Testing with the CO+NO reaction showed high conversion to N$_2$ and CO$_2$ with no N$_2$O. This was compared to pre-formed CoRh nanoparticles which displayed very poor activity. However, only limited testing was done with no redox cycling or oxidative treatments. Also, it was unclear what the Rh loading was. The group is currently moving on to the characterisation of supports to understand reactivity differences between grafted complexes such as Re and Zr alkyl complexes. A good summary of the activity differences between grafted complexes such as Re and Zr alkyl complexes. A good summary of the characterisation of Al$_2$O$_3$ surfaces using IR and N$_2$, H$_2$, and CH$_4$ adsorption was given. He also discussed the role of adsorbed H$_2$O on Al$_2$O$_3$ in creating basic sites which provide binding sites for complexes and the role of DNP for surface enhanced NMR to investigate surface chemistry using an example of surface site characterisation of zeolites.

Materials

Tae-Sik Oh (University of Pennsylvania) presented ‘Exsolution Behavior of Transition Metal Catalysts from Perovskite Host Lattices’. This group had previously investigated (La$_{0.4}$Sr$_{0.4}$)(Ti$_{0.97}$Ni$_{0.03}$)O$_3$–δ perovskites and found that Ni can only be segregated from the (110) surface as there need to be A cation vacancies, a B cation and B oxygen vacancies. ‘Ex-solved’ Ni particles appear to show much less carbon nanotube formation as they are anchored more strongly (CNT formation requires ‘lift-off’ of the growth particles). LaFe$_{0.95}$Pd$_{0.05}$O$_{3.3}$ was also investigated and the formation of PdFe nanoparticles was observed on reduction.

Sibo Wang (University of Connecticut, USA) gave a talk entitled ‘ZnO/Perovskite Core-Shell Nanorod Arrays Based Monolithic Catalyst for Hydrocarbon Oxidation at Low Temperature’. It had been previously shown that ZnO nanorods can be epitaxially grown on ceramic surfaces which is claimed to eliminate diffusion limitations. Nanoparticles of perovskite (LaMnO$_3$, LaCoO$_3$, La$_2$NiO$_4$) were coated onto the surfaces of the ZnO nanorods and the arrays tested for C$_3$H$_8$ oxidation. The perovskites on the ZnO showed a lower light-off when compared to the perovskites alone. The addition of Pt improved the low temperature oxidation further.

In her talk ‘Ion Beam Surface Engineering for High Active Nanocatalysts’ Nancy Artioli (Université de Caen, France) described the use of ion bombardment to improve the reducibility of CeZrO$_x$ and Pt/CeZrO$_x$. IR spectroscopy was used to investigate vacancy formation in Ce$_{0.7}$Zr$_{0.3}$O$_2$ through analysis of the surface OH vibrations. Ion beam treatment appears to form a higher number of O vacancies and higher O mobility.

Ming Li Ang (National University of Singapore) presented ‘Highly Active Ni/xNa/CeO$_2$ Catalyst for Water-Gas Shift Reaction: Effect of Sodium on Methane Suppression’. Generally Ni is not a good candidate for water-gas shift as it has high methanation activity. The addition of Na inhibits methanation with Ni/CeO$_2$ catalysts. Up to a certain level Na appears to promote Ni reducibility, with XPS showing electron donation to Ni. In situ DRIFTS shows that Na inhibits the formation of Ni subcarbonyl species which are proposed to be key for methanation reactivity. It was also shown that Na promotes CeO$_2$ sintering up to 2 wt% after which there is no further effect. It was speculated that 2 wt% Na is the solubility limit of Na in CeO$_2$.

Yolanda A. Daza (University of South Florida, USA) discussed the use of H$_2$ reduction and CO$_2$ re-oxidation cycles for CO$_2$ capture studies on LaSrCoFeO$_3$ perovskites in her talk ‘Intensified Reverse Water Gas Shift Chemical Looping on La$_{0.75}$Sr$_{0.25}$Co$_{1-y}$Fe$_{y}$O$_3$...
Perovskite Oxides. Under the cycling conditions (500°C reduction and >650°C re-oxidation) the pure Co containing perovskite is not stable, so Fe was added to stabilise it. Fe inhibits the Co reducibility. Although the LaSrCoFeO₃ is stable under repeated cycles, there is a loss in conversion attributed to both sintering and C (possibly CO₃⁻) laydown. The addition of Cu improved H₂O formation from H₂ reduction but did not change CO formation from CO₂ re-oxidation. It was suggested that the extra vacancies formed by the addition of Cu are more stable.

Sean Hunt (MIT) presented ‘Bimetallic Transition Metal Carbide Nanoparticles as Active, Stable, and Versatile Electrocatalysts’. Practical WC materials are often surface terminated with graphitic carbon which limits their usefulness. An alternative preparative method was shown that relied on forming WOₓ nanoparticles, coating them in a porous SiO₂ shell, carburising and etching the SiO₂ with HF/EtOH to give WC nanoparticles. Similar nitrides can be made by substituting CH₄/H₂ for NH₃ in the carburising step. The route is also able to form carbides of other transition metals such as Mo and Ti. The WC nanoparticles supported on carbon are active for electrochemical MeOH oxidation, although less active than Pt.

Conclusions
This review has given a brief overview of the numerous talks and posters presented, largely in the area of environmental catalysis but also some of those catalysts in zeolite and other structures, at the conference. A significant amount of work was focused on materials preparation and fundamental understanding, along with the development of new characterisation techniques. As shown in this review, there is also research into applications which do not utilise pgms for emission control reactions. Overall, the talks the reviewers attended were of a good quality and gave a good feel for the breadth of the US catalysis scene.

References

The Reviewers
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Desirée Durán-Martín is a Senior Scientist in Johnson Matthey Technology Centre. She graduated in Chemical Engineering from the University of Málaga, Spain, and has a PhD in Physical Chemistry from Autonomous University of Madrid, Spain. In 2011, she joined the Emission Control Research Group at Johnson Matthey. Her current research is focused on the control of NOx emissions from diesel engines, with special interest in the development of novel materials and fundamental understanding of the structure-activity relationships.
“Mesoporous Zeolites: Preparation, Characterization and Applications”

Edited by Javier Garcia-Martinez (Universidad de Alicante, Spain) and Kunhao Li, (Rive Technology, USA), Wiley-VCH Verlag GmbH & Co KGaA, Germany, 2015, 574 pages, ISBN: 978-3-527-33574-9, £120.00, €162.00, US$215.00

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Introduction


The book was edited by Professor Javier Garcia-Martinez of Universidad de Alicante, Spain, and Kunhao Li, Project Leader at Rive Technology, USA. The two have broad experience of zeolites and in particular mesoporous zeolites. It is the first in a series and aims to bring to light the fast emerging field of mesoporous materials and their applications. To expand on this, various examples are included which demonstrate that mesoporous materials eliminate diffusion limitations. The book successfully fulfils these aims.

It is composed of 16 chapters that can be divided into six general topics: accessing micropores; nanozeolites and nanomaterials; mesoporous aluminosilicates; hierarchical zeolites; characterisation of mesoporous or hierarchical zeolites; and industrial applications of mesoporous zeolites.

Accessing Micropores

This is mainly covered in Chapter 1 authored by Professor Joaquín Pérez-Pariente et al. of Instituto de Catálisis y Petroleoquímica, Spain. The chapter gives an overview of diffusional limitations experienced by reactants or products in and out of the zeolite micropores. The chapter covers how these limitations can be overcome by three different but complementary strategies. The first two strategies involve reduction of crystal size of already existing material and creating large pores (mesopores) or cracks in the existing crystal. This enables large bulky molecules to access the active sites. The last approach is synthesis of new zeolite materials containing mesopores. Strategies such as controlling nucleation and growth by use of carbon black, blocking agents, synthesis in presence of pore forming agents and post synthesis methods such as removal of specific tetrahedral atoms are also covered in this chapter.
Nanozeolites: Synthesis and Applications

In my view, this is one of the most interesting topics in this book. It is covered in detail in Chapters 2 and 3. Chapter 2 is by Professor Heloise de Oliveira Pastore et al. of Instituto de Química, Brazil, and Universidade Federal de São Carlos, Brazil, while Chapter 3 is by Professor Trong-On Do et al. of Laval University, Canada.

Chapter 2 covers fundamentals, advantages and disadvantages of micrometre and nanometre sized zeolites. In the chapter, the authors detail how changes in chemical composition influence particle size of zeolite A. Among the nanosized zeolites included in this chapter are FAU, EMT, LTA, BEA, pentasil and aluminophosphates/silicoaluminophosphates. A table of the effect of different synthesis conditions on crystal size, with references, is included in this chapter.

Chapter 3 is on progress and strategies in synthesis of nanozeolites. Among them are synthesis from clear solution where the ratio between the rate of nucleation and the rate of growth is controlled. To synthesise nanozeolites, high nucleation rates and stabilisation of nuclear entities is required. The former is dependent on temperature, alkalinity and ageing while the latter is mainly dependent on structure directing agents. Other strategies covered in Chapter 3 include use of growth inhibitor, confined space synthesis and use of organic media. Towards the end of the chapter, the authors cover some of the recent advances in nanozeolites including but not limited to cracking of gas oil.

Mesoporous Aluminosilicates

Chapter 4 discusses efforts put towards improvement of mesoporous aluminosilicates since the discovery of M41S by Mobil scientists (1, 2). A review of various strategies (such as wall thickening, aluminium incorporation, surface silylation and zeolite/mesoporous composite materials) used to improve the properties of mesoporous aluminosilicates, in particular acidity and hydrothermal stability, are detailed in this chapter by Yu Liu of Dow Chemical, USA. Examples of the application of zeolite/mesoporous materials in cracking large hydrocarbons such as n-dodecane and vacuum gas oil (VGO) are included.

Hierarchical Zeolites

Hierarchical zeolites contain both micropores and mesopores. Various strategies of creating hierarchical zeolites are discussed in Chapters 5–9 and Chapter 14. Chapter 5 by Professor David P. Serrano et al. of Instituto IMDEA Energia, Spain, focuses on strategies of synthesising hierarchical zeolites using organosilanes. In this chapter, different types of organosilanes (simple organosilanes, silylated polymers and amphiphile organosilanes) and their effects are discussed.

Perturbation of zeolite crystallisation by addition of polymers or organosilanes is described in Chapter 6 by Professor Feng-Shou Xiao et al. of Zhejiang University, China. The chapter details how sources of silicon and aluminium, reaction conditions and type of template influence the size and location of mesopores, crystal morphology and crystallinity.

Chapter 7 by Zhuopeng Wang et al. of University of Massachusetts Amherst, USA, primarily focuses on synthesis of hierarchical zeolites in a confined space mainly using carbon as the hard template. Crystallisation techniques such as vapour phase transport (VPT) and steam assisted crystallisation (SAC) are also covered in this chapter. A summary of representative framework types synthesised using the confined space method is presented in table form.

While Chapter 7 is on the ‘bottom-up’ strategy, Chapter 8 by Masaru Ogura et al., University of Tokyo, Japan, focuses on ‘top-down’. The chapter also reviews different opinions on the ‘top-down’ mechanism. The main treatment method covered in this chapter is desilication, where the effects of alkali concentration, temperature and duration of treatment are critical to the type of mesopores formed. Although other zeolite types are covered, the main focus is on ZSM-5. In addition to synthetic approaches, the catalytic performances of various desilicated materials are presented.

Figure 1 shows scanning electron microscopy (SEM) of mesoporous mordenite zeolite obtained by de-ironation through heat treatment.

Chapter 9 is by Professor Irina Ivanova et al. of Moscow State University, Russia. Chapter 9 is very similar to Chapter 8 in that it focuses on the ‘top-down’ method, except that after desilication, it covers an extra step of zeolite recrystallisation and the role played by surfactants. The composite product shows improved
hydrothermal stability and catalytic activity compared to the mesoporous aluminosilicates.

While Chapters 5–9 cover the generation of hierarchical zeolites mainly by desilication, Chapter 14 by Professor Jerzy Datka et al. of Jagiellonian University, Poland, explores both desilication and dealumination. It also investigates the nature of the formed acidity including various techniques used for measuring acidity.

**Characterisation of Mesoporous and Hierarchical Zeolites**

Discovery of new materials poses significant challenges with regard to proper characterisation. Characterisation and the challenges associated with mesoporous zeolites are covered in Chapters 11, 12 and 13.

Recent advances in characterisation of mesoporous zeolites by gas adsorption are covered in Chapter 11 by Matthias Thommes et al. of Quantachrome Instruments, USA. In this chapter the choice of adsorptive and the adsorption mechanism are discussed along with data analysis to determine surface area, pore size distribution and porosity. In the summary section, the authors consent that pore size analysis of zeolites and hierarchically structured micro-meso porous materials is a challenge.

Fundamentals of diffusion and diffusion measurements (micro, macro, macro/meso, macro/micro, meso/meso, and meso/micro) including pulsed field gradient nuclear magnetic resonance (PFG-NMR) are explored in Chapter 12 by Professor Jörg Kärger et al. of Universität Leipzig, Germany.

Principles and use of techniques such as SEM, high-resolution transmission electron microscopy (HR-TEM) and transmission electron microscopy (TEM), rotation electron diffraction and electron tomography in analysis of complex structures such as zeolites is discussed in Chapter 13 by Professor Xiadong Zou et al. of Stockholm University, Sweden. An example of the use of electron tomography to quantify mesopores and platinum nanoparticles in mesoporous zeolite Y is included in this chapter.

Fig. 1. Dark field SEM images of mesoporous mordenite zeolite obtained through de-ironation
Industrial Application of Mesoporous Zeolites

Similarly to Chapter 9, Chapter 10 by Professor Javier Garcia-Martinez et al. of Universidad de Alicante, Spain, demonstrates how mesopores can be tuned by using surfactants of different size. The chapter also includes details on the commercialisation of the first mesoporous zeolites in a fluid catalytic cracking unit by Rive Technology. The use of mesoporous zeolites for biomass conversion to fuels and chemicals is reviewed by Professor Kostas S. Triantafyllidis et al. of University of Thessaloniki, Greece, and Chemical Process and Energy Resources Institute (CPERI), Greece, in Chapter 15. Areas covered in this chapter include the use of mesoporous zeolites in catalytic fast pyrolysis of lignocellulosic biomass, cracking of vegetable oils, methanol to hydrocarbons, methanol to dimethyl ether, methanol to gasoline, methanol to olefins and hydrosisomping of biomass derived feeds.

To conclude is Chapter 16 by Roberto Milini of Eni SpA, Italy, on industrial perspectives for mesoporous zeolites.

Summary

This book is interesting and very informative. It broadly covers all areas of mesoporous materials: synthesis, characterisation and application. The book is meant for someone with knowledge of zeolites and microporous materials. In my view, one of the areas not fully addressed in this book is the enormous cost associated with the templating agents and potential loss of materials during desilication or dealumination. A review on what is been done to reduce the costs is also missing.

References


The Reviewer

Charles Kanyi is a Senior Scientist at Johnson Matthey Process Technologies (JMPT), USA. He holds a Bachelor’s and Master’s degree in Science from Moi University, Kenya, and PhD degree in Materials Chemistry from State University of New York at Binghamton, USA. Currently, he is working on several projects among them zeolite and zeolite based catalysts.
The Discoverers of the Isotopes of the Platinum Group of Elements: Update 2016

A deletion of the isotope $^{209}\text{Pt}$ and the inclusion of new isotopes found for Rh and Pd

In the 2012 review (1) the isotope $^{209}\text{Pt}$ was included based on a claim to its discovery by Kurcewiz et al. which was reported in a preprint (2). However when the actual paper was published (3) it was considered that the evidence for $^{209}\text{Pt}$ was unsatisfactory and it was no longer included. Therefore the number of known isotopes for platinum has been amended in Table I. In addition one further isotope each for rhodium and palladium have been identified and are included in Table II and Table III respectively.

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| Table I  Total Number of Isotopes and Mass Ranges Known for Each Platinum Group Element to 2016 |
|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Element | Number of known isotopes | Known mass number ranges |
| Ru | 40 | 85–124 |
| Rh | 39 | 89–127 |
| Pd | 39 | 91–129 |
| Os | 43 | 161–203 |
| Ir | 42 | 164–205 |
| Pt | 43 | 166–208 |

| Table II New Isotope for Rhodium |
|---------------------------------|---------------------------------|---------------------------------|
| Mass Number | Half-life | Decay mode | Year of discovery | Discoverers | Reference |
| 127 | 20 ms | $\beta^-$ | 2015 | Lorusso et al. | 4 |

| Table III New Isotope for Palladium |
|-----------------------------------|---------------------------------|---------------------------------|
| Mass Number | Half-life | Decay mode | Year of discovery | Discoverers | Reference |
| 129 | 31 ms | $\beta^-$ | 2015 | Lorusso et al. | 4 |

$\beta^-$: beta or neutron decay for neutron rich nuclides is the emission of an electron and an anti-electron neutrino caused by a neutron in the nucleus decaying to a proton so the mass number of the daughter nuclide remains the same but the atomic number increases by one.
References


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John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.
Optimisation of the Recrystallisation Annealing Regime of Pd-5Ni Alloy

Using experimental design and statistical analysis to understand the metallurgical properties of palladium alloy for ammonia oxidation catchment gauze applications

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In this paper, changes in the mechanical properties of Pd-5Ni alloy are analysed after recrystallisation annealing in order to determine the optimal conditions for a thermomechanical processing regime for this alloy. The temperature and annealing time were varied and the resulting changes in hardness, tensile strength, relative elongation and proof strength were monitored. By using the simplex-lattice method and analysing experimental data, a fourth degree mathematical model-regression polynomial was defined and isolines of changes in the mechanical properties of the investigated alloys were designed depending on the conditions of heat treatment after rolling.

Introduction

Metal meshes, usually of platinum-rhodium or platinum-rhodium-palladium alloy, are used as ammonia oxidation catalysts for the production of nitric acid. These catalysts are exposed to very rigorous conditions: high temperature, high pressure, gas turbulence and the influence of oxygen, which can lead to rapid destruction of the catalysts and the reduction of their service life. Depending on the operating conditions in the reactor (temperature, pressure and ratio of oxygen to NH₃), losses of platinum group metals (pgms) from the catalytic meshes occur due to the formation of volatile oxides PtO₂, PdO and RhO₂ which are taken away by the gas stream (1, 2). Empirically, these losses are in the range 0.035–0.065 g/tHNO₃ for reactors operating at atmospheric pressure, or 0.32–0.39 g/tHNO₃ for reactors working under high pressure. Most of these losses are irreversible, and only 35–40% of the metal can be recycled by periodic cleaning of gas installations of adhered dust, and replacing and processing of the filter filling.

In order to reduce such incurred losses of platinum metals, due to their high cost (3), manufacturers and researchers in many countries have made significant efforts to develop processes for the efficient capture and recycling of products of oxidation of platinum metals resulting from the production of nitric acid, and...
in other, related, high-temperature catalytic processes (4). One of these methods is the use of Pd catchment gauzes or recovery gauzes arranged in conjunction with conventional Pt catalysts. The role of the Pd catchment gauze is to reduce the volatile PtO$_2$ from the gaseous stream to metal form, and retain the Pt metal on the surface of the Pd.

By placing the Pd catchment gauze just behind the platinum catalysts in the reaction zones, the resulting volatile PtO$_2$ reacts with Pd according to Equation (i):

$$2\text{Pd} + \text{PtO}_2 \rightarrow \text{Pt} + 2\text{PdO}$$  (i)

Due to the higher affinity of Pd for oxygen relative to Pt, when there is contact between PtO$_2$ and Pd there is an exchange of oxygen. The Pt metal is then caught on the surface of the Pd mesh and kept there. Incorporation of Pt in the surface layers of the Pd catchment gauzes is further supported by the oxidation and evaporation of the alloying element in the Pd alloy at the temperature of ammonia oxidation, which assists in the retention of Pt on the Pd catchment gauze. These are the basic assumptions about the mechanism by which the process of capturing Pt using Pd catchment gauzes takes place.

Initially the catchment gauzes were made from palladium-gold alloys (4–6), while more recently palladium-nickel alloys have been used (7). Pd-Au catchment gauzes have a relatively short service life and can withstand only two campaigns before their complete destruction (1). Because of the short lifetime of the Pd-Au gauze and the high cost of both Au and Pd (up to 50% of the investment in Pt), Pd-Ni catchment gauzes are an attractive alternative. Compared to Au, Ni has a lower cost and produces comparable catalytic activity when used as an alloying element with Pd. The mechanical properties of Pd can be significantly improved by alloying with Ni and applying an appropriate thermomechanical treatment regime. Pd-Ni alloys in the solid-state create a continuous series of solid solutions (8).

The aim of this study was to determine the optimal recrystallisation parameters for annealing the Pd-5Ni alloy by testing the dependence of the mechanical and structural properties on the temperature and time of recrystallisation annealing. This will allow alloys of satisfactory mechanical properties to be obtained for further cold plastic processing or rolling. In this paper, the simplex method (9,10) was applied for the selection of an optimal heat treatment regime after rolling, for which previous studies at IRM Bor enabled selection of the factors and their levels (11). The simplex plans by Scheffe (12–14) were used to devise suitable experimental space allowing complex models of the investigated dependencies to be obtained (15–22).

### Experimental

For the preparation of the samples, Pd powder of 99.99% purity and Ni in the form of thin sheets of 99.95% purity were used. The Ni content in the prepared samples was 5% by weight. Starting materials were first compressed on a hydraulic press in order to achieve better compactness of the material, and then the melting and casting of the samples were performed in a medium frequency induction furnace, in a magnesium oxide pot of dimensions $h_1 \times h_2 = 85 \times 80$ mm, $d_1 \times d_2 = 65 \times 55$ mm, under vacuum. The melting point of the Pd-5Ni alloy is 1520ºC. Prior to casting, the batch was overheated between 350–400ºC. To control the composition of the cast alloy an X-ray fluorescence analyser Niton™ XL3t-950 was used. Homogenisation annealing was performed in an electric resistance furnace chamber type LP08 at 900ºC for 30 min. After that, rolling of samples was performed in duo-stand rolls with calibrated rollers of cross-sectional dimension $1.7 \times 1.7$ mm (with 97% reduction) and with intermediate annealing (900ºC, 15 min). Thermal treatment of the Pd-5Ni alloy samples after rolling in the form of a wire consisted of recrystallisation annealing and was performed in accordance with the given regimes (Table II).

The optimisation parameters were Vickers hardness (HV), ultimate tensile strength ($R_m$), yield strength ($R_{0.2}$%), and relative elongation (A). Influential factors are recrystallisation annealing temperature (T) and recrystallisation annealing time ($\tau$). For each combination of factors three repeated readings in a random order were performed. To select the optimum heat treatment conditions after rolling a simplex plan with fifteen experimental points and a fourth degree polynomial for the mathematical model were applied. Hardness measurements were performed on a combined instrument for measuring
the Vickers hardness and Brinell hardness, from WPM (Werkstoffprüfmaschinen), Germany, with a hardness measurement range from 5 to 250 daN. Determination of tensile strength, relative elongation and yield strength (system responses) were performed on an Instron® 1332 materials testing machine of 100 kN. The tubes of test material were clenched by mechanical jaws and stretched at a rate of 10 mm s⁻¹. Before testing all tubes were cut to a length of 150 mm.

Mathematical processing of data obtained using the simplex method was performed with the help of specially developed software in the Delphi programming environment. Using the above software, mathematical models to describe the influence of annealing parameters on the hardness of the Pd-5Ni alloy were obtained. The adequacy of the model was determined on the basis of Student's criteria in control points (12, 13, 19, 20, 22, 23). Examination of the microstructure was performed on samples measuring 1.7 × 1.7 mm, which were prepared according to standard procedure: grinding, polishing (Zentrifugenbau RÖWAG polishing machine) with 0.05 μm Al₂O₃ powder and etched for a few seconds with a solution of 1 g CrO₃ + 20 ml HCl. Optical microscopy was performed on a metallographic microscope Epytip 2 (Carl Zeiss Jena, Germany), at 400× magnification. Changes in grain size with increasing temperature were monitored using the program Image-Pro® Plus for image analysis.

Results and Discussion

The X-ray spectrum of the sample of Pd-5Ni alloy is shown in Figure 1, and the results of the analysis are given in Table I. The results and analysis of the spectrum show that the cast alloy contains 95% Pd and 5% Ni, and hence it can be concluded that there was no loss or contamination of the alloy during casting. Table II shows a matrix of the simplex plan of the experiment with 15 experimental points and heat treatment regimes and the results of the experiment. By analysing the experimental results using specially developed software in the Delphi programming environment,
The dependence of the system response (HV, Rm, Rp0.2%, A) on the input factors (temperature environment, the dependence of the system response and annealing time) was obtained in the form of Equations (ii)–(v):

\[
Y_{HV} = 120.33x_1 + 113x_2 + 87.33x_3 - 14.66x_1x_2 + 58x_1x_3 - 2.26x_2x_3 + 12.453x_1x_2^2 (x_1 - x_2) - 50.667x_1x_3(x_1 - x_3) + 31.28x_2x_3(x_2 - x_3) + 44.453x_1x_2(x_1 - x_2)^2 + 52.587x_1x_3(x_1 - x_3)^2 + 65.947x_2x_3(x_2 - x_3)^2 + 541.520x_1x_2x_3 + 1.653x_1x_2^2x_3 - 797.68x_1x_2x_3^2
\]  
Equation (ii)

\[
Y_{Rm} = 306x_1 + 304x_2 + 296x_3 + 4x_1x_2 - 20x_1x_3 - 8x_2x_3 - 5.33x_1x_2(x_1 - x_2) - 80x_2x_3(x_2 - x_3) + 176x_1x_3(x_1 - x_3) + 213.33x_2x_3(x_2 - x_3)^2 + 576x_1^2x_2x_3 - 368x_1x_2^2x_3 - 613.33x_1x_2x_3^2
\]  
Equation (iii)

\[
Y_A = 34x_1 + 48x_2 + 45x_3 + 24x_1x_2 + 22x_1x_3 - 2x_2x_3 + 69.33x_1x_2(x_1 - x_2) + 50.667x_2x_3(x_2 - x_3) - 40x_1x_3(x_1 - x_3) - 74.667x_1x_2(x_1 - x_2)^2 - 77.33x_1x_3(x_1 - x_3)^2 - 88x_2x_3(x_2 - x_3)^2 - 376x_1^2x_2x_3 + 40x_1x_2^2x_3 + 272x_1x_2x_3^2
\]  
Equation (iv)

\[
Y_{Rp0.2\%} = 120x_1 + 134x_2 + 132x_3 + 12x_1x_2 + 44x_1x_3 - 12x_2x_3 + 18.7x_1x_2(x_1 - x_2) + 10.67x_2x_3(x_2 - x_3) + 144x_1x_3(x_1 - x_3) + 298.67x_1x_2(x_1 - x_2)^2 + 90.67x_1x_3(x_1 - x_3)^2 + 272x_2x_3(x_2 - x_3)^2 + 141.33x_1^2x_2x_3 + 744x_1x_2^2x_3 - 317.33x_1x_2x_3^2
\]  
Equation (v)

To check the adequacy of the selected models the control points \(K_1(0.16; 0.15; 0.69)\) and \(K_2(0.459; 0.166; 0.375)\) were used, where additional tests were performed under the following experimental conditions: \(T_1 = 887.5{}^\circ{}C, \tau_1 = 30\text{ min} \) and \(T_2 = 825{}^\circ{}C, \tau_2 = 27.5\text{ min}\). The analysis showed the adequacy of the fourth degree model for all observed mechanical properties by Student's criteria for the credibility coefficient of 0.995 and 14 levels of freedom in the control points \(t_a(\alpha; K_1) > t_{0.995; 14}\) and \(t_aK_2 < t_{0.995; 14}\). On the basis of these checks it can be claimed with a probability of 99.5% that the adopted mathematical model is adequate and that the model parameters are relevant to the selected heat treatment regime.

Certain mechanical properties are changed variously under the influence of the diffusion processes that take place during annealing (11, 24, 25).

Using Equations (ii)–(v) and specially developed software in the Delphi environment, isoline diagrams of level \(Y_i = f(x_1, x_2, x_3), i = HV, Rm, Rp0.2\%\) were constructed. Isolines represent the set of temperature and time points which give the same values for the optimisation parameters. Changes in the mechanical properties of the investigated alloy correspond to the lines appearing at a given level within the system, depending on the conditions of heat treatment after rolling (Figure 2).

The results of mathematical processing confirm that the changes in mechanical properties (HV, Rm, A, Rp0.2%) of Pd-5Ni alloy at a constant deformation degree of 97% depend strictly on the temperature and annealing time, defined by a fourth degree regression polynomial according to Equations (ii)–(v). Analysis of
the investigation results shows that the alloy annealed at 900°C for 30 min has satisfactory values for hardness (HV = 89.9), ultimate tensile strength (R_m = 308 MPa), yield strength (R_p0.2% = 134 MPa) and elongation (A = 49%), which is a key factor in the application of palladium gauzes for ‘capture’ of platinum at high temperatures.

Figure 3 shows the structural changes which occur during annealing of the Pd-5Ni alloy after cold rolling at a constant deformation degree of 97% depending on the temperature at a constant time (30 min). The polyhedral grain structure characteristic of a plastically deformed and then annealed alloy can be seen.

Recrystallisation grain size depends on the annealing temperature at a constant time (30 min), and as a rule, the higher the annealing temperature the larger the recrystallised grain, at the same degree of deformation (25). This was confirmed by our results (Figure 4).

Based on the investigations performed here, parameters for recrystallisation annealing of Pd-5Ni alloy can easily be set to provide adequate mechanical and structural characteristics for use as a catchment gauze in the catalytic oxidation of ammonia (26–28). For economic and technological reasons the following parameters were chosen as optimal for further plastic
processing: annealing temperature of 900°C, annealing time of 30 min.

Conclusions

This paper describes the application of experimental design and statistical analysis in studying the effects of recrystallisation annealing parameters on the mechanical properties of Pd-5Ni alloy. The simplex method was used to plan experiments examining the impact of changes in process variables (temperature and annealing time) on the mechanical and structural properties of the Pd-5Ni alloy at a constant deformation degree of 97%. A fourth degree empirical mathematical model was defined to describe the process, on which basis the values of HV, Rm, A, Rp0.2% within the selected values of temperature and annealing time could be predicted. The optimal conditions at the recrystallisation annealing were found to be: recrystallisation annealing temperature of 900°C and time of 30 min at which satisfactory values for hardness (HV = 89.94), ultimate tensile strength (Rm = 308 MPa) and yield strength (Rp0.2% = 134 MPa) were achieved at a maximum relative elongation (A = 49%).

The above results could be considered a contribution to the characterisation of Pd-5Ni alloy, and are also of importance for selecting the optimal technology to obtain products based on this alloy. However it should be noted that the above alloy has not yet been sufficiently investigated in terms of the determination of structural and mechanical properties depending on the applied thermomechanical processing regime, and further work is recommended in this area.

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Fig. 3. Microstructure of Pd-5Ni alloy, after rolling and annealing at: a) 820°C; b) 850°C; c) 900°C; and d) 950°C. All magnifications are 400×

Fig. 4. Change in the size of recrystallised grains with temperature for τ = 30 min
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Improvement of Noble Metal Based Photocatalysts by Spray Pyrolysis Processes

A review of progress in photocatalytic materials for water treatment applications

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Oxidation technologies and advanced oxidation processes (AOPs) have been regarded as a competitive method for the remediation of persistent pollutants in water. Among AOPs, the use of photocatalysis has particularly attracted interest in recent decades. However, attempts to improve the efficiency of photocatalysts in terms of both enhanced activity and applicability under visible light have proved challenging. In this context, there is a need for processes able to achieve the synthesis of innovative nanostructured materials meeting these criteria with reproducibility and scalability in mind. The aim of this review is to focus on two themes of interest, namely noble metal based catalysts and spray pyrolysis (SP) processes. Several alternative SP methods have been reported and these will be described. The emphasis is placed on the recent use of SP for the synthesis of noble metal/semiconductor nanomaterials and their enhanced photocatalytic activity. Recent innovations in the design of SP processes and their potential to further improve noble metal-based photocatalysts are also examined. Finally, the possibility of using SP processes as a flexible tool to achieve immobilisation of photocatalysts onto substrates and in reactor for real water treatment application is considered.

1. Introduction

With population growth and economic development, there is an increasing demand for potable water. Because of the scarcity of the resource and new sources of contamination, access to clean water is a major environmental challenge worldwide. Moreover, the presence in water of an emerging class of persistent organic compounds such as pharmaceuticals, personal care products and endocrine disrupters that cannot be decomposed by current water treatment technologies, is a major health concern. In search of affordable and efficient processes for water decontamination, photocatalysis has proven to be a good strategy for the degradation of a large range of organic compounds and microorganisms. A great effort has been dedicated to the development of semiconductor-based photocatalysts over the last few decades. Among others, titania (TiO₂) and zinc oxide (ZnO) show the ability to mineralise organic pollutants, are stable, environmentally friendly and cheap. However, the major limitations of these semiconductors are their inability to absorb visible light and the fast recombination of photogenerated holes (h⁺) and electrons (e⁻) at lattice defects, leading to relatively low quantum efficiency. The improvement of photocatalysts and the design of an efficient catalyst recovery strategy have been reported to be two of the key technical issues that have held back heterogeneous
photocatalysis technology from being implemented at larger scale for water treatment (1).

So far, different strategies have been applied to improve the performance of photocatalysts. These include doping with transition metals (2), anionic doping (3), sensitisation with dye (4), and coupling with carbon nanotubes or graphene (5), low band gap semiconductors (6, 7) or noble metals (8). The latter has been reported as an efficient way to enhance the photocatalytic activity under ultraviolet (UV) light and the resulting materials usually show improved activity towards pollutant degradation compared to the bare semiconductor counterpart (8). Moreover, the ability to absorb visible light by different mechanisms when combined with plasmonic nanoparticles makes these segregated materials attractive for future application. Noble metal supported on semiconductor photocatalysts have been prepared by hydrothermal techniques (9), photodeposition (10), wet impregnation (11), sol-gel (12, 13) and precipitation (14) methods. The production of such supported material has also been carried out by SP processes and this will be the subject of this article.

Hence, the aim of this paper is to update the review recently published by Teoh (15) with a particular focus on: (a) SP-made TiO₂ and to a lesser extent ZnO, combined with noble metals for water application under UV and visible light irradiation; (b) the recent advances in SP processes that may help to develop innovative photocatalysts; and finally (c) the possibility of using SP processes to directly coat substrates with photocatalysts to enable usage in a reactor and offer a practical solution to using this technology in the real world.

2. Spray Pyrolysis Processes

The control of size, chemical phase and phase composition is critical for the design of innovative photocatalysts. SP processes are particularly well suited to produce dried nanostructured materials without requiring post treatment. Many materials including metal oxide nanoparticles, mixed oxides, supported catalysts and doped metal oxides have been produced by SP processes in a very reproducible way (16). As well as allowing access to non-thermodynamic materials, SP processes produce no liquid byproducts, do not require post treatment, are scalable and cost effective. For these reasons, SP processes proved to be excellent methods to produce nanomaterials on a large scale (17–19). The TiO₂ benchmark P25, from Evonik, is a good example of a photocatalyst produced at the industrial scale by vapour-fed aerosol flame synthesis (VAFS). This flame-assisted process consists of feeding a volatile precursor in its gas phase (i.e. titanium tetrachloride (TiCl₄)) in a supported flame that initiates the precursor’s decomposition to nuclei that further grow through surface growth and coalescence to give nanoparticles. However, in many cases, finding a suitable volatile metal precursor can be a limitation. As an alternative, flame-assisted spray pyrolysis (FASP) techniques such as ultrasonic spray pyrolysis (USP) allow this challenge to be addressed. USP consists of a nebuliser used to produce an aerosol of cheap water-soluble precursor, which is then brought to the external flame using a carrier gas. Alternatively to a flame process, a tube furnace can also be used for the combustion of the precursor (20).

In addition to the flame-assisted methods previously described, SP processes include methods that allow the use of a large range of organometallic precursors dissolved in organic solvent. This alternative approach, including flame spray pyrolysis (FSP) (Figure 1), can be described as a self-sustained technique. FSP consists of injecting an organic solution containing metal precursors through a nozzle ignited by a supporting flame fed by a mixture of O₂ and methane or ethylene. The combustion of the solvent allows for the decomposition of the metal precursors and serves as a combustible to sustain the flame. The design of the equipment depends on the application either for particle collection on a glass filter/sock collection system or for the deposition of a nanomaterial on a substrate and more details can be found in existing comprehensive reviews (21, 22).

3. Supported Noble Metals Under Ultraviolet Light

3.1 Theoretical Background

It was reported that photocatalytic performance can be increased by improving the separation of photogenerated charges, hindering charge carrier recombination and facilitating the charge transfer through a heterojunction (23, 24). Deposition of noble metals on a metal oxide semiconductor is a common approach to reach this goal and to further improve quantum efficiency of the photocatalysts. When a hybrid noble metal/semiconductor is irradiated with a UV source and excited by a wavelength of energy above or
equal to the semiconductor’s band gap, electrons from its valence band (VB) are transferred to the conduction band (CB) and then further transferred interfacially to the noble metal deposits, where the electrons are trapped. As illustrated below, noble metal deposits accumulate negative charges from the semiconductor’s CB and Fermi level shift to a more negative potential close to the CB until it reaches equilibrium (Figure 2) (25, 26). This phenomenon results in a better charge separation and an enhancement of the photocatalyst’s performance. The barrier formed at the noble metal/semiconductor interface is known as the Schottky barrier and it is worth noting that the height of the barrier can be influenced by the difference of work function between noble metal and semiconductor. From that point of view, platinum is expected to be the best candidate for electron trapping among noble metals (27, 28).

3.2 Noble Metals on Titania Support

Among the literature, reports on the synthesis of noble metals deposited on metal oxides by SP processes...
can only be found from the last decade with earlier work from Mädler, Stark and Pratsinis on the gold/titania (Au/TiO₂) and gold/silica (Au/SiO₂) systems (29). When tested for photocatalysis application, these materials usually show promising results in terms of performance compared to commercial benchmarks. The mechanism of their formation relies on the fact that the metal oxide support generally nucleates first at high temperature followed by the sequential deposition of the more volatile platinum group metal (pgm) in the flame either by direct nucleation on the semiconductor or by homogenous nucleation followed by deposition as described by Strobel and Pratsinis (Figure 3). This is likely to be applicable to other noble metals due to their high vapour pressure compared to the support materials (30). Teoh et al. reported the FSP synthesis of Pt/TiO₂ with high metal dispersion and tuneable size of Pt deposits by varying the Pt loading. A Pt loading of 0.5 at% appears to be optimum for the mineralisation of sucrose under UVA irradiation and showed better performance compared with the benchmark P25. It was suggested that a lower Pt loading diminishes the number of sites where photogenerated electrons can be efficiently transferred and interact with an electron acceptor in the medium, hence hindering the charge separation and thus the oxidative pathway through photogenerated holes. At higher Pt loadings, in addition to the screening effect of Pt deposits preventing the optimum irradiation of TiO₂, it was suggested that the presence of an increasing amount of negatively charged Pt may improve the recombination of photogenerated holes leaving fewer holes available for photooxidation and hindering photocatalytic activity as a consequence (31). It is worth noting that the formation of nanoparticles in a highly oxidative flame results in nanostructured materials with noble metal deposits in an oxidised state. This was further investigated, as 0.5 at% Pt/TiO₂ was analysed by X-ray photoelectron spectroscopy (XPS) before and after photocatalytic mineralisation of different organic substrates, namely formic acid, phenol and methanol, demonstrating the influence of the Pt oxidation state on the kinetics of the photocatalytic reactions (32).

Tiwari et al. have synthesised Pt/TiO₂ with a setup involving a flame fed with titanium isopropoxide (TTIP) and acetylacetonate-based aerosols and found that the optimum loading for methyl orange degradation in aqueous phase under UVA lies between 0.5 wt% and 1 wt% Pt, which is consistent with the results described above. Interestingly, bare TiO₂ contains a mixture of anatase and rutile, and in this flame-assisted procedure the addition of Pt dopant led to the suppression of the total rutile fraction while in the case of the FSP-made materials presented above, X-ray diffraction (XRD) showed no disappearance of rutile phase with the addition of Pt. The doping of TiO₂ with 0.5 wt% palladium was also investigated and appeared to be detrimental to the photocatalytic activity, the methyl orange degradation rate being even lower compared to bare TiO₂. It was suggested that the low performance of Pd/TiO₂ could be either due to the nature of the dye or to the fact that 0.5 wt% Pd may be above the optimum loading for methyl orange degradation. The oxidation state of Pd may also have an influence but has not been the object of further study. A bimetallic composite 0.5 wt% Pd-Pt/TiO₂ was synthesised and showed an intermediate photocatalytic activity compared to Pd/TiO₂ and Pt/TiO₂ (33).

Recently, an attractive strategy has been employed by Paulauskas et al. to combine doped 0.4 at% Pt/TiO₂ with 14 at% Al and 7 at% Sn to further improve...
the degradation rate of methyl orange. A series of nanocomposites: platinum-aluminium/titania (Pt-Al/TiO₂), platinum-tin/titania (Pt-Sn/TiO₂) and their undoped derivatives, respectively 14 at% Al/TiO₂ and 7 at% Sn/TiO₂, were prepared by FSP. The results showed that among Pt/TiO₂-based photocatalysts, Pt-Sn/TiO₂ shows the highest degradation rates compared to Pt/TiO₂ and the commercially available benchmark P25 (34).

As an alternative to flame assisted methods, Haugen et al. used SP equipment for the atomisation of an aqueous solution of precursors followed by calcination in a tube furnace between 800°C and 1000°C at short residence time to produce TiO₂, Ag/TiO₂ and Au/TiO₂. In some cases, the materials were further calcined for 3 h between 550°C and 900°C. Methylene blue was used to assess the photocatalytic activity under UV light irradiation and the results showed that the as-prepared TiO₂ photocatalysts containing a non-negligible quantity of amorphous TiO₂ show a similar activity to the reference P25. Despite being more crystalline, the calcined materials showed a lower photocatalytic activity. It was suggested that the higher amount of rutile in the as-prepared samples could be responsible for this trend. Interestingly, in this study, no improvement of photocatalytic activity was found in the case of noble metal/TiO₂ materials. It was suggested that the rather large size of Au and Ag crystallites in the calcined materials (20–30 nm and 5 nm respectively) were acting as recombination centres (35).

3.3 Noble Metals on Zinc Oxide Support

Compared to TiO₂, the synthesis and testing of ZnO-based photocatalysts by SP methods has been studied to a lesser extent. Height et al. compared the performance of Ag/ZnO nanomaterials prepared by FSP and wet impregnation methods. On a mass basis, FSP-made nanomaterials showed higher photocatalytic activity toward discolouration of methylene blue under UV light irradiation compared to wet-made materials and the TiO₂ P25 benchmark. For both synthesis methods, a Ag loading of 3 at% was found to be optimal for the conversion of methylene blue. For FSP-made nanomaterial, the photocatalytic performance was increased when the ratio of the liquid precursor feed rate to the O₂ dispersion gas flow rate was highest. A higher liquid to gas ratio increases the flame height and the residence time of the nanomaterial at higher temperatures, thus resulting in materials with fewer crystal defects as supported by XRD and ultraviolet-visible (UV-vis) absorption measurements (36).

Recently, Siriwong et al. synthesised a series of Pd-doped ZnO materials by one-step FSP. Photocatalysts were tested for the degradation of three different substrates under UV light irradiation and the results showed that a loading of 0.5 at% Pd was the optimum for the degradation of methanol, glucose and sucrose (37). Pawinrat, Mekasuwandumrong and Panpranot synthesised Pt/ZnO and Au/ZnO by FSP and tested their activity on the degradation of methylene blue under UVA irradiation. Photoluminescence emission studies showed that the recombination rate of Au/ZnO was lower than for Pt/ZnO; these results were consistent with better photocatalytic performance of Au/ZnO compared to Pt/ZnO. The low performance of the latter was in accordance with the literature and was attributed to the ohmic nature of the contact between Pt and the semiconductor ZnO resulting in the poor ability of Pt deposits to store photogenerated electrons hence to increase electron-hole separation lifetime as occurs in the Pt/TiO₂ system (38).

4. Supported Noble Metals Under Visible Light

4.1 Theoretical Background

In addition to increasing charge carrier separation and improving overall quantum yield, decorating a semiconductor with plasmonic nanoparticles such as Au and Ag is also beneficial for photocatalysis as it allows visible light absorption. Due to the ability of plasmonic noble metals to concentrate and scatter photons, the absorption of TiO₂ can be extended to visible light through localised surface plasmon resonance (LSPR). LSPR is the strong coherent oscillation of the plasmonic particle’s free electrons when in phase with the electric field of incident light. Figure 4 shows an

Fig. 4. Illustration of a localised surface plasmon (Reprinted with permission from (39). Copyright (2003) American Chemical Society)
illustration of LSPR where light interacts with a particle smaller than its wavelength. The resulting localised plasmon oscillates around the particle at a certain frequency (40).

When a plasmonic nanoparticle/semiconductor nanostructure is exposed to visible light, different mechanisms may take place:

(i) the electron transfer between the plasmonic nanoparticle and the conduction band of the semiconductor can be induced by LSPR in a similar mechanism to sensitisation

(ii) when the electronic transfer is diminished due to non-conductive separation between the plasmonic metal and the semiconductor, LSPR may induce an enhancement of the electromagnetic field near the surface of the plasmonic particle that increases the charge carrier formation in the nearby TiO$_2$ region

(iii) the photon’s path length may be increased at the surface of the semiconductor by the scattering of noble metal nanoparticles.

Enhancement of the absorption is influenced by the loading, the size and the shape of the plasmonic particles. An extensive coverage of plasmonic photocatalysis can be found in comprehensive reviews (8, 28, 41).

4.2 Silver and Gold on Titania Support

Compared to coimpregnation and deposition-precipitation techniques, SP processes can provide benefits for the design of supported catalysts both in terms of size distribution and uniformity of deposits (42). This could be an advantage for the design of visible light active photocatalysts. However, to the best of our knowledge, only a limited number of plasmonic photocatalysts made with SP processes have actually been studied under visible light irradiation for the photodegradation of pollutants. A few examples of these materials have however been reported for other applications under visible light.

This includes work undertaken by Gunawan et al. in which FSP-made Ag/TiO$_2$ could be used as a reversible photoswitch for antimicrobial applications. The application relies on control of the oxidation state of silver. Exposure of Ag$^0$ deposits to visible light (>450 nm) allows the electrons to migrate to the TiO$_2$ support through LSPR hence oxidising Ag$^0$ to Ag$^+$. The process is reversible under UV light irradiation (43). This work gives a particular insight into oxidation state and leaching behaviour of FSP-made Ag/TiO$_2$ that is relevant for potential photodegradation applications under visible light irradiation. The leaching of noble metals has been reported in several articles, especially in the case of Ag/TiO$_2$ photocatalysts. This is a matter of concern for sustainable water purification applications since it could be the cause of a loss of photocatalytic performance over time and the release of toxic Ag$^+$ into the water stream (44, 45).

Interestingly, some studies suggest that a combination of both Au and Ag plasmonic metals could show improved stability against surface oxidation and hinder Ag$^+$ leaching. First, Hannemann and coworkers demonstrated by complementary analysis, including extended X-ray absorption fine structure (EXAFS) spectroscopy, that Au and Ag could form alloyed nanoparticles by FSP synthesis. X-ray absorption near edge structure (XANES) spectra could give information on Ag oxidation state and suggested that Ag was slightly more oxidised in the absence of Au (46). In addition, a recent study investigating LSPR and leaching of FSP-made Ag-Au nanoalloys confirmed this trend and showed that Ag$^+$ leaching was minimised with an alloy containing over 50 at% Au (47). The Au-Ag/TiO$_2$ system has been little studied for water application, although a few examples exist in the literature. This includes one study on Au-Ag/TiO$_2$ nanomaterials made by microemulsion that show promising results for the degradation of phenol under visible light irradiation compared to their monometallic counterparts, but there was no mention of potential Ag leaching (48).

These examples show that SP routes have potential for the production of photocatalysts active under visible light irradiation.

5. Modified Flame Spray Pyrolysis Techniques

Progress has also been made toward the development of the FSP technique in order to allow the fine-tuning of size, chemical composition and architecture of the nanostructured materials. Changing the catalyst characteristics would allow for the optimisation of their activity.

5.1 Quench Cooling Technique

It is highly desirable to be able to tune the size and shape of a noble metal on a semiconductor substrate as these parameters greatly influence the absorption of visible light. In the case of plasmonic deposits, the scattering mechanism and the overall photocatalytic activity
may be adjusted in this way. Schulz et al. developed a quench-cooling device to independently tune the TiO₂ support and the deposits of Pt nanoparticles on its surface. The device consists of a ring placed axially around the flame, adjustable to 2 to 12 cm from the burner outlet of a FSP rig (Figure 5(a)). A cooling gas is injected from the ring to quench the flame temperature at an early stage (Figure 5(b)). By tuning the distance between the burner and the quenching ring, it was possible to modulate both the dispersion and the average diameter of the Pt nanoparticles. The benefits are particularly interesting at high Pt loading (up to 10 wt%) since the average Pt diameter is better controlled compared to unquenched experiments (49).

In the work conducted by Tiwari et al., a similar quenching approach to tune the specific surface area of 1 wt% Pt/TiO₂ was investigated. Results show a decrease of the surface area from 88 to 74 m² g⁻¹ when using a quenching ring located at 5 and 10 cm from the burner respectively. Compared to the experiments described above, the same precursor (TTIP) was used as a Ti source but in this latter study, the precursor was introduced in the vapour phase rather than as liquid droplets for FSP. Consequently, the mechanisms of nanoparticle formation, described in Figure 6 (22), may yield different particle characteristics. The authors investigated the influence of the quenching ring position toward the photocatalytic performances. The photocatalysts obtained were assessed under UV irradiation and results show that the rate for methyl orange degradation decreases with the distance at which the quenching ring is located from the burner, the highest rate being when the ring is located at the lowest position (5 cm). The authors demonstrated that this trend originates from the nanomaterials physical properties and showed that by taking surface area into account the modified rate constants were similar (33).

Alternatively, to provide cooling gas, a second injection ring can be used to feed the flame with a volatile precursor to dope the semiconductor or alternatively to achieve a partial reduction by feeding with H₂.

5.2 Routes to Modified Titania

Tuning the band gap of a semiconductor is key to allow a photocatalyst to extend its absorption to the visible light region. However, the introduction of a foreign cationic dopant in the semiconductor framework may act as a recombination centre and hinder photocatalytic activity (50). As an alternative, the synthesis of substoichiometric titania (TiOₓ) which contains oxygen vacancies, VO-Ti³⁺, appears to be a good way to achieve visible light harvesting without including any impurity elements usually required to induce this effect (51). Recently, black and blue coloured defective titania nanomaterials were successfully synthesised using different routes including solvothermal process (52, 53), crystallisation/reduction process (54)
and spark plasma sintering (55). Compared to pristine or commercial TiO<sub>2</sub>, the improvement of the photocatalytic efficiency under visible light irradiation either for the degradation of dyes or for the selective photooxidation of methylcyclohexene to ketones were achieved in every case.

Modified FSP technique can also be run under controlled conditions to produce nanomaterials under rich or lean O<sub>2</sub> environment. It has been demonstrated that by closely controlling the O<sub>2</sub>/N<sub>2</sub> atmosphere around an enclosed flame, the polymorphic anatase/rutile ratio could be finely tuned. In the most anoxic conditions (i.e. sub-stoichiometric O<sub>2</sub> content), oxygen vacancies were induced and promoted the highest content of TiO<sub>2</sub> rutile, up to 94 wt% (56). Using a combination of anoxic conditions and a quench cooling ring, Pratsinis and coworkers demonstrated the possibility of inducing oxygen vacancies and producing blue TiO<sub>2</sub> in one step. These particles showed long-term colour stability suggesting that the defects are located both inside and at the surface of the particles (57, 58). As an alternative to the quench cooling process, Huo et al. synthesised surface doped TiO<sub>2</sub> with Ti<sup>3+</sup> by reducing the particle surface in situ. In a one-step VAFS process, TiCl<sub>4</sub> was brought to the flame with a N<sub>2</sub> flow and was ignited by a supported flame; a second injection ring placed 15 cm above the nozzle introduced H<sub>2</sub> above the flame to generate reduced Ti<sup>3+</sup> near the surface. The resulting blue titania showed enhanced photocatalytic activity under visible light irradiation compared to P25 and pristine TiO<sub>2</sub> (59). However, the stability over time of such a reduced surface could be of concern for practical applications.

Another approach involving noble metal and taking advantage of the ‘strong metal-support interaction’ (SMSI (60)) effect has been recently undertaken
by Fujiwara et al. to produce sub-stoichiometric AgTiO$_2$-TiO$_x$ by FSP in a single step under low oxidative flame conditions. The resulting ‘black titania’ consists of the distorted crystalline TiO$_x$ phases (Ti$_4$O$_7$ and Ti$_3$O$_5$) on Ag nanoparticles supported on TiO$_2$. According to the authors these materials were obtained as a result of fine control of the O$_2$ flow against precursor feed rate and the presence of a large amount of intermediate combustion products during the synthesis, allowing the reduction of TiO$_2$ to TiO$_x$. The SMSI between Ag and TiO$_2$ induces the formation of a TiO$_x$ overlayer that covers, at least partially, the Ag nanoparticles. Interestingly, the plasmonic resonance band due to Ag$^0$ could not be observed by diffuse reflectance absorption and this was attributed to the SMSI suggesting that the contribution of the plasmonic nanoparticle is minimal. Consequently, improved visible light absorption and photocatalytic activity against Cr$^{6+}$ reduction and methylene blue degradation were attributed to TiO$_x$ at the surface of Ag (61).

5.3 Anionic Doping by Flame Spray Pyrolysis

The doping of TiO$_2$ with non-metallic elements, such as fluorine and sulfur, is of great interest since it was reported to hinder charge carrier recombination and to increase electron lifetime hence improving the photocatalytic activity of TiO$_2$-based material (3, 62–67). Moreover, nitrogen doping can enhance the absorption of visible light (68–70). Common wet chemistry methods for anionic doping make use of post thermal treatment that affects chemical properties and specific surface area (SSA) (71). In addition, reproducibility is a matter of concern. FSP can achieve anionic doping in one step either by direct injection or by the use of a second injection ring. As an example, Jiang, Scott and Amal reported the F-doping of TiO$_2$ by direct injection of F and titanium precursors by FSP. An enhancement of photocatalytic activity toward degradation of acetaldehyde in the gas phase under UV irradiation was reported (72). Recently, Chiarello et al. co-doped Pt/TiO$_2$ with F in a single step also by direct injection of precursors. Compared to its F-free counterpart, the resulting F-doped material appears to be more efficient to photocatalytically produce H$_2$ from methanol under UV irradiation. It is worth noting that in this particular case, the ideal amount of F is 5 at% and an increase above 10% is detrimental to the photocatalytic activity due to the formation of structural defects improving charge carrier recombination (73). Due to the high enthalpy of the flame and the fast reaction rate, doping with nitrogen or sulfur precursor is difficult to achieve by direct injection as the dopant element is likely to be oxidised to nitrogen oxides (NOx) and sulfur oxides (SOx). It is therefore desirable to introduce the precursor downstream at a greater distance from the burner where the temperature is lower according to the temperature profile of a FSP unquenched flame (Figure 5) (49). With the aim of achieving the preparation of nitrogen-doped TiO$_2$ by FSP in a single step, Huo et al. first produced TiO$_2$ by FSP and introduced a solution of ammonia above the flame by means of a spray nozzle (Figure 7). The resulting material consists mostly of the anatase polymorph (90.8%) and XPS results suggest that the presence of nitrogen is due to the replacement of oxygen atoms by nitrogen near the TiO$_2$ surface. The introduction of nitrogen increases the visible light absorption as shown by UV-vis spectroscopy. This material was not tested for water application but the study of dye sensitised solar cell (DSC) performance demonstrates a decrease in the charge recombination rate for the anionic doped TiO$_2$ (74).

These engineering changes to the flame spray process have shown that complex materials can be obtained in one step yielding superior activity and
demonstrating the importance of the technique to deliver unique catalysts. Further complexity to the process was developed with the use of two separate nozzles to bring more flexibility to FSP and to control at which steps of nucleation or growth a noble metal can encounter the metal oxide semiconductor in the flame.

5.4 Double Flame Spray Pyrolysis

Even better control of size and chemical composition of a noble metal deposit on a support can be achieved by spraying two solutions of precursors in two separate FSP nozzles. Complex heterostructures such as platinum/barium/alumina and cobalt/molybdenum/alumina can also be obtained in this way (Figure 8) (75, 76). The technique, known as double FSP, allows the particle growth of the catalyst or material components to be individually tuned, and mixing to be controlled at different stages by adjusting the geometry and precursor mixtures for each individual nozzle. In the Pt/Ba/Al2O3 system, the location of Pt and Ba deposits on the Al2O3 support are crucial factors for NOx storage-reduction (NSR) and a double nozzle introduces greater flexibility for the design of such a catalyst. Indeed, the use of a single nozzle leads to the dispersion of amorphous Ba material throughout Al2O3 (Figure 9(a)), while the use of two nozzles allows the formation of both Al2O3 and Ba species in their respective flames before mixing occurs, thus leading to the synthesis of the desired crystalline barium carbonate (BaCO3) dispersed on Al2O3 nanoparticles (Figure 9(b)). In addition, it was demonstrated that the internozzle distance has a strong impact both on the amount of Ba in the form of BaCO3 and on the Pt dispersion as both values decrease with decreasing internozzle distance due to the influence of the second flame’s heat contribution at shorter distance (65).

A recent study focused specifically on the impact of the nozzle arrangement. When there is large spacing between nozzles (20 cm) simulation and Fourier transform infrared (FTIR) measurements of the temperature profile along the flame axis show that there is no increase in the flame temperature either close to the burner or at the intersection of both flames, suggesting that the temperature profile is similar to that of a single flame. On the other hand, when the distance decreases to 10 cm, the temperature increases by up to 300 K compared to a single flame configuration possibly due to a decrease of the effect of cooling by the surrounding air at the point of intersection. However, according to XRD results, the increase in the flame temperature has no effect on the crystallinity and anatase/rutile ratio of titania.

H2 chemisorption measurements show that the dispersion of Pt deposits is lowered by the double flame arrangement compared to direct injection of both precursors in a single flame. This work clearly emphasises the importance of aerosol mixing in the synthesis of the desired noble metal supported on metal oxide nanostructured material (77). From a design of photocatalyst point of view, the advantage of double FSP lies in the possibility to tune the TiO2 physicochemical properties in a separate flame without affecting the size and the dispersion of Pt deposits on the support.

6. Designing Immobilised Photocatalysts

Many experimental studies of photocatalysis reported in the literature are slurry-based whereby a TiO2 based catalyst is suspended in an aqueous media to be tested for the photodegradation of pollutants under a radiation source. For large scale applications, the design of photoreactors for slurry and immobilised systems has been the subject of various papers and reviews (1, 78–80). Although advances in slurry-based reactors have been reported (81), the post separation difficulties associated with the powder form of the TiO2 catalyst from the treated water often remains a challenge. To that effect, various methods have been employed to immobilise the photocatalysts and many techniques have been used to form thin films onto a wide range of substrates including sol-gel, chemical
vapour deposition, sputtering, pulsed laser deposition, electrospray deposition and SP (82–94).

6.1 Flame Spray Pyrolysis Deposition

One recent review summarises the methods for the preparation of nanoscale TiO₂ films for water remediation applications (95). FSP is the method of interest in this review. This technique allows a flexible and scalable process for synthesis and deposition of thick nanostructured coatings on large surfaces in a very short time. The reagents are pyrolysed prior to deposition onto the substrate. The precursors are dissolved or suspended in a liquid medium and sprayed by gas or ultrasonic assisted means. The evaporation and decomposition of the reagent solutions are carried out either by self-sustained spray combustion with an organic based solution ignited by a pilot flame or, for an aqueous based solution, an external heat source such as a H₂ flame is supplied. The products from such processes are often collected as powders although there are also reports on their direct deposition onto a wide range of substrates (96, 97).

The chemical (98) and mechanical strength of such films in the reactor environment is critical for ‘real-life’ applications. Direct FSP deposition tends to yield low mechanical stability films; however in situ film annealing with an impinging flame produced much improved strength (99, 100). Alternatively the substrate may be heated during the deposition to provide a degree of annealing and thus mechanical strength (101). Depending on the substrate temperature, a porous film is either preserved or collapses into more compact structures by sintering (102). A modification of the FSP process was also reported recently in which it was coupled with supersonic expansion to allow deposition under mild conditions, avoid a high substrate temperature and obtain a coherent film (103).

A small number of reports have been found regarding thin films containing noble metals and these are reviewed below. Keskinen et al. reported the H₂/O₂ FASP of TiO₂-Ag thin film on steel and glass plates. A range of flame to substrate distances and deposition times were studied together with subsequent deposition of TiO₂ and Ag or direct deposition of both components at once. Analysis revealed that metallic Ag is highly enriched and sintered on the surface of the TiO₂ crystallite in the two-step method compared to the one-step method which yielded more dispersed discrete Ag nanoparticles. The TiO₂ films were made of mostly anatase and the crystallite size was in the region of 10 nm. Grain size decreased with Ag doping. The films were tested for the photodegradation of stearic acid. The Ag-TiO₂ film prepared in a single step showed a higher value of the formal quantum efficiency (FQE) compared to TiO₂. The films were then wiped and retested. The activity dropped dramatically and this was associated with removal of the powder demonstrating the low mechanical strength of such a deposition technique unless some annealing.

Fig. 9. Transmission electron microscopy (TEM) pictures of Pt/Ba/Al₂O₃ made with: (a) one nozzle; (b) two nozzles. The red areas indicate the presence of Ba (Reprinted with permission from (75). Copyright (2006) American Chemical Society)
treatment is carried out, as described in the previous paragraph. After removing the loose particles, the thin film produced closest to the nozzle showed the highest activity. According to the authors, the shorter collection distance during deposition might have made the particles more adherent to the substrate as the film had been exposed to a higher temperature (104).

Mädler et al. reported the formation of a Pt-SnO2 thin film by FSP of Pt and Sn precursors directly deposited onto Al2O3 sensor substrates by thermophoresis. They describe the advantage of using this technique over other deposition methods since it can deliver one-step high-temperature synthesis of single or doped materials, defined as functionalised and without the need for post-annealing as in conventional SP.

The films were described as porous (up to 98% porosity) with tin oxide grain size ~10 nm. The thickness of the films could be varied from 9 to 40 μm using different deposition times without affecting the high porosity. Pt doping did not affect the SnO2 grain size, crystallinity or the porous film structure. These films were tested as CO sensors (105).

Thybo et al. flame sprayed a metal precursor solution made of gold-triphenylphosphine nitrate and Ti-tetraisopropoxide in a mixture of tetrahydrofuran and isooctane to produce a 1 wt% Au/TiO2 catalyst, which was directly deposited onto a range of substrates usually used in the fabrication of microfluidic reactors, including Si, Ti, Al, Si3N4 and H:Si. The substrate holder was cooled at different temperatures and this seemed to influence the deposition rate. Photolithography was used to make patterns with a resolution better than 100 μm, indicating that the flame spray technique is suitable for the functionalisation of micron sized channels used in microfluidic systems. An optimal nozzle to support distance was determined to allow uniform radial deposition of catalyst onto the support.

The surface area of the films was about 350 m² g⁻¹; higher than those obtained from powders collected on a filter. This is most likely due to the quenching of the particles deposited nearer the tip of the flame on a cooled substrate which would reduce the particle collisions and coalescence. The adhesion of films was not quantitatively determined and it is difficult to ascertain the actual strength of the bond of the thin films onto the substrates. The catalyst coated substrate incorporated into a microfluidic system was tested in situ for the gas phase oxidation of CO to CO2 (106).

This last example shows that FSP could be an efficient method to prepare reactors which could be adapted to be illuminated with an appropriate light source and used for the continuous decontamination of water wastes.

### 6.2 Spray Pyrolysis Deposition

An alternative process to FSP is the SP method which is a versatile low cost technique that also enables deposition onto large areas. A liquid is atomised by gas, ultrasonic or electrostatic means. The formed droplets travel to the substrate during which time the solvent may evaporate. Once the shrinking droplets reach the surface of the hot substrate, the droplets undergo pyrolytic decomposition. The volatile byproducts and solvents escape in the vapour phase and sintering and crystallisation of the clusters of crystallites yield a film. There are many parameters controlling the quality of the thin films and these are summarised in reviews (107, 108). For noble metal containing thin films prepared by this method, literature reports have been found to include either simultaneous deposition or subsequent deposition of the semiconductor and the noble metal (109). These are reported for other usage than photocatalysis for degradation of water pollutants; however they are introduced in this review as they may be a good source of interesting materials for photodegradation applications. Tarwal and Patil prepared Au-ZnO thin films onto indium tin oxide (ITO) coated glass substrates by spraying an aqueous solution of silver nitrate and zinc acetate together onto the pre-heated substrate at 450°C. Upon addition of Ag at various loadings, the thin films become generally more compact and uniform with smaller crystallites. The authors describe the optical characteristics of the thin films using UV-vis spectroscopy with a band edge ~380 nm for pure ZnO and the presence of an absorption peak within the range 530–570 nm due to the presence of Ag nanoparticles. The transmittance is somewhat decreased in the films which contain Ag, possibly due to grain boundary scattering. The photoelectrochemical properties of the thin films were studied and improvements in performance of the Ag-ZnO thin film over that of pure ZnO were attributed to surface plasmon resonance enhanced absorption phenomena (110).

Mohite and coworkers developed Au-doped TiO2 thin films by spraying non-aqueous based solutions of Au and Ti onto a heated substrate at 450°C. The Au doping was varied from 1 to 4 at%. The process parameters and optimum Au doping were determined using photoelectrochemical methods. The Au doped...
The refractive index of the TiO$_2$ matrix (113). These to 620 nm. This was associated with the increase in shift of the surface plasmon resonance band from 570 size of the Au nanoparticles.

The annealing at 400ºC has a minor in annealed at 400ºC and no loss of Au was observed. The thin temperature of 400ºC. The thin components directly onto a heated substrate. The Au content in the thin TiO$_2$ and no Au was detected in increasing deposition temperature from 260 to 300ºC and interestingly, the [Au]/[Ti] ratio decreases with the incorporation of Au in the TiO$_2$ matrix.

The degradation effect on benzoic acid was claimed to be 49% higher in 3 at% Au-doped TiO$_2$ than in the pure TiO$_2$ thin film photoelectrodes, although no data was presented for these. The enhanced photocatalytic activity was attributed to the widening of the response of the photocatalyst into the visible region as a result of Au doping. It was also reported that Au doped TiO$_2$ could be reused for five cycles of experiments without the need for a post-treatment while the degradation efficiency was retained (111).

Acik et al. used a preparation in which they first deposited the TiO$_2$ by a sol-gel chemical spray pyrolysis method whereby a solution of titanium(IV) isopropoxide and acetylacetone in ethanol was pulsed onto the preheated glass substrates at a growth temperature of 400ºC.

Au nanoparticles were then formed by spin coating a solution of chloroauric acid (HAuCl$_4$) onto the TiO$_2$ films; the resulting composites were then dried and finally annealed. The particle size of the Au particles was found to increase with increasing Au concentration. The TiO$_2$ films were about 120 nm in thickness and made of a mixture of amorphous and crystalline anatase. The authors planned to adapt the preparation of these Au nanoparticles TiO$_2$ thin films for thin plasmonic coatings for photovoltaic applications (112).

The same authors also described more recently the preparation of Au doped thin TiO$_2$ films by spraying both components directly onto a heated substrate. The Au content in the thin films was determined and interestingly, the [Au]/[Ti] ratio decreases with increasing deposition temperature from 260 to 300ºC and no Au was detected in films prepared at deposition temperature of 400ºC. The thin films were finally annealed at 400ºC and no loss of Au was observed. The annealing at 400ºC has a minor influence on the size of the Au nanoparticles.

The UV-vis spectra were studied and showed a red shift of the surface plasmon resonance band from 570 to 620 nm. This was associated with the increase in the refractive index of the TiO$_2$ matrix (113). These coatings could be of interest for photocatalysis but were not tested for this particular application.

It is clear from this section that interesting noble metal containing materials and thin films can be developed. However, further work is needed to investigate the adhesion and lifetime of these thin films for the demanding environment of ‘real life’ applications.

7. Conclusion

Implementation of photocatalysis for water treatment is challenging as it requires the design of robust and efficient photocatalysts both in terms of photocatalytic activity and in the ability to absorb a wide range of light. SP processes can address issues in terms of cost-effective access to defect-free, finely tuned catalysts at a large scale, the economic considerations being mostly dependent on the cost of the precursors. The self-sustained method, FSP, is more versatile because a wider range of precursors can be used to deliver nanostructured photocatalysts. In addition, FSP has recently been the object of exciting engineering developments which bring even more possibilities such as co-doping, direct anionic doping and separate tuning of metal oxide substrate and noble metal deposits.

Overall, there is great potential for SP-made noble metal based photocatalysts which offer improved activity under UV irradiation compared to bare TiO$_2$ counterparts as well as absorption of visible light via the plasmonic effect. However, the photocatalytic activity is also influenced by a set of parameters such as particle size, polymorph ratio, crystallinity, noble metal content and surface chemistry. More insights into the complex influence of these parameters will have to be gained to design improved noble metal/metal oxide photocatalysts in a rational way. SP processes could ultimately combine the ability to make complex composites and to directly deposit these onto suitable substrates resulting in a very efficient way of preparing photocatalytic components for reactors. As this review has highlighted, very little testing on FSP made thin films has been carried out as yet for water depollution and key characteristics such as film adhesion must be further investigated to provide durable composites for this application.

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12th International Conference on Materials Chemistry

Highlights of materials chemistry research

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Materials chemistry is concerned with establishing connections between structure, properties, processability and performance of molecular materials, including organic compounds and polymers, supramolecular architectures and nanoporous substances. Encompassed within this diverse field are molecular magnets, graphene, optoelectronic devices, artificial photosynthesis, chemical sensors, speciality polymers, fluorescent labels, functional membranes, composite conjugated hybrids and molecular sieves. The field relies heavily on sophisticated organic synthesis but readily embraces computational chemistry in order to delve more deeply into the properties of the materials. The topic provides an important interface between atomic, molecular and supramolecular behaviour and the functions of the substance under examination. All manner of molecular materials are considered, ranging from thin films to organogels to solids with microscopic cavities. The 12th International Conference on Materials Chemistry was held between 20th–23rd July 2015 at the University of York, UK, and covered the full range of topics, with six plenary lectures supported by twenty-four keynote lectures and over a hundred invited or contributed talks (1). In addition, some 370 posters were presented. The conference was co-chaired by Duncan Bruce (University of York) and Dermot O’Hare (University of Oxford, UK).

Platinum Group Metals

 Materials chemistry relies heavily on the synthesis of new molecular building blocks, mostly organic or organometallic compounds equipped with particular functions. A vast array of such substances was reported during the conference, a large fraction of which required the use of platinum, palladium or rhodium catalysts for the key assemblage steps. Most notably, homogeneous Pd catalysts underpinned the construction of new molecular architectures based on Heck or Suzuki reactions, Negishi or Sonogashira coupling, Stille reactions or Buchwald-Hartwig amination. Cyclisation reactions, catalysed by Pt and utilising new alkyne derivatives, provided easy access to routes to a plethora of novel structures possessing advanced properties. In addition, ruthenium and iridium complexes were used extensively to generate triplet emitters and/or photocatalysts. In sessions covering progress in artificial photosynthesis, Pt- and Ru-based reagents proved to be the most effective catalysts for H2 and O2 liberation from water. A common theme running throughout the conference was that, while the properties and functions of the new materials were described in detail, the essential chemistry leading to their synthesis remained in the background. Thus, the
platinum group metals (pgms) were less prominent than would have been the case if the main focus had concerned synthesis.

Even so, the pgms made numerous key contributions to the conference. Among the many excellent presentations, we draw attention to the newly developed Pt- and Ir-containing multimetallic triplet emitters reported by Gareth Williams et al. (Durham University, UK). These compounds are based on cyclometallated Ir(III) and Pt(II) complexes and important differences in the recorded photophysical properties are noted between mononuclear and multinuclear species (Figure 1). Such materials have applications in organic light-emitting diodes (OLED) and bioimaging. Somewhat related multiple chromophoric assemblies were reported by Anthony Harriman and Raymond Ziessel (Newcastle University, UK), with the main emphasis being placed on the development of artificial light-harvesting arrays (Figure 2). The use of Ru(II) complexes as photosensitisers for the visible light induced oxidation of water was reported by Dominic Walsh et al. (University of Bath, UK). In this latter study, the oxygen-evolving catalysts were formed from manganese dioxide (MnO₂) and cobalt oxide (CoOₓ). High rates of water oxidation were described by Richard Walton (University of Warwick, UK) using novel forms of ruthenium(IV) oxide (RuO₂) and iridium(IV) oxide (IrO₂).
These catalysts were employed in the form of mixed-metal pyrochlores and have possible applications in water electrolyzers. Photochemical water oxidation was reported by Borbala Kiss et al. (University of Liverpool, UK). The active substrate was formed by Rh substitution into the yttrium titanate (Y₂Ti₂O₇) pyrochlore and it was noted that oxygen evolution rivalled that observed from tungsten trioxide (WO₃) but with much improved light harvesting capability. Despite the enormous effort expended on the search for new oxygen-evolving catalysts, it is clear that the optimum performance is derived from RuO₂ and IrO₂ based materials.

Interesting results were reported by Richard Baker et al. (University of St Andrews, UK) regarding the preparation of Pd-based catalysts for methanol reforming. Here, the support was a high surface area, nanostructured ceria while the adsorbate was Pd or PdO. In certain cases, samarium was also doped into the ceria support. These materials appear to exhibit impressive performance for both methane combustion and alcohol reforming under relatively mild conditions. The synthesis of Pt-functionalised tin dioxide (SnO₂) sheets for propan-2-ol gas detection was described by Igor Djerdj (Rudjer Boskovic Institute, Croatia).

### Soft Materials

Photoresponsive soft materials were described by Yann Molard et al. (University of Rennes 1, France) and by Etienne Borré et al. (University of Strasbourg, France). Such materials, especially when engineered in the form of organogels, could have important applications in luminescence-based technologies. Incorporating the pgms into these soft materials is not a straightforward procedure but could lead to novel matrices with useful optoelectronic applications. Likewise, Pt(II) and Pd(II) ions can be used to assemble metallo-supramolecular structures with interesting optical properties. Used in the form of a gel, these compounds give rise to stimuli-responsive systems with sensing properties. In fact, this is a particularly active research field, fuelled by the recognition that the key features of organogels have not been adequately exploited to date. The presence of certain pgms switches on the possibility for luminescence sensing, such as the in situ detection of molecular oxygen. Extension of Pt(II)-based ensembles into polymeric matrices was considered by Kevin Chan et al. (The University of Hong Kong, China), with particular reference to electronic energy transfer processes.

The photophysical properties of such Pt(III) polyynes can be modulated by incorporating an azobenzene spacer into the conjugated ligand, as illustrated by Raya Al-Balushi and Muhammad Khan (Sultan Qaboos University, Oman). When substituted with fullerenes, these materials could provide improved performance of organic photocells. Replacing Pt(II) with Ir(III) leads to marked changes in the luminescence properties, as described by Ruth Daniels et al. (Northumbria University, UK), while mixed Pt(II)-Ir(III) complexes favour intramolecular triplet energy transfer.

### Photochemical Dissociation of Water

The possible generation of a useful fuel via the photochemical dissociation of water continues to attract attention. One of the tried-and-tested methodologies for H₂ generation involves the ultraviolet (UV)-photolysis of titanium dioxide (TiO₂) coated with deposits of Pt. This system has been around for more than four decades but new results were presented by Greta Haselmann et al. (University of Münster, Germany). Here, the Pt deposit plays the key role of catalyst for proton reduction (Figure 3). Related work was presented by Michael Nolan, Alexander Cowan and Dave Adams (University of Liverpool) and concerned the replacement of the TiO₂ semiconductor with photoconductive perylene bisimide gelators.

![Fig. 3. Typical colloidal particle proposed for photochemical dissociation of water into hydrogen and oxygen.](http://dx.doi.org/10.1595/205651316X689954)
Conclusion

Overall, the meeting was a huge success. The venue was excellent, access to lecture rooms was easy, and the large number of delegates catered for in a relaxed but competent manner. Poster sessions were well organised and disciplined. The plenary lectures were outstanding.

References


The Reviewer

Anthony Harriman started his career in artificial photosynthesis at the Royal Institution in London, UK, in 1974, working under Sir George Porter. He spent a total of 14 years at the Royal Institution, including terms as Dewar Research Fellow, 1977–1988, and Assistant Director of the Davy-Faraday Research Laboratory, 1982–1988. He moved to the University of Texas at Austin, USA, in 1988 to become Director of the Center for Fast Kinetics Research. This was followed by a short stay at the Université Louis Pasteur in Strasbourg, France. In 1999, he took up the position of Professor of Physical Chemistry at Newcastle University, UK. He has maintained a strong interest in artificial photosynthesis. Among his many awards are the Corday-Morgan Medal and Prize, 1984, the first Prix Grammaticakis-Neumann en Photochimie, 1985, and the RSC Chemical Dynamics Award, 2011. He has published more than 400 papers in the areas of molecular photophysics, artificial photosynthesis and electron/energy transfer.
Uranium Remediation by Ion Exchange and Sorption Methods: A Critical Review

Various types of solid phase sorbents are studied and evaluated

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The solid phase materials or sorbents applied to the removal of uranium from industrial waste streams and surface waters are reviewed. The speciation of the element in the environment is discussed. A series of examples on uranium remediation from the recent literature using the different kinds of solid phase sorbents are reviewed in detail and evaluated. The criteria for making the best choice of ion exchanger are discussed with suggestions for further evaluation of the described technologies.

1. Introduction
1.1 General Background on the Element

As the world’s consumption of energy increases there has been an increased interest in nuclear energy. Uranium is one of the most common elements used in nuclear reactors as well as in weapons and other military uses. It is the heaviest and most abundant naturally occurring radioactive element, making up 2.4 mg kg\(^{-1}\) of the earth’s crust. It can be easily dissolved, transported and precipitated within ground and surface waters by slight changes in the environment. With half-lives of millions to billions of years, uranium atoms slowly break down to a host of radioactive byproducts: thorium-230, radium-226, radon-222 and the radon daughters: lead-210 and polonium-210 (1, 2). For uranium to be used as an energy source, the ore must be enriched to obtain higher concentrations of a particular isotope, \(^{235}\text{U}\). \(^{235}\text{U}\) is fissionable and releases a large amount of energy in the form of heat but also produces large amounts of radioactive waste. Currently, the spent uranium can only be stored, reprocessed or disposed of underground (3).

\(\text{U(IV)}\) is stable in reducing environments, is slightly soluble and is the least mobile form of uranium. Uraninite (\(\text{UO}_2^{2+}\)) is the most common reduced mineral species and is the main ore mineral in many uranium deposits (2). \(\text{U(VI)}\) is stable in oxidising environments and its compounds are the most soluble and therefore the most mobile (4, 5). It can also form complexes with hydroxides, carbonates, sulfates and phosphates (5). Therefore, in the presence of oxygen \(\text{U(IV)}\) is oxidised to \(\text{U(VI)}\) which allows the uranium to dissolve in water as the uranyl cation (\(\text{UO}_2^{2+}\)). The dissolution of uraninite is shown in Equation (i).

\[
2\text{UO}_2(s) + 4\text{H}^+(aq) + \text{O}_2(g) \rightarrow 2\text{UO}_2^{2+}(aq) + 2\text{H}_2\text{O}(l)
\] (i)
1.2 Uranium Speciation

Recovery of uranium from surface and ground water waste streams depends strongly on the type of uranium species in solution. Determining the distribution of these species is a complex analytical problem and various extraction techniques are required to determine speciation (6–8). These species can be in the form of colloids or dissolved ions. Extraction is therefore not an ideal method for determining uranium speciation because the process can change the original species present (8). In aqueous environments uranium speciation can be determined by computational modelling and analytically. However, analytical methods remain to be improved. Therefore much of the speciation of uranium is determined by thermodynamic speciation modelling that uses the equilibrium constants or the Gibbs free-equation to arrive at species distribution (8). We present here three Eh-pH diagrams that illustrate the variability of speciation under different environmental conditions.

The speciation diagram for uranium where the total [U] = 1 M is shown in Figure 1 (9). In a reducing environment the major species in solution is neutral UO$_2$ over a wide range of pH, making ion exchange useless under these conditions as a method of uranium recovery. This occurs in humic soils. Under oxidising conditions, as in surface waters, the uranyl cation, UO$_2^{2+}$, is predominant only at very low pH and would be an important species in acid mine drainage, accompanied by hydroxide-bridged cationic uranium cluster species. At higher pH hydrolysis of uranyl leads to the formation of neutral oxo-hydroxo-species such as UO$_2$(OH)$_2$ (Figure 1). Thus in the absence of other coordinating ions ion exchange would be limited for uranium remediation.

At low total [U] the speciation changes drastically. The UO$_2^{2+}$ along with crystalline U$_4$O$_9$ are the major species in an oxidising environment up to about pH = 5.5 (Figure 2) (10, 11). Above this pH neutral and anionic hydroxyl complexes are the major species and in reducing environments UO$_2$ is again the major species. Thus at low [U] the uranyl cation becomes more dominant making cation exchange more useful in the absence of other ligands such as sulfate and carbonate.

In air, with carbon dioxide concentrations of 0.3% the picture changes again. UO$_2^{2+}$ is still the dominant species up to about pH = 5, but above pH = 7 anionic carbonate complexes become important, making anion exchange a viable option (Figure 3) (12). The exceptional stability of these carbonate complexes makes their formation favourable over a wide range of concentrations such as those referred to in Figures 1 and 2. Modelling of these uranium solutions suggests that under reducing conditions UO$_2$ exists in its hydrated form, shown as U(OH)$_4$ in Figure 3.

To summarise, because the UO$_2^{2+}$ is a strong Lewis acid it can complex with many different compounds via oxygen atoms especially in natural waters. At dilute concentrations (<$10^{-6}$ M) UO$_2$(OH)$^+$ is the dominant hydrolysed species and above this concentration a mixture of UO$_2$(OH)$_2$, U$_4$O$_9$(OH)$_4$ and UO$_2$(OH)$_5$ forms are also observed. In seawater, uranium exists in...
the form of carbonate complexes, such as $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)^-$ (12).

In consideration of the discussion above it is imperative that a detailed study of the environment must be taken into account when considering a U remediation project. This type of sensitivity is not peculiar to U, but is also important for other metals in their higher oxidation states such as manganese, vanadium, molybdenum and tungsten. It should be noted here that that acid mine drainage in general is often characterised by high sulfate which complexes with uranium. These are discussed in Section 2.1. Although 1 M total $[\text{U}]$ is never found in waste streams, comparison of Figure 1 with Figures 2 and 3 provides a view towards the sensitivity of uranium to changes in concentration.

### 2. Examples of Uranium Recovery with Polymer Based Adsorbents

Ion exchange resins based on organic polymers, specifically polystyrene, are by far the most widely used solid phase sorbents for remediation and recovery of toxic and valuable metals. The functional groups used for uranium are varied and include amidoxime on polystyrene and on acrylic based copolymers and fibres (13–15). Most recently, magnetic core-shell particles coated with functionalised polymers have been employed for uranium recovery (16, 17). The three case studies discussed here use commercially available polystyrene resins and focus on the three types of uranium streams encountered in the industries associated with uranium mining and processing: (i) ore processing; (ii) recovery of uranium from industrial waste; (iii) recovery of uranium from acid mine drainage.

#### 2.1 Recovery of Uranium From Acid Leaches of Ores as Sulfate Complexes

The overall process used for uranium ore enrichment and recovery is given in Scheme I and the chemical composition of the ore is given in Table I (18). The ore was leached with 50 g l$^{-1}$ $\text{H}_2\text{SO}_4$ and the final pH adjusted to 1.5 with ammonia. At this pH a clear solution was obtained that contained 1.163 g l$^{-1}$ U, 1 g l$^{-1}$ Fe, 25 ppm V and 0.52 g l$^{-1}$ P. 150 mL of ammonia was required to neutralise 4 l of leach solution. The conditions for treating the 4 l of leach by ion exchange are given in Table II.

The Type I strong base anion resin, Amberlite® IRA-400, that has a trimethyl ammonium ion on cross-linked polystyrene in the chloride form was used for the ion exchange step. The ion exchange process used to extract uranium from the leaching solution is based on the high binding constants of the anionic sulfate complexes of uranium relative to the anion on the anion exchange resin (chloride) primarily due to their higher negative charge. The uranium is fixed in the form of carbonate complexes, such as $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)^-$ (12).

In consideration of the discussion above it is imperative that a detailed study of the environment must be taken into account when considering a U remediation project. This type of sensitivity is not peculiar to U, but is also important for other metals in their higher oxidation states such as manganese, vanadium, molybdenum and tungsten. It should be noted here that that acid mine drainage in general is often characterised by high sulfate which complexes with uranium. These are discussed in Section 2.1. Although 1 M total $[\text{U}]$ is never found in waste streams, comparison of Figure 1 with Figures 2 and 3 provides a view towards the sensitivity of uranium to changes in concentration.

#### Table I. Composition of the Uranium Ore (18)

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>U</th>
<th>PO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>65</td>
<td>15</td>
<td>10</td>
<td>0.01</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

#### Table II. Conditions for Fixation of the Ore Leach on the Ion Exchange Column (18)

<table>
<thead>
<tr>
<th>Condition, units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal diameter of resin column, cm</td>
<td>0.5</td>
</tr>
<tr>
<td>Height of resin bed in column, cm</td>
<td>43</td>
</tr>
<tr>
<td>Resin volume, ml</td>
<td>20</td>
</tr>
<tr>
<td>Flow rate, ml min$^{-1}$</td>
<td>2.23</td>
</tr>
<tr>
<td>Retention time, min</td>
<td>3.6</td>
</tr>
<tr>
<td>Bed volume, ml</td>
<td>20</td>
</tr>
</tbody>
</table>
this process noncompetitive with the alternative, solvent extraction (20).

2.2 Recovery of Uranium from Carbonate Solutions of Industrial Waste Streams

Uranium carbonate industrial waste streams from a Brazilian nuclear production plant were treated by an ion exchange process using a Type II strong base anion exchange resin, IRA-910A with a dimethyl 2-hydroxyethyl functional group (21). The stream needed to be boiled for 6 h to lower the total carbonate concentration before it could be treated. In order for ion exchange to be effective total carbonate concentration has to be <5 g l\(^{-1}\).

Table III describes the chemical composition of the waste stream before and after carbonate removal. The breakthrough and stripping profiles under various loading rates and with different stripping solutions are shown in Figure 4. Flow rate did not have a big effect on breakthrough but stripping with various carbonate solutions did.

The best strip was with 3 M carbonate, which gave a U concentration of 2.7 g l\(^{-1}\), a respectable concentration factor of about 43. Interestingly, the uranium-depleted effluent could be used for the strip and gave a concentration of 2.3 g l\(^{-1}\) after dilution from 2.3 M to 1.3 M carbonate concentration. The final effluent contained <4 mg l\(^{-1}\) uranium which met the plant specifications but is well primarily as a 3:1 complex and to a lesser extent as a 2:1 complex (Equations (ii)–(iv)) (19):

\[
\begin{align*}
\text{UO}_2^{2+} + \text{SO}_4^{2-} &\rightleftharpoons \text{UO}_2\text{SO}_4 \quad (K_1 = 50) \quad \text{(ii)} \\
\text{UO}_2^{2+} + 2\text{SO}_4^{2-} &\rightleftharpoons [\text{UO}_2(\text{SO}_4)_2]^{2-} \quad (K_2 = 350) \quad \text{(iii)} \\
\text{UO}_2^{2+} + 3\text{SO}_4^{2-} &\rightleftharpoons [\text{UO}_2(\text{SO}_4)_3]^{4-} \quad (K_3 = 2500) \quad \text{(iv)}
\end{align*}
\]

The uranium fixation reaction is shown in Equation (v):

\[
4\text{RX} + [\text{UO}_2(\text{SO}_4)_3]^{4-} \rightleftharpoons R_4\text{UO}_2(\text{SO}_4)_3 + 4\text{X}^- \quad \text{(v)}
\]

where R = resin; X = HSO\(_4^-\); Cl\(^-\); NO\(_3^-\).

The major species in solution is the uranyl trisulfate tetra-anion. In principle, this anion will take up four strong base sites and so loading effective concentrations of the feed will be limited. The high charge on this anion also leads to poor stripping. Thus, although the capacity of the resin was high at 67.2 g U l\(^{-1}\) resin, the concentration factor was negative. The final strip solution had 1.0 g U l\(^{-1}\) and was 1.63 g U l\(^{-1}\) solution before ion exchange. Stripping the column required over 200 ml of dilute nitric acid. Anionic ferric sulfate complexes competed with the U sulfate complexes. The percent recovery from the feed was only 75%. The overall process is fairly efficient but the poor capacity of the resin and the large amount of the expensive nitric acid needed for stripping could make this process noncompetitive with the alternative, solvent extraction (20).
above the Brazilian government’s recommended release level of 0.02 mg l\(^{-1}\) (see Table IV). However, it should be pointed out that without further dilution or a polishing step this level of uranium is still highly dangerous from a toxicity point of view, especially if the effluent is discharged into surface waters. The authors did not specify this.

An older report on the removal of uranium carbonate from industrial waste is discussed here as it contains important information on the effect of competing ions and used a more dilute uranium carbonate feed (22). The authors used a strong base anion exchange resin and although they did not specify the exact nature of the resin it is assumed here that it was a Type II resin.

### Table III. Chemical Composition of the Waste Stream Before and After Carbonate Removal (21)

<table>
<thead>
<tr>
<th>Analyses</th>
<th>Units</th>
<th>Original industrial effluent</th>
<th>Industrial effluent after carbonate removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>mg l(^{-1})</td>
<td>43</td>
<td>63</td>
</tr>
<tr>
<td>(\text{CO}_3^{2-})</td>
<td>g l(^{-1})</td>
<td>170.9</td>
<td>4.0</td>
</tr>
<tr>
<td>F(^-)</td>
<td>g l(^{-1})</td>
<td>0.35</td>
<td>0.5</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>g l(^{-1})</td>
<td>78.4</td>
<td>9.0</td>
</tr>
<tr>
<td>Fe</td>
<td>mg l(^{-1})</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Na</td>
<td>mg l(^{-1})</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>10.1</td>
<td>9.7</td>
</tr>
</tbody>
</table>

*Unless indicated, units are expressed in mg l\(^{-1}\) (except pH)

\(^b\)Permissible level not defined by Brazilian legislation CONAMA 357/2005

### Table IV. Chemical and Radiochemical Analysis of the Acid Mine Water (23)

<table>
<thead>
<tr>
<th>Determination</th>
<th>Acid mine water(^a)</th>
<th>Permissible level</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>12.0</td>
<td>0.02</td>
</tr>
<tr>
<td>Th</td>
<td>0.8</td>
<td>b</td>
</tr>
<tr>
<td>(^{226})Ra</td>
<td>3.5 Bq l(^{-1})</td>
<td>b</td>
</tr>
<tr>
<td>Mn</td>
<td>173.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca</td>
<td>158.0</td>
<td>b</td>
</tr>
<tr>
<td>Mg</td>
<td>8.9</td>
<td>b</td>
</tr>
<tr>
<td>Al</td>
<td>170.4</td>
<td>b</td>
</tr>
<tr>
<td>Zn</td>
<td>41.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe</td>
<td>180</td>
<td>15.0</td>
</tr>
<tr>
<td>(\text{SO}_4^{2-})</td>
<td>1400</td>
<td>b</td>
</tr>
<tr>
<td>F(^-)</td>
<td>110</td>
<td>10.0</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>57.0</td>
<td>b</td>
</tr>
<tr>
<td>pH</td>
<td>2.7</td>
<td>6.0–9.0</td>
</tr>
</tbody>
</table>

\(^a\)Unless indicated, units are expressed in mg l\(^{-1}\) (except pH)

Fig. 4. (a) Breakthrough and (b) elution profiles for uranium recovery from industrial waste (21)
Based on the fact that the more recent studies used this type of resin. Two feed solutions were tested. Solution A contained 0.010 M carbonate and comparable amounts of bicarbonate, chloride, and sulfate as their sodium salts while Solution B contained only 35 × 10⁻⁴ M carbonate and both solutions contained 7 × 10⁻⁴ M uranium added as UO₂(NO₃)₂ (Table V).

When tested individually all the ions in Solution A as well as UO₂(CO₃)₄⁻ showed adsorption isotherms that obeyed the Langmuir and Freundlich models starting with the chloride form of the resin. Correlation coefficients were very good, with the Freundlich model showing a better correlation for UO₂(CO₃)₄⁻, 0.99 versus 0.87 for the Langmuir model. These equilibrium studies allowed the establishment of a selectivity order for the competing ions: UO₂(CO₃)₄⁻ >> NO₃⁻ >> SO₄²⁻ ~ CO₃²⁻ > HCO₃⁻ > Cl⁻ with selectivity coefficients of 537, 98, 7.5, 7.4, and 5.2. The pH at which this order of selectivity was established was not provided for the equilibrium isotherm studies but maximum loading of UO₂(CO₃)₃⁴⁻ occurs at pH = 6.5–7.0. Table VI shows the pH dependence of uranium loading for Solutions A and B. It can be seen that the presence of competing ions had only a slight effect on uranium loading, peaking at 6.5–7.0 in agreement with the reported selectivity values (Table VI). Subsequent spectroscopic studies suggested that at the optimal loading a portion of the uranium is converted to U₂O₇²⁻. The lower charge on this species accounts for the increased loading of uranium at pH = 6.5–7.0.

Although uranium loading showed a clear maximum at pH = 6.5–7.0 stripping with neutral salts such as NaCl or NaNO₃ only recovered ~60% of the uranium loaded at this pH. Stripping with additional ethanol or HCl did not recover any significant amounts of uranium. Stripping with Na(NO₃)₃ was very efficient for columns loaded at pH = 9, but loading was much lower at this pH (Table VI). The authors did not consider using a carbonate leach at high pH as suggested by the observed selectivity coefficients and by the equations governing the conversion of UO₂(CO₃)₃⁴⁻ to the apparently nonexchangeable U₂O₇²⁻ in the resin phase (Equation (vi)):

\[
2R₄UO₂(CO₃)₃ + 6OH⁻ → R₂U₂O₇ + 3R₂CO₃ + 3CO₃²⁻ + 3H₂O \quad (vi)
\]

where R = resin site.

Overall taking the two studies together, it would appear that loading at pH = 6.5–7.0 and stripping with

### Table V. Composition of the Feed Solutions and Column Configuration (22)

<table>
<thead>
<tr>
<th>Run</th>
<th>Solution components, mol l⁻¹</th>
<th>pH</th>
<th>Na₂CO₃</th>
<th>NaHCO₃</th>
<th>NaCl</th>
<th>Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.010</td>
<td>3.0–9.0</td>
<td>0.025</td>
<td>0.015</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>35.70 × 10⁻⁴</td>
<td>5.0–9.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Concentration of uranium: 7.14 × 10⁻⁴ mol l⁻¹ UO₂(NO₃)₂.

Column configuration: ID = 0.8 cm, length = 10 cm. Resin weight = 0.5 g

### Table VI. pH Dependence of Uranium Loading for Solutions A and B (22)

#### Uranium loading capacity from composition of A at different pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>6.5</th>
<th>7.0</th>
<th>8.0</th>
<th>9.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg U g⁻¹ dry resin</td>
<td>199</td>
<td>223</td>
<td>271</td>
<td>370</td>
<td>352</td>
<td>235</td>
<td>183</td>
<td>171</td>
</tr>
<tr>
<td>Relative loading capacity</td>
<td>1.16</td>
<td>1.30</td>
<td>1.58</td>
<td>2.16</td>
<td>2.06</td>
<td>1.37</td>
<td>1.07</td>
<td>1</td>
</tr>
</tbody>
</table>

#### Uranium loading capacity from composition of B at different pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>5.0</th>
<th>6.0</th>
<th>6.5</th>
<th>7.0</th>
<th>7.5</th>
<th>8.0</th>
<th>9.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg U g⁻¹ dry resin</td>
<td>49</td>
<td>300</td>
<td>398</td>
<td>423</td>
<td>392</td>
<td>188</td>
<td>179</td>
</tr>
<tr>
<td>Relative loading capacity</td>
<td>0.27</td>
<td>1.68</td>
<td>2.22</td>
<td>2.36</td>
<td>2.19</td>
<td>1.05</td>
<td>1</td>
</tr>
</tbody>
</table>
carbonate at pH >9.0 would be the best approach, even in the presence of significant amounts of competing ions.

2.3 Removal of Uranium from Acid Mine Drainage using Strong Base Ion Exchange Resins

This study compared the effectiveness of Type I (Dowex™ Marathon™ A) with Type II (Amberlite® IRA-410u) strong base resins (Figure 5) for the removal of uranium from high sulfate acid mine drainage (23). Table IV shows the chemical and radiochemical profile of the waste stream. The uranium is present as sulfate complexes and considering the large excess of sulfate and the low pH the major species in solution is likely UO$_2$(SO$_4$)$_3^{4-}$ (Equations (ii)–(iv)). The other ions in solution are present as cations except for sulfate, silicate and fluoride which have lower negative charges but could compete with the UO$_2$(SO$_4$)$_3^{4-}$. Column experiments were performed on 5.0 ml volumes of each resin at pH values of 2.7 and 3.9 in a 1.2 cm ID column at a flow rate of 24 BV h$^{-1}$ (Figure 6). The Type II resin IRA-410u performed significantly better than Dowex™ A (Table VII). Both resins performed at only about 40–60% of their theoretical value (1 equiv. g$^{-1}$ for IRA-410u and 1.3 equiv. g$^{-1}$ for Dowex™) probably because of the interference of other anions. However, the authors were unclear about whether these theoretical values took into account the higher negative charges on the sulfate complexes. Performance was slightly better for both resins at the higher pH. Sulfate and fluoride levels were monitored and revealed that indeed sulfate does compete but fluoride does not (Figures 7(a) and 7(b)).

The authors report an economic analysis of the uranium recovery based on the adsorption data. However, this is meaningless in the absence of elution data, especially in light of the poor stripping reported for the sulfate complexes above (21). The value of this study is the demonstration that Type II resins work better than Type I strong base resins and that unbound sulfate competes with the uranium sulfate complexes. No cycle testing is provided. In the absence of this data the scale up analysis reported in the paper is of little value.

3. Uranium Removal Materials Based on Silica and Other Inorganic Matrices: Overview

In the past 20 years there has been considerable development in the area of silica gel based chelator materials for metal ion removal and recovery. This is due, in part, to the development of new methods for synthesising silica gels but also because silica gel offers some advantages over the widely used and highly developed polymer based materials (Section 2). Silica gel does not shrink or swell with changes in pH or temperature and has a hydrophilic surface that affords faster mass transfer kinetics (24).
proprietary. The silica gels available commercially for use as solid-phase sorbents can be made in a wide range of particle sizes (25–500 μm) and all have high porosities and surface areas. Table VIII illustrates the physical properties of the midrange particle sizes available from different suppliers (24). Amorphous silica gels can also be made as nanoparticles (25). As expected, these have much lower porosities but higher total surface areas. Amorphous silica gels can also be made by the sol-gel route using siloxanes (Si(OR)₄) and functionalised siloxanes (SiR(OR)₃) that provide direct functionalisation of the surface (26). This approach offers more control over pore-size distribution, a parameter that can affect the uniformity of mass transfer kinetics in ion exchange applications. The sol-gel method can afford much narrower pore size distributions (26). Most recently, it has been shown

On the other hand, strong alkali degrades silica while polystyrene is quite stable at high pH. In general, polystyrene shows more resistance to mechanical shock but has a higher cross section for neutron capture limiting its use for actinide separations and recoveries. Each matrix has its advantages and disadvantages and these will be summarised later in this review.

Silica gels used as solid phase sorbents are of two general types, amorphous silica gels and mesoporous silica gels. Amorphous silica gels are made by the fusion of sodium carbonate and silicates at high temperature (~1100ºC) to produce sodium silicate (water glass), which is dissolved in water and then reprecipitated with acid under carefully controlled conditions. The porosity, particle shape and size are very sensitive to the precipitation conditions and subsequent curing. The conditions for precipitation used in industry are

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Diameter, mm</th>
<th>Pore diameter, Å</th>
<th>Pore volume, ml g⁻¹</th>
<th>Porosity, %</th>
<th>Surface area, m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crosfield</td>
<td>90–105</td>
<td>267</td>
<td>2.82</td>
<td>84.7</td>
<td>422</td>
</tr>
<tr>
<td>Qingdao Haiyang</td>
<td>150–250</td>
<td>194</td>
<td>2.39</td>
<td>85.0</td>
<td>493</td>
</tr>
<tr>
<td>Qingdao Meigao</td>
<td>180–250</td>
<td>378</td>
<td>2.86</td>
<td>85.3</td>
<td>303</td>
</tr>
<tr>
<td>Nanjing</td>
<td>180–250</td>
<td>164</td>
<td>2.30</td>
<td>85.8</td>
<td>561</td>
</tr>
<tr>
<td>Nanjing Tianyi</td>
<td>80–250</td>
<td>150</td>
<td>2.28</td>
<td>85.6</td>
<td>526</td>
</tr>
</tbody>
</table>
that rice hull ash can be converted to amorphous silica gel by simply extracting the material with 1 M sodium hydroxide and then precipitating with acid. The resulting gel can be converted into useful solid phase sorbents but lack the mechanical strength of the commercially available amorphous gels (27).

Mesoporous silica gels differ from amorphous silica gels in that they are ordered phases made by the sol-gel method using a templating agent, usually a detergent such as cetyl ammonium bromide (28) or more recently block copolymers containing hydrophilic and hydrophobic segments (29). The block copolymers provide the option of removing the template by solvent extraction while the ionic detergent requires calcination at 400–500ºC. Both methods provide highly ordered phases of nanoparticles with pore diameters in the 2–10 nm range with very high surface areas (>700 m² g⁻¹) and good mechanical strength. Commercially available mesoporous silica gels are marketed by many suppliers as MCM-41 and SBA-15, which differ slightly in their physical properties. Because these mesoporous silica gels are made by the sol-gel method they offer the opportunity of direct surface functionalisation using Si(OR)₃ and SiR(OR)₃ (26, 29).

For the purposes of uranium recovery and remediation the cheaper more porous amorphous silica gels are probably a better choice than the mesoporous gels, while for catalysis the higher surface area and more mechanically strong mesoporous materials, and the related zeolites, are a better choice. In comparing the silica matrix with the polymer based materials described in Section 2, the latter have seen a much wider use, but as described at the beginning of this section silica gel offers some distinct advantages.

3.1 Commercially Available Silica Based Ion Exchange Materials

Steward Advanced Materials, USA, offers Self Assembled Monolayers of Mesoporous Silica (SAMMS®) functionalised with 3-propane thiol for gold, silver and mercury recovery. The ordered silica pores are very small but form a high surface area-ordered material. The silica matrix is made using a detergent template followed by calcination. These materials were developed at Pacific Northwest Labs by the group of Glen Fryxell and have been used in a variety of metal capturing applications, including uranium that will be discussed in Section 3.3.2. The materials show high capacity but are difficult to strip and are expensive to produce. This material has not seen widespread use in the base metals industry. There are many studies on their use for actinide metal recovery, but none on the commercial scale.

IBC Advanced Technologies, USA, makes both polystyrene and silica based materials modified with macrocyclic ligands that are highly selective for a given metal. The ligands work on so-called molecular recognition technology (MRT) and are based on size selectivity rather than covalent binding constants. They are quite expensive but according to their website this technology has seen a wide range of applications in the mining industry. The company has presented the results of these projects at numerous conferences but access to the actual data is limited and their product web pages come up blank.

SiliCycle Inc, located in Quebec, Canada, markets a selection of metal scavenging agents based on silica gel modified with propyl groups bearing a purportedly selective metal scavenging agent. Ligand loadings vary from 0.3 to 1.2 mmol g⁻¹, slightly lower than related polymer based materials. They have lower bulk densities than polystyrene sorbents similar to silica polyanime composites (SPC) (vide infra). Pore size is quoted at 6 nm, in the same range as that reported for both amorphous and mesoporous silica gels with particle sizes in the range of 40–60 μm. The website does not provide metal capacities or longevity data for the materials. The website offers quantities of up to 500 g but states that bulk quantities are available. These amino propyl resins (SiliaBond® Amine) do not stand up well to repeated use and the EDTA modified propyl silanes (SiliaMets® Triaminetetraacetic Acid (TAAcOH)) actually lose capacity with increasing pH (30). Finally, all of these products list very general metal selectivity according to the website without any quantitative data on preferences within mixtures. Metals are listed as scavengers or preferred scavengers. No uranium selective adsorbents are listed on the website. The main application of these materials is most likely the removal of excess metals after a bench scale chemical reaction.

Johnson Matthey Plc is currently developing a series of silica polyanime composites (SPC) that use a chloropropyl/methyl silane mixture to modify an amorphous silica gel surface that is subsequently treated with polymeric amines, and then further modified with metal selective ligands (31, 32). The polyanime surface is much more robust than the aminopropyl modified surface in that the multipoint anchoring provides a more stable composite surface and elevating the metal...
capturing ligand away from the surface eliminates ligand interactions with the surface. This group of sorbents has been extensively compared with polystyrene analogues and offer distinct advantages. Separations are sharper as a result of better column utilisation factors, no shrink-swell during pH changes and lower bulk densities (33). Functionality is available over a range of metal selective ligands, including analogues of the strong base resins (34, 35) and amino phosphonic acid groups that have been applied to uranium remediation (*vide infra*) (36). These materials have been employed on a large scale by the mining industry for remediation and recovery of transition metals.

### 3.2 Silica Based Hybrid Materials for Uranium Recovery

The literature is full of sorbents based on mesoporous and amorphous silica gels. Their surfaces allow a wider degree of functionalisation relative to organic polymers because the silanisation step offers an almost infinite choice of functional groups that can be further modified (37–39). Here, we have chosen representative examples of inorganic and hybrid materials that have been specifically designed for uranium recovery from waste streams.

#### 3.2.1 Uranium Recovery with Chelator Ligands Bound to Amorphous Silica

Murexide is a commonly used organic indicator that changes colour on complexation with metals. Recently, this commercially available ligand has been bound to silica gel and has shown a high affinity for uranyl ion and for thorium (*Scheme II*) (40). These investigators used acid-activated amorphous silica (6 nm pore diameter, 63–212 μm). The resulting murexide composite showed very good capacities for uranyl ion over a wide pH range with a maximum batch capacity of 1.13 mmol g\(^{-1}\) at pH = 5.5. Flow capacities of ~0.5 mmol g\(^{-1}\) were realised at relatively rapid flow rates of 10 ml min\(^{-1}\). The material could be regenerated efficiently with 0.1 M HCl but no cycle testing is reported and the actual loading of the murexide ligand is not reported. This could have been easily done by nitrogen analysis before and after reaction of murexide with the amino propyl modified silica. The most appealing aspect of this new ligand is its high degree of selectivity for uranyl ion. It shows exceptionally high selectivity values for uranium versus other anions and cations (selectivities of 70–1000) with only Zr\(^{4+}\) and Th\(^{4+}\) and the anions VO\(^{3-}\), PO\(^{4-}\), and C\(_2\)O\(^{4-}\) causing significant interference (Table IX).

Another class of ligand that has shown excellent properties for uranyl ion recovery are the carboxylate modified cyclams bound to silica (*Figure 5*) (41). The silica gel used was Kieselgel 60 (bead size 0.2–0.5 mm, 35–70 Mesh, specific area 550 m\(^2\) g\(^{-1}\)). These composites were made by either adding the cyclam to a 3-chloropropyl group on silica followed by reaction of the remaining three N atoms with an acrylic acid or by preassembly of the trimethoxysilyl-tris-acrylate ligand to the chloropropyl surface.

#### Table IX. Tolerance for Competing Ions for the Murexide Modified Silica Gel (40)

<table>
<thead>
<tr>
<th>Foreign ion</th>
<th>Tolerance limit(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(^+), Cl(^-), Na(^+), NO(_3)(^-), CH(_3)CO(_2)(^-)</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>I(^-), SO(_4)(^{2-}), Cd(^{2+}), Ti(^{4+}), Mg(^{2+}), Ca(^{2+}), Ni(^{2+}), Cu(^{2+}), Pb(^{2+}), Zn(^{2+})</td>
<td>1000</td>
</tr>
<tr>
<td>La(^{3+}), Ce(^{3+}), Al(^{3+}), MoO(_4)(^{2-}), Cs(^+)</td>
<td>100</td>
</tr>
<tr>
<td>Fe(^{3+}), Co(^{2+}), Zn(^{2+}), Cr(^{3+})</td>
<td>70</td>
</tr>
<tr>
<td>VO(_3)(^-), PO(_4)(^{3-}), C(_2)O(_4)(^{2-})</td>
<td>7</td>
</tr>
<tr>
<td>Th(^{4+}), Zr(^{4+})</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\)The concentration ratio of the foreign ions to the U(VI) ions

![Image](image-url)
Different cyclams were grafted to silica gel and the best performance was obtained with the cyclam shown in Figure 5. As expected from the Eh-pH diagrams (Figures 1 to 3) in the introduction the highest uranium capacity was obtained at pH = 4–5 (dynamic $K_d = 158 \text{ ml g}^{-1}$ at pH = 4). This study reports regeneration studies with very little loss in capacity over nine load regeneration cycles, with typical loadings of 0.25 mmol UO$_{2}^{2+}$ g$^{-1}$ gel. However, the stripping kinetics were poor; even though complete recovery was realized in the nine cycles, large volumes of 2 M nitric acid were required.

A schematic diagram for a continuous extraction of uranium in the presence of other actinides is shown in Figure 8 and used two 12 l columns one loaded with unmodified silica gel for use as a pre-filter and the second loaded with the cyclam modified silica. This system was used to capture a mixture of U, Am and Pu at concentrations typical for radioactive waste. All three metals were removed to below detection limit.

Interestingly, the distribution coefficient almost doubles on going from 298 K to 353 K. This may be characteristic of all amorphous based silica gels as it has been observed with related silica polyamine composites (42). Overall, this study is the most complete evaluation of a solid phase uranium adsorbent and lacks only selectivity studies relative to other ions that are associated with uranium waste streams.

A silica polyamine composite modified with an amino phosphonic acid functional group has been used to selectively recover uranium from a mock solution that profiles the acid mine drainage found in the gold mine tailing around Johannesburg, South Africa (43). The previously reported polyamine composite, BPAP, is schematically represented in Figure 9 (36). Amorphous silica with a 180–250 μm particle size distribution, a 38 nm average pore diameter and a 303 m$^2$ g$^{-1}$ surface area was used for this study.

The mock solution was run through a 5 ml column with a flow rate of 1.0 ml min$^{-1}$ at pH = 2.5. The mock solution contained 175 mg l$^{-1}$ Fe, 55 mg l$^{-1}$ Zn, 18 mg l$^{-1}$ Ni, 81 mg l$^{-1}$ Co, 78 mg l$^{-1}$ Mn, 123 mg l$^{-1}$ U, 41 mg l$^{-1}$ Cu, 195 mg l$^{-1}$ Ca and 82 mg l$^{-1}$ Mg. After 15 bed volumes (75 ml) were passed through the solution, all the metals except Fe and U reached their feed concentrations. Stripping with 2 M H$_2$SO$_4$ was not effective but stripping with 2 M Na$_2$CO$_3$ removed all of the uranium along with some of the Fe and Ca. The strip solution contained only minor amounts of the divalent transition metals and the Fe and Ca could be precipitated as their hydroxides and carbonates by subsequent pH adjustment. Thus, the divalent transition metals mainly passed through the column but Fe$^{3+}$ and Ca$^{2+}$ co-loaded with UO$_{2}^{2+}$. On stripping with carbonate all of the uranium is removed as soluble UO$_4$(CO$_3$)$_{m-}$ (n = 2, 3; m = 2, 4) complexes. The wt% uranium is increased from 17% in the feed to 45% in the strip (Figure 10).

For this process to be useful the remaining Fe$^{3+}$ and Ca$^{2+}$ must be removed to fully regenerate the column. This could be done with EDTA as has been previously shown (44). The valuable aspect of this report is that the BPAP can be used to effectively separate uranyl cation from divalent transition metal ions.

Fig. 8. Schematic drawing for continuous extraction experiments: 1 contaminated solution (A) or concentrated solution (B); 2 peristaltic pump; 3 column filled with silica gel-bound macrocycles; 4 thermostated jacket; 5 decontaminated solution (A) or 2 N nitric acid solution (B) (41)

Fig. 9. Schematic representation of the amino-phosphonic acid modified silica polyamine composite, BPAP (36)
two different mesh sizes of MnO\textsubscript{2} (70–200 μm and <5 μm) and MnO\textsubscript{2} adsorbed onto a polystyrene sulfonic acid resin.

The materials were used as sorbents for the radioactive isotopes of actinide and lanthanide elements present in trace amounts in seawater (3 pbb for U) and the Columbia River (~70 pbb for U). Experiments were conducted in batches (for example, lanthanides together with other isotopes: \textsuperscript{234}Th, \textsuperscript{237}Np, \textsuperscript{233}Pa and \textsuperscript{233}U) and determined using either gamma emission or liquid scintillation. Standard solutions were used and compared with the data from Columbia River water and Galveston Bay water in order to evaluate the contribution of organics and other ions to the observed distribution coefficients. Samples were counted until the counting error of the fitted peak area was less than 10%, which typically required counting times on the order of 102 to 103 min. The activity of each analyte was used to determine a mass-weighted distribution coefficient (\(K_D\), l kg\textsuperscript{-1}), Equation (vii):

\[
K_D = \frac{A_S}{A_W} \frac{V}{m}
\]

where \(A_S\) is the total activity of the isotope retained in the sorbent, \(A_W\) is the total activity remaining in solution, \(V\) is the volume of the batch experiment (50 ml), and \(m\) is the mass of sorbent in kg.

Distribution coefficients are reported for all six of the isotopes in the standard solutions for each adsorbent in both the river water and seawater. There are relatively small differences between ions but the big differences are between the adsorbents and type of water. We discuss only the data for uranium here (Table X).

3.3.2 Uranium Recovery with Chelator Ligands Bound to Mesoporous Silica

A recent study surveyed the effectiveness of variously functionalised MCM-41 mesoporous silica gels (75–250 μm particle size, 480 m\textsuperscript{2} g\textsuperscript{-1}, 7 nm pore diameter) and compared them with polystyrene chelator resins having the same functionality and with various forms of MnO\textsubscript{2} (45). Three functional groups were tested: sulfonic acid (SCX), iminodiacetic acid (IDAA, referred to as EDTA in the Tables) and 3,4-hydroxypyridinone (HOPO\textsuperscript{−}) (Figure 11). Ligand loadings were 0.67, 0.29 and 1.3 mmol g\textsuperscript{-1} respectively, using (MeO)\textsubscript{3}Si(CH\textsubscript{2})\textsubscript{3}R (R = functional group) procedures.

These modified SAMMS\textsuperscript{®} were compared with two polystyrene resins: a strong base anion exchange resin (SAX) and Chelex\textsuperscript{®} 100 (EDTA, actually IDAA),
A wide variety of cations. The IDAA (EDTA) chelator worked better on the polystyrene than on the SAMMS® and the SCX SAMMS® is no better than blank silica. HOPO SAMMS® showed the best all around performance for both river water and seawater. Most interesting is that the anion exchange resin performed relatively well for both samples but the authors ignored this in their conclusion, as well as a detailed discussion of solution pH. Given the complex nature of uranium speciation this was a significant fault with this otherwise elegant and informative study. More work needs to be done to evaluate saturation capacities and the stability of the sorbents.

A recent report from the group that pioneered the development of SAMMS® compares the performance of the mesoporous phase MCM-41 with amorphous silica gel for loading of the HOPO ligand or a benzyl protected HOPO ligand and subsequent uranium capture (Scheme III) (46).

It was thought that protection of the phenolic OH would improve the efficiency of the coupling step between HOPO and the aminopropyl silane. Two different types of silica were used for these experiments, a surfactant templated mesoporous silica MCM-41, and an amorphous, chromatographic silica (Davisil®, 634 and 635, Aldrich). The batch of MCM-41 has a specific surface area of 800 m² g⁻¹, an average pore size of 3.5 nm (very uniform pore size distribution), and a pore volume of 1.29 cm³ g⁻¹. The smaller pores of MCM-41 are more easily crowded during monolayer deposition, but the very high surface area of this support suggests that it might be possible to get a higher functional loading in the SAMMS® made using this support.

The biggest difference in log Kᵝ is between the two water sources, where the values are much lower for the bay water than for the river water by about two orders of magnitude on average. This suggests there are more interfering ions in the seawater and is a very valuable contribution. Between the different sorbents, the polystyrene sulfonic acid with MnO₂ (SCX-MnO₂) was by far the best for the river water and the worst for the seawater, pointing to the affinity of this adsorbent for a wide variety of cations. The IDAA (EDTA) chelator worked better on the polystyrene than on the SAMMS® and the SCX SAMMS® is no better than blank silica. HOPO SAMMS® showed the best all around performance for both river water and seawater. Most interesting is that the anion exchange resin performed relatively well for both samples but the authors ignored this in their conclusion, as well as a detailed discussion of solution pH. Given the complex nature of uranium speciation this was a significant fault with this otherwise elegant and informative study. More work needs to be done to evaluate saturation capacities and the stability of the sorbents.

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A recent report from the group that pioneered the development of SAMMS® compares the performance of the mesoporous phase MCM-41 with amorphous silica gel for loading of the HOPO ligand or a benzyl protected HOPO ligand and subsequent uranium capture (Scheme III) (46).

It was thought that protection of the phenolic OH would improve the efficiency of the coupling step between HOPO and the aminopropyl silane. Two different types of silica were used for these experiments, a surfactant templated mesoporous silica MCM-41, and an amorphous, chromatographic silica (Davisil®, 634 and 635, Aldrich). The batch of MCM-41 has a specific surface area of 800 m² g⁻¹, an average pore size of 3.5 nm (very uniform pore size distribution), and a pore volume of 1.29 cm³ g⁻¹. The smaller pores of MCM-41 are more easily crowded during monolayer deposition, but the very high surface area of this support suggests that it might be possible to get a higher functional loading in the SAMMS® made using this support.
Also, the highly uniform pore size distribution makes it possible to monitor dimensional changes in pore size with each reaction. The amorphous Davisil® silica gels used had specific surface areas of 480 m² g⁻¹, and an average pore size of ~6.0 nm (broad pore size distribution, up to ~20.0 nm), and a pore volume of 1.67 cm³ g⁻¹. The difference between Davisil® 634 and 635 is their granulation – Davisil® 634 has 75–150 μm particles (100 to 200 mesh), while Davisil® 635 has 150–250 μm particles (60–100 mesh). The larger pores of the Davisil® silica make this support more amenable to making monolayers with large bulky ligands, like the benzyl-protected HOPO ligands.

The authors experimented with the impact of different methods of cleaving the protecting group and found that this had little effect on mass weighted K_D using the usual formula (47). The type of medium (blood, plasma, river water) had a major effect on the efficiency of U(VI) with the highest being the more homogeneous river water (Table XI).

The most important result of this study is that the amorphous silica gel performed better in every medium and regardless of the method of deprotection. Even without using the protecting group the amorphous silica-HOPO performed better than the protected MCM-41-HOPO. This makes an important point with regard to silica adsorbents and remediation. Porosity, not uniformity is the key property for a good solid phase sorbent. Less porous ordered phases are better suited to structural investigations and catalysis where they give better resolution of the environment and better stereoselectivity.

A different approach, using functionalised polymers adsorbed onto ordered silica phases has been reported (48). An ordered nanoporous silica (MSU-H) with a hexagonal array structure that has a specific surface area of ~700m² g⁻¹ and nanopores of ~4 nm in average diameter was used in the study. Three common polymers: poly(ethyleneimine), carboxymethyl, poly(ethyleneimine) and polyacrylic acid were used in the study. The silica gel was activated by treatment with hydrochloric acid and then the polymers were mixed with the gel for a set period of time. After washing and drying the polymer-silica composite was exposed to solutions of uranyl ion of various concentrations. Very poor distribution coefficients are reported (~10²) for all three polymers and most importantly, 15% of the uranium leached off the material after one day. No stripping data is reported and it is likely that the polymer would have desorbed with any reagent that was capable for recovery of the uranium. This report is presented here as an example of what does not work for designing a solid phase sorbent for uranium.

### 3.4 Layered Sulfide Materials for Uranium Capture

An entirely different type of sorbent based on layered sulfides is reported here for comparison with the more developed polymer and silica based sorbents discussed so far. Very recently, the layered sulfide material, K₂MnSn₂S₆ (KMS-1) has been shown to be an effective ligand for Rb⁺, Cs⁺ and UO₂²⁺ (49, 50). The metal ions exchange for potassium that sits between layers of MnS₆ (0.32 occupancy) or SnS₆ (0.68 occupancy). The exchange is driven by the greater affinity of the larger cations for the soft sulfur atoms on the surface of each

### Table XI. The Effect of Cleavage Method of the Benzyl Protecting Group, the Type of Silica Used and the Adsorption Medium on the Distribution Coefficient for U(VI) with HOPO Modified Surfaces (46)

<table>
<thead>
<tr>
<th>Silica</th>
<th>Cleavage method</th>
<th>Matrix</th>
<th>K_D</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>Old²</td>
<td>Buffer</td>
<td>&gt;100,000</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Old</td>
<td>Blood</td>
<td>7000</td>
</tr>
<tr>
<td>D-634</td>
<td>None (Bz ether)</td>
<td>River water</td>
<td>5800</td>
</tr>
<tr>
<td>D-634</td>
<td>Old</td>
<td>River water</td>
<td>10,000,000</td>
</tr>
<tr>
<td>D-634</td>
<td>New</td>
<td>River water</td>
<td>100,000,000</td>
</tr>
<tr>
<td>D-634</td>
<td>New</td>
<td>Blood</td>
<td>55,000</td>
</tr>
<tr>
<td>MCM-41</td>
<td>New</td>
<td>Plasma</td>
<td>32,000</td>
</tr>
<tr>
<td>MCM-41</td>
<td>New</td>
<td>Blood</td>
<td>6100</td>
</tr>
<tr>
<td>D-635</td>
<td>Unprotected</td>
<td>River water</td>
<td>&gt;10,000,000</td>
</tr>
<tr>
<td>D-635</td>
<td>Unprotected</td>
<td>Plasma</td>
<td>10,000</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Unprotected</td>
<td>Plasma</td>
<td>12,000</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Unprotected</td>
<td>Blood</td>
<td>8900</td>
</tr>
</tbody>
</table>

²18 h at 25ºC, ³Reference (58), ⁴4 days at 25ºC, ⁵New = 50–60ºC for 18 h
layer. In the case of UO$_2^{2+}$, the rod-like shaped ion lies horizontally between the layers in order to directly interact with the S atom (Figure 12).

The material can reduce uranium levels from a variety of sources over a wide range of pH to very low levels, even in the presence of other cations (Table XII). In most cases 98–99% of the uranium is removed and an average of 84% where other cations are present at very high levels. Thus, KMS-1 is very effective for removal of trace levels of U from real-world water samples. KMS-1 is:

(a) inexpensive and easy to make (51), (b) very stable in the atmosphere and water, (c) highly selective for UO$_2^{2+}$ with very fast sorption kinetics, (d) easily regenerated with 2 M Na$_2$(CO)$_3$, an affordable and environmentally friendly method, and (e) reusable for at least six cycles. The material lost about 40% of its capacity after the first regeneration cycle but then remained constant for remaining five. It represents one of the most promising solid phase adsorbents for efficient and cost-effective treatment of wastes and groundwater containing highly toxic U levels. For removal of low levels of uranium it stands out relative to the other adsorbents discussed in this review, but it would not be suitable to an industrial or mining environment where much higher levels of uranium must be processed and where a 40% loss in capacity after one cycle is not acceptable.

4. Concluding Remarks

This review focused on the application of the two main types of solid phase adsorbents used for uranium

![Fig. 12. Proposed mechanism for displacement of K$^+$ by UO$_2^{2+}$ (49, 50)](image)

| Table XII. Removal of UO$_2^{2+}$ by KMS-1 from Various Water Sources (49) |
|------------------|------|-----------------|-----------------|-----------------|
| Sample                        | pH   | Adsorption, ml g$^{-1}$ | U concentration, ppb | Removal, % |
| Distilled water, 0.34 M NaCl   | 3    | 1000             | 2500           | 12–22         | 99.1–99.5   |
| Distilled water, 0.15 M NaNO$_3$ | 6.5  | 1000             | 3250           | 103–128       | 96.1–96.8   |
| Potable water$^b$              | 7    | 100              | 36             | 0.5–0.7       | 98.1–98.6   |
| Lake Michigan water$^c$        | 7.3  | 100              | 34.2           | 0.9–1.1       | 96.8–97.4   |
| Contaminated seawater, Gulf of Mexico | 8.2  | 16–50            | 1308           | 1.2–6.5       | 99.5–99.9   |
| Contaminated seawater$^d$, Pacific Ocean | 8.2  | 20–50            | 1278           | 1.1–2.0       | 99.8–99.9   |
| Contaminated seawater, Gulf of Mexico | 8.2  | 100              | 39             | 5.3–8.5       | 78.3–86.5   |
| Original seawater$^e$, Gulf of Mexico | 8.2  | 100              | 3.8            | 0.6–0.9       | 76.3–84.2   |

$^a$Range of concentrations obtained from three different experiments

$^b$Potable water as found in Evanston, IL, contains 10.7 ppm of Na$^+$, 32.9 ppm Ca$^{2+}$, 8.5 ppm Mg$^{2+}$, 7 ppm K$^+$, and other ions of insignificant concentrations

$^c$Water samples from Lake Michigan, Evanston, IL, contain 20 ppm Na$^+$, 24 ppm Ca$^{2+}$, 8.8 ppm Mg$^{2+}$, 2.7 ppm K$^+$ and other ions of insignificant concentrations

$^d$The cations with the highest concentrations in these seawater samples were Na$^+$ (8557 ppm), Mg$^{2+}$ (820 ppm), K$^+$ (500 ppm) and Ca$^{2+}$ (262 ppm)

$^e$The cations with the highest concentrations in these seawater samples were Na$^+$ (9486 ppm), Mg$^{2+}$ (897 ppm), K$^+$ (556 ppm) and Ca$^{2+}$ (274 ppm)
The Achilles heel of the inorganic exchangers is high pH, silica in particular degrades rapidly at pH>13. Organic-inorganic hybrid materials slow this process down but do not eliminate it (53).

In choosing the right ion exchange resin for a given application the properties of the waste are of primary concern. Total suspended solids should be less than 4 mg l\(^{-1}\) or prefiltering is necessary for both organic and inorganic exchangers. The waste should have a low dissolved ionic solids content of less than 1–2 g l\(^{-1}\). In the specific case of radionuclides, they need to be in the anionic form to be suitable for ion exchange with strong base anion exchangers. This can usually be done with pH adjustment but this will raise the total ion content and may affect removal efficiency (52).

For uranium removal from industrial waste or groundwater containing high levels of sulfate or carbonate the commercially available strong base anion exchange resins are currently the best option as discussed in Section 2. However, strong base silica polyamine composites with a higher tolerance for solutions with high ion concentration (upper limit for

<p>| Table XIII. A Comparison of the General Properties of Organic and Inorganic Ion Exchangers (52) |
|-------------------------------------------------|-----------------|-----------------|-----------------------------|</p>
<table>
<thead>
<tr>
<th>Property</th>
<th>Organic exchangers</th>
<th>Inorganic exchangers</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal stability</td>
<td>Fair to poor</td>
<td>Good</td>
<td>Inorganics are especially good for long term stability</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Good</td>
<td>Fair to good</td>
<td>Specific organics and inorganics are available for any given pH range</td>
</tr>
<tr>
<td>Radiation stability</td>
<td>Fair to poor</td>
<td>Good</td>
<td>Organics are very poor in combination with high temperatures and oxygen</td>
</tr>
<tr>
<td>Exchange capacity</td>
<td>High</td>
<td>Low to high</td>
<td>The exchange capacity will be a function of the nature of the ion being removed, its chemical environment and the experimental conditions</td>
</tr>
<tr>
<td>Selectivity</td>
<td>Available</td>
<td>Available</td>
<td>For some applications, such as caesium removal, inorganics can be much better than organics, owing to their greater selectivity. Ion selective media are available in both organic and inorganic forms</td>
</tr>
<tr>
<td>Regeneration</td>
<td>Good</td>
<td>Uncertain</td>
<td>Most inorganics are sorption based, which limits regeneration</td>
</tr>
<tr>
<td>Mechanical strength</td>
<td>Good</td>
<td>Variable</td>
<td>Inorganics may be brittle or soft or may break down outside a limited pH range</td>
</tr>
<tr>
<td>Cost</td>
<td>Medium to high</td>
<td>Low to high</td>
<td>The more common inorganics are less costly than organics</td>
</tr>
<tr>
<td>Availability</td>
<td>Good</td>
<td>Good</td>
<td>Both types are available from a number of commercial sources</td>
</tr>
<tr>
<td>Immobilisation</td>
<td>Good</td>
<td>Good</td>
<td>Inorganics can be converted to equivalent mineral structures, organics can be immobilised in a variety of matrices or can be incinerated</td>
</tr>
<tr>
<td>Handling</td>
<td>Good</td>
<td>Fair</td>
<td>Organics are generally tough spheres, inorganics may be brittle; angular particles are more friable</td>
</tr>
<tr>
<td>Ease of use</td>
<td>Good</td>
<td>Good</td>
<td>If available in a granulated form both types are easy to use in batch or column applications</td>
</tr>
</tbody>
</table>
polystyrene is 4 meq ml$^{-1}$) are under development and may prove competitive for these applications (35).

As stated clearly in Section 3.3.2 mesoporous materials are not a good choice for remediation projects. These materials and the related zeolites have found a wide range of applications in catalysis, medicine and many other fields. Their smaller pore sizes make them more difficult to regenerate, they do not tolerate bulky ligands well and the lower porosities generally lead to slower exchange kinetics (47). In addition they are more expensive to make.

For the inorganic exchangers discussed here to make an impact on uranium remediation, investigators need to focus more on testing regeneration and evaluation of usable lifetime. In fact, for the particular examples presented in Section 2 on polystyrene resins this is also an issue. In the nuclear industry regeneration and resin lifetime are central issues (52). Large-scale remediation of uranium waste streams is just beginning to receive attention and the processes and procedures developed in the nuclear industry should serve as model for this emerging field (52).

References

34. V. Kailasam and E. Rosenberg, Hydrometallurgy, 2012, 129–130, 97

Further Reading
Edward Rosenberg received his doctorate at Cornell University, USA, and held post-doctoral fellowships at the University of London, UK, and the California Institute of Technology, USA. He is the author of 180 peer-reviewed publications, five book chapters, eight patents and one book in the areas of environmental and organometallic chemistry. He has received awards for his research and student mentoring from the University of Montana, USA, and has had visiting faculty fellowships in Italy, Israel and South Africa.

William G. Pinson earned his PhD in Chemistry in 2012 at the University of Montana under Professor Ed Rosenberg. He then did post-doctoral research at the University of Montana until 2014 on recovery and regeneration of petroleum cracking catalysts, followed by a nine-month post-doctoral position at the Department of Metallurgical Engineering at Montana Tech, carrying out research on flotation of rare earth elements using novel collectors. Currently Dr Pinson is working for the Government Publishing Office in Washington DC as a Research Scientist in materials science and product processing.

Ranalda Tsosie is Diné from Tó’likan, Arizona, USA. She is currently a third year graduate student at the University of Montana, in Interdisciplinary Studies with a focus in Chemistry and Environmental Science. Her research interests are directed toward the development of remediation technology for the specific use in groundwater and metal ion cleanup efforts.

Hlanganani Tutu received a PhD degree in Environmental Chemistry from the University of the Witwatersrand, South Africa, in 2006, an institution that he has worked for since then. Professor Tutu’s research interests span geochemical modelling of solutes transport, designing remediation strategies and chemometric data modelling. He teaches courses in general chemistry, environmental chemistry and geochemical modelling, has supervised a number of research projects and published over 100 peer-reviewed articles.

Ewa Cukrowska is a Professor of Environmental and Analytical Chemistry at the University of the Witwatersrand. Professor Cukrowska received MSc and PhD degrees from the Maria Curie-Skodowska University in Poland in 1982. Her research interests include speciation of trace elements in industrial, environmental, and biomedical samples with emphasis on the development and application of different analytical techniques and remediation methods. She also has interest in: studies of metal transport and fate, effects of seasonal changes on contaminant behaviour and biological uptake. She teaches courses in general, analytical and environmental chemistry and has published over 200 publications.
International Symposium on Zeolites and Microporous Crystals 2015

Recent advancements in zeolite research

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The International Symposium on Zeolite and Microporous Crystals 2015 (ZMPC2015) was held at the Sapporo Convention Center, Japan, from 28th June to 2nd July 2015 and had 435 attendees from 32 countries, with 75% from Japan, China, Korea or Taiwan. 396 presentations covered all aspects of zeolites and microporous crystals over four days. Catalysis and synthesis were the two main themes (46% of all presentations) with the others being: new porous materials; membranes and films; adsorption and diffusion; characterisation; novel applications; industrial applications; layered materials; computational chemistry; post-synthetic treatment; crystallography; and ion exchange. There were six plenary talks along with 17 keynote and 94 oral presentations that took place in three parallel sessions. There were two poster sessions for 250 posters and recent research reports.

Synthesis

‘Innovations in Zeolite Synthesis and Applications at UOP’ was presented by John Qianjun Chen (UOP, USA). Using the charge density mismatch (CDM) approach, UOP scientists have invented and patented more than 50 new zeolite materials referred to as UOP zeolitic materials (UZMs). The CDM approach starts with a clear reaction mixture that cannot crystallise. A couple of economical structure-directing agents (SDAs) are then added, such as alkali or tetramethylammonium cations. Strict control over the concentration of the crystallisation SDAs allows one to have great control over the rates and extent of condensation, often resulting in nanocrystals and crystals of unique morphologies. Crystallite dimensions are typically 500 Å to 20 Å.

Tsuneji Sano (Hiroshima University, Japan) presented ‘High Potential of Hydrothermal Conversion Route as an Alternative Method for Zeolite Synthesis’. Based on the hydrothermal conversion of one zeolite type into another type this presentation described recent investigations of the synthesis of several types of zeolites by hydrothermal conversion in the presence and absence of organic structure-directing agents (OSDAs). FAU could be converted to RUT, *BEA, CHA or OFF; USY to CHA; and FAU to LEV or MAZ. The presence of seeds sped up the conversion and led to a core/shell structure. The structural similarity between the starting zeolite and the final crystallised zeolite is a crucial factor for hydrothermal conversion, for example all having 4MR. Separately, a tetraethylphosphonium (instead of nitrogen based) cation was used to synthesise a high-silica AEI zeolite with high thermal/hydrothermal stability.
‘Green Sustainable Science and Technology Supported by Worldwide Researchers’ Community for Micro- and Meso-porous Materials’ was presented by François Fajula (CNRS, University of Montpellier, France). Fajula is the current president of the International Zeolite Association (IZA) and spoke about the conversion of methanol to olefins through reaction intermediates and coke precursors, the identification of the active sites responsible for the carbonylation of methanol on mordenite and of the selective reduction of nitrogen oxides (NOx) on Cu-SSZ-13. He also spoke about preparation of zeolite nanocrystals or crystals with multimodal hierarchical porosity, pulse field gradient NMR and the need for further advanced characterisation of zeolites.

Manuel Moliner (Instituto de Tecnología Química, Spain) presented ‘Rationalizing the Synthesis of Small Pore Zeolites with Large Cavities’. The ability to place the silicon atoms selectively in isolated form (desired due to higher acid strength) will mostly depend on the properties of the OSDA selected for the SAPO synthesis, such as size, shape, rigidity or charge distribution. Therefore, extracting an ‘SAR’ value from $^{29}$Si NMR spectra makes no sense as two SAPOs could have the same framework SAR but different distributions due to different OSDAs. A second part of the talk discussed Cu-SAPO-34, the hydrothermal stability of which has been considerably increased by properly modifying the synthesis conditions to favour the selective distribution of isolated Si species in the framework positions by direct synthesis methodologies (1).

Cong-Yan Chen (Chevron Energy Technology Co, USA) presented ‘Investigation of Shape Selective Properties of SSZ-87 and Other Zeolites via Hydrocarbon Adsorption and Catalytic Test Reactions’. This talk from Chevron contained two interesting pieces of information. First, there was a new synthesis approach to yield alkali-free borosilicate zeolites using boric acid and ammonium fluoride, with both boron and fluoride as part of the synthesis product (2). Al can substitute B in zeolite frameworks if the pores are large enough to allow the hydrated Al cations to enter. As a result, the borosilicate zeolites can be converted to their aluminosilicate counterparts with acid sites strong enough to catalyse various hydrocarbon transformation reactions. Second, 2,2-dimethylbutane adsorption has proven to be a useful tool to provide valuable information for the determination of the unknown structures of many new zeolites. The initial rate of adsorption and subsequent slower adsorption rate gives information on ring sizes and spatial restrictions.

Toshiyuki Yokoi (Tokyo Institute of Technology, Japan) presented ‘Control of Location of Al atoms in the Pores of ZSM-5 Based on the Rational Choice of Organic and Inorganic Cations’. The type of OSDAs and the presence or absence of Na cations during crystallisation affects the location of Al atoms in the framework; for example the acid sites in tetrapropylammonium [TPA] are selectively located at the intersections because the negative charges of Al atoms in the MFI framework are balanced by large TPA cations, which is located in the intersections during the crystallisation of ZSM-5 (3).

Shaheen Anis (Masdar Institute of Science and Technology, Abu Dhabi) presented ‘Fabrication of Micro and Nanozeolite Fibers Through Electrospinning’. Anis fabricated zeolite-Y microfibres (≥600 nm) and zeolite LTL nanofibres (<100 nm) through electrospinning, which is an economic and versatile method for fabricating fibres. SEM images reveal a rough morphology for both zeolite-Y microfibres and LTL nanofibres, which is highly desirable for strong catalytic activity. The ratio of zeolite: polyvinylpyrrolidone (PVP): ethanol was 1:1:8 by weight. Calcination in a furnace at 475°C for 2 h removed the polymer without affecting the zeolite, characterised by BET and XRD.

Jorge Gascon (Delft University of Technology, The Netherlands) presented ‘Rational Design of Structured Catalysts and Membranes’. Polymer membranes and inorganic membranes both have their pros and cons; mixed matrix membranes offer the best of both (4). Gascon also introduced the use of metal-organic frameworks (MOFs) as hard templates for the direct synthesis of carbon-metal nanoparticle composites displaying unrivalled stability in different conversions involving carbon nanotubes, from Fischer-Tropsch synthesis to the electroreduction of CO$_2$ (5).

Characterisation

Yuriy Roman-Leshkov (Massachusetts Institute of Technology, USA) presented ‘Lewis Acid Zeolites for Biomass Conversion: Insights on Reactivity, Characterization, and Stability’. Roman-Leshkov used dynamic nuclear polarisation (DNP) to characterise Sn-Beta zeolites without isotopic enrichment in a matter of hours, instead of a weekend. DNP was also used to obtain complex 2D spectra for elucidating adsorption geometry between nuclei from adducts and active sites in zeolites. Titanium, zirconium, tin and hafnium were
probed as Lewis acid sites, however the DNP results from Zr and Hf were not great. bCTbk dissolved in 1,1,2,2-tetrachloroethane was used as the DNP radical and solvent. Finally, results on TMPO as an acid-site probe molecule were presented. $^{1}H-^{31}P$ heteronuclear correlation (HETCOR) experiments differentiated between open and closed sites.

Matthias Thommes (Quantachrome Instruments, USA) presented ‘Progress and Challenges in the Physical Adsorption Characterization of Mesoporous Zeolites’. This talk from Quantachrome was on state-of-the-art physical adsorption techniques based on argon 87 K adsorption, applied to hierarchically structured zeolites and other materials. A novel methodology for the analysis of the adsorption hysteresis was applied to argon isotherms from a surfactant templated mesoporous Y zeolite in order to quantify the percentage of ‘open’ and ‘blocked’ mesoporosity.

Emiel Hensen (Eindhoven University of Technology, The Netherlands) presented ‘Design of Hierarchical SSZ-13 Zeolite by Fluoride-modulated Growth’. Creating mesoporosity in SSZ-13 results in improved catalytic performance in the MTO reaction. However, the characterisation employed was of the most interest; SEM, TEM, confocal fluorescence microscopies, COads FT-IR, MTO activity testing, methanol/propylene adsorption and positron emission tomography (PET) of $^{11}$C-methanol. This last technique was used to observe, in situ, a methanol pulse moving through a fixed bed reactor.

‘H$_2$-Activation Ability of Zn$^{2+}$ Caused by MFI: Effects of Al–Al Distance and Curvature Originated from MFI-Pore-Structure’ was presented by Akira Oda (Okayama University, Japan). Oda reported that the H$_2$ activation ability of Zn$^{2+}$ ion-exchanged in MFI is controlled by the two dominant factors derived from the ion-exchangeable site in MFI: Al–Al distance and specific nature endowed by the curvature originated from pore-structure. This was achieved using molecular orbital theory and observation of the Zn4s and O2p XPS peaks.

Kaname Yoshida (Japan Fine Ceramics, Japan) presented ‘High Resolution Imaging of Zeolites with Aberration Corrected (S)TEM’. Aberration-corrected high resolution TEM (AC-HRTEM) imaging is very effective in imaging of zeolitic frameworks consisting of comparatively light elements such as Si, Al and O. Each crystalline sample was crushed in an agate mortar with ethanol, and collected on a TEM microgrid support. Two C$_S$ values of $\pm 15 \mu m$ were employed to AC-HRTEM imaging. Imaging with positive (PCS) and negative (NCS) values form dark and bright atomic images, respectively. In order to compensate the very low signal-to-noise ratio (SNR) of image contrast, all images were processed with a Bragg filter. The heavy element Cs$^+$ captured at the centre of S8R was clearly seen in all images; however, Na$^+$ delocalised near the centre of S8R could not be visualised absolutely in high-angle annular dark field (HAADF)-STEM mode.

Silica
Giuseppe Bellussi (Eni SpA, Italy) presented ‘Hybrid Organic-inorganic, Crystalline or Pseudo-ordered, Porous Silicates’. Bellussi talked about periodic mesoporous organosilica (PMO) and eni carbon silicate (ECS) materials (6). The synthesis of ECS is often promoted by the presence of boric acid. Boron does not enter in the crystalline framework, but boric acid promotes the hydrolysis of the silica precursor thus accelerating the formation of pure crystalline phases. The silica to alumina ratio (SAR) of the materials obtained so far is low, close to 1, and this composition has prevented the obtainment of the acidic form of ECS materials. Interestingly, the structure of ECS-3 was determined by automated diffraction tomography (ADT) and ECS-20 contains an O$_3$ environment.

‘Synthesis and Structural Study of the Complex Macroporous Photonic Structure by Electron Microscopy’ was presented by Lu Han (Shanghai Jiao Tong University, China). To solve the complex hollow structure, the three-dimensional (3D) electrostatic potential map of the macroporous silica was obtained from the Fourier synthesis of the crystal structure factors taken from transmission electron microscopy (TEM) images. A 3D reconstruction was obtained from 160 reflections. TEM images were simulated using a 3-term nodal equation. These studies demonstrate that electron crystallography is the only way to solve the complex structure at such length scale.

Atsushi Fukuoka (Hokkaido University, Japan) presented ‘Low-Temperature Oxidation of Ethylene by Platinum Nanoparticles supported on Mesoporous Silica’. The researchers studied platinum catalysis of ethylene oxidation at low temperature. The effect of supports was investigated using 5% Pt at
25°C, catalytic activities were ranked as follows: Pt/MCM-41 > Pt/SiO₂ > Pt/Al₂O₃ > Pt/TiO₂ > Pt/ZrO₂. A mechanism for the oxidation of ethylene by supported Pt catalysts was also proposed.

**Catalysis**

Michael Tsapatsis (University of Minnesota, USA) presented ‘2-Dimensional Zeolites: from High-quality Exfoliated Nanosheets for Thin Film Formation to Self-pillared Nanosheets for Catalysis and Adsorption’. Scale-up of membranes to separate para-/ortho-/meta-xylene is a big hurdle. Tsapatsis introduced an approach to hierarchical zeolite catalysts and adsorbents, which does not rely on sacrificial hard or soft templates and can be accomplished by single-step synthesis. The approach relies on rotational intergrowths and produces self-pillared nanosheets, which exhibit performance similar to other reported 2D assemblies. Thickness of the 2D nanosheets were determined by rel-rod mapping using TEM diffraction patterns over a tilt-series, see Figure 1 (7).

Raul Lobo (University of Delaware, USA) presented ‘Novel Active Sites and New Opportunities in Zeolite Catalysis’. Lobo spoke about methane oxidation on small-pore copper-zeolites and noted that diffuse-reflectance ultraviolet-visible (UV-Vis) spectroscopy revealed that the structure of the Cu sites is similar between the three zeolites investigated (SSZ-13, SSZ-39 and SSZ-16) but different from Cu-ZSM-5. Another topic was on the synthesis of benzene from methane using MoCₓ nanoparticles embedded in the pores of H-ZSM-5. They decoupled the chemistry that occurs on the MoCₓ nanoparticles from the oligomerisation/aromatisation reaction by preparing a variety of catalysts in non-acidic zeolites.

Zhongmin Liu (Chinese Academy of Sciences, China) presented ‘Recent Progress on Fundamental Researches of MTO Reaction’. The hydrocarbon pool mechanism, in which organic species confined in the zeolite cage or at the intersection of channels act as co-catalysts, has been regarded as a rational explanation for formation of C–C bonds in methanol conversion (8). Methylbenzenium cations and methylcyclopentenyl cations have been speculated to be the most important active intermediates involved in the ‘hydrocarbon pool’ mechanism. Although a reaction network was proposed, there still remain many scientific challenges, such as how the first C–C bond forms, what happens in the induction period, what are the exact relations among different reaction routes, how coke forms, and how to control the coking reaction in the reaction network.

Shang-Bin Liu (Institute of Atomic and Molecular Sciences, Taiwan) presented ‘Brønsted-Lewis Acid Synergy during Selective Catalytic Reduction of Nitric Oxide over Lanthanide-metal Incorporated Iron-based ZSM-5 Zeolite’. The catalysts were characterised by X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET) surface area analysis, electron microscopy (EM) and X-ray photoelectron spectroscopy (XPS), whereas their acidic properties were analysed by ammonia temperature-programmed desorption (NH₃-TPD), pyridine infrared (IR), and ³¹P magic-angle spinning nuclear magnetic resonance (MAS NMR) of adsorbed trimethylphosphine oxide (TMPO) as a probe molecule. CeFe-ZSM-5 catalyst exhibited the optimal NO
conversion exceeding 95% over a temperature range of 300°C to 500°C. The superior selective catalytic reduction (SCR) activity observed for the CeFe-ZSM-5 has been attributed to the synergistic effect from the Brønsted acidity of MFI zeolites and strong Lewis acidity induced by the presence of incorporated active Fe³⁺, Ce³⁺ and/or Ce⁴⁺ ion species.

Kristof De Wispelaere (Ghent University, Belgium) presented ‘Combined Theoretical and Experimental Study on the Influence of Zeolitic Acid Strength on the Methanol Conversion Process’. Two AFI catalysts with different acid strength, H-SSZ-24 and H-SAPO-5, were tested for methanol to hydrocarbons (MTH) catalysis (9). It was found that the strongly acidic H-SSZ-24 is more selective towards aromatic products and light alkenes than the moderately acidic H-SAPO-5. Furthermore, it was found that while aromatic hydrocarbon pool species appear to play an important role in H-SSZ-24, these are of less importance in the weaker acid H-SAPO-5. AFI was chosen over the more typical CHA (SAPO-34) as AFI can be fed aromatics, which cannot enter the CHA supercages.

Javier Ruiz-Martínez (Utrecht University, The Netherlands) presented ‘The Role of Methoxy and Aromatic Species during the Methanol-to-Olefins Reaction over SAPO-34’. The authors presented a novel operando approach combining UV-vis and IR spectroscopy with online mass spectrometry to investigate the chemistry of the species formed during the methanol to olefins (MTO) reaction (10). It was found that the accessibility of SAPO-34 is linked with the amount of methoxy species, whereas the formation of polyaromatic species that block the pores is the main cause of deactivation. Furthermore, the reaction pathways responsible for the formation of olefins and polyaromatics coexist and compete during the whole MTO process.

Ferdi Schüth (Max-Planck-Institut für Kohlenforschung, Germany) presented ‘Porous Polymers as Catalysts and Catalyst Support’. Several syntheses, gas adsorption properties and catalytic performance of porous polymers were discussed. Notably, a 1000 m²g⁻¹ Pd/polyphenylene catalyst proved a very good solid catalyst for the Suzuki coupling of substrates which are very difficult to activate, such as methane to methanol (11). Hollow graphitic spheres containing platinum were also investigated for oxygen reduction reaction in fuel cells. This Pt@C catalyst does not deactivate with cycling and the hollow sphere is essential in a real fuel cell for effective mass transport, see Figure 2 (12).

**Conclusions**

From a characterisation perspective, XRD, TEM and MAS NMR were the most popular techniques, all of which were presented in at least 15 separate talks attended by the reviewer. The TEM was especially advanced, incorporating electron crystallography and tomography. SEM and FTIR were also well represented, followed by UV-vis. AFM and XPS data were only shown in three talks, whilst Raman appeared once, suggesting that these techniques have potential to be further exploited by the community.

Overall, ZMPC2015 was well attended and well organised. We saw an excellent array of talks and posters that covered all the latest developments in the field of zeolites and microporous crystals, especially regarding catalysis and synthesis. The next conference will be held in Yokohama, Japan, in 2018.

**References**

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### The Reviewer

Nathan Barrow is currently a Principal Scientist in the Advanced Characterisation department at the Johnson Matthey Technology Centre, Sonning Common, UK. He graduated with an MPhys in 2006 from the University of Warwick, UK, where he remained to gain a PhD in SSNMR. In 2010 Barrow was a Knowledge Transfer Partnership associate between the University of Warwick and Johnson Matthey, helping to install and run an SSNMR service. His current research focuses on applying advanced characterisation to materials such as zeolites, alumina, glasses and batteries.
A Comparative Study of N₂O Formation During the Selective Catalytic Reduction of NOx with NH₃ on Zeolite Supported Cu Catalysts


The decreased N₂O formation on the small pore zeolite, Cu-CHA, in the SCR of NOx with NH₃ was studied by comparing with a large pore Cu-BEA zeolite catalyst. The N₂O yield rises with a rise in the NO₂/NOx ratios of the feed gas for both catalysts, implying N₂O is formed via the decomposition of NH₄NO₃. TPD showed that NH₄NO₃ was more stable on Cu-CHA compared to Cu-BEA. Surface nitrate groups are vital for NH₄NO₃ formation and this was confirmed by in situ FTIR spectra on the stepwise (NO₂ + O₂) and (¹⁵NO + NH₃ + O₂) adsorption and reaction, and product distribution analysis using isotope-labelled reactants. Cu-CHA was found to be significantly less active than Cu-BEA in catalysing NO oxidation and the later formation of surface nitrate groups.

Local Organization of Fe³⁺ into Nano-CeO₂ with Controlled Morphologies and its Impact on Reducibility Properties


Ce₁₋ₓFeₓO₂₋ₓ/₂ solid solutions were prepared by two different methods. Surface area, lattice parameter, particle shape and local Fe³⁺ organisation were found to depend on the preparation method and the Fe content. A microwave preparation method was used and caused a large amount of Fe³⁺ to exist in isolated distorted octahedral sites affecting a large number of Ce⁴⁺ nearest neighbours and leading to highly mobile oxygen vacancies. Therefore these samples had a lower solubility limit and a larger variation of the cell parameter compared to conventionally prepared samples. The findings can be extended to provide understanding of reactivity and redox properties (for automotive exhaust catalysts and photocatalysis), ionic conductivity (for solid oxide fuel cells) and magnetic interactions (for spintronic applications) in other transition metals.


In this study exhaust energy is captured from a high temperature engine exhaust stream to aid catalytic endothermic fuel reforming reactions where hydrocarbon fuel is converted to hydrogen-rich reformate. The reformate is then reused in the engine, providing a source of hydrogen to improve the engine combustion process – known as the reformed exhaust gas recirculation (REGR). This method has much potential for modern gasoline direct injection (GDI) engines. A full scale gasoline prototype reformer incorporated with a multi-cylinder GDI engine was presented by the authors. The prototype reformer performance was analysed by the reformate composition, the temperature distribution across the catalyst, the reforming process efficiency and the amount of exhaust heat recovery accomplished.

Fine Chemicals: API Manufacturing

Palladium-Catalyzed α-Arylation Reactions in Total Synthesis


Palladium-catalysed α-arylation of carbonyl compounds is a powerful new methodology for synthesising natural products and active pharmaceutical ingredients (APIs). Increased yields, improved scope, decreased number of steps and alternative starting materials are all made possible. This microreview highlights the importance of the method for a number of challenging examples, and raises to the attention of synthetic chemists the value of palladium-catalysed α-arylation as a key step in choosing a route to structurally important molecules.
NEW BUSINESSES: BATTERY TECHNOLOGIES

Synthesis of Multimodal Porous ZnCo₂O₄ and its Electrochemical Properties as an Anode Material for Lithium-Ion Batteries


A simple method to synthesise multimodal porous ZnCo₂O₄ microspheres through PVP assist solvothermal self-assembling process was proposed by the authors. This was then characterised by XRD, SEM, TEM and XPS, and a potential formation mechanism was suggested. Lithium ion batteries were fabricated using the ZnCo₂O₄ microspheres as an anode material. The results show that the porous microstructure gives an outstanding electrochemical performance with high capacity and long-life cycling stability. A large reversible capacity of 940 and 919 mAh g⁻¹ was retained after 100 cycles at a low charge-discharge rate of 0.1 C and 0.2 C (100 and 200 mA g⁻¹) respectively.

NEW BUSINESSES: FUEL CELLS

Platinum/Carbide Interactions: Core-Shells for Catalytic Use


Various transition metal carbides were studied by DFT for possible application as core materials in core-shell nanoparticulate fuel cell catalysts. The fcc forms of TiC, NbC, TaC and hcp WC were selected and compared to β SiC. The interaction of model surfaces with Pt were calculated. Pt overlayers on carbides were found to be thermodynamically feasible. The results were explained in terms of the modulation of the carbide and Pt electronic structures. WC and SiC were found to support Pt overlayers and therefore may be suitable for Pt encapsulation. Pt adsorption took place on fcc (111) carbide surfaces in all cases, but not on fcc (100). The carbide supports also affected oxygen binding on the Pt overlayer, the implications for the ORR are discussed. WC may be most suitable for a core material. Several of the Pt–WC surfaces showed reduced oxygen adsorption energies, and should provide similar ORR activity to Pt catalysts.

PRECIOUS METAL PRODUCTS: NOBLE METALS

TEM Characterization of Simultaneous Triple Ion Implanted ODS Fe12Cr


To aid the design of advanced fusion reactors it is important to understand the behaviour of oxide dispersion strengthened (ODS) ferritic/martensitic steels under irradiation. TEM was used to investigate the effects of irradiation on a simultaneous triple ion implanted ODS Fe12Cr steel. The grain and dislocation structures, oxide nanoparticles and other secondary phases present in the steel were the focus of the study. Irradiation of the ODS steel was carried out at room temperature using Fe⁶⁺, He⁺ and H⁺ at the JANNUS-Saclay facility to a damage of 4.4 dpa. The ODS nanoparticles had high stability under these irradiation conditions.

PROCESS TECHNOLOGIES

The Adsorption of Ethene on Fe(1 1 1) and Surface Carbide Formation

S. Booyens, L. Gilbert, D. Willock and M. Bowker, Catal. Today, 2015, 244, 122

During Fischer-Tropsch synthesis of higher hydrocarbons from synthesis gas (CO + H₂), ethylene is adsorbed and decomposed on a Fe(1 1 1) surface. This investigation into the nature of the process used a molecular beam reactor and XPS. At a range of substrate temperatures (373–873 K), ethylene was found to decompose fully to atomic carbon and gas phase hydrogen, and carbon deposited on the surface was found to undergo fast diffusion into the subsurface region leaving surface sites free. Fast carbon removal could be achieved with oxygen above ~600 K; the carbon was evolved as CO, with no evidence of CO₂ production. CO on the surface at those temperatures has a very short lifetime.

Dual Doping Effects (Site Blockage and Electronic Promotion) Imposed by Adatoms on Pd Nanocrystals for Catalytic Hydrogen Production


Doping of metal nanoparticles with additives such as polymers or metallic adatoms can be used to optimise the electronic and geometric properties of catalytic materials. Rational nanocatalyst design can be improved by a greater understanding of doping effects at the atomic level interaction(s). Using the decomposition of HCOOH to H₂/CO₂ over metallic Pd nanoparticles as a probe reaction, three different metal additives were studied: Bi, Te and Ag. Each was found to produce a different doping effect. Bi atoms reside on higher index sites, leading to reduced HCOOH dehydration; Te atoms occupy terrace sites, reducing the rate of dehydrogenation; Ag atoms are not site specific and at high coverage, their strong electronic effects promote activity on the decreased number of surface Pd sites.

Effect of Mill Type on the Size Reduction and Phase Transformation of Gamma Alumina

The impact of size reduction mechanisms on $\gamma$-$\text{Al}_2\text{O}_3$ catalyst support brought about by various stress modes was investigated. Three different mill types were studied and air jet milling was found to be most efficient in decreasing particle size from $d_{90}$ of 37 $\mu$m to 2.9 $\mu$m in comparison with planetary ball milling (30.2 $\mu$m) and single ball milling (10.5 $\mu$m). The samples were characterised by XRD and TEM. Phase transformation to the undesirable $\alpha$-$\text{Al}_2\text{O}_3$ occurs during planetary ball milling, therefore, there is a big decrease in the surface area from 136.6 m$^2$ g$^{-1}$ to 82.5 m$^2$ g$^{-1}$ as shown by the BET method. This was caused by the large shear stresses under high shear rates.

**Discrete Element Modelling (DEM) Input Parameters: Understanding their Impact on Model Predictions Using Statistical Analysis**

In the DEM, the choice of the particle property input parameters and/or their cross-correlation presents a difficulty. The authors study the effect of the DEM input particle properties on the bulk responses for the discharge of particles from a flat bottom cylindrical container onto a plate using a parametric multi-level sensitivity process. Particle properties such as Young's modulus, friction parameters and coefficient of restitution were altered to investigate the impact on material repose angles and particle flow rate. Both the final angle of repose and particle flow rate are determined by inter-particle static friction followed by inter-particle rolling friction coefficient. The suggested process gives a systematic method that can be used to demonstrate the significance of particular DEM input parameters for a chosen system and then possibly aid their selection or calibration.

**Understanding the Structure Directing Action of Copper-polyamine Complexes in the Direct Synthesis of Cu-SAPO-34 and Cu-SAPO-18 Catalysts for the Selective Catalytic Reduction of NO with NH$_3$**

The direct synthesis of Cu-containing microporous SAPO materials using complexed Cu$^{2+}$ cations in linear polyamines was investigated. The authors studied the complexing ligands: DETA, HEEDA, TETA, 232, 323, TEPA and PEHA. A comparative exercise of the syntheses was undertaken using analogous Ni-polyamine complexes. Both SAPO-18 and SAPO-34 materials were prepared using Cu$^{2+}$ and Ni$^{2+}$. SAPO-18 was prepared with Cu$^{2+}$ (232), Ni$^{2+}$ (232) and Ni$^{2+}$ (TETA) but the majority of the polyamine complexes were prepared by direct crystallisation to SAPO-34. UV-visible, EPR spectroscopy and computer simulation were used to investigate the coordination geometry of the complexes. SAPO-18 was preferred by the smaller square planar complexes or octahedral species (with two water molecules) of 232 and TETA. The extra-framework Cu$^{2+}$ and Ni$^{2+}$ cations in SAPO-18 and SAPO-34 frameworks were caused by calcination. Thermal template degradation happens via nitrile intermediates in Ni-SAPO-18 and was shown by *in situ* synchrotron IR spectroscopy. The extra-framework Cu$^{2+}$ and Ni$^{2+}$ cations freed by calcination were located by Rietveld structural analysis.