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By Peter J. Clark, Giuseppe Forte, Mark J. H. Simmons and E. Hugh Stitt
We have previously described some of Johnson Matthey’s core competencies in modelling (1) and the control of advanced materials at the atomic scale (2). The third of these competencies, and a vital component of the company’s strategy to develop high performance solutions to its customers’ problems, is characterisation of materials.

Materials characterisation is a huge and diverse field. One place perhaps to start is at the beginning, and the first principle to consider is the depth to which characterisation supports new materials discovery:

- Measuring a material’s property allows experimental improvement in the property;
- Making unique measurements allows differentiation by improvement in unique areas;
- Insight into compositional and structural origins of material properties enables rationally designed improvement.

Taking a model heterogeneous catalyst, of a metal supported on an oxide support (such as platinum on alumina), hydrogen chemisorption allows for empirical exploration of preparation strategies leading to increased surface area. As well as the support it is essential to control Pt content between preparations to ensure commercial efficiency, thus even for a relatively simple material the number of measurements needed to achieve empirical success increases rapidly.

The “unique” measurements are measurement capabilities developed for a bespoke solution to a particular question or performed with instrumentation or facilities which have a high barrier to access. Returning to the model material, the optimum metal surface area available depends upon nanoparticulate Pt dispersed over the alumina surface. Transmission electron microscopy (TEM) coupled with automated image processing can count and describe particle size, shape and dispersion. TEM is not a unique technique, yet developed know-how in sample preparation, data collection, image processing and data interpretation varies widely between practitioners. Reliable access to material properties such as particle size distribution at nanoscale is key to enabling empirical optimisation and opens the potential for control of both size and distribution.

Within the third category, the delivery of insight requires an internal connection between a compositional or structural property and the behaviour of a material. Hence most “in situ” and “operando” approaches sit within this area. Taking the Pt on alumina model further, observation of nanoparticle sintering in response to changing temperature can be achieved with commercially available equipment. Direct observation conducted with a time capture component yields significantly more insight than empirical approaches.

There is therefore another level in the characterisation hierarchy to pursue:

- Making measurements that yield temporally limited structure (reactive intermediates), kinetic or energetic values during operando studies enables the in silico modelling of materials and the prediction of performance based on proposed materials structure.

There is much fertile research ground to explore in the gap between current modelling capability (1) and a full description of a material integrated across length scales.

**Characterisation Driving Innovation**

The above pressures would tend to suggest that characterisation demand will continually drive towards the delivery of the ultimate, since the richness of the information has a direct impact on the ease with which materials discovery can be accomplished. The predictable trade-off is with cost and time.

**Figure 1** describes the dilemma. At the pinnacle of the triangle is the delivery of intellectual property (IP) in materials development. Empiricism (discovery through systematic exploration of the preparation variables) is
furthest away from IP and requires significantly more (albeit lower complexity) characterisation support. It is no surprise that, as characterisation complexity increases, so does the stimulation towards insight and designed improvement, hence one moves closer to the delivery of IP with fewer measurements. But cost increases and the availability or throughput drops.

Not implicit in the understanding of this model is the bias from which it is observed. One challenging thought is that “characterisation” has traditionally operated as a service activity to the synthetic researcher: i.e. people make materials, then analyse, activity test and try to work out what the results mean to formulate the next experiment. This “perspiration approach” requires a huge bias in delivery of capability in order to drive innovation. Generally speaking, more of the picture of a material is needed before the further stage can be formulated and hence the demand for measurement provision is exponential. The exponent is exacerbated by materials complexity, which increases with the need to achieve new performance requirements. The risk is that a gap between capacity to make materials, and the capacity for characterisation, limits the rate of improvement.

The alternative turns this on its head: model-led characterisation demands materials to confirm hypotheses, enabling predictive optimisation. Fewer materials are synthesised yet insightful measurement stimulates the inventive step (the “inspiration approach”). More research support is committed to development of characterisation methods which are consistent with insight delivery for complex materials.

### Rewarding Collaborations

We already see this happening. Increasingly, academic and industrial researchers are either demanding or beginning to develop characterisation methodologies to support solutions to their problems. The market is shifting to meet the arising need. Characterisation development is a rewarding area for collaborations: the intellectual challenge to extract predictive information from materials is high, and has high impact, yet the exploitation of insightful methods can be separated from commercial materials development through use of the simple yet realistic model systems which are needed to drive the cutting edge.

One area where this is already yielding a rich collaboration is the rapidly developing partnerships centred at national research facilities. In Johnson Matthey’s case, the Harwell campus in the UK incorporating Diamond Light Source, ISIS the neutron source and the Lasers for Science facilities all have capabilities to enhance characterisation development. The UK Catalysis Hub consortium is also on campus and is developing researchers with the capacity to develop characterisation methodologies. Working in this environment, providing rich problems and collaboration support opens up great promise for the development of future solutions to the four objectives for characterisation.

So here we should celebrate this issue based on characterisation methods. The thread that binds them is the development of methodologies seeking to acquire information about increasingly complex systems, towards finding answers to critical problems for real-world applications.

### References


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Surface Selective $^1$H and $^{27}$Al MAS NMR Observations of Strontium Oxide Doped $\gamma$-Alumina

Surface binding sites of strontium oxide on $\gamma$-alumina identified for the first time

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High-surface area $\gamma$-alumina is industrially used as a catalyst support. Catalytically active elements are doped onto the support, where they can bind to AlO$_4$, AlO$_5$ or AlO$_6$ sites on the surface. Pretreating the surface with alkaline earth oxides can alter the availability of these surface sites, hence affecting the catalytic activity. The surface binding sites of strontium oxide (SrO) on $\gamma$-alumina were previously unknown. Direct $^{27}$Al magic angle spinning nuclear magnetic resonance (MAS NMR) could not detect AlO$_5$ sites at 9.4 T, so $^1$H–$^{27}$Al cross-polarisation (CP) MAS NMR was used to preferentially select the surface environment signals. We directly observed the three surface environments on dehydrated $\gamma$-alumina as a function of SrO impregnation up to 4 wt% SrO. We found that Sr$^{2+}$ preferentially binds to AlO$_5$ and AlO$_6$ surface sites. $^1$H MAS NMR revealed SrO impregnation causes a reduction in the terminal (−0.3 ppm) and bridging (2.2 ppm) hydroxyl environments, as well as the promotion of a new peak in between these sites, at 0.5 ppm. By using $^1$H–$^{27}$Al CP/MAS NMR the relative proportions of surface sites on $\gamma$-alumina can be determined, allowing an optimal level of SrO doping that can saturate all the AlO$_5$ sites. Importantly, this provides a method of subsequently depositing catalytically active elements on just the AlO$_4$ or AlO$_6$ sites, which can provide a different catalytic activity or stability compared to the AlO$_5$ binding site.

1. Introduction

Over 80 million tons of alumina are produced annually, which is used industrially for the production of aluminium and in applications requiring high melting point, excellent mechanical strength, electrical resistivity or chemical inertness (1). There are several polymorphs of alumina and the thermal transformations between them are well known (2). $\gamma$-Alumina in particular has a favourable combination of high surface area, pore size distribution and acid/base characteristics, which makes $\gamma$-alumina a common industrial catalyst support (3).

Specific applications of $\gamma$-alumina in catalysis include as a binder for zeolite catalysts in fluid catalytic cracking (4), as iron/copper/potassium (FeCuK) support for Fischer-Tropsch catalysis (5) and as a platinum support for dehydrogenation of jet fuel (6) or carbon monoxide oxidation (7). Three-way catalysts (TWC), which are widely used on gasoline engines to reduce CO, nitrogen oxides (NOx) and hydrocarbon emissions, include $\gamma$-alumina as part of the mixed oxide support because of its high surface area and relatively good thermal stability under hydrothermal conditions (8, 9). Barium oxide (BaO) and lanthana are commonly...
used as stabilisers for alumina in TWC. An additional advantage of adding alkaline earth oxides to γ-alumina is the improvement of NOx storage for TWC (10, 11). Thus, the investigation of SrO structure on the surface of γ-alumina is one of practical importance. The matter is complicated as despite the massive production and industrial use of γ-alumina, the surface topography of γ-alumina is still under debate (12). Nevertheless, there is clear agreement that three main aluminium coordination environments exist on the surface: AlO₄, AlO₅ and AlO₆.

Solid-state nuclear magnetic resonance (SSNMR) of alumina is informative as the aluminium environments give distinct ²⁷Al peak positions; AlO₄ ≈ 60 ppm, AlO₅ ≈ 30 ppm and AlO₆ = 0 ppm. As ²⁷Al is a quadrupolar nucleus (13), the observed chemical shifts vary as a function of magnetic field strength, but remain distinct at all high fields (14). Studies on γ-alumina have been reported for the past 25 years, both using direct ²⁷Al NMR (15–17) as well as using ¹H to ²⁷Al CP NMR (12, 18, 19). More recently, dynamic nuclear polarisation (DNP) has been used to enhance the ²⁷Al NMR signals from the surface of γ-alumina, calculations have shown that the ²⁷Al CP signal is from the very first surface layer or primostrato (20, 21). This is in agreement with a deuteration experiment that concluded the CP signal does not come from interstitial or sub-surface hydrogens (18). Some computational studies disagree as the surface ²⁷Al nuclei are reported to have a large quadrupolar coupling, which broadens the ²⁷Al signal and makes CP ineffective (16, 22). However, the models used for these calculations did not account for surface rearrangement, which will favour less strained symmetric environments, as has been seen in alumina (23).

Penta-coordinated aluminium environments, i.e., AlO₅, exist on the surface of γ-alumina and can be observed using CP NMR (19, 21) or directly using high-field NMR measurements (24–27). Interestingly, little or no AlO₅ was observed by DNP NMR despite being a surface enhanced measurement, presumably because the alumina was mixed with an aqueous solution that reacted with the AlO₅ sites (20, 21). These AlO₅ sites have been shown to be the anchoring point for platinum oxide (26). Concerning alkaline earth oxide doping, AlO₅ has a one-to-one correlation against the number of BaO molecules impregnated on to γ-alumina (27). Hence, the surface AlO₅ sites are of great interest to the catalyst scientist.

Although no hydrogen atoms exist in the bulk of γ-alumina, the surfaces ((111), (110) and (100)) are terminated by hydroxyl groups. Knözinger and Ratnasamy extended the earlier work of Peri who identified five types of hydroxyl environment on a hydroxylated ideal γ-alumina surface (28, 29). This model was again extended by Tsyganenko and Mardilovich who added a sixth environment, reproduced in Figure 1. (Note that in this article we refer to AlIV as AlO₄).

Many workers have reported ¹H NMR spectra of γ-alumina and attempted to assign peaks to specific hydroxyl environments. As-received γ-alumina contains a significant amount of physisorbed water throughout its porous structure, which overwhelms the ¹H NMR signal from the surface hydroxyls. Thus, all ¹H NMR experiments on γ-alumina must necessarily be performed after the sample has been heated above 250°C to remove water and consequently the γ-alumina will be partially dehydroxylated. This is significant as penta-coordinated environments such as OH⁵, OH⁶⁵ and OH⁶⁶⁵, will be present that require assignment despite not having a particular Knözinger and Ratnasamy type (30–32). One limitation of this ¹H NMR technique is the requirement for drying, as the environments formed might not be present during, for example, a subsequent incipient wetness treatment to load the support with a catalytically active species.

Initial studies reported peaks of around −0.3 ppm, 2.4 ppm, 4.0 ppm and higher, which were assigned to the most basic OH group (type Ib), a more acidic group (type II), the most acidic (type III) and finally hydrogen-bonded protons, respectively (33, 34). Later studies appreciated the presence of AlO₂ with assignments of −0.2 ppm to −0.5 ppm: OH⁴, 1.5 ppm to 2.5 ppm: OH⁴⁵,
2.5 ppm to 4.0 ppm: OH\textsuperscript{nnn} and higher shifted hydrogen-bonded protons (12, 35, 36). These assignments are in agreement with the earlier studies, clearly showing the trend of increasing chemical shift going from terminal (\(\mu_1\)) to bridging (\(\mu_2\)) to \(\mu_3\) OH environments.

To date, there have been no reports on the surface aluminium environments of any alumina that has been impregnated by SrO. The catalytic activity of a \(\gamma\)-alumina support, doped with an active species, will be affected by strontium doping that causes the surface environments to rearrange. For example, by blocking the AlO\(_5\) sites, an active species can anchor to a weaker aluminium binding site (AlO\(_4\)/AlO\(_6\)), thus changing the catalytic activity. Accurate understanding of alkaline earth oxides on the surface of \(\gamma\)-alumina must explain changes in the aluminium coordination populations as well as \(^1\)H NMR assignments. The scope of this article is to present novel NMR spectra on a strontium alumina system and suggest possible surface environments to explain those spectra. These hypotheses could be tested by future infrared measurements as well as \textit{ab initio} calculations.

2. Experimental Results

1 wt\%, 2 wt\% and 4 wt\% SrO on \(\gamma\)-alumina (Sasol) samples were prepared by incipient wetness impregnation using strontium nitrate (Alfa Aesar) dissolved in sufficient water. Following addition of the nitrate solution to the alumina, the samples were dried at 105\(^\circ\)C before being calcined at 500\(^\circ\)C for two hours.

Powdered samples were dried under vacuum at 350\(^\circ\)C overnight, before being packed in air-tight zirconia rotors under an inert atmosphere and were spun at 14 kHz in a static magnetic field strength of 9.4 T. A widebore Bruker 4 mm broadband (BB)/1H MAS probe was used. Spectra were normalised by mass and number of scans and all acquired on a Bruker Avance III console using TopSpin 3.1 software. All experiments used a 2 s recycle delay.

\(^1\)H spectra were acquired (256 scans) with one rotor period spin echo experiment (37) and referenced to the low-ppm peak of adamantane-d\(_{16}\) at 1.73 ppm. Pulse lengths were 3 \(\mu\)s (90\(^\circ\)) and 6 \(\mu\)s (180\(^\circ\)) at \(\nu_{RF} = 83\) kHz. 

\(^{27}\)Al spectra were referenced to yttrium-aluminium garnet (YAG) AlO\(_6\) at 0.8 ppm (38). Direct acquisition (128 scans) used a 1.5 \(\mu\)s (\(<30^\circ\)) pulse at \(\nu_{RF} = 50\) kHz. CP spectra (7168 scans) used a 1.5 ms contact pulse. \(^{27}\)Al \(\nu_{RF} = 12\) kHz and \(^1\)H \(\nu_{RF} = 36\) kHz to satisfy the Hartmann-Hahn condition (39, 40). The low radio-frequency (RF) field gives selective spin-locking of the central transition (\(m = \frac{1}{2} \) to \(-\frac{1}{2}\)), but under MAS, lineshapes will be distorted (41, 42). Proton decoupling did not improve resolution and was not used.

### 2.1 \(^{27}\)Al Nuclear Magnetic Resonance

Directly acquired \(^{27}\)Al spectra of the bulk are given in Figure 2. Peaks corresponding to AlO\(_4\) and AlO\(_6\) were clearly visible, present in an approximately 1:2 ratio by integration, which does not account for spinning sideband intensity. The contribution of surface AlO\(_5\) environments was undetectably small against the background bulk signals. After normalising by sample mass, there was no significant variation in the bulk aluminium environments. This indicates that the SrO impregnation did not affect the structure of the \(\gamma\)-alumina nor form a strontium-aluminate phase.

Primostrato \(^{27}\)Al CP spectra are given in Figure 3. Focusing initially on the undoped alumina; in contrast to the bulk spectra, the presence of AlO\(_5\) was clearly visible. The ratio of AlO\(_4\) and AlO\(_6\) sites showed a preference for AlO\(_6\) sites at the surface of \(\gamma\)-alumina.

Although CP NMR spectra are not quantitative, the quadrupolar parameters of AlO\(_4\) and AlO\(_6\) were similar enough to allow for qualitative comparison. This is strong evidence that a surface rearrangement has taken place, i.e., the surface structure is not the same as the bulk structure.

The effects of SrO doping are also pronounced, with variation seen in all three types of aluminium environment. With the addition of 1\% SrO there was an enhancement of AlO\(_4\) signal, no change to the AlO\(_5\) signal and a reduction in AlO\(_6\) signal. For the \(\gamma\)-alumina with 2\% SrO the AlO\(_4\) signal was enhanced even more.
whilst there was a reduction in AlO₅ and AlO₆ signals. This trend continued for the 4% SrO sample.

Generally, a reduction in CP ²⁷Al signal could be caused by several factors: (a) an actual physical reduction in that type of environment; (b) the removal of nearby hydrogen to that environment (as the magnetisation is transferred to aluminium from hydrogen) or (c) a distortion of the aluminium site symmetry causing extreme quadrupolar broadening and rendering the signal ‘invisible’. The likelihood of these different factors occurring upon Sr doping will be discussed below.

2.2 ¹H Nuclear Magnetic Resonance

The processed spectra are given in Figure 4. For the undoped γ-alumina three main environments were seen, in agreement with previous studies (12, 33, 35). These were assigned as HO-µ¹ at −0.3 ppm, HO-µ² at 2.2 ppm and HO-µ³ at 4.3 ppm. Hydrogen-bonded environments also existed at higher chemical shifts, but in a lesser amount to the main environments.

Systematically doping γ-alumina with SrO produced an additional peak at 0.5 ppm whilst simultaneously reducing the terminal and bridging hydroxyl environments at −0.3 ppm and 2.2 ppm, respectively. The hydrogen-bonded and HO-µ³ environments appeared unaffected by the SrO doping.

As there are several specific types of surface hydroxyl group and the peaks appeared asymmetric, the spectra were deconvolved. At least seven peaks were required to obtain a good fit, although the lack of resolution meant that such a fit was ambiguous. Two of the fitted spectra are shown in Figure 5. The purpose of the fits is to show that a full structural model of the surface of γ-alumina must account for at least seven hydroxyl environments. Also, the fits show approximately how the various environments change upon doping with SrO.

Further experiments were performed to help assign the additional peak at 0.5 ppm. A strontium hydroxide (Sr(OH)₂) species was ruled out, as measurements on this material gave much higher chemical shifts. Both X-ray photoelectron spectroscopy (XPS) and chemical testing (addition of acid caused carbon dioxide evolution) indicated the presence of strontium carbonate (SrCO₃), which being energetically stable, is a likely surface species.

Hence, the 4% SrO γ-alumina sample was dosed with CO₂ overnight to promote a carbonate environment. The resulting ¹H NMR spectrum is given in Figure 6. A loss
of intensity for the HO-μ¹ environment was observed and a new peak at 5.2 ppm was gained. This peak corresponds to an aluminium carbonate OH signal (12). Clearly the presence of Sr did not inhibit the adsorption of CO₂ on γ-alumina but significantly, this mechanism did not occur for atmospheric amounts of CO₂. This suggests the 0.5 ppm peak was not related to carbonate species.

In conclusion, SrO doping systematically affected the proton environments on γ-alumina, modifying the previously identified HO-μ¹ and HO-μ² hydroxyls and producing a new peak at 0.5 ppm. Although this new environment has not been identified, the correlation with SrO doping suggests the hydroxyls are proximate to some strontium compound, which will be discussed below.

3. Discussion

We first discuss the changes in the ²⁷Al CP/MAS NMR spectra upon SrO doping shown in Figure 3. The addition of SrO appears to preferentially replace the hydroxyls located at AlO₂ and AlO₆ sites. This preference could be because of the energetic favourability of Sr²⁺ towards the more electronegative AlO₅ and AlO₆ sites. Consequently, the reduction in CP signal from the AlO₅ and AlO₆ sites is simply because of a reduction in nearby protons that the magnetisation would otherwise be transferred from. Whether Sr is present as isolated atoms or in SrO clusters is unclear from the ²⁷Al NMR.

An increase in AlO₄ CP signal upon SrO doping is harder to explain. One possibility for enhanced signal is to introduce additional hydroxyls. However, directly bonded hydroxyls would increase coordination causing the signal to appear elsewhere, which has not been observed. Another possibility is that the presence of SrO promotes a structural rearrangement of higher coordination aluminium to AlO₄. This would be the opposite of condensation reactions typically seen when dopants are added to alumina and a plausible mechanism has not been forthcoming (43).

Two possibilities remain. One is that the addition of SrO causes AlO₄ sites to become more symmetric. This reduces their quadrupolar broadening giving rise to a more effective magnetisation transfer from ¹H to ²⁷Al. Thus, previously ‘invisible’ AlO₄ sites appear in the primostrato spectra when SrO is added. Further experiments at multiple fields or using multiple quantum magic angle spinning (MQMAS) could be performed to determine the quadrupolar parameters and test this possibility. The other possibility is that SrO, replacing AlO₂ and AlO₆ hydroxyls, could then prohibit the fast exchange of protons across the surface, facilitating CP from the remaining protons on AlO₄ sites (16).

Next we discuss the changes in the ¹H spectra upon SrO doping shown in Figure 4. As mentioned above, the peak at 0.5 ppm grew in proportion with the quantity of SrO doped, which suggests these hydroxyls are proximate to some Sr compound. Additional experiments have ruled out the assignment of Sr(OH)₂ or SrCO₃. Furthermore, the chemical shift is in between the typical terminal and bridging environments. Combined with the unchanging environments above 4 ppm, these findings lead us to conclude that the peak at 0.5 ppm is from a shifted OH⁻ or OH⁻⁺ site.

As the most reactive/electronegative OH⁵⁻, OH⁶⁻, OH⁵⁶⁻ and OH⁶⁶⁻ environments have most likely been replaced by SrO, these are probably not an accurate assignment for the 0.5 ppm peak. The presence of an OH⁴⁻ environment is generally energetically unfavourable, so this too can be ruled out. This leaves us with modified OH⁴⁻ and/or OH⁴¹⁴ environments.

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One issue with assignment is that the Sr form is currently unknown. SrCO₃, SrO clusters or Sr²⁺ ions are possibilities. These three particular possibilities are shown in Figure 7, next to an OH⁴⁻ environment. As the deconvoluted proton spectrum in Figure 5 suggested just one environment for the peak at 0.5 ppm, the likelihood is that just one of these mechanisms was present in our system.

Further evidence that favours the assignment of OH⁴⁻ comes from the CO₂ dosing results shown in Figure 6. As it has been shown that CO₂ preferentially goes

Fig. 6. Normalised ¹H solid-state MAS NMR spectra of γ-alumina doped with 4% SrO
to the OH^4 sites (12), the dramatic intensity loss of the 0.5 ppm peak strongly suggests this was a OH^4 environment.

4. Conclusion

The need for further research into the nature of the Sr environment and more comprehensive ^1^H peak assignments, is clearly indicated. This could be achieved through higher resolution ^1^H NMR experiments as well as ^1^H–^27^Al correlation experiments. NMR data can be combined with infrared measurements to probe the hydroxyls. Raman microscopy and transmission electron microscopy (TEM) may also be used to elucidate the Sr environment. Ideally, the experimental data can all be used to create accurate surface models for density functional theory calculations to further explain the mechanisms at work in this system.

In conclusion, ^1^H–^27^Al CP MAS NMR has shown that doping γ-alumina with SrO covers AlO_5 and alters the surface AlO_4:AlO_6 ratio. ^1^H MAS NMR revealed SrO impregnation caused a loss or shifting, of the terminal and bridging hydroxyl environments, with a new peak at 0.5 ppm hypothesised to be a modified OH^4 environment. These changes to surface chemistry will strongly affect where catalytically active metals are subsequently deposited. Such tunability for a common industrial catalyst support, like γ-alumina, is of great interest to the catalyst scientist.

5. Acknowledgements

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References

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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.
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After graduating from the University of Southampton, UK, Nicola Collis joined Johnson Matthey working on catalyst preparation for fuel cells where she looked at generating robust metal alloy particles for proton exchange membrane fuel cell applications. Nicola subsequently transferred to emission control research where she specialises in metal solution chemistry and support surface chemistry, focusing on how to design catalyst particles and control metal-support interactions during catalyst preparation.
Erratum

The Effects of Hot Isostatic Pressing of Platinum Alloy Castings on Mechanical Properties and Microstructures

It has come to our attention that an image in a recent article published in this journal (1) was incorrectly attributed. The image caption should read as follows. The authors sincerely apologise for the error in attribution.

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Fig. 3. HIP Unit, courtesy ABRA Fluid AG, Switzerland
"New Trends in Cross-Coupling: Theory and Applications"

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This massive volume with a most appropriate title will lead the user to say: ‘I read, I understand modern trends, I will apply’. After perusing it, the reader is encouraged to give a quiz to their students or colleagues: what is the largest scale Heck reaction to date? Why is a reaction in water not a fully ‘green’ process? What are the problems of scale up flow reactions? How much palladium may there be in the over-the-counter drug ibuprofen? What are the major caveats for a chemist using transition metal catalysis? among many other questions.

Colacot has gathered thirteen academic and industrial chemists with their respective coauthors who are at the forefront of the various reactions that comprise the cross-coupling theme to serve as a cornucopia of fundamental and practical knowledge. With forewords by three chemists, prominent in their own right in the field, this collection of chapters will bring up-to-date all those interested in teaching and practicing the chemistry which has largely superseded the classical reactions of the pre-1970 era.

Although multi-authored, a uniformity of presentation prevails, perhaps owing to the fact that all chapters have been independently reviewed by two to three experts.

Individual authors teach the reader about the breadth of the cross-coupling landscape, the still incomplete mechanistic knowledge and the important practical characteristics of new areas: the rapid acceptance of continuous flow reactions, the increasing attempts to be ‘green’ and the requirements of metal detection in active pharmaceutical ingredients (APIs), the latter, a humbling read for the academic researcher.

The authors ask the reader to linger on mechanistic aspects before leaping into the less cerebral-requiring synthetic data. The present reviewer ponders that since the advent of transition metal reactions, revision of retrosynthetic strategy as taught by Corey and others is required. As suggested by the Editor, this compendium will ‘rejuvenate the entire area of cross-coupling’; it may be argued that ‘re’ is not required – the area is still in its rapidly developing infancy.

Review of Fundamentals

Following historically insightful brushstrokes on ‘how we got here’ in the foreword by Professor Barry Trost (Stanford University, USA) and in the preface by Tom Colacot, the fundamentals of the broad canvas of cross-coupling are described. In Chapter 1, Carin Johansson Seechurn (Johnson Matthey Catalysis and Chiral Technologies, UK), Andrew DeAngelis and Tom Colacot (Johnson Matthey Catalysis and Chiral Technologies, USA) define the basic terminology, such as turnover number (TON) and valence bond picture, sketch the discovery tree with due recognition,
including names of some widely unknown chemists, and set the stage for both industrial and academic chemists’ palates to view the recent state (mainly the last five years) of transition metal-catalysed cross-coupling reactions and to taste the next courses of surprises in the near future.

Chapter 2 by DeAngelis and Colacot serves as a perfect primer for the rapid advances that have occurred in the last decade in the design and development of ligands that have reached sophisticated levels of application in catalytic cross-coupling reactions where Pd is king. In agreement with Crabtree (1), who perceptually taught in his textbook that ‘to pick suitable spectator ligands’ is the key to the art, the reader learns about steric, electronic effects and bite angle consequences (a table of 29 ligands) and is then taken on a tour (for example in industrial context, Figure 1) on useful modern ligands: bulky Ar₃P, chelating bisphosphines, biaryl monophosphines, N-heterocyclic carbenes (NHCs) and chiral ligands. Copious examples in C–C but also C–N and C–O coupling reinforce the schematically explained, mechanistically significant points.

Chapter 3 by Carin Johasson Seechurn, Hongbo Li and Tom Colacot, the last chapter of collaboration from the very able Johnson Matthey chemists, authoritatively instructs in the rapidly emerging evolution of preformed Pd catalysts (isolated, pure Ln₃PdX ligands). A refresher course on the 18 electron rule, with examples and exceptions is followed by a section on complex stability which is photographically illustrated by the decomposition of ‘tetrakis’ with time, events very familiar in practicing laboratories. Mechanistic studies, still incomplete, promise to play a crucial part in the provision of improved precatalyst procedures on large scale that will undoubtedly help process economics of these reactions. The chapter concludes with valuable tables of recommended precatalysts and their use in specific cross-couplings.

Ligands

In the hefty Chapter 4, Anthony Chartoire (Econic Technologies, UK) and Steven Nolan (University of St Andrews, UK) focus on the NHCs, the new kid on the block in ligands. Appreciation is gained of the influence of pKₐ, steric and electronic effects on NHCs and a journey is provided of the cross-coupling name reactions for which they are effective and those as yet little studied (Kumada-Corriu, Hayashi, copper-free Sonogashira, discovered by Heck, C–S coupling, α-arylation). For informed chemists, conspicuously absent so far in the literature are also the C–O coupling and the asymmetric Suzuki-Miyaura reactions.

In Chapter 5, Mark Stradiotto (Dalhousie University, Canada) summarises the impact of sterically demanding phosphine ancillary ligands on achievement of monoarylation in Pd-catalysed Buchwald-Hartwig amination and α-arylation reactions. The long-sought NH₂⁺ equivalent in anionic aromatic chemistry is overcome by the amination reaction which also supercedes the classical electrophilic aromatic substitution (SₑAr) nitration–reduction route to amines. Thus monoarylation of ammonia is especially useful in the synthesis of bioactive heterocycles and that of hydrazine gives a new twist to the Fischer indole reaction. The completely chemoselective synthesis of amines, bearing primary and secondary amines, through use of Stradiotto’s heterobidentate ligands cannot be easily achieved by classical methods. A useful feature of this chapter is the brief outlines for each topic discussed.

Fig. 1. Kilogram-scale Suzuki-Miyaura reaction using Pd(2)Cl₂ (Reproduced by permission of The Royal Society of Chemistry)
C–O and C–S, Suzuki-Miyaura Cross-Coupling and Carbohalogenation

In Chapter 6, James Stambuli (Ohio State University, USA) discusses C–O and C–S bond formation reactions, areas that have progressed less than the corresponding C–C and C–N coupling processes. As gleaned also from other chapters, copper catalysis is making an impact on the C–O and C–S coupling reactions. Best choices of ligands are defined, including those that prevent thiolate attack on the Pd centre and most recent replacements for Pd (manganese, cobalt, nickel and rhodium) are noted. From this chapter, we appreciate that a long road has been travelled to give improvements and alternatives to the nucleophilic aromatic substitution (S_NAr) and ancient Ullmann procedures.

Chapter 7 by David Petrone, Christine Le, Stephen Newman and Mark Lautens (University of Toronto, Canada) provides a detailed view of the C-halogen reductive elimination process from transition metal complexes and then delves deeply into the carbohalogenation reaction. Surprisingly, the reductive elimination to form new or reform existing C-halogen bonds is a poor cousin to the equivalent oxidative addition in terms of synthetic use and its mechanism is incompletely understood and controversial. The review focuses on the Pd(0/II) species in these transformations as a background for the carbohalogenation reaction to which Lautens’ group has made substantial contributions. Provided is a scheme displaying commendably the mechanistic divergences between the Heck and the new carbohalogenation process, numerous examples of synthetic utility (indoles via gem-dihalo olefin coupling stand out, Scheme I), including aspects of selective coupling of polyhalogenated systems, containing Handy’s predictive guide, and density functional theory (DFT) corroboration of the experimental results. The chapter shows a flourish of considerable new synthetic potential.

The brief but instructive Chapter 8 by Alastair Lennox and Guy Lloyd-Jones (University of Edinburgh, UK) is the present best source for the mechanistic understanding of the Suzuki-Miyaura cross-coupling, named the ‘gold standard’ for biaryl construction, which can be appreciated by the given examples of ‘blockbuster’ drugs whose synthesis critically incorporates this reaction. A survey of 40,000 reactions in the preparation of this review is a sound basis for discussion of mechanistic aspects for which evidence is currently weak or not available, for example, for the transmetalation step. The requirement for boron preactivation and the practical aspects of various boron coupling reagents, including the recently introduced and promising triisopropylborate and cyclic triol salts are features also to be appreciated. The categorisation of Suzuki-Miyaura couplings into three groups is tentative but practically useful.

Mizoroki-Heck and Beyond

Chapter 9 (>100 pp) by Irina Beletskaya and Andrei Cheprakov (Moscow State University, Russia) is a masterful, well organised and definitive review of the Heck reaction that the authors use in a generic sense to cover the family of reactions, the main one of which is

![Scheme I. Synthesis of 2-substituted indoles via Pd-catalysed tandem C–N/C–C coupling of gem-dibromoolefins (Reproduced by permission of The Royal Society of Chemistry)](image-url)
of course the Mizoroki-Heck reaction (~50 pp). (For an opinion of the value of the Heck reaction see Fuhrhop and Li:

“Synthesis: the preparation of large molecules from smaller ones by the formation of C-C bonds. The Wittig, Heck, and Diels-Alder reactions are all the methods a beginner needs to know. Most compounds can be made by these reactions if they are followed by intelligent functional group interconversions (FGIs)” (2)).

After a historical account, rightfully acknowledging chemists along the path to Heck’s discovery, the diversity of this dominant C–C bond forming reaction is unfolded, always by reference to mechanism which the authors are eminently qualified to analyse. The differences between the Heck, general cross-coupling, and C–H activation reactions is such an area of mechanistic ambiguity that it demands further studies. Carbynylation and decarbynylation (‘masked carbanion’, discovered by Blaser and Spencer (3)) reactions are demystified. The Mizoroki-Heck reaction is given a deserved comprehensive presentation and includes many elements of theoretical and practical value, some perhaps unappreciated, for example: mechanistic pathways using mono- and bidentate ancillary ligands, the functioning of Pd nanoparticles as precatalysts, the qualitative rules for ligand acceleration, the status of the Pd(II)/Pd(IV) mechanism and the new developments in copper-catalysed reactions. The increasingly used oxidative Heck and Fujitawa-Moritani reactions are given merited coverage. The most intriguing deborylative (Heck discovery, 1975), desilylative and destannylative Heck reactions are remarkably evolving methods of new synthetic opportunities. In spite of the authors’ modest concluding comment, this chapter provides the depth and the breadth of the Heck reaction that will be read with great benefit for some time (for a personal account, see (4); for obituaries see (5, 6)). 456 References are listed and a SciFinder search for 2010–2015 reveals 3371 hits; therefore, this chapter is perceptively discriminating no doubt due to the authors’ command of the area.

Chapter 10 by Xiao-Feng Wu (Leibniz Institute for Catalysis, Germany) and Christopher Barnard (Johnson Matthey, UK) concentrates on the Heck, Sonogashira, Suzuki and C–H activated carbonylation reactions. With respect to the Heck carbonylation, there is no overlap with Chapter 9; in fact, Chapter 10 presents useful intramolecular, including heterocyclic, versions. In spite of a partial mechanistic understanding, all of these methods provide different retrosynthetic thinking, especially for the construction of alkyynes by the classical Grignard and Friedel-Crafts reactions. A litany of new reactions is schematically indicated with the following highlights: the use of arylidiazonium coupling partners, the preparation of $^{11}\text{C}$ and $^{12}\text{C}$ labelled ketones (although lacking examples of industrial reactions), and the advantages of NHC complexes. Perhaps most significant are the results from the rapidly evolving C–H activation-carbonylation process whose application to the synthesis of substituted and heteroanuallated aromatics will certainly see further advances.

Chapter 11 by Ben Glasspoole (Sigma-Aldrich, USA), Eric Keske and Cathleen Crudden (Queen’s University, Canada) address work on the Suzuki-Miyaura cross-coupling reaction from perspectives of: (a) stereospecific coupling of chiral organoborons; (b) chiral electrophile partners for stereospecific couplings; and (c) racemic electrophiles in dynamic resolution tactics. All three topics are expertly tackled from which may be arguably underlined: the challenges ($\beta$-hydride elimination and their invisibility for symmetrical nucleophiles, steric effects) faced in reactions of secondary aliphatic boranes (overcome in Crudden’s group); the coupling of racemic and enantioenriched allylic boranes (provided in tabular data); the use of benzylcarbamates and esters to displace the need for enantiomerically pure alkyl halides in coupling with organoboron derivatives; the power of Ni-catalysed radical-mediated asymmetric arylation of racemic $\alpha$, $\gamma$, and $\delta$-chloroamides; and the initial demonstration of arylation of tertiary halides. The chapter critically discusses the highs and the lows of current methods for stereo-selective and -specific $sp^2$-$sp^3$ and $sp^3$-$sp^3$ bond formation which are of growing significance in new synthetic method development.

C–H Activation

In Chapter 12, Upendra Sharma, Atanu Modak, Soham Maity, Arun Maji and Debabrata Maity (Indian Institute of Technology Bombay, India) discuss a topic of high current activity – the direct arylation by C–H activation which, it should be noted, is formally not a cross-coupling reaction. With a very good historical preamble on today’s named coupling methods using two prefunctionalised substrates, presented critically is the moving frontier of the C–H activated arylation methods based on using one
prefunctionalised system. The chapter has a strong mechanistic orientation, for example Figure 2. The subdivision by metal (Pd, Rh, Ru, Ir, Cu) shows clearly that Pd is king of the catalytic highway. Examples of illustrative reactions are outlined, mechanistic pictures are presented, and, notably, experimental needs, costs, catalysts and ligands are examined. A glossary of acronyms, for example chemical manganese dioxide (CMD) appears early in the book but is not defined until later. Also, a table of directing groups, giving an eye blink view of the section on directing scaffolds, would have been valuable. Sections on direct arylation of heterocycles and of sp3 bond C–H activation represent tips of the iceberg of current research, as are the initial results of remaining challenges, such as erasable and traceless directing groups, which are described in this well formulated chapter.

**Flow and Green Cross-Coupling and APIs**

The review (Chapter 13) on cross-coupling chemistry in continuous flow by Timothy Noël and Volker Hessel (Eindhoven University of Technology, The Netherlands) begins with an instructive table on the pros and cons of this new technology over batch processes. Presented by two experts in this rapidly emerging field that, of necessity, involves also chemical engineers, the reader receives step-by-step instruction on how to set up a flow experiment, be aware of technical difficulties and hazards and be concerned about safety issues on scale. The myth of reactions in water being ‘green’ is laid to rest by considering that it needs to be treated before release into the environment. Laudably, examples for Pd, Cu and Fe catalysed flow reactions are presented with comparison of cost and toxicity, as are comparisons of batch vs. flow procedures. The ‘metal-free’ reaction, as currently often carelessly stated in the literature, is given the proper caveat by need for fluorescence or inductively coupled plasma mass spectrometry (ICP-MS) metal detection that apparently may be carried out by a first year student (see also review of Chapter 16 below). As this chapter emphasises, the benefits of flow will occur with increased attention to gas-liquid coupling reactions, more efficient operation, increased engineering automation, and introduction of flow chemistry courses in curricula.

Chapter 14 by Kevin Shaughnessy (University of Alabama, USA), which takes up the ‘green’ theme in depth, will be valuable reading especially for academics. As stated in the introduction, the philosophy in industry has changed since passing of the Pollution Prevention Act by the US government in 1990 from ‘how to deal with hazardous substance’ to ‘how to design processes of minimum waste and hazard’. The chapter focuses on using various solvents with emphasis on water, even though its ‘green-ness’ is questioned (see also review on Chapter 13 above). Shaughnessy makes many important points, some of which are very familiar to both academic and industrial chemists (for example, atom economy, protecting group avoidance, toxicity) and some not to academics (for instance environmental (E) factor = mass of waste/mass of product, life-cycle assessment (LCA))
= a cradle to grave evaluation from raw materials to materials returned back to Earth). Although examples of large scale reactions appear to be absent, aspects of cross-coupling in aqueous media are given thorough treatment in which choice of hydrophilic or hydrophobic metal-ligand combinations and surfactant-mediated reactions (original observation by Jefferey) are highlighted. Heterogeneous, recyclable catalysis such as nanoparticles, which are clearly of value in industry, and other green alternative solvents, such as polyethylene glycol (PEG) and ionic liquids, as well as novel conditions such as microwave and thermomorphic techniques receive coverage. Although all chemists are innately ‘green’, commandments such as solvent minimisation, E factor and LCA which are currently not given sufficient attention, especially by academics, are vital and appreciated points from reading this chapter.

Chapter 15 by Javier Magano (Pfizer Global Research & Development, USA) and Joshua Dunetz (Gilead Sciences, Inc, USA) is a well-placed wide-ranging review, with 171 references, of recent large-scale cross-coupling reactions in service of the synthesis of pharmaceuticals. With a forceful table of statistics regarding numbers of >100 mmol reactions carried out in the 2000–2013 period, the impact of the 2010 Nobel Prize in Chemistry is truly respected and is undeniably shown by a table of commercial drugs which are synthesised by C–C (mainly), C–N and C–S coupling methods, for example Scheme II. There follow sections on some of these household name reactions that offer instructive details in schemes and commentary. The value of organic synthesis is alive in this chapter for sharing with students and laypersons alike. A brief section on C–H activation processes (only four to date of the review) is evidence of rapid application of this evolving methodology. A discussion of preferred metals (currently Pd > Cu > Ni > Fe) and a glossary of abbreviations terminate this welcome chapter.

In the significant and fittingly last chapter (Chapter 16), Kazunori Koide (University of Pittsburgh, USA) defines the necessary standards for metal removal for APIs (for Pd = 10 ppm, for example, 2 µg of Pd in a 200 mg ibuprofen tablet) and the trials and tribulations in this achievement which are a process chemist’s nightmare since scrupulous metal removal can delay scale up campaigns. This major problem has led to the development of new fluorimetric and colorimetric analytical methods, many in the Koide laboratories, for the detection of trace amounts of Pd. These are delineated by required criteria and are illustrated. The synthesis of Pd sensors and chemodosimeters are exemplified which, rather appropriately, illustrates cases involving Suzuki-Miyaura and Sonogashira couplings as the key steps. An informed synthetic organic chemist surveying this chapter may be tempted to devise new ‘ideal metal detection’ molecules.

Conclusion

To conclude, the volume under review amassed by Colacot is a magnum opus of contemporary organic chemistry. The studious chemist of this volume, should receive a 95% grade (as with yields, there is no 100%) on the quiz posed at the beginning of this review. Dipping into sections of interest will provide the practicing chemist with knowledge and insight from scientists in the trenches of the areas discussed. Whether in a university or industrial lab, the chemist will take information from this compendium into the lab (if allowed) and immediately profit.

<table>
<thead>
<tr>
<th>Active ingredient name</th>
<th>Commercial name</th>
<th>Structure</th>
<th>Type of coupling</th>
<th>Applicant</th>
<th>Indication</th>
<th>FDA approval date</th>
<th>Exclusivity expiration date (USA)</th>
</tr>
</thead>
<tbody>
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<td>Losartan potassium</td>
<td>Cozaar</td>
<td><img src="image" alt="Losartan structure" /></td>
<td>Suzuki-Miyaura. Also used for structurally similar drugs</td>
<td>Merck</td>
<td>Angiotensin II receptor antagonist for the treatment of high blood pressure</td>
<td>28th April 1995</td>
<td>Generic (August 2009)</td>
</tr>
</tbody>
</table>

Scheme II. Losartan drug synthesised by Suzuki-Miyaura cross-coupling reaction (Reproduced by permission of The Royal Society of Chemistry)
References

4. R. F. Heck, Synlett, 2006, 18, 2855

“The Reviewer

Victor Snieckus was born in Lithuania and fled with his parents to Germany during World War II. He obtained the BSc at the University of Alberta, Canada; graduate degrees at the University of California, USA, under the supervision of D. S. Noyce, and University of Oregon, USA, with Virgil Boekelheide and carried out postdoctoral studies at National Research Centre, Canada with O. E. Edwards. He taught at the University of Waterloo, USA, until 1998 and then moved to Queen’s University, Canada, as the inaugural Bader Chair of Organic Chemistry. He continues fundamental research as Bader Chair Emeritus as well as Director of Snieckus Innovations, an institute for the synthesis of small molecules for the pharmaceutical and agrochemical industries. He is a recipient of the American Chemical Society Cope Scholar Award, Arfvedson-Schlenk Preis of the Gesellschaft Deutscher Chemiker (GDCh), Canadian Society for Chemistry Bernard Belleau and Alfred Bader Awards, is a Lithuanian Academy of Sciences Laureate, and is a Royal Society of Canada Fellow.
1. Introduction

This symposium was organised by Chalmers University of Technology, Sweden, to commemorate the first 20 years of research at Competence Centre for Catalysis (KCK). The Frontiers in Environmental Catalysis conference was held on 24th September 2015 at Chalmers University of Technology. All previous and current KCK employees were invited, together with representatives of KCK’s member companies and few invited speakers. About 50% of the invited people attended, resulting in about 120 participants. Among them were four Johnson Matthey delegates (including the present reviewer, having been a post-doctoral fellow at KCK). Although Johnson Matthey is no longer part of KCK, a collaboration project on the study of methane oxidation is ongoing between Johnson Matthey Technology Centre, Sonning Common, UK and Professor Per-Anders Carlsson (KCK, Sweden) resulting in two poster presentations at the symposium.

The aim of this review is to summarise the oral presentations relevant for emission control applications and provide the reader with useful references for further reading. The topics covered by the poster presentations will also be mentioned to give an overview of the current research at KCK.

2. Oral Presentations
2.1 Twenty Years with KCK

An introductory talk to celebrate the history of KCK, an interdisciplinary research centre within heterogeneous catalysis since 1995, was given by the director of KCK, Professor Magnus Skoglundh (Chalmers University of Technology). The diversity of the centre was emphasised: it was originally composed of Chemical Engineering, Chemical Reaction Engineering and Applied Physics departments at Chalmers University of Technology, and recently it was further expanded by Eva Olsson’s microscopy group. The research is focused on catalysis for emission control with a growing interest in energy related areas. KCK is financially supported by Chalmers University of Technology, the Swedish Energy Agency and the member companies: AB Volvo, ECAPS AB, Haldor Topsøe A/S, Scania CV AB, Volvo Car Corporation AB and Wärtsilä Finland Oy.

On a similar note, Pär Gabrielson’s (Haldor Topsøe, Denmark) talk on ‘The Impact of KCK from an Industrial Perspective’ stressed the role played by KCK on students’ education and how it prepares them for employment in the catalysis and aftertreatment industry. This is confirmed by statistics, with 70% of PhDs employed by industry of which 45% are member companies. The remaining 30% of PhDs are employed by other organisations.
2.2 Automotive Aftertreatment

Galen Fisher (University of Michigan, USA) presented ‘Progress and Challenges in Automotive Emission Control’. Fisher is one of the members of the KCK’s international advisory board. His talk concentrated on current challenges facing the automotive emission control industry such as improving the low-temperature activity of three-way catalyst (TWC) and nitrogen oxides (NOx) traps. Moving the TWC design from a supported metal to a metal core surrounded by an inert shell was shown to prevent poisoning and metal sintering (1). Johnson Matthey was cited in relation to the development of palladium/cerium based low-temperature NOx adsorbers, characterised by lower nitrous oxide (N2O) production compared to platinum-based catalysts and preferential storage of nitrogen oxide (NO) vs. nitrogen dioxide (NO2) (2). Fisher discussed how the new aftertreatment technologies use layering/zoning strategies as well as diffusion effects to decrease emissions.

Jonas Jansson (AB Volvo, Sweden) presented ‘Exhaust Aftertreatment for Heavy Duty Diesel Engines – Current Trends and Future Challenges’. The evolution of the aftertreatment systems for heavy duty diesel vehicles at Volvo was discussed. The original configuration diesel oxidation catalyst (DOC) + diesel particulate filter (DPF) + selective catalytic reduction (SCR) has been recently substituted by close-coupled DOC + SCR on filter (SCRF®) (or passive NOx adsorber (PNA) + SCRF®), allowing an enhancement of the light-off performances. The location of the catalysts and of the urea tank depends on the geographical area where the vehicle is commercialised.

2.3 Advanced Characterisation

Stig Helveg (Haldor Topsoe) presented ‘Electron Microscopy Advances for Catalysis’. Helveg introduced the cutting-edge technology of in situ and operando transmission electron microscopy (TEM) imaging (3). A nanoreactor was designed at Haldor Topsoe in collaboration with TU Delft, The Netherlands, and was functionalised with a micrometre-sized gas-flow channel, transparent windows to allow the electron beam to reach the sample and with a heating device (4). This device allows the collection of images at 1 bar, solving the pressure gap issue typical of traditional TEM imaging. The time resolved TEM images and measurement of the outlet gas composition by mass spectrometry (MS) results in a powerful way of studying correlations between a catalyst structure and its activity. The research of oscillatory catalytic reactions, such as carbon monoxide oxidation, was reported as an example of successful application of this technique (5). In this case a link between catalyst activity and shape of platinum nanoparticles has been found (shape dynamics from squared to circular). Sintering mechanisms and kinetics can also be investigated with the same technique.

Anders Nilsson (Stockholm University, Sweden) presented ‘Fundamental X-ray Studies of Catalytic Reactions’. The understanding of the nature of the interaction between water and metals, which is of interest in heterogeneous catalysis, was described (6). Professor Nilsson developed a library of X-ray absorption spectroscopy (XAS) and X-ray Raman scattering (XRS) spectra that spans the liquid part of the water phase space and several important aqueous solutions. This was used as a reference to identify hydroxyl species involved in catalytic reactions such as hydrogen oxidation in fuel cell applications.

Per-Anders Carlsson presented ‘Studies of Catalysts at Work’. This talk focused on the use of synchrotron facilities (European Synchrotron Radiation Facility (ESRF), France; MAX IV, Sweden and PETRA III, Germany) to examine catalytic reactions. Some examples were given of various spectroscopic techniques (extended X-ray absorption fine structure (EXAFS), high-energy X-ray diffraction (HEXRD), Fourier transform infrared (FTIR) and MS) to distinguish the adsorbed species and simultaneously coordinate catalytic activity to changes in the catalyst oxidation state (7, 8) (Figure 1). The possibility of exploiting the structure gap, from ideal surfaces to big particles, small clusters and single atoms, to improve the understanding of catalytic reactions was also mentioned. Active areas of interest are total methane oxidation and partial selective methane oxidation to methanol.

2.4 Reaction Engineering and Molecular Modelling

Louise Olsson (Chalmers University of Technology) presented ‘Studies of Aging Mechanisms for NH3-SCR Catalysts using Experiments and Kinetic Modelling’. Sulfur poisoning and regeneration on copper-SSZ13 were studied and performed in collaboration with Cummins Inc. A three-site kinetic model was necessary to describe ammonia storage and oxidation during temperature programmed desorption (TPD) experiments (9). A connection was
also found experimentally between the rate of SCR reaction and Cu loading, that was introduced in the kinetic model. A sulfur exposure study showed that sulfur dioxide (SO₂) can be adsorbed on Cu sites (S₁-SO₂), resulting in a decreased catalytic activity. The experimental observation of more NH₃ stored in the presence of sulfur was elucidated with the formation of adsorbed ammonium-sulfur species (S₁-(NH₃)₂-SO₂). The gradual decomposition of these species leads to catalyst regeneration and also provides an alternative route to the SCR reaction. This mechanism was successfully included in a kinetic model.

Henrik Grönbeck (Chalmers University of Technology) presented ‘Catalysis from First-Principles Calculations’. A recent work combining X-ray photoelectron spectroscopy (XPS) measurements and first-principle calculations suggests that the most active phase for methane oxidation on Pd-based catalyst is a double layered PdO(101) structure (10). Density functional theory (DFT) calculations show that CH₄ repulsion from the surface is quite strong when only one monolayer of PdO is present, but it can be overcome after a second monolayer is created therefore explaining the better activity observed experimentally. A micro-kinetic model for CH₄ oxidation was also built from first principles, able to predict reaction orders in methane, water, and oxygen as well as apparent activation energies in good agreement with a range of experimental findings (11). Interestingly, different reaction steps were found to be limiting depending on the temperature: water inhibition, CH₄ desorption, CH₃ dissociation or CH₄ dissociation with increasing temperature. Different activation energies depending on the temperature were found also experimentally, which supports the modelling results.

3. Poster Presentations

29 posters were presented during the poster session, covering two main research areas: emission control and energy conversion.

One of the main focuses in emission control research was the understanding of ageing and sulfur poisoning mechanisms as well as deactivation during operation, for lean NOx trap (LNT), SCR and hydrocarbon oxidation catalysts. The SCR of NOx in the presence of excess oxygen by NH₃/urea (NH₃-SCR) or hydrocarbons (HC-SCR), and NOx storage reduction (NSR) using mixed lean/rich operation were explored. Posters on passive SCR and SCR coated DPFs were also presented. Another subject of interest is the catalytic oxidation of soot and methane in particular the inhibiting effect of H₂O on the latter.

Moving to the energy conversion theme, research is ongoing in the synthesis of methanol from direct selective oxidation of methane on Cu-zeolites as well as selective hydrogenation of oxygenates.

In many cases activity studies were accompanied by kinetic modelling and/or first principles calculations to support the interpretation of the experimental results.
4. Conclusions

The contribution by representatives from both academia and industry to the symposium made it an overall successful event. The range of presentations was diverse and covered the most relevant topics in environmental catalysis, with an emphasis on future challenges. The Chalmers’ KCK demonstrated once again to be one of the leading groups in environmental catalysis research.

References


The Reviewer

Djamela Bounechada graduated in Chemical Engineering at Politecnico di Milano, Italy, in 2008 with a thesis combining experimental and modelling studies of SCR of NOx by ammonia (NH3-SCR) for automotive applications. She obtained a doctorate degree from the same university in 2012, with a thesis on strategies for enhanced methane oxidation in the exhausts of natural gas vehicles. After two years as a post-doctoral Fellow at Chalmers University of Technology, she joined Johnson Matthey Technology Centre (Sonning Common, UK) in 2014, as part of the reaction engineering research team.
7th International Gold Conference

Recent developments in gold research from heterogeneous catalysis to biomedical imaging

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Introduction

The 7th International Gold Conference takes place every three years and in 2015 was hosted by the Cardiff Catalysis Institute at Cardiff City Hall, UK, from 26th to 29th July. Scientists from all over the world gathered to discuss the latest advances in gold chemistry. Over three days, the conference covered different aspects from homogeneous and heterogeneous catalysis to biomedical imaging. The conference had more than 200 attendees from academia and industry and was divided into three parallel sessions with 72 talks and nearly 100 posters.

This review will focus mainly on the industrially relevant heterogeneous catalysis and to some extent biomedical applications.

Gold in Catalysis

Catalysis by Au has rapidly increased importance in chemistry since Masatake Haruta (Osaka National Research Institute (ONRI), Japan) and Graham Hutchings (Cardiff University) found that Au can be used as a catalyst in various reactions. Historically, Au was known to be a transition metal rich in coordination numbers but compared with other metals, bulk Au was thought to be chemically much less reactive. However, this changed in 1973 when Bond et al. (1) reported the hydrogenation of olefins over supported Au catalysts; subsequently Haruta and Hutchings independently found that supported nanosized Au catalysts are surprisingly active for low temperature carbon monoxide oxidation and for the hydrochlorination of acetylene to vinyl chloride monomer (2, 3). The most important aspects of Au catalysts are the high activity at low temperatures, promotion by water and unique selectivity. The catalytic activity of Au nanoparticles (NP) can be further tuned by careful choice of the support material. There are many examples of Au NP loaded on semiconductor materials to exhibit high CO oxidation activity at temperatures below 0°C, activity which has not been reached by other metals (4–8).

Low Temperature CO Oxidation by Gold

At the beginning of the 1980s, Haruta reported that Au NP deposited on semiconductor oxides such as titanium dioxide (TiO₂), iron(III) oxide (Fe₂O₃), cobalt(II,III) oxide (Co₃O₄) and nickel oxide (NiO) exhibit markedly high catalytic activity for CO oxidation even at temperatures as low as 200 K (7). The contributing factors to this high activity are still disputed. Haruta studied low-temperature CO oxidation with Au and platinum NP supported on TiO₂ prepared by different methods and found that activity is dependent on the
preparation method. Interestingly, hemispherical Au particles adhering to the support, prepared by deposition-precipitation methods, exhibited greater activity than spherical particles having little interaction with the support prepared using impregnation and photochemical methods. Pt catalysts did not show such variation in activity with the preparation method, indicating that only the metal is involved in CO conversion. These data indicate that metal-support interactions play a crucial role in Au-catalysed CO oxidation at low temperature (9). Another important aspect is the size of the NP. It has been found that the optimal inside diameter range for maximum activity is between 0.5 and 5 nm (9), supporting Kubo’s prediction five decades ago that small NP would behave differently from the bulk (10). Metal NP smaller than 2 nm show a discrete energy band structure similar to those of semiconductors.

The promoting effect of moisture has been intensively studied and it has been found that it promotes CO oxidation at room temperature but is not indispensable at temperatures below 273 K, depending on the support. Semiconducting supports such as TiO₂, manganese(IV) oxide (MnO₂), Fe₂O₃, Co₃O₄, NiO, zinc oxide (ZnO), zirconium dioxide (ZrO₂) and cerium(IV) oxide (CeO₂) exhibit high activity at temperatures below 273 K in the absence of water. However, insulating, non-reducible metal oxides such as aluminium oxide (Al₂O₃), silicon dioxide (SiO₂) or titanium carbide (TiC) show moderate
activity and require a significant amount of moisture (11). A detailed study on the influence of moisture and NP size on CO oxidation over supported Au catalysts, including kinetic studies has been published (11).

As an extension to low-temperature CO oxidation over supported Au catalysts, Professor Bert Chandler (Trinity University, USA) presented a new process for eliminating CO from hydrogen feeds with minimal hydrogen oxidation, the so-called preferential oxidation (PROX) process with Au/TiO2 and Au/Al2O3 catalysts. CO PROX over Au catalysts has been investigated in two ways: firstly, the fundamentals of CO oxidation are studied in the absence of H2 (at low conversion); secondly the CO oxidation reaction is studied at industrially useful conversions and temperatures (close to 80ºC) in the presence of H2 (PROX). In both cases, the reaction is greatly affected by the presence of water in the feed and formation of carbonates on the catalyst surface. In a recently published study, the Chandler group established that the CO oxidation reaction is co-catalysed by weakly adsorbed water at the NP perimeter (12, 13).

In situ characterisation of CO oxidation over bimetallic Au-Ag/TiO2 catalysts was presented by Catherine Louis (Centre National de la Recherche Scientifique (CNRS)-University Pierre et Marie Curie (UPMC), France). Bimetallic Au-Ag NP supported on TiO2 showed higher activity and stability for CO oxidation at room temperature than monometallic Au and Ag catalyst. The best performances were obtained by Au-Ag/TiO2 catalysts with an Au:Ag ratio of 1:0.8 after activation in H2 at 550ºC. Transmission electron microscopy (TEM) showed that the average metal particle size increases with the temperature of activation and micro-energy dispersive spectroscopy (EDS) performed on individual particles indicated that the metal particles become more bimetallic. Ultraviolet (UV)-visible spectroscopy performed during in situ reduction indicated that the bimetallic particles formed gradually as temperatures increased. The evolution of the surface composition of the metal particles studied by X-ray photoelectron spectroscopy (XPS) and CO diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) revealed an increasing proportion of silver atoms during activation under H2 (14).

Other Industrially Relevant Processes with Gold Catalysts

Peter Johnston presented the latest progress in the development and commercialisation of Au catalysts for vinyl chloride monomer (VCM) production. He showed that Au supported on activated carbon as catalyst for the hydrochlorination of acetylene shows superior activity to the current mercury(II) chloride (HgCl2) on carbon. He explained the importance of the migration to the new, mercury-free process taking into consideration the environmental and handling problems due to the toxic nature of the Hg catalyst. He described the progress in developing ultra-low Au catalysts for this application (3, 15, 16).

Another important industrial process is glycerol oxidation. In recent years, the catalytic transformation of alcohols into fuels and other valuable chemicals has played an important role in the quest to more sustainable processes. It is well known that oxidation of glycerol is a complex process leading to a complex mixture of products including six potential C3 oxygenated products. Chunli Xu (Shaanxi Normal University, China) presented the effect of the acid/base nature of supports on the selectivity of glycerol oxidation over supported Au-Pt bimetallic catalysts. Various supports, including acidic (TiO2 and CeO2), basic (magnesium oxide (MgO), magnesium hydroxide (Mg(OH)2), magnesium carbonate (MgCO3), Mg(OH)2, ZnO and calcium carbonate (CaCO3)) and amphoteric (Al2O3 and hydrotalcite), were reported. The results showed that the acid-base properties of the supports significantly affected product selectivity. The selectivity to glyceraldehyde was inversely proportional to the strength of basic sites on the supports while the
selectivity to tartronic acid, glycolic acid and glyoxalic acid was directly proportional to the strength of basic sites of supports. In contrast, the selectivity to glyceric acid was neither proportional to the strength of basic sites of supports nor proportional to the strength of acid sites of supports (17).

Two other talks on alcohol oxidation were presented by Emiel J. M. Hensen (Eindhoven University of Technology, The Netherlands) studying the synergy between Au NP and Cu+ in MgCuCr2O4-spinel supports (17). XPS and extended X-ray absorption fine structure (EXAFS) characterisation results show that the synergy involves close interaction between metallic and surface Cu+ species stabilised in the support. MgCuCr2O4 is more stable under reaction conditions than MgCuAl2O4. The use of MgCuAl2O4 leads to segregation of Cu and formation of copper(II) oxide (CuO). Au/MgCuCr2O4 is also an active catalyst for the selective oxidation of propylene to acrolein (selectivity close to 90%). Density functional theory (DFT) study of the reaction mechanism explained the dynamic nature of Au atoms at the interface of the Au clusters with the support. Adsorption of propylene leads to the formation of an isolated Au atom that strongly binds propylene. The reaction proceeds by activation of the allylic C–H bond by an adsorbed O2 molecule. Detailed analysis of the electronic structures of the reaction intermediates in the catalytic cycle show that the critical role of Cu is the decrease of the desorption energy of acrolein (18–21).

On the same subject of selective oxidation of alcohols to aldehydes or ketones, Feng Wang (Waterloo Institute for Nanotechnology, Canada) discussed the effect of crystallinity of Au NP supported on CeO2 for the conversion of alcohols to aldehydes or ketones and amines to imines via oxidative dehydrogenation. Both types of reactions achieve moderate to excellent yields. Importantly, regardless of Au size and surface area of CeO2 support, the study reveals that the active plane for C–H and N–H bond activation is the (110) plane on nanorod ceria. Characterisations by Raman and XPS show that positively charged Au dominates in nanorod Au/CeO2 possibly via the interaction with oxygen vacancy sites. Au NP supported on CeO2(110) crystal planes were more reactive than on CeO2(111) and (100) in the oxidative dehydrogenation of alcohols. Kinetic analysis and a Hammett plot suggest that hydride transfer is involved and the cationic Au is catalytically active. The Au/CeO2 catalysts were initially evaluated in the oxidation of benzyl alcohol to benzaldehyde showing around 99% selectivity for benzaldehyde (22, 23).

Another important catalytic process is low-temperature C–C bond activation. Hidehiro Sakurai (Osaka University, Japan; and Japan Science and Technology Agency) has shown that bimetallic Au/Pd alloy nanoclusters stabilised by a hydrophilic polymer, poly(N-vinylpyrrolidone) (PVP), have unusual catalytic activity towards the activation of the C–Cl bond at room temperature under aqueous conditions. The reaction does not occur with either Au or Pd single metal clusters, indicating that a synergistic alloy effect plays a key role. In addition, alloy clusters exhibited unique reactivity when aryl bromide was used as coupling partner. With Pd-rich catalyst the reaction occurs through conventional catalysis by leaching of Pd from alloy clusters (24–26).

The selective hydrogenation of acetylene to ethylene over SiO2-supported Au alloyed Pd single-atom catalyst (SAC) was discussed by Tao Zhang (Chinese Academy of Sciences, China). This industrially important process uses mainly Pd-based catalysts but suffers from poor selectivity. The speaker showed that conversion of acetylene to ethylene can be achieved with high selectivity using Au alloyed Pd SAC on SiO2 support. In situ DRIFT spectra of CO adsorption and EXAFS results give evidence of the formation of Au-Pd interaction. The data fitting results gave only Pd-Au interactions in the AuPd0.025/SiO2 catalyst, providing direct evidence for the isolation of Pd atoms. This new catalyst improved the catalytic performance of the acetylene conversion by 95% compared to the monometallic Au/SiO2 catalyst and ethylene selectivity by 100% compared to the monometallic Pd catalyst (27).

Two other relevant talks were delivered by Florencia C. Calaza (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) and Wilm Jones (The UK Catalysis Hub, UK; and Cardiff University, UK) on carbon dioxide activation by negatively charged two-dimensional (2D) Au clusters; and photocatalytic H2 production using core-shell AuPd promoters with controlled shell thickness, respectively. The adsorption and activation of CO2 on various Au clusters grown on Ag(001)/supported MgO films were reported using
XPS, temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS). It has been found that the adsorption of CO₂ in the presence of 2D Au clusters with negatively charged perimeters is reversible and that these species are stable up to slightly above room temperature. When heated beyond 380 K, the clusters appear to take on more three-dimensional (3D) morphologies. The negative charge on the 2D clusters is responsible for the activation of CO₂. Furthermore, isotope labelled compounds were used (¹³CO₂, ¹⁸CO₂ and ¹⁸O₂ for labelling the oxide surface) to identify the presence of different species on the surface (28). Au NP supported on TiO₂ followed by the deposition of thin layers of one and two monolayer equivalent of Pd was studied for photocatalytic H₂ production. Deposition of Pd was performed by a photodeposition method as well as sodium borohydride (NaBH₄) reduction (SR). The photocatalytic performance was evaluated using the reforming of ethanol as a model. TEM analysis demonstrates that all metal NP were deposited on the TiO₂ homogeneously for all samples. Analysis by XPS confirmed the presence of metallic Au and Pd with the lack of any significant PdO. The absence of PdO suggests the Pd is associated with Au, as segregated Pd would likely oxidise. The association of Pd with Au was also supported by EXAFS results which show Pd existing in a Au-rich environment with no significant Pd–O and Pd–Pd interactions (29).

**Gold in Sensing Applications**

One of the sessions focused on sensing applications using Au as the active material. Malcolm Kadodwala (Glasgow University, UK) delivered a particularly interesting talk titled ‘Biosensing with a Twist: Detection and Characterization of Biomaterials with Sculpted EM Fields’, on ultrasensitive detection and characterisation of biomolecules using Au to create plasmonic nanomaterials (30–32). ‘Metal Oxide Supported Gold Nanoparticles for Gas Sensing Applications’ delivered by Katia Fajerwerg (Paul Sabatier University, France), focused on Au/ZnO and Au/TiO₂ for CO and propane detection (33, 34). Another presentation on sensing with Au was delivered by Emilie Lebon-Taillhades (Laboratoire de Chimie de Coordination, France; and Sciences et Technologies pour l’Aéronautique et l’Espace, France). She introduced a new strategy for nitrate monitoring in aqueous media using Au nanostructured electrodes (35). ‘Gold-decorated MW-CNT Modified Electrodes for Glycerol Electroanalytical Detection and Transformation’ was presented by Laura Prati (University of Milan, Italy). She mentioned that carbon nanotubes could be decorated with Au NP using sol immobilisation or deposition precipitation. More details can be found in the literature (36).

**Gold in Clinical Diagnostics and Treatments**

Using nanotechnology-based systems for diagnosing and treating specific diseases is increasing in popularity in recent decades and it is particularly relevant for personalised medicine, allowing a disease to be detected at an early stage and a suitable therapy to be directed toward the target tissue. The unique properties of Au play an important role in this area. A series of presentations were delivered by experts including Laura Maiore on synthesis, characterisation and evaluation of Au complexes as antimicrobial compounds (37) and Meike Roskamp (Midatech Pharma Plc, UK) on Au anticancer drugs. Midatech Pharma are using ultra-small targeted sugar-coated Au NP as delivery agents and have their own manufacturing facility for large scale NP under good manufacturing practice (GMP) conditions (38). In the same area of drug delivery, Federica Scalletti delivered a talk on the fabrication of Au nanorods for incorporation into nanocapsule systems (39). Another presentation in the same field was by Sebastian Kopitzki (Midatech Pharma Plc) on targeted treatment of liver diseases. This study focuses on attaching the targeting and chemotherapeutic agents to ultra-small glycol-coated Au NP. It has been shown that after administration and circulation in the body the targeted Au NP accumulate in the liver, where the small NP show increased tumour penetration potential (40). In the diagnostics area, Yasuro Niidome (Kyushu University, Japan) presented a study on liver tissue mass spectrometry imaging using Au NP. He showed that the highly stable chemical nature of Au and the high sensitivity of mass spectrometry enabled the Au nanorods to serve as a mass marker in body tissue (41, 42).

**Conclusion**

This review presents only a fragment of the presentations and posters disclosed. The increasing popularity of the conference, combined with the large number of key stakeholders present, highlighted the
importance of Au catalysis. It has been shown that the most important characteristics of Au catalysts: the high activity at low temperatures, promotion by water and unique selectivity can be further tuned by careful choice of support, different promoters or catalysis conditions. The range of applications in the conference, from replacing mercury in VCM production to diagnosing and treating medical conditions, presents an optimistic message that Au catalysis and applications will play a crucial role in a sustainable future.

References

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The Use of Annular Dark-Field Scanning Transmission Electron Microscopy for Quantitative Characterisation

A review of techniques developed for a high resolution study of bimetallic catalysts and other materials

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Small metallic nanoparticles used for polymer exchange membrane fuel cells (PEMFC) represent a characterisation challenge. Electron microscopy would seem the ideal technique to analyse their structure at high resolution. However, their minute size and sensitivity to irradiation damage makes this difficult. In this review, the latest techniques for overcoming these limitations in order to provide quantitative structural and compositional information are presented, focusing specifically on quantitative annular dark-field (ADF) scanning transmission electron microscopy (STEM) and quantitative energy dispersive X-ray (EDX) analysis. The implications for the study of bimetallic fuel cell catalyst materials are also discussed.

1. Introduction

It is well established that catalyst nanoparticles are critical to the success of PEMFC; indeed it is the cost of the platinum loading which currently limits their wide-scale use. To help the search for better catalysts, with higher catalytic activity and specificity and lower cost, steady improvement in characterisation abilities is essential. Since the technique’s infancy (1), ADF STEM has been utilised for the study of catalysts due to the strong dependence of signal intensity on atomic number (see Figure 1). This so-called ‘Z-contrast’ has enabled differentiation of individual heavy atoms from lighter, and even crystalline, supports well before atomic resolution was even possible, as first demonstrated by Crewe, Wall and Langmore (1) and later by Nellist and Pennycook (2) among others. STEM suffers from the inherent problem of many other high resolution techniques, where the particularly small area investigated may not be representational of the whole sample. However the technique does provide the local atomic scale information which is essential to completely understand catalysts at the same length scales as their chemical reactions.

This paper will introduce the key advantages and limitations of STEM for materials characterisation. Some of the more recent advances and developments in the field of quantification, where the machines are beginning to be used much more as analytical tools rather than high resolution cameras, will also be discussed.
2. The Fundamentals of Scanning Transmission Electron Microscopy

STEM is a process where pre-specimen lenses focus the beam into a small probe that is scanned in a raster pattern across the sample (see Figure 2(a)). This is similar to scanning electron microscopy (SEM) (3) except that here the transmission signal is collected and it is customary to use an electron transparent transmission electron microscopy (TEM) thin foil, producing significantly improved resolution because beam-spreading or particle scattering events are reduced in thin samples. There are a variety of signals emitted by the sample due to excitation from the high energy electron probe (see Figure 2(b)). One of the major advantages of STEM is the ability to detect several of these signals in parallel. The collection of several signals in parallel is particularly beneficial for beam sensitive samples, such as catalysts, as they will often damage or reconstruct during analysis due to the high energy provided by the electron beam. This means that sequential images will not present the same sample structure, especially at atomic resolution.

A small on-axis detector, with an outer collection angle typically less than 5 mrad, produces a bright-field (BF) STEM image. The origin of the image contrast is the interference between overlapping Bragg disks (these disks are green in Figure 2(a)). Due to the theory of reciprocity (5) BF-STEM, with a convergent illumination and a small on-axis detector, is analogous to BF high resolution TEM, with a small point source and a large detector collecting the resultant scattered beams. A disadvantage of both methods is that they suffer contrast inversions with defocus and thickness, and
difficulties associated with image interpretation of a coherent signal (4). A recent approach aims to produce a more incoherent BF image by using an annular detector, referred to as annular bright-field (ABF). The theory is that ABF is more sensitive to lighter elements like oxygen or lithium (6–8), although the exact origin of the image contrast is still a matter of debate so whether or not quantitative intensity information can be extracted is uncertain.

Using an annular detector to only collect the electrons scattered to higher angles, typically larger than 80 mrad, often referred to as high angle annular dark-field (HAADF), produces a coherency loss in the signal detected. Originally, Howie proposed (9) that the cause of this coherency loss was thermal diffuse scattering (TDS) at larger detector angles becoming the more dominant scattering mechanism over elastic or Bragg scattering. However, it was later demonstrated that the process of integration of the signal over a large annular detector, and therefore a large range of scattering angles, is the cause of the coherency loss. Any dynamical elastic diffraction of electrons scattered onto the detector will have no effect on the final image as the intensity is only redistributed elsewhere in the detector and is still integrated into the total collected signal (10). ADF STEM produces an image with atomic number sensitivity or Z-contrast following power law relationship Z^α, where α is between 1 and 2 depending on the angular range of electrons collected (11) and relative Debye-Waller factor between atoms among other things. Many early attempts at intensity quantification have relied on accurately characterising this exponent.

2.1 Aberration Correction

Unlike optical lenses, electromagnetic lenses contain inherent aberrations that are unavoidable (4, 12, 13). When aberration correction is discussed it normally refers to correction of the positive spherical aberration, C₆ or C₃, in which the rays furthest from the optic axis are focused more by the lens field. In early instrumentation, namely TEM, resolution was improved by using higher accelerating voltages (14) in order to minimise the sample interaction volume, a process which inevitably had its own limitations due to the resulting high damage rates. Later it was combated by using a so-called high-resolution or narrow gap pole piece with a much smaller C₃ of 0.7 mm (15). However, the narrow gap produces large restrictions on specimen holders, including tilt ranges and in situ cells and limits the possible additional detectors for microanalysis. The most recent solution is an aberration corrector, where a series of non-round lenses are used to counteract the aberrations, similar to the lenses in glasses for eyesight improvement. In STEM this results in not only a reduced probe size (improving resolution) but also an increase in the current density within this corrected probe (16), causing an enhanced signal-to-noise ratio (SNR) during imaging and significant improvement in counts for microanalysis. Aberration correctors allow microscopes to keep their large pole piece gaps and are now commercially available, existing in microscopes around the world (16–19).

3. Quantification of Annular Dark-Field Images

ADF STEM images are easy to interpret qualitatively due to the Z-contrast nature of the technique and the absence of any contrast inversions with thickness. The information they can provide when images are treated as data sets and analysed quantitatively is only just beginning to be explored. Often what people mean by ‘quantification’ is a comparison with simulated images. Anderson et al. (20) scaled simulated images to fit with experimental data rather than acquire them on an absolute scale. Darji and Howie (21) have also discussed the necessity of correcting experimental data; in this case for additional scattering from a crystalline substrate, as they believed this was the origin of the mismatch between experiment and simulation. Meanwhile for TEM there is a widely accepted mismatch between simulation and experimental intensity known as the Stobbs factor (22).

The earliest attempts on quantification were by Retsky (23) and Isaacson et al. (24) in the 1970s, comparing the integrated intensity of heavy metal atoms or small clusters to those values calculated from first principle quantum mechanics. Work on small metallic clusters has often assumed that the integrated ADF intensity of a cluster scales linearly with the number of atoms it contains (25, 26). Therefore if the intensity of a single atom is known, dividing the total intensity of a cluster by this value yields the cluster size in atoms. It is an acceptable approximation for amorphous and off-axis clusters where it can be assumed that no channelling (see below) is occurring. However, it is overly simplistic to assume such linearity for on-axis crystalline particles and neglecting coherency effects in calculations is likely to cause significant errors.
3.1 Channelling
For direct interpretation of images and accurate quantification, on a column by column basis, cleanly resolved atomic resolution images are required. This necessitates viewing the sample down a low order zone-axis (27). When atoms are aligned in this way, parallel to the incident electron probe, they provide a small lensing and therefore focusing effect on the beam (28) (see Figure 3). The subsequent atoms in the atomic column then experience a more focused probe than the first atom; resulting in the amount of scattering to the detector initially increasing faster than linearly with respect to the number of atoms. Therefore the contribution of the second atom in a column to the integrated intensity (the summed value of all the pixels within the image which represent one feature) or the total scattering cross section (29) of the column is larger than the contribution of the first and so on. Along a longer column, oscillations in intensity are seen (30) and the process is often referred to as channelling. TDS simultaneously leads to a reduction in the electron intensity along a column which is often referred to as absorption. Channelling has considerable implications for ADF STEM if not taken correctly into account (27, 29, 31, 32). Heavier atoms provide a stronger lensing effect than lighter atoms, which means that in columns containing a mixture of atom types the specific sequence of the atoms in the column will affect the resulting intensity scattered out to the detector (33).

In certain circumstances channelling can be exploited to expose subtle sample changes; for example it has been used advantageously to map the height of dopant atoms within an atomic column based on their contribution to the image intensity (34–37).

3.2 Detector Calibrations
The more common method of ADF STEM quantification utilises a detector normalisation method pioneered by Singhal, Yang and Gibson (26), and LeBeau and Stemmer (38), as such it is essential to be able to understand and map the efficiency of the STEM detectors. Commercially available ADF detectors consist of a scintillator, a glass light pipe and a photomultiplier tube (PMT). The scintillator is normally either a powder Y2SiO5 doped with cerium, a single crystal made of yttrium aluminium garnet (YAG) or, more commonly, yttrium aluminium perovskite (YAP). Electrons hitting the scintillator are converted into a photon cascade. The photons are directed to a PMT through the light pipe and converted into an electrical signal, which can be controlled to vary the ‘contrast’ in the final image. A constant voltage (direct current offset) may be added by a preamplifier, controlling the ‘brightness’ in the final image. Finally the output is digitised by an analogue to digital converter and sent to the computer. When aiming for a truly quantitative comparison with simulations it is important to map and understand the detector efficiency, as most simulation software packages normally assume a perfect detector, modelled by a uniform efficiency mask.

The more common method of detector mapping relies on using a confocal arrangement, referred to as STEM ‘alignment’ mode. The post specimen lenses are adjusted to translate an image of the probe at the specimen plane onto the detector plane (see Figure 4(b)). This produces a fine convergent beam which can be scanned over the detector; recording the detector output with respect to probe position provides a map of the detector efficiency. The gain and DC offset are optimised from the detector map such that the maximum range of signal is achieved without saturating the detector or clipping any of the pixels in the vacuum (38).

The alternative ‘pencil beam’ method of detector scanning (26) may provide a more realistic map in angle space (because of how the beam passes through the post specimen optics); the beam is travelling tilted from the optic axis. This was the more traditional method of detector mapping used in dedicated STEMs where no post specimen lenses were present due to the way in which the beam passes through the post-specimen optics. The convergence angle of a
A typical STEM probe is around 20 mrad, whereas the angle of scattering out to the detector can be up to ten times that. These scattered electrons will interact with post-specimen lenses at a very large tilted angle where lens aberrations are normally worse, making it beneficial to map the detector in angle space. However, it is more difficult to set up and thus its use so far has been limited to dedicated STEM machines.

When using detector normalisation for quantitative analysis it is important to be aware of the linearity of the detector response (38–40). In particular, altering the detector contrast does not produce a linear variation (41) in the detector signal, which is why contrast and brightness settings are normally kept constant between detector mapping and experimental images.

The majority of image intensity detector normalisation methods rely on the detector responding linearly with the number of incident electrons. Care should be taken not to rely too heavily on this linearity alone. During experimental image acquisition the detector will see a diffuse electron flux (see Figure 4(a)) at a much lower intensity, whereas during detector mapping the whole beam is scanned over it in a fine probe. To combat this it is prudent to drop the probe current by a known amount during the detector mapping (42) and subsequently incorporate a ratio of the probe currents into the quantification method. Lowering the current also helps to minimise damage to the detector and makes a greater contrast range available in the final experimental image, which is particularly useful for imaging nanoparticles or other low dimensional materials.

Working from the premise that real detectors are asymmetric in their collection efficiency (43, 44) there needs to be a way to compensate for this to improve matching with simulations. Rosenauer et al. (39) use a two-dimensional (2D) profile estimate of their detector asymmetry to simulate images with an asymmetric detector; however this approach is only possible with certain simulation packages. The flux weighting method developed by Martinez et al. (45) aims to improve the detector normalisation by accommodating for this asymmetry in the experimental images rather than adjusting the simulations.

3.3 Recent Advances in STEM Quantification

LeBeau and Stemmer are generally acknowledged as the originators of a resurgence of interest in detector calibrations and recording images on an absolute intensity scale (see Figure 5) (38). Their method relies on a full characterisation of microscope imaging parameters and detector responses in order to achieve direct comparison with simulations (46), although defocus has been fitted empirically from selecting the simulated image which fits most closely to experimental images.

Quantitative comparison between experiment and simulation has only become possible due to improvements in parallelisation of simulation software, first on central processing units (CPU) and then graphical processing units (GPU). Such parallelisation makes it possible to produce accurate simulation reference libraries in reasonable time-scales using the more accurate (but more computer intensive) frozen phonon approach rather than absorptive potential (47).

From a detector efficiency map like the one presented in Figure 6(b), the average pixel intensity in the active region (the area coated with the scintillator, predominantly blue in Figure 5(b)) can be considered to represent one hundred percent of the total electron beam, whilst the average intensity of the background region (anywhere in the image detector image considered not to be the active region) represents no-beam and is also known as the black-level. Normalising experimental images using these maps results in images being scaled as a fraction of the incident beam which has been scattered out to the detector.

An improvement to this has been developed by calculating the scattering cross-section (29) or...
Gaussian volume (31, 48) of each atomic column within an image. Scattering cross-sections are calculated by integrating the normalised intensity over one atomic column, using a Voronoi polygon (49, 50) or otherwise, and multiplying by pixel area. This creates a value with area units that represents the probability of electrons interacting with that column and scattering out to the ADF detector, much in the way that other cross-sections behave in particle physics. Gaussian volumes are mathematically identical to cross-sections (51), only instead of integrating the intensity in a polygon method, a 2D Gaussian curve is fitted to the

Fig. 5. (a) One of the first ADF STEM images normalised to the incident beam. The sample is a gold wedge and the white numbers represent the assigned atom counts based on direct comparison with simulation; (b) the associated detector efficiency map in units of fraction of the average intensity of the active region. (Reprinted with permission from (46). Copyright (2010) American Chemical Society)

Fig. 6. (a) Image of a silver nanoparticle embedded in an aluminium matrix, the dots represent the estimated position of the atomic columns with those assigned as silver marked in red; (b) histogram of the scattered intensities of the Ag columns. The black solid curve shows the estimated mixture model; the individual components are shown as dashed curves; (c) the ICL criterion evaluated as a function of the number of Gaussians in a mixture model. The minimum at 10 components represents the optimum number of components (Reprinted by permission from Macmillan Publishers Ltd: Nature (59), copyright (2011))
image intensity of each column and the integrated volume under this curve is used. Using these volumes or cross-sections for quantification still requires comparison with simulations but is a lot more robust to defocus, tilt, source size and other aberrations (29, 32, 48). Although the robustness of such an integration or averaging over a unit cell has been commented on before (20, 39, 52), it was not until the scattering cross-section work (29, 32, 48, 51) that it was mathematically proven and robustly tested through a series of simulations. Scanning distortions may still affect the quantification accuracy; recent advances in non-rigid image registration may provide the solution to this (53–55).

An alternative technique to direct comparison with simulation is one based on statistical parameter estimation theory (56), pioneered by Van Aert et al. (57). The theory relies on the inherently quantised nature of a histogram of integrated intensities from an experimental image (58). For a single element scenario, for example the silver particle in Figure 6, the integrated intensities should naturally be quantised in the histogram due to the fact that each column contains an integer number of atoms. These discrete values become somewhat smeared by Poisson noise and other random errors; however, it should still be possible to decompose the histogram of all the integrated intensities into a series of Gaussian components through statistical estimation and a maximum likelihood criterion. The critical component of this algorithm is a ‘cost function’ to minimise the total number of Gaussians incorporated, otherwise the best solution would be an infinite number of Gaussians. The integrated classification likelihood (ICL) criterion is used for this purpose and provides a local minimum at the optimum number of components (Figure 4(c)).

The main advantage of ICL is that it does not require the experimental images to be intensity normalised. A systematic error or scaling can easily be incorporated or alternatively it can be used as an independent method of atom counting. The limitations of the ICL approach have also been covered by Van Aert (51) and De Backer et al. (60). In particular the field of view and therefore the number of observations per Gaussian component greatly affect the ability of the ICL criterion to estimate the correct number of components. This is critical for investigations of nanomaterials where their finite size severely limits the number of observations available per component, but could potentially be overcome by combining several images for incorporation into the histogram (31).

3.4 Three-Dimensional Reconstruction

The traditional method for three-dimensional (3D) reconstruction is electron tomography (61), developed from X-ray tomography (62). A 3D structure is reconstructed from a tilt series of images using one of a variety of possible reconstruction algorithms (63, 64). The main requirement is for the micrographs to be ‘true projections of the structure’ (65) such that image intensities are a monotonic function of sample thickness. Therefore the use of TEM or BF-STEM is not desirable because Fresnel fringes and diffraction contrast are a significant problem. Tomography was initially developed for biological samples (66, 67) and is regularly used to determine the location of catalysts particles on their supports (68–73). Once the 3D shape has been reconstructed important information such as surface area, volume and thickness distributions can be measured for particles (74). Carrying out tomographic reconstructions by this method subjects the sample to high amounts of electron dose from the hundred images required for a single reconstruction and the dose inflicted during any tilting and re-centring processes between frames.

The more recent method of discrete tomography (75) significantly reduces the number of necessary projections to less than 10, even in the presence of noise or defects, through the use of ‘prior knowledge’. Atomic resolution discrete tomography (59) uses the prior knowledge that the particles have crystalline structure, contain no voids and surface steps and kinks are minimised. This is primarily carried out by defining each crystallographic point as a boxed region and then only one atom may lie within each box. Van Aert et al. were the first group to publish atomic resolution discrete tomography data on their embedded silver nanoparticle (59) and also the core of core-shell semi-conductor nanocrystals (76). In their research they found that two or three quantified HAADF STEM images down crystallographic orientations (for example [100], [010] and [110]) gave sufficient information to reconstruct the particle, provided the atoms are restricted to a particular, in this case face-centred cubic (fcc), crystalline structure. Their quantitative STEM method (57) was used on each projection image to estimate the number of atoms before carrying out a reconstruction. It is, however, important to note that both of the example particles used to demonstrate this method had been
embedded in another material, thereby limiting the surface mobility and improving the dose tolerance for such reconstructions to be carried out.

A more recent alternative to tomography has been designed specifically for the study of free standing catalysts where the mobility of surface atoms between sequential images will be high. Using the method of quantitative STEM with scattering cross-sections, an automated procedure has been developed for peak finding (to find each atomic column location within an image) and subsequently estimating the number of atoms they contain (77). Armed with the atomic column locations and the number of atoms it becomes possible to estimate the 3D structure from only one experimental image (see Figure 7). The same assumptions described above for atomic resolution discrete tomography are combined with atomic spacing in the beam direction predicted from bulk crystal information. A significant advantage to this approach is the requirement of only one experimental image for 3D information. This not only provides reduced dose capabilities but also increases throughput, leading to the ability to reconstruct a time series of images (77) or several particles in one sample (47, 78).

4. Composition Analysis

The STEM image intensity contains both composition and thickness information which can be difficult to differentiate. A particular example of this is acid leached platinum cobalt nanoparticles; the increased ADF image intensity of the heavy metal shell is swamped by the loss in intensity due to the large reduction in sample thickness at the particle surface (79, 80). The challenge facing quantification of bimetallic systems is how to incorporate additional

Fig. 7. Particle 3 – normalised experimental ADF image (a) of a Pt/Ir particle with the calculated cross-section map; (b) the 3D reconstructed particle is shown parallel to the beam direction; (c) perpendicular to the beam direction at from two angles 90° from each other (d) and (e). For ease of comparison with a Wulff construction the (d) projection has had the faces coloured in, {111} purple, {100} blue, {110} red
information or assumptions in order to separate out the thickness and composition contributions from the ADF STEM signal. For PEMFCs in particular it is desirable to understand how much Pt there is and its location on the particle surfaces.

A combination of sequential high resolution STEM images and multi-slice simulation has been successfully implemented by Ortalan et al. (81) on iridium-rhodium clusters, using intensity ratios to predict possible combinations of Ir and Rh in each column. This procedure, however, was only possible due to the small size of the clusters investigated (containing a maximum of three atoms per column); at larger particle sizes with an exponential increase in the number of possible combinations this approach quickly becomes unrealistic. Carlino and Grillo (82, 83) demonstrated that it is possible to use a section of sample with known composition to interpolate the thickness where composition is unknown to estimate composition changes on a relative scale. Rosenauer et al. have extended this approach at atomic resolution analysis (49, 84). However, this technique is rather limited to the semiconductor multilayer systems for which it was designed, where areas of known composition are present in the same image. Molina (85, 86) and Hernández-Maldonado et al. (87) have demonstrated approaches using a series of carefully controlled reference samples with accurately known composition, although this comes with its own problems of being able to manufacture such standards.

With these restrictions to quantitative ADF STEM for compositional analysis it is therefore useful to look at the other available signals which an electron microscope can provide. Elemental analysis of catalyst particles began as early as 1983 (88). The advantage of using so-called microanalysis in the electron microscope is the ability to achieve compositional information at the same length scale as the electron micrographs thereby providing invaluable local microstructural information of a sample. Here the focus is on EDX, one of the two microanalysis techniques which can be carried out within a TEM/STEM. EDX analysis relies on the excitation and ejection of an inner shell electron within an atom in the sample. An outer shell electron fills the subsequent hole whilst emitting an X-ray of characteristic energy. The EDX signal has significantly worse SNR than ADF but the elemental information is much more readily separable. The alternative technique, electron energy loss spectroscopy (EELS), provides higher count rates but in many cases can prove challenging to use for mapping of several elements at the same time. This is especially true for heavy elements like Pt (89) where the ionisation edge is very high energy. Microanalysis is a region where STEM demonstrates advantages over TEM due to the focused probe providing localised information and the ability to collect ADF and microanalysis signals simultaneously.

Aberration correction has produced a significant advancement for microanalysis, particularly in the realms of 2D elemental mapping due to the significant increase in current density within the finer corrected probe. However for samples prone to beam damage this high current density is a problem. For mapping in particular, one must be aware of the damage being caused by the long acquisition times in order to improve total counts (90). From experience (47) it has been found that this damage can be minimised through using sequential fast scanning, where several fast acquisitions of a line scan or map are combined, to reduce the dwell time per pixel per scan while still maintaining the total live time necessary for high counts. Ideally sub-pixel scanning is also used so the beam is never stationary over the sample. It is unclear why such an approach yields lower damage unless the lower dose rate per pixel allows sufficient time for the charge or heat to dissipate away from the analysis region into the remainder of the sample.

Even without aberration correction Prestvik et al. carried out some of the earliest investigations into STEM-EDX analysis of bimetallic nanoparticles where individual platinum-rhenium particles sized 0.5–2.5 nm were imaged and the percentage Pt was plotted against particle size (91). EDX mapping has been used to demonstrate the localisation of sulfur on the nanoparticles in ‘poisoned’ catalysts (90). In more recent years EDX of 5 nm core-shell nanoparticles mapping has been able to differentiate the layered structure very effectively (89); however the atomic columns are not resolved due to the trade-off between resolution and counts. Deepak et al. (89) have demonstrated the use of multivariate statistical analysis (92) to improve their quantification, mining their data cube for independently varying compositions.

The new generation of EDX detectors has provided a huge advancement for the field of TEM microanalysis. The improved detector design of these silicon drift detectors (SDD) (93–95) allows for larger devices and therefore increased solid angles for X-ray collection. They are also often windowless which allows them
to be located closer to the sample thereby increasing the improved solid angle of collection (up to 1.3 srad, whereas previous generation detectors only reached up to 0.3 srad). The improvement in X-ray count rates is sufficient that atomic resolution maps (96–99) and X-ray tomography (100) are now both regularly possible in reasonable time scales. Tran et al. are among the first to apply these new detectors to nanoparticles (101), allowing them to map their copper-gold nanoparticles ranging 1–10 nm in diameter. No comment or attempt is made towards quantification of the alloy ratio apart from establishing their particles as random alloys.

5. Quantification of Energy Dispersive X-ray

SDD have opened up a new era in microanalysis. Combining their improved collection efficiency with the higher current densities provided by aberration correction (16, 19) yields a huge increase in X-ray counts leading to the potential for improved quantitative analysis. This is particularly relevant when investigating catalyst nanoparticles where only a small number of counts are generated from the low mass of sample.

Quantification through direct comparison with simulations (98) must take into account both X-ray absorption and subsequent re-fluorescence. This requires knowledge of, or estimation of, local thickness and density (although this can be neglected for thin specimens such as nanoparticles). The detector geometry and detection efficiency must also be included in quantification calculations, including both the solid collection angle and the take-off angle.

5.1 k-Factors and ζ-Factors

The original ratio approach to EDX quantification in TEM thin films was first proposed by Cliff and Lorimer nearly forty years ago (102). The Cliff-Lorimer or k-factor, \( k_{AB} \), relates the atomic fractions, \( C_A \) and \( C_B \), of constituent elements A and B to their measured X-ray intensities, \( I_A \) and \( I_B \) (Equation (i)).

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \tag{i}
\]

In the technique’s infancy a ratio approach was essential due to the mechanical and electrical instabilities present in the early analytical electron microscopes and therefore the low X-ray counts detected. Electron microscope capabilities are now considerably improved, especially the beam current stability. Despite this the k-factor approach remains the primary method for EDX quantification due to its incorporation into the majority of commercial analysis software. Most EDX software allows a quantification option, however it is a rather ‘black box’ approach meaning it is not necessarily clear which methods of count extraction are being used.

The k-factors used in software have normally been calculated from first principle quantum mechanics. These theoretical k-factors have a minimum estimated systematic error of around 10% (103) but this could be as high as 20% (104). The only way to reduce such an error is to calculate an experimental k-factor by analysing a set of known samples with very similar density and thickness at a range of compositions to create a calibration curve (~±1% error is achievable). Unfortunately, this is time consuming and there is an inherent difficulty in manufacturing such samples where the composition is homogenous on the nanoscale and correspond to the macroscopic chemical composition determined by other methods.

An alternative to the k-factor approach is the ζ (zeta)-factor (104, 105) method first proposed in 1996 by Watanabe et al. (105). Designed for thin film specimens it makes use of pure element standards which are rather more readily available than the alloy alternatives, Equation (ii):

\[
\rho t = \zeta_x \frac{I_x}{C_x D_e} \tag{ii}
\]

\( \zeta_x \) is the factor connecting \( I_x \), the raw X-ray counts, to \( pt \), the total density multiplied by sample thickness. \( C_x \) is the weight fraction of \( x \), with a similar relationship holding independently for other elements in the system. It assumes that the characteristic X-ray intensity from element A, \( I_A \), is proportional to the mass-thickness of the sample. This holds well as long as X-ray absorption and fluorescence are negligible, which is the case for thin specimens; for thicker specimens an absorption correction should also be incorporated (106), (Equation (iii))

\[
D_e = N_e \phi e \tau \tag{iii}
\]

\( D_e \) is the total number of electrons seen by the sample during acquisitions defined in terms of \( N_e \), the number of electrons in a unit electric charge (or 1/e), the probe current, \( I_p \), and the acquisition time, \( \tau \). The ζ-factor, therefore, is independent of acquisition time, beam current, composition and mass-thickness providing it with units of kg electron m\(^{-2}\) photon\(^{-1}\).
It is vital to know the beam current at the time of analysis by a direct measurement (for example, Faraday cup) in order to calculate the dose. Whilst this method may seem less trivial as it requires thickness calibration and current measurements it does have the significant advantage that pure element thin films can be used as standards (107), which are often more routinely available. This method can prove more accurate than the k-factor method and is an absolute value rather than a ratio based on other elements within the system. It can also be used as a method of instrumentation comparison, to evaluate which microscopes have better analytical capabilities.

5.2 Accuracy Limitations

The key problem with STEM EDX of nanoparticles (108–110) is the limited count rate because of the small number of atoms excited. For example, in early maps produced by Lyman (88) in 1987 the number of counts from a background area pixel was 7 whilst the maximum number of counts from a Pd pixel was only 36 (giving a \( \sqrt{N} \) error of 18.5%). The problem with EDX is finding the balance between high beam currents for improved analytical resolution which increases the probe diameter or keeping the probe diameter small for improved spatial resolution but which results in poor counting statistics. E et al. (42) confirmed that the limiting factor for EDX of nanoparticles will be in achieving high enough counts of characteristic X-rays where beam sensitive samples place restrictions on the length of acquisition possible. A low number of counts results in poor statistics, reducing the reliability of quantification. There is a thickness dependent error in quantification (80) because a thicker region of sample will produce more raw X-ray counts and so have a smaller statistics error.

Another fundamental limitation for accurate STEM EDX quantification is absorption of X-ray photons before they are able to escape the sample, although this becomes less of a problem for thinner samples like nanomaterials. The absorption rate is element specific, so could cause an error in the quantification results. Work by Watanabe and Williams (104) has demonstrated the effects of both the sample thickness and X-ray line selection on EDX quantification. For the very small sample thicknesses of nanoparticles any K or L lines will provide sufficient quantification accuracy; however the M-lines may still provide small absorption errors and should therefore be avoided where possible. For elements with an atomic number lower than 30, quantification should only be carried out with the K-lines as the L-lines also begin to drop below the safe limit. Often the degree of absorption occurring within the sample can be estimated through the K-line to L-line height ratios because the L-lines begin to be absorbed much sooner, thereby changing the peak height ratios.

5.3 Energy Dispersive X-ray Cross-sections

The most recent method for quantification is by calculating cross-sections. EDX partial cross-sections (79) provide a robust measure which is easy to compare with the scattering cross-sections used for ADF STEM quantification (23, 29, 77) and ionisation edges in EELS (111–113). In sufficiently thin samples, not aligned along a low order zone-axis, so that channelling, X-ray absorption and fluorescence can be neglected, the number of X-ray counts is linearly proportional to sample thickness. The EDX partial cross-section of a single atom can therefore be determined from a polycrystalline pure element wedge sample with known wedge angle using Equation (iv) (79):

\[
\sigma_x = \frac{e}{\pi n_x \tan(\theta)} \frac{dl_x}{dx}
\]  

where \( e \) is unit electronic charge, \( i \) is the probe current, \( \tau \) is the total pixel dwell time, \( n_x \) is the atomic density of the element \( x \) and \( \theta \) is the wedge angle. \( \frac{dl_x}{dx} \) is the gradient extracted from a line profile showing integrated X-ray counts plotted against distance into the sample. Further details about this calibration method and its accuracy can be found in the literature (79).

Cross-sections are specific to a given microscope setup, including the solid-angle and collection efficiency of the EDX detector, as well as the microscope operating voltage, making them a good comparison tool between analytical TEMs. Such calibrations are also dependent on the specific X-ray peaks used, as well as the chosen energy window and background subtraction method, but this is also true for \( k \) and \( \zeta \)-factors. The cross-section approach can provide atomic counts on an absolute scale which negates the need for knowledge of sample thickness, particularly useful for nanoparticles where the exact thickness can be difficult to determine.

EDX cross-section quantification has been applied to acid leached PtCo nanoparticles in order to determine the depth of the Pt enrichment produced by the leaching process (79, 80). With Pt(Pd) core-shell nanoparticles it is possible to characterise the non-uniformity of the Pt shell (see Figure 8). The intended two-monolayer
coverage actually results in a thicker than two-monolayer coverage over part of the particle surface. The Pt shell is applied after the particles have been deposited onto the carbon support which limits the amount of coverage which can occur due to the position of the particles’ contact with the particle support.

6. Conclusions

The new developments in STEM characterisation now make it possible to pursue sub-particle and even atomic resolution compositional and structural information about nanomaterials in a genuinely quantitative manner. Whilst this approach should still be combined with more broad-beam techniques, such as X-ray or infrared spectroscopy, with much better statistical representation, the movement towards automation is beginning to allow for several particles to be analysed. Such atomic-scale information is invaluable in the work towards catalyst understanding and design. The beam sensitive nature of catalyst nanoparticles puts restrictions on the acquisition time for microanalysis. However in STEM multiple signals can be collected in parallel. Therefore creating a cross-section method for quantification which is comparable across multiple signals opens the way for combining the information they provide to yield more fruitful results.

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Applications of Neutron Scattering in Catalysis

Where atoms are and how they move

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Neutron scattering is a severely underused technique for studies of catalysts. In this review we describe how and why neutrons are useful to catalysis. We illustrate the range of systems that have been studied by both elastic and inelastic neutron scattering. These range from structural studies of adsorbates in zeolites to determination of the structure of surface adsorbates, characterisation of nanoparticles, the measurement and mechanism of diffusion and spectroscopic characterisation of adsorbed species. We conclude with how to access neutron facilities and some future prospects for the application of these techniques to industrially useful materials.

Why Neutron Scattering?

Neutron scattering is undoubtedly a severely underutilised capability in catalysis research. This is probably for two main reasons: there is a lack of understanding of what the technique can provide and it is seen as being the province of purely academic research, largely for condensed matter physics. These perceptions are not correct: there is a wealth of information that can be provided to the chemist, surface scientist and other specialisms within both academic and industrially focused research. There are a small number of centres for neutron scattering worldwide, since the production of sufficient neutrons for useful science requires highly specialised facilities. The aim of this review is to show that even within the constraint of a limited number of facilities, neutron scattering can usefully contribute to many areas of catalysis that range across structure determination at the micro- to the nanoscale and atomic and molecular dynamics from the femtosecond (vibrational spectroscopy) to the sub-microsecond (diffusion) timescale.

Neutron Properties and their Applications

The usefulness of neutron scattering arises from the properties of the neutron, which is an uncharged particle of mass 1.00866 amu (almost the same as the hydrogen atom 1H, 1.00782) with a magnetic moment. Neutrons are scattered by the atomic nuclei of the sample and, since the nucleus of an atom is only ~0.1% of the diameter of the atom, to a neutron most of a material is empty space. Hence neutrons only interact weakly with matter and as a result are highly penetrating; for example the attenuation at 1.81 Å (which corresponds to the peak flux from a research reactor) by 1 mm of aluminium is less than 1%.
For neutron diffraction studies it is straightforward to study light elements in the presence of heavy ones. The scattering cross section is both atom and isotope dependent, Figure 1, and is not a monotonic function of atomic number as it is for X-ray scattering. Hydrogen-in-metal systems are perhaps the most important example of systems which are ideal for study using neutron techniques, but it is also a valuable way to determine the precise location of oxygen in heavy metal oxides in fields ranging from high-temperature superconductors to oxide ion conductors in fuel cells.

Bond distances are generally more accurate from neutron scattering data than from X-ray techniques, particularly for bonds involving hydrogen, since the maximum electron density is not located at the atomic position but is displaced towards the heavier atom. Thus C–H and O–H distances measured by X-ray diffraction are typically 0.1 Å shorter than those measured by neutron diffraction.

It is also possible to distinguish elements that are adjacent in the periodic table, such as Al$^{3+}$ and Si$^{4+}$, as commonly found in microporous materials. These elements have identical scattering power for X-rays (since they have the same number of electrons) but different neutron cross sections, 1.503 vs. 2.167 barn (1 barn = $1 \times 10^{-28}$ m$^2$) respectively, hence providing contrast.

The atomic nucleus acts as a point-like scatterer, unlike the electron cloud, which is of finite size compared to the wavelengths used. The consequence of this is that the neutron cross section is independent of the scattering angle, $2\theta$, in contrast to the X-ray case where the X-ray cross section has a form factor that decreases with increasing scattering angle. Thus the smaller $d$ spacing information is relatively better determined in a neutron experiment compared to a similar X-ray experiment. This results in more precise atomic thermal parameters being determined from powder neutron data than from the powder X-ray data.

The most striking difference in cross section occurs for $^1$H and $^2$H, hydrogen and deuterium: $\sigma_{\text{coh}} = 1.76$ ($^1$H), 5.59 ($^2$H) barn, $\sigma_{\text{inc}} = 80.27$ ($^1$H), 2.05 ($^2$H) barn ($\sigma_{\text{coh}} = \text{coherent scattering cross section, } \sigma_{\text{inc}} = \text{incoherent scattering cross section}$). Hence hydrogen is overwhelmingly an incoherent scatterer while deuterium is primarily a coherent scatterer. Coherent scattering gives information on long range properties such as structure while incoherent scattering is a local probe. The neutron may be scattered without a change in energy (elastic scattering) as in diffraction, or there may be exchange of energy between the sample and the neutron (inelastic scattering). The latter may be coherent or incoherent, but for any material containing hydrogen, the incoherent scattering dominates. Since much of catalysis involves the transfer of hydrogen from reactant to product, the sensitivity to hydrogen is a major advantage of the technique. However, for structural studies it may be necessary to use deuterated materials, since the incoherent scattering from hydrogen results in a significant background that complicates the data analysis. For inelastic scattering, it is only the exceptionally large value of $\sigma_{\text{inc}}$ that makes catalysis studies feasible.

In short, neutron scattering can be summarised as: “where atoms are and how they move”.

### Elastic Scattering – Where Atoms Are

Elastic scattering of neutrons covers length scales that span from 1 to 5000 Å. This ranges from the atomic scale for structure determination to typical sizes of colloids. The investigation of structure is the major use of neutrons in this area, particularly by powder diffraction. The location of $n$-heptane in silicalite-1 (1) provides an example of what can be achieved. This system shows an inflection in the adsorption isotherm at a loading near four molecules per unit cell that has been ascribed to a commensurate freezing of $n$-heptane in the sinusoidal channels of silicalite-1. To investigate the unusual behaviour, the adsorption of C$_7$D$_{18}$ was followed in situ by powder neutron diffraction. (Deuterated heptane was used to reduce the incoherent background). The results show that the straight channels are first filled, then near
four molecules per unit cell, the molecules also fill the sinusoidal channels, Figure 2. Thus the diffraction data show that the inflection point in the isotherm is due to self-blocking of the channels at junctions.

Diffraction methods are well-suited to operando measurements and this is already utilised for neutron diffraction studies of batteries (2) and proton conductors (3). Studies of catalysts are also feasible as shown by a recent study of the activation and subsequent working of a commercial Cu/ZnO/Al2O3 methanol synthesis catalyst (4, 5). Due to their pyrophoric nature, commercial Cu/ZnO/Al2O3 catalysts are prepared in the completely oxidised form as CuO/ZnO/Al2O3 and the first step in methanol synthesis is activation of the catalyst by reduction of CuO to metallic Cu. The activation process is shown in Figure 3 following the reduction of CuO and the growth of Cu. It has been proposed that defects play an important role in the active Cu phase but Cu would be expected to be mobile enough under the reaction conditions, T = 493–573 K, P = 3.5–10 MPa, for these to anneal out. In situ neutron diffraction was able to show that the nanostructured Cu generated by reduction of the CuO precursor has a high concentration of stacking faults and also that they were stable under industrial methanol synthesis conditions (5).

Pair distribution function (PDF) analysis or total scattering analysis (6) is a well-established technique for the structural characterisation of poorly- or non-crystalline materials including nanoparticles. Figure 4 shows a comparison between the
Inelastic Scattering – How Atoms Move

As shown in Figure 6, inelastic scattering covers a vast range of length and time scales. For catalysis, the most relevant are quasielastic neutron scattering (QENS) which probes whole-body motions (such as diffusion) on and within materials and neutron vibrational spectroscopy or inelastic neutron scattering (INS), which probes the motion of atoms and molecules within a material.

Quasielastic scattering (10) is a very low energy inelastic process which usually manifests itself as a broadening of the elastic line and is most commonly the result of diffusional (translational or rotational) motion of atoms. Translational and rotational diffusion occur simultaneously but on different timescales. The energy resolution of a spectrometer, $\Delta E$, and the timescale, $\tau$, of the motion are related by the Heisenberg uncertainty principle: $\Delta E \times \tau = \hbar / 2\pi$. Thus resolution and timescale are inversely related and the slower the motion, the higher the required resolution. QENS spans the range $10^{-11} \leq \tau \leq 10^{-7}$ s, which requires $10^{-5} \leq \Delta E \leq 10^{-8}$ cm$^{-1}$. 

Fig. 4. The neutron diffraction differential correlation function, $D_N(Q)$, for as received hydrous palladium oxide (red). The blue curve is a simulated correlation function based on a model of a 18 Å nanoparticle of PdO. Reprinted with permission from (7). Copyright (2010) American Chemical Society

Fig. 5. Difference pair distribution function, $\Delta D(R)$, for hydrogen on Raney nickel (purple) at room temperature. This is the Fourier transform of the normalised difference of the catalyst before and after addition of hydrogen. (The peak at ~1.00 Å is non-physical and results from a truncation error in the Fourier transform.) Also shown is the pair distribution $D(R)$ function (red) generated from a periodic-DFT calculation of H on Ni(111). The spectrum is abscissa scaled so that the large peaks at 2.54 Å have the same amplitude. No ordinate scaling has been applied, all the distances come directly from the $ab\ initio$ calculation (9). Reproduced by permission of the Royal Society of Chemistry
No single spectrometer can access all of this range and typically three are needed: direct-geometry time-of-flight (τ ~ 10−11 s), backscattering crystal analyser (τ ~ 10−9 s) and neutron spin echo (τ ~ 10−7 s).

Understanding the diffusion behaviour of molecules in microporous materials is important for the design of membranes for separations and for catalysts, particularly for applications in the petrochemical industry. QENS is ideally suited for the measurement of diffusion constants in technologically relevant materials (11). The QENS timescales also match those accessible by classical molecular dynamics (MD) simulations which can provide insight into the diffusion mechanism. However, until very recently (12), the agreement between observed and calculated diffusion constants could differ by as much as two-to-three orders of magnitude, Figure 7. The improvement is the result of using fully atomistic models for both adsorbate and framework, adsorbate loadings that match those used experimentally and a flexible framework that deforms as the molecule moves through the channel.

The diffusion of branched alkanes has been much less studied than the n-alkanes. However, an understanding of the diffusion of branched alkanes is crucial to understand the effect of molecular shape on both catalytic cracking and molecular sieving in zeolites. 2-methylpropane (isobutane) is the simplest branched alkane and its diffusion in silicalite has been studied by a variety of experimental and computational methods. The diffusion is sufficiently slow that the neutron spin echo technique and long MD runs are required. Figure 8(a) shows the neutron spin echo results (13) compared with fits for 3D and 1D diffusion models. This immediately shows that 2-methylpropane is able to explore both the straight and sinusoidal channels, in contrast to previous results that indicated the molecule was confined to the straight channels. The MD results support this conclusion and show that from an initial configuration where the 2-methylpropane molecules were placed in the large cages at the intersections of the straight and sinusoidal channels, the system evolves to have both types of channel populated, Figure 8(b).
The conversion of methanol to hydrocarbons over acid zeotype catalysts is an attractive route to increased value products. Industrially, the process uses a SAPO or ZSM-5. The mechanism of the process is still debated but an early step is the formation of methoxy by reaction of methanol with an acid site. The mobility of methanol in the catalyst is clearly important and was the focus of a QENS study that compared the mobility of methanol in the industrial catalyst, H-ZSM-5, and zeolite HY which has the same Si:Al ratio (30) (14). Figure 9 compares the results of the two systems obtained with a backscattering spectrometer crystal analyser. It can be seen that the two systems behave completely differently. Zeolite HY shows a significant broadening at room temperature, consistent with simple Fickian diffusion through the material. In contrast, in H-ZSM-5 methanol is immobile on the timescale of the spectrometer.

To attempt to understand the striking difference in behaviour, INS spectra of the same samples that were used for the QENS measurements were recorded. INS spectroscopy has no selection rules, hence all modes are allowed. However, the intensity of a mode depends on the incoherent cross section and the amplitude of motion of the atoms in the mode. Both of these are large for normal hydrogen (1H), see Figure 1, thus the spectrum is dominated by modes that involve hydrogen displacement. This has a corollary that most elements that occur in catalysis such as transition metals, metal oxides or carbon are largely invisible, so the spectra do not exhibit cut-offs due to lattice absorption (as occurs with many supports with infrared spectroscopy) and the entire 0–4000 cm⁻¹ range is available.

For HY, Figure 10(a) and 10(b), it can be seen that the characteristic spectral features of methanol: C–O–H deformation at 750 cm⁻¹, CH₃ rocking mode at 1150 cm⁻¹, C–H bends at 1500 cm⁻¹, C–H stretches at 3000 cm⁻¹ and O–H stretch at 3200 cm⁻¹ are largely preserved on absorption into HY. The O–H stretch broadens consistent with hydrogen bonding to the framework hydroxyls, which downshift to ~3400 cm⁻¹ from 3650 cm⁻¹ in the clean zeolite. This indicates a relatively weak interaction between methanol and HY,
allowing free diffusion as seen by QENS. In contrast, in H-ZSM-5, Figure 10(c) and 10(d), while the C–H related modes (rock, bend, stretch) are all present, the C–O–H and Si–O–H deformations and the methanol and framework O–H stretch all disappear upon adsorption of methanol. This indicates that reaction between methanol and the H-ZSM-5 hydroxyls has occurred to generate bound methoxy, Equation (i):

$$\text{CH}_3\text{OH} + \text{Si–O–H} \rightarrow \text{Si–O–CH}_3 + \text{H}_2\text{O}$$ (i)

The reaction occurs at room temperature, suggesting a very low activation barrier, with water removed in the He/methanol gas stream used to prepare the samples.

On almost any working catalyst that involves reaction of hydrocarbons, over time there is a build-up of a hydrocarbonaceous overlayer, which may be detrimental to the catalyst activity by blocking access to the active sites or may be integral to its operation by controlling the flow of reactants to the surface. The overlayers are difficult to study with light-based spectroscopies due to strong absorption and/or fluorescence. These are irrelevant to INS spectroscopy and it has been used to study the overlayers on Ni/Al$_2$O$_3$ methane reforming catalysts (17–19). As part of the work, a method to quantify and speciate hydrogen on the surface of the catalyst was developed (17).

An even more challenging system for conventional spectroscopies is the Fischer-Tropsch synthesis of alkanes from synthesis gas. Historically, this has used an iron-based catalyst, although supported cobalt catalysts are becoming widely used. Cobalt is in limited supply, so iron catalysts are still of interest. Figure 11(a) shows the INS spectrum (20) of a technical-grade iron-based Fischer-Tropsch catalyst taken from the Sasol Ltd coal-to-liquids plant at Secunda, South Africa, whilst the reactor was operating under steady-state conditions. The most surprising feature of the spectrum is that it shows distinct bands, i.e. it is molecular-like. The spectrum exhibits bands characteristic of both aliphatic and aromatic functionalities. This is most clearly seen in the C–H stretch region, Figure 11(b),

![Fig. 10. INS spectra of solid methanol (green line), the empty dehydrated zeolite (blue line) and methanol loaded into the zeolite (purple line) at incident energies of: (a) and (c) 5240 cm$^{-1}$; and (b) and (d) 2016 cm$^{-1}$. The arrow in (a) shows the downshift of the framework hydroxyls on hydrogen-bonding to methanol. (The spectrometer is described in (15, 16)). Reproduced from (14) with permission from The Royal Society of Chemistry](http://dx.doi.org/10.1595/205651316X691230)
where bands below (aliphatic) and above (aromatic) 3000 cm\(^{-1}\) are seen. The intensity of an INS mode is directly proportional to the number of oscillators, thus aliphatic and aromatic C–H stretch modes have the same intensity per C–H, unlike infrared spectroscopy where aliphatic and aromatic C–H stretch modes can have very different extinction coefficients making quantitative comparison problematical. From Figure 11(b) it can be seen that there is an approximately equal number of hydrogen atoms bonded to sp\(^2\) and sp\(^3\) hybridised carbon.

As a model system for Fischer-Tropsch catalysis, CO methanation (Equation (iii)) has been investigated:

\[
3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (\text{ii})
\]

Starting from a pre-catalyst (hematite, \(\alpha\)-Fe\(_2\)O\(_3\)), under reaction conditions (6 hours, 623 K, He 600 ml min\(^{-1}\), H\(_2\) 150 ml min\(^{-1}\), CO 75 ml min\(^{-1}\), 1.1 bar) the active catalyst evolves in the same way as the industrial material. For INS studies of catalysts, sample quantities are in the range 10–50 g, as compared to the usual microreactor scale of 10–50 mg. To generate the 1000-fold larger samples required, a large scale gas handling facility with online mass spectroscopy has been developed, Figure 12 (21) together with a range of cells for the different pressure and temperature regimes that are encountered, Figure 13. Figure 11(c) shows the C–H stretch region after six hours methanation (21, 22), the similarity to the commercial system is evident. This approach provides a tractable method to study a very complex process.

In Figure 4 it was shown that hydrous palladium oxide, PdO\(_2\)H\(_2\)O, has a core of nanocrystalline PdO. This leaves the role of water unresolved. Figure 14(a) compares the INS spectra of high density amorphous ice (Figure 14(a), line A) with PdO\(_2\)H\(_2\)O (Figure 14(a), line B) (7). The similarity of the spectra suggests that the water is present as a disordered shell on the PdO nanoparticle. However, there is an additional peak at \(~1000\) cm\(^{-1}\) that is more apparent after drying at 373 K under vacuum (Figure 14(a), line C). This is assigned to a Pd–O–H deformation mode (the corresponding O–H stretch can be seen with a different spectrometer) and indicates a layer of hydroxyls at the surface. This system was modelled with periodic density functional theory as a two layer slab of PdO capped with hydroxyls and a layer of water, Figure 14(b). It can be seen that the INS spectrum generated from this model (Figure 14(a), line D) shows reasonable agreement with the experimental data (Figure 14(a), line C), although it does not capture the disorder in the water layer. The structure that emerges from the combined diffraction, spectroscopy and modelling

Fig. 11. (a) INS spectra of an iron-based Fischer-Tropsch catalyst taken from an operating plant. The sample was Soxhlet extracted in toluene for 24 hours to remove hydrocarbon product; (b) same sample as (a) showing equal numbers of aliphatic and aromatic C–H bonds; (c) a model iron-based Fischer-Tropsch catalyst, A before and B after six hours methanation (21, 22). Reproduced from (20) and (21) with permission of Wiley-VCH Verlag GmbH & Co and the Institute of Physics, respectively
Fig. 12. A photograph of the gas handling apparatus (blue panel), that is housed within a walk-in fume cupboard. The furnace is located to the left hand side of the gas panel and is mounted on a heavy-duty lab-jack. A cell is in the furnace, which is connected to the gas panel by heated lines that terminate in high-temperature valves, which may be used to isolate the cell. The reaction may be followed by online mass spectrometry using the Hiden RGA on the trolley at the left of the picture. Toxic gas (H₂ or CO) monitors (black boxes on the walls on the extreme left and right of the picture) are integral to automatic safety shutdown safeguards. A more complete description is given elsewhere (21).

Fig. 13. INS cell designed to carry out high-temperature and high-pressure (600°C, 20 bar) reactions. The cell body is made of Inconel™. Similar designs are used for less severe operation: 316 stainless steel (300°C, 5 bar), aluminium (100°C, 1 bar) and TiZr (100°C, 1 bar). The background scattering from the cell decreases in the order given. TiZr is not suitable for use with hydrogen due to rapid embrittlement above ~50°C (21).
study is that hydrous palladium oxide is not Pd(OH)$_2$ but that it is best described as ~18 Å diameter particles of nanocrystalline PdO with a monolayer or so of hydroxyls capped by 4–7 layers of water. Transmission electron microscopy (TEM) shows that the very small nanocrystallites are agglomerated into larger clusters which reduces the effective surface area.

It was pointed out that Pearlman’s catalyst is commonly formulated as palladium(II) hydroxide supported on carbon, Pd(OH)$_2$/C. This is a versatile reagent that is effective for hydrogenation, hydrogenolysis and C–C coupling reactions. In view of the results for hydrous palladium oxide, there was a strong suspicion that the commonly accepted formulation of Pearlman’s catalyst was incorrect. Knowledge of the state of the palladium is important in trying to understand the mechanism of the reactions since recent work has suggested that the catalyst functions by leaching of palladium into solution.

5 wt% and 20 wt% Pearlman’s catalyst were measured by INS in the as-supplied wet state and after drying in vacuum (23). In the wet state, only water was visible. Vacuum drying removed most of the water and allowed the spectral features to be observed. Figure 15 compares the INS spectra of the dried catalysts after subtraction of the spectrum of the bare carbon with that of dried hydrous palladium oxide. The similarity is obvious: TEM showed lattice spacings typical of PdO hence Pearlman’s catalyst is better described as carbon supported hydrous palladium oxide. Interestingly, the TEM and X-ray photoelectron spectroscopy (XPS) study showed a minor fraction, ca. 13–17%, of nearly metallic palladium. Since Pearlman’s catalyst is generally used in non-aqueous environments this species may simply be a spectator species in the C–C coupling reactions that are a major use of the catalyst. This supports work that showed that Pd/C is a much less effective catalyst for C–C coupling reactions than Pearlman’s catalyst.
How to Access Neutron Scattering Techniques

Neutron scattering facilities occur across the globe, Figure 16, (24) but the pre-eminent facilities are: ISIS in the UK (25), the Institut Laue Langevin (ILL) in France (26), the Spallation Neutron Source (SNS) in the USA (27) and J-PARC in Japan (28). All of these, and most of the smaller centres, operate a system of “free at the point at use”. Generally, beamtime is awarded via a competitive proposal system with application dates in the spring and autumn. If time is awarded, then the user is responsible for travel, subsistence and the preparation of samples but there is no charge for the actual beamtime. (Depending on the nationality of the user, the facility may partially or wholly cover these costs). This access mechanism requires that the work is made publicly available, generally by publication. The facilities also allow beamtime to be purchased and the work is then subject to a confidentiality agreement.

A proposal generally consists of a two page science case plus experimental requirements and safety considerations. For new or inexperienced users, it is essential to discuss the proposal with an established user or the instrument scientist to avoid failure of the experiment. This is especially the case for catalysis experiments. The requirements include:

- Sufficient sample quantity (g not mg are generally needed)
- A large number of active sites (the minimum for current inelastic instruments is 1 mol% of hydrogen in the beam)
- At least one of the surface species must be hydrogenous.

Even for experienced users, the first experiment at the start of a new project is often unsuccessful. In this case, the problem may be that the physical characteristics are different on the gram scale (for example, different space velocities or plugging). However, the experienced user learns from the problem and subsequent experiments are generally successful.

Fig. 16. The location of neutron scattering centres in 2015, coloured by continent. Reproduced from (24) with permission of Neutronsources.org

Future Prospects

It will be obvious that most of this review concerns inelastic scattering. Partly this reflects the bias and interests of the authors but it is also a reflection of the current landscape. Inelastic scattering is more widely used even though it is less sensitive than elastic scattering. This arises because the energy analysis methods all involve rejecting most of the neutrons in either the incident or scattered beam. QENS studies are routinely carried out at varying temperatures to yield activation energies as well as diffusion constants and insight into the diffusion mechanism (Fickian, jump or immobile). To date most INS studies have used a ‘react and quench’ approach (14, 17–22) to provide a snapshot along the reaction coordinate. This is largely because of the need to measure spectra at low temperature (<50 K) to obtain the best results. However, recent work (29) has shown that in favourable cases it is possible to obtain time resolved results at ambient temperature or above. The time resolution is very modest (10s of minutes) but this will improve as the instruments’ sensitivities improve.

Elastic scattering by contrast has been massively underused in studies of catalysts. The technique is well-suited to operando measurements: realistic temperatures and pressures are accessible, the penetrating nature of neutrons means that there is a wide choice of materials for cell design, time resolution of minutes or better is available and hydrogenous reactants and products give strong signals. An example where neutron diffraction studies are potentially very useful, would be to follow the evolution of an iron-based Fischer-Tropsch catalyst from the hematite pre-catalyst
to the working catalyst which includes other iron oxides, iron carbides, metallic iron and carbon, under *operando* conditions. Neutrons are sensitive to the light elements as well as the heavy ones, Figure 1, so phase identification should be more certain. Although it has not been discussed here, small angle neutron scattering (SANS) covers the size range typical of supported catalysts and the pores in microporous materials. Real time study of pore filling is clearly feasible.

Neutron scattering is a flux limited technique and there is a continual push to improve sensitivity by increasing the detector coverage, increasing the incident flux by better neutron transport from source to sample and by building more powerful facilities. The latest facilities, SNS (27) and J-PARC (28), are nearly a factor of 10 brighter than the previous generation. The European Spallation Source (ESS, (30)) under construction in Sweden will offer at least another factor of 10.

The other way that more information will be extracted from the data is via better modelling. Throughout this paper the link with atomistic modelling has been demonstrated; neutrons are particularly strong here because neutron observables are readily calculable as a result of the simple interaction between the neutron and the sample. Neutrons and modelling are a synergistic couple; the neutron data is an exacting test of the model and the modelling allows deeper insight into the process. QENS and MD simulations such as shown in Figure 8 are a good illustration of the synergy.

**Conclusions**

Neutron scattering is a very versatile tool that is underused for studies of catalysts. While it is applicable to most elements it has a particular focus on light elements, especially hydrogen. Thus it is highly complementary to synchrotron studies with X-rays that excel for the heavier elements. Neutron scattering provides observables that are readily calculable, thus modelling and neutron scattering are a natural partnership. This review has highlighted the detailed information that can be extracted from QENS and INS studies. Elastic neutron scattering has much to offer catalysis, particularly in the areas of *operando* studies of catalyst activation and deactivation, pore filling of micro- and mesoporous materials and the location of hydrogen or hydroxyls in materials. Neutrons are a resource that are much simpler to access than is generally believed, new users with interesting problems are always welcome!

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This book represents the latest magnum opus in a line of multi-author books on process tomography, with the first dating from 20 years ago. Following in the tradition of Beck and Williams (1) this book presents a comprehensive overview of process relevant tomographic modalities, reconstruction techniques and industrial applications. The editor Professor Mi Wang has done an excellent job in obtaining contributions from many leaders in the field.

The technical scope and application of process tomography has grown enormously since the landmark Beck and Williams book (1) from a technology of significant potential to one of substantial impact. While it may be true that medical tomography is notably leading, the challenges of applying tomographic approaches at meaningful scale for the process industries and the complications of using it on manufacturing plant or even offshore, all within the tighter cost constraints of the manufacturing industry are steadily being overcome. There are now a number of companies that specialise in supplying the equipment or services into the process industries. Geir Anton Johansen (Bergen University College, Norway) for example highlights three different commercially available gamma tomography-based offerings. Equally there are competitive offerings for electrical resistance and capacitance tomography, purpose-developed for process tomography. Process tomography is no longer a pet research area and a research tool, but rather it is now becoming an important measurement approach for industry. This book is therefore timely, coming at a time when industrial activity is markedly increasing and while the pace of academic progress is being maintained.

Modalities

The book is broken down into three sections: modalities, image reconstruction and applications. The section on modalities is meticulous, including well established and exploited routes such as soft field electrical capacitance and impedance (including resistance) tomographies and hard field X-ray and gamma ray techniques (Figure 1) as well as electromagnetic induction, magnetic resonance and radioisotope methods. Attention is also given to
Applications

The final section of the book presents eleven chapters on different applications in process tomography. They vary a little in their thrust and aspect according to their titles. Some are quite specific in terms of modality and subject of interrogation: for example a chapter each on X-rays and electrical capacitance tomography for gas-solid fluidised beds. Others are particular only in the application but wide ranging in the modalities used: general chapters on tomography for bubble columns and trickle bed reactors, reaction engineering (mixing processes) and microreactors. The final category of chapter is the general industry sector summaries: tomography in mineral transportation, oil and gas industry (two chapters, the first of which actually focuses on oil field and well imaging, and explains the otherwise incongruous inclusion of the earlier chapter on sensor networks), food inspection and the nuclear industry. There is also a stand-alone chapter on tomographic velocimetry; which seems somehow out of place dealing as it does with the basic principles of the methods and may better have been included in the opening section. Some of the chapters are however slightly more restrictive in their subject matter than their titles may suggest. The report on food inspection actually considers only X-ray based systems.

While it is easy to be critical of the unevenness of this final section it should not be seen to detract from the overall impact; the collation provides a wide-ranging review of the application of various tomographic modalities to a number of different measurement problems and operations relevant across the process industries such as flows, filtering, mixing, drying processes and chemical reactions inside vessels and pipelines. The editor has assembled a broad cross-section of applied process tomography written by leading practitioners.

Summary

In conclusion this compilation presents a broad coverage of tomographic techniques that can be applied to process measurements. The method sections feature a diverse range of modalities and provide in depth analysis of their respective techniques, equipment and data processing. There is detailed study of some aspects of image reconstruction and an extensive investigation of process tomography in

Fig. 1. The Tracerco Discovery™ tool for sub-sea pipe inspection by gamma-ray tomography (Image courtesy of Tracerco)
applications. The new book thus offers an up to date compendium that will be invaluable to those involved in process tomography research and those looking to utilise tomographic methods for process measurement either as a research tool or for industrial application.

Reference

The Reviewer
E. Hugh Stitt is a Scientific Consultant at Johnson Matthey Technology Centre, Billingham, UK. He is a Visiting Professor at the University of Birmingham, UK, and at Queen’s University Belfast, Fellow of the Institution of Chemical Engineers and a Fellow of the Royal Academy of Engineering. He has 25 years of industrial research experience across a variety of themes related to catalytic reaction engineering and catalysts with over 100 refereed publications.
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The aim of this book “Ball Milling towards Green Synthesis” is to highlight the importance of ball milling as a potential route to produce organic materials. The book was published by the Royal Society of Chemistry and edited by Brindaban Ranu and Achim Stolle. In this book, applications, projects, advantages and challenges related to ball milling for specific organic syntheses are reviewed. In principle the book should interest researchers working in general mechanochemistry: however in this reviewer’s opinion most of the chapters are aimed more at the organic chemist. The book is very well structured for researchers focused on organic synthesis, allowing them to go directly to a specific subject. Also, the book has a very formulaic structure; every chapter systematically describes specific organic syntheses, with experimental procedures, yields and advantages of using ball milling over other techniques. Each chapter describes the ball milling conditions in detail, including specifications of different milling equipment (Figure 1), which may be of interest for general research on the technique. The main reactions described in this book are related to the following processes: carbon–carbon and carbon–heteroatom bond formation, oxidation-reduction, organocatalytic reactions, dehydrogenative coupling, synthesis of peptides and polymeric materials. One key point of the book is that it highlights how ball milling can be used not just for particle size reduction applications but for creating chemical reactions since the energy induced by the mechanical treatment is high enough to induce transformations. In all chapters the authors point out that mechanochemical reactions lead to economic advantages over existing technologies providing the same products.

The content of this book is arranged in ten chapters, which are based on different organic chemistries. Each chapter is divided into several sections related to specific organic syntheses or reactions. All chapters show how successfully the technique can be used to obtain specific organic products, and information is provided about experimental procedures and yields as well as a comparison with conventional routes such as solution chemistry, microwave and ultrasound methods.

Bond-forming Processes
Chapter 1, ‘Carbon-Heteroatom Bond Forming Reactions and Heterocycle Synthesis under Ball
Milling’ by Brindaban C. Ranu, Tanmay Chatterjee and Nirmalya Mukherjee (Indian Association for the Cultivation of Science, India) covers carbon–heteroatom (C–N, C–O, C–S, C–Cl, C–Br) bond formation and synthesis of heterocycles under ball milling. The authors show examples of the quantitative formation of different organic materials of commercial interest such as imines, azines, hydroquinone and hydrazine. It is pointed out that chemical reactions with fullerenes in solution are difficult to perform. Ball milling gives the opportunity to carry out the synthesis in the solid state. It was found that this method provides better results than performing the reaction in solution.

Chapter 2, ‘Carbon–Carbon Bond Forming by Ball Milling’ by Katharina Jacob, Robert Schmidt and Achim Stolle (Friedrich-Schiller University Jena, Germany), shows how carbon–carbon bonds can be formed by ball milling to produce compounds such as diphenylacetylene or biphenyl derivatives, which are used in medicine, drug design and electronics. The advantages of this method over conventional routes such as microwave or ultrasound-assisted synthetic routes are highlighted. Shorter reaction times and previously unknown molecular transformations have been reported. Reactions between carbon electrophiles and organometallic nucleophiles, known as cross-coupling reactions, were carried out in different high energy mills, with different milling times, media size and media materials, giving increased selectivity compared to solution based techniques.

**Solvent-Free Synthesis**

Chapter 3, ‘Oxidation and Reduction by Solid Oxidants and Reducing Agents using Ball-Milling’ by Giancarlo Cravotto and Emanuela Calcio Gaudino (University of Turin, Italy) deals with several oxidation and reduction reactions in the solid state by application of ball milling, generally under solvent-free conditions. Again the authors emphasise the efficiency and scalability of the ball milling process as well as the absence of solvents and the low energy consumption. The different examples shown in this chapter confirm that technical parameters such as volume, size of the reactor, material and number of milling balls have a clear effect on the final product. Vibration or revolutions, speed and milling time also needed to be optimised in order to improve yields.

Chapter 4, ‘Asymmetric Organocatalytic Reactions under Ball Milling’ by Elizabeth Machuca and Eusebio Juaristi (Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico) highlights some advantages of the application such as the ability to carry out reactions in the absence of solvent, with an immediate reduction in costs and handling procedures. A very interesting finding is that by-products and potentially toxic wastes are frequently reduced. The shorter heating time, implying energy savings, is once again highlighted, as well as the frequent observation of reduced reaction times.

Chapter 5, ‘Cross Dehydrogenative Coupling Reactions by Ball Milling’ by Jingbo Yu, Zhijiang Jiang and Weike Su (Zhejiang University of Technology, China) confirms how ball milling can promote cross dehydrogenative coupling (CDC) and asymmetric CDC reactions. This method efficiently provides C–C bonds directly from C–H bonds.

**Protection and Synthesis**

In Chapters 6, 7, 8 and 9 the authors demonstrated that different processes such as amino acid derivation or protection, peptide synthesis, polymers and cellulose processing could greatly benefit from mechanochemical synthesis. According to the authors it is expected that further studies with ball milling on these areas will lead to significant advances.
Chapter 7, ‘Ball-milling Mechanochemical Synthesis of Coordination Bonds: Discrete Units, Polymers and Porous Materials’ by Tomislav Friščič (McGill University, Canada) discusses the importance of the in situ analysis of mechanochemical reactions. It is well known that this has been largely limited to temperature and pressure measurements on mechanically induced self-sustaining reactions or monitoring pressure changes in reactions adsorbing or releasing gas, but some progress has been made by the use of penetrating synchrotron X-ray radiation studies.

Technical Implications

Chapter 10, ‘Technical Implications of Organic Synthesis in Ball Mills’ by Achim Stolle explains that ball mills are characterised by different parameters, regardless of the type of process. This information is of value not just for organic synthesis but for general applications. The author lists a large number of influencing variables including chemical parameters, technological parameters such as the milling media and process parameters such as temperature or pressure. The chemical parameters include all those variables that are directly related to the chemical reactions taking place in the mill.

Summary

In general the book is a summary of the preparation of several organic materials by ball milling. The book would be a very good reference for scientists focused on organic synthesis who are interested in reducing costs and increasing the efficiency of existing reaction processes. Using different examples, the book highlights how mechanochemistry can replace conventional processes for the preparation of organics and green materials for various applications. This book is not a basic text about ball milling or organic synthesis; it is aimed at people with experience in either organic synthesis or ball milling. Several examples confirm that technical parameters such as volume, size of the reactor, material and number of milling balls have a clear effect on the final product. All this is in line with our findings in the field of dry milling for inorganic materials synthesis. An important point described in this book is related to in situ analysis. Due to mechanical forces and equipment configuration, in situ analysis has been largely limited and milling reactions have been mainly followed by temperature and pressure measurements on mechanically induced self-sustaining reactions or by monitoring pressure changes in reactions adsorbing or releasing gas. Some progress on highly penetrating synchrotron X-ray radiation is reported. Overall the book is a positive review about ball milling for organic materials development.

The Reviewer

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Introduction

“Hierarchical Nanostructures for Energy Devices” is part of the Royal Society of Chemistry Nanoscience & Nanotechnology Series. The editors Seung Hwan Ko and Costas P. Grigoropoulos have published more than 60 articles together with a strong focus on laser processing of nanomaterials and hierarchical surface coatings.

This book highlights the advantages of hierarchical arrangements for energy conversion, and particular attention is paid to nanowire-based materials and their manufacturing techniques. Inspiration is found in nature, where hierarchical structures are present whenever energy transfer processes have to be optimised. Divided into 13 chapters, the book shows relevant applications as well as physical fundamentals and the unique characteristics of nanostructured materials.

Developing and commercialising sustainable energy conversion systems are among the major issues of today’s society. In the past decade, research associated with energy devices has concentrated on developing new materials for these applications. As progress has become sluggish, there is a stronger focus on the three-dimensional arrangement of nanostructures.

Hierarchical nanostructure designs in various applications are introduced, together with their advantages compared to zero-dimensional (0D), one-dimensional (1D) or two-dimensional (2D) nanostructures. Typical improvements are the increased surface-to-volume ratio and diffusion optimisation for chemical species. In general, hierarchical structures strongly increase the efficiency of many physical and chemical devices.

Chapters 1 and 2 introduce the topic with fundamental considerations and the physics of nanomaterials. Chapter 3, ‘Nanotechnology’s Wonder Material’ describes carbon nanotubes and their growth process. Chapters 4 to 11 are each dedicated to one application of hierarchical structures: solar cells, fuel cells, thermoelectric devices, piezoelectric energy harvesting, photoelectrochemical cells (PEC), supercapacitors, field electron emission devices and sensors. Chapter 12 shows other applications like hierarchical adhesives, superhydrophobic surfaces and metal nanowire percolation networks. The final chapter summarises the book and gives an outlook on the great potential of hierarchical designs in future applications.
This review focuses on the applications of hierarchical nanostructures rather than the fundamentals of nanotechnology and quantum effects, which however should always be considered when developing nanomaterials. Figure 1 shows the change in melting temperature of gold nanoparticles compared to bulk material, exemplary for changing properties of nanostructures.

![Graph showing melting temperature as a function of gold particle size](image)

**Fig. 1.** The graph shows the melting temperature as a function of the gold particle size. The melting point strongly decreases when the particle size falls below 5 nm (Reprinted with permission from (1). Copyright (1976) by the American Physical Society)

### Solar Cells

Chapter 4, ‘Hierarchical Nanostructures for Solar Cells’ examines dye-sensitised solar cells (DSSC, Grätzel cell). Solar cells are typically divided into three generations. The first generation is the widely used crystalline silicon solar cell (mono- or multi-crystalline), which account for more than 90% of the worldwide market. Thin-film solar cells are referred to as the second generation; their market share is around 8%.

A third generation of solar cells is currently on the rise due to its low manufacturing costs and higher flexibility compared to conventional silicon solar cells, namely DSSC or organic photovoltaic (OPV). These solar cells usually involve a platinum catalyst at the counter electrode to utilise a redox reaction, where the yield can be improved by nanostructures (2). The anode is typically made from titanium dioxide (TiO₂) or zinc oxide (ZnO), both of which are wide band-gap semiconductors. The electrons emerging from the reaction of the photosensitive dye with sunlight are transferred into the conduction band of the semiconductor. By using hierarchical TiO₂ or ZnO nanostructures (Figure 2) on the anode, the performance can be boosted: higher carrier mobility (nanowire structures lead to less recombination), large surface area to adsorb more dye molecules and capture more sunlight (compare the principle of a tree) and light scattering layers to efficiently capture more sunlight by multiple scattering.

### Fuel Cells

In November 2014, Toyota presented the world’s first commercially available fuel cell car at the Los Angeles Auto show (4). Fuel cells are seen as one of the most promising future technologies to replace combustion engines due to their much higher efficiency. Besides transportation, fuel cells can also be used in combined heat and power (CHP) or power-to-gas systems to convert and store energy efficiently.

Chapter 5, ‘Hierarchical Nanostructures for Fuel Cells and Fuel Reforming’, explains the two most common types of fuel cells: polymer electrolyte membrane fuel cells (PEMFC) and solid oxide fuel cells (SOFC). The main advantages of SOFC are their high conversion efficiency and direct conversion of hydrocarbons instead of hydrogen. Furthermore, these systems do not require expensive precious metals on the electrodes. SOFC are mainly used for stationary power generation due to their high operating temperature and the related lengthy heat-up process.

PEMFC is mostly used for automotive applications due to its low operating temperature. These fuel cells usually use hydrogen (anode reaction) and oxygen from air (cathode reaction) to run the system, Equation (i):

$$H₂ + 0.5O₂ → H₂O$$  \(i\)

Another approach is to directly convert alcohols, which leads to potentially higher efficiencies and increased energy densities compared to hydrogen fuel cells. The conversion of a primary fuel into H₂ can be avoided. These types of fuel cells are a sub-category of PEMFC and are usually referred to as direct alcohol fuel cell (DAFC); typically the fuel is methanol or ethanol. However, the complete dissociation from ethanol to CO₂ remains challenging. The complete reaction of methanol to CO₂ is shown in Equation (ii):

$$CH₃OH + H₂O → CO₂ + 6H^+ + 6e^-$$  \(ii\)

In simple terms, the efficiency of fuel cells can be improved by increasing the catalytic activity of the
Fig. 2. Scanning electron microscopy pictures of the ZnO nanowire hierarchical nanostructures for DSSC: (a) vertically aligned nanowire carpet; (b) short branched nano weeping willow tree; (c) long branched nano weeping willow tree; (d) pseudo-coloured SEM picture of the long branched nano weeping willow tree. Magenta coloured nanowire represents backbone nanowire after first growth and purple coloured nanowires represent branch nanowires after second growth; (e) current-voltage curve of DSSC made from the long branched nano weeping willow trees of ZnO nanowires (© IOP Publishing. Reproduced with permission. All rights reserved)
electrodes. Hierarchical structures strongly increase the active surface area and hence the number of catalytically active sites. They also enhance the diffusion of the fuel to the electrode site and raise the mass activity since only the top layer consists of the catalytically active material (core-shell principle).

**Thermoelectric Materials and Devices**

Chapter 6, ‘Thermoelectric Materials and Devices’, introduces the materials, their applications and explains the benefits of nanostructures in thermoelectric devices.

Thermoelectric devices convert thermal energy into electrical energy and vice versa. The effect is based on differences in the Fermi levels at the point of contact of two metals or semiconductors. The Fermi level is a measure of the affinity of the electrons to leave a material: the electrons flow from the material with a higher Fermi level to the material with the lower Fermi level. When a temperature gradient between the two materials creates an electrical potential, it is referred to as the Seebeck effect. The reverse effect, where an electrical potential is applied to create a temperature difference, is called the Peltier effect.

Practical applications are found in power generation, energy harvesting, cooling and heating. Typical materials used in thermoelectric devices are bismuth telluride (Bi₂Te₃), lead telluride (PbTe) and silicon-germanium (SiGe). All these materials are semiconductor alloys, which were found to be more efficient than insulators or metals. The ideal thermoelectric material has a high electrical and a low thermal conductivity.

Besides the pioneering work from the US National Aeronautics and Space Administration (NASA) in the 1950s to power their spacecraft with thermoelectric energy, the biggest commercial success to date is the thermoelectric refrigerator. These are mainly used in small solid state devices in order to cool down the hot spots in a central processing unit (CPU).

The possibility of generating energy from waste heat is another hot topic and is often referred to as energy harvesting. However, the low energy conversion efficiency, which is typically in the range 3% to 10%, is often too low for the required energy.

Nanostructures are being widely investigated to increase the conversion efficiency. The mean free pathway of an electron is in the range of 10 nm, whereas a phonon has a mean free pathway of around 100 nm. When using structures smaller than 100 nm the thermal conductivity is reduced but the electrical conductivity is unaffected thus leading to a more efficient thermoelectric device (5).

**Piezoelectric Energy Harvesting**

Chapter 7, ‘Piezoelectric Energy Harvesting Nanofibers’ reports key accomplishments in nanofibre generators composed of polyvinylidene fluoride (PVDF) and lead zirconate titanate (PZT). In the last few years, autonomous piezoelectric power generators have gained much attention due to the miniaturisation of electrical devices and medical implants. Independence from a space consuming battery and eliminating the need to recharge or replace these systems are the main driving forces in developing energy harvesting solutions with piezo materials.

Research is devoted to three different kinds of piezoelectric nanogenerators: film-based, nanowire-based and nanofibre-based. Film-based piezoelectric materials, for example aluminium nitride (AlN) or PZT (6, 7) are commonly applied by thin-film deposition or spin-on methods. Nanowire-based piezoelectric materials are typically made of semiconductors like ZnO, zinc sulphide (ZnS), gallium nitride (GaN) or cadmium sulphide (CdS). By coupling their semiconducting and piezoelectric properties, mechanical strains are directly converted into electrical energy.

Ceramic PZT and polymeric PVDF are the two most promising materials in making piezoelectric nanofibres. The key manufacturing techniques to produce these nanofibres are either near-field or far-field electrospinning. PZT is known for its exceptional piezoelectric properties; however the manufacturing process via electrospinning requires solvents, which lower the density and the overall power efficiency. PVDF has lower piezoelectric performance, but has the advantages compared to PZT of flexibility, biocompatibility, fibre length and weight. High-temperature annealing is also not required for PVDF.

Piezoelectric energy harvesting is still in the early stages of research due to its limited power output. Success will depend on low energy systems and advanced microelectronic technologies. Recent studies with multiple layers of nanofibres have the potential to produce enough energy to drive miniaturised electrical devices. New approaches, using real mechanical actuation sources like the human heartbeat also show promising results for practical uses. Another interesting approach is the support of energy storage systems.
like batteries, where an energy harvester could potentially enhance the overall lifetime of, for example implantable devices. A possible breakthrough in nanofibres is predicted by the chapter’s author in the field of wearable electronics (smart watches, displays), where these devices are directly powered by human motions.

**Photoelectrochemical Cells**

Chapter 8, ‘Hierarchical Nanostructures for Photo-Electro-Chemical Cells’ is closely related to the previous chapter on solar cells. The most famous PEC is the aforementioned Grätzel cell (DSSC). Besides photovoltaics, PEC are often used for hydrogen generation by splitting of water.

In the beginning of the chapter the importance of hierarchical arrangements for catalysis and photogenerated electrons is emphasised. The cell efficiency was enhanced by a factor of 4 to 5 through hierarchical structures compared to non-hierarchical nanowire structures. Hierarchical structures enable higher light harvesting as well as a longer effective path for photons to be absorbed by improving scattering and trapping. It strongly increases the chemical reactions and the diffusion of species to the electrode sites. Another important fact is that hierarchical structures are usually constructed by hybridising two or more different materials. For example, the integration of a material with different band structures can increase the range of photon absorption. In terms of catalysis, different materials can trigger different reactions at the same potential and, for example, avoid electrode poisoning.

In the following sub-chapters several fabrication strategies for hierarchical structures are introduced. The chapter finishes with theoretical considerations and examples of hierarchical structures for PEC applications.

**Supercapacitors**

Chapter 9, ‘Hierarchical Nanostructures: Application to Supercapacitors’ considers two types of supercapacitors (sometimes referred to as ultracapacitors, **Figure 3**): electrical double-layer capacitors (EDLC) and pseudocapacitors, and the different nanomaterials for supercapacitor electrodes such as activated carbon and carbon-based nanomaterials like carbon nanotubes and graphene. Supercapacitors are electrochemical capacitors that bridge the gap between electrolytic capacitors and batteries. The power density of supercapacitors is significantly higher than that of lithium-ion batteries and the time needed to charge such a device is much shorter. Supercapacitors also allow a large amount of charge and discharge cycles. The main disadvantage, however, is the much lower energy density in supercapacitors.

Supercapacitors usually complement a primary energy source like fuel cells, batteries or combustion engines. Typical applications are power harvesting from regenerative braking systems, power back-up, providing burst power for heavy operations and voltage stabilisation in start/stop systems of automotive vehicles.

Hierarchical nanostructures increase the energy that can be stored by a supercapacitor per geometrical surface area. The hierarchical designs enable these devices to be more compact and efficient.

**Sensors**

Chapter 11, ‘Sensors’ introduces three types of sensors: gas sensors, biosensors and optical surface enhanced Raman spectroscopy (SERS) sensors, where hierarchical designs play an important role. Sensors are analytical components that convert physical or chemical input signals into appropriate
electronic output signals. In order to increase sensor performance and obtain high surface-to-volume ratios, nanostructures are widely used in chemical sensor applications. Limitations of nanostructures are found in the lower nanometre scale due to degradation and aggregation effects of the structures.

Hierarchical designs increase the surface-to-volume ratio without decreasing the size of the nanostructures. Additionally diffusion and mass transport of chemical species to the surface are improved. This leads to higher sensitivity, better resolution and faster response times of sensor elements. Figure 4 shows a picture of hierarchical platinum nanostructures, which are applied to increase sensitivity and selectivity of non-enzymatic glucose sensors.

Conclusions

The book gives a great introduction into important energy conversion technologies, where the efficiency is increased by using hierarchical nanostructures. Most of the inventions are related to improved electrochemical reactivity, but other areas like piezo and energy harvesting technology are also investigated. In pacemakers or neurostimulators applications, hierarchical (or fractal) structures to increase the energy transfer have been state-of-the-art for more than ten years and the ideas behind this have spread to many other technology areas. The book is ideal for people working in catalysis and/or energy related fields and want to find inspiration for new developments.

References


“Hierarchical Nanostructures for Energy Devices”
Patrick Daubinger works for Johnson Matthey Medical Components in technical sales and business development. He obtained his Masters degree from the University of Freiburg, Germany, in 2013, where he was conducting research on hierarchical platinum nanostructures for biosensor applications. His work on hierarchical nanostructures resulted in various publications and he holds a patent in this field.

Johnson Matthey Piezo Products

Johnson Matthey Piezo Products, based in Germany, has been developing, producing and selling piezoelectric ceramics, components, atomizers and piezo modules for more than 45 years. Piezos can be combined with electronics and mechanics and tailored in accordance with customers’ individual requirements for various applications world-wide. The products are used in industry, in textile machines, in automobiles, in medical and other applications.

Johnson Matthey is a globally leading supplier of bending actuators.

The Piezo Bending Actuator, Sensor and Energy Harvester: Working Principles

When two piezoelectric ceramic plates are bonded together with a supporting material and counter-actuated, this results in a pronounced deformation of the composite similar to the case of a bimetal. Its design enables deflections of several millimetres. Forces up to several Newton and a short cycle time of a few milliseconds can be achieved. Therefore, the piezo bending actuator can be employed as a high performance and fast-reacting control element.

Piezo ceramic benders can also be used as sensors. Bending generates a charge or voltage on both ceramic layers. Connecting both ceramic layers in parallel results in adding their charges together. Thus they are suitable for measuring both large and small movements, vibrations and accelerations and for energy harvesting.

Johnson Matthey’s piezo benders usually have a working life of more than a billion cycles.

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In the Lab

Synchrotron Radiation Based Solid Phase Characterisation of Industrial Catalysts and Materials

Johnson Matthey Technology Review features new laboratory research

Tim Hyde is a Principal Scientist in the Advanced Characterisation Department at the Johnson Matthey Technology Centre, Sonning Common, UK. His research interests focus on the development of synchrotron radiation-based characterisation using in particular X-ray absorption spectroscopy (XAS) on a range of applications in environmental catalysis, process technologies and battery research. He has co-authored over 50 papers and four patents.

About the Research

Beginning in the 1960s and 1970s, the advantages of using synchrotron radiation for spectroscopy and diffraction were realised by an ever-growing scientific community. While the original accelerators were built for particle physics applications, their relevance to materials science, biology and medicine soon became apparent. Synchrotron light has since become an ideal tool for many types of research including numerous industrially related applications. Some of the experimental techniques utilised at synchrotron beamlines include: pair distribution function (PDF) structural analysis of crystalline and amorphous materials; macromolecular X-ray crystallography; small angle X-ray scattering; XAS; tomography; imaging and photoemission spectroscopy.

One specific characterisation technique utilised by Johnson Matthey is XAS. This technique consists of various data regions, among which X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) are the most useful in obtaining chemical information. XANES is sensitive to the oxidation state, local coordination geometry and the nature of ligands present in the first coordination sphere, while EXAFS provides information about the radial distribution of localised atoms surrounding a central absorbing atom of interest. By analysing these oscillations, the local structural environment of a specific absorbing atom can be revealed without hindrance from other atoms present and is irrespective of the chemical complexity of the system. Since EXAFS requires a tuneable X-ray source, data are

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always collected at synchrotron beamlines such as Diamond Light Source, Harwell, UK, or the European Synchrotron Radiation Facility (ESRF), at Grenoble, France, that are specially optimised for the purpose. Benefits of the XAS technique include:

(a) atom specificity since each element has an unique absorption edge;
(b) does not depend on long-range structural order, so that any liquid or solid material can be investigated; and
(c) does not depend on concentration of the absorbing element, so even concentrations at ppm levels can be studied.

Hence XAS has proven an ideal technique to provide structural insight into catalytic systems and materials of technological relevance to Johnson Matthey. Applications in areas such as environmental catalysis, supported bimetallics and in situ systems have been studied and are now discussed.

Given recent emerging concerns about the bioavailability and toxicity of anthropogenic platinum compounds emitted into the environment from sources including vehicle emission catalysts (VEC), the solid phase platinum species present in a variety of unused (fresh) and used (road aged) gasoline three-way catalysts (TWC) and light and heavy duty diesel VECs were investigated. The localised Pt environments present in catalysts from both North American and European origins were explored by Pt L2- and L3-edge XAS. EXAFS studies at these edges revealed the presence of mainly oxidic species in the fresh catalysts while metallic and bimetallic components were found to be the dominant species in the respective road aged catalysts. Importantly, supporting Cl K-edge X-ray absorption spectroscopy confirmed the absence of chlorine associated with platinum. Hence from these studies the presence of environmentally significant quantities of chloroplatinate species in VECs could be discounted.

In another study, the location and quantification of Cr$^{6+}$ and Cr$^{3+}$ in Cr-doped Fe$_2$O$_3$ high temperature shift (HTS) catalysts were determined by ex situ XAS and laboratory XPS. Levels of Cr$^{6+}$ were found to increase on samples heated to 400°C. At 500°C the material crystallised to form haematite, and concomitantly the Cr$^{6+}$ became unstable and reduced to Cr$^{3+}$. XPS indicated that the residual Cr$^{5+}$ after 500°C calcination was located at the surface and was probably formed from reoxidation of Cr$^{3+}$ during cooling to room temperature. Specific Cr K-edge XANES pre-edge features and EXAFS Cr-O bond lengths confirmed and quantified both octahedral Cr$^{3+}$ and tetrahedral Cr$^{6+}$ in the 500°C calcined material.

Bimetallic palladium-mercury alloys are formed at elevated temperatures of 204°C as Hg is adsorbed during coal gasification over supported Pd-based sorbents. Different adsorption capacities were proposed on alumina and silica supports as significant differences were found in the nature of the alloy formed following Hg exposure on the respective sorbents. By EXAFS analysis, on exposure of the supported Pd sorbents to Hg-containing fuel gas the Pd/Al$_2$O$_3$ sorbent produced a single homogeneous solid solution of Pd–Hg. The Pd/SiO$_2$ produced an alloy of varying composition with particles containing predominantly a Pd core and an Hg–Pd alloy at the periphery of the particle. This was explained as due to lower dispersion of Pd on the SiO$_2$ support and subsequently restricted Hg diffusion through the particle.

High synchrotron beam intensities allow for time- and temperature-resolved in situ studies, where characterisation techniques can often be combined to provide additional insight under industrially relevant reaction conditions. The formation of nano-sized zinc oxide from zinc peroxide was followed through the ZnO$_2$ decomposition temperature range of 180–250°C by in situ XAS and X-ray diffraction (XRD) techniques and the structure and nature of the PdO-Pd transformation supported on alumina was followed from ambient to 900°C and subsequent cooling using in situ XAS and PDF techniques. The phase compositions of the Pd components were established at various temperatures by quantitative analysis of the PDF data. Above 850ºC it was found that PdO had converted to metallic Pd, with the extent of reduction of the order ca. 70% Pd metal and ca. 30% PdO. Complementary in situ XANES and EXAFS experiments supported and quantified the observations that residual PdO was detected at elevated temperatures. Hysteresis in the transformation upon cooling was confirmed from XAS studies where reoxidation occurred below 680ºC (Figure 1).

Through such non-proprietary studies, Johnson Matthey has now established expertise in synchrotron radiation-based structural methodologies. This is being implemented over a diverse range of systems from fundamental characterisation studies of materials to characterisation-based innovation of proprietary catalysts.
Selected Publications


Johnson Mathey Highlights

A selection of recent publications by Johnson Matthey R&D staff and collaborators

EMISSION CONTROL TECHNOLOGIES

Understanding the Gas Transport in Porous Catalyst Layers by Using Digital Reconstruction Techniques

Internal transport limitations are studied in supported porous catalytic layers to understand their effect on the performance of a catalytic reactor, specifically an automotive catalytic converter. The results are considered generally applicable. 3D digital reconstruction and complex mathematical modelling were applied and case studies are presented to illustrate their use in optimising transport properties in a porous supported catalyst.

Incorporation of Square-planar Pd$^{2+}$ in Fluorite CeO$_2$: Hydrothermal Preparation, Local Structure, Redox Properties and Stability

Low-temperature hydrothermal synthesis was used to prepare a number of nanocrystalline Pd-substituted ceria-type fluorites of the form Ce$_{1-x}$Pd$_x$O$_{2-δ}$ (0.05 ≤ x ≤ 0.15). Efforts to attain a higher value of Pd substitution results in PdO being formed as a secondary phase. X-ray absorption near edge structure revealed that Ce and Pd were in the +4 and +2 oxidation states respectively, therefore proposing oxide deficiency as the mechanism of charge balance. Pd$^{2+}$ has local square-planar coordination which was confirmed by the extended X-ray absorption fine structure (EXAFS) analysis at the Pd K-edge. A structural model, consistent with earlier modelling investigations, can be fitted in which the mean fluorite structure was kept but with Pd$^{2+}$ sitting in the square faces of oxide ions available in the local cubic geometry of Ce. Pd is well dispersed in the nanocrystalline ceria particles as shown by TEM analysis and in situ powder XRD indicated that upon heating in air the samples continue to be stable up to 800°C.

Heavy Duty Emission Control System Analysis and Optimization for Future Demands


This paper, presented at SAE 2015 World Congress & Exhibition, reviews emission control systems for heavy duty diesel (HDD) applications to meet post-EuroVI/US10 legislation. It focuses on systems containing SCR and covers the optimisation of the system for both fuel consumption and catalyst efficiency. Pros and cons are considered and it is concluded that all current legislative requirements may be met using optimised SCR containing systems.

Thermal Decomposition of Bulk and Supported Barium Nitrate

The decomposition of anhydrous bulk barium nitrate to produce O$_2$ and NO plus small quantities of NO$_2$, N$_2$ and N$_2$O was found to take place principally at 630°C. Lower temperature decomposition took place after dispersing on Al$_2$O$_3$ and TiO$_2$. This procedure also increased the complexity of the decomposition products as well as causing increased N$_2$O production due to reaction of adsorbed gases on the supports.
FINE CHEMICALS: CATALYSIS AND CHIRAL TECHNOLOGIES


An anion templated Grubbs’ II-catalysed RCM clipping mechanical bond forming process was used to synthesise a mixed halogen- and hydrogen-bonding hetero-[2]catenane. The interlocked catenane host was able to bind and sense anions, and form strong associations with acetate and dihydrogen phosphate as shown by 1H NMR spectroscopy and fluorescence titration experiments.

NEW BUSINESSES: BATTERY TECHNOLOGIES

Transforming Anatase TiO2 Nanorods into Ultrafine Nanoparticles for Advanced Electrochemical Performance


Although the smaller diffusion pathways for ions and electrons are frequently the main reason for nanostructuring lithium-ion active materials, there are also other, less-expected phenomena happening when leaving the microscale to go into the nanoscale. The authors investigate one of these phenomena – the thermally induced fragmentation (i.e. ‘chopping’) of oleic acid-capped anatase TiO2 nanorods perpendicular to the [001] direction. As a result of the fragmentation, ultrafine TiO2 nanoparticles with improved (001) facets are formed. These ultrafine nanoparticles have a fantastic rate performance and cycling stability, even for cathodic cut-off potentials as low as 0.1 V, due to the altered surface facets ratio and the beneficial utilisation of carboxymethyl cellulose as binder.

NEW BUSINESSES: FUEL CELLS

Properties of the Hydrogen Oxidation Reaction on Pt/C Catalysts at Optimised High Mass Transport Conditions and its Relevance to the Anode Reaction in PEFCs and Cathode Reactions in Electrolysers


A model is developed for use in simulation studies of fuel cell and electrolyser systems using Pt/C catalyst with ultra-low loadings (0.84–3.5 μgPt cm⁻², Johnson Matthey’s HiSPEC 9100). The dependence of the hydrogen reaction on pH and H₂ concentration may be understood using this model. Using a high mass transport floating electrode technique allowed features of the HOR and HER to be elucidated for the first time. Fine structure has been resolved in the H₂ adsorption region and the features correlated to functions of the H₂ and H⁺ concentration, anion concentration, potential scan limit and temperature.

PRECIOUS METAL PRODUCTS

A Density Functional Study of Oxygen Vacancy Formation on α-Fe₂O₃(0001) Surface and the Effect of Supported Au Nanoparticles

S. W. Hoh, L. Thomas, G. Jones and D. J. Willock, Res. Chem. Intermed., 2015, 41, (12), 9587

The PBE + U calculations of Au nanoparticles supported on the α-Fe₂O₃(0001) surface were investigated and the authors found that the periphery atoms of Au₉ particles became oxidised via the dissociation of O₂ at the metal-oxide interface. The metal particle was shown to significantly decrease the defect formation energy for surface oxygen vacancies in the oxide support especially when the nanoparticle is in a semi-oxidised state. The defect formation energy depends on the distance of the vacancy from the metal particle so the smallest defect formation energies are calculated for oxygen vacancies formed under the Au nanoparticle. For Au₁₀/α-Fe₂O₃(0001) forming the vacancy under the cluster involves a defect formation energy of 2.13 eV (relative to ½O₂(g)) and this falls to 0.86 eV when the perimeter of the particle is oxidised. These values are substantially less than that for the bare α-Fe₂O₃(0001) of 3.04 eV.

PROCESS TECHNOLOGIES

NiO/CaAl₂O₄ as Active Oxygen Carrier for Low Temperature Chemical Looping Applications

J. A. Medrano, H. P. Hamers, G. Williams, M. van Sint Annaland and F. Gallucci, Appl. Energy, 2015, 158, 86

A commercial Ni-based catalyst has been tested for chemical looping to capture CO₂ more efficiently from chemical processes at low temperature. Its behaviour at low temperature has been investigated and it was found to require pre-treatment at higher reduction temperature as an activation step. The oxygen carrying capacity is thereby increased, improving reactivity. Redox kinetics were found to be adequate for low temperature applications up to 200 cycles. The kinetic rates for gas-phase and gas-solid reactions are also available to use for prediction of performance in such applications.

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


Air jet milling, planetary ball milling and single ball milling were employed to investigate the effects of stress modes on particle size reduction in γ-alumina, a frequently used catalyst support. The size reduction achieved was...
greatest for air jet milling, from a $d_{90}$ of 37 $\mu$m to 2.9 $\mu$m. Single ball milling produced a size reduction to 10.5 $\mu$m. The planetary ball milling procedure gave the least size reduction to 30.2 $\mu$m and also caused phase transition to unwanted $\alpha$-alumina. The shear rates are known to be higher in planetary ball milling compared to other types of milling, and this is thought to account for the differences.

A Kinetic Analysis Methodology to Elucidate the Roles of Metal, Support and Solvent for the Hydrogenation of 4-phenyl-2-butanone over Pt/TiO$_2$


The choice of solvent affects the rate and selectivity (ketone vs. aromatic ring) of the hydrogenation of 4-phenyl-2-butanone over a Pt/TiO$_2$ catalyst. A crucial kinetic model for this multi-phase reaction, taking into account statistical analysis, has been proposed. A 2-site model was found to be the most suitable, illustrating aromatic hydrogenation (over a Pt site) and ketone hydrogenation (at the Pt/TiO$_2$ interface). The selected solvent has little effect on the ketone hydrogenation rate constant, however it strongly influences aromatic hydrogenation due to solvent-catalyst interaction. Reaction selectivity was also corresponded to a fitted product adsorption constant parameter. The role of solvents in affecting reactant adsorption and reaction selectivity was shown by the kinetic analysis method.

Characterising the Rheology of Non-Newtonian Fluids using PFG-NMR and Cumulant Analysis


A new method to rheometry using pulsed field gradient (PFG) NMR which increases the application of MR rheometry to single-axis gradient hardware was proposed by the present authors. In this study the use of flow propagators was difficult due to the introduction of artefacts during Fourier transform which occur when realistic sampling procedures are limited by experimental and hardware constraints and especially when specific spatial and temporal resolution are needed. In this paper, the authors outline a process involving the cumulant analysis of the acquisition data directly, therefore, avoiding the introduction of artefacts and shortening data acquisition times. A model-dependent method was developed taking into account the pipe-flow characterisation of fluids showing non-Newtonian power-law rheology, which includes using an analytic expression illustrating the flow propagator in terms of the flow behaviour index. This process was found to be resilient to the signal-to-noise ratio (SNR). The simulated results were validated by an experimental investigation on shear-thinning aqueous xanthan gum solutions where the rheology could be correctly characterised using a power-law model across the experimental shear rate range of 1–100 s$^{-1}$. The calculated flow behaviour indices were found to be within 8% of those acquired using spatially-resolved velocity imaging and within 5% of conventional rheometry.
Towards 3D-Electrical Capacitance Tomography for Interface Detection

Thresholding method improves accuracy for real-world 3D process monitoring

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The application of three-dimensional electrical capacitance tomography (3D-ECT) for the in situ monitoring of a hard boundary or interface has been investigated using imaged phantoms that simulate real-life processes. A cylinder-in-tube phantom manufactured from polyethylene (PE), a low di-electric and non-conductive material, was imaged using the linear back projection (LBP) algorithm with the larger tube immersed at varying intervals to test the ability of the technique to image interfaces axially through the sensor. The interface between PE and air is clearly imaged and correlates to the known tube penetration within the sensor. The cylinder phantom is imaged in the centre of the sensor; however, the reduction in measurement density towards the centre of the ECT sensor results in reduced accuracy. A thresholding method, previously applied to binary systems to improve the imaged accuracy of a hard boundary between two separate phases, has been applied to the 3D-ECT tomograms that represent the PE phantom. This approach has been shown to improve the accuracy of the acquired image of a cylinder of air within a non-conductive PE tube.

1 Introduction

The ability to accurately and quickly monitor the evolution of physical and chemical changes within products during manufacturing has been the subject of much interest in both academic and industrial research communities. Enhanced process monitoring allows an engineer to implement better control thereby increasing efficiency, improving material and energy usage and increasing product quality. Electrical tomography has been developed over the last few decades with the purpose of delivering real time, in situ measurements of phase distributions within a process vessel or pipe. It provides spatially resolved information on the distribution of material properties (permittivity, conductivity, density) within a cross-sectional plane through the sensing zone represented by a pixel grid known as a tomogram. In the majority of cases to date two-dimensional (2D) images have been sufficient to provide the required process information for the user;
however, 3D tomography provides spatial information in both radial and axial planes yielding greater process insight. The compromise when applying 3D methods as opposed to 2D is increased computing time, greater complexity of hardware and requirement for advanced reconstruction algorithms.

Electrical tomography is categorised as a ‘soft-field’ method. The distribution of the electric field within the sensor is unknown thus forming a non-linear relationship between the measured capacitances at the boundary of the sensor and the material distribution within the sensor. ECT is a specific form of electrical tomography applicable to systems with a non-conductive continuum and an insulating process vessel wall. It utilises a concentric ring of uniformly spaced electrodes fixed to the outside of a non-conductive vessel wall. The signal-to-noise ratio (SNR) of the system is dependent upon the area of each electrode therefore studies have been conducted that determine the optimal size of ECT electrodes (1). Guard electrodes are also required to prevent process materials outside the sensing zone having an effect upon the electric field distribution (2). The number of electrodes used within the sensor ring is a compromise between the required size of electrode to deliver the required SNR, the diameter of the electrode array (directly related to the diameter of the process vessel) and the desired reconstructed image accuracy, with a greater number of electrodes delivering increased spatial resolution. There are two critical parameters when designing an ECT sensor: the ratio of permittivity of continuous and dispersed phases and the thickness of the sensor liner (3). When either of these phases has a high relative permittivity there is an increased electrical flux deflection at the boundary of the ECT sensor that results in the relationship between material permittivity and measured capacitance becoming non-linear, typically at relative permittivity values \( \varepsilon_{\text{mat}} > 15 \). To image these materials a new sensor was developed that applies internal rather than external electrodes to measure the boundary inter-electrode capacitance. This system has been used to image an air/de-mineralised water phantom and a water continuous oil-in-water dispersion designed to mimic process equipment in the oil industry such as separators and extraction units (3). Whilst the configuration of the sensor solves the boundary linearity problem, it removes the non-intrusive advantage that traditional ECT has over competing methods. In the majority of the process industries it is unlikely that a pipe or unit will be taken offline for electrode fitting, and indeed due to the hazardous nature of the chemicals used any potential for containment risk is unacceptable. Liquid hold up within a gas/liquid packed bed has been investigated using twin-plane ECT for application within chemical reactors. Initial measurements using single plane ECT were conducted to determine liquid drainage dynamics and determine their relationship with the gas velocity and packing particle size. Extensive calibrations were performed using twin plane ECT so as to accurately map bed hydrodynamics across the dual sensing zones and the use of tracer led residence time distribution (RTD) combined with ECT analysis to obtain hydrodynamic performance data was also investigated (4).

Image refinement of 2D tomograms of high dielectric materials using commercially available ECT equipment has previously been addressed by the present authors (5, 6). The focus of that study was to vary the threshold value and optimise the image based upon image error as a function of the threshold. Two known methods for determining image error were compared: pixel-by-pixel (PbP) (Equation (i)) and areal (Equations (ii) and (iii)):

\[
e_{\text{PbP}} = \frac{100}{N} \sum_{i=1}^{N} \left( \frac{|\mu_{\text{image}} - \mu_{\text{real}}|}{\mu_{\text{real}}} \right)
\]

where \( e_{\text{PbP}} \) is the error using the PbP approach, \( N \) is the total number of pixels, \( \mu_{\text{image}} \) is the imaged pixel value of pixel \( i \) in the tomogram and \( \mu_{\text{real}} \) is the theoretical pixel value of pixel \( i \) in the real system. The areal analysis is given as two stages; the first calculates the area of the image occupied by the phantom:

\[
A_{\text{image}} = A_{C} \frac{\sum \mu_{\text{image}}}{N} |\mu_{\text{image}}|_{\text{c}}
\]

where \( A_{\text{image}} \) is the area of the image and \( A_{C} \) is the cross-sectional area of the circular sensor chamber. The second stage calculates the error as a ratio of the difference between the areas of the imaged and real object to the area of the real object:

\[
e_{A} = \frac{|A_{\text{image}} - A_{\text{phantom}}|}{A_{\text{phantom}}}
\]

where \( e_{A} \) is the image error calculated using the areal approach and \( A_{\text{phantom}} \) is the area of the phantom. These two methods were compared to determine the sensitivity of image error to threshold value. The
important conclusions were: (a) the optimal threshold values calculated using each method are consistent, demonstrating robustness; and (b) the calculated image error using the areal approach is much lower as it is not constrained to the pixel resolution. A similar study was conducted with the aim of defining ‘limited region tomography’ (7, 8). This is a method based upon defining a region to which the reconstruction is applied using a narrowband pass filter. The accuracy of the image is increased by limiting the image area, thereby reducing the number of unknown pixels and enhancing the resolution. This approach has so far been applied predominantly for detection of deposits and scaling in pipes, although the potential applications stretch to any purpose whereby imaging of the whole tomographic plane is not essential. However, this method is currently not a commercially available technology.

The definitions of 3D and ‘pseudo-3D’ tomography are confusing and often misapplied in the existing literature on this subject. Until recently there was a lack of precision hardware and capable software that could obtain full 3D-ECT data, that is to say acquire and reconstruct electrode measurements in the axial, radial and angular dimensions (assuming cylindrical coordinates). Prior to suitable commercial equipment being available, 2D tomograms were stacked to obtain ‘pseudo-3D’ images of a process. The term ‘pseudo’ is used as there are no electrode measurements across the axial plane (9).

An electrical capacitance volume tomography (ECVT) approach has been used to monitor the hydrodynamics of the drying of wet granules with the purpose of being used in the pharmaceutical industry. From the 3D data gained the granule moisture content and drying medium velocity were calculated (10).

The majority of work so far in applied 3D-ECT research has used back-projection approaches for simplicity, however there has been some work done on a volumetric 3D approach using alternative reconstruction algorithms. A neural-network multi-criterion optimisation image reconstruction technique (NN-MOIRT) algorithm has been developed that effectively applies the optimisation approach across a Hopfield neural network (11). The results have been compared favourably with existing reconstruction algorithms such as the iterative filtered back projection technique (IFBPT) and the iterative linear back projection (ILBP) algorithm. The NN-MOIRT algorithm was then applied to a three phase bubble column so as to image multi-phase flows and showed the enhanced accuracy of this method for 3D-ECT applications (12). The same group then used this approach to investigate the dynamics of spiral bubble plume motion in the entrance zone of bubble columns and three-phase fluidised beds (13). The NN-MOIRT approach was again combined with volumetric ECT to investigate a jet of air, issued from a single orifice, within a poppy seed bed of internal diameter 50 mm. The ECVT results were thresholded to yield optimal images and then compared directly with magnetic resonance imaging (MRI) data showing consistency at high air flow rates, although the ECVT was less sensitive than MRI to changes at lower air flow. Standard deviation measurements across the ECVT images gave 7 mm in the radial plane and 8 mm in the axial plane, at least an order of magnitude higher than MRI. From this it may be concluded that significant further improvement is required for ECT to be considered an accurate imaging technique (14).

In another study, moving objects were imaged using 3D-ECT. Images of a rod and a ball were separately moved down the central axis and periphery of the sensor (15). A Gauss-Newton reconstruction algorithm was used, another approach that is not yet commercially available and is largely confined to academia, yielding an image error of approximately 10% although this increased by 2% when the imaged objects were at the sensor periphery. Interestingly, a parallel study was conducted that arrived at the same conclusion in that the image error at the wall was greater than in the centre of sensor. The reasoning for this observation is that the incidence of convergence of electric field lines is greater in the sensor centre than at the periphery leading to greater measurement integrity in the centre (5). An iterative non-linear reconstruction algorithm has also been applied to 3D-ECT measurement data and compared with traditional linear back projection; suffice to say the non-linear algorithm showed significantly improved results (16).

The academic group responsible for the previously mentioned ‘limited region tomography’ (7, 8) also investigated using a novel ECT sensor coupled with a resolution analysis method to determine the sensitivity of image error and resolution to electrode and sensor design (17). This study provides a step change in the protocols used to design 3D-ECT sensors and certainly gives greater impetus to the argument for increased use of this technology in industry.

Given the usefulness of the information gathered, there is potential for 3D-ECT to be integrated into engineering processes (18). However, so far there
have been few works published using a commercial instrument. 2D-ECT has so far been applied to a wide range of engineering processes, however the majority of published work has been carried out on academic instruments in either single or dual plane configuration. Few ECT instruments are commercially available and the capability for 3D image reconstruction amongst these is very low, the main reason being a lack of image accuracy which is problematic for real-world industrial applications. Indeed the implementation of a reconstruction package into a useable graphical user interface (GUI) has only recently been published (19).

The present paper addresses this need by applying commercially available 3D-ECT technology to image a series of mobile phantoms. The phantom used is a simple cylinder-in-tube setup that demonstrates both a moving object and a hard boundary, in this case the interface between polyethylene and air. A methodology, initially developed on 2D-ECT images, that improves image accuracy using optimised binary thresholds is then applied to the 3D-ECT tomograms.

2 Materials and Methods for 3D-ECT Imaging

The objectives of this work were to determine the usefulness of ECT as an online measurement tool for interface detection within a 3D sensing zone and to investigate the capability of a commercially available ECT instrument to deliver 3D images of a transient system including an evolving interface.

2.1 Cylinder-in-Tube Phantom Configuration

In order to show the development of a hard interface in the radial plane moving axially through the sensor a series of phantom experiments were designed. Phantoms are objects of known dimensions that simulate a desired process or system. A triple plane ECT sensor was used comprising a polyether ether ketone (PEEK) cylinder of inner diameter 156 mm with three planes of eight electrodes implanted to the outside of the wall and encased in stainless steel. A cylinder-in-tube PE phantom was used to simulate the interface. The PE tube had diameter 142 mm with an annular core of diameter 30 mm, tube wall thickness 62 mm and length 300 mm. The PE cylinder was 30 mm in diameter and 300 mm long with a flanged base having a diameter of 160 mm. The schematics for these phantoms are given in Figure 1.

The small cylinder (Figure 1(b)) and sensor were raised above the large tube (Figure 1(a)) and imaged at penetration intervals of \( \frac{1}{8} \) of the length of the small cylinder. Once the whole of the large tube had been removed, the sensor was imaging just the small cylinder with a large air gap between the sensor wall.
and the phantom. The $1/8$ penetration intervals were measured and marked onto the polyethylene cylinder shown in Figure 2(b).

Figure 2(a) shows the large tube housed within the PEEK-lined ECT sensor. There is an air gap of 1 mm between the PE large tube and the wall of the sensor. As this is present during the sensor calibration it has no impact on the reconstructed ECT data. The $1/8$ intervals of the length of the small cylinder at which the large tube was imaged are shown in Figure 2(b) as markings on the small cylinder.

2.2 ECT Setup and Configuration

The ECT instrument used for this work was an Industrial Tomography Systems (ITS) m3c 24 input channel unit. Individual electrodes were connected from the sensor to the instrument ports using Bayonet Neill-Concelman (BNC) cables. The first step in processing of electrical tomography data is normalisation of the capacitance data according to Equation (iv):

$$C_n = \frac{C - C_l}{C_h - C_l}$$  \hspace{1cm} (iv)

Where $C_n$ and $C$ are the normalised and measured capacitance values respectively, and $C_h$ and $C_l$ are capacitance values from the high permittivity and low permittivity reference frames respectively. The reference frames are taken prior to measurement and for both experimental series the conditions for these are given in Table I.

The low permittivity reference frame is taken prior to the high permittivity reference frame and once both are acquired process data can be recorded. The phantom experiment was imaged for 30 frames at each of the large tube holding intervals thus building a series of images of penetration depth of the small cylinder.

![Fig. 2. Individual components of cylinder-in-tube phantom: (a) thick-walled PE tube within PEEK-lined ECT sensor; (b) 40 mm diameter PE cylinder with flanged base](image)

<table>
<thead>
<tr>
<th>Experimental series</th>
<th>High permittivity reference frame(^a) material</th>
<th>$\varepsilon_r$</th>
<th>Low permittivity reference frame(^a) material</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phantom</td>
<td>PE</td>
<td>2.2–2.4</td>
<td>Air</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\(^a\) $\varepsilon_r$ = Relative permittivity
A reconstruction algorithm is required to calculate the spatially resolved material data from electrical boundary measurements. In commercial ECT equipment there has previously been just one algorithm available to use: the LBP algorithm. This is a single-step algorithm that requires less computing power due to its simplicity and delivers fast results; however the reconstructed images are inaccurate (5). It assumes a linear relationship between the capacitance and permittivity vectors as given in Equation (v):

\[ g = S^T \lambda \]  

where \( g \) is the normalised permittivity vector, \( \lambda \) is the normalised capacitance vector and \( S^T \) is a linear approximation to the inverse of the sensitivity matrix, \( S \) (20). This equation is solved by discretisation across a pixel grid containing 1024 pixels that is reduced to 812 pixels as the corners are filleted for circular images. Although LBP has several drawbacks, it is the most commonly used method in industry and is therefore used for reconstructing data within this paper.

2.3 3D-ECT Tomogram Image Processing

A true 3D-ECT measurement acquires charge data in both the radial and axial direction for each stimulus, yielding an output of a 3D tomogram composed of 32 × 32 × 32 voxels (corresponding to pixels in 3D space). Each voxel represents a volume portion within the sensor and is assigned a value in the interval between 0 and 1. In order to identify the geometrical shape placed in the sensor, a binary gating method is applied. This method, widely applied in MRI and in 2D-ECT, consists of dividing the tomogram into a number of zones equivalent to the number of phases. In this study one zone represents the volume occupied by the phantom and the second is composed of the surrounding gas phase (5). Once the image has been thresholded it is possible to compare it with a previously built reference to evaluate the image error. The advantage of using phantoms is that their exact geometry is known and therefore a digitalised reference image as basis for comparison for error analysis is accurate and simple to construct.

The data processing methods applied in the refinement of 2D images have been applied also to the 3D-ECT tomogram analysis. The objective of the gating method is to find the optimum threshold value to allow generation of the binary matrix that describes the object with the minimum error. A reference image has been created to allow the comparison between the reconstructed tomograms and the real object, this image is given in Figure 3.

The PbP approach, defined as voxel-by-voxel in 3D tomography, compares the corresponding voxels in the reconstructed and in the theoretical images (Figure 3) and is described by the same equation as PbP analysis (Equation (i)). The areal approach (Equations (ii) and (iii)) is extended to the third dimension by evaluating the volume occupied by the phantom in the image, Equation (vi):

\[ V_{image} = V_C \sum \mu_{image} \frac{1}{N} \mu_{image}^{\text{ref}} \]  

where \( V_{image} \) is the volume of the image and \( V_C \) is the total volume of the sensor chamber. The volumetric error is calculated by evaluating the ratio of the difference between the volumes of the imaged and the real object and the volume of the real object, Equation (vii):

\[ e_{\nu} = \frac{V_{image} - V_{phantom}}{V_{phantom}} \]  

where \( e_{\nu} \) is the image error calculated using the volumetric-areal approach and \( V_{phantom} \) is the volume of the phantom.
3 Results and Discussion

The phantom experiments use PE, with a low relative permittivity, to simulate an interface so the 3D-ECT reconstruction can be trialled using the basic LBP algorithm to ascertain its efficacy before application to high di-electric media. Therefore these experiments are used solely to examine whether 3D-ECT is capable of monitoring an interface.

3.1 3D-ECT Reconstruction using LBP

The ECT three-plane sensor is attached to the flanged base of the small cylinder therefore the phantom is defined as the large tube being inserted into the sensor with the PE/air interface being the top of the PE large tube. The tomograms are shown in Figure 4.

The images displayed in Figure 4 are cross-section tomograms whereby the electrode measurements from the three planes of uniform electrodes are reconstructed and subsequently discretised to give 16 image planes. In pseudo-3D tomography this form of image is strongly discouraged as the lack of axial inter-electrode capacitance data nullifies any assumptions required to use an inter-plane interpolation approach. This is not the case in 3D-ECT as inter-electrode capacitances on different planes have been measured. Figure 4(a) shows the system at full immersion, that is to say the small cylinder is fully immersed.

![Cross-section sliced 3D tomograms of cylinder-in-tube phantom experiment](image)

Fig. 4. Cross-section sliced 3D tomograms of cylinder-in-tube phantom experiment: (a) fully immersed phantom; (b) $\frac{7}{8}$ immersed; (c) $\frac{3}{4}$ immersed; (d) $\frac{5}{8}$ immersed; (e) $\frac{1}{2}$ immersed; (f) $\frac{3}{8}$ immersed; (g) $\frac{1}{4}$ immersed; (h) $\frac{1}{8}$ immersed; (i) fully withdrawn
immersed in the large tube. The colour scheme of these charts indicate low permittivity regions as being blue and high permittivity regions as being red, however the corners of the square pixel grid are included in these reconstructed images and coloured blue. These pixels are present in all the cross-section slice tomograms, however they are not representative of the circular sensor (in 2D-ECT these are typically removed from the image) and are therefore excised from all analyses.  
The large tube is withdrawn from the ECT sensor at intervals of \(\frac{1}{8}\) penetration. It can be seen in Figure 4(b) that a reduction in the mean conductivity across the electrode plane occurs and continues through the other images within Figure 4 as the phantom moves through the sensor. The small cylinder is present inside the cylinder at all times even as the large tube is removed from the sensing zone. The first evidence of the presence of the small cylinder phantom is in Figure 4(e) where a series of voxels in the centre of the top cross-section planes of the 3D image register an increase in the permittivity. Moving from Figure 4(e) to Figure 4(h) it is clear this area of high permittivity spreads down the 3D tomograms in this series. This has to be attributed to the presence of the small cylinder in the centre of the sensor, however the shape of the high permittivity region is not clear which is unsurprising given that the air gap between the cylinder and the sensor wall is 51 mm. The air gap affects the linearity assumption used in the sensitivity matrix. However, it is surprising that the small cylinder is affecting the inter-electrode electric field given the size of this air gap. The images given in Figure 4 have been smoothed to a high degree that gives the impression of soft edges in the process.  
To better represent the interface between low and high permittivity phases iso-surface plots of the same experiment are presented in Figure 5. Iso-surface plots were calculated from volumetric data (given in Figure 4) and represent constant scalar data within a scalar 3D distribution. In the case of the phantom experiments this is represented as the interface between PE and air. Initially, in Figure 5(a), the sensor was at the equivalent of a high permittivity reference frame as the large tube was fully immersed in the sensor. The four rectangular regions at the sensor boundary are image artefacts and enclose the high permittivity region; they are able to be excised from the images but have been retained to give clarity as regards to the phase distribution. As the large PE tube was removed from the sensor the interface was clearly shown to progress down the sensor. Figure 5(d) shows the presence of the small cylinder at the top of the image, indicating that although the large tube was \(\frac{5}{8}\) immersed in the sensor and the small cylinder occupied the centre of the void behind the interface, it was not clearly detected by the sensor. When the large tube reached \(\frac{1}{4}\) immersed (Figure 5(g)) the small tube was imaged as a rounded cone and the interface of the large tube and air was clearly present at the bottom of the sensor. The imaged shape of the small cylinder was consistent from Figure 5(e) to Figure 5(h) and was only imaged as a cylinder once the large tube was fully removed from the sensor in Figure 5(i). This result is symptomatic of a number of limitations of the technique in its current state: the limit of the software to drive a maximum of three planes; the reconstruction algorithm when imaging hard boundaries; and the low permittivity ratio between the two phases (\(\sigma_{air} = 1, \sigma_{PE} = 2.3\)). ECT therefore images the permittivity difference between phases by keeping this difference high and the ability of the instrument to detect a hard boundary theoretically increases.  

3.2 Binary Image Refinement of 3D-ECT Tomograms  
Following on from the evaluation of accuracy of 2D-ECT tomograms, a similar error analysis has been applied to the cylinder-in-tube experiment. The reference image for the voxel-by-voxel analysis was shown in Figure 3. The voxel values are extracted from the tomographic data and processed using MATLAB® (MathWorks® Inc). The voxel-by-voxel error and the volumetric error are calculated for several values in the interval between 0.2 and 0.7 in order to evaluate the optimal value in terms of minimum error.  
As shown in Figure 6 in both cases it is possible to reach very low errors and the optimum threshold value does not change substantially. It is 0.501 according to the voxel-by-voxel analysis (Figure 6(a)) and 0.547 by applying the volumetric analysis (Figure 6(b)). This characteristic is an important sign of the robustness of the reconstruction and leads to the conclusion that the results do not change substantially if the threshold value is fixed for either error analysis methodology. In fact, using the voxel-by-voxel method to compare the errors when choosing the threshold value at the minimum of Figure 6(a) and Figure 6(b), gives values of 0.0306 and 0.0316 respectively. This confirms the strength of the volumetric analysis which unlike the voxel-by-voxel...
Fig. 5. Iso-surface plots of PE cylinder-in-tube phantoms: (a) fully immersed large tube phantom; (b) \( \frac{7}{8} \) immersed; (c) \( \frac{3}{4} \) immersed; (d) \( \frac{5}{8} \) immersed; (e) \( \frac{1}{2} \) immersed; (f) \( \frac{3}{8} \) immersed; (g) \( \frac{1}{4} \) immersed; (h) \( \frac{1}{8} \) immersed; (i) fully withdrawn

Fig. 6. Binary sensitivity to thresholds of 3D-ECT tomograms of polymethyl methacrylate (PMMA) cylinders: (a) voxel-by-voxel error analysis; (b) volumetric analysis
analysis does not need precise geometric information relative to the position of the phantom or objects within the sensor.

In Figure 7 the iso-surface plots display the reconstructed interface between the phantom and the gas phase using the threshold value suggested by the voxel-by-voxel analysis (Figure 7(a)) and the volumetric analysis (Figure 7(b)).

The obtained images from both analyses are very similar with both unable to display a geometric cylindrical shape, a limitation of the spatial resolution provided by single-step reconstruction algorithms. The permittivity difference between the air and PE is approximately two thereby reducing the SNR of the measurement and leading to lower image accuracy. The data post-processing improves the image accuracy as the images in Figure 7 represent the cylindrical phantom more closely than those in Figure 5(i). To reduce image error the two available options with the current ECT instrumentation are to use an alternative reconstruction algorithm or to improve the phase permittivity difference.

4 Conclusions

This paper examines recent innovations in the field of 3D electrical capacitance tomography and the application to 3D-ECT of previously used 2D-ECT post-processing methods that improve tomogram accuracy of imaged geometric phantoms. Firstly, development work of the data processing techniques applied to 2D-ECT was examined and shown to be effective, then using a similar phantom system the 3D-ECT method was used to acquire 3D tomograms and a similar analysis was adopted. It has been shown that commercially available ECT equipment has the capability to image a mobile object and yield information on the location of a hard boundary in 3D space.

The images were optimised using a previously published method whereby the threshold value of the image was optimised by correlation with image error. A voxel-by-voxel approach to calculating image error was compared with a volumetric approach demonstrating the robustness of the latter as it does not require precise geometric information to provide improved tomographic accuracy. The image accuracy of ECT is a function of the spatial resolution that is dependent upon both the software (reconstruction algorithm and data processing) and hardware (electrodes and data acquisition system (DAS)) used in the measurement. When these are improved the quality of the reconstructed images improves thereby making this method more applicable to chemical processes.

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Fig. 7. 3D-ECT iso-surface plots with applied optimal threshold value and dashed lines showing object location: (a) voxel-by-voxel threshold value = 0.501; (b) volumetric threshold value = 0.547
References


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