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Johnson Matthey has a long history and track record of designing and supplying specialist coatings into a wide range of application areas and substrate types. A common theme is the requirement to deposit precise amounts of materials. This is key for expensive platinum group metals and for the resulting coating to provide a function such as catalytic, conductive, protective or optical.

Building Insight

Scientists in Johnson Matthey have built up insight into chemical interactions and speciation at the interfaces of solids, gases and liquids. This knowledge has been used to improve processes, construct new and improved catalysts and surface coatings and enhance manufacturing capability.

Key to the understanding is characterisation of the surfaces and interfaces across the length scales: from nano (atomic) scale, through the micron ranges to macro scales on the mm and cm lengths. On the nanoscale, chemical bonds and molecular interactions are probed via a range of electron optical techniques such as high-resolution transmission electron microscopy (HR-TEM), scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS), all used widely in Johnson Matthey.

Materials of interest come in phases from crystalline through to amorphous and combinations thereof. Having the capability to characterise both using X-ray diffraction (XRD) and solid-state nuclear magnetic resonance (SSNMR) coupled with electron adsorption spectroscopy techniques gives us a full picture of solid state materials in current and future products. Specific areas of study have been, for example, surface or bulk crystallisation in glass phases for Johnson Matthey’s automotive glasses and metal-matrix composite parts, and catalytic transformations both in the gas and liquid phases.

Of particular interest to Johnson Matthey is investigation of catalytic function in real time under reactive gas/liquid environments. Cells that can be inserted into spectrophotometers or used with some of the analytical techniques mentioned above have led the way to in situ data acquisition giving rise to product understanding at the catalytically active sites. This is key to being internationally competitive for activity and selectivity of desired products and ensuring the catalyst minimises byproducts that require removal from the reaction streams, thus driving towards more sustainable products and processes.

A Track Record of Success in Coatings

Some of the earliest coating products in Johnson Matthey came from the Hatton Garden site in London, UK, around the 1920s. These were in the form of inks and pastes to produce decorative precious metal films, mostly involving gold. The inks would contain finely divided or micronised gold powders or soluble gold precursors in organic media comprising natural resins and organic solvents. The inks were applied by screen printing onto ceramic or glass and fired to elevated temperatures to remove the organic fragments and reveal bright lustrous films.

As electron optical techniques became more informative, they allowed the gold film structure and bonding mechanisms onto ceramic or pottery type substrates to begin to be elucidated, giving insight into bonding mechanisms of gold onto metal oxides and allowing improvements to be designed. Surprisingly, from these complex ink mixtures precise gold coating thicknesses could be obtained by a combination of careful control of ink rheology and an intimate knowledge of screen...
printing technology. These early products were the forerunners of today’s specialist surface coatings.

**Latest Research**

The research is continuing today. In this issue further examples can be seen from the contributing authors, namely: *in situ* spectroscopic studies of methanol steam reforming catalysis probing both surface and bulk (1); coating technologies for continuous flow reactors (2); using SSMNR studies to again determine surface and bulk structure of catalytic supports (3); or using molecular probes to determine acid sites in zeolites (4). All of these papers enhance our knowledge of surface properties and advanced coatings technologies to deliver active species where they are most wanted and effective.

Enjoy your read.

**References**

“Surface Treatments for Biological, Chemical and Physical Applications”


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Introduction

“Surface Treatments for Biological, Chemical and Physical Applications” was written to provide an up to date overview of surface modification techniques, with a specific leaning towards applications rather than pure science. The tone of the book strikes a good balance between accessible and technical, and is targeted towards a range of audiences, from undergraduate students to interested individuals. As such, the first three chapters form a basic grounding in surface science and terminology. The later chapters comprise comprehensive reviews of applications of several different surface modification techniques, from chemical separation membranes to biosensors.

The editors, Mehmet Gürsoy and Mustafa Karaman, are both academics in a Chemical Engineering department, though each chapter has a different set of authors from a broad range of disciplines. This is indicative of the applicability and importance of controlled surface modification across several fields. The book is written in good English, and has a well thought out balance of diagrams and text. All diagrams in the book are clear and are related directly to the text.

Surface Science Basics

The first three chapters provide a solid grounding in surface science terminology as well as providing an introduction to the broad range of applicability of controlled surface modification. The first chapter, authored by the editors, is titled ‘Surfaces in Nature’, presenting surface structures of a number of organisms, as well as attempts to mimic such natural surfaces. Biomimicry, the act of copying or mimicking biological systems, is increasingly being used in the design of high-tech surface structures. The authors neatly sum up the motivation for biomimetics by quoting Da Vinci:

“Although human genius through various inventions makes instruments corresponding the same ends, it will never discover an invention more beautiful, nor more ready, nor more economical than does nature, because in her inventions nothing is lacking and nothing is superfluous.” (1).

Having outlined the broad motivation behind biomimetic surfaces, Chapter 1 continues with several examples from literature, under the title ‘Inspiring Natural Surface Structures’. Examples include: self-cleaning, antifouling, fog harvesting,
anti-reflective and adhesive surfaces. In order, these manufactured surfaces were inspired by, or templated from: lotus leaves, shark skin, Namib desert beetles, moth eyes and gecko feet. One interesting observation made by the author is that nature often produces multiple useful functionalities from the same nano- or microstructure, for example gecko foot skin, which exhibits both high adhesion and superhydrophobicity.

The second chapter, ‘Chemical and Physical Modification of Surfaces’, introduces a range of surface modification techniques, starting with vapour deposition processes before moving on to wet coating techniques, which includes electrophating and dip coating. Each different method is accompanied by clear cartoon schematics, with the underlying physical and chemical processes described well. This chapter is especially useful because it highlights the advantages and limitations of a broad range of surface treatment techniques.

The third and final chapter of surface science basics discusses ‘Surface Characterization Techniques’. This, like the previous chapter, takes the form of a list of analytical techniques explained in the context of their usefulness for surface science. That this book is targeted at non-specialists is especially apparent in this chapter, as even routine techniques such as scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy are explained in detail.

Emerging Chemical and Physical Applications

The remaining chapters focus on specific applications of surface modification. The first of these (Chapter 4) is titled ‘Surface Modification of Polymeric Membranes for Various Separation Processes’, authored by Woei-Jye Lau et al. Membranes are here defined as: “a selective barrier between two phases that separate based on the different permeation rates of subjected components”. Such interfaces are ideal opportunities for using surface modification to improve for example filtration efficiency, activity and corrosion resistance. This is, in part, due to the separation processes being controlled primarily by the physical and chemical properties of the top layer (the surface) of a membrane. There are many examples given, covering solid-liquid, liquid-liquid and gas-gas separation processes. One example is summarised in Figure 1. Zhu et al. (2) grafted a zwitterionic polyelectrolyte brush from a

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Fig. 1. (a) Schematic illustration of the preparation of poly(3-(N-2-methacryloxyethyl-N,N-dimethyl) ammonatopropansulfone (PMAPS)-grafted poly(vinylidene fluoride) (PMAPS-g-PVDF) membranes for separating dispersed oil from water; (b) water and oil wettability. Photographs of an oil water droplet (3 ml) dropped onto the original PVDF membrane (A) and PMAPS-g-PVDF membrane (B) and their contact angles. An underwater oil (1,2-dichloroethane) droplet on PMAPS-g-PVDF membrane showing a CA of 158° (C). Reproduced from (2). Copyright The Royal Society of Chemistry
poly(vinylidene fluoride) (PVDF) membrane, with an aim to remove dispersed oil from bulk water. By grafting this brush, they were able to produce a membrane which showed a significantly increased oil filtration, attributed to a high surface energy combined with a low water contact angle.

Chapter 5, authored by Epameinondas Leontidis, reviews the use of Langmuir-Blodgett (LB) films for sensors and in biomedical applications, and then draws comparisons with organic films produced using the layer-by-layer (LbL) method. There is some feeling that LbL methods have supplanted LB-generated films, due, in part, to the ease with which LbL films can be generated. The author outlines the strengths and limitations of both techniques, commenting that they should be considered as complementary rather than as competitors (Figure 2).

Chapter 6, ‘Surface Modification of Biopolymer-Based Nanoforms and Their Biological Applications’, authored by Susana C. M. Fernandes, considers the chemical surface modification of biopolymer-based nanoforms, such as nanocrystalline cellulose and chitin. Cellulose and chitin are the two most abundant biopolymers on earth, with well-known chemistry and the ability to self-assemble into hierarchical structures at several length scales. Unlike other nanomaterials, which can be more dangerous than their larger forms, nancellulose and nanochitin, nanometre crystalline fibrils with diameter ~10 nm, are biodegradable, biocompatible and non-cytotoxic. A selection of different chemical functionalities are discussed, including antimicrobial surfaces and novel composites containing these biomaterials.

Chapter 7 is a relatively short chapter on ‘Enzyme-based Biosensors in Food Industry via Surface Modifications’, authored by Nilay Gazel and Huseyin B. Yildiz. Enzyme-based biosensors, sensors which use enzymes as part of the detection mechanism for probing biological processes, rely on the immobilisation of enzymes onto a variety of substrates. This chapter outlines a few chemical and physical methods to immobilise these highly selective macromolecules onto several different substrates, from metals and polymers to carbon nanotubes.

The final chapter, Chapter 8, considers ‘Heterogeneous Catalysis from the Perspective of Surface Science’. The authors, Aydin Cihanoğlu, Diego Hernán Quiñones-Murillo and Gizem Payer, in keeping with the tone of the book provide a comprehensive grounding in catalysis, as well as...
discussing methods of producing and characterising catalytic surfaces. This chapter is a particularly useful overview of catalyst preparation methods, summarising a large number of procedures and characterisation techniques.

Conclusions

The mix of general introduction and applications-focused literature review helps to achieve the intended broad appeal of the book. This book could be used as an accessible introduction to surface science, but could also be a handy reference for a more experienced researcher, with several practical hints and tips. The quality of the writing does vary from chapter to chapter, as one would expect from a research-focused textbook, occasionally drifting into lists of related papers without much further analysis or commentary. On the whole, however, this is a clear, concise and useful introduction to surface science and would be a good addition to the bookshelf for anyone that would want to use surfaces in some way.

References


About the Reviewer

Alex de Bruin joined Johnson Matthey in January 2017 as a Research Scientist at Johnson Matthey’s Technology Centre, Sonning Common, UK, after completing a PhD in colloid science and nanomaterials at Bristol University, UK. His current research is split between extrusion paste chemistry and fundamentals of washcoat processing, employing a range of surface science techniques to control the rheology of complex fluids.
Historical Review of the Swiss Precious Metals Control Act Focused on Platinoids

In Switzerland, platinum and palladium finenesses have been submitted to federal control respectively since 1914 and 1995

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"Make possible the loyal execution of any honest order"

Numa Droz, Member of Swiss Parliament and Federal Councillor (1877)

Precious metals are subject to great scrutiny from lawmakers because of their financial and strategic importance. Gold and silver coins have been hallmarked since ancient times but the platinum group metals (pgm) were only known from 1748, therefore their hallmarking and fineness control is more recent. This paper reviews the legal history of pgm control in Switzerland where precious metal refiners’ and fine watchmakers’ lobbying impacted Swiss regulations on precious metals trade. Platinum and palladium have been regulated since 1914 and 1995 respectively while the other pgms (rhodium, iridium, osmium and ruthenium) are not.

Introduction

Platinum and palladium trade control and hallmarking in the UK have been discussed in earlier issues of this journal (1–2). In Switzerland, manufacturers, smelters or sellers of silver, gold, platinum and palladium items are subject to the Precious Metals Control Act (3).

Every aspect related to precious metal is evoked in this Act: hallmarking, assaying or refining. A Precious Metals Control Ordinance and an Ordinance on the Fees for Precious Metals Control complete the Act (4–5). The Act has no fiscal dimension: protection against fraud is the main goal of the Precious Metals Control Act and the Ordinance on the Fees governs only stamping fees and determination of fineness fees. Purity is guaranteed by the manufacturer hallmark and fineness is determined by a federal licensed trade assayer working for an Assay Office or a manufacturer. The precious metal control is organised within four federal Assay Offices (Geneva, Chiasso, Bienne and Zürich), one cantonal office (La Chaux-de-Fonds) and the Central Office in Bern where the General Directorate of Customs is located. Except Zürich, all offices are in cantons with horology or precious metal industries (6).

First Federal Laws

Geneva was the first Swiss location to establish legal control over precious metals: an ordinance of 1424 settled the requirements of silverware fineness and hallmarking. From the seventeenth century, an important watchmaking industry developed in Geneva and in the Jura mountains, especially in the district of Neuchâtel where the first law on gold fineness was established in 1754. With the emergence of the Federal State,
horologists started lobbying the Federal Assembly for better control over gold and silver fineness to maintain their commercial reputation (7).

At that time, the Swiss Federal State was a recent construction: the first Constitution was established in 1848 and lawmakers were reluctant to draft federal regulations and preferred to leave precious metal control to cantonal authorities. On 1st July, 1850, a petition of 548 firms, factories or craftsmen of La-Chaux-de-Fonds requesting a federal hallmark was addressed to the National Council. On 16th August, 1850 the Federal Council pleaded to the National Assembly the rejection of such a proposition because it was contrary to trade freedom and every citizen was to feel free to buy lower-quality, better or cheaper watch cases. The petition was ruled out but the industrialists of the Neuchâtel district continued lobbying (7).

A second Federal constitution was drafted in 1874 and the Federal State gained in importance and in influence. The economic situation was difficult for watchmakers: due to American and French concurrence, unscrupulous Swiss producers cheated on gold purity of watch cases causing great harm to the reputation of Swiss watches. The industrialisation of American watch producers made them more competitive and they seriously threatened Swiss horologists (7–8).

In 1876–1877, 2154 watchmakers or subcontractors of Romandy and Bern signed a petition to introduce control measures while their arguments were exposed in a leaflet of 80 pages (Figure 1) (7–8).

The representative of the Neuchâtel district, Numa Droz, successfully proposed a new silver and gold control: in 1880, the first federal law was enacted to assure a defined fineness for watch cases made of silver and gold (9). Article 4 of the rules of procedure mentioned that every object made of gold or silver was required to have the same fineness except external decorative parts made of silver or platinum (8). No other precious metal was mentioned.

In 1886, a second law was enacted regulating silver and gold scraps (10). In the presentation of the law, it was written "one may add platinum, if that substance is used extensively, which is not the case" (11). Indeed, platinum was not widely exploited in 1886 (the global production for the 1881–1885 period was 12,725 kg for an average price of 2000 CHF kg⁻¹ (12)). Within thirty years, the situation evolved. In the 1890s–1900s, reputable jewellers such as the Frenchman Louis Cartier or the American firm Tiffany & Co started to promote platinum-made jewellery (13). Platinum became very fashionable because of its colour and its improved crimping qualities compared to gold. The platinum price overtook the gold price in 1906 because of the wide demand for jewellery which consumed 70% of the global platinum production in 1922 (12).

**Platinum Control**

At the end of 1909, several industrialists petitioned the Federal Council to impose a strict regime of regulations on platinum watch cases. Their request was motivated by the sale of poor alloys supposed to imitate real platinum (14). In 1911, the Swiss Embassy in Paris reported the recent French Finance Law in the Federal Gazette. Hallmarking of platinum became mandatory in France, platinum standard fineness was established at 950‰ and iridium was accounted as platinum (15).

In 1913, the representatives of the jewellery and horology industries petitioned for a strict control of platinum works (16). Quoted to 7000–8000 CHF kg⁻¹, platinum was in competition
with white gold (3000–4000 CHF kg\(^{-1}\)), an alloy of gold (750‰) and cheaper metals such as nickel or palladium (16). The Chambre Suisse de l’Horlogerie was consulted and responded positively to a control on platinum. Consequently, the Federal Council enacted a decree in February 1914 on the optional hallmarking of platinum. The decree was not limited to horology but included all platinum-made items, the minimal fineness had to be 950‰ and the responsibility mark was a chamois head (Figure 2(a)) which was delivered by the assay offices after assaying (17–18).

Table I gives an account of the gold, silver and platinum watch cases hallmarked during the period 1913–1920 (19, 20). The initial decrease of gold and silver hallmarked cases was explained by World War I and the difficulties for the watchmaking industry to obtain raw materials. Platinum prices increased from 5000 CHF kg\(^{-1}\) at the beginning of 1915 to more than 8000 CHF kg\(^{-1}\) a few months later because of the restrictions imposed by belligerents on platinum exports. In spite of those hurdles, the total value of platinum items made in Switzerland amounted to 200,000 CHF in 1915 (20 million CHF and 5.5 million CHF respectively for gold and silver-made objects) (19).

The platinum price continued to soar between 1916–1920 (Table II) (20). In consequence, platinum scrap was included in the dispositions of the Act of 1886. The Federal Council invoked the dramatic platinum price increase over 30 years: from 2000 CHF in 1886, its value reached over 10,000 CHF in 1916 (see Table II).

Table I Number of Gold, Silver and Platinum Watch Cases Hallmarked in Switzerland (1913–1920) (19)

<table>
<thead>
<tr>
<th>Year</th>
<th>Hallmarked watch cases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gold</td>
</tr>
<tr>
<td>1913</td>
<td>815,038</td>
</tr>
<tr>
<td>1914</td>
<td>474,296</td>
</tr>
<tr>
<td>1915</td>
<td>318,982</td>
</tr>
<tr>
<td>1916</td>
<td>688,497</td>
</tr>
<tr>
<td>1917</td>
<td>630,301</td>
</tr>
<tr>
<td>1918</td>
<td>1,010,037</td>
</tr>
<tr>
<td>1919</td>
<td>1,100,746</td>
</tr>
<tr>
<td>1920</td>
<td>1,005,437</td>
</tr>
</tbody>
</table>

Table II Platinum Prices in Switzerland (1916–1920). 1913 Was Added for Comparison (20)

<table>
<thead>
<tr>
<th>Year</th>
<th>Gold price, CHF kg(^{-1})</th>
<th>Silver price, CHF kg(^{-1})</th>
<th>Platinum price, CHF kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1913</td>
<td>3500</td>
<td>96</td>
<td>7500</td>
</tr>
<tr>
<td>1916</td>
<td>3520</td>
<td>118</td>
<td>12,200</td>
</tr>
<tr>
<td>1917</td>
<td>3600</td>
<td>140</td>
<td>21,000</td>
</tr>
<tr>
<td>1918</td>
<td>3640</td>
<td>170</td>
<td>27,000</td>
</tr>
<tr>
<td>1919</td>
<td>4000</td>
<td>213</td>
<td>21,000</td>
</tr>
<tr>
<td>1920</td>
<td>3900</td>
<td>170</td>
<td>16,000</td>
</tr>
</tbody>
</table>

Two other reasons explained the extensive lawmaking during World War I: (a) War-induced rarity of platinum forced the Federal Council to regulate platinum supplies to avoid metal deprivation (21). Platinum watch cases were still very prized and every platinum item (sheet, hook, wire or pin) was collected for the domestic industry (22).

Fig. 2. (a) Chamois head: first Swiss platinum hallmark (1914–1933); (b) Swiss platinum hallmark for foreign products (1917); (c) Ibex goat head: platinum hallmark (1933–1995); (d) Hare head: Swiss platinum hallmark for foreign products (1933); (e) Saint Bernard dog head: single official hallmark for all precious metals and all fineness standards (1995–)
to the Central Powers. France (24), platinum sales were strictly forbidden by the Parisian company Desmoutis, Lemaire & Co, in 1910s, 80% of the Russian platinum was refined the main provider of platinum to Switzerland and manufactured objects in platinum. As France was the gold price and it became less attractive (12). Dentists had widely adopted platinum due to its physicochemical properties (rustproofing, high melting point and favourable stretching coefficient): 40% of US platinum imports were used for dental applications in 1891. After 1906 the platinum price exceeded the gold price and it became less attractive (12).

In Switzerland, fraudsters started to collect out-of-use dentures to extract their platinum frames to sell to the Central Powers, which paid the highest price for war reasons (22). Dentists had widely adopted platinum due to its physicochemical properties (rustproofing, high melting point and favourable stretching coefficient): 40% of US platinum imports were used for dental applications in 1891. After 1906 the platinum price exceeded the gold price and it became less attractive (12).

In 1917, official hallmarking was extended to all manufactured objects in platinum. As France was the main provider of platinum to Switzerland and the first refiner of Russian platinum (in the early 1910s, 80% of the Russian platinum was refined by the Parisian company Desmoutis, Lemaire & Co, France (24)), platinum sales were strictly forbidden to the Central Powers.

To ensure compliance, the Chambre Suisse de l’Horlogerie asked the Federal Council to enact a regulation on hallmarking. On 2nd February, 1917, the first decree was brought into force to hallmark ingots, watch cases, jewellery and tools made of platinum (25).

A second decree on 15th August, 1917 imposed a specific mark on all imported items made of gold, silver and platinum. During the war, foreign companies used to import items into Switzerland and re-export them as Swiss manufactured objects while their fineness was sometimes dubious. Such a specific mark (Figure 2(b)) avoided any mistake between Swiss and foreign platinum-made jewels or watch cases (26).

Precious Metal Control Act of 1933

After the difficulties experienced during WWI, modernisation of the Precious Metal Control Act was proposed in 1925 (22). The draft law considered platinum as a precious metal like gold and silver. The Message of the Federal Council summarised the reasons to enact successive decrees on platinum control. The price of platinum was lower compared to gold when the first Act was drafted in 1880: no control was needed at that time. The platinum price increased because its applications were no longer limited to the electrical and chemical industries but started being used in jewellery. The limited number of platinum fields (Russia) increased the price while the demand for platinum kept growing especially with the development of wristwatches.

The draft law also proposed the possibility to sell platinum alloys with a fineness between 950‰ and 333‰ if it was clearly presented as an alloy with the trademark and the real fineness engraved on the object. The denomination ‘platinum alloy’ was denied to lower fineness objects (22). No fineness tolerance was accorded for watch cases: foreign countries did not accept tolerances and watchmakers did not want confusion between domestic and foreign markets. 950‰ was kept as the standard fineness and any trace of iridium was considered as platinum. The draft law was special in the sense that official fineness control was made compulsory for silverware and goldsmithing.

Further discussions occurred between industrialists and the Federal Council and the final law was drafted in 1931 to be promulgated on 20th June, 1933 and to enter into force on 1st July, 1934 together with an ordinance (27–29). The legislation was softened: official hallmarking was only mandatory for watch cases. Personal hallmarking was imposed on any platinum-made objects (such as jewellery and optics). 950‰ was the only authorised fineness and the letters PT (minimum height 1 mm) had to be inscribed on every platinum-made object to avoid any confusion with white gold (28).

Like older regulations, iridium in platinum was considered as platinum (28). Iridium was used to harden platinum (5–10%) and its separation from platinum was too tedious to be performed. Furthermore, its price was high enough to consider it (unofficially) as a precious metal in the 1910s–1930s. In the early 1920s, the main US producer states (New York, New Jersey and Illinois) had drafted a regulation for platinum-made objects imposing a minimal 925‰ standard fineness which included not only iridium but all platinum group metals. However, palladium was more affordable than platinum (US$78 against US$116.50 in 1923 (12)) and jewellers increased palladium content in their products, raising concerns about cheaper substitution (30).

Plated articles were mentioned in the Act of 1933: they were defined as objects made of silver or ordinary metal with a layer of 8 μm of platinum or...
gold (fineness ≥ 500‰). The fabrication method (mechanical or electrolytic) had to be specified. Imitations (objects made of platinum below the standard legal fineness or plated) may be described as platinised but without fineness or misleading indications (28).

The platinum symbol for export was changed to an ibex goat head (Figure 2(c)) and imported watch cases were marked with a hare head (Figure 2(d)). No fiscal dimension was introduced: every tax related to hallmarking was intended to cover the costs of the Offices for Precious Metals Control. The Precious Metals Control Act of 1933 was intended to be very pragmatic and no significant modification occurred before 1993.

International Conventions

In 1972, seven European countries (nineteen in 2017) adopted a common mark through the Vienna Convention (31). Each object made of silver, gold or platinum marked with the Common Control Mark was allowed for importation into any contracting State without fineness control. Swiss watch cases intended for the British market had previously been systematically controlled by the UK Assay Office and re-exported to Switzerland to receive their mechanism before final exportation to the UK. Such complications were cancelled when both countries applied to the Convention (31). In Switzerland, the Convention entered into force on 27th June, 1975 (32, 33). At that time, only silver, gold and platinum were classified as precious metals (31). A 2001 amendment entered into force in 2010 introduced palladium as a precious metal (32). As late as 2012, 10 participants out of 19 recognised palladium as a precious metal (33). The Convention Secretariat of the Vienna Convention, which supervises the activities relating to the Convention, is located in Geneva, Switzerland (33).

Between 1935 and 2011, Switzerland separately adopted five bilateral conventions (still active) with Austria, France, Italy, Spain and Russia for mutual recognition of official control marks of watch cases or jewellery (34).

Palladium Control

In 1993, an important revision of the Precious Metals Control Act was operated to adapt the law to new international regulations and economic considerations (35). Two years earlier, ISO 9202:1991 (Jewellery – Fineness of Precious Metal Alloys) was drafted and classified palladium as a precious metal. To be consistent with such norm, the Federal Council proposed during the revision of the Precious Metals Control Act to add palladium among the precious metals subjected to Federal Customs Administration control. Two finenesses for palladium were accepted: 500‰ and 950‰ as defined in the ISO 9202:1991 standard and two finenesses for platinum were added: 850‰ and 900‰ (35). Controversies on possible competitions with white gold, platinum or gold were not taken into account (35).

Palladium was mentioned as early as 1918 in a decree on the Fees for Precious Metal Control where it was measured together with gold and silver but was not classified as precious metal (36). Palladium production increased during the second half of the twentieth century: around 1950, the annual global production was estimated to be 6 tonnes against more than 200 tonnes in 2016 (37, 38). In the 1940s–1950s, the mining of palladium-rich nickelous ores motivated Canadian producers like the International Nickel Company to promote palladium in jewellery as an alternative to platinum (38). Consequently, Canada was the first country to classify palladium as a precious metal in 1950 (38).

Palladium supplies are now mainly used by the automotive sector (80% of global palladium production in 2016) and palladium demand for jewellery amounted to less than 7 tonnes in 2016 (37). That demand has been declining: this was very striking in China where the market was nonexistent in 2016 while the demand for palladium jewellery in this country peaked at 38 tonnes in 2005 (37). The hardness and brittleness of palladium together with the ranking of its price between those of silver and gold made it less attractive to jewellers and investors (39).

Iridium was excluded from the new Act and was no longer treated as platinum because new analytical techniques enabled a separate quantification of iridium. Iridium-platinum alloys are still entitled to platinum hallmarking in other jurisdictions: for example iridium-platinum alloys are treated as platinum in France while Canadian regulations entitle iridium or ruthenium-platinum alloy to platinum hallmarking if the total precious metal content is minimum 950‰ (40, 41).

As for platinum, articles made of palladium must show the complete name of the metal or an abbreviation such as ‘Pd’ (‘Pt’ for platinum). The official national hallmark for watch cases sold in Switzerland was changed to a Saint Bernard dog head (Figure 2(e)) (35).
Palladium was the first precious metal to have a precise definition given by the Federal Council:

"With a grey-white colour, palladium belongs chemically to the six precious metal of the platinum-group. It is used today mainly in electrotechnics and petrochemistry. Mixed with low amount of copper or other metals, it acquires remarkable properties (for example inalterability, hardness, brightness). These qualities make palladium interesting for jewel-manufacturing, watches, etc, especially since its price is between silver and gold prices" (35).

The Federal Message of 1993 defined precious metals in the following terms:

"...strongly-resistant metals from the chemical point of view. Their physical properties play also an important role as their aesthetic characteristics. Precious metals are gold, silver and the platinum-group metals, namely platinum, palladium, rhodium, iridium, ruthenium and osmium" (35).

After the revised Act entered into force in 1995, no other precious metal was subjected to legal control in Switzerland although ruthenium and rhodium coating is allowed on precious metals (42). One has to admit that the Federal Act against Unfair Competition of 1986 protects Swiss consumers against any dishonest sale of fake osmium, iridium, ruthenium or rhodium ingots (43). In comparison, the US Code of Federal Regulations Part 23 Guides for the Jewelry, Precious Metals, and Pewter Industries is more precise and imposes strict measures to jewellers:

“(a) It is unfair or deceptive to use the words “platinum,” “iridium,” “palladium,” “ruthenium,” “rhodium,” and “osmium,” or any abbreviation to mark or describe all or part of an industry product if such marking or description misrepresents the product’s true composition. The Platinum Group Metals (PGM) are Platinum, Iridium, Palladium, Ruthenium, Rhodium, and Osmium.

[...]

(c) The following are examples of markings and descriptions that are not considered unfair or deceptive:

(1) The following abbreviations for each of the PGM may be used for quality marks on articles: “Plat.” or “Pt.” for Platinum; “Irid.” or “Ir.” for Iridium; “Pall.” or “Pd.” for Palladium; “Ruth.” or “Ru.” for Ruthenium; “Rhod.” or “Rh.” for Rhodium; and “Osmi.” or “Os.” for Osmium” (44).

Conclusion

Platinum and palladium as well as gold and silver are subject to strict control by the Swiss customs administration. Precious metal control was mainly introduced because of a need to protect consumers when these expensive platinum group metals started to be widely used by jewellers. Switzerland was first influenced by the French hallmarking of platinum after its value surpassed that of gold, while palladium control was achieved to comply with international standards (ISO 9202:1991 and its subsequent revisions). The actual law, originally drafted in the 1930s, was modernised in 1995 but its core remained unchanged, illustrating the early pragmatism of Swiss legislators. The timetable of introduction is summarised in Table III. Self-regulation has been the main method of precious metal control: for example apart from watch cases, precious metals may be certified by a sworn assayer and this person is responsible in front of the federal authorities. This self-compliance is highly regarded by Swiss refiners, contributing to the success of this industry (45).

Although major changes in Swiss precious metal legislation are very unlikely, an extension of hallmarks for the remaining platinum group metals is a hypothesis that cannot be ruled out. As discussed before, laws were issued to protect industrialists and consumers from fraud and unfair competition. If a new precious metal began to gain significant market share, regulations would have to be drafted to maintain trust between sellers, buyers and investors.

Acknowledgements

The Swiss Central Assay Office is gratefully acknowledged for providing historical and technical information.

References

1. Platinum Metal Rev., 1975, 19, (2), 63
3. ‘Federal Act on the Control of the Trade in Precious
Table III Timetable of Platinum Group Metals Control in Switzerland (1880–2017)

<table>
<thead>
<tr>
<th>Year</th>
<th>Fineness and platinum group metal</th>
<th>Hallmarking for platinum group metal made articles (such as jewellery, optics and horology)</th>
<th>Official hallmark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precious Metal Finess Control Act of 23rd December, 1880</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Federal Council Decree of 2nd February, and 16th June, 1917</td>
<td>Platinum (950‰, iridium included)</td>
<td>Official hallmarking mandatory</td>
<td>Mandatory for exported and imported items</td>
</tr>
<tr>
<td>Precious Metal Control Act of 20th June, 1933</td>
<td>Platinum (950‰, iridium included). PT is marked on every article</td>
<td>Responsibility hallmarking mandatory</td>
<td>Mandatory for Swiss or foreign watch cases marketed in Switzerland</td>
</tr>
<tr>
<td>Revision of 1933's Act 1st August, 1995</td>
<td>Platinum (999, 950, 900, 850‰), palladium (999, 950, 500‰). Articles of platinum or palladium must also bear a reference to the type of precious metal used (Pd, Pt). Iridium not included</td>
<td>Responsibility hallmarking mandatory</td>
<td>Mandatory for Swiss or foreign watch cases marketed in Switzerland</td>
</tr>
</tbody>
</table>

Metals and Precious Metal Articles (Precious Metals Control Act, PMCA), SR 941.31, The Federal Council of the Swiss Government, Bern, Switzerland, 20th June, 1933

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Dynamic Nuclear Polarisation Enhanced
Solid-State Nuclear Magnetic Resonance
Studies of Surface Modification of γ-Alumina

Enhanced solid-state NMR technique significantly reduces experiment time
for surface studies

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Dynamic nuclear polarisation (DNP) gives large (>100-fold) signal enhancements in solid-state nuclear magnetic resonance (solid-state NMR) spectra via the transfer of spin polarisation from unpaired electrons from radicals implanted in the sample. This means that the detailed information about local molecular environment available for bulk samples from solid-state NMR spectroscopy can now be obtained for dilute species, such as sites on the surfaces of catalysts and catalyst supports. In this paper we describe a DNP-enhanced solid-state NMR study of the widely used catalyst γ-alumina which is often modified at the surface by the incorporation of alkaline earth oxides in order to control the availability of catalytically active penta-coordinate surface Al sites. DNP-enhanced $^{27}$Al solid-state NMR allows surface sites in γ-alumina to be observed and their $^{27}$Al NMR parameters measured. In addition changes in the availability of different surface sites can be detected after incorporation of barium oxide.

Introduction

Solid-state NMR is a powerful method for studying the molecular structure and dynamics of a broad range of advanced materials. NMR suffers from low sensitivity, because of the small nuclear spin polarisations involved even with high magnetic fields so that long acquisition times or large sample volumes are often required. The problem of sensitivity becomes overwhelming for dilute species, so that measurements of surface sites, molecules at interfaces or isotopes with low natural abundance are often impossible. Fortunately, weak NMR signals can be enhanced by DNP, which involves transfer of electron spin polarisation from radicals implanted in the sample to nearby nuclei (1–4). This process requires the saturation of the electronic Zeeman transitions at microwave frequencies and is most efficient at low temperatures (<100 K).

Until recently DNP has been limited to low magnetic fields because of the lack of high-frequency, high-power microwave sources.
However, developments in the design of extended interaction klystrons (5, 6) and gyrotrons (7) have made DNP spectrometers operating at $^1$H NMR frequencies up to 900 MHz possible. Commercial DNP-enhanced solid-state NMR spectrometers have been available since 2010, leading to an increase in publications as shown in Figure 1 illustrating the emergence of DNP, particularly as a surface science technique. The substantial enhancements (routinely >100-fold) obtained with DNP make NMR studies of dilute species feasible for the first time, enabling a >10,000-fold time saving, making impossible NMR experiments viable and prompting many new NMR applications, for example, to surfaces (8–13).

γ-Alumina is widely used as an industrial catalyst support, chosen because of its high surface area, good thermal stability, favourable pore-size distribution and useful acid/base properties (14). Catalytically active elements doped onto the support bind to several sites with varying coordination environments at the surface. Pre-treatment of the alumina with alkaline earth and rare earth oxides alters the availability of these different sites, allowing control over the catalytic activity (15). For example, BaO and lanthanum oxide are commonly added as stabilisers to the alumina supports used in three-way catalysts for vehicle emission control (16).

Solid-state $^{27}$Al NMR is a powerful technique to characterise the local environment in a wide range of materials, including clays, glasses, zeolites and other microporous systems (17). $^{27}$Al magic-angle spinning (MAS) NMR spectra of transition alumina usually show peaks at approximately 67 ppm and 9 ppm which are assigned to tetrahedrally (AlO$_4^-$) and octahedrally (AlO$_6^-$) coordinated aluminium, respectively. Surface-selective $\{^1$H$\}$-$^{27}$Al cross polarisation (CP) (15, 18–21) has revealed a further signal at about 30 ppm which is assigned to fivefold coordinated aluminium sites (AlO$_5^-$) in the first surface layer.

$^{27}$Al MAS NMR of BaO-modified γ-alumina shows a decrease in the proportion of fivefold co-ordinated aluminium as the amount of doping increases (22), suggesting that doping with BaO blocks access to these reactive sites. However, recent computational studies (23) indicate that only a fraction of the surface aluminium may be observed using $\{^1$H$\}$-$^{27}$Al CPMAS NMR, since CP favours symmetric sites, although the authors did not account for surface reconstruction (24) or for increased motional flexibility at the alumina surface (22). Furthermore, the linewidths of $\{^1$H$\}$-$^{27}$Al CPMAS spectra (15) are not narrower than in direct excitation spectra, as would be the case if CP filtered out the response from asymmetric sites. Hence, the nature of the surface sites of γ-alumina, their modification by other oxides and even the utility of $^{27}$Al MAS NMR for studying them are still a matter for debate.

DNP results in surface selectivity because the polarisation source is a radical or bi-radical dissolved in a solvent which wets the surface of the sample. At low temperatures, the solvent usually forms a glassy matrix, and transfer mechanisms transport the polarisation to nuclei in the sample surface. In this case polarisation transfer from the biradical to surface $^{27}$Al nuclei is achieved by spin diffusion through the dipolar-coupled $^1$H network in the frozen organic solvent followed by $\{^1$H$\}$-$^{27}$Al CP. The selectivity means DNP is expected to be an effective method for the study of surface sites in γ-alumina. However, previous DNP-enhanced $\{^1$H$\}$-$^{27}$Al CPMAS spectra of γ-alumina (21, 25) did not show a significant AlO$_5^-$ peak, possibly owing to hydration of the surface during the sample preparation.

In this paper we describe a new DNP-enhanced $\{^1$H$\}$-$^{27}$Al CPMAS study of γ-alumina and BaO-modified γ-alumina in which a significant AlO$_5^-$ peak is observed for the first time with DNP. Sample preparation (see Supplementary Information (SI) in the online version of this article) was found to be critical for optimising the DNP enhancement. It should also be noted that the current study was carried out at higher magnetic field (14.1 T compared to 9.4 T) to provide improved resolution of $^{27}$Al environments.
and with different DNP polarising agents to previous work.

**Results and Discussion**

**Figure 2** shows the conventional $^{27}$Al MAS spectrum of bulk γ-alumina recorded in just 24 s with a total of 24 scans. The signal to noise ratio is very high as expected for a bulk sample, but only two $^{27}$Al peaks are observed at approximately 70 ppm and 10 ppm, which can be assigned to the AlO$_4$ and AlO$_6$ sites in the γ-alumina structure, respectively.

In order to illustrate the advantages of the method **Figure 3** shows (black) the DNP-enhanced $^1$H-$^{27}$Al CPMAS spectra of γ-alumina wetness impregnated with a solution of the biradical TEKPoi (26) in 1,1,2,2-tetrachloroethane (TCE) as described in the SI. This spectrum shows an extra $^{27}$Al peak at about 30 ppm which can be assigned to the surface AlO$_5$ sites. The lack of significant line broadening with DNP demonstrates that wetting with the radical solution does not have a detrimental effect on the NMR spectrum.

Following convention the DNP-enhanced spectrum (‘microwave on’) is compared to an identical one recorded with the gyrotron turned off (the ‘microwave off’ spectrum) (red), and an enhancement $\varepsilon$ of 36 can be measured for DNP (see SI) for the AlO$_6$ site which equates to a 1300-fold saving in time. The surface selectivity of DNP-enhanced $^1$H-$^{27}$Al CPMAS means the AlO$_5$ site, which is not observed at all in the bulk, is now clearly visible in the spectrum.

The DNP-enhanced $^{27}$Al CPMAS spectrum in **Figure 3** exhibits lines with a characteristic asymmetric lineshape which is evidence of disorder and a distribution of electric field gradients (27). This means that the high-field tail of the asymmetric AlO$_6$ line overlaps with the AlO$_6$ peak and two-dimensional experiments are required to improve the resolution and separate them (28). Since $^{27}$Al is a quadrupolar nucleus with $I = 5/2$, the approach of choice is the cross-polarisation multiple-quantum MAS (CP-MQMAS) experiment (29) which is described in more detail in the SI. The large signal enhancements obtained with DNP make surface-selective two-dimensional CP-MQMAS experiments feasible.

A DNP-enhanced CP-MQMAS spectrum of γ-alumina is shown in **Figure 4(a)**, and the three surface $^{27}$Al peaks are clearly resolved. In MQMAS experiments the two-dimensional lineshapes observed depend on the isotropic chemical shift $\delta_{iso}$ and quadrupolar coupling $C_Q$, as well as the distributions in these parameters arising from disorder. The quadrupolar coupling is determined by the electric field gradient (EFG) which in turn results from the distribution of charges around the observed nucleus.

Czjzek et al. (30, 31) derived the joint distribution $p$ of the principal EFG tensor component $V_{zz} = hC_Q/eQ$ and the asymmetry parameter $\eta$ in the case of a statistical distribution of charges around the observed nucleus, shown in Equation (i):

$$p(V_{zz}, \eta) = \frac{V_{zz}^4}{\sqrt{2\pi\alpha^5}} \left(1 - \frac{\eta^2}{9}\right) \exp \left[ -\frac{V_{zz}^2}{2\alpha^2} \left(1 + \frac{\eta^2}{3}\right) \right]$$ (i)
Fig. 4. DNP-enhanced two-dimensional sheared \(\{1^H\}\)-\(^{27}\)Al CP-MQMAS spectra of: (a) \(\gamma\)-alumina; and (b) BaO-modified \(\gamma\)-alumina. All three \(^{27}\)Al lines are fully resolved in the two-dimensional spectra. There were 100 \(t_1\) increments with 120 co-added scans for each. Heteronuclear decoupling was applied using the swept-frequency two-pulse phase modulation (SW\(f\)-TPPM) sequence with a \(^1\)H radiofrequency (rf) amplitude of 90 kHz during \(t_1\) and \(t_2\). The z-filter delay was 20 \(\mu\)s. The non-selective \(^{27}\)Al coherence transfer pulse after \(t_1\) was 1.5 \(\mu\)s in duration with a rf amplitude of 88.6 kHz, and the selective \(^{27}\)Al pulse before \(t_2\) was 11.5 \(\mu\)s in duration with a rf amplitude of 22.0 kHz. Other parameters were as for Fig. 3, except for: (b) the relaxation delay was 5.1 s. Experimental details are given in the SI.

where the parameter \(\sigma\) is directly proportional to the average value of the quadrupolar product \(P_Q = C_Q(1 + n/3)^{1/2}\) for the joint distribution.

The DNP-enhanced CP-MQMAS spectrum in Figure 4(a) suggests that for the AlO\(_4\) site the distribution in isotropic chemical shift induced by the disorder dominates, since the observed broadening is parallel to the ‘chemical shift axis’ of the two-dimensional spectrum. On the other hand for the AlO\(_6\) site the distribution in the electric field gradient dominates since the observed broadening is along the ‘quadrupolar induced shift axis’ of the two-dimensional spectrum. The interaction between these distributions complicates the interpretation of MQMAS spectra in terms of disorder, so for fitting using the DMFit package (32) a Gaussian distribution of isotropic chemical shift is assumed which is uncorrelated with the Czjzek distribution of \(C_Q\). The fit parameters were an amplitude factor, the isotropic position, the width of the Gaussian chemical shift distribution and the average value of \(P_Q\) from the Czjzek distribution.

Initially, the full DNP-enhanced two-dimensional CP-MQMAS spectrum was fitted, and the chemical shift distribution fixed before fitting the DNP-enhanced MAS spectrum to allow the intensity for each site to be obtained by integrating over the resulting lineshape. It should be noted that given the complicated polarisation transfer mechanisms associated with DNP, \(\{1^H\}\)-\(^{27}\)Al CP and the MQMAS experiment, this spectrum should be thought of as at best semi-quantitative.

Figure 5(a) shows (top) the two-dimensional fit (red) to the spectrum of Figure 4(a) (black), as well as (bottom) the one-dimensional fit (red) to the spectrum of Figure 3 (black). The corresponding fit parameters are given in Table I and these confirm the substantially larger isotropic chemical shift distribution for the AlO\(_4\) site compared to AlO\(_6\). Wischert et al. (23) have demonstrated that \(\{1^H\}\)-\(^{27}\)Al CPMAS is sensitive to strongly hydrated surface sites and that catalytically important Al centres with high quadrupolar couplings are not always observed, and this might also be the case here.
Fig. 5. Fits to data using the DMFit package (32): (a) γ-alumina: (top) two-dimensional fit (red) to the DNP-enhanced $^{1}{H}$-27Al CP-MQMAS spectrum shown in Fig. 4(a) (black), (bottom) one-dimensional fit (red) to the DNP-enhanced $^{1}{H}$-27Al CPMAS spectrum shown in Fig. 3(a) (black); (b) BaO-modified γ-alumina: (top) two-dimensional fit (red) to the DNP-enhanced $^{1}{H}$-27Al CP-MQMAS spectrum of BaO-modified γ-alumina shown in Fig. 4(b) (black), (bottom) one-dimensional fit (red) to the DNP-enhanced $^{1}{H}$-27Al CPMAS spectrum of BaO-modified γ-alumina shown in Fig. 6 (black). Further details of the fitting are described in the text and the resulting parameters are shown in Table I.

Table I Czjzek Model Fitting Parameters for Different 27Al Sites

<table>
<thead>
<tr>
<th>Site</th>
<th>Relative Intensity</th>
<th>$\delta_{iso}$, ppm</th>
<th>$\Delta$, ppm</th>
<th>$&lt;P_Q&gt;$, MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al₂O₃</td>
<td>$\text{AlO}_4$</td>
<td>0.10 ± 0.02</td>
<td>77.5 ± 0.2</td>
<td>16.0 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$\text{AlO}_5$</td>
<td>0.13 ± 0.02</td>
<td>37.2 ± 0.2</td>
<td>6.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$\text{AlO}_6$</td>
<td>0.78 ± 0.02</td>
<td>14.0 ± 0.2</td>
<td>7.2 ± 0.3</td>
</tr>
<tr>
<td>BaO/$\gamma$-Al₂O₃</td>
<td>$\text{AlO}_4$</td>
<td>0.16 ± 0.02</td>
<td>77.4 ± 0.2</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$\text{AlO}_5$</td>
<td>0.08 ± 0.02</td>
<td>34.0 ± 0.2</td>
<td>12.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$\text{AlO}_6$</td>
<td>0.76 ± 0.02</td>
<td>13.7 ± 0.2</td>
<td>7.4 ± 0.3</td>
</tr>
</tbody>
</table>

*a* Errors obtained for each fitting parameters from the DMFit package. Errors quoted are largest obtained for all sites.

*b* Integral over the fitted lineshape. Note that because of the complicated polarisation transfer processes associated with DNP, $^{1}{H}$-27Al CP and MQMAS only the relative intensities within a particular spectrum can be compared.

*c* Isotropic position.
Figure 6 shows a comparison between DNP-enhanced $^1$H-$^{27}$Al CPMAS spectra of (red) BaO-modified and (black) unmodified γ-alumina (from Figure 3) normalised so that the overall spectral intensity is preserved. The AlO$_5$ peak decreases in intensity while the AlO$_4$ peak increases after pretreatment with BaO, as found previously by $^{27}$Al MAS NMR for BaO (33) and by $^1$H-$^{27}$Al CPMAS for SrO (15). This suggests that the reactive surface AlO$_5$ environment provides a preferential nucleation site for Ba (22). Figure 4(b) shows a DNP-enhanced CP-MQMAS spectrum of BaO-modified γ-alumina which is similar in appearance to that for unmodified γ-alumina in Figure 4(a). Figure 5(b) shows (top) the two-dimensional fit (red) to the spectrum of Figure 4(b) (black), as well as (bottom) the one-dimensional fit (red) to the BaO-modified γ-alumina spectrum of Figure 6 (black).

The results of fitting to the Czjzek model are given in Table I, and the similarity between the parameters obtained for the two samples suggests that modification with BaO does not significantly modify the local environment of the Al surface sites. However, the width of the distribution of chemical shifts for the AlO$_5$ site increases with modification by BaO, while $<P_Q>$ decreases. This could indicate that BaO adds preferentially to the most distorted AlO$_5$ sites. In addition to changes in the chemical shift and quadrupolar parameters, the relative intensities confirm that the proportion of AlO$_5$ sites has decreased after surface modification by BaO, while the proportion of AlO$_4$ sites has increased.

Conclusions

DNP-enhanced solid-state NMR is an emerging technology for surface science, capable of enhancing surface NMR signals to achieve greater than 1000-fold savings in experiment time. This enabling technology is applicable to many catalyst materials, where structural information about the surface can be critical to the understanding of chemical processes.

In the example presented here, bulk NMR measurements of undoped and doped alumina showed no change. However, $^1$H-$^{27}$Al CPMAS NMR of alumina is surface-specific and showed that adding BaO reduced the intensity of the AlO$_5$ sites. To reveal more insight about the surface environments, two-dimensional CP-MQMAS experiments were required, but these would require prohibitively long experiment times with conventional NMR. Following a novel sample preparation involving grinding in a glovebox prior to radical impregnation, the DNP enhancement obtained was sufficient for acquisition of the required CP-MQMAS spectra in less than one day with sufficient signal-to-noise for fitting to structural models.

A Czjzek model revealed the chemical shift and quadrupolar coupling distributions of the three surface environments. These showed little difference between pristine γ-alumina and its BaO-modified counterpart with only a reduction in the intensity of the AlO$_5$ signal and a concomitant increase for AlO$_4$. This suggests that upon BaO modification the remaining alumina sites are unperturbed by the presence of BaO. These results can be used to refine DFT models of BaO-modified γ-alumina surfaces, to provide insight for further chemical reactions such as doping of metals, or to aid understanding of metal-support interactions and subsequent catalytic testing.

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Marco Mais obtained his Bachelor’s degree at the University of Cagliari, Italy and his Master’s degree in Physical Chemistry at the University of Pisa, Italy. He is currently studying for a PhD at the University of Nottingham, UK funded by an EPSRC industrial CASE studentship “Dynamic Nuclear Polarisation MAS NMR Studies of Catalysts” in collaboration with Johnson Matthey, UK. His research is primarily focused on surface analysis of a wide range of catalysts and catalytic supports with solid-state NMR and DNP-enhanced solid-state NMR. He also worked in NMR relaxometry and the application of alternative numerical approaches for ill-posed problems that arise from dynamic NMR studies. He is a member of the Italian National Group of Magnetic Resonance.

Subhradip Paul obtained his MSc and PhD in solid-state NMR at the Tata Institute of Fundamental Research (TIFR), Mumbai, India. Afterwards he carried out postdoctoral research in the field of solid-state NMR at Ohio State University, USA, and in the field of DNP-enhanced solid-state NMR at Alternative Energies and Atomic Energy Commission (CEA), Grenoble, France before moving to the University of Nottingham, UK where his current position is Facility Manager of the Nottingham DNP MAS NMR Facility. During his research career he has primarily worked on methodology development in solid-state NMR and its further application in important systems for structure elucidation. He has also worked on theoretical aspects of DNP-enhanced solid-state NMR and the development of pulse sequences applicable in systems at their natural isotopic abundance.

Nathan Barrow is currently a Principal Scientist in the Advanced Characterisation department at Johnson Matthey, Sonning Common, UK. He graduated with an MPhys in 2006 from the University of Warwick, UK, where he remained to gain a PhD in solid-state NMR. In 2010 he was a Knowledge Transfer Partnership associate between the University of Warwick and Johnson Matthey helping to install and run a solid-state NMR service. His current research focuses on applying advanced characterisation methods to materials such as zeolites, alumina, glasses and batteries.

Jeremy Titman carried out NMR research at the University of Cambridge, UK and the Max-Planck-Institut für Polymerforschung, Germany, before moving to the University of Nottingham, UK where he is currently Associate Professor and Reader in Magnetic Resonance. During over 25 years of research activity, he has developed a large number of new methods in solid-state NMR and has applied them to a broad range of problems in chemistry and materials science. He is currently Deputy Director of the UK 850 MHz Solid-State NMR Facility.
Accessibility and Location of Acid Sites in Zeolites as Probed by Fourier Transform Infrared Spectroscopy and Magic Angle Spinning Nuclear Magnetic Resonance

Understanding heterogeneous catalysts using probe molecule experiments

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The understanding of location and accessibility of zeolite acid sites is a key issue in heterogeneous catalysis. This paper provides a brief overview of Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) characterisation of acidity in zeolites based on the application of test molecules with a diverse range of basicity and kinetic diameters. Many zeolites, including ZSM-5 and BEA, have been characterised by monitoring the interaction between the zeolite acid sites and test molecules, such as 1,3,5-trisopropylbenzene, pyridine and alkylpyridines, to probe the location, accessibility and strength of the Brønsted acid sites. 1,3,5-trisopropylbenzene can be used to distinguish Brønsted acid sites located on the external and internal surface in most medium and large pore channel zeolites. Brønsted acid sites on the external surface of medium pore zeolites can also be quantified using 2,6-di-tert-butyl-pyridine and 2,4,6-trimethylpyridine. It is concluded that using a combination of probe molecules, including co-adsorption experiments, affords differentiation between acid sites located in channels and cavities of different sizes and on the external and internal surfaces of various zeolitic structures.

1. Introduction
Zeolites are crystalline solids with a well-defined structure consisting of molecular scale pores and channels. Their primary units such as SiO$_4$ and AlO$_4$ tetrahedra are linked by oxygen atoms at their vertices, creating a variety of microporous framework structures (1). The AlO$_4$ units impart a negative charge within the framework that must be balanced by cationic species (2). These cationic species are retained by steric effects and electrostatic interactions and can be exchanged with other cations, making zeolites highly valuable as cation-exchangers (2–4).

Zeolites have been widely used within the chemical and petrochemical industries as heterogeneous catalysts. This is due to their unique set of characteristics such as high adsorption capacity, intrinsic acidity, hydrothermal stability and shape selectivity.

Detailed understanding of their acidic properties is important for the design, modification and practical application of zeolite based catalysts. Generally, the most important properties for catalytic reactions are the type, strength, distribution, concentration and accessibility of
acid sites. Whilst the microporous nature of zeolites imparts some of their essential properties, such as high surface area, adsorption capacity and shape-selectivity, the presence of micropores can also lead to diffusional limitations, shorter catalyst lifetime and poor activity (5, 6).

To achieve the full potential of a zeolite catalyst, it is important to maximise the accessibility of active sites and transport efficiency for both the feed molecules and products in catalytic reactions. This can be achieved by employing zeolites with different structures and pore systems, and by introducing mesoporosity in addition to the existing network of micropores. These materials, the so-called hierarchical zeolites, developed, synthesised and modified in numerous ways have received considerable attention (7–10). The aim of this article is to review recent work evaluating acid site location and accessibility in zeolites with different pore systems, focusing on understanding the interactions between acid sites and probe molecules, particularly using FTIR and solid-state NMR, and providing examples of characterisation data for BEA and MFI zeolites using a variety of probe molecules.

2. Location and Accessibility of Acid Sites

The accessibility and location of acid sites in many ways determine the catalytic performance of zeolites. Acid sites hosted on the external surface of a zeolite are commonly accessible; the accessibility within the microporous system is dependent upon the dimensions of the pore space relative to the guest molecule. This relationship is closely linked to the local geometry of the acid sites, position of the Al atoms and chemical environment (11, 12).

2.1 Infrared Spectroscopy

Infrared (IR) spectroscopy studies using adsorption of probe molecules is one of the most important tools for comprehensive characterisation, including the nature, strength and accessibility of acid sites in zeolite based catalysts. The nature and the strength of the Brønsted acid sites (BAS) (i.e. bridging OH groups) and Lewis acid sites (LAS) in zeolites has been addressed in detail (11, 13–18); this section is focused on evaluating the location and accessibility of acid sites.

Busca and co-authors (19) carried out a range of experiments using pivalonitrile as a probe molecule to distinguish acid sites on internal and external surfaces in MCM-41, FER and MFI type materials (20, 21). Other nitriles such as propionitrile, isobutynitrile (22), 2,2-diphenylpropionitrile, benzonitrile and ortho-tolunitrile (23) were also utilised in order to assess the acid site accessibility in a number of zeolitic structures. When compared with other probe molecules such as pyridines and amines, nitriles interact with acid sites less strongly, creating a relatively weak bond with the BAS and LAS.

A variety of hydrocarbons have also been used (24); their interaction with acid sites is relatively weak resulting in the formation of a hydrogen bond between the hydrocarbon and a zeolite OH group. Alkenes and aromatics achieve stronger interactions than saturated hydrocarbons, which are still weak in comparison with other classes of probe molecules. The location and strength of BAS in ZSM-5 zeolites were evaluated by comparing the data obtained for cyclohexane and benzene with those for 1,3,5-trimethylbenzene. It was concluded that the mesoporosity influences only the accessibility of the acid sites by shortening the diffusion pathways, while the strength of the interaction with the probes, reflecting the strength of the acid sites, remains unaffected.

Another approach to understanding the site accessibility in zeolites is co-adsorption of probe molecules with different sizes. Adsorption of a small probe molecule (for example carbon monoxide (CO)) after pre-adsorption of a larger probe molecule was the subject of several studies in mordenite (25, 26). This zeolite exhibits two types of channels: 12-membered ring main channels and 8-membered ring channels connected by 8-membered ring side pockets (27). Pyridine can interact with the acid sites in the main channels of MOR but not with those inside the smaller side pockets, whereas CO interacts with all acid sites in the pore system. Consequently, by co-adsorbing these two probes, CO provides information about the strength of Brønsted acid sites in different locations, and the steric hindrance of pyridine gives evidence for the location of the acid sites (26). Co-adsorption of CO and nonane was also used to examine the spatial distribution of platinum in the micropores and mesopores of bi-functional Pth-MFI catalysts (28). This technique involves nonane pre-adsorption between two successive CO chemisorption experiments.

Nesterenko et al. (29, 30) and Bleken et al. (31) presented a methodology based on co-adsorption of alkylpyridines and CO for the analysis of acid site distribution in dealuminated mordenites and MFI zeolites. The use of these probe molecules with
increasing steric hindrance allows discrimination between acid sites located on internal and external surfaces. Both pyridine and alkylpyridines are protonated by BAS. However, due to steric hindrance induced by the bulky substituents, the alkylpyridine probes do not interact with LAS (32). These bulky probe molecules also have limited access to some micropores and consequently are suitable to obtain information about the BAS in different locations (14).

Many reports have been published on the application of 2,6-di-tert-butylpyridine (29, 33–35), 2,6-dimethylpyridine (29, 36–39) and 2,4,6-trimethylpyridine (30, 40–42) for zeolite characterisation. For instance, adsorption of pyridine and 2,4,6-trimethylpyridine was used to detect traces of coke in MFI catalysts, and to determine which acid sites are specifically perturbed by coke molecules (43). In the latter study, the authors found that coke deposits, resulting from ortho-xylene isomerisation, do not perturb BAS but perturb non-acidic silanol groups inside the micropore system. Using the same approach, Barbera et al. (41) confirmed that the presence of coke could influence catalyst deactivation. Both studies clearly distinguish between internal and external silanol groups and show that silanol defects play an important role in coke formation over MFI catalysts. Corma et al. (34) used the 2,6-di-tert-butylpyridine to investigate the external surface of many zeolitic structures. 2,6-di-tert-butylpyridine can enter the 12-membered channels of BEA but not the 10-membered ring channels of ZSM-5 and MCM-22. Therefore, it can be used to identify acid sites situated on the external surface of medium pore zeolites.

2,4,6-trimethylpyridine and 2,6-dimethylpyridine were used in a novel approach introduced by Thibault-Starzyk et al. (44), to quantify the accessibility of acid sites in ZSM-5 samples prepared with different degrees of intracrystalline mesoporosity. This approach is based on the calculation of the accessibility index (ACI), the ratio between the number of BAS detected by substituted pyridines and the total number of BAS in the zeolite detected by pyridine (Py). The results showed that the formation of mesoporosity reduces the average length of micropores and leads to an increase in the availability of acid sites at the pore mouths. This methodology has been successfully used to evaluate the accessibility of acid sites in both nanocrystalline zeolites and in zeolites with relatively large crystal size (44, 45).

Recently, this approach was also applied to other probe molecules, for example 2,6-di-tert-butylpyridine was used to quantify external BAS in various parent and modified zeolites indicating that the extended mesoporosity and decrease in average length of micropores resulted in increasing accessibility of BAS (35). Pivalonitrile adsorption was used to quantify both BAS and LAS, including multivalent transition metal cations hosted in zeolites, which are considered as active sites in redox reactions (46).

The quantitative analysis and interpretation of accessibility studies requires careful consideration. Indeed, the key to quantitative measurements is the use of molar absorption coefficients (ε). For some test molecules, there is a lack of ε values in the literature, and for most, the values reported show a significant degree of variation. Furthermore, the interaction of the probe with the zeolite can be complicated by pore blockage as some probe molecules can adsorb at the pore mouth of the zeolite and restrict access to the internal pores that once were accessible (47). Also, the strength of interaction with some molecules, such as pyridine and acetonitrile, could lead to ‘extraction’ of the protons from inaccessible positions, making them accessible (48, 49). For this reason, some molecules with a relatively large kinetic diameter can access acid sites in small pores of a zeolite. For example, Armaroli et al. (39) reported different behaviour using probes of similar size (2,6-dimethylpyridine and meta-xylene) in ZSM-5. 2,6-dimethylpyridine enters the pores of the ZSM-5 zeolite more readily as compared to meta-xylene. In addition, Traa et al. (50) suggested that the flexibility and the shape of the molecule in relation to the shape of the pore openings should also be considered.

Overall, the optimisation of the experimental procedures and the application of a combination of probe molecules are imperative for the successful evaluation of the location and strength of acid sites in different zeolite based materials.

### 2.2 Magic Angle Spinning Nuclear Magnetic Resonance

Both FTIR and 1H NMR can directly probe the acidic proton, which can be used to differentiate BAS and terminal hydroxyls (51). However, the accessibility (location), strength and distribution of acid sites cannot be easily measured by NMR. Basic probe molecules such as pyridine-\(d_5\) and \(^{13}\)C-acetone have been used to adsorb on the acid sites and reveal
their relative strength (52, 53). However, \(^1\text{H}\) has a small chemical shift range giving poor differentiation, and \(^{13}\text{C}\) (1.1% naturally abundant) is an insensitive nucleus requiring expensive enriched reagents. Thus, an approach involving \(^{31}\text{P}\) was sought, which has both a large chemical shift range and high sensitivity being 100% naturally abundant.

Trimethylphosphine (TMP) was first used in 1985 by Lunsford et al. and has since been used as a probe molecule for BAS and LAS in a variety of solid acid catalysts (54). TMP can chemisorb on BAS and LAS or physisorb on weakly acidic hydroxyls, each giving a distinct chemical shift range for each type of interaction. Although TMP is a sensitive probe for Lewis acid characterisation, a small Brønsted acid chemical shift range and volatility of the probe molecule have limited the popularity of this approach.

Trimethylphosphine oxide (TMPO), which is a solid at room temperature not susceptible to oxidation, retains the benefits of using \(^{31}\text{P}\) NMR and offers a greater chemical shift range for BAS characterisation. The applicability of TMPO probe molecules was first shown for zeolites by Rakiewicz et al. in 1998 (55). Over the past 20 years there have been many \(^{31}\text{P}\) NMR studies of phosphorus containing probe molecules, especially for the industrially relevant zeolites Beta and ZSM-5 shown in our examples (56–64).

A typical procedure for loading a zeolite with TMPO is to first dehydrate the zeolite, then add TMPO dissolved in dichloromethane (CH\(_2\)Cl\(_2\)) under an inert atmosphere, before heating the sample above the melting point of TMPO (140°C) (65). However, we and others (66) have also had success in a solvent-free method, by just adding TMPO at elevated temperatures, which has the added advantage of avoiding any solvent-zeolite interactions. It has been noted that a slight excess of TMPO is crucial in ensuring a complete coverage of acid sites during the experiment (67).

By varying the length of the alkyl chain, internal and external acid sites can be discriminated (68). The kinetic diameter of TMPO is 0.55 nm (55), whereas the butyl equivalent, tributylphosphine oxide (TBPO), is 0.82 nm (69), which is larger than the pore size in ZSM-5.

Unlike TMP, the chemical shift ranges for TMPO interacting with Brønsted and Lewis sites overlap. However, the TMPO adsorption to Lewis sites is weak and it can be readily displaced by water. Thus, acquiring two spectra with and without hydration allows one to determine Brønsted versus Lewis acidity (70).

As NMR is inherently quantitative, by knowing the quantity of TMPO added, a deconvolution of spectral peaks directly gives the concentration of acid sites. Furthermore, the \(^{31}\text{P}\) chemical shift of the peaks is linear with Brønsted acid strength (proton affinity), allowing both relative and absolute acid strength to be known (71).

### 3. Experimental Method

Ammonium forms of zeolites BEA (CP814E, BEA framework, Si:Al = 12.5) and ZSM-5 (CBV8014, MFI framework, Si:Al = 40) were obtained from Zeolyst International, USA. Prior to FTIR studies, the zeolites were pressed into self-supporting discs (~8–10 mg) and pretreated \textit{in situ} in an IR cell at 450°C under vacuum (10\(^{-5}\) Torr) for 5 h. The adsorption experiments with different probe molecules were monitored by Thermo Scientific™ Nicolet™ iSTM10 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector, at a spectral resolution of 4 cm\(^{-1}\). An excess of probe molecules was admitted by injection of 1.0 μl into the IR cell. Physisorbed molecules were subsequently removed by evacuation at the adsorption temperature. Adsorption of 1,3,5-triisopropylbenzene (C\(_{13}\)H\(_{24}\), Acros Organics, Belgium, 95%) was performed at room temperature. Pyridine (C\(_5\)H\(_5\)N, Acros Organics, 99.5%), 2,6-di-tert-butyl-pyridine (C\(_{13}\)H\(_{14}\)N, Sigma-Aldrich, USA, 97%), 2,6-dimethylpyridine (C\(_8\)H\(_9\)N, Sigma-Aldrich, 99%) and 2,4,6-trimethylpyridine (C\(_{6}\)H\(_{12}\)N, BDH reagents, UK, 95%) were adsorbed at 150°C. Desorption profiles were obtained by evacuating the sample at increasing temperatures in 50°C steps.

The obtained IR spectra were analysed (including integration, subtraction and determination of peak positions) using Thermo Scientific™ OMNIC™ Series Software. All the spectra presented in this work were normalised to 10 mg sample mass.

For MAS NMR experiments, the two zeolite samples were dehydrated at 350°C under vacuum (10\(^{-5}\) Torr) overnight. A slight excess of TMPO was added to the zeolites in an argon glovebox, followed by a treatment at 165°C for a few hours to melt the TMPO and distribute it throughout the sample. Solid-state NMR spectra were acquired at a static magnetic field strength of 9.4 T on a Bruker Avance™ III console using TopSpin® 3.1 software. A widebore Bruker 4 mm BB/1H WVT MAS probe was used, tuned to 161.98 MHz and referenced to ammonium dihydrogen phosphate at 0.9 ppm. The samples were packed into...
4. Results and Discussion

4.1 Acidity Measurements on ZSM-5 and BEA Zeolites

MFI structure is characterised by two types of 10-membered ring channels: straight channels with a nearly circular opening of 5.3 Å × 5.6 Å and sinusoidal channels with an elliptical opening of 5.1 Å × 5.5 Å. BEA is a large pore size zeolite with smaller 12-membered ring channels with a cross-section of 5.6 Å × 5.6 Å and larger 12-membered ring channels with a cross-section of 7.7 Å × 6.6 Å.

FTIR spectra of zeolites BEA and ZSM-5 show two major peaks at 3745 cm⁻¹, with a shoulder at ~3735 cm⁻¹, and 3610 cm⁻¹ (Figure 1(a)). The band at 3610 cm⁻¹ is assigned to acidic bridging Si-OH-Al groups and the bands at 3745 cm⁻¹ and 3735 cm⁻¹ are attributed to external and internal silanol groups (Si-OH), respectively. The separation of external and internal silanol groups is more noticeable in the spectra of the BEA zeolite. The interaction of pyridine with ZSM-5 and BEA zeolites results in a complete disappearance of the band at 3610 cm⁻¹ corresponding to bridging Si-OH-Al groups and a decrease in the intensity of the band assigned to Si-OH groups. This means that pyridine can access all the acid sites of BEA and ZSM-5 providing an overall concentration of acid sites.

In the range of 1400–1700 cm⁻¹, chemisorbed pyridine is revealed by the following sets of bands: 1545 cm⁻¹ and 1637 cm⁻¹ is due to pyridinium ion (PyH⁺), two bands assigned to pyridine coordinated to Lewis acid sites (PyL) at 1456 cm⁻¹ and 1622 cm⁻¹ and the superposition of signals of Lewis and Brønsted acid sites at 1491 cm⁻¹ (Figure 1(b)). The concentrations of Brønsted and Lewis acid sites (Figure 2) have been calculated from the intensities of peaks at 1545 cm⁻¹ for BAS and 1456 cm⁻¹ for LAS. The total concentrations of acid sites for ZSM-5 and BEA parent zeolites are about 350 μmol g⁻¹ and 760 μmol g⁻¹. ZSM-5 zeolite with Si:Al = 40 has less Al in the structure compared to BEA with Si:Al = 12.5, and consequently, a lower total concentration of acid sites. The concentration of LAS in ZSM-5 is ~12% of the total number of acid sites. BEA zeolite presents similar amounts of BAS and LAS, 340 μmol g⁻¹ and 420 μmol g⁻¹, respectively. These data are corroborated by ²⁷Al MAS NMR experiments indicating a higher amount of extra-framework aluminium in BEA compared to the ZSM-5 zeolite.

The type and concentration of acid sites can be readily determined from FTIR spectra of pyridine adsorbed on zeolites. Their strength can be evaluated by the temperature programmed desorption of pyridine, ammonia or other probe molecules. However, such measurements give only an effective strength as the probe molecules can re-adsorb on available acid sites during the desorption process. Clearly, the observed apparent strength would be affected by the concentration of acid sites, the size of the micropores as well as by a number of experimental parameters. In contrast, ³¹P MAS NMR spectra of TMPO-loaded zeolites...
provide a direct measure of the strength of acid sites given by the chemical shift of the phosphorus signal. These data are also quantitative, but they do require complete coverage of the zeolite by TMPO, and therefore rely on the appropriate dosing procedure being followed.

Figure 3(a) shows $^{31}$P MAS NMR spectra of TMPO dosed ZSM-5 by two different methods, one where TMPO was first dissolved in CH$_2$Cl$_2$ and the other where TMPO was added directly. Both methods produce similar results, whereas the solvent-free method avoids any potential solvent-zeolite interaction. A small excess of physisorbed TMPO is visible around 46 ppm, giving confidence that the accessible acid sites are completely covered. Two types of strong Brønsted site are observed, around 77 ppm and 69 ppm, along with a weaker Brønsted site at 54 ppm. Lewis acid sites from the extra-framework aluminium appeared around 65 ppm. There also appeared to be a very strong Lewis acid site at 84 ppm, but at a very low concentration. The assignment of BAS and LAS was based on literature data (70).

Figure 3(b) presents $^{31}$P MAS NMR spectra of TMPO dosed BEA zeolite, obtained via the solvent-free method. A small quantity of mobile TMPO is visible around 31 ppm, suggesting physisorbed TMPO is also present around 46 ppm, but overlapping with Brønsted or Lewis acid sites. Strong BAS can be clearly seen around 75 ppm, along with very strong LAS at 85 ppm. Additional LAS appeared around 65 ppm, as seen for ZSM-5. For BEA, the determination of Lewis versus Brønsted was based on hydrating the sample to observe which peaks disappear. The greater quantity of LAS in BEA over ZSM-5 agrees with the pyridine-FTIR and $^{27}$Al NMR results.

Fig. 3. $^{31}$P Solid-state MAS NMR spectra of: (a) ZSM-5 dosed with TMPO, with and without using CH$_2$Cl$_2$ as a solvent; (b) BEA dosed with TMPO without solvent
Further work would be required to obtain accurate data for the concentration of each type of the detected sites. This would involve precise weighing of the samples and TMPO dose that was not undertaken for this study. Additionally, a quantitative analysis of the acid sites present on the internal and external surfaces could be performed by using bulkier probe molecules such as TBPO.

### 4.2 Accessibility of Acid Sites in ZSM-5 and BEA Zeolites

Adsorption of 1,3,5-triisopropylbenzene (kinetic diameter of ~8.5 Å) at 30°C on ZSM-5 and BEA zeolites (Figure 4) leads to a significant reduction in the intensity of the Si-OH band at 3745 cm⁻¹. In the case of BEA (Figure 4(c)) there is a clear separation between external SiOH groups at ~3745 cm⁻¹, which are interacting with the hydrocarbon molecules, and internal silanols at ~3735 cm⁻¹, which are not. At the same time, the Si-OH-Al band at ~3610 cm⁻¹ appears to be almost unchanged. However, the difference spectra (Figures 4(b) and 4(d)) show a low intensity negative peak at ~3610 cm⁻¹ detected for both zeolites. This negative peak corresponds to the acidic Si-OH-Al groups on the external surface interacting with the probe molecule with the formation of a hydrogen bond. These data demonstrate that 1,3,5-triisopropylbenzene, which is too large to enter

![Fig. 4. (a) FTIR spectra of ZSM-5 before, A, and after, B, 1,3,5-triisopropylbenzene adsorption at 30°C; (b) difference spectrum of ZSM-5 before and after adsorption of the probe; (c) FTIR spectra of BEA before, A, and after, B, 1,3,5-triisopropylbenzene adsorption at 30°C; (d) difference spectrum of BEA before and after adsorption of the probe](image-url)
the 10- and 12-membered channels of ZSM-5 and BEA, respectively, can be used to quantify the BAS located on the external surface.

FTIR spectra of ZSM-5 zeolite following adsorption of 2,6-dimethylpyridine, 2,4,6-trimethylpyridine and 2,6-di-tert-butyl-pyridine at 250°C are presented in Figure 5. All the substituted pyridines interact with terminal SiOH groups on the external surface reducing the intensity of the band at 3745 cm⁻¹. The band of Si-OH-Al is virtually unaffected in the case of 2,4,6-trimethylpyridine and 2,6-di-tert-butyl-pyridine adsorption, but does decrease noticeably following adsorption of 2,6-dimethylpyridine, indicating that the latter probe can access some of the BAS inside the micropore system. 2,6-di-tert-butyl-pyridine and 2,4,6-trimethylpyridine are not able to enter the micropores of ZSM-5. The difference spectra in the OH region show a low intensity negative peak at ~3610 cm⁻¹ after 2,4,6-trimethylpyridine and 2,6-di-tert-butyl-pyridine adsorption, which corresponds to the small fraction of bridging OH groups located on the external surface of the zeolite or near the pore mouths.

Adsorption of 2,6-dimethylpyridine (Figure 5(c), Spectrum A) leads to the appearance of two bands around 1600–1680 cm⁻¹ (72). 2,4,6-trimethylpyridine adsorption (Figure 5(c), Spectrum B) gives rise to the band at ~1634 cm⁻¹ with a shoulder at ~1649 cm⁻¹ resulting from the interaction with BAS; two low intensity bands at 1619 cm⁻¹ and 1575 cm⁻¹ are assigned to the probe adsorbed on Si-OH groups (42). The spectra of 2,6-di-tert-butylpyridine (Figure 5(c), Spectrum C) show a band at 1615 cm⁻¹ attributed to the probe bonded to BAS (35). Based on the assignment of these bands and

![Fig. 5. (a) FTIR spectra of ZSM-5 before, A, and after adsorption of alkylpyridines: 2,6-dimethylpyridine, B, 2,4,6-trimethylpyridine, C, and 2,6-di-tert-butyl-pyridine, D; (b) difference spectra in the OH region after adsorption of alkylpyridines: 2,6-dimethylpyridine, A, 2,4,6-trimethylpyridine, B, and 2,6-di-tert-butyl-pyridine, C; (c) difference spectra in the region of the aromatic ring vibrations of alkylpyridines: 2,6-dimethylpyridine, A, 2,4,6-trimethylpyridine, B, and 2,6-di-tert-butyl-pyridine, C](image-url)
the extinction coefficient values available in the literature (30, 35, 37), the number of BAS accessible to these probe molecules and the corresponding accessibility indices have been calculated assuming 1:1 interaction with the BAS (Table I). The total amount of BAS is obtained by probing the zeolites with pyridine (44). 2,6-dimethylpyridine, being bigger than pyridine, probes 47% of the total amount of BAS; 2,4,6-trimethylpyridine can access 8% and 2,6-di-tert-butyl-pyridine only 5%. These results agree with previously published reports on the adsorption of alkylpyridines on ZSM-5 zeolites (35, 44). The diffusion of 2,6-dimethylpyridine, with the kinetic diameter of 6.7 Å, in the micropores of ZSM-5 zeolite (maximum pore size of 5.6 Å) is restricted, depending on the temperature and duration of the experiment it can access up to about 50% of the BAS. These data confirm that the accessibility of the acid sites in the zeolite micropores is controlled by both molecular sieving and strength of interaction between the probe molecule and the acid site. The relatively large size of 2,6-di-tert-butyl-pyridine (7.9 Å) and 2,4,6-trimethylpyridine (7.4 Å) prevents their access to BAS in the micropores of ZSM-5.

In the case of BEA zeolite, the FTIR spectra demonstrate that all three substituted pyridines are protonated on all Si-OH-Al and some Si-OH groups, as they interact with all BAS on the external surface and in the micropores of zeolite BEA. Indeed, the size of the substituted pyridines are similar to the dimensions of the larger pores in the BEA structure (7.7 Å × 6.6 Å) allowing their access to the BAS in the micropore system.

### Table I

<table>
<thead>
<tr>
<th></th>
<th>Py a</th>
<th>Lu b</th>
<th>Coll c</th>
<th>DTBPy d</th>
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<tr>
<td>Concentration of accessible BAS, μmol g⁻¹</td>
<td>305</td>
<td>143 e</td>
<td>25</td>
<td>14</td>
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<tr>
<td>Accessibility index, %</td>
<td>100</td>
<td>47</td>
<td>8</td>
<td>5</td>
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*a* Py = pyridine  
*b* Lu = 2,6-dimethylpyridine  
*c* Coll = 2,4,6-trimethylpyridine  
*d* DTBPy = 2,6-di-tert-butylpyridine  
*e* Depends on the temperature and duration of the adsorption experiment

### 5. Conclusions

Characterisation of the acidic properties of zeolites has received a great deal of attention in recent decades. FTIR and MAS NMR are now established as major analytical techniques providing detailed information on the type, concentration, accessibility and location of acid sites. This work demonstrates several examples of FTIR and NMR evaluation of the acidic properties of ZSM-5 and BEA zeolites using a range of test molecules under *in situ* conditions. For instance, the accessibility and the number of acid sites on the internal and external surfaces has been determined using adsorption of bulky probe molecules monitored by FTIR, hence providing a clear method for the detailed examination of the acid sites in MFI and BEA structures. The application of ³¹P MAS NMR to the analysis of the interactions between TMPO as a probe molecule and the zeolite has provided in-depth information about the type and the strength of the acid sites.

This work can be further extended to include detailed characterisation of new and modified zeolite-based catalysts, particularly utilising a combination of several techniques. In addition, the experimental method should be optimised to improve the accuracy of the quantitative analysis under *in situ* and realistic reaction conditions and for cross validation of the data obtained from different techniques.

### Acknowledgements

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### References


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The Discoverers of the Isotopes of the Platinum Group of Elements: Update 2018

New isotopes found for Ru, Rh and Pd

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In the 2014 review (1) discovery circumstances for $^{85}$Ru and $^{86}$Ru were referenced only in the form of a preprint but have now been reported in the open literature (2). For the most recently discovered isotopes the discovery years for both $^{128}$Rh and $^{90}$Pd are the manuscript dates of the given references whilst for $^{125}$Ru, $^{130}$Pd and $^{131}$Pd the common discovery year corresponds to the original description of these isotopes in a RIKEN Accelerator Progress Report (3). In addition the existence of the isotope $^{89}$Rh has been confirmed by Čeliković et al. (4).

No half-lives have been reported for the new isotopes but their very detection indicates that they are all likely to be ‘particle stable’ – that is resistant to proton or neutron decay. The discovery circumstances of the new isotopes are given in Table I where the decay modes are estimated for the particular isotope mass.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass number</th>
<th>Decay modes</th>
<th>Year of discovery</th>
<th>Discoverers</th>
<th>Reference</th>
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<td>Ru</td>
<td>125</td>
<td>$\beta^-$</td>
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<td>Shimizu et al.</td>
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<tr>
<td>Rh</td>
<td>128</td>
<td>$\beta^-$</td>
<td>2017</td>
<td>Shimizu et al.</td>
<td>(5)</td>
</tr>
<tr>
<td>Pd</td>
<td>90</td>
<td>EC + $\beta^+$ ?</td>
<td>2016</td>
<td>Čeliković et al.</td>
<td>(4)</td>
</tr>
<tr>
<td>Pd</td>
<td>130</td>
<td>$\beta^-$</td>
<td>2014</td>
<td>Shimizu et al.</td>
<td>(5)</td>
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<tr>
<td>Pd</td>
<td>131</td>
<td>$\beta^-$</td>
<td>2014</td>
<td>Shimizu et al.</td>
<td>(5)</td>
</tr>
</tbody>
</table>

Notes on Decay Modes

EC: Orbital electron capture in which the nucleus captures an extranuclear (orbital) electron which reacts with a proton to form a neutron and a neutrino, so that the mass number of the daughter nuclide remains the same but the atomic number decreases by one

$\beta^+$: Positron decay in which a positron and a neutrino are emitted as a proton in the nucleus decays to a neutron. As with EC the mass number of the daughter nuclide remains the same but the atomic number decreases by one. However this type of decay mode cannot occur unless the decay energy exceeds 1.022 MeV (for example, twice the electron mass in energy units)

$\beta^-$: Beta decay in which an electron and an anti-electron neutrino are emitted as a neutron in the nucleus decays to a proton so that the mass number of the daughter nuclide remains the same but the atomic number increases by one

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Table II  Total Number of Isotopes and Mass Ranges for Each Platinum Group Element to 2018

<table>
<thead>
<tr>
<th>Element</th>
<th>Number of known isotopes</th>
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<td>Ru</td>
<td>41</td>
<td>85–125</td>
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<tr>
<td>Rh</td>
<td>40</td>
<td>89–128</td>
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References


The Author

John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.
“Atomic Layer Deposition in Energy Conversion Applications”

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Introduction

“Atomic Layer Deposition in Energy Conversion Applications” is a series of reviews presented as nine chapters that focus on the applications of atomic layer deposition (ALD) for photovoltaics, electrochemical energy storage and photo- and electrochemical devices. These have been edited by Julien Bachmann whose research is based on the fabrication of nanostructured materials and interfaces to study the key mechanisms within energy conversion systems. Developed in the 1970s, ALD is a deposition technique whereby thin-film growth is achieved by alternating the exposure of a substrate surface to pulses of chemical precursors, resulting in the sequential deposition of sub(monolayers). The process has potential application in fields ranging from catalysis to batteries and fuel cells.

The book is organised into five main sections. Part I introduces the concept of ALD and the growth characteristics and conformality of ALD processes. Part II, which comprises three chapters, explores the use of ALD for the preparation of functional layers in commercial solar cells. Part III consists of three chapters where the recent advances in thin-films fabricated by ALD for fuel cells, water-splitting electrocatalysts and lithium-ion batteries are reviewed. The final section is presented in two chapters where an overview of ALD for photoelectrochemical and thermoelectric energy conversion is provided.

Principles of Atomic Layer Deposition

Chapter 1, presented by J. Dendooven and C. Detavernier (Ghent University, Belgium), provides an overview to ALD including the basic principles of the deposition process and the in situ characterisation techniques frequently used in ALD research. This chapter will be of particular interest to general readers.

The first section of Chapter 1 describes several advantages that the ALD technique offers over more common deposition methods (for example, chemical vapour deposition (CVD) and physical vapour deposition (PVD)) that are the result of the unique self-saturating nature of the process. Of these are the control of layer thickness at the Ångström level and the ability to deposit conformal coatings onto high aspect ratio (AR) structures with holes, trenches and pores. The essential characteristics of layer-by-layer growth in the ALD process are highlighted as growth per cycle (GPC), saturation, temperature window and linearity, where under ideal conditions ALD is characterised by a linear increase in the amount of deposited material as a function of the number of pump cycles.

In the following section of Chapter 1, the authors discuss the range of in situ characterisation techniques that are used to study the growing film during ALD. The most common of these is the quartz crystal microbalance (QCM) which monitors the mass of deposition by measuring a shift in the resonant frequency of an oscillating piezoelectric...
crystal. Other methods include quadrupole mass spectroscopy (QMS), spectroscopic ellipsometry (SE), optical emission spectroscopy (OES), as well as a variety of X-ray based synchrotron techniques.

The final section of Chapter 1 reviews the conformality of the ALD process. The deposition of ultrathin coatings on the interior of nano-sized pores is explored using both meso- and microporous thin films, where the growth is monitored by the in situ techniques described earlier in the chapter.

Applications in Photovoltaics

Part II comprises three chapters where the opportunities for ALD in silicon heterojunction (SHJ) solar cells are explored.

In Chapter 2, B. Macco et al. (Eindhoven University of Technology, The Netherlands) investigates the role of ALD Al2O3 passivation layers in p-type doped SHJ cells. Al2O3 nanolayers prepared by ALD have been shown to account for ~1% absolute increase in the conversion efficiency of commercial solar cells. This has been attributed to both the excellent chemical and field-effect passivation offered by the material. However, as the interface properties are strongly dependent on the thickness and processing conditions of the film, there is a balance between achieving complete surface coverage to prevent rapid deterioration and maximising light transmittance through the cell. The optimal thickness of the layer is determined to be >5 nm for plasma ALD and >10 nm for thermal ALD.

Chapter 2 also reviews the preparation of transparent conductive oxides (TCO) by ALD with examples of In2O3 and ZnO for the front side and rear side of a SHJ cell, respectively. The physics and requirements of TCOs for SHJ cells are discussed, and the advantages of ALD TCOs in high volume manufacturing (HVM) are highlighted. In the later part of the chapter, novel passivating tunnelling contacts and carrier-selective materials based on metal oxides such as MoOx, WOx, NiOx, and TiOx are reviewed.

The author concludes that the precise control of film growth and film composition offered by ALD render it a very promising deposition method of functional layers for a variety of materials in HVM. The success of the ALD Al2O3 passivating layer over the last few years has resulted in the development of high-throughput reactors which are capable of meeting industrial demands. In addition, other materials prepared by ALD for the passivation of Si have been explored including HfO2, SiO2, and Ga2O3.

Chapter 3 focuses on the use of ALD for light absorption. In this chapter, A. Martinson (Argonne National Laboratory, USA) discusses each of the key sources of major solar light absorption deficiencies: reflectivity, indirect semiconductor band gaps and transmission of photons with energy less than that of the band gap. The author follows by describing the unique characteristics that make ALD favourable for the preparation of solar absorbing materials. Of these is the ability of ALD to orthogonalise light harvesting and charge extraction. The conformal coating ability of ALD means that ultrathin films can be arranged in high density parallel to the direction of illumination. This unusual configuration allows for greater light absorption from ever-thinner absorber films. In the later part of the chapter, Martinson reviews a variety of absorbing metal oxides and metal chalcogenides that can be grown by ALD, ranging from CuInS2 to Bi2S3. This chapter is particularly useful to both the general reader and those beginning research in the field as it provides a general overview of the light absorbing process in photovoltaic devices in addition to recent advances in ALD solar absorbers.

In the final chapter of Part II, Guerra-Nuñez et al. (EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; ETH Zürich, Nanoscience for Energy Technology and Sustainability, Switzerland) present the most relevant research on ultrathin films of metal oxides deposited onto nanostructured surfaces by ALD. These films are designed to engineer the interfaces within photovoltaic devices such as dye-sensitised solar cells (DSSC), quantum-dot-sensitised solar cells (QDSSC), colloidal quantum-dot solar cells (CQDSC), organic solar cells, perovskite solar cells and photoelectrochemical cells for water splitting, with the purpose of minimising recombination losses. The review mostly focuses on the application of ALD in DSSCs, investigating the use of both TiO2 as a compact layer at the TCO/metal oxide interface and Al2O3 as a blocking layer at the metal oxide/absorber interface. It is concluded a 5–10 nm thick amorphous TiO2 film that is both uniform and pinhole-free is the optimal configuration to block the back transfer of electrons to the hole-transport material (HTM). Increasing the thickness and crystallinity of the TiO2 film reduces the light transmittance and efficiency of blocking properties due to the presence of grain boundaries, and thus reduces the power conversion efficiency (PCE). In the later parts of the chapter, examples where ALD has been used to deposit blocking films directly onto nanotubes/nanowires in DSSCs and in water-splitting devices are briefly discussed.
Conclusions

The book is intended to provide an overview of the opportunities offered by ALD in the energy conversion field and the requirements for it to become a promising candidate in high volume manufacturing. It should therefore be of interest to general researchers within the semiconducting industry as well as ALD specialists.

The Reviewer

Sabrina Elix joined Johnson Matthey in 2017. She is currently a Process Development Chemist at Johnson Matthey, Royston, UK. Her work focuses on the scale-up and process optimisation of new catalyst products for the company's worldwide manufacturing facilities.
Recent Developments in the Structural Characterisation of Disordered, Mesoporous Solids

Novel hybrid methods provide greatly increased information on this important class of solids

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The accurate and precise characterisation of disordered, mesoporous solids continues to be an ongoing challenge due to the high level of complexity of such materials. Common, indirect methods, such as gas sorption and mercury porosimetry, still offer relatively cheap, and, most importantly, statistically representative characterisations of macroscopic samples. This work reviews and expands upon recent developments aimed at increasing, and cross-validating, the information obtained from such methods. This involves developing a better understanding of the pore-pore cooperative effects that emerge only in extensive, disordered pore networks to better interpret raw characterisation data, and to use these effects to deliver more information on the void space. This work also describes novel hybrid methods that also greatly increase the information that indirect methods can deliver on complex mesoporous solids.

1. Introduction

Many materials of industrial interest are both mesoporous and disordered over many length scales. These materials include heterogeneous catalysts and adsorbents, absorbents, gas and oil reservoir rocks (such as shales), controlled drug release devices and tissue engineering scaffolds. Such materials present a challenge for characterisation because the pore sizes are of the order of nanometres, while the particle sizes are of the order of millimetres to metres, and the correlation length, above which the statistical descriptors of the pore structure become constant, can take any value in this range, or there may even not be one.

This typical level of complexity means that, even though various different microscopy methods have been developed to directly examine the void space at nanoscale, these methods are still impractical for obtaining statistically representative descriptors for macroscopically sized samples, such as even just single catalyst pellets or rock fragments. This is because obtaining nanometre scale resolution in tomographic and microscopic methods (for example electron tomography (1), or dual-beam microscopy (2)) means the sample size typically has to be of the order of micrometres in size or even less. Microscopic and tomographic methods also tend to be slow and expensive. There is thus still a need for characterisation methods that deliver descriptors of nanoscale structure that are statistically representative for macroscopic samples.

There are several such macroscopic techniques such as gas sorption, mercury porosimetry and thermoporometry. However, given that these techniques are indirect, they have potential issues of uncertainty in the correct interpretation of raw data. Further, the underlying physical processes involved in these characterisation methods can be complex, with new, idiosyncratic effects.
arising just for disordered materials. These effects are specific to disordered materials because they are linked to the structural heterogeneity. Hence, studies of these physical processes on more ordered materials, such as templated (3) or nano-cast (4) porous media, where independent validation is possible, is often not sufficient to properly interpret data for disordered pellets. These idiosyncratic effects include advanced adsorption and network-based delayed condensation in gas sorption, mercury snap-off and entrapment in porosimetry, and advanced melting in thermoporometry.

While complicating the interpretation of these characterisation data types for disordered materials, these effects also offer the potential to extract more information on void spaces than has been typical in the past. Further, the often idiosyncratic physical origins of these effects particular to one technique means that a combination of methods offers the potential for independent validation of data from indirect methods.

While comparisons of statistical descriptors, such as voidage fractions or pore size probability density functions (distributions), from different indirect methods is common practice in the literature, the full integration of data sets via truly hybrid methods is rare. More recently, truly hybrid methods such as integrated gas sorption and mercury porosimetry (5), or combined mercury porosimetry and thermoporometry (6), have been developed. These hybrid methods typically consist of a series of different experiment types conducted on the same sample. For example, gas sorption may be conducted on a sample following porosimetry, once the entrapped mercury has been frozen in situ, or the entrapped mercury can form the probe fluid for a subsequent thermoporometry experiment. Hybrid methods present a much tougher test of the consistency of interpretation of data from the component indirect methods than simple comparisons of separate data sets. The combined hybrid data sets can also be used to obtain additional unusual pore space descriptors, such as pore length (7).

It is the purpose of this work to describe the physical principles underlying the common indirect characterisation methods, and discuss the key issues this raises concerning interpretation for disordered solids, and how they may be dealt with. It will then describe recently developed hybrid experimental protocols and their analysis. This work will argue that, rather than causing yet more problems for data interpretation, when properly understood, the idiosyncratic physical effects discovered in application of indirect techniques to disordered pore networks present an opportunity to derive additional information from them.

2. Basic Characterisation Methods and their Idiosyncratic Effects in Disordered Porous Solids

2.1 Gas Sorption

Gas sorption pore size characterisation is based upon the capillary condensation process, whereby the critical pressure for the phase transition between vapour and liquid is lowered by confinement. The condensation pressure, \( P_c \), for within a void space of radius \( r_p \), is generally given by the Kelvin equation,

\[
\ln \left( \frac{P_c}{P_0} \right) = - \frac{k \gamma V_m \cos \theta}{RT(r_p)} \quad (i)
\]

where \( P_0 \) is the saturated vapour pressure at which condensation occurs for the bulk, \( k \) is a geometry parameter and depends on the pore type (for a cylindrical pore open at both ends \( k = 1 \); and for a cylindrical pore with one dead-end and a hemispherical meniscus, \( k = 2 \)), \( \gamma \) is the surface tension and \( V_m \) is the molar volume of the condensed liquid phase, \( \theta \) is the contact angle with which the liquid meets the wall, and \( T \) is the absolute temperature.

It is generally assumed, for nitrogen, that the adsorbed condensate is perfectly wetting the surface such that the contact angle is zero, and thus the \( \cos \theta \) term is unity (8). Hence, from Equation (i), a key first assumption is thus pore shape/geometric. However, knowledge of the material synthesis process, or microscopy, can often provide the relevant information. Further, molecular simulations suggest that as the length of open pores increases the increased pore potential from growing interactions with the greater amount of solid means that long open pores behave like dead-end pores (9). This suggests that for macroscopic samples the assumption of dead-end pores is appropriate. However, it is also noted that, as will be described below, nitrogen condensation in some pores of macroscopic catalyst support pellets shifts to lower pressures when they are turned into dead-end pores, suggesting they were not behaving that way beforehand (10).

Further, before a pore completely fills via capillary condensation, a multi-layer film builds up on the surface, thereby decreasing the core void space
dimension. This must be taken account of when calculating pore sizes since the core void dimension controls condensation pressure.

The film, or \( t \)-layer, thickness is generally obtained from a universal \( t \)-curve, such as that of Halsey, or Harkins-Jura (8). \( t \)-Curves are generally obtained for adsorption on non-porous materials with relatively flat surfaces, while under the severe confinement within mesoporous solids the walls have severe curvature. The impact of this surface curvature on film thickness at a given pressure was addressed in the analysis of Broeckhoff and de Boer (11). Kruk et al. (12) showed that the Kelvin equation for a hemispherical meniscus geometry, along with a correction for the statistical film thickness, gives quite good agreement with the actual pore size of MCM-type silicas from nitrogen adsorption. The agreement was made even better in the pore size range from ca. 2 nm to 6.5 nm, if an additional correctional constant was added to the Kelvin equation.

A common feature of gas sorption data for mesoporous solids is the presence of hysteresis, whereby the pressure required for the main desorption step is generally lower than the pressure at which condensation originally occurred (8). The cause of the hysteresis has been a long running subject of study, with the promise of extracting additional information on pore systems (8). Even just for simple single pore systems a variety of mechanisms have been proposed.

From \textbf{Equation (i)}, the condensation and evaporation pressures for the same adsorbate in the same pore, or the condensation pressures for the same adsorbate in open/closed pores of the same diameter, or identical pores with different wetting properties, can be related via the ratio, \textbf{Equation (ii)} (13):

\[
\ln \left( \frac{P}{P_0} \right) = \frac{k_1 \cos \theta_1}{k_2 \cos \theta_2} \ln \left( \frac{P}{P_0} \right) = \frac{1}{\delta} \ln \left( \frac{P}{P_0} \right) \quad (\text{ii})
\]

where the subscripts 1 and 2 refer to either condensation and evaporation, respectively, or two different pores of the same radius. Cohen proposed that in an open cylindrical pore, with a fully wetting surface, condensation occurred \textit{via} a cylindrical sleeve meniscus (where \( k_1 = 1 \)), while desorption occurred \textit{via} a hemispherical meniscus (where \( k_2 = 2 \)), and the cos\( \theta \) terms both equal unity (14). Hence, in that case, the relative pressure for evaporation is the square of the relative pressure for condensation, and \( \delta = 2 \). For a wetting equilibrium sorption system, with no hysteresis, the power would be unity. For less wetting surfaces (where the cos\( \theta \) term can vary) the power would be less than two. Further, the condensation and evaporation pressures obtained by the analysis by Broeckhoff and de Boer (11) are such that \( \delta = 1.5 \) (13).

While, prior to full condensation, in large (macro-) pores, the model of adsorbate spatial distribution consisting of a distinct liquid-like film on the walls and a vapour-like core is generally sufficient, when the pore becomes small enough such that the opposite wall potentials begin to overlap significantly this becomes unrealistic. This overlap occurs in the mesopore range, becoming significant for pores of sizes below 10 nm (15).

When the pore wall potentials overlap the apparent discontinuous meniscus boundary between liquid-like and vapour-like phases becomes smeared out, and there is more a continuous distribution of adsorbate density across the pore. Non-local density functional theory (NLDFT) has been used to predict the condensation and evaporation transitions in such circumstances (15). Comparisons of the predictions of NLDFT with experimental data for (more) ordered porous materials, such as templated silicas with arrays of straight cylindrical pores, like MCM-41 and SBA-15, have suggested that condensation occurs at the adsorption spinodal, while desorption occurs at the equilibrium transition (15).

For pressures thus derived from NLDFT, the value of the parameter \( \delta \) in \textbf{Equation (ii)} is 1.8 (13). However, hysteresis widths, as measured by the parameter \( \delta \) in \textbf{Equation (ii)}, for different materials vary over the full range of values from 2 to 1.5, and even below, so none of the aforementioned theories supplies a complete description of sorption processes.

NLDFT is partially empirical because the surface potential has to be calibrated from experimental data, typically, for example for silicas, using adsorption on non-porous fumed silicas (16). Hence, the predictions of condensation pressures for NLDFT must be affected by factors such as surface chemistry and roughness that affect wetting. Previous work (17) has also allowed the cos\( \theta \) term in \textbf{Equation (i)} to be a free-fitting parameter, and, by doing so, it has been shown that a corrugated, cylindrical pore geometry can give rise to all of the IUPAC standard hysteresis loop types, thereby suggesting differences in pore wetting can explain differences in isotherm shape. Further, different adsorbates can be used for pore size characterisation, such as nitrogen and argon.
and these may have different values of the $\cos \theta$ term in Equation (i) for different surfaces (13). This can be exploited for structural characterisation, as will be seen below.

For more complex void spaces there is a further contribution to hysteresis from pore-pore co-operative effects. The most well-known such contribution is the so called pore-blocking or ink-bottle effect (18). Pore-blocking is said to arise because, for evaporation to occur, the condensate must have access to a free meniscus.

In a dead-end, ink-bottle geometry the larger (bottle) body only has access to the exterior via the narrow (bottle) neck. The pressure for evaporation from the neck will be lower than that in the body. Since it would not then have access to a free meniscus, the condensate in the body becomes meta-stable when the pressure drops below that required for desorption from an open pore of the same size. The condensate in the body can only desorb once the pressure drops sufficiently for the neck condensate to become unstable itself and desorb, thereby causing the free meniscus to retreat back to the entrance to the pore body, which will then immediately desorb.

In a more complex, disordered, interconnected pore network, a given pore may have many potential access routes to the surface, and thus the penetration into the network of the free meniscus as pressure declines is modelled using percolation theory (18). This approach has been used to derive pore network connectivity. It should be noted that in desorption a further key effect that can arise is cavitation, which occurs when the pore necks guarding a larger pore body are below a critical size, generally considered to be approximately 4 nm for nitrogen (19).

In cavitation, the meta-stable condensate in the pore body is stretched until it reaches the limit of stability and spontaneously converts to vapour even though the pore neck remains filled with liquid. This typically gives rise to a steep desorption step at a relative pressure of 0.4 for nitrogen (19). The position of this step is thought to be only dependent on properties of the adsorbate, and thus delivers no information on the void pace (beyond that it contains pore necks <4 nm guarding larger pore bodies).

It has been common practice, as in the aforementioned percolation analysis, to presume that there is a simple monotonic relationship between condensation pressure and pore size during adsorption. This is the same as treating an interconnected network of pores as a parallel pore bundle, similar to the overall arrangement of pores in MCM-41 (3). However, this neglects the potential for pore-pore co-operative effects in adsorption. Two such effects are advanced adsorption and delayed condensation.

The idea underlying advanced adsorption was originally proposed by de Boer (20). The basic mechanism for advanced adsorption can be demonstrated from a consideration of the simplest pore network, namely the through cylindrical pore body accessed by two cylindrical pore necks at either end of the body, with the central axes of all through cylinders aligned along the same straight line. Capillary condensation would be initiated at the cylindrical sleeve menisci in the pore necks. Once the necks fill with condensate they create a complete hemispherical meniscus at both ends of the pore body, which previously only had a largely cylindrical sleeve meniscus. Hence, if the condensation pressure for the pore necks via a cylindrical sleeve meniscus exceeds that for condensation via a hemispherical meniscus in the pore body then both will fill at the same pressure.

According to the Cohan equations, that means that if the pore body radius is less than twice that of the pore neck then both will fill at the same pressure (14). Hence, the apparent pore size distribution derived from the adsorption isotherm for such a system would be much narrower than reality.

The advanced condensation effect has also been predicted from molecular simulations of capillary condensation in void spaces with corrugations or irregular geometry, and is also known as the cascade effect (21). Advanced adsorption can be detected where the adsorbate occupancy of neighbouring pores of different sizes can be simultaneously observed, either directly or indirectly. As will be seen below, magnetic resonance imaging (MRI) can be used to observe occupancy of different neighbouring pore sizes when these are each part of extended regions of similar pore size that adjoin each other. Alternatively, as will be described in Section 3.1, the presence of advanced adsorption at the pore scale can be inferred indirectly by utilising complementary information from an independent technique like mercury porosimetry.

For porous catalyst supports where there is a macroscopic heterogeneity (>10 µm) in the spatial arrangement of pore sizes this advanced adsorption effect has been directly observed via MRI using nuclear magnetic resonance (NMR) relaxation time as an independent measure of condensate ganglia characteristic dimension, and, thence, filled pore
size at a given pressure (22). The typical resolution of the images is between 10 µm and 100 µm, so the images map macroscopic variation in microscopic properties.

For water adsorption in a sol-gel silica material, it was shown, using the fractal BET equation to quantify the shape of the multi-layer region with the surface fractal dimension, that multi-layer build-up was similar for water and nitrogen (22). This agrees with simulations of water adsorption in hydroxylated silica nanopores which suggest low pressure adsorption via pervasive multi-layer build-up, rather than isolated ganglia (23). However, it was observed, for water sorption, that there was not a monotonic relationship between filling pressure for condensation and pore size, and filled pores were spatially correlated.

The relaxation time distribution obtained for partially saturated samples, at relative pressures below that needed for complete pore filling, contained relaxation times from the uppermost tail of the distribution for complete saturation (22). This suggested that some of the largest pores containing condensed phase became completely filled at lower pressure than some of the smaller pores. Hence, partial pore filling is unlikely to explain the results. It was also found that the critical ratio of body to neck size for advanced condensation to occur may be substantially higher than two, and thus advanced adsorption may have more impact on pore size distribution (PSD) accuracy than otherwise thought.

A further pore-pore co-operative effect arising during adsorption is (network derived) delayed condensation (24). Delayed condensation occurs when the pore potential in a given pore is reduced below that for a section of void of the same geometry but with completely solid walls, due to side-arms branching off that pore leaving gaps in the walls. For networks consisting of pore bodies at nodes, and pore necks forming lattice branches, the condensation pressure for a pore body of a given size depends upon how many of the adjoining necks are filled. In such a system the apparent characteristic pore dimension obtained from gas adsorption would be different to that controlling invasion of a meniscus of non-wetting fluid or Knudsen diffusion.

The potential impact of co-operative phenomena on PSD accuracy has been explored by simulation of adsorption within pore network models (25). Matadamas et al. (25) have simulated the effects of delayed and advanced adsorption in pore body-pore neck network models with a range of pore connectivities and overlaps between pore body and neck size distributions. They compared the actual void space descriptors for the underlying models with those derived by standard analysis methods from the simulated isotherms, and showed that delayed condensation gave rise to a significant error in the accuracy of the PSD obtained. This finding means that indirect pore characterisation methods must address pore-pore co-operative effects to obtain accurate pore size distributions.

The existence of pore-pore co-operative effects in adsorption may explain apparent discrepancies between previous findings from NMR relaxometry studies of sorption hysteresis and pore blocking theory (26). In NMR relaxometry studies of partially saturated samples, the measured NMR relaxation time is dominated by the two-fraction, fast-exchange type relaxation of the liquid confined to the ganglia (27), and, thus, is sensitive to the characteristic size (i.e. smallest overall dimension) of the ganglia. This is because the residence time of a given water molecule is much larger in the confinement of the high density liquid phase compared to the short residence time in the sparsely populated, low density gas phase.

For water sorption in a silica sample, it was found that, at the same level of saturation of the void space on the adsorption and desorption boundary isotherms, the NMR relaxation time of the condensate was the same (26). This suggests that the spatial arrangement of condensate in the void space was the same on each branch at the same saturation. This result conflicts with conventional monotonic filling and pore blocking theory mechanisms for adsorption and desorption, respectively, which suggest more larger pore bodies should still be filled on desorption (18). This would mean that the measured relaxation time should be larger for the desorption branch than the adsorption branch at the same saturation level. However, as the aforementioned descriptions of pore blocking and advanced condensation show, if the material contains ink-bottle pores then the pore neck and pore body can both fill and empty at the same pressure. Hence, with advanced condensation as well as pore blocking, the condensate configuration would be expected to be the same on both adsorption and desorption branches of the hysteresis loop, as observed.

Scanning curves are an experimental technique for obtaining additional pore structural information beyond that delivered by the boundary isotherms (28). Scanning curves consist of experiments where the increase in pressure is halted before the sample
saturation with condensate is complete, and then the pressure is reversed (known as descending scanning curves), or experiments where the sample is first pore filled with condensate and then the pressure is reduced but this reduction is halted part way down the boundary desorption branch of the hysteresis loop and then the pressure is increased again (known as an ascending scanning curve).

The observed behaviour of scanning curves tends to fall into one of two broad classes. These classes are scanning curves that cross directly from one boundary curve to the other, and those that head for one of the hysteresis closure points. Scanning loops consist of curves where the direction of change of pressure is again reversed before the scanning curve gets to the other boundary isotherm or a hysteresis closure point. Scanning curves potentially deliver information on the relative juxtaposition of pores of different sizes because desorption requires the presence of a free vapour-liquid meniscus. If the sample is only partially saturated when desorption commences, liquid condensate may desorb into the remaining internal vapour pockets as well as the exterior. The occurrence and spatial distribution of these vapour pockets will determine the size and nature of the difference in form between the scanning curve and boundary isotherm. Hence, scanning curves have been used to validate random pore bond networks used to determine pore network connectivity (29).

The availability of high resolution sorption apparatus has facilitated the increased use of scanning curves to enhance the amount of information derived from gas sorption (30). Scanning curves have been used to infer indirectly the presence of advanced adsorption and delayed condensation phenomena for nitrogen sorption in SBA-15 (24). More recently, besides percolation theory, molecular simulations have been used to aid interpretation of scanning curves (31), particularly for more chemically heterogeneous systems (32).

2.2 Mercury Porosimetry

Mercury porosimetry is based on the phenomenon that mercury is non-wetting for most surfaces, and thus an external hydrostatic pressure must be applied to force mercury into pores. The pressure, $P_{Hg}$, required is inversely proportional to the pore radius, $r$, as given by the Washburn equation, shown in Equation (iii) (8):

$$ P_{Hg} = \frac{-2\gamma \cos \theta}{r} \quad (iii) $$

where $\gamma$ is the surface tension, and $\theta$ is the contact angle. The contact angle varies from surface to surface due to differences in surface chemistry and roughness (33). Unless the contact angle is fixed independently mercury porosimetry is strictly only a relative technique, although many materials have very similar intrusion contact angles of between 130° and 140° (33). The contact angle for a given material can be obtained from the macroscopic sessile drop experiment. However, for closely confined systems like mesoporous solids the contact angle and surface tension can be functions of pore radius. Hence, previous workers (34) have used mesoporous controlled pore glasses (CPGs) as model materials, for which it was possible to calibrate the pore radius independently using electron microscopy, to obtain semi-empirical relations of the form shown in Equation (iv) (33):

$$ r = \frac{-A + \sqrt{A^2 - 2BP_{Hg}}}{P_{Hg}} \quad (iv) $$

where the parameters $A$ and $B$ are given in Table I.

<table>
<thead>
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<th>Material</th>
<th>Advancing meniscus</th>
<th>Retreating meniscus</th>
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<td>$B, \text{ nm}^2$</td>
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Table I Parameters for Insertion into Equation (iv)\(^a\)

\(^a\) The advancing meniscus values have a pore radius range of applicability of 6–99.75 nm and the retreating values have a range from 4–68.5 nm (33)

Raw mercury porosimetry data typically exhibits hysteresis, whereby mercury extrudes from the sample at a lower pressure than was needed for it to intrude (8). In addition, some mercury may be retained in the sample, known as entrapment. The hysteresis commonly has two contributions, known as contact angle hysteresis and structural hysteresis.

Contact angle hysteresis arises because advancing mercury menisci have larger contact angles than retreating menisci (33), as can be seen directly in the sessile drop experiment when the sample platform is tilted and the mercury droplet is allowed to move downhill. The contact angle hysteresis can also be measured using model materials, such as for the CPGs in Table I. Simulations suggest that, for a given surface chemistry, the width of contact
angle hysteresis is determined by the degree of surface roughness (35). Hence, materials with similar surface fractal dimensions to CPGs have contact angle hysteresis that can be removed using Equation (iv) and the values of its parameters given in Table I derived from calibration using CPGs.

Structural hysteresis is associated with entrapment and is due to less mercury extruded than intruded over the same pressure range. For mercury to retreat from a given sample it must retain a continuous connection to the bulk reservoir. However, the mercury meniscus can break, or snap-off under certain circumstances (36). Experiments suggest that when the mercury thread is forced to go through a narrow neck adjoining a larger pore body the meniscus may snap-off in the neck (37). It has frequently been observed that there is often a critical pore body-to-neck ratio above which snap-off occurs, which is typically >6 (38). Experiments on glass micromodels have shown that the mercury meniscus may also break at the boundary of macroscopic heterogeneities in the spatial distribution of pore sizes, such that regions of large pores isolated in a continuous network of smaller pores will entrap mercury (36).

A combination of MRI experiments to map the macroscopic heterogeneity in the spatial distribution of pore sizes in a catalyst support pellet, with computerised X-ray tomography (CXT) to map the spatial distribution of entrapped mercury, has shown that this effect gives rise to entrapment in such materials (39). Simulation of mercury entrapment in structural models derived from the MRI images suggested that the occurrence of the snap-off process at the boundaries of adjoining regions of sufficiently disparate pore sizes caused entrapment as observed in the CXT images.

It is possible to use calibrated relations such as Equation (iv) to deconvolute contact angle hysteresis from structural hysteresis. For example, it has been found that Equation (iv) can completely remove the hysteresis in porosimetry data for powdered samples of silica pellets, suggesting it is purely contact angle related in origin (40). However, MRI studies showed that, when whole, these pellets possessed macroscopic heterogeneities in the spatial distribution of porosity and pore size (41). For porosimetry on the whole pellets, some hysteresis and entrapment was retained after application of Equation (iv) to the raw data, and thus this means the macroscopic heterogeneity gave rise to structural hysteresis (40). Given that mercury hysteresis and entrapment are related to structural features it can thus be used to derive information on these properties of materials, which is especially useful for chemically heterogeneous materials not amenable to fully quantitative MRI methods.

When void spaces are highly interconnected and pore sizes are such that a mercury saturation of 100% can be achieved at the top of the intrusion curve, then the mercury menisci will coalesce throughout the sample, and the mercury threads will all be continuous. In order for the mercury to retract from the sample when the pressure is lowered, there must be free menisci from which extrusion can begin.

Where there has been complete coalescence of menisci on intrusion these free menisci must be re-formed by snap-off (42). This means that lowering the pressure stretches the mercury until snap-off occurs. Experiments in straight cylindrical channels (of diameter 4 µm) drilled into glass have shown that, where there is no particularly distinguished location in a pore, this snap-off may occur multiple times within the same pore (43). Simulations have shown that where larger pores are joined via smaller pores snap-off will occur in the smaller pores, but additional delay in retraction pressure, beyond that associated with contact angle hysteresis, will occur (35). This results in a characteristic residual triangular hysteresis at the top of porosimetry data analysed using Equation (iv), where there is a sharp drop in the retraction curve after a horizontal plateau delay relative to the more continuous intrusion (35).

Mercury porosimetry is sometimes mistakenly dismissed as error-prone or misleading because of the so-called pore-shielding or pore-shadowing effect (44). This arises because mercury must enter the sample from the periphery and, if the only access to larger pore bodies in the sample interior is via smaller pore necks on the periphery, then the mercury pressure must first be raised to that required to enter the small necks to intrude the sample as a whole. Hence, an over-simplistic interpretation of the data would mean the volume of larger pore bodies would be attributed to the smaller necks.

However, for some applications, such as fluid permeation in reservoir rocks or adsorption separation processes, the size of pores on the surface of the sample, as delivered first by porosimetry intrusion curves, is often the key rate-controlling parameter (45). Further, in some materials, extrusion of the mercury is controlled by the shielded pore body size and structural hysteresis results such that the
The pore body size can be obtained from the retraction curve (already corrected for contact angle effects) (46). Alternatively, as will be seen below, where the mercury becomes entrapped in shielded pore bodies, it can be used as the probe fluid for thermoporometry to determine the body size.

### 2.3 Thermoporometry

Thermoporometry uses the principle that when a fluid is confined to a porous medium, the freezing and melting points of that fluid are altered. Commonly, the change in the phase transition point for a small crystal, relative to the bulk, varies inversely with crystal size (47). When a crystal confined within a cylindrical pore is melting, the relevant form of the Gibbs-Thompson equation suggests that the melting point depression $\Delta T_m$ will be given by Equation (v) (47):

$$
\Delta T_m = T_m^\infty - T_m(x) = -\frac{4\sigma_{sl}T_m^\infty}{x\Delta H_f\rho_s}\cos(\phi)
$$

where $T_m(x)$ is the melting point in a pore of diameter $x$, $T_m^\infty$ is the bulk melting temperature, $\Delta H_f$ is the bulk enthalpy of fusion, $\sigma_{sl}$ is the solid-liquid surface tension, $\rho_s$ is the solid phase density, and $\phi$ is the contact angle (typically assumed to be 180° for liquid-solid). This equation is frequently simplified to the form shown in Equation (vi):

$$
\Delta T_m = k/x
$$

where $k$ is known as the Gibbs-Thompson constant. Probe fluids for thermoporometry typically include water, or hydrocarbon liquids such as cyclohexane or decane, or mercury. The ideal probe liquid should have a large value of $k$, and a simple liquid-solid phase transition, such that it is clear when a given pore is molten or frozen. For water, experiments in templated silica materials have suggested a $k$ value of 52 nm K (48). In previous work (6), it has been found that for melting of a mercury crystal, via a hemispherical meniscus, the value of $k$ was 90 nm K.

Before recent work (6), mercury thermoporometry was only used to study the microscopic structure of confined mercury ganglia, rather than for pore structure characterisation. Borisov et al. (49) found that a thin liquid-like layer is formed on the surface of confined, solid mercury ganglia over the temperature range 195 to 229 K. This liquid-like layer forms the seed site for initiating melting of the solid cores at a higher temperature depending on characteristic size. It is presumed this liquid-like layer is one molecular diameter thick, and thus the effective crystal size in Equation (vi) becomes $x-t$, where $t$ is the thickness of the liquid-like layer.

Thermoporometry experiments can be performed using either differential scanning calorimetry (DSC) (6), or using NMR (49, 50). In the case of DSC the melting or freezing transition is detected via the flow of latent heat of fusion, while for NMR the transition is detected via the large decrease in relaxation time for solids compared to liquids, and so the NMR signal from the frozen solid can be removed by a relaxation time filter. The advantage of using NMR is that thermoporometry can be combined with pulsed-field gradient (PFG) NMR to create the hybrid method known as NMR cryodiffusometry, which can be used to link pore structure and transport directly (51, 52).

Thermoporometry can be used to directly determine pore shape since analysis by Petrov and Furo (53) has suggested that for phase transitions in through cylinders the melting point depression should be twice that of the freezing point depression. For example, the overall network architecture, and the cylindrical shape of constituent nanopores, within a small region of the sol-gel silica sphere Q1 have been independently determined by noting the similarity in the form of the images of cross-sections of the real void space obtained from focused-ion beam (FIB) SEM methods (such as the example shown in Figure 1) with simulated images obtained from sectioning a random pore bond network (shown in Figure 2) (2).

---

**Fig. 1.** EM image of the back wall of a trough cut in the surface of a sample of Q1, revealing the cross-section through the internal nanoscopic pore structure of the material. Reprinted from (2). Copyright (2017), with permission from Elsevier.
Figure 2. (a) View of a random, cylindrical pore-bond network model with 512 nodes and 1726 cylindrical pores; (b) view of simulated random planar section through network in (a). The discrete black and white ovoids correspond to small and large pores, respectively, and the continuous grey matrix corresponds to solid. Reprinted from (2). Copyright (2017), with permission from Elsevier.

Figure 3 shows the NMR thermoporometry data for a sample of Q1 fully saturated with deionised water as the probe fluid. The large vertical step at low temperature is the freezing transition for the pore fluid, the large step at intermediate temperature is the melting transition for the pore fluid, while the small step at 273 K is the melting and freezing transition for the bulk water film on
the exterior of the sample pellets. The slope in the top plateaus is caused by the Curie effect (47). The melting point depression of the point of inflexion of the freezing curve (6 K) was twice that of the freezing curve (12 K). According to the analysis of Petrov and Furo (53), this suggests the pores are cylindrical in geometry, in line with the imaging data. This suggests the pore geometry that happens to be observed in the image field of view is also more pervasive throughout the sample.

Freezing in thermoporometry is an invasion percolation process like gas desorption, and thus can also be used to obtain pore connectivity using percolation theory (18, 50). By analogy with gas adsorption, thermoporometry melting curves can be theorised to be affected by an advanced melting phenomenon in ink-bottle type pore geometry (54). For melting to be initiated there should be a free meniscus with molten phase. In thermoporometry, for a fully saturated, through-pore, wetting sample, melting is generally initiated from a cylindrical sleeve shaped meniscus at the boundary between the non-freezing layer at the pore wall and the ice in the pore core. However, if a smaller neck in a through ink-bottle geometry melts it creates a complete hemispherical meniscus at the entrance to the larger pore body. If the melting point for the pore body, via a hemispherical meniscus, is lower than the melting point via a cylindrical sleeve shaped meniscus for the pore neck, then both will melt together. This effect has also been predicted by computer simulation of melting in disordered porous media (55).

The existence of this effect has been confirmed by experiments on whole and powdered samples of mesoporous pellets independently (via MRI) shown to possess macroscopic heterogeneities in the spatial distribution of pore sizes larger than the powder particle size (30 µm) (54). The sharply increasing melting curve for the whole pellet sample became more gently sloping when the sample was fragmented, and thus the direct contact between regions of small and large pores that was previously facilitating advanced melting was broken.

3. Hybrid Methods
3.1 Integrated Gas Sorption and Mercury Porosimetry

As mentioned above, integrated gas sorption and mercury porosimetry consists of a series of gas sorption and porosimetry experiments conducted in series on exactly the same sample each time, with any entrapped mercury frozen in situ after a porosimetry step (5), since nitrogen adsorption is carried out at 77 K and the freezing point of bulk mercury is around 234 K. The stages of the experiment are shown schematically in Figure 4. The gas sorption isotherms from after mercury entrapment can be subtracted from those obtained beforehand to obtain the isotherms for just the region of the sample affected by the entrapment. The virtue of this integrated experiment is that the mercury porosimetry data provides detailed independent information on the void space where the mercury became entrapped.

![Figure 4. Schematic diagram of integrated gas sorption and mercury porosimetry experiment. The stages of the experiment are: A Empty sample; B First gas sorption experiment; C Empty sample; D Hg porosimetry; E Hg entrapment; F Second gas sorption experiment. Reprinted from (43).](https://doi.org/10.1595/205651318X696710)

The method can be further combined with CXT to reveal the macroscopic spatial distribution of entrapped mercury (43, 56). This further development has some similarities to the past low melting point alloy (or Wood’s metal) intrusion technique that uses electron microscopy to look at spatial distribution of frozen, intruded alloy (57). Figure 5 shows CXT projection images of the entrapped mercury within samples of a mesoporous, sol-gel silica sphere. From gas sorption, this material had a unimodal pore size distribution with the peak...
at around 30 nm. Glass micro-model experiments (36) suggest that, in samples with heterogeneities in the spatial distribution of pore size, mercury tends to get entrapped within isolated regions of the largest pores that are surrounded by regions of smaller pores due to snap-off of the mercury menisci at the periphery of the region of larger pore sizes. Hence, the CXT images can effectively provide maps of the location of the largest pores, and, thence, reveal spatial correlations in pore size, which may be related to manufacturing route. For example, sol-gel spheres are often grown from central seeds, and these may be evident in the CXT images.

Entrapped mercury is meta-stable, and, thus, a key issue for hybrid methods is whether the mercury moves around between the end of the porosimetry experiment and the start of the next experiment, such as gas sorption or thermoporometry. The driving force for this potential movement is the minimisation of the surface energy of the entrapped phase. However, the potential for, and rate of, mercury migration can be studied using either the integrated method itself, or other complementary techniques (58).

Gas sorption experiments have been conducted both immediately after porosimetry, and a week later, and while for some materials no significant variation in isotherm shape has been observed, for others significant changes did occur over this time (58). Mercury entrapped following porosimetry experiments with shorter equilibration times tends to be more unstable and likely to move than that entrapped in the course of experiments with longer equilibration times. The sample mean grain size of entrapped mercury ganglia can be obtained using small-angle X-ray scattering (SAXS), and, for example, for the sample of pellets from the batch of sol-gel silica spheres denoted Q1 this was found to be 5.71 ± 0.71 nm and 5.88 ± 0.11 nm for immediately after the integrated experiments, and seven days later, respectively (58).

This suggests that the ganglia of entrapped mercury did not change significantly in characteristic size over this period. SAXS has the virtues that the sample preparation is minimal, it does not need to be frozen before the experiment is conducted, and the scattering pattern can be obtained quite quickly, so a result can be obtained very rapidly after sample discharge from the porosimeter. CXT images can also be obtained immediately after porosimetry, and some time later, and compared in order to detect any migration of entrapped mercury occurring over macroscopic length scales.

Integrated experiments have been used to obtain pore length distributions (7), and reveal differences in mercury entrapment mechanism between samples (59). In particular, integrated experiments have been used to detect pore-pore co-operative effects, as discussed below.

Nitrogen sorption scanning curves for samples before and after mercury entrapment have been used to demonstrate the presence of the advanced
condensation effect for nitrogen adsorption (43). Specific amount adsorbed is expressed per unit mass of silica even after mercury entrapment to make the data-sets easily comparable. To produce scanning curves that are only for the pores affected by mercury entrapment, the experimental gas sorption data points following mercury porosimetry were subtracted from the equivalent data points before mercury porosimetry.

Figure 6(a) shows the desorption scanning curves, starting at relative pressure 0.948, for all condensate-filled pores in sol-gel silica S1 (solid line) and for those affected by entrapped mercury (closed squares). Further, Figure 6(b) shows the adsorption scanning curves, starting at relative pressure 0.894, for all empty pores in S1 (solid line) and for the pores affected by entrapped mercury (open diamonds). The scanning curves for all pores start to descend or ascend immediately, but reach the other boundary isotherm before the final hysteresis closure point, so some pores have reversible condensation, while others do not. The final intersection point of the scanning curve is the composite of the terminus of the curves for both types. The adsorption and desorption scanning curves for just the pores affected by entrapped mercury cross directly horizontally between the boundary curves. Pores which give rise to directly crossing ascending and descending scanning curves appear to be independent, like the through cylindrical pores in MCM-41. This is because, for independent pores, condensation would occur in just one step via the cylindrical sleeve-shaped meniscus, and desorption in just one step via a hemispherical meniscus. However, the pores that entrap mercury in S1 are actually part of a complex interconnected network.

In order to account for the apparent independence of the pores that entrap mercury, they must empty of condensate by the pore blocking mechanism, but also fill with condensate by the advanced adsorption mechanism. Consideration of sorption within the simple pore model presented in Figure 7 will demonstrate why the capillary condensation and evaporation mechanisms for S1 must be as just stated (43).

The pore model is made up of three pore segments, A, B and C, in which, following a mercury porosimetry experiment, pore C becomes filled with entrapped mercury. The sizes of the pores are in the order pore C > pore B > pore A, and the pressure of the system is shown as P0 or P1, where P1 > P0. At pressure P0 no nitrogen has condensed within the pore model. As the pressure is increased to P1, pore A fills with condensed gas via a cylindrical-sleeve type meniscus. Since pore B then acquires a closed end, the condensate meniscus in pore A can then invade pore B and pore C by the advanced adsorption mechanism. This means pore C, which entraps mercury (following mercury porosimetry) fills at the same pressure as pore A. When the pressure is subsequently lowered, pore C and B could only empty once the liquid condensate within pore A had evaporated. This is because of the aforementioned pore blocking mechanism, and pore A will empty at pressure P0 by a hemispherical meniscus. Hence, pore C, which entraps mercury (following mercury porosimetry) would empty at the same pressure as pore A. Therefore, pore C would appear as an independent pore in a gas sorption experiment. Further, the capillary condensation and
evaporation in pore C would happen at pressures anticipated for a pore of size A.

A comparison of the mercury intrusion curves for whole and powdered samples of S1 showed that the pores that entrapped mercury were shielded by pores from 1 nm to 2 nm smaller than themselves (60). This is within the range of critical sizes predicted by the Cohan equations (14). Pore A does not behave like a dead-end pore following entrapment in pore C due to the intermediate still empty pore B.

The aforementioned findings, from the integrated experiment with scanning curves, has revealed a lower limit to the resolution possible for the pore size distribution with gas sorption. Materials with an apparently narrow PSD may, in fact, have a much wider distribution concealed by advanced adsorption effects. However, the integrated experiment showed that mercury extrusion was still sensitive to the pore size variation present that went undetected by gas sorption.

The integrated experiment has demonstrated that argon and nitrogen wet the surface of entrapped mercury differently (13). The multi-layer region of the adsorption isotherm can be analysed using a fractal version of the BET equation that takes account of surface roughness and quantifies it using a surface fractal dimension parameter. When mercury becomes entrapped within an amorphous, mesoporous solid, it blocks access to much of the rough surface of the solid, and creates many other smooth metallic surfaces. Hence, if the adsorbate multi-layer film wets the mercury significantly, it will expand across it and the average surface roughness will decline. In contrast, if the adsorbate does not wet the smooth mercury surface well, the surface film will largely remain confined to the rough surface. Hence, in the case of the former adsorbate, the surface fractal dimension will decline following mercury entrapment, while, in the latter case, the fractal dimension will remain the same. The former effect is what has been observed for nitrogen and the latter for argon (13).

When mercury becomes entrapped within a pore adjoining the end of a through cylindrical pore, that particular through-pore then becomes a dead-end pore. However, the capillary condensation pressure of an adsorbate within the pore will only be reduced (as according to Equation (i)), through a change in the transition from occurring via a cylindrical-sleeve meniscus to via a hemispherical meniscus, if the adsorbate wets the new dead-end. This effect has been observed for nitrogen, but does not also arise for argon (which does not wet the new dead-end), in a hierarchical macro-/meso-/micro-porous silica-alumina catalyst pellet (10).

Similarly, for a through pore with intersections with side pores along its walls, the resulting holes in the pore potential will only be patched by entrapment of mercury in the side pores if the adsorbate wets that mercury. Hence, the difference in wetting between nitrogen and argon can be used to detect the delayed condensation effect (2). If some pore volume accessibility is lost to both nitrogen and argon, but only nitrogen isotherms show a decrease in capillary condensation pressure following mercury entrapment, then the delayed condensation effect is occurring. This effect is shown schematically in Figure 8.

This predicted effect has been observed for nitrogen and argon adsorption in a sol gel silica Q1 (2). As can be seen in Figure 9, when the incremental amount of nitrogen adsorbed after mercury entrapment is subtracted from that adsorbed over the same pressure step before porosimetry, and these differences are added cumulatively with increasing pressure, then a large negative peak appears at lower pressures and a
Nitrogen Argon

Before porosimetry

Pressure

After porosimetry

Incremental adsorbed amount

Cumulative difference plot (before-after)

Fig. 8. Schematic diagram showing the anticipated impact of entrapped mercury on the form of cumulative difference in incremental amount adsorbed (before mercury minus amount afterwards) plots for nitrogen and argon. The cumulative difference plot below also includes the broadening expected due to the presence of a range of pore sizes where the effect might happen. Reprinted from (2). Copyright (2017), with permission from Elsevier.

(a) Cumulative difference in amount adsorbed, cc STP g⁻¹

(b) Cumulative difference in amount adsorbed, cc STP g⁻¹

Fig. 9. Cumulative difference in amount adsorbed plots for adsorption of: (a) nitrogen; and (b) argon on typical samples from batch Q1. Reprinted from (2). Copyright (2017), with permission from Elsevier.

A negative peak in such plots corresponds to a pressure range where the amount adsorbing has increased following porosimetry. Since entrapped mercury is blocking access to previously open voids, thereby reducing adsorption capacity, the only way this can apparently happen is if the condensation pressure for some pores that remain open shifts significantly. In the case of nitrogen, still open
Pores neighbouring those with entrapped mercury have shifted lower in capillary condensation pressure, but this has not happened to anything like the same degree for argon.

The pores where the condensation corresponding to the negative peak is occurring have had the holes in their walls patched with wetting filler (mercury), and thus now have a much increased pore potential, and the delayed condensation effect has been removed. The relative pressure for the negative peak in Figure 10 of around 0.84 is approximately the square of the relative pressure of 0.93 for the positive, suggesting a discrepancy in pore size of a factor of around 2, and thereby gives an estimate of the size of the error in the pore size that the delayed condensation effect creates. The size of the negative peak gives an estimate of the volume of pores affected by delayed condensation.

### 3.2 Combined Mercury Porosimetry and Thermoporometry

As mentioned above, mercury entrapped during porosimetry can be used as the probe fluid for thermoporometry (6). The mercury saturation at the end of a porosimetry experiment can range from 100% to 0%. In order to successfully relate the thermoporometry data to the porosimetry data it is important that the mercury does not redistribute before or during the thermoporometry experiment. However, it has been suggested that mercury in partially saturated samples may retreat from some pores during the freezing process (63). The volumetric thermal contraction of liquid mercury on cooling from 298 K to 234.4 K is around 1%, while that for solid mercury on cooling from 234.4 K to 77 K is 0.4%. Hence, any significant retreat must be a dewetting phenomenon. This effect can be tested for by multi-cycle thermoporometry.

In multi-cycle thermoporometry the same sample is repeatedly frozen and melted several times in series. If the freezing process is inducing mercury migration, such as a retreat from smaller pores, this should become evident from a progressive shift in the melting peak position over repeated freeze-thaw cycles. An example of a set of results of such experiments is shown in Figure 11. It

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![Fig. 10. Plot of difference in incremental amount adsorbed at particular relative pressures obtained by subtracting the isotherm obtained after porosimetry from that obtained beforehand for a sample from batch Q1. Reprinted from (2). Copyright (2017), with permission from Elsevier.](image1)

![Fig. 11. Mercury DSC thermoporometry melting curves obtained with temperature ramp rates in the order 0.5 (red dot-dashed line), 0.8 (green dashed line), 1.0 (purple dotted line), and 1.5 (solid blue line), °C min^{-1}, for copper-zinc oxide catalyst during repeated freeze-thaw cycling experiment on same sample. The sharp peaks at approx. −39°C correspond to the melting of the reference bulk mercury added to sample pan. The sample was cooled to −80°C at the start of each phase of the cycling.](image2)
can be seen that repeated freeze-thaw cycles did not give rise to a significant shift in melting peak position. It was also found that over the ranges tested the temperature ramp rate for DSC also did not affect peak position.

Since mercury tends to become entrapped in shielded (or shadowed) pores then mercury thermoporometry can be used to de-shield mercury porosimetry PSDs without the need for pore network modelling, which requires a priori knowledge of pore connectivity to determine pore accessibility (6). The DSC thermoporometry data provides the PSD of the shielded pores. Comparisons between mercury porosimetry and thermoporometry can also be used to determine whether the parameters in Equation (iii) and Equation (v) vary differently with pore size relative to each other (64).

4. Conclusions

It has been demonstrated that pore-pore co-operative effects are present for a variety of characterisation techniques for disordered materials, such that the occurrence of these effects can be cross-validated between different techniques. Hybrid combinations of the various common indirect characterisation methods have been shown to vastly expand their power to deliver descriptors of complex disordered porous solids. It has been seen that the physical effects idiosyncratic to porous materials with interconnected pore networks, such as advanced condensation and melting, can also expand the range of information on pore structures and the processes occurring within them.

References

The Author

Sean Rigby obtained his first degrees and PhD in Chemical Engineering from the University of Cambridge, UK. He then worked for the catalyst business, Katalco/Synetix, of ICI for four years as a process engineer and product research manager, and managed the catalyst characterisation department. Thereafter, Sean joined the University of Bath, UK, as a lecturer and worked there between 2000 and 2010. He subsequently moved to the University of Nottingham, UK, where he is currently Professor of Chemical Engineering and Director of the Geo-energy Research Centre. Sean’s research interests include structural characterisation and transport processes in porous media, heterogeneous catalysis, thermal and electromagnetic methods of heavy oil recovery, controlled drug delivery and carbon sequestration.
Johnson Matthey Highlights

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

Cohesive Strength Measurement of Catalyst Layer: Uniform Drying and On-Line Monitoring

Automotive catalyst coatings are generally deposited on the inside walls of a ceramic or metallic monolith. The strength of the coating layer is an important consideration to improve lifetime and activity levels of the catalytic converter. Both cohesive and adhesive failure modes are possible for the coated catalyst layer. A method to quantify the individual cohesive strength using a uniform drying system is proposed here. The behaviour was observed using on-line monitoring of a washcoat layer drying process. It was found that the cohesive strength varies with particle size, pH of catalyst suspension and drying rate of the suspension.

Formation of Size-Dependent and Conductive Phase on Lithium Iron Phosphate During Carbon Coating

Carbon coating by pyrolysis of an organic substance on lithium iron phosphate particles at high temperature is used to improve conductivity in active materials for Li-ion batteries. However, the process causes formation of secondary phases. The conductive phase was observed during coating and was found to be dependent on size, temperature and annealing atmosphere. Its formation depends on the reducing capacity in the carbon coating process. The work is expected to enable control of phase composition and tuning of the quality during manufacture.

Effect of Mixing Conditions on the Wet Preparation of Ceramic Foams

Scale-up of ceramic foams was studied using an agitated baffled vessel fitted with an up-pumping pitch blade turbine and a bottom round sparger. The effect of mixing parameters on the foam properties was determined. Flow conditions were carried out in low to mid transitional regime. DoE was used to create the screening experiments with different sparging time, air flow rate, impeller speed and impeller diameter. Rheology results were found to be useful for at-line measurement to control the structure of the material produced.

Ideal Versus Real: Simulated Annealing of Experimentally Derived and Geometric Platinum Nanoparticles

The structures of commercially available Pt catalysts were determined using electron microscopy and are here compared with geometric cuboctahedral and truncated octahedral structures using classical and quantum atomistic simulations. The potential energy surface at different temperatures and the effect of annealing on catalytic activity on nanoparticles with different geometries and sizes was examined using a simulated annealing procedure. Annealing both experimental and geometric nanoparticles produced structures similar in shape and predicted activity, using oxygen adsorption as a measure. Annealing is predicted to increase the catalytic activity in all cases except the truncated octahedra, where it has the opposite effect.
Importance of Support Stability

Levulinic Acid with Formic Acid/Formate Mixtures:

Ru/ZrO2 Catalysts for Transfer Hydrogenation of

2018, 14, (13), 1703734

Ru/ZrO2 catalysts. Ru/ZrO2 with γ-valerolactone using equimolar formate/formic acid in water and Ru/ZrO2 catalysts. Ru/ZrO2 with loadings <3 wt% were more active than those with higher loadings. Catalyst stability was investigated. A sol-gel process was used to prepare the catalysts in order to prevent metal leaching by trapping the Ru particles in the support. However the catalyst became deactivated after one run. There was no agglomeration of Ru particles although the ZrO2 support was found to have converted from predominantly tetragonal crystal to monoclinic phase and there was a decrease in the surface Ru/Zr ratio. Doping with 0.1 wt% SiO2 stabilised the tetragonal phase of zirconia and enabled the catalyst to retain its activity.

Improving Biomass Pyrolysis Economics by Integrating Vapor and Liquid Phase Upgrading


Carbon species on a commercial iron-based Fischer-Tropsch synthesis catalyst were studied using in situ XANES, in situ DRIFTS, TPH-MS, GC-MS and STEM-EDX. Re-oxidation or transformation of the active Hägg iron carbide phase did not lead to deactivation under the applied conditions. Sintering of this phase occurred over time on stream with increasing temperatures due to a hydrothermally-assisted process. Carbon species such as aliphatic hydrocarbons from wax and oxygenate compounds such as alcohols, aldehydes, ketones and carboxylates were on the catalyst surface. Carboxylate species resisted hydrogenation at 280ºC and the strongly adsorbed carbon species remaining on the catalyst surface from wax products were mainly α-olefins and branched carboxylic species.

Identification of Carbon Species on Iron-Based Catalysts During Fischer-Tropsch Synthesis


Electrochemical reduction of CO₂ may be a route to C–C coupling to produce platform chemicals and represents the biggest challenge to this route. Nanostructured iron(III) oxyhydroxide on N-doped C support can be used to produce high Faraday efficiency and selectivity to acetic acid at low potential. Electron microscopy, operando X-ray spectroscopy and DFT simulations were used to correlate the activity to N-coordinated iron(II) sites. Evolution of H2 could be correlated to the formation of metallic Fe and was the dominant reaction path.

Operando Spectroscopy Study of the Carbon Dioxide Electro-Reduction by Iron Species on Nitrogen-Doped Carbon


Economics.

In this perspective article, a combination of approaches for partial deoxygenation of bio-oil by catalytic fast pyrolysis with subsequent coupling and hydrotreating are investigated in detail. Some oxygen is removed during catalytic fast pyrolysis and the remainder removed by downstream hydrotreating, accompanied by carbon–carbon coupling reactions in either the vapour or liquid phase to improve carbon efficiency toward value-driven products (fuels or chemicals). The economic impact of partial deoxygenation by catalytic fast pyrolysis is explored as an integrated part of a two-stage process. Finally, including production of high-value co-products will be examined as a method of improving the overall pyrolysis-based biorefinery economics.

Development of Suitable CuO-Based Materials Supported on Al₂O₃, MgAl₂O₄, and ZrO₂ for Ca/Cu H₂ Production Process


Performance of Preformed Au/Cu Nanoclusters Deposited on MgO Powders in the Catalytic Reduction of 4-Nitrophenol in Solution

CuO-based materials supported on Al$_2$O$_3$, MgAl$_2$O$_4$ and ZrO$_2$ were prepared by different routes. Their performance for sorption enhanced reforming for H$_2$ production coupled to a Cu/CuO chemical loop was tested. The Al$_2$O$_3$ or MgAl$_2$O$_4$ supported materials synthesised by coprecipitation and mechanical mixing with Cu load ~65 wt% were stable. However ZrO$_2$ was not suitable for coprecipitation under these conditions. Pellets with high chemical and mechanical stability, high oxygen transport capacity and good mechanical properties were prepared by coprecipitation and can be scaled up.

**A One-Dimensional Model for Square and Octo-Square Asymmetric Particulate Filters with Correct Description of the Channel and Wall Geometry**

T. Watling, SAE Technical Paper, 2018-01-0951, 2018

This paper presents the first model to correctly describe the geometry of square and octo-square asymmetric particulate filters (PF), where the inlet channel is wider than the outlet channel in order to accommodate ash. Expressions are presented to describe the solid fraction of the PF, channel cross section and perimeter for both clean and soot/ash loaded conditions. The error introduced by assuming the inlet channels are square rather than octahedral depends on the substrate, but can be significant. Pressure drop across the wall and soot cake are also provided.

**Effects of H$_2$S and Phenanthrene on the Activity of Ni and Rh-Based Catalysts for the Reforming of a Simulated Biomass-Derived Producer Gas**


Rh and Ni-based catalysts for reforming methane and phenanthrene were tested. The feed composition was designed to replicate the producer gas from wood gasification. Phenanthrene was used to represent tar. H$_2$S was added at the higher range of typical values. At 900ºC, 200 ppm of H$_2$S caused much greater loss of methane reforming activity than that caused by 200 ppm of phenanthrene. The rate of methane consumption in the presence of both poisons varied linearly with the Rh metal surface area. The rate of methane consumption per unit of metal surface area was about five times higher on Rh than on Ni.
In Situ and Operando Spectroscopy: A Powerful Approach Towards Understanding Catalysts

Revealing reaction mechanisms to find the correlation between structure and surface composition

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The improvement of catalytic processes is strongly related to the better performance of catalysts (higher conversion, selectivity, yield and stability). Additionally, the desired catalysts should meet the requirements of being low cost as well as environmentally and user-friendly. All these requirements can only be met by catalyst development and optimisation following new approaches in design and synthesis. This article discusses three major approaches in the design and development of catalysts: (a) high-throughput synthesis; (b) reaction kinetic studies; (c) in situ and operando spectroscopy for studying catalysts under process conditions. In contrast to approaches based on high-throughput synthesis and reaction kinetic studies, an emerging approach of studying catalysts under process conditions using in situ and operando spectroscopy and transferring the gained knowledge to design of new catalysts or the optimisation of existing catalysts is not yet widely employed in the chemical industry. In this article, examples of using in situ or operando spectroscopy for studying the surface and bulk of catalysts under process conditions are discussed, with an overview of applying in situ X-ray absorption spectroscopy (XAS), in situ infrared (IR) spectroscopy and in situ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) for monitoring the bulk and surface composition of PdZn/ZnO and Pd2Ga/Ga2O3 methanol steam reforming catalysts.

1. Approaches for Catalyst Development

1.1 Discovery of a ‘Lucky Catalyst’ via High-Throughput Synthesis

Research and development of more efficient and sustainable catalysts, either the development of novel catalysts or optimisation of existing ones, is a vital part of industrial and academic research. One of the most common approaches for catalyst development is the synthesis of a large number of catalysts, followed by screening of their catalytic activity (known as high-throughput synthesis) (1, 2). A high-throughput synthesis approach is the most common method of catalyst discovery and optimisation and can be strongly boosted by the combinatorial design of experiments and using robotic equipment to synthesise and test catalysts (3–8). One of numerous catalysts prepared using high-throughput synthesis might be very active for a particular reaction (a ‘lucky catalyst’). However, employing such an approach...
alone without understanding activity-controlling factors often does not lead to a gain in knowledge or deep understanding of factors driving the activity and selectivity of catalysts (for example the nature of active sites and reaction mechanisms).

Understanding the structure-performance relationships of catalysts is a crucial step for the successful development of the next generation of more efficient catalysts and covers different aspects. Some research lines focus on the preparation of catalysts by varying certain parameters (for example preparation methods, elemental composition or loading) and then correlate catalytic properties of the synthesised materials with their structure, reducibility or tendency to adsorb or desorb the educts and products for a particular reaction. Combining knowledge of a catalyst's performance with its structure adds substantially to the understanding of catalytic systems and the potential to transfer knowledge to similar processes or products. Yet this approach provides rather a macroscopic picture of the structure-performance relationships of catalysts, omitting the detailed microscopic insights into the activity-controlling factors driving a particular reaction.

1.2 Reaction Kinetic Studies

Another line of research focuses on microscopic insights and explores the nature of the reaction sites of a catalyst and the mechanisms of reactions (9, 10). The commonly used methodology is based on a detailed study of reaction kinetics (reaction rates and rate laws). It takes its roots back to 1921 when the mechanisms of the catalytic action of platinum in the reactions of carbon monoxide oxidation and hydrogen oxidation were described with the help of kinetics by Irving Langmuir and presented at a Discussion of the Faraday Society held in September 1921 at the Institution of Electrical Engineers in London, UK (11). Langmuir’s work was later elaborated by Cyril Hinshelwood. The combined work of Irving Langmuir and Cyril Hinshelwood is known today as the Langmuir-Hinshelwood mechanism and is one of the most common reaction mechanisms describing numerous catalytic reactions (12). According to the Langmuir-Hinshelwood mechanism, a catalytic act is a reaction between two molecules, adsorbed on neighbouring sites (12).

Some years later, in 1938, Dan Eley and Eric Rideal proposed the Eley-Rideal mechanism, in which a catalytic act is a reaction between an adsorbed molecule and a molecule from the gas phase (13). Later works of Mars and van Krevelen on reducible oxides in 1954 suggested another mechanism that today is called the Mars-van-Krevelen type redox mechanism. According to the Mars-van-Krevelen mechanism, one reactant forms a chemical bond with the catalytic surface; the other reactant reacts directly from the gas phase. A vacancy that is formed when the reaction product desorbs was thought to be filled with an atom from the bulk (14). However, nowadays it is generally accepted that the vacancy created by the reaction is filled with the first reactant again.

The type of mechanism depends on the type of catalyst. The Mars-van-Krevelen type redox mechanism typically applies to reducible metal oxide catalysts, where lattice oxygen is involved in the reaction cycle and generation of vacancies is a crucial reaction step. The Eley-Rideal and Langmuir-Hinshelwood mechanisms typically describe non-reducible oxides and metal nanoparticle catalysts, where a network of elementary reaction steps involves adsorption of reactants on the catalyst surface, a catalytic reaction and desorption of products. As is demonstrated in the review of Rob Berger et al., in the chemical industry knowledge of the reaction kinetics is of primary importance for: (a) catalyst development; (b) process development; (c) process optimisation; and (d) mechanistic research (12). 29% of the utilisation of kinetic data in industry is dedicated to catalyst development (12). For mechanistic studies and advanced catalyst development, a precise description of the reaction rate is required at the level of elementary steps. This calls for advanced kinetic studies such as fast transient kinetic investigations (employing a temporal analysis of product reactor) (15) and advanced kinetic modelling studies (16–18).

1.3 The In Situ and Operando Approach

Although studying the kinetics of reactions is a powerful tool for identifying steps of the reaction cycle and for obtaining hints about active sites, it does not allow a complete picture of the reaction mechanism to be obtained. Often several reaction mechanisms can run in parallel; therefore, an exact identification of the reaction mechanism is not feasible. Moreover, for heterogeneous catalytic reactions, the identification of active sites is rather vague especially for solid catalysts because of their complexity. Often solid catalysts are multicomponent and multielement materials. Furthermore, the structures of solid catalysts are usually not well defined; thus, several sites might serve as active
sites and as a result, different reaction pathways might simultaneously run on different reaction sites or in different temperature regimes.

The complementary methodology based on the use of in situ and operando techniques for studying the catalyst under reaction conditions can overcome some of the limitations of the traditional kinetic methodology and provide a broader insight into the complex network of reaction pathways, thereby strongly contributing to understanding the structure-performance relationships of catalysts, the nature of active sites, reaction mechanisms, the structure of working catalysts and, based on the knowledge gained, the design of new catalysts (19–21).

Why is it so important to study catalysts under process conditions? Solid catalysts are very dynamic under working conditions when high temperatures and pressures are applied. Freshly prepared catalysts often undergo structural changes under activation and pretreatment conditions and further under reaction conditions. Thus, simply speaking, catalysts ‘adjust’ to the reaction environment (22). Monitoring such environment-induced changes of catalysts and understanding why they happen should be taken into account during the design of catalysts.

The traditional approach to gain insights into environment-induced changes was and is still in many cases to study catalysts ex situ (meaning outside, off site, out of place). However, this does not allow a clear picture of working catalysts to be obtained (Figure 1). The famous saying of Gabor Somorjai highlights this, stating that knowing the ‘before-reaction part’ or ‘after-reaction part’ “is like studying a life with access only to the prenatal and postmortem states” (23). Moreover, exposing the catalyst to ambient conditions might again change the catalyst’s structural and electronic properties and lead to data misinterpretation (Figure 1).

A more informative way is to monitor the catalyst directly under reaction conditions, in situ (meaning on site, in position, undisturbed) (23). Watching the catalyst under reaction conditions by physical-chemical methods and simultaneously recording catalytic data using a mass spectrometer or a gas chromatograph allows the catalytic properties to be correlated directly with electronic and structural changes in the catalyst. This approach is called ‘operando’ (24–26). An in situ approach is not only used for studying catalysts under working conditions, but can also be applied to the preparation of catalysts. For instance, application of tomographic energy dispersive diffraction imaging during the calcination of [Ni(en)(H₂O)₄]Cl₂/γ-Al₂O₃ and [Ni(en)₃](NO₃)₂/γ-Al₂O₃ hydrogenation catalyst bodies was used to study the changes in the structural composition of the catalysts at the macroscopic level (27).

An operando or in situ approach allows one to study the “birth, life and death” of catalysts, a concept that was recently introduced by Bert Weckhuysen (22). According to his concept, “birth” refers to the stage when a catalyst is prepared, as it is essential to understand how catalytic solids are formed; “life” describes how a catalyst functions...
and performs in a catalytic reaction; "death" explains how a catalyst undergoes deactivation.

Generally, operando investigation of catalysts can include spectroscopic techniques (for example Raman spectroscopy, infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), XAS, ultraviolet-visible (UV-Vis) spectroscopy and electron paramagnetic resonance (EPR) spectroscopy), but also microscopy (for example environmental transmission electron microscopy or environmental scanning electron microscopy, X-ray diffraction (XRD) and X-ray total scattering). A number of research groups have demonstrated the strength of combining several in situ techniques for the investigation of a range of catalytic systems under reaction conditions to identify dynamic changes to the catalysts under varying conditions (Figure 2) (28–35). Therefore, many efforts and the attention of the operando community are directed towards developing an integrated or combined approach, simultaneously applying several techniques (for example IR, Raman, XRD and XAS), for studying catalysts under reaction conditions.

Such an approach is successfully employed in the BM01B beamlines at the European Synchrotron Research Facility (ESRF), where in situ XRD, XAS and Raman spectroscopy are combined (36). Other synchrotron facilities have also been taking steps in this direction. Table I summarises the most commonly used hard X-ray synchrotron beamlines from the European synchrotron facilities where opportunities for operando and in situ studies of catalysts are provided. Using an integrated approach requires special reaction cells that allow in situ experiments to be carried out either simultaneously or sequentially in the same cell. Therefore, many efforts are directed toward the development of cells that can be used for combined measurements, in particular focusing on the cell design to obtain good agreement between the catalytic activity and selectivity of a catalyst measured in a conventional reactor and in a spectroscopic cell (37–39).

2. The Need to Understand the Surface of Catalysts Under Process Conditions

The increased interest in the in situ and operando approach for studying catalysis is demonstrated by the increased number of research papers where in situ and operando techniques are employed (40). A lot of money is currently invested into the building and improvement of synchrotron facilities to provide dedicated beamlines for in situ and operando studies and the topic regularly appears on the agenda at catalysis conferences. Moreover, a dedicated conference on operando

![Diagram of in situ and operando spectroscopy approach](https://doi.org/10.1595/205651318X15234323420569)

Fig. 2. Combined in situ and operando spectroscopy approach for studying catalyst under process conditions. Adapted with permission from (32)
Table I  Hard X-ray Synchrotron Beamlines from the European Synchrotron Facilities that Provide Opportunities for Operando and In Situ Studies of Catalysts

<table>
<thead>
<tr>
<th>Beaml ine</th>
<th>Energy range, keV</th>
<th>Techniques</th>
<th>Facility name</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>P07 The High Energy Materials Science</td>
<td>30–200</td>
<td>XRD, PDF, SAXS, 3D-XRD, tomography</td>
<td>PETRA III</td>
<td>DESY, Germany</td>
</tr>
<tr>
<td>P22 Hard X-ray Photoelectron Spectroscopy</td>
<td>2.4–30</td>
<td>Ambient pressure HAXPES</td>
<td>PETRA III</td>
<td>DESY, Germany</td>
</tr>
<tr>
<td>P64 Advanced X-ray Absorption Spectroscopy</td>
<td>4–44</td>
<td>EXAFS, Q-EXAFS, RXES</td>
<td>PETRA III</td>
<td>DESY, Germany</td>
</tr>
<tr>
<td>P65 EXAFS Beamline</td>
<td>4–44</td>
<td>EXAFS, XANES</td>
<td>PETRA III</td>
<td>DESY, Germany</td>
</tr>
<tr>
<td>ID22 High Resolution Powder Diffraction</td>
<td>6–80</td>
<td>XRD, PDF, anomalous diffraction, anomalous scattering</td>
<td>European Synchrotron Radiation Facility</td>
<td>Grenoble, France</td>
</tr>
<tr>
<td>ID22 Energy Dispersive X-ray Absorption Spectroscopy</td>
<td>5–27</td>
<td>XAS, EXAFS, FTIR, MicroXANES</td>
<td>European Synchrotron Radiation Facility</td>
<td>Grenoble, France</td>
</tr>
<tr>
<td>ID26 High Brilliance X-ray Spectroscopy</td>
<td>2.4–27</td>
<td>XAS, XES, IXS, REXS, XMCD, RIXS</td>
<td>European Synchrotron Radiation Facility</td>
<td>Grenoble, France</td>
</tr>
<tr>
<td>BM23 XAS Beamline</td>
<td>5–75</td>
<td>EXAFS, XRD, XRF, XMLD, MicroXANES, XANES, XAFS</td>
<td>European Synchrotron Radiation Facility</td>
<td>Grenoble, France</td>
</tr>
<tr>
<td>BM26A Dubble Dutch-Belgian XAFS Beamline</td>
<td>5–50</td>
<td>XAS, XRD</td>
<td>European Synchrotron Radiation Facility</td>
<td>Grenoble, France</td>
</tr>
<tr>
<td>BM31 The Swiss-Norwegian Beamline</td>
<td>4.9–70</td>
<td>XAS, HRXRD, Raman</td>
<td>European Synchrotron Radiation Facility</td>
<td>Grenoble, France</td>
</tr>
<tr>
<td>SAMBA</td>
<td>6–35</td>
<td>XAS, Raman, UV-Vis, XRD, differential scanning calorimetry</td>
<td>SOLEIL</td>
<td>Paris, France</td>
</tr>
<tr>
<td>LUCIA</td>
<td>0.6–8</td>
<td>XAS, Raman</td>
<td>SOLEIL</td>
<td>Paris, France</td>
</tr>
<tr>
<td>ROCK</td>
<td>4.5–40</td>
<td>XAS, Raman, UV-Vis, XRD, differential scanning calorimetry, Q-EXAFS</td>
<td>SOLEIL</td>
<td>Paris, France</td>
</tr>
<tr>
<td>I11</td>
<td>6–25</td>
<td>HRXRD</td>
<td>Diamond Light Source</td>
<td>Oxfordshire, UK</td>
</tr>
<tr>
<td>B18</td>
<td>2.05–35</td>
<td>XAS, XRF, XRD</td>
<td>Diamond Light Source</td>
<td>Oxfordshire, UK</td>
</tr>
<tr>
<td>I15-1</td>
<td>40, 65, 76</td>
<td>XRD, PDF</td>
<td>Diamond Light Source</td>
<td>Oxfordshire, UK</td>
</tr>
<tr>
<td>X10DA SuperXAS</td>
<td>4.5–35</td>
<td>XAS (QEXAFS), HRXES, PXEX, pump-sequential-probes XAS</td>
<td>Swiss Light Source</td>
<td>Paul Scherrer Institute, Switzerland</td>
</tr>
<tr>
<td>PHOENIX X07MA/B</td>
<td>0.8–8/04–2.0</td>
<td>High quality EXAFS for low-Z elements</td>
<td>Swiss Light Source</td>
<td>Paul Scherrer Institute, Switzerland</td>
</tr>
</tbody>
</table>

Continued
spectroscopy was launched in 2003 in Lunteren, The Netherlands, and successfully takes place every three years.

Despite numerous studies on catalysts using in situ and operando investigations including those using combined techniques, very limited knowledge exists in the literature about the surface composition of catalysts under reaction conditions, as most of the techniques characterise the bulk of the catalysts. The changes in surface composition, however, are the most relevant for explaining catalytic events that take place at catalyst surfaces (41). Importantly to note, the average bulk structure of materials does not represent the surface composition as was demonstrated in a recent study by Karim et al. on the size-dependent redox behaviour of iron, where it was shown that during oxidation iron grows in layers, forming Fe(0)/FeO/Fe3O4/Fe2O3 core-shell structures (42).

Dynamic surface variations under reaction conditions for catalysts are often not taken into account (for example, surface segregation processes). Assumptions are mainly made on the basis of the average bulk structure that leads to misleading conclusions on the active phase, active sites, role of promoters or deactivation mechanisms, thus hindering further optimisation and development of catalysts. As an example, despite intensive studies of high temperature water gas shift (HTWGS) iron-based catalysts, the nature of active sites and the HTWGS reaction mechanism (redox vs. associative) are still subject to ongoing debate. Open questions and contradictory results concern the interaction of chromium oxide with iron oxide (the formation of a Cr-enriched shell around the iron oxide phase, magnetite, vs. strong interaction of Cr3+ with magnetite) as a way of stabilising iron oxide against sintering (28, 29, 43).

To study catalysts, often operando IR spectroscopy is combined with bulk techniques such as XAS, Raman and XRD. Operando IR spectroscopy is a crucial technique for studying surface adsorbed species, particularly important for revealing reaction intermediates (39, 44); however, it does not provide insights into the redox properties of the catalyst surface. One of the most important factors that governs the catalytic activity, selectivity and stability of catalysts in particular for redox reactions is the redox properties (the oxidation state and interplay between oxidation states during the reaction) of the surface.

XPS is one of the most powerful spectroscopic tools for obtaining chemical information about the surfaces of solid materials. It is based on the photoelectric effect theory (the ejection of electrons from the surface in response to incident photons). This technique is also known as electron spectroscopy for chemical analysis (ESCA). The ESCA term was introduced in 1967 (45) by the Swedish physicist Kai Siegbahn, who in 1954 recorded the first high energy resolution XPS spectrum of cleaved NaCl (46), to highlight the importance of obtaining chemical information like oxidation states for materials investigated.
with XPS. In 1981 Siegbahn was awarded the Nobel Prize in Physics as acknowledgment “for his contribution to the development of high-resolution electron spectroscopy”.

Traditionally, XPS is known to be an ultra-high vacuum (UHV) technique that can only operate at pressures below $10^{-9}$ mbar because of the strong scattering of photoelectrons by gas molecules. However, the first ‘non-UHV’ XPS experiments were performed in the Kai Siegbahn research group (47, 48). In 1973 Kai Siegbahn together with his son Hans Siegbahn published a study in which the first spectrum of a liquid (formamide) was presented (47). In 1979 Wyn Roberts published a study entitled “A ‘High-Pressure’ Electron Spectrometer for Surface Studies”, where he described the development of the first photoelectron spectrometer capable of studying solid surfaces in the presence of gas up to 1.3 mbar (49). A new type of photoemission spectrometer, based on several differential pumping stages with electrostatic lenses between the sample surface and the photoelectron detection, was developed by the groups from the Advanced Light Source, Berkeley, California, USA, and the Fritz Haber Institute of the Max Planck Society, Berlin, Germany (50). A schematic representation of the differential pumping system of the NAP-XPS setup from the Innovative Station for In Situ Spectroscopy (ISISS) beamline, BESSY II, is given in Figure 3. This setup enables operation at pressures close to ambient (up to 20 mbar).

Although these pressures are still far away from pressures used in industrial fixed-bed flow reactors, NAP-XPS experiments can model the reaction environment and allow the dynamic variations of a catalyst surface and its catalytic properties to be studied (52–56). Today, NAP-XPS is the most powerful technique for studying the surface of redox catalytic materials under process conditions (57), particularly when employing synchrotron radiation as a light source. Using the tuneability of synchrotron radiation, different information depths can be studied by NAP-XPS ranging from ~0.5 nm to 3 nm, which is not achievable with routinely available lab-based XPS. Table II summarises the most commonly used soft X-ray synchrotron beamlines, where opportunities for operando and in situ NAP-XPS, ambient pressure XPS (AP-XPS) and XAS studies of catalysts are provided.

To gain improved understanding of redox-based catalytic systems, one can combine in situ NAP-XPS or near edge X-ray absorption fine structure (NEXAFS) for surface-specific chemical information with in situ Raman, XRD or XAS studies which provide information on local coordination environment, structure and oxidation state of the bulk of a material.

3. In Situ and Operando Studies Providing Information on Surface and Bulk Properties of Working Catalysts

There are only a few operando studies reported in the literature in which XAS, XRD or Raman and NAP-XPS were performed on the same catalytic system, giving valuable insights into bulk versus...
Table II  Soft X-Ray Synchrotron Beamlines (Worldwide) that Provide Opportunities for Operando and In Situ Studies of Catalysts (NAP-XPS/AP-XPS and XAS)

<table>
<thead>
<tr>
<th>Beamline</th>
<th>Energy range, keV</th>
<th>Techniques</th>
<th>Facility name</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPO</td>
<td>0.05–1.5</td>
<td>NAP-XPS</td>
<td>SOLEIL</td>
<td>Paris, France</td>
</tr>
<tr>
<td>23-ID-2 in situ and operando Soft X-ray Spectroscopy</td>
<td>0.25–2</td>
<td>AP-XPS, XAS</td>
<td>National Synchrotron Light Source</td>
<td>Brookhaven National Laboratory, US</td>
</tr>
<tr>
<td>9.3.2 Ambient-Pressure Soft X-Ray Photoelectron Spectroscopy (S-APXPS)</td>
<td>0.2–0.9</td>
<td>AP-XPS, XAS</td>
<td>Advanced Light Source</td>
<td>Lawrence Berkeley National Laboratory, US</td>
</tr>
<tr>
<td>B07</td>
<td>0.05–2.8</td>
<td>NAP-XPS, NEXAFS</td>
<td>Diamond Light Source</td>
<td>Oxfordshire, UK</td>
</tr>
<tr>
<td>HIPPIE</td>
<td>0.3–2000</td>
<td>AP-XPS</td>
<td>MAX IV 3 GeV storage ring</td>
<td>MAX IV, Sweden</td>
</tr>
<tr>
<td>SPECIES</td>
<td>0.027–1.5</td>
<td>AP-XPS, NEXAFS, XAS</td>
<td>MAX IV 1.5 GeV storage ring</td>
<td>MAX IV, Sweden</td>
</tr>
<tr>
<td>ISIS8</td>
<td>0.08–2.0</td>
<td>NAP-HE-XPS</td>
<td>BESSY II</td>
<td>Helmholtz-Zentrum Berlin, Germany</td>
</tr>
<tr>
<td>EMIL</td>
<td>0.08–10</td>
<td>PES, PEEM, HAXPES, XES, XRF, XRD, ambient-pressure-HAXPES</td>
<td>BESSY II</td>
<td>Helmholtz-Zentrum Berlin, Germany</td>
</tr>
<tr>
<td>BL24 CIRCE</td>
<td>0.1–2</td>
<td>NAP-XPS</td>
<td>ALBA</td>
<td>Barcelona Synchrotron Park, Spain</td>
</tr>
<tr>
<td>Mobile station operates between PHOENIX X07MA and SIM X11MA beamlines</td>
<td>0.005–8</td>
<td>APPES</td>
<td>Swiss Light Source</td>
<td>Paul Scherrer Institute, Switzerland</td>
</tr>
</tbody>
</table>

surface properties. As examples, recent studies by Israel Wachs’ group demonstrate the importance of employing a surface sensitive technique like NAP-XPS for studying HTWGS and shed light on iron-based HTWGS catalysts in combination with in situ XAS and Raman (28, 29). Looking at data from the respective techniques in isolation could lead to wrong conclusions. Examples from our own work at the Institute of Materials Chemistry, TU Wien, Austria, comprise preferential CO oxidation (PROX) on Co3O4 and CeO2-Co3O4 catalysts studied by operando NAP-XPS and XAS (30). During PROX both the bulk and surface of Co3O4 were fully oxidised up to 523 K, while in CO the surface reduction of Co3O4 occurred from 373 K. Preferential oxidation of CO to CO2 in an excess of H2 was suggested to follow predominantly the Mars-van-Krevelen mechanism. Promotion of Co3O4 with 10 wt% CeO2 increased the reduction temperatures in CO and H2 and enhanced the PROX activity. Since CeO2 is a less active material, this can only be explained by higher activity of the Co-O-Ce ensembles and creation of oxygen vacancies as detected by NAP-XPS in Ce 3d spectra.

In another recent work, we utilised NAP-XPS to study the surface composition of Cu-promoted Ni/ZrO2 catalysts in methane atmosphere at mbar pressures and relevant reaction temperatures. An important result from this work was that the surface composition changed from a Cu-enriched state after reduction to a Ni-enriched surface in methane at T>~700 K which was the active state (58). The surface segregation of Ni0 was driven by the strong interaction between Ni and carbon and was corroborated by density functional theory (DFT) calculations (59).
4. **Operando FTIR, XAS and NAP-XPS Investigation of Methanol Steam Reforming on Pd-Based Intermetallic Compounds: Surface vs. Bulk**

An exemplary study will be discussed here in more detail to illustrate the insights into catalyst structure and composition under reaction conditions and the reaction mechanism gained from the *operando* approach using surface sensitive methods. In the discussed work we aimed at obtaining a detailed understanding of the fundamental processes occurring at the surface and in the bulk of ZnO and Ga2O3 supported Pd nanoparticles applied as methanol steam reforming (MSR) catalysts (60–69). In addition, the work should contribute to the improvement and development of active, selective and stable catalysts for the production of clean (CO-free) hydrogen, which can be used for example in proton exchange membrane fuel cells.

Our goal was to understand the selectivity of the desired MSR reaction (Equation (i)) producing CO2 and H2 and the unwanted methanol decomposition (MDC) (Equation (ii)) yielding CO and H2, by combining information on surface and bulk composition, structure and electronic properties under reaction conditions obtained by *operando* XAS, XRD and NAP-XPS with mechanistic understanding obtained by Fourier transform infrared (FTIR) spectroscopy.

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + 3\text{H}_2 \quad (i) \\
\text{CH}_3\text{OH} & \rightleftharpoons \text{CO} + 2\text{H}_2 \quad (ii)
\end{align*}
\]

**4.1 Active and Selective Phase Under Reaction Conditions: *Operando* XAS and NAP-XPS**

By *in situ* quick-extended X-ray absorption fine structure (QEXAFS) spectroscopy we followed in real time how the Pd/ZnO nanoparticles dynamically adapt to the surrounding atmosphere (62), which presented the first direct proof for the formation of PdZn alloy in methanol/water starting from Pd/ZnO without prior high temperature reduction. PdZn alloying occurred via spillover and reduction of the ZnO by H2 generated in the reaction and was accompanied by a simultaneous change in reactivity, from an unselective state characteristic of metallic Pd to a highly selective state due to the formation of a PdZn intermetallic compound (IMC). The XAS near-edge region is shown in Figure 4 and resembles the progressive transition from the structural and electronic properties characteristic of Pd to those of the tetragonal Pd:Zn IMC with a 1:1 stoichiometry occurring with time on stream in methanol/water. By combining time resolved *in situ* QEXAFS with FTIR spectroscopy we could clarify the processes occurring when switching...
between reducing (methanol, H₂) and oxidising (alloy formation and decomposition with ZnO island formation on the Pd nanoparticle surface) atmospheres (62). The studies on powder catalysts were complemented by surface science work on single crystal-based UHV grown model systems (PdZn surface alloys), which were in excellent agreement with the PdZn/ZnO powder catalysts and DFT calculations (67).

For the related system Pd/Ga₂O₃ the combination of techniques of different surface sensitivity, namely in situ XRD, synchrotron-based in situ XPS, FTIR and XAS, were used to identify the formation of the MSR-selective intermetallic Pd₂Ga phase under relevant reaction conditions as well as upon reduction at medium temperature around 573–673 K (63, 65). One of the major advantages of XAS in catalysis is its suitability for in situ studies, due to the high penetrating power of the hard X-rays used. Fitting the extended fine structure function identified Pd₂Ga as the active phase present under MSR conditions (65). Interestingly, different intermetallic phases exhibited a different reactivity (63) with Pd₂Ga showing the best catalytic performance.

Since the catalytic properties of a material are mainly determined by its composition and the structure and properties of the surface and near-surface region, we have further characterised the Pd₂Ga/Ga₂O₃ catalyst by applying synchrotron radiation-based NAP-XPS as a surface sensitive technique. Upon reduction in H₂ or in the H₂ produced from methanol a species attributed to zerovalent Ga evolved in the Ga 3d binding energy range shifted by 2.2 eV relative to Ga³⁺, whereas the Pd 3d signal was shifted by ca. 0.5 eV to higher values upon IMC formation because of the charge transfer from Ga to Pd (Figure 5). The composition of the surface was in very good agreement with the Pd:Ga stoichiometry 2:1 (Figure 5). Depth profiling by varying the incident photon energy and thereby the kinetic energy of emitted photoelectrons reveals equal relative amounts of Ga⁰ and Pd with a ratio of about 2:1 and therefore uniform distribution in the experimentally accessible depth range (63).

4.2 Stability and Origin of Unwanted CO Formation: Operando FTIR

Special attention was paid to the stability of the PdZn and Pd₂Ga surfaces. Importantly, in situ FTIR spectroscopic results reveal for the very first time the limited stability of the intermetallic surfaces (PdZn and Pd₂Ga) under MSR reaction conditions (61, 63). Besides intermetallic PdZn and Pd₂Ga the presence of domains of metallic Pd catalysing the unwanted methanol decomposition to CO and H₂ was detected in both catalysts (Figure 6). Metallic Pd and Pd present within the IMC can be distinguished by CO adsorption. While linear, bridge and hollow bonded CO are characteristic for adsorption

![Figure 5](https://doi.org/10.1595/205651318X15234323420569)
Fig. 6. Time-resolved in situ FTIR spectra obtained in flowing methanol over Pd\textsubscript{2}Ga/Ga\textsubscript{2}O\textsubscript{3} at: (a) 373 K; and (b) 523 K reaction temperatures after reduction at 673 K. The CO stretch vibration range is displayed for spectra recorded every 5 min in 1 vol% methanol in He. Besides on-top CO adsorbed on intermetallic Pd\textsubscript{2}Ga, bridge and hollow bonded CO on metallic Pd is present indicating partial instability of Pd\textsubscript{2}Ga in the methanol feed, which is more pronounced at lower reaction temperatures. Adapted with permission from (61)

4.3 Insights into the Reaction Mechanism: Operando FTIR

Vibrational spectroscopy was applied to investigate the reaction mechanism of MSR over Pd\textsubscript{2}Ga/Ga\textsubscript{2}O\textsubscript{3} (64). The mechanistic study explored the interaction of the catalyst with methanol and water by combining temperature-programmed, steady state and concentration modulation FTIR experiments. A different surface chemistry on low temperature reduced (unselective) Pd/Ga\textsubscript{2}O\textsubscript{3} and high temperature reduced (selective) Pd\textsubscript{2}Ga/Ga\textsubscript{2}O\textsubscript{3} was detected. Formation of intermediate surface formate species was observed at much lower temperatures on Pd\textsubscript{2}Ga/Ga\textsubscript{2}O\textsubscript{3} (Figure 7) and was attributed to reactive oxygen sites in the Ga\textsubscript{2}O\textsubscript{3} surface modified by the high temperature reduction and IMC formation. The presence of H\textsubscript{2}O strongly affected the stability of the formates.

A reaction mechanism involving the interconversion of formate species was proposed, as described in more detail elsewhere (64). This work provides important new insights into the reaction mechanism of MSR and emphasises the crucial role of the oxide support. The reaction seems to predominantly proceed on the reduced Ga\textsubscript{2}O\textsubscript{3} surface near the IMC nanoparticles or at the interface and is promoted by the intermetallic particles. An additional and necessary effect of IMC formation is the slowdown of the unwanted MDC to CO and H\textsubscript{2} on metallic Pd.

4.4 Reactivity of the Oxide Support

Concerning the reactivity of the oxide support, special attention was paid to the role of oxygen vacancies. This was investigated by applying
different reducing pretreatments with subsequent quantification of vacancy sites by titration with O\textsubscript{2}. This approach was successfully applied to study the defect chemistry of Ga\textsubscript{2}O\textsubscript{3} (68, 69). Strongly related to the work on MSR, the reactivity of Ga\textsubscript{2}O\textsubscript{3} for reverse water gas shift (RWGS), a follow-up reaction of the MSR products CO\textsubscript{2} and H\textsubscript{2} and potential source of unwanted CO, was investigated by combining FTIR spectroscopy and temperature-programmed methods. By looking in detail at the interaction of Ga\textsubscript{2}O\textsubscript{3} in different defective states in terms of nature and concentration of vacancies with H\textsubscript{2}, CO, CO\textsubscript{2}, water and their mixtures, the reactivity of Ga\textsubscript{2}O\textsubscript{3} for water gas shift (WGS) and RWGS was explored. Ga\textsubscript{2}O\textsubscript{3} is catalytically active for these reactions, with the reaction most likely proceeding via oxygen vacancies. Ga\textsubscript{2}O\textsubscript{3} on its own (without metal promotion) is capable of H\textsubscript{2} activation; formed oxygen vacancies can then be re-oxidised by CO\textsubscript{2} yielding CO in the catalytic RWGS reaction.

The molecular level understanding of the reaction mechanism, the factors controlling selectivity and the correlation of catalyst structure and composition with catalytic properties enable a more scientific approach to catalyst optimisation on a rational basis. Only the combination of various \textit{operando} methods providing complementary information on the composition of the catalyst surface, the reacting species and the catalytic properties allowed an almost complete picture of the surface chemistry of PdZn/ZnO and Pd\textsubscript{2}Ga/Ga\textsubscript{2}O\textsubscript{3} MSR catalysts to be obtained.

5. Perspectives: A Combined Approach for the Successful Development of the Next Generation of More Efficient Catalysts

The work described in this paper clearly demonstrates the importance of combining several \textit{operando} techniques in studying catalysts under steady state as well as dynamic conditions for revealing reaction mechanisms and for finding correlations between the structure and surface composition and the activity and selectivity of catalysts. In particular surface-sensitive information is crucial. Moreover, the presented results highlight the great potential of \textit{in situ} NAP-XPS for obtaining redox and structural information on the (near) surface changes of catalytic materials for different information depths.
For the successful development of the next generation of more efficient catalysts, it is essential to combine three approaches (Figure 8): (a) high-throughput synthesis in combination with correlating catalytic performance with the electronic and geometric structure of synthesised materials (structure-performance relationship); (b) reaction kinetic studies; (c) in situ and operando investigation of catalysts under reaction conditions. Using such a combined approach and interconnecting the obtained information is a powerful research tool that can boost the research and development of more efficient catalysts with the desired catalytic properties.

In situ / operando spectroscopy & diffraction

**High-throughput synthesis**

**Reaction kinetics**

Fig. 8. Combined approach, which includes high-throughput synthesis, reaction kinetic studies and in situ and operando spectroscopy, for catalyst development

### Glossary of Techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
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<tr>
<td>APPES</td>
<td>ambient pressure photoelectron spectroscopy</td>
</tr>
<tr>
<td>AP-XPS</td>
<td>ambient pressure X-ray photoelectron spectroscopy</td>
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<tr>
<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
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<tr>
<td>ESCA</td>
<td>electron spectroscopy for chemical analysis</td>
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<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>HAXPES</td>
<td>hard X-ray photoelectron spectroscopy</td>
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<tr>
<td>HRXRD</td>
<td>high-resolution X-ray diffraction</td>
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<td>IR</td>
<td>infrared</td>
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<td>IXS</td>
<td>inelastic X-ray scattering</td>
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<tr>
<td>NAP-HE-XPS</td>
<td>near-ambient pressure high energy X-ray photoelectron spectroscopy</td>
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<td>NAP-XPS</td>
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<td>NEXAFS</td>
<td>near edge X-ray absorption fine structure</td>
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<td>PDF</td>
<td>Pair distribution function</td>
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<td>PEEM</td>
<td>photoemission electron microscopy</td>
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<td>PES</td>
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RIXS  resonant inelastic X-ray scattering
RXES  resonant x-ray emission spectroscopy
SAXS  small angle X-ray scattering
UV-Vis ultraviolet-visible
XANES X-ray absorption near edge structure

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References

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Cycling Non-Aqueous Lithium-Air Batteries with Dimethyl Sulfoxide and Sulfolane Co-Solvent

Evaluating influence of sulfolane on cell chemistry

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Despite considerable research efforts, finding a chemically stable electrolyte mixture in the presence of reduced oxygen species remains a great challenge. Previously, dimethyl sulfoxide (DMSO) and sulfolane (tetramethylene sulfone (TMS))-based electrolytes were reported to be stable for lithium air (Li-O_2) battery applications. Recently lithium hydroxide (LiOH) based chemistries have been demonstrated to involve supressed side reactions in water-added ether- and DMSO-based electrolytes. Herein, we investigate the impact of DMSO-based electrolyte and sulfolane co-solvent on cell chemistry in the presence of water. We found that DMSO-based electrolyte leads to formation of a peroxide-hydroxide mixture as discharge products and the removal of both LiOH and lithium peroxide (Li_2O_2) on charging from 3.2–3.6 V (vs. Li^+/Li) is observed. In the presence of sulfolane as co-solvent, a mixture of Li_2O_2 and LiOH is formed as major discharge products with slightly more LiOH formation than in the absence of sulfolane. The presence of sulfolane has also significant effects on the charging behaviour, exhibiting a clearer 3 e^-/O_2 oxygen evolution reaction profile during the entire charging process. This work provides insights into understanding the effects of the primary solvent on promoting LiOH formation and decomposition in lithium iodide (LiI) mediated non-aqueous Li-O_2 batteries.

1. Introduction

The non-aqueous Li-O_2 battery has drawn considerable scientific attention due to its higher theoretical energy density compared to the values achieved by conventional Li-ion batteries (1–3). The successful operation of a Li-O_2 battery necessitates the reversible formation and decomposition of a discharge product, typically Li_2O_2 (4–6). However, this process is often limited by the considerable parasitic reactions caused by highly reactive reduced oxygen species, reaction intermediates (such as lithium superoxide (LiO_2)) and the final product Li_2O_2 (7). These undesired reactions are accelerated at high charge overpotentials (8, 9) and addressing such a fundamental issue remains a major challenge hindering its commercial implementation. One promising strategy to address this issue is the formation of chemically more stable discharge products, so that fewer side-reactions occur. Recently, LiOH formation and...
decomposition has been proposed as an alternative mechanism to cycle non-aqueous Li-O₂ batteries using LiI as a redox mediator, in a water-added ether-based electrolyte (10), and with ruthenium-catalysed cells with water-added DMSO-based electrolyte (11).

The search for chemically stable electrolytes against reactive reduced oxygen species with the appropriate physicochemical properties is another crucial research topic in this field. In this regard, a wide range of solvents such as carbonates, ethers and sulfones have been investigated so far (7, 12, 13). In particular, sulfur-containing solvents such as DMSO and sulfolane have shown to be promising candidates for Li-O₂ batteries because they possess high oxidation potentials (4.8 V and 5.6 V vs. Li⁺/Li, respectively), and high boiling points (189°C and 285°C, respectively) (14–16). Although initial studies have reported good reversibility of cells with either DMSO or sulfolane-based electrolytes via formation and removal of Li₂O₂, various issues related to cell performance were reported in later studies (13, 17). In the case of DMSO, its electrochemical instability with Li metal anodes has been reported as a major issue. It has been suggested that the addition of N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (PyR₁₄TFSI) ionic liquid can mitigate this issue (18) through the formation of a stable solid electrolyte interphase (SEI) via TFSI⁻ anion decompositions (19) as well as lowering the charging overpotential by stabilising superoxide species (20). Similarly, sulfolane-based electrolytes have shown to promote the reversible formation and removal of Li₂O₂ but capacity fading was observed due to the accumulation of side-reaction products such as LiOH and lithium carbonate (Li₂CO₃) (13).

Early chemistries reported for DMSO-based electrolytes were equivalently described as promoting Li₂O₂ with significant amounts of side-reactions (17, 21). In order to increase stability the formation of LiOH as discharge product has been attempted with DMSO-based electrolytes. Ru-catalysed Li-O₂ cells cycled with LiTFSI/DMSO in the presence of added water exhibited a dominant LiOH chemistry with suppressed side-reactions, but the charging process undergoes dimethyl sulfone (DMSO₂) accumulation rather than oxygen evolution reaction (11).

In this report, we investigate the effect of sulfolane as co-solvent in DMSO based electrolytes containing LiI as redox mediator, LiTFSI salt with water and PyR₁₄TFSI as additives in non-aqueous Li-O₂ batteries. A range of ex situ and operando techniques were used to evaluate the influence of sulfolane on cell chemistry, and especially whether it promotes dominant and reversible LiOH chemistry.

### 2. Experimental

Electrospun carbonised polyacrylonitrile (C-PAN) electrodes were prepared using a standard recipe for preparation of carbon nanofibers with an electrode diameter of 18 mm and the typical carbon loading around 1.2 mg cm⁻². Polyacrylonitrile (Sigma-Aldrich, average M_w = 150 k) was dissolved at 7.5 wt% in dimethylformamide (DMF) and electrospun using a custom-built device onto aluminium foil wrapped on a rotating drum at >1 kV cm⁻¹ field strength. The resulting electrospun mat was dried in a vacuum oven at 50°C for 12 h, then stabilised by heating in air at 5 K min⁻¹ up to 300°C and held for 1 h. Sections were cut to size, allowing for shrinkage, and carbonised in flowing N₂ by heating 10 K min⁻¹ to 1200°C and held for 2 h. The resulting electrodes were dried at 110°C under vacuum for 20 h in a Büchi oven and stored in a dry argon glove box for further use.

Electrodes were assembled into cells for testing in an argon glove box using EL-CELL differential electrochemical mass spectrometry (DEMS) hardware with 1.55 mm EL-CELL glass fibre separator, lithium metal anode (Alfa Aesar, 99.9% metals basis) and 360 μl of electrolyte. The electrolyte used is a mixture of 5000 ppm water, 0.9 M PyR₁₄TFSI, 0.7 M LiTFSI and 0.05 M LiI in DMSO solvent and a 1:1 DMSO:sulfolane mole ratio for the sulfolane-containing electrolyte. Added water content was carefully chosen on the basis of recent studies (10, 11) and the water content of 5000 ppm is sufficient to promote dominant LiOH formation up to the discharge capacity of 5.35 mAh. Cell temperature was controlled at 25°C and all cell testing was potential limited at 2.2–3.7 V. Exhaust gas was continuously analysed using Stanford Research Systems UGA/RGA200 with a heated capillary and channel electron multiplier (CEM) gain 200. Cell purge gas flow rate was 5 ml min⁻¹ at 1.5 bar with cell charge performed in pure argon and cell discharge in 20% oxygen in argon. Mass signal response was calibrated against standard concentrations to confirm linearity while background levels and drift were subtracted using a linear fit before and after the target dataset.
X-ray diffraction (XRD) measurements were carried out using a Panalytical Empyrean with Cu Kα1 radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) images were recorded with a Hitachi S-5500 in-lens field emission electron microscope. Post-mortem electrode characterisations were performed with samples to avoid air exposure during transfer and data acquisition. In the case of SEM, electrodes were exposed to air for a maximum of 20 s prior to insertion into the high vacuum chamber. For nuclear magnetic resonance (NMR), electrodes were scrapped and packed in an argon glovebox.

Solid-state NMR data were acquired at 11.7 T on a Bruker Avance™ III HD spectrometer using a 2.5 mm HX probehead. A rotor synchronised Hahn-echo pulse sequence was used to acquire ¹H and ⁷Li magic angle spinning (MAS) spectra with a spinning speed of 30 kHz, with recycle delays of 150 s and 20 s for ¹H and ⁷Li, respectively. Radiofrequency (RF) field strength was 100 kHz and either 256 transients for ¹H or 128 transients for ⁷Li were acquired. ¹H and ⁷Li chemical shifts were externally referenced to solid adamantane at 1.87 and Li₂CO₃ at 0 ppm, respectively.

(a) (b) (c) (d)

![Graphs showing capacity and potential](image)

![XRD patterns](image)

**Fig. 1.** Electrochemical first discharge and charge profiles of Li-O₂ batteries using C-PAN electrodes cycled with 5000 ppm water-added 0.9 M Pyr14TFSI/0.7 M LiTFSI/0.05 M LiI/DMSO: (a) with; and (b) without sulfolane co-solvent, and their corresponding XRD patterns of cycled C-PAN electrodes, shown as (c) and (d), respectively. The cycling rates are all 0.1 mA cm⁻² (160 mA g⁻¹). The XRD patterns of reference LiOH and Li₂O₂ compounds (blue and green traces and also shown as blue triangles and green diamonds on the top of the XRD patterns, respectively) are also shown for comparison.
3. Results and Discussion

Figures 1(a) and 1(b) show the galvanostatic discharge and charge profiles of the first cycle of Li-O\textsubscript{2} cells using the electrolyte 0.9 M Pyr\textsubscript{14}TFSI/0.7 M LiTFSI/0.05 M LiI/DMSO with 5000 ppm water added in the presence and absence of a sulfolane co-solvent, respectively. In both cases a similar discharge plateau was observed at around 2.7 V, although slightly lower (2.6 V) for the sulfolane-containing cell. The charge process was noticeably different; the cell without sulfolane charged in a single plateau from 3.4 V to 3.6 V, whereas the sulfolane-added cell showed a more sloped charge profile, starting at 3.2 V and finishing at 3.7 V. The observed oxygen reduction voltages are consistent with the values generally reported in the literature (13, 22) as well as the charging voltages with that of LiI-mediated oxygen evolution reaction, essentially the redox potential of I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-} (3.5 V versus Li/Li\textsuperscript{+}) in DMSO-based electrolytes. In the absence of the LiI mediator, the cell charging voltages in the cells DMSO or sulfolane-based electrolyte usually exceed 4.0 V (16, 22).

The XRD patterns of electrodes after the first discharge in the presence and absence of sulfolane are shown in Figures 1(c) and 1(d), respectively. Both cases indicate the formation of a mixture of LiOH and Li\textsubscript{2}O\textsubscript{2} as discharge product. Similarly, SEM images (Figures 2(a) and 2(c)) of the corresponding discharged electrodes reveal two distinct morphologies, suggesting a mixture of discharge products. As previously reported, distinguishing LiOH and Li\textsubscript{2}O\textsubscript{2} mixtures by morphologies is possible if the grown particle size is large enough; electrochemically produced LiOH typically presents various morphologies, including cones, discs, large sheets and flowers (10, 23), whereas Li\textsubscript{2}O\textsubscript{2} typically displays toroidal and platelet shapes (5). After charging, XRD patterns in both cases (Figures 2(c) and 2(d)) show that the intensity of reflections corresponding to LiOH and Li\textsubscript{2}O\textsubscript{2} decreases significantly, more distinctly in the sulfolane-containing case, indicating that most
of the crystalline discharge products are removed. The SEM images of the charged electrodes indicate that some solid residues remain adsorbed on the surface of the carbon electrode as particles and thin films. In the sulfolane-absent case (Figure 2(b)), most of the discharge products appear to be removed from the carbon fibres of C-PAN electrodes, whereas sulfolane-containing cells (Figure 2(d)) display electrode surfaces more noticeably covered by particles and thin films after charging.

To further characterise the chemical nature of reaction products formed during cell cycling, solid-state \(^1\)H and \(^7\)Li NMR measurements (Figure 3) were performed on the cycled electrodes characterised by XRD and SEM. In both sulfolane-absent and present cases, the \(^7\)Li NMR spectra of discharged electrodes (red and orange traces, respectively, in Figure 3(b)) show a single broad resonance centred at 0.7 ppm, consistent with the presence of a mixture of Li\(_2\)O\(_2\) (0.4 ppm) and LiOH (1.1 ppm). The corresponding discharged \(^1\)H NMR spectra exhibit a major resonance at ~1.5 ppm, assigned to lithium hydroxide, more dominant and intense in cells containing sulfolane, and a minor one at 8.3 ppm, assigned to formate (10, 24). Other distinct resonances are present in the range 1–4 ppm, with the resonances at 2.5 ppm and 1–2 ppm attributed to DMSO and Pyr\(_{14}\)TFSI of residual electrolyte, in agreement with the literature (25). Despite rinsing the electrodes after cell disassembly with acetonitrile and overnight drying under vacuum, the highly viscous nature of the ionic liquid-containing electrolyte inevitably results in severe adsorption of Pyr\(_{14}\)\(^+\) cations onto the C-PAN electrode after cycling, showing significant contributions on the \(^1\)H NMR spectra. Furthermore, decomposition of Pyr\(_{14}\)\(^+\) cations by superoxide attack is known to generate various \(^1\)H resonances in a 4–6 ppm range (highlighted in magenta in Figure 3(a)) (25). After charging, the \(^7\)Li NMR spectra of both cases (Figure 3(b)) are consistent with the removal of Li-containing species from the electrodes, whereas the \(^1\)H NMR spectrum shows that the intensity of the LiOH peak is significantly reduced. These observations are consistent with the formation and removal of a mixture of LiOH and Li\(_2\)O\(_2\) from the electrodes during cell discharge and charge, respectively. The comparison of the

![Fig. 3. Solid-state: (a) \(^1\)H; and (b) \(^7\)Li MAS NMR spectra of the cycled C-PAN electrodes from cells using 5000 ppm water-added 0.9 M Pyr\(_{14}\)TFSI/0.7 M LiTFSI/0.05 M LiI/DMSO electrolyte with and without sulfolane co-solvent. The magenta-shaded areas on the \(^1\)H spectra indicate the \(^1\)H shifts of Pyr\(_{14}\)\(^+\) ions and their related decomposed chemical species and residual water. A broad \(^1\)H resonance at ~4 ppm is assigned to protons in the C-PAN electrode](https://doi.org/10.1595/205651318X15233499272318)
charged $^1$H NMR spectra of both sulfolane present and absent cases suggest a higher extent of parasitic reactions occurring in the former case, in good agreement with the SEM data.

In order to investigate the charging mechanism involved in removing the LiOH and Li$_2$O$_2$ mixture, operando DEMS experiments were performed. The Faradaic efficiency profiles of the oxygen evolution reaction (OER) during galvanostatic charging of LiI-mediated cells with and without sulfolane are shown in Figures 4 and 5, respectively. In both cases, oxygen evolution is observed from the beginning of charge at approximately 3.4 V with an e$^-$/O$_2$ molar ratio at around three for the first half of the charge capacity. This oxygen evolution rate is consistent with the decomposition of equivalent amounts of Li$_2$O$_2$ through a two-electron and LiOH through a four-electron mechanism, respectively (Equations (i)–(iv)):

\begin{align*}
3\text{I}^- & \rightarrow \text{I}_3^- + 2e^- \\
\text{Li}_2\text{O}_2 + \text{I}_3^- & \rightarrow 2\text{Li}^+ + 3\text{I}^- + \text{O}_2 \uparrow \\
6\text{I}^- & \rightarrow 2\text{I}_3^- + 4e^- \\
4\text{LiOH} + 2\text{I}_3^- & \rightarrow 4\text{Li}^+ + 6\text{I}^- + 2\text{H}_2\text{O} + \text{O}_2 \uparrow
\end{align*}

Beyond the midpoint of charge capacity, the DEMS profiles in both cases are noticeably different; in the sulfolane-absent case, the oxygen evolution rate is reduced continuously as the cell voltage rises above 3.5 V. This suggests that the charging process deviates from the aforementioned desirable oxidation reactions and side reactions involving less or no O$_2$ evolution pathways may occur, such as the formation of iodo-oxygen species (26, 27), and dimethyl sulfoxide (DMSO$_2$) (11). In the case of cells containing sulfolane the oxygen evolution rate is maintained at an overall Faradaic efficiency.

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Fig. 4. Operando differential electrochemical mass spectrometry measurements on charging the Li-O$_2$ batteries on the first (left) and second (right) cycle using a 5000 ppm water-added 0.9 M Pyr$_{14}$TFSI/0.7 M LiTFSI/0.05 M LiI/DMSO electrolyte with sulfolane co-solvent. The left and right axes indicate the detected oxygen (normalised) and CO$_2$ (not normalised) evolution rates, shown as blue and red traces, respectively.
of 3 e-/O₂ with a slight deviation until the end of charge, 3.7 V. In both cases, the DEMS profiles are reproducible for the second charge with no significant CO₂ evolution detected. The observation of a 3 e-/O₂ OER process rather than a 2 e-/O₂ expected for Li₂O₂ decomposition, alongside the absence of CO₂ evolution and consistency in charging DEMS profiles might be associated with the partial removal of LiOH during the OER in cells containing sulfolane as co-solvent but further work is required to understand the charging mechanisms.

4. Conclusions

In this report, we have investigated the effect of sulfolane as co-solvent in Li-O₂ cells cycled with LiI/H₂O/LiTFSI/Pyr14TFSI/DMSO electrolyte. A mixture of Li₂O₂ and LiOH is formed during cell discharge, with the presence of sulfolane slightly increasing the formation of LiOH as shown by solid-state ¹H NMR and SEM. On charging, the decomposition of both Li₂O₂ and LiOH is observed with oxygen evolution being monitored by DEMS measurements. The observation of residual discharge products after a full charge confirms the effect of parasitic reactions to the faradaic efficiency. Further work is required to optimise the more stable LiOH chemistry, and to understand the associated OER mechanisms for the successful commercial development of rechargeable Li-O₂ batteries.

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References


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Stress Whitening in Polyester Melamine Coatings

Role of time and temperature in industry thermosetting polymer coatings

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Stress whitening is a long-standing problem and scientific work has focused on evaluating causes of this in bulk polymer systems. In this paper we focus on this optical defect exhibited by a complex thermosetting polyester melamine coating system used extensively in the pre-coated metal industry. There are several mechanisms proposed for how stress whitening occurs and hence there is uncertainty over the causes in the systems mentioned. The most likely explanation given to date is that a number of proposed micro-mechanisms exist, which one is occurring is entirely dependent on the system being investigated. The work presented shows that the presence of dissimilar particles is the cause of the stress whitening. The proposed mechanism for whitening and its disappearance in this case is a time and temperature dependent change in density, i.e. cracking or voiding, where the cracks are outside the range that scatters light with an increase in temperature.

1. Introduction

1.1 Pre-coated Steel

Pre-coated steel, produced by coil coating, has uses within a number of industry sectors including architecture, transport and the domestic appliance (DA) market (1–3). The coil coating market in Europe uses approximately 180–200 kilotonnes of paint per annum which is worth almost €1 billion (1). This work focuses on the requirements of the DA market in which polyester melamine pre-coated systems are utilised. Pre-coated sheets are formed during the fabrication of panels into the desired shape. During this forming stage high strains will be experienced by the coating. Forming can lead to various defects including cracking, tearing and voids (4–7). In some systems a visual problem called stress whitening can arise from these defects (3).

Pre-coated steel consists of several layers. In this instance the substrate is pre-treated cold rolled steel with a two-coat polyester system on top, as seen in Figure 1. The basecoat provides the colour and other functional features such as corrosion protection, the top coat acts as a

---

Fig. 1. Schematic diagram of a domestic appliance (DA) coating system
further barrier layer as well as adding any surface finishes required by the customer (1, 8). The basecoat is grey silver and the topcoat is a clear lacquer. Both coatings consist of a polyester resin crosslinked with hexa(methoxymethyl)melamine (HMMM), standard additives such as a catalyst and required functional additives, such as a structuring agent (1, 8). The polyester crosslinks with the melamine via a transetherification reaction which is thermally activated (1, 8). It is very important that the correct temperature and dwell time are used for the material, if the temperature is too low then the melamine will not crosslink enough and the melamine is also found not to distribute evenly (8). If the temperature is too high or the dwell time too long then the coating over-crosslinks, meaning it is too rigid for forming and the coating will crack, the coating often becomes brittle and has poor adhesion as well. At extremes of time or temperature, thermal degradation, shown by yellowing, occurs (1, 8, 9).

1.2 Stress Whitening

Stress whitening is the effect seen when an initially non-white polymeric material undergoes mechanical deformation, applying stress to the system, which then causes the material to exhibit a greater optical brightness and appear white, as can be seen in Figure 2. This effect is caused by light scattering: a variation in the reflection of light from either the surface or the bulk caused by a change in the coating (10–17). Features shown to cause stress whitening have been found to be around the range of visible light in size by Misra and co-workers (11, 18). However results within the present authors’ research group generally agree more with Thiele et al. (19) who find scattering materials have particle sizes around 170–360 nm, which is around the range of visible light halved.

There are several proposed changes which are attributed to stress whitening. The two categories they fall into are structural changes or changes in density (15, 16). Structural changes are seen in semi-crystalline polymers and are associated with changes in crystal orientation (15, 16). Cherry et al. (15) have concluded that the primary mechanism by which high density polyethylene (HDPE) stress whitens is a change in structure, associated with permanent plastic deformation. Changes in density have been seen in a plethora of polymers and include voids, crazes or cavities among others (11). Owing to the nature of the coating as a thermosetting system and therefore amorphous (8) in structure, only changes in density will be investigated in the present study.

As an example of differing density mechanisms in different polymers, Young and Lovell (14) have found stress whitening in high impact polystyrene (HIPS) and rubber toughened poly(methyl methacrylate) (RTPMMA). HIPS exhibited more whitening than RTPMMA. Scanning electron microscopy (SEM) micrographs of the two materials were compared and crazes emanating from dissimilar rubber particles in bulk polymer surface were seen in HIPS, however no crazing was visible in RTPMMA. The RTPMMA has much smaller rubber particles at 200–300 nm. The authors concluded this was the reason no crazes were emanating from the rubber. Their secondary conclusion, that cavitation within the nanoparticulate rubber was the cause of observed whitening, is in agreement with the findings of Breuer et al. (16), who evaluated rubber-modified polyvinyl chloride (PVC) which was shown to be stress whitening by cavitation occurring in the rubber modifiers. Contrary to the conclusions of Young and Lovell (14), the further work conducted by Breuer et al. (16) found that variation of the polymer was most likely to be the cause of a change in mechanism as opposed to the size of rubber particles, which the group have associated with the extent of stress whitening. Breuer et al. (16) also cited the crazing mechanism as the source of stress whitening in polystyrene.

Misra and co-workers (10, 11, 18, 20) have published a number of studies on stress whitening, including investigation on polyethylene and polybutylene and the effects of various additives on these polymers. Misra et al. (10) have stated that the primary factors influencing stress whitening are composition, molecular weight, percentage crystallinity and phase transformation. The effects seen in materials in regions of tensile...
strain where stress whitening is visible include, but are not limited to wedges, tearing, crazes, cracking and fibrillation. In an early paper Misra et al. (21) concluded that small voids will scatter more visible light and yield a whiter appearance whereas larger voids absorb in the visible light range and reduce whitening; however Misra et al. (11, 22) later went on to state the complexities of the relationship between light scattering and deformation and the dependence upon refractive index, surface roughness and the already mentioned void size.

There are limited publications discussing stress whitening in thermoset polymers (3, 23), and these do not explore the mechanism of whitening or contain a useful level of detail; however stress whitening has been seen as a prevalent problem within the thermoset coatings industry for many years.

1.3 Summary of Literature Findings

From the preceding review it has been found that, to date, research has investigated stress whitening in homopolymer systems (15, 24) or single modifier polymer systems (10, 12, 16, 20, 24–26). Complex systems such as coatings have not been investigated to confirm whether or not the same mechanism(s) are occurring. Tensile strain in coatings has been heavily investigated (4, 27); previous foci have been essential work of fracture (3, 28), fracture mechanics (29) and other physical properties such as viscoelastic responses (2, 30), however there has not previously been a focus on evaluating visual concerns in coatings. This work is the start of research into the visual phenomenon of stress whitening appearing in complex coatings systems, with the aim of identifying the cause of stress whitening and determining its potential mechanism(s).

1.4 Hypothesis

Industry hypothesises that stress whitening in coatings is largely due to heterogeneous particles in the bulk resin mixture. These could be mineral additions for pigmentation or strengthening, anti-corrosive pigments or a range of other additives and extenders (1). Given the mechanisms presented for various polymer systems, the heterogeneous particles hypothesis seems a reasonable assumption; however it is important to monitor both the bulk system and the additives currently included as both can affect the mechanism and occurrence of stress whitening.

In order to establish the exact cause of stress whitening in DA systems the coatings used were consecutively reconstructed by adding different component parts, such as catalysts, to the bulk resin. Functional agents were added separately, and in combination, to determine the cause of stress whitening. Once this was completed and the cause attributed, then a likely mechanism for stress whitening was established.

1.5 Strategic Choices

The coating used was a DA coating, which had been known to stress whiten under set circumstances. The ingredients in the coating were needed to achieve the specifications of the DA market. These include a polyester melamine crosslink resin system as the main polymer, solvents, a structuring agent and a liquid dispersion of particles used as a slip additive. Table I highlights key details of the resin mixture and the two heterogeneous additives.

<table>
<thead>
<tr>
<th>Table I Topcoat Components</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
</tr>
<tr>
<td>Resin mixture</td>
</tr>
</tbody>
</table>

Additive 1

<table>
<thead>
<tr>
<th><strong>Name</strong></th>
<th><strong>Purpose</strong></th>
<th><strong>State</strong></th>
<th><strong>Appearance</strong></th>
<th><strong>Approximate particle size, μm</strong></th>
<th><strong>Glass transition temperature T&lt;sub&gt;g&lt;/sub&gt; °C</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive 1</td>
<td>Structuring agent</td>
<td>Powdery solid</td>
<td>Opaque white</td>
<td>Up to 80</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Additive 2

<table>
<thead>
<tr>
<th><strong>Name</strong></th>
<th><strong>Purpose</strong></th>
<th><strong>State</strong></th>
<th><strong>Appearance</strong></th>
<th><strong>Glass transition temperature T&lt;sub&gt;g&lt;/sub&gt; °C</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive 2</td>
<td>Slip additive</td>
<td>Dispersion of particles</td>
<td>Opaque white</td>
<td>n/a</td>
</tr>
</tbody>
</table>
2. Method

2.1 Coating Procedure

In stress whitened systems previous studies have shown that there is a correlation between defect formations from tensile strain and the presence of dissimilar particles in the polymer system. In these coatings the most likely cause of stress whitening is a particular additive. The formulae of two polyester melamine paints, which make up the two coat DA system, were analysed, and the most likely particular additives were noted.

To determine if stress whitening was linked to any particles in the systems, different combinations of the coatings were made. The focus was on the presence or absence of these particular additives in the system in order to verify which ones, if any, were causing stress whitening. All possible variations were investigated. Table II shows the differing combinations made for the topcoat. The full topcoat system featured a basic polyester melamine resin mixture, including solvents, catalyst and defoamer, which was homogeneous. The slip additive and structuring agent, also included, were both heterogeneous to the resin mixture.

Table II Topcoat Formulation Combinations

<table>
<thead>
<tr>
<th>Name of coating</th>
<th>Included in coating</th>
<th>Resin mixture</th>
<th>Slip additive</th>
<th>Structuring agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating 1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Coating 2</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>✓</td>
</tr>
<tr>
<td>Coating 3</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Coating 4</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

2.2 Panel Manufacture

Panels of the various coating permutations were manufactured; the substrate used was 0.6 mm thick cold rolled steel. The basecoat and topcoat were applied using a standard draw down method. The basecoat had a dry film thickness (DFT) of $13 \pm 3 \mu m$. The topcoat had a DFT of $15 \pm 3 \mu m$.

The following method of curing, for the coatings, mimics a coil line cure. For the basecoat, panels were placed in a paint oven at $300^\circ C$ for 35 s and then removed and quenched with a heat sink. For the topcoat, panels were placed in a paint oven at $300^\circ C$ for 40 s and then removed and quenched in water. The basecoat peak metal temperature (PMT) was $216–224^\circ C$. The PMT for the topcoat was $241–249^\circ C$.

The panels underwent basic industrial quality control tests, which showed the additions or lack of have no overall effect on the mechanical performance of the system. However, there was a difference in surface appearance. Coatings 1 and 2 containing the structuring agent had a wrinkled or textured surface, whereas Coatings 3 and 4 produced a smooth and shiny surface. Coating 1 had a more patterned wrinkled surface than Coating 2 and is reminiscent of Swiss cheese.

2.3 Induction of Stress Whitening

For this system, the method of inducing stress whitening required samples to be cooled to $-20^\circ C$ and stress applied. To determine the best method of applying stress, Coating 1, as the full system, underwent various tensile tests. The tests chosen were all industry standards for testing coatings (1). The most consistent test results were seen with either a cylindrical or conical mandrel bend, as seen in Figure 3. The cylindrical mandrel bends a sample not more than 1 mm thick and 50 mm wide through an angle up to $180^\circ$ over a period of 2–3 s. Different width cylinders exist, in this case a diameter of 16 mm was used. This causes a shallow bend angle of $160^\circ \pm 3^\circ$. The conical mandrel bend consists of a 20 cm long metal cone with an initial diameter of 3.2 mm increasing up to 38 mm, the mandrel conforms to the DIN EN ISO 6860 test standard. Erichsen cup draw tests and tensile pull tests among others were also investigated; however it was not possible to consistently whiten Coating 1, ruling out the use of these methods.

Fig. 3. (a) Conical and (b) cylindrical mandrels used to induce stress whitening
2.4 Microhardness Testing Procedure

In order to explore any influence of particle hardness, each coating underwent microhardness testing, as well as samples of the additives. Hardness testing was completed using a Fischer microhardness tester at 19 ± 0.5°C where the diamond tip forms a 2 µm indent into the surface. Once 2 µm has been reached the indenter is held in place for approximately 60 s and then removed. A probe in the indenter feeds results back to the WIN-HCU® software, which processes the hardness curves and provides a measurement of hardness. The software made nine random indents across the surface of the panel using this method, which then generated an average hardness as well as the standard error. To ensure comparability, this method was used for both the coating panels and the additives. To increase reliability, three panels of the same sample were manufactured, all of which underwent hardness tests. The results were collated and an average value determined. These results will be discussed in Section 3.2.

2.5 Scanning Electron Microscopy Procedure

SEM was used to evaluate nanofeatures on the coating surfaces. SEM imaging of samples was conducted on a Jeol 7800F FEG-SEM. The operating parameters were 2 kV accelerating voltage with the lower electron detector set with +300 V bias at an approximate working distance of 7–10 mm.

Samples were prepared from the desired coated panels by cutting a small section from the middle. The top was then cleaned using compressed air. Samples were mounted on an appropriate platen for the SEM and secured using electroless silver paint, also referred to as Silver DAG (Agar Scientific Ltd, UK). Finally, the mounted samples are sputter coated with 2–3 nm of platinum using an Agar high resolution sputter coater.

3. Results and Discussion

3.1 Stress Whitening Results

In every system that stress whitened, whitening was found to be transient and was no longer evident upon warming to room temperature or after a prolonged period at the lowered temperature. Re-cooling the samples did not make whitening re-appear.

The topcoat combinations were tested. None of the coatings stress whitened at room temperature. Both Coatings 1 and 2 (Table II) exhibited stress whitening after being cooled to −20°C for at least 1 h, and bent, as seen in Figure 4. Whitening did not last for more than a minute when in ambient conditions and did not last for more than one month when immediately re-stored at −20°C. A conical mandrel and a cylindrical mandrel both induced stress whitening in the samples. The stress whitening appeared speckled in both Coatings 1 and 2. For Coating 1 specifically the white speckles appeared to be at the base of the craters or 'Swiss cheese' like holes. A single additive was shown to be responsible for stress whitening, this was additive one or the structuring agent.

Fig. 4. Transient stress whitening caused by structuring agent

Mandrel testing revealed that the basecoat did not stress whiten for any combination, it was ruled that only the topcoat stress whitened. However the silver pigment in the basecoat may have enhanced the appearance of stress whitening in the topcoat. Characterisation of the coatings was conducted to test for property variation and to highlight any differences between the additive and the coating. The only consistent element between Coatings 1 and 2 that was not present in Coatings 3 and 4 was the structuring agent, producing the conclusion that the presence of the structuring agent causes stress whitening.

3.2 Microhardness Testing Results

The hardness results listed in Table III show no statistically significant variation between Coatings 1 through to 4; however the additives were significantly softer than the coatings. Given that the structuring agent was found to be the source of stress whitening, it is notable that the coating was significantly harder than the structuring agent. Variation in hardness can produce different reactions...
to strain, where a hard system has a short elastic response followed by a viscoelastic and plastic response; a soft system is more likely to have a greater elastic response, with only a small amount of viscoelastic or plastic response occurring. The presence of heterogeneous particles has been cited as the initiation point for various defects.

### Table III Hardness Measurements Accrued from Micro-Hardness Tester

<table>
<thead>
<tr>
<th>Sample</th>
<th>Marten’s Hardness, N mm⁻²</th>
<th>Standard deviation, N mm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating 1</td>
<td>170</td>
<td>22</td>
</tr>
<tr>
<td>Coating 2</td>
<td>175</td>
<td>25</td>
</tr>
<tr>
<td>Coating 3</td>
<td>164</td>
<td>14</td>
</tr>
<tr>
<td>Coating 4</td>
<td>176</td>
<td>5</td>
</tr>
<tr>
<td>Slip additive</td>
<td>19</td>
<td>3</td>
</tr>
<tr>
<td>Structuring agent</td>
<td>24</td>
<td>9</td>
</tr>
</tbody>
</table>

#### 3.3 Scanning Electron Microscopy Analysis

SEM images have been captured for all of the samples. These were before bending or tensile testing had occurred. The SEM images were used as a comparison to isolate whether any particles can be seen that correlate to the structuring agent. SEM was also used as a stage of elimination, as any particles or surface artefacts only present in Coatings 3 or 4 were not causing stress whitening and so can be ruled out in the other systems. The 20–70 µm circular craters visible in Coatings 1 and 3 are an example of an artefact not associated with the structuring agent, meaning they cannot be the cause of whitening. The circular craters in fact correspond in size with either a single particle or an agglomeration of the slip additive and are most likely caused by this. Figures 5 to 8 show overview SEM micrographs of Coatings 1 through 4.

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**Fig. 5.** SEM micrograph of Coating 1 before bending. Coating 1 is the full system and the micrograph features surface artefacts associated with both slip additive and structuring agent. It also has features which do not appear in any of the other coatings, these are the amorphous shapes which are around 100 µm

**Fig. 6.** SEM micrograph of Coating 2 before bending. Coating 2 only contains resin mixture and structuring agent. The circular depressions with smaller approximately 30 µm circular artefacts within them are associated with the structuring agent

**Fig. 7.** SEM micrograph of Coating 3 before bending. Coating 3 contains only resin mixture and slip additive. The circular concave artefacts are attributed to either single particles or agglomerates of the slip additive. They have a size range of approximately 20–70 µm

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Figure 9 shows a surface artefact only found in Coatings 1 and 2. This is the most likely artefact that can be attributed to the structuring agent, which is the cause of stress whitening. These artefacts will be the point of focus in SEM studies of the bent coatings.

Figure 10 is a schematic representation of the proposed mechanism for stress whitening in this heterogeneous polyester melamine coating. Given the transient nature of the stress whitening, a feasible hypothesis is that the particles of structuring agent and the polymer are responding differently to the stress on the system. The different responses are time dependent, i.e. kinetic, meaning the initial response is not the material’s final response and after a short time the material reaches equilibrium. At this equilibrium the conditions for stress whitening are no longer present, unlike in the initial response, meaning stress whitening is no longer visible. This would also account for the lack of stress whitening at a warmer temperature, as the system will go through elastic and visco-elastic changes far more quickly than when at –20°C.

The most likely scenarios are either a self-healing effect where any nano-cracks or defects present in the correct range are sealed by the final time-dependent viscoelastic response of the resin matrix and particle to the strain applied; or the nano-cracks or defects in the coating have become larger than the range which interferes with light scattering.

![Fig. 8. SEM micrograph of Coating 4 before bending. Very few if any surface artefacts are visible. There are no repeating artefacts across the entire sample, leading to the conclusion that any individual artefacts are either dirt or specific surface defects into the coating](image1.png)

![Fig. 9. SEM micrograph of Coating 2 before bending. This shows a close-up of the approximately 30 µm surface artefact, which is potentially structuring agent](image2.png)

![Fig. 10. Proposed mechanism of stress whitening in heterogeneous coating system](image3.png)
reflection as equilibrium is reached in cases where the two materials have different end reactions to strain. Due to the transient nature of the stress whitening, determining which is true for this system is challenging.

4. Conclusions

In conclusion, the structuring agent present in the coating caused stress whitening when tensile strain occurred in the system. The structuring agent is a softer particle, which is not detectable by microhardness in the bulk coating system. Previously industry has only observed stress whitening in systems with harder heterogeneous particles. Stress whitening is caused by light scattering off defects present in the coating; the most likely defects are voids or nano-cracks around the heterogeneous structuring agent particles, which act as an initiation point for defects. The transient nature of the stress whitening is most likely attributed to this difference in hardness. SEM micrographs show surface features indicative of a potential point of defect, surface comparison has ruled out many surface artefacts.

Acknowledgments

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Dr Chris Lowe moved from photo-resists to drugs for African cows and then to paints that cure under the influence of UV light. These early experiences have informed his research interests into areas such as structure property relationships for both weathering resistance and mechanical properties, adhesion and the lack of it and the application of spectroscopic tools in general to issues with paint.

Professor David T. Gethin DSc, CEng, FLechE, FLSW, undertakes fundamental and applied research in all aspects of printing and coating processes with a key interest in the deposition of functional materials. This includes the formulation of inks, their deposition using the appropriate processes and metrology of the printed layers or devices. This work covers a range of technology readiness from laboratory scale exploration to scale up for industrial application.
Additive Layer Manufacturing of Catalytic Static Mixers for Continuous Flow Reactors

Versatile technique provides economic and practical advantages to the flow chemist

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With a design guided by computational fluid dynamics (CFD), additively manufactured from base metals and coated with metal catalysts using cold spray technology or electroplating, catalytic static mixers are used to replace fixed bed columns in continuous flow reactors. We have shown their versatility in gas-liquid hydrogenations and homogeneous transfer hydrogenations and review here their preparation, stability and wider use in catalytic transformations using flow reactors. Additive manufacturing provides complex mixer structures that can be retrofitted to existing reactor geometry and reduces manufacturing costs by removing abrasive blasting steps in the mixer fabrication process. The rough surface profile of the mixers aids with high metallurgical bonding of the catalyst coating, as shown by the low catalyst leaching levels reported here.

Flow Chemistry – Economic Benefits

Over the last decade, much attention has been focused on continuous flow reactors as a process intensification method to reduce costs. Because of the efficient heat transfer into or out of the narrow tubing used in these reactors, production of by-products is reduced and often eliminated. This in turn leads to less need for purification steps, reducing waste streams and power consumption for a process. Others have noted improved safety aspects such as no vapour headspace, reduced over-all footprint and lower initial capital expenditure as additional economic benefits to using flow reactors (1–5). Reactions at elevated temperatures or pressures that might once have been the domain of specialist toll manufacturers could now be brought in-house with dedicated process lines (6, 7).

Continuous flow hydrogenations were some of the earliest reactions investigated in flow reactors (8–10), resulting in the manufacture of dedicated hydrogenation units from several manufacturers (11, 12). However, these solutions continued to use cartridges or packed columns, essentially fixed-bed reactors.

Hydrogenations – Fixed-Bed Reactor Limitations

Fixed-bed reactors have been a mainstay of catalytic reaction processing for many decades. While easy to construct and implement, they suffer from a number of shortcomings when designing a continuous flow process (1, 9, 13–15). Pressure drop (back-pressure) across a fixed-bed reactor is a major concern when developing a flow process, especially with a viscous medium. This can result in lower throughputs in order to work within the limitations of existing equipment such as pumps, tubing or tubing connectors. Irregular temperature gradients or hotspots are difficult to remove, especially when scaling to larger production units.
CSIRO has been pursuing a new approach that uses established tubular reactor technology retrofitted with purposely designed and additively manufactured catalytic inserts. These are known as catalytic static mixers (CSM) (16). Metal deposition methods such as cold spraying or electroplating are used to coat the base metal scaffold with the catalyst. These metal scaffolds have good mechanical stability, being less brittle than ceramics and more scratch resistant than plastics. They are also compatible with a broader range of solvents and temperatures compared to most plastics and composite materials.

Moreover, the use of additive manufacturing processes means that the CSM can be designed for an existing reactor geometry to optimise surface contact, mixing and flow. Here, two custom built reactors are used for hydrogenations, both previously described in other publications (16–18). These contain stainless steel tubing of 6 mm inner diameter and are heated electrically. The smaller unit houses four CSM with a reaction volume of 14 ml (Mk1 reactor) and the larger capacity reactor houses twelve CSM with a 40 ml reaction volume (Mk2 reactor).

**Computational Fluid Dynamics**

CFD was used to design a mixer with optimised mixing and heat transfer, along with maximum surface area for catalyst deposition. Our simulations for homogeneous liquid and liquid-liquid phases show good performance with low Reynolds numbers typically below 2300. The details of this design and modelling work will be the subject of a forthcoming publication in the fluid dynamics literature.

Three designs were tested:
- **D1** (a continuous mesh style)
- **D2** (with a helical groove along the length of the CSM)
- **D3** (a commercial design from Cambridge Reactor Design Ltd, UK) (16).

**Figures 1 and 2** illustrate the CAD drawing and CFD calculations, respectively, for D1.

**Additive Manufacture**

Base scaffolds were additively manufactured on an Arcam A1 electron beam melting printer using aluminium alloy, titanium alloy (Ti-6Al-4V), cobalt-chromium alloy (CoCr) or 316L stainless steel powder. An electron beam was used to melt and fuse the metal powders, layer-by-layer, into three-dimensional parts (16–17, 19) as shown in **Figure 3**. The finished scaffolds for D1 and D2 are shown in **Figure 4**. The scaffolds were inserted into metal tubes as illustrated in **Figure 5**.

Without the need for additional abrasive blasting to create increased surface roughness, the base mixer could be coated in catalyst using either cold spray coating or electroplating.
(a) Cold Spray Coating

Cold spray coating is a technique that sprays metal powders at supersonic speeds onto a target resulting in the metal particles bonding to the target substrate. It produces very stable, controlled coatings. A commercial cold spray unit from Plasma Giken Co Ltd, Japan, was used and base scaffolds were coated with base metals (for example, copper and nickel) as well as precious metals (for example, palladium, platinum and gold).

Coating qualities were analysed by scanning electron microscopy (SEM) and optical microscopy (Figures 6(a) and 6(b)) and CSM of high porosity and high metallurgical bonding were used for further investigation in catalytic reactions. This commercial system was subsequently modified with a custom-made target holder to rotate the scaffold at speeds up to 300 rpm (17). This modification improved surface coverage of the catalyst on the accessible surface of the scaffold, as well as increasing productivity in processing multiple scaffolds. For additional characterisation data, see previous publications (16–18).

(b) Electroplating

More traditional electroplating using solutions of copper, nickel, palladium or platinum salts were used to provide very high internal plating of the CSM base scaffold (16–18). An example of the electroplated scaffold with copper is shown in Figure 7.
SEM images (Figures 6(c) and 6(d)) were used to confirm thickness distribution and, together with X-ray tomography at the Australian Synchrotron, to analyse the morphology and porosity of the scaffolds. Preparation and characterisation procedures have been published previously (16–18).

**Gas-Liquid Hydrogenations**

The first application looked at heterogeneous hydrogenations combining a substrate in a liquid phase with hydrogen gas. With a continuous flow reactor, it is possible to conduct hydrogenations under pressure, but by reducing the volume of material being reacted at any one time, dramatically improve safety considerations compared with hydrogenations using a regular batch reactor. For this work, electrically heated tubular reactors were used that could hold either four or twelve CSM inserted into 6 mm ID stainless steel tubing. A reactor schematic is shown in Figure 8.

**Substrate Stability**

Early experience in additive manufacturing in metal within our group came from creating medical implants such as heels or sternums (20–21). These used a titanium alloy, so this was initially chosen as a substrate for the CSM scaffolds. However it became clear that this titanium alloy was subject to hydrogen embrittlement after a few exposures to pressurised hydrogen reactions at temperature (22–24) (Figure 9). Therefore 316L stainless steel was selected as an alternative. This required investigation of new conditions on the electron-beam printing machine, but once these were determined, the problems of CSM scaffold embrittlement were eliminated.

**Hydrogenation Examples – Initial Investigations**

Initial investigations looked at the hydrogenation of oleic acid (OA), vinyl acetate (VAc) and cinnamaldehyde (CAL) (see Scheme I for...
cinnamaldehyde hydrogenation pathway. Nickel catalyst was applied by cold spray coating and electroplating, as well as platinum catalyst by electroplating, on the titanium alloy, cobalt-chromium alloy and stainless steel (316L) base scaffolds.

While the nickel catalysts generally afforded lower yields and turnover frequencies (TOF) compared to the platinum catalysts, it was apparent that when comparing nickel coated mixers prepared using electroplating to ones prepared using cold-spray, the cold-spray approach resulted in higher values for yields and TOF. We attribute this to the much smoother surface coatings seen in the electroplated mixers which could contribute to reduced surface area on which the substrate can interact with the catalyst. The results for these substrates are shown in Table I.

A broader range of substrates and functional groups was then investigated (17). For example, the individual isomers of nitroanisole and chloronitrobenzene are cleanly reduced to the corresponding aniline, with the exception of $p$-nitroanisole (Table II).

For substrates such as phenyl acetylene where multiple products could be produced, the reaction parameters could be tuned to select one product over another, for example favouring styrene over ethyl benzene (Table III). The results from other functional groups, such as imines, diazo compounds, ketones, nitriles and various vinyl systems can be seen in previous publications (16–17).

Active Pharmaceutical Ingredients – Linezolid

The antibiotic linezolid is used to treat the antibiotic resistant strains vancomycin-resistant enterococci (VRE) and methicillin-resistant Staphylococcus aureus (MRSA). Part of the manufacturing process is a reduction of an aromatic nitro group to an amine as illustrated in Scheme II. A challenge with the existing methodology is the removal of the palladium catalyst by filtration upon completion of the hydrogenation and recovery of the catalyst.

By replacing the Pd/C fixed bed reactor with a palladium coated CSM, the reduction step could be completed with high yield (>99%) and no leaching of the catalyst, making this a highly efficient heterogeneous catalytic reactor (25).
Table I Reaction Conditions (Reactor Pressure, Liquid Flow Rate, Gas/Liquid Ratio and Residence Time) and Results (Conversion, Turnover Frequency (TOF) and Space Time Yield, (STY)) from Hydrogenation Experiments using Nickel and Platinum Catalysts (16)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Results</th>
<th>Activation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(p_R, \text{bar})</td>
<td>(V, \text{ml min}^{-1})</td>
<td>(G/L)</td>
</tr>
<tr>
<td>1</td>
<td>OA</td>
<td>Ni-EP-CoCr-D1</td>
<td>16</td>
<td>0.5</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni-EP-CoCr-D1</td>
<td>20</td>
<td>0.5</td>
<td>5.00</td>
</tr>
<tr>
<td>3</td>
<td>OA</td>
<td>Ni-EP-Ti-D1</td>
<td>16</td>
<td>0.5</td>
<td>3.60</td>
</tr>
<tr>
<td>4</td>
<td>OA</td>
<td>Ni-CS-Ti-D1</td>
<td>16(\text{a})</td>
<td>0.5</td>
<td>3.60</td>
</tr>
<tr>
<td>5</td>
<td>OA</td>
<td>Ni-CS-Ti-D1</td>
<td>16(\text{a})</td>
<td>0.3</td>
<td>6.67</td>
</tr>
<tr>
<td>6(\text{b})</td>
<td>OA</td>
<td>Ni-CS-SS-D3</td>
<td>16(\text{b})</td>
<td>0.2</td>
<td>10.50</td>
</tr>
<tr>
<td>7(\text{c})</td>
<td>VAc</td>
<td>Ni-CS-SS-D3</td>
<td>22(\text{c})</td>
<td>0.5</td>
<td>5.00</td>
</tr>
<tr>
<td>8(\text{d})</td>
<td>VAc</td>
<td>Pt-EP-Ti-D2</td>
<td>24(\text{d})</td>
<td>0.5</td>
<td>5.00</td>
</tr>
<tr>
<td>9(\text{e})</td>
<td>VAc</td>
<td>Pt-EP-Ti-D2</td>
<td>16(\text{e})</td>
<td>0.5</td>
<td>5.00</td>
</tr>
<tr>
<td>10(\text{f})</td>
<td>CAL</td>
<td>Pt-EP-Ti-D2</td>
<td>20(\text{f})</td>
<td>0.5</td>
<td>5.00</td>
</tr>
<tr>
<td>11</td>
<td>OA</td>
<td>Pt-EP-Ti-D2</td>
<td>16</td>
<td>0.5</td>
<td>3.60</td>
</tr>
<tr>
<td>12</td>
<td>OA</td>
<td>X-X-Ti-D1</td>
<td>16</td>
<td>0.3</td>
<td>6.67</td>
</tr>
<tr>
<td>13</td>
<td>VAc</td>
<td>X-X-Ti-D1</td>
<td>16</td>
<td>0.3</td>
<td>5.00</td>
</tr>
</tbody>
</table>

All reactions were conducted at 140°C. For entries 2, 7, 8, 9, 10 and 13, EtOH was used as solvent, for all others EtOAc was used. For entries 2, 7, 8, 9 and 13, the substrate concentration was 2 M, for all others it was 1 M

\(a\) \(p_R\) was varied between 16 bar and 20 bar resulting in conversions between 8.3% and 14.8%

\(b\) \(G/L\) was varied between 0.92 and 10.50 resulting in conversions between 1.1% and 55.3%

\(c\) \(p_R\) was varied between 10 bar and 22 bar resulting in conversions between 12.5% and 73.6%

\(d\) \(p_R\) was varied between 14 bar and 24 bar resulting in conversions between 57.9% and 92.1%

\(e\) Entry 9 was repeated multiple times with and without activation prior to reaction; with activation conversions were between 88.3% and 100.0%; without activation conversions were between 63.5% and 95.1%

\(f\) CAL was converted to 88.7%, giving a range of different hydrogenation products: HCOH \(16.1\%\), COH \(60.6\%\), HCAL \(7.3\%\), CAL \(11.3\%\), others \(4.6\%\) (See Scheme I)

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Table II Hydrogenation of Individual Isomers using Pd-EP-D2 in Mk2 Reactor

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yields</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="OMe-NO2.png" alt="Image" /></td>
<td><img src="OMe.png" alt="Image" /></td>
<td><img src="NH2-Cl.png" alt="Image" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yields</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="Cl-NO2.png" alt="Image" /></td>
<td><img src="Cl.png" alt="Image" /></td>
<td><img src="NH2-Cl.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Adapted from (17) by permission of the author.

Table III Hydrogenation of Phenyl Acetylene using Ni-CS-D3 and Mk2 Reactor

<table>
<thead>
<tr>
<th>Conc., M</th>
<th>Pressure, bar</th>
<th>Gas/liquid ratio, v/v</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>12</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>24</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Adapted from (17) by permission of the author.

Scheme II. Making linezolid with a CSM
Leaching of Catalyst – Results of ICP-OES Monitoring

Over the lifetime of the catalysts, some of which were in operation for up to 2000 h, several leaching tests were conducted. For these, usually an extended run with a common substrate such as VAc (scale: 1 l or more, concentration: 2 M) was used and the combined product from this hydrogenation reaction was collected and analysed for conversion and leaching of metals by inductively coupled plasma-optical emission spectrometry (ICP-OES) (18). The leaching results are shown in Table IV.

Deactivation of the catalyst in the first few hours of operation of a VAc reduction using a CSM coated in nickel using cold spray was also briefly investigated (Figure 10). An initial drop in activity was seen, but a plateau was reached after 150 min and only around 5% of initial activity was lost. This points to the need to activate and pre-condition the catalyst before use as experiments without activation generally showed lower activity than those where the catalyst was activated.

Table IV Average Concentrations for Metals Leached from a Nickel Coated and Palladium Coated CSM Measured by ICP-OES. Base Scaffold was 316L Stainless Steel in Each Case (18)

<table>
<thead>
<tr>
<th>Nickel CSM – Cold Spray</th>
<th>Average conc., ppb</th>
<th>Palladium CSM – Electroplate</th>
<th>Average conc., ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>27</td>
<td>Pd</td>
<td>&lt;0.18</td>
</tr>
<tr>
<td>Ni</td>
<td>123.1</td>
<td>Cr</td>
<td>25.2</td>
</tr>
<tr>
<td>Fe</td>
<td>408.1</td>
<td>Cu</td>
<td>6.65</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>Mn</td>
<td>0.98</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>Mo</td>
<td>0.35</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>Ni</td>
<td>44.1</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>Fe</td>
<td>32.4</td>
</tr>
</tbody>
</table>

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Fig. 10. Normalised activity levels of Ni cold sprayed onto a stainless steel CSM: VAc (2 M EtOH), H₂ (16 bar), 120°C, 1 ml min⁻¹
Homogeneous (Single Phase) Transfer Hydrogenation

We have also looked briefly at transfer hydrogenation using ammonium formate as the hydrogen source. The early results still need to be optimised, but the smaller reactor containing four of the palladium electroplated CSM using design D1 afforded a series of aniline derivatives by selectively reducing the nitro-groups of the compounds shown in Table V. Additional results for other substrates are listed in a previous publication (17).

Fabrication Costs

A typical CSM printed for a 15 cm length of 6 mm ID tubing found in a mid-sized flow reactor currently costs between 10% to 70% of the cost to make a comparable static mixer using conventional manufacturing techniques (prior to coating in catalyst) by removing additional welding steps. This is already exceedingly cheap for what is essentially a custom item, but would scale readily if transferred to a production environment, where costs are expected to decrease further by a factor of 1.5 to 10 when additively manufacturing these devices for mass manufacture.

Additional costs then come from the catalyst load and some typical quantities for a 15 cm × 6 mm CSM are shown in Table VI. It should be noted that the inherent rough surface profile of the additively manufactured mixers removes the need for an intermediate abrasive blasting step, which further saves on fabrication cost.

Future Directions

CSM is one of the products stemming from a continuous flow manufacturing focus in our labs, culminating in the construction of a new 400 m² flow chemistry facility being built onto existing infrastructure at CSIRO’s Clayton, Australia, site. CSIRO will provide manufacturing partners with access to the latest in flow chemistry and process technology so that they can rapidly develop continuous manufacturing processes to synthesise small molecules, polymers and other materials. We will be partnering with chemical manufacturers in the pharma, fine chemistry, food and polymers spaces to utilise CSM in a variety of applications.

We are currently exploring the use of copper, nickel, platinum, gold and ruthenium coatings as catalysts for a variety of chemical transformations such as oxidations, hydrogenations and coupling reactions.

Conclusion

This short review article has examined how CSM have been prepared for use in continuous flow hydrogenation reactors by making use of in-house computational fluid dynamic design capability, metal additive manufacturing and catalyst coating abilities at CSIRO. While 316L stainless steel is the obvious choice of scaffold for most chemistries,

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conversion, %</th>
<th>P, bar</th>
<th>TOF, h⁻¹</th>
<th>STY, g l⁻¹h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitrobenzene</td>
<td>36</td>
<td>20</td>
<td>1.72</td>
<td>65</td>
</tr>
<tr>
<td>4-nitrotoluene</td>
<td>87</td>
<td>20</td>
<td>4.17</td>
<td>176</td>
</tr>
<tr>
<td>4-nitroanisole</td>
<td>100</td>
<td>12</td>
<td>4.76</td>
<td>225</td>
</tr>
<tr>
<td>3-nitroanisole</td>
<td>20</td>
<td>12</td>
<td>0.96</td>
<td>45</td>
</tr>
</tbody>
</table>

Conditions: 130°C, 0.33 M in MeOH, 1 ml min⁻¹. Adapted from (17) by permission of the author

<table>
<thead>
<tr>
<th>Base material</th>
<th>Weight, g</th>
<th>Metal/Coating method</th>
<th>Weight with catalyst, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti alloy – design D1</td>
<td>11.3</td>
<td>Ni / CS</td>
<td>13.3</td>
</tr>
<tr>
<td>SS 316 – design D3</td>
<td>15.6</td>
<td>Ni / CS</td>
<td>18.9</td>
</tr>
<tr>
<td>Ti alloy – design D2</td>
<td>16.2</td>
<td>Pt / EP</td>
<td>16.6</td>
</tr>
</tbody>
</table>

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other alloys using titanium, aluminium or cobalt-chrome could also be used. But we found, as have others, that the titanium alloy was not suitable for use in hydrogenation reactions due to its limited stability after prolonged exposure to hydrogen.

Either cold-spray technology or electroplating may be used to coat the CSM scaffolds with metal catalysts, with little leaching being observed after several months for either technique. SEM studies indicated that the former method produces a rougher coating and thus higher surface area, while the latter method coats more of the internal surfaces of the scaffold.

The CSM performed well in gas-liquid hydrogenations and homogeneous transfer hydrogenations, on a variety of substrates and with improvements in the space time yield (STY) for these reactions. Selective hydrogenation could be achieved by careful tuning of the hydrogenation conditions, allowing, for example, the reduction of phenyl acetylene to either styrene or ethylbenzene. Significantly, the combination of design capability, additive manufacturing in metal and stable catalyst coating has provided a safe alternative to fixed bed reactors for existing hydrogenation continuous flow reactors. We remain excited to see this approach extended to other catalytic reactions in continuous flow reactors.

Acknowledgements

CSIRO would like to thank Bashir Harji of Cambridge Reactor Designs, UK, for the design of our Mk1 hydrogenation reactor. The authors would like to thank Darren Fraser for the animation stills of the Arcam electron-beam printer and the additive manufacturing of the CSM scaffolds, Mike Horne and Bita Bayatsarmadi for electroplating the mixers, Andrew Urban for cold spraying the mixers and Dayalan Gunasegaram for the CFD images of the mixers, all of CSIRO, Australia. Finally, we would like to thank Antoine Avril for the photographs of the disintegrated Ti-mixers and Antony Carafa for data processing of the extended run experiments.

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Shravan Singh is an electronic engineer and currently works as Business Development Manager at CSIRO Manufacturing. Prior to joining CSIRO, Shravan worked for himself as an entrepreneur and has years of experience in optical metrology, having worked at leading metrology institutes in South Africa and the USA in technical and management roles. He forms part of a multidisciplinary team at CSIRO that includes intellectual property, commercialisation and legal experts, helping CSIRO researchers translate their work into the market.

Simon Saubern trained originally as an organic chemist and, with a keen interest in high-throughput experimentation, facilitated CSIRO’s early flow chemistry capability. He has several years’ experience working with continuous flow reactors on industrial processes, particularly in the field of polymer synthesis. Dr Saubern is part of the multidisciplinary FloWorks team, evaluating novel technologies applied to synthesising polymers in flow reactors and using statistical methods to optimise reaction conditions.