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Highlights from Faraday Discussion on Designing Nanoparticle Systems for Catalysis, London, UK, May 2018

Rosa Arrigo, [ID] *[ab] Andrew J. Logsdail [ID] *[c] and Laura Torrente-Murciano [ID] *[d]

The 2018 Faraday Discussion on "Designing Nanoparticle Systems for Catalysis" brought together leading scientists to discuss the current state-of-the-art in the fields of computational chemistry, characterization techniques, and nanomaterial synthesis, and to debate the challenges and opportunities going forward for rational catalyst design. The meeting was a vivid discussion of how the communities accummulate knowledge and on how innovativeness can be combined to have a stronger scientific impact. In the following, we provide an overview of the meeting structure, including plenaries, papers, discussion points and breakout sessions, and we hope to show, to the wider scientific community, that there is great value in continued international discussion and scientific collaboration in these fields.

Introduction

When attending a Faraday Discussion meeting, one immediately gets a sense of scientific continuation. Following a tradition established over 100 years ago, in 1907, with the first Faraday Discussion on "Osmotic Pressure" [DOI: 10.1039/TF9070300012] the meeting symposiums have had a distinctive format that makes them a unique experience amongst all other scientific dissemination forms. Indeed, the scientific papers presented in these events are provided in advance for all the attendees to read; then, during the meeting, the papers' authors have the opportunity to briefly present their manuscripts within five minutes, followed by an extensive discussion of the work

[a] Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK.
  E-mail: rosa.arrigo@diamond.ac.uk
[b] Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK
[c] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK.
  E-mail: LogsdailA@cardiff.ac.uk
[d] Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, CB3 0AS, Cambridge, UK.
  E-mail: lt416@cam.ac.uk

including impacts and future directions. This special format has the great advantage that it provides a broad overview on specific topics, allowing a direct critical analysis by the wider international scientific community.

There could have been no better place to host this 2018 discussion, about "Designing of Nanoparticle systems for Catalysis", than at Burlington House in London, which is the home of the Royal Society of Chemistry (RSC) (Fig. 1). Surrounded by the book-filled shelves of the RSC Library, an international representation of over 120 delegates convened on the 16th May, all eager to exchange opinions and visions on how to design and engineer structures for selective and efficient chemical synthesis.

Fittingly, the event commenced with recognition that the 2018 Faraday Lectureship Prize was awarded from the RSC to Prof. Graham Hutchings, the chairperson of the event. This prize is awarded every two years for exceptional contributions to physical science, for which Prof. Hutchings is a worthy recipient.[1] In his subsequent introductory speech, Prof. Hutchings introduced the three main themes of the meeting: the control of nanoparticle synthesis, the challenges of

Fig. 1 Façade of Burlington House, Piccadilly, London; home of the Royal Society of Chemistry.

characterization, and the use of theory as a guide in our search for novel nanoparticle-based catalysts. Therein, the meeting was declared open.

Opening lecture

The introductory lecture was given by Prof. Bruce Gates, from the University

of California, Davis (USA), who is a world-leading figure in the design of supported metal clusters for catalysis and also the author of excellent catalysis textbooks.[2] In his talk, Prof. Gates shared his vision and strategies on how to attain the needed molecular foundation for application-oriented synthesis of supported clusters and nanoparticles (NPs), giving several detailed examples that showcase when the goal of design could be achieved. He introduced the concept of nuclearity of supported catalysts and identified two extreme cases representing different foundations of chemical science: precisely synthetized single-site metal atoms, and larger nanoparticles. The reactivity of atomically dispersed metal species is well described by organometallic chemistry. On the other hand, for larger NPs, surface dynamics and restructuring typical of the corresponding bulk systems are to be expected and thus these are normally considered using surface science approaches. Clusters and small NPs exist in a large variety of shapes and sizes between these two delimiting cases. The chemical interactions between the nano-structures and the support onto which they are immobilized provide further opportunities to fine-tune the catalytic properties; moreover, both ligands on the surface of the metal as well as on the support itself, can also play an important role in catalysis. In contrast to most of the supported NPs obtained by wet impregnation followed by thermal annealing, almost always inhomogeneous in shapes and sizes, well-defined few-atoms metal clusters can be obtained *via* the direct adsorption of ligated molecular metal clusters or the deposition of size-selected metal clusters from the gas-phase onto an oxide support.[3] Adsorption-based synthetic methodologies enable the precise control of the system's structural properties in the initial state, and also meaningful monitoring of the structural modifications at the molecular scale, thus providing model systems with which one can develop a fundamental understanding of catalytic phenomena. Indeed, Prof. Gates stressed the importance of starting from a well-defined system and the use of several characterization techniques to study the structural dynamics of clusters

under catalytic reaction conditions (*i.e.*, *in operando*).

Prof. Gates makes extensive use of state-of-the-art characterization techniques, including high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM). He acknowledged that the foundations of the science of clusters and single atoms on supports would not be nearly as strong as they are now without the technological advancement of the modern transmission electron microscope (TEM). Due to atomic scale resolution and a high sensitivity to atomic number contrast, HAADF-STEM allows the direct visualization of heavy metal atoms forming clusters or NPs on light-atom supports in a 2-dimensional projected image. More recent advanced image processing and complementary spectroscopy now allows reconstruction of a 3-dimensional model of the analysed object, and sometimes even the structure of the metal–support interface. One of the key questions addressed during his talk was the effect of nuclearity on the catalytic activity. As a first example, Prof. Gates discussed atomically dispersed Au supported on CeO_2 for carbon monoxide oxidation.[4] By means of *operando* X-ray absorption fine structure spectroscopy, he showed that a sharp increase in the conversion coincides with the formation of Au–Au dimers from an initial $Au(CH_3)_2(acac)$ complex, and that it proceeds to the steady state, in which the coordination number of Au increases slowly up to gold nanoclusters. The next example was the selective hydrogenation of butadiene using isolated rhodium dimer complexes, which showed the contrast in catalytic properties between isolated rhodium atoms and extremely small rhodium clusters supported on zeolite H-Y. Here, $Rh(C_2H_4)_2$ complexes catalyse both the dimerization and hydrogenation of ethene, and a controlled thermal treatment to produce rhodium clusters of only a few atoms boosts the activity for hydrogenation, eliminating the dimerization.[5] Another interesting study that exemplifies the high precision attainable by *in situ* methodologies for chemical speciation is the case of Ir tetramers with bulky calixarene phosphine ligands, used for ethylene hydrogenation, where it was possible to identify

that apical Ir atoms in Ir_4 tetrahedra can catalyse the hydrogenation reaction whereas the basal Ir atoms are inactive.[6]

The last point made by Prof. Gates was on the issue of the catalysts' stability under the reaction conditions. Synthetic strategies to encapsulate NPs in micro-porous materials, such as zeolites or metal organic frameworks, are being explored to improve stability against sintering and coking resistance. As concluding remarks, Prof. Gates emphasized how *in situ* spectroscopy and transmission electron microscopy are formidable techniques to promote fundamental understanding; however, in view of generating further knowledge, site precision synthesis is a pre-requisite for establishing robust structure–function correlations.

Session 1: Theory as a driving force to understand reactions on nanoparticles

The discussions themselves began with six papers grouped into two sequential sessions, with a wide span of discussion topics focusing on the use of computational modelling in catalytic applications. Prof. Rutger van Santen (Eindhoven University of Technology, The Netherlands) presented his work first, which had the broad title of ''*The challenge of catalyst prediction*'', where he emphasised his belief that current computational approaches need to accurately predict both the transient initiation as well as deactivation processes on (and within) catalysts [DOI: 10.1039/c7fd00208d]. Quantitative data could then be fed into microkinetic models to provide a more complete description of catalytic mechanisms. The provision of experimentally comparable observables, rather than qualitative trends, is a very topical issue in the field of computational catalysis; a specific mention in the discussion was made on the recent work of Phillipe Sautet and the consideration of transient catalyst structures on the observable rate constants and reaction turnovers.[7] There was an inevitable suggestion of the use of machine learning to facilitate insight, given that vast

amounts of data could need analysing in these approaches. Limitations were noted in the ability of computational approaches to produce enough accurate data to warrant such an approach in catalysis. Indeed, these discussion points became a persistent theme throughout all the theory-led discussions.

In the first session, there was also a presentation from Prof. Roy Johnston (University of Birmingham, UK), entitled "*Modelling free and oxide-supported nanoalloy catalysts: comparison of bulk-immiscible Pd–Ir and Au–Rh systems and influence of a TiO₂ support*", and from Dr David Willock (Cardiff University, UK), entitled "*Structural behaviour of copper chloride catalysts during the chlorination of CO to phosgene*". The work of Johnston *et al.* focuses on the stability of differing chemical configurations for bimetallic nanoparticles, using a fixed nanoparticle morphology cut from the bulk FCC crystal, and supported on the rutile (110) surface of TiO₂ [DOI: 10.1039/c7fd00213k]. In both systems studied (Pd–Ir and Au–Rh), the strongest surface interactions were observed when the non-noble metal interacted with the support surface, commensurate with the monometallic results, thus paving a way to introducing support-induced elemental segregation in the nanoparticles, and providing a rationale towards improving the anchoring of nanoparticles. The discussion debated the value of limiting the models to those outlined, exploring whether the bulk crystal fragment is representative at these low nuclearities, as surface wetting by the nanoparticles may be expected; a detailed discussion of charge distribution at the interface was also considered, and how this will affect reactivity. In the latter case, it was noted that other substrates preferred in catalytic applications, such as alumina or haematite, are much less ordered and so expanding the work to make it more relevant to catalytic applications remains challenging. In contrast, the work of Willock *et al.* includes a comparison between experiment and theory for the reactivity of attapulgite-supported Cu(II)Cl₂ [DOI: 10.1039/c8fd00005k]. In the experiment, CO exposure leads to oxidation of the reagent to CO₂ for the as-received catalyst; however, Cl pre-treatment leads to the synthesis of

phosgene. This reactivity is linked back to the formation of surface defects during the Cl pre-treatment, with density functional theory (DFT) simulations corroborating XANES data to show that this could lead to Cl⁻ surface defects. Such defects result in Cu(I) and Cu(II) ions at the surface, with DFT showing a strong CO interaction with the former allowing the formation of the COCl₂ product. Due to the more applied nature of this work, compared to that of Johnston *et al.*, the discussion in turn moved towards the role of free energies and entropy in determining rates; furthermore, the periodic nature of the studied catalyst, rather than a discrete nanoparticle, left questions about the role of supports and/or promoters for improving the catalytic reactivity.

After a short coffee break, with much intense discussion already about the advantages and drawbacks of computational approaches, the session reconvened with more computational-focused investigations. Prof. Nora de Leeuw (Cardiff University, UK) introduced a comparative DFT study of small Ni nanoclusters on ZrO₂ and YSZ(111) surfaces [DOI: 10.1039/c7fd00217c]. On both of these supports, the nanoparticles formed pyramidal structures rather than wetting the surface, with charge transfer returning as a topic of debate for the support–nanoparticle interaction. The Ni atoms interact most strongly with the electronegative O in the support, forcing geometric changes in the YSZ. These support-interacting atoms are typically positively charged, whereas Ni atoms furthest from the support become slightly negative; such subtle differences could easily affect the reactivity. The use of kinetic Monte Carlo approaches leads to a conclusion that surface aggregation would occur under medium temperatures, with sintering occurring independently of the initial surface coverage. When the floor was opened, the debate here reverted to similar themes encountered for the work of Johnston *et al.* with the focus on the importance of realistic models of the support and also the reaction environments, particularly solvents, identified as areas for further work.

Perhaps one of the most of the widely debated papers of the day followed, when Mr Wilke Dononelli (Carl von Ossietzky

Universität Oldenburg, Germany) introduced his work on CO and O₂ adsorption on Group XI nanoparticles using both DFT and high-level coupled-cluster [CCSD(T)] approaches [DOI: 10.1039/c7fd00225d]. The work used exemplar models for the nanoparticles, containing 13- and 55-atom structures, and considered Au, Ag and Cu monometallic compositions. For CO adsorption the results of the 55-atom system are similar to a high index (321) surface, whereas the differences are much greater for the 13-atom system (up to 0.6 eV for Cu). The authors postulate a naïve assumption that the PBE approach of DFT would lead to overbinding but QM/QM calculations, with CCSD(T) used for the adsorption site, give almost identical results. The dissociation barriers for O₂ were identified as being prohibitively high, thus showing that direct molecular reactions (Eley–Rideal) are more suitable for CO oxidation than the surface-mediated Langmuir–Hinshelwood type mechanisms.[8] Inevitably, when the floor opened for questions, there was much debate about the role of CCSD(T) in acting as a benchmarking guide for DFT. In particular, opinions were sought on how high-level theory could be used to improve or standardise empirical corrections to DFT, *e.g.* commonly used Hubbard- or Grimme-type corrections. However, it is noted that cautionary comments were also raised: CCSD(T) cannot be assumed as a "silver bullet" that could solve all modelling problems, given the complex nature of ensuring accuracy with this higher-level approach.

Finally in this session, Dr Arun Chutia (University of Lincoln, UK) presented his work on "*The electronic properties of Au clusters on CeO₂(110) surface with and without O-defects*" [DOI: 10.1039/c8fd00002f]. This work returned to the topics of metal nanoparticles and their interaction with supporting materials, specifically focusing on Au atoms and dimers on a low-energy ceria surface. It was observed from DFT calculations that the charge state of the adsorbate can be strongly altered by the presence of O-defects in the ceria, varying between cationic and anionic forms, with a density of states analysis used to validate the observations. Specifically, Au⁺ exists in the absence of defects,

with charge transfer to the Ce atom of the support, whereas adsorption over O vacancies results in Au⁻. Strong similarities to the work of Prof. De Leeuw *et al.* were developed in the post-presentation discussion, with emphasis on characterising the charge transfer effects and how these will alter the catalytic chemistry. For instance, alternative probe CO molecules were suggested, as these are responsive to charge transfer and can be linked to experimental spectroscopic techniques. Further discussion also covered the role of the nanoparticle-supporting ligands on the structure and surface-interaction of the nanoparticles. Although this topic was not covered in any of the computational work presented, it is of key importance if the results are to be related to experiment.

To complete Day 1, then followed a series of "quick-fire" flash introductions to precede the evening's poster presentation. Twenty presenters were given just one minute and one slide to pitch their work to the audience, with a rapid turn-over between presenters, leading to a mixture of presentation styles and details that only whetted the appetite for the subsequent session. Then followed two hours of poster-mediated discussion, with over 30 posters presented (Fig. 2). The debate was flowing and engaging, the attendees consumed by questions and discussions, either of the day's work or poster content. Even once the evening's session had closed, the debate continued on to some of London's other fine "meeting" establishments, though conclusions were drawn (or at least postponed) in time for everyone to get home and prepare for the following day's discussions.

Session 2: The challenges of characterizing nanoparticulate catalysts

One of the big dreams that scientists in the field of catalysis share is the full understanding of the catalytic phenomenon at the molecular level. This search has intrigued chemists from the dawn of this science, when it was realized that materials manifesting catalytic activity towards a reaction remain unaffected by

Fig. 2 After some excellent presentations and debate, discussions continued at the end of day 1 with the poster session.

the reaction itself unless they are deactivated.[9] Nowadays, scientists are developing sophisticated spectroscopic and imaging techniques for attaining the needed time- and space-resolutions to follow the structural dynamics taking place at the reactive interface during the catalytic turn-over. Thus, it is timely that Session 2 is dedicated to the application of *in situ* methodologies to catalysis, with a critical assessment of capability and limitations.

With this perspective, the second day started with a session chaired by Prof. Mike Bowker and a talk delivered by Prof. Carlo Lamberti (University of Turin, Italy) on time-resolved *operando* studies of carbon-supported Pd nanoparticles (NPs) under hydrogenation reactions by X-ray diffraction and absorption [DOI: 10.1039/c7fd00211d]. In this work, by a combination of X-ray powder diffraction (XRPD), extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge spectroscopy (XANES) and volumetric analysis in a wide range of sample temperatures and H_2 equilibrium pressures, the authors are able to identify the structure of these NPs under reaction conditions as composed of an ordered core and a disordered shell. XRPD patterns reveal a direct structure–reactivity relationship during the ethylene hydrogenation reaction,

where periodic oscillations of the lattice parameter of the crystalline core of the NPs correspond to oscillations in the mass fragment signal of C_2H_4 and C_2H_6 recorded simultaneously in the mass spectrum. Advanced analysis of the ΔXANES spectra allows the detection of carbon-containing molecules adsorbed at the surface of the NPs. Finally, some insights into the catalyst deactivation mechanism were also provided where the local temperature and hydrogen concentrations drive the formation and disappearance of the β-phase and thus of the catalytic activity.

Following that, Dr Annette Trunschke (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany), discussed a paper that focused on the investigation of the structural dynamics of $(Mn,Fe)O_x$-promoted Rh nanoparticles under the hydrogenation of CO to higher alcohols [DOI: 10.1039/c7fd00215g]. Dr Trunschke started her talk by referring to the computational chemistry contribution from the group of Prof. Nørskov[10] in which the authors failed to find a catalyst for the hydrogenation of CO to ethanol. This experimental work demonstrates that, on Rh catalysts, support and promoters (Fe,Mn) make this reaction possible. By applying a combination of integral techniques such as temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and Fourier transform infrared (FTIR) spectroscopy together with local analysis by using high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX), the authors conclude that the active sites are associated with either a $(Mn,Fe)O_x$ ($x < 0.25$) phase or species at the interface between Rh and its co-catalyst $(Mn,Fe)O_x$, whereas Rh^0 is poisoned due to the strong adsorption of CO under the reaction conditions. In the conclusion, this contribution showed that it is indeed possible to break scaling relations by creating new interfaces of metal nanoparticles with a co-catalyst (support, promoters).

The last talk before the break was delivered by Dr Michele Carrosso (University of Turin, Italy) who presented the work titled "*Looking for the active hydrogen species in a 5 wt% Pt/C catalyst: a*

challenge for inelastic neutron scattering" [DOI: 10.1039/c7fd00214a]. Therein, by coupling H_2 adsorption measurements with inelastic neutron scattering, the authors were able to determine the H speciation on both the metal and the carbon support with unprecedented structural detail, including the demonstration, for the first time, of molecular H_2 physisorbed on the metal surface, as well as the atomic H spill-over from the metal to the carbon surface.

Topics of the discussion session included how to ascertain, from integral techniques, the correct NP structural model when presented with two equally valid chemical configuration models: *e.g.* discriminate between the ordered-core/disordered-shell structures from a broad NP size distribution, where the small NPs could account for the disordered part. Indeed, there was a general consensus from the audience on the importance of the application of complementary characterization techniques, with accessibility championed through the model of the Harwell Science and Innovation Campus in the UK. A more general discussion was characterized by an historical digression on the use of the XAFS techniques from the EXAFS "boom" in the early 1980s to nowadays, when XANES is gaining increasingly interest especially for diluted systems. This modern shift has been enabled by the modern capability of theory to predict XANES spectra, with an outlook into the future in which machine-learning approaches can revolutionize the way to interpret XANES data.

Part B of this session was devoted to the study of catalytic systems based on Au nanoparticulate systems. Dr Yaroslav Odarchenko (University College London and Research Complex at Harwell, UK) opened the session by discussing his use of grazing incidence X-ray scattering *in operando* to study CO oxidation over a well-defined 2D-system composed of monodispersed gold nanoparticles periodically arranged on a single crystal SiO_2 substrate [DOI: 10.1039/c8fd00007g]. By using grazing angles, this intrinsically bulk technique is able to provide surface structural information. The authors show the peculiar modification of the Au NPs, which flatten due to the enhancement of the NPs' wetting area under the reaction conditions. The findings support a dual model of active sites located at the metal/support interface, in which the CO is activated at the Au metal site and the O_2 is activated at the interface with the support.

Following that, the talk delivered by Prof. Valerii I. Bukhtiyarov (Boreskov Institute of Catalysis and Novosibirsk State University, Russia) was the only example in this conference on the application of *in situ* surface sensitive X-ray spectroscopy to study CO oxidation over bimetallic Pd–Au/HOPG systems [DOI: 10.1039/c7fd00219j]. By means of near ambient pressure XPS, in combination with the on-line detection of the gases by means of mass spectrometry, the authors were able to capture the dynamic segregation of Pd towards the surface under the reactive mixture and at a temperature below the reaction temperature. The surface segregation was associated with the strong chemisorption of CO on Pd, whereas the reversible segregation of Au to the NP surface and the formation of Pd–Au alloys were observed under a CO oxidation regime. The next talk of the session was given by Prof. R. A. Nome (Institute of Chemistry, Brazil), where the authors used hollow Ag–Au NPs of well-defined size and composition synthesized by a galvanic replacement method and characterized by means of UV-Vis and ultrafast spectroscopy, with the goal of contributing new insights into their composition dependent catalytic activity [DOI: 10.1039/c7fd00220c]. Therein, the authors propose an original approach which could ultimately allow the precise determination of the surface composition of bimetallic NPs under the reaction conditions. In particular, the authors study the fundamental molecular motion of NPs by means of ultrafast time-resolved spectroscopy, which depends on their structural composition. They validate this approach for the specific case of the Ag–Au NPs, with pump–probe spectroscopy used to extract fundamental electron–phonon coupling time constants as a function of the nanoparticle composition. The authors also performed all-atom molecular dynamics simulations of model hollow Ag–Au core–shell NPs to characterize the stability and equilibrium structure, and to obtain an atomic view of the NP surface composition. The basic atomistic and electron-lattice dynamics of the core–shell Ag–Au NPs aid the mechanistic understanding and performance optimization of Au–Ag NPs catalysts.

The last talk of the session was given by Mr A. L. Bugaev (University of Turin, Italy), who, similarly to the first talk, used a combination of *in situ* XRPD and XAS to investigate the synthesis of Pd nanoparticles inside UiO-67 for ethylene hydrogenation [DOI: 10.1039/c7fd00224f]. The authors were able to prove that the Pd(II) species of the precursor are initially coordinated to the N site of the ring but lose their coordination with the framework upon hydrogenation, instead coalescing to form NPs entrapped in the cage of the MOF structure. The entrapment of the NPs within the cage of the UiO-67 enabled a much higher stability against coking.

The last part of this session was dedicated to capturing the catalytic process by microscopy techniques. After a lively lunch, the session was opened by Prof. Haio-Joachim Freund (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) who delivered a clear and important message that, in order to isolate the effect of the various components of a catalyst, *in situ* characterization should focus on a systematic approach, which looks at systems with an increasing level of complexity to finally approach the real system [DOI: 10.1039/c7fd00209b]. Prof. Freund elaborated on two systems: (a) the design of a model system for the Phillips catalyst (Cr/SiO_2) for ethylene polymerization and (b) Au NPs on MgO(100)/Ag(100). For the first example, after many years of attempts, it is now possible to investigate the mechanistic aspects of this reaction at the atomic scale thanks to recently developed thin silica films grown on metals as a well-defined silica support. Indeed, beautiful high-resolution scanning tunnelling microscopy (STM) images of the bilayer film are reported in the paper. Therein, the authors also discussed surface sensitive data obtained by XPS, noting that a simple discussion based on binding energy (BE) chemical shifts could be misleading without associating complementary characterization techniques.

In the second example, the authors studied the dynamics of the Au NPs on MgO, under low pressure CO_2, by means of STM. In this way, they were able to observe the reaction, which is confined to the rim of the particles where the molecules of CO_2 adsorb and convert into oxalate species as confirmed by infrared reflection–absorption spectroscopy (IRAS).

The session was concluded with the contribution by Dr Stig Helveg (Haldor Topsoe, Denmark) on the detailed study of step edge structures on $TiO_2(001)$ by means of atomic resolution TEM and STM [DOI: 10.1039/c7fd00222j]. After a careful analysis, taking into account the electron dosage and impact of this on the structure of the material, the authors were able to identify double step edges and several small differences in the periodicity of the "ad-molecule" (ADM) structures along and across the double step edges. This ADM structure is a surface reconstruction which covers the surface with rows of TiO_3 replacing bridging O to relieve the large tensile stress of unreconstructed surfaces. The structural agreement between single crystals and NPs holds promise that this combined STM and TEM approach can be used to study complex catalytic systems. In the general discussion, it was emphasised that these *in situ* electron microscopy experiments remain challenging and therefore should be considered as the current state-of-the-art.

Session 3: Control of catalytic nanoparticle synthesis

The day continued with the third session of the meeting, regarding the synthesis of nanoparticles for catalytic reactions, chaired by Prof. Bob Tooze.

The first part of the session was opened by Prof. Laura Prati (Università degli Studi di Milano, Italy) who introduced her work entitled "*Gold as a modifier of metal nanoparticles: effect on structure and catalysis*" where she presented the preparation of bimetallic Au-based particles (Pt, Pd, Ru and Cu) on a carbon support by the sol-immobilisation method, which is known to provide a good control of

size [DOI: 10.1039/c7fd00223h]. Despite similar metal dispersions, the selection of the second metal was of key importance for the resulting activity. Au–Pd and Au–Cu bimetallic systems show a clear synergistic effect in the oxidation of benzyl alcohol; in contrast, the addition of Pt to Au seemed to have a detrimental effect on the catalytic performance, whereas Au and Ru do not seem to form alloys but instead core–shell structures. The second paper entitled "*One pot microwave synthesis of highly stable AuPd@Pd supported core–shell nanoparticles*" was presented by Dr Jennifer K. Edwards (Cardiff University, UK). In this work, microwave decomposition of metal precursors was presented as a one-step quick synthetic method to form well-defined metal nanoparticles without the need for additional reducing agents and minimum post-synthesis washing steps [DOI: 10.1039/c8fd00004b]. In the case of bimetallic particles, this method led to the formation of an Au core surrounded by an Au–Pd shell, in contrast to the bimetallic alloy formation achieved by the sol-immobilisation methods. Even more interesting is the high stability of these core–shell bimetallic nanoparticles, which show constant activity in several consecutive runs for the synthesis of hydrogen peroxide. The session continued with the presentation of Dr Laura Torrente-Murciano (University of Cambridge, UK) entitled "*Continuous synthesis of hollow silver–palladium nanoparticles for catalytic applications*", where a novel flow system for the continuous synthesis of nanoparticles with tuneable sizes was presented [DOI: 10.1039/c8fd00001h]. This innovative approach consists of a number of coiled flow inverter (CFI) microreactors connected in series which enable, for the first time, the separation of the nucleation, growth of cores and galvanic displacement stages leading to the formation of reproducible hollow bimetallic alloy nanoparticles. Bimetallic Ag–Pd hollow particles show a higher activity than their monometallic and solid Ag–Pd alloy counterparts in the reduction of 4-nitrophenol used as a model reaction. These results open the door to the design, understanding and exploitation of hollow nanoparticles in catalysis.

A lively general discussion followed these presentations, prompted by the diversity of the methods, focusing on the ability to tailor the reactivity of nanoparticles by exploring synergistic effects induced by the metal–metal interaction in binary alloys. The role of the reducing agents in the synthesis of the bi-metallic systems was highlighted, and especially their effect on determining the metal's distribution within the NPs (*e.g.* the formation of alloys, core–shell and hollow structures). In this regard, flow reactors offer the opportunity of quickly varying not only the physical parameters (*e.g.* temperature) but also the chemical environments within milliseconds. The control achieved in the design of metal nanoparticles by these different methods, at the core of this event, was stressed, in addition to the importance of using theory to predict not only the resulting structures but also their respective reactivities. As expected when considering synthetic methods for nanoparticles, comments about their scalability were raised. In this context, flow protocols can be designed for the translation of the different synthetic procedures where scalability can be easily achieved by increasing the number of reactors in series.

The discussion extended through the coffee break, after which the session continued with two additional presentations. The first talk was by Dr Scott Rogers (University College London, UK) on a paper entitled "*Supported metal nanoparticles with tailored catalytic properties through sol-immobilisation: applications for the hydrogenation of nitrophenols*", where the importance of carefully adjusting the conditions of colloidal synthesis, *i.e.* temperature and solvent, was further emphasised for the manipulation of the catalyst structure and reactivity. The principle was illustrated for the synthesis of Pd nanoparticles supported on TiO_2, with smaller particles achieved at lower temperatures, presenting a higher activity towards the hydrogenation of *p*-nitrophenol and increased stability on consecutive runs; slightly bigger NPs are formed at high temperatures, where aggregation seems to take place [DOI: 10.1039/c7fd00216e]. The following work was introduced by Prof. Philip Davies (Cardiff University, UK)

who emphasised the role of the support and its functionality in the design of nanoparticle-based catalysts in their paper entitled "*The deposition of metal nanoparticles on carbon surfaces: the role of specific functional groups*". In their work, they use highly ordered pyrolytic graphite crystals (HOPG) as model surfaces to understand the effects of specific functional groups including hydroxyl, ether and carbonyl groups on the formation of Au nanoparticles. In this elegant approach, by a combination of AFM and XPS characterisation, they demonstrate the direct involvement of hydroxyl groups in the reduction of gold ions, whereas carbonyl and ether groups promote the nucleation of Au^{3+} ions [DOI: 10.1039/c7fd00210f]. These results reveal the actual effects of previously reported carbon acid treatments, providing the initial rationale behind the effect of oxygen species on the support to stabilise gold nanoparticles.

The enormous complexity of supported nanoparticle-based catalysts was the focus of the following discussion. In general, the importance of *in situ* characterisation during the synthesis of nanoparticles was acknowledged for revealing the effect of key synthetic parameters such as temperature, solvent, metal precursors, support functionality, reducing agents, *etc.*, and to understand and consequently control the resulting catalytic systems.

This stimulating day concluded with the conference dinner at the Royal Society in a more informal manner, including the famous celebration of the Loving Cup tradition (Fig. 3).

Session 4: Application of new nanoparticle structures as catalysts

The final day of the event was focused on the applications of new nanoparticle-based catalysts, chaired by Prof. Chris Hardacre. The session was opened by Prof. Chris-Kriton Skylaris (University of Southampton, UK), with a talk entitled "*DFT calculation of oxygen adsorption on platinum nanoparticles: coverage and size effects*", which investigates the

Fig. 3 Attendees are presented with the outlines of the Loving Cup ceremony of the Faraday Discussions, where toasts are given to the memory of Mr Marlow, Angela and Tony Fish, and to the Faraday Division.

nanoparticle structure and chemistry of the state-of-the-art catalysts for hydrogen fuel cell electrodes [DOI: 10.1039/c7fd00218a]. Addressing indirectly the question of optimal nanoparticle sizes, the authors acknowledged that the scope of the problem is beyond standard computation and focused on the effects of O coverage on the chemical properties. In their work, it was observed that, as nanoparticle sizes grow, the adsorption energies decrease and converge to bulk surface values, correlating also with the d-band properties. The subsequent discussion focused heavily on the capabilities of the methodology developed and used by Prof. Skylaris, namely the linearly scaling ONETEP package and the recent implementation of a linear-scaling implementation for metals,[11] provoking memories of Wilke Dononelli's presentation of CCSD(T) on Day 1. Such approaches are beneficial for large systems, beyond the maximum of 309 atoms addressed by Skylaris and co-workers in this meeting's presentation, and can help to improve the understanding of chemistry on large nanoparticles. From a chemical perspective, several calls were made to look at benchmarking of these results with experiments, and consideration of whether a surface oxide has successfully formed; both ideas were acknowledged as being of value in future work.

In the second presentation, Dr Katharina Brinkert (California Institute of Technology, USA) discussed the development

of technologically advanced III–V semiconductor absorbers coupled *via* an interfacial film to an electrocatalyst layer for photoelectrochemical (PEC) cells for H_2 production from water [DOI: 10.1039/c8fd00003d]. The authors demonstrate that shadow nanosphere lithography (SNL) is an auspicious tool to systematically create three-dimensional electro-catalyst nanostructures on the semiconductor photoelectrode, through controlling the NP morphology and optical properties. First, results are demonstrated by means of the photoelectrochemical production of hydrogen on p-type InP photocathodes where hitherto applied photoelectrodeposition and SNL-deposited Rh electrocatalysts are compared based on their *J–V* and spectroscopic behaviour. The authors show that smaller polystyrene particle masks achieve higher defect nanostructures of rhodium on the photoelectrode, which leads to a higher catalytic activity and larger short circuit currents. The ensuing discussion considered then the future steps for this exciting work.

After the morning tea break, the session continued with the presentation by Prof. Paul Sermon (Brunel University, UK) entitled "*Nanoengineering ABO₃ active sites from low-energy routes (TX100-stabilised water-in-oil microemulsions, surface segregation and surface complexation on colloidal AlOOH/sol–gel Al₂O₃ surfaces) for pollution control catalysis*" where water-in-oil microemulsions were used for the formation of $BaCeO_3$ and $LaCoO_3$ particles, with

applications in CO and propane oxidation and phenol removal from aqueous streams respectively [DOI: 10.1039/c8fd00006a]. Such alternative synthetic routes as the use of microemulsions opens the door to novel, reproducible and controllable ways of producing perovskite-type nanoparticles for a wide range of applications. The last talk of this session was given by Prof. Andrea E. Russell (University of Southampton, UK) discussing the paper entitled "*Effects of heat treatment atmosphere on the structure and activity of Pt₃Sn nanoparticle electrocatalysts: a characterisation case study*" [DOI: 10.1039/c7fd00221a]. The authors address the effect of thermal post-synthesis treatment on the quantitative and qualitative composition of Pt_3Sn NPs by applying an approach of multiple bulk and surface sensitive characterization techniques. A correlation of the structural features of these samples with the electrocatalytic performance for CO, methanol, ethanol and 1-butanol oxidation was also drawn. This talk stimulated further discussion as to what would be the most appropriate methodology for obtaining an accurate chemical speciation and quantitative composition of the NPs. Obviously, there is not a general answer to this question; however, the comforting outcome of this study is that for the NPs investigated, the different methodologies indicate the same qualitative trend in composition amongst them.

Concluding remarks

The event was concluded with an inspiring and stimulating lecture by Prof. Cynthia Friend (Harvard University, USA) where she elegantly summarised the community's aspiration to predict catalysts' reactivity and selectivity based on fundamental understanding (Fig. 4). In order to achieve this ultimate goal, atomistic models are of paramount importance to enable the design of real systems. Within this context, theoretical developments, including reaction kinetic models, are presented as a driving force for the understanding of reactions on the surface of nanoparticles. There are different flavours of DFT approaches, where models vary in terms of detail and thus accuracy, creating the need for

Fig. 4 Picture of the community during the concluding remark lecture by Prof. Cynthia Friend.

experimental validation of theoretical methods for electronic structure calculations. Close collaboration between experimentalists and theorists is thus of key importance. In particular, accurate measurements of adsorption energies (calorimetry, TPD), bond distances (diffraction, EXAFS, imaging), vibrational frequencies (IR, Raman), chemical shifts and electronic structures are necessary information for benchmarking theoretical models and validating reaction mechanisms. These efforts should be combined with the modelling of nanoparticles and their interaction with the supports, not only considering model surfaces but also taking into consideration structural complexities (the presence of defects, vacancies and charge transfer). During the event, it was evident that there is a plethora of methods for the synthesis of metallic nanoparticles, especially focused on binary systems, ranging from well-established synthetic strategies such as wet impregnation and sol-immobilisation routes, to novel approaches such as microwave synthesis, microemulsions and flow systems. It was noted that special attention should be paid to the activation pretreatments and their implications to gain the necessary knowledge related to the evolution of the systems. Two approaches can be adapted towards this aim: single crystal model systems, including thin-film integrated with spectroscopy methods, as well as real models. Indeed, *in situ* and *operando* methods provide knowledge of how catalysts evolve under catalytic

conditions. A combination of imaging and spectroscopy provides unique and highly valuable insights into catalyst changes, the structure and composition of materials and their dependency on ambient gas pressure and process temperatures. Metastable states can present surprisingly high reactivities, but also present the challenge of their stabilisation. The importance of reaction kinetics, including the elucidation of elemental steps and the material structural rearrangement, was identified as an additional important focus area for the design of future catalytic systems.

The complexity of some of the above mentioned challenges could be facilitated by better benchmarking and standardisation protocols for both theoretical and experimental studies, which identify the key characteristics of improved and enhanced catalysts. In this context, exciting contributions can be expected from the application of statistical approaches and machine learning contributions for future catalyst discovery and synthesis.[12] This final stimulating lecture provided fertile ground for thoughts to the community that departed after the closure of the meeting until the next Faraday Discussion event in the field: "Reaction mechanisms in catalysis" to be held in Burlington House, London during 22nd–24th April 2020.

Conclusions

This Faraday discussion meeting, focused on the design of nanoparticle systems

for catalysis, was a unique opportunity to bring together the community in a highly scientific and stimulating manner. Its individual format, focused on deep and critical discussion, helps not only to evaluate the state-of-the-art of the field, but also, and most importantly, to set the guidelines for future developments. Without a doubt, a combination of new and controllable synthetic routes guided by *in situ* characterisation techniques and theoretical predictions is required to tackle the complexity of supported nanoparticle catalytic systems.

Acknowledgements

Notes and references

1 http://www.rsc.org/ScienceAndTechnology/Awards/FaradayLectureshipPrize/2018-Winner.asp.
2 B. C. Gates and F. C. Jentoft, *Advances in Catalysis*, Academic Press, Amsterdam, 2013, vol. 56.
3 A. Kulkarni, R. J. Lobo-Lapidus and B. C. Gates, *Chem. Commun.*, 2010, **46**(33), 5997–6015.
4 V. Aguilar-Guerrero and B. C. Gates, *Chem. Commun.*, 2007, 3210–3212.
5 P. Serna and B. C. Gates, *J. Am. Chem. Soc.*, 2011, **133**(13), 4714–4717.
6 A. Palermo, A. Solovyov, D. Ertler, A. Okrut, B. C. Gates and A. Katz, *Chem. Sci.*, 2017, **8**, 4951.
7 G. Sun and P. Sautet, *J. Am. Chem. Soc.*, 2018, **140**(8), 2812–2820.
8 L. M. Molina and B. Hammer, *Phys. Rev. Lett.*, 2003, **90**, 206102.
9 A. J. B. Robertson, *Platinum Met. Rev.*, 1975, **19**, 64.
10 A. J. Medford, A. C. Lausche, F. Abild-Pedersen, B. Temel, N. C. Schjødt and J. K. Nørskov, *Top. Catal.*, 2014, **57**, 135–142.
11 J. Aarons and C.-K. Skylaris, *J. Chem. Phys.*, 2018, **148**, 074107.
12 https://science.energy.gov/~/media/bes/pdf/reports/2017/BRN_CatalysisScience_rpt.pdf.