Fourier-transform ion cyclotron resonance (FT-ICR) analysis called frequency chasing, where the frequency of each individual ion is tracked to observe the drifts that arise due to the long transients required to perform CDMS in the Orbitrap. Through observing the frequencies of each individual ion, frequency drifts can be accounted for and corrected.

Frequency chasing accommodates the recording of very long transients to over 4 s while reducing artefacts in the spectrum, thus allowing for higher resolution and precision for native mass spectra of MDa ions. By tracking the frequency of the ions through the entire path length, the changes to the frequency due to solvent loss and charge stripping can be used to give direct information on the charge and mass of the trapped ion. Hepatitis B virus (HBV) capsid is composed of 180 or 240 subunits arranged with T (triangulation number) = 3 (3 MDa) or $T = 4$ (4 MDa) icosahedral symmetry, respectively. By combining longer transient times and frequency drift correction, a ~23-fold increase in effective ion sampling and a twofold improvement in mass measurement precision and resolution can be realized.

Native mass spectrometry has been instrumental for the characterization of intact large proteins and protein complexes, and it can contribute significantly to structural biology research. As such, native mass spectrometry has many applications, especially for biotechnology, virology and medicine. However, analysis of large biomolecules can be limited due to mass spectrometry instrumental issues and the biophysics of ion behaviour in mass analysers. The efforts reported by Heck and co-workers clearly demonstrate that single-molecule Orbitrap-based CDMS can make the high-resolution analysis of large MDa-sized biomolecules achievable, and it suggests future strategies to further improve the performance of Orbitrap-CDMS, including measuring transients beyond the 4 s limit. Who knew that "all good things come to those who wait," even for native mass spectrometry? John Fenn's "flying elephants" have never been viewed so clearly.

Muhammad A. Zenaidee[1] ✉ and **Joseph A. Loo**[2] ✉
[1]*Australian Proteome Analysis Facility, Macquarie University, New South Wales, Australia.*
[2]*Departments of Chemistry and Biochemistry and Biological Chemistry, UCLA-DOE Institute, and Molecular Biology Institute, University of California-Los Angeles, Los Angeles, CA, USA.*
✉*e-mail: muhammad.zenaidee@mq.edu.au; JLoo@chem.ucla.edu*

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Competing interests

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INTERMETALLIC COMPOUNDS

Catalytic site seeing

Understanding how surface structure affects catalyst selectivity is limited by the ability to synthesize atomically precise active-site ensembles. Now, by using intermetallic Pd–Zn, a series of well-defined multinuclear Pd–metal–Pd catalytic sites have been generated and studied, providing insights into their selectivity for the semi-hydrogenation of acetylene.

Max Mortensen and Siris Laursen

For over a century, researchers in the field of heterogeneous catalysis have sought to understand and develop compositionally complex materials that exhibit specific and highly tunable surface chemistry. The palette of materials available to the community has progressed from supported monometallic late-transition-metal nanoparticles and naturally occurring zeolites to multimetal alloy nanoparticles and synthetic mesoporous materials (synthetic zeolites and metal organic frameworks), providing new surface and reaction-site chemistry[1]. Understanding and developing intermetallic compound catalysts — which are compositionally ordered, crystalline solids composed of metals, post-transition metals and metalloids — is the next evolution in catalytic materials design.

In comparison to transition-metal alloys, intermetallic compounds present a wide range of improved properties, from well-defined compositions, to improved high-temperature stability, to highly tunable electronic structures. Intermetallic compound catalysts also present a range of surface-reaction-site properties that are directly dependent on the electronic bonding within the solid and the organization of elements at the crystal surface. In the parlance of surface chemistry, intermetallic compounds can present surface reactivity similar to that of the parent elements with tunable reaction-site ensemble size and geometry (through the ensemble effect), slightly modified site reactivity (through the ligand effect) and completely new reaction-site chemistry that is not naturally observed over the parent elements (through strong electronic effects)[2,3]. Gaining fine control over the reactivity and geometric organization of surface elements to both understand and leverage these effects, and thus manipulate catalytic performance, is of paramount interest in intermetallic compound catalysis. However, few studies have demonstrated appropriate control over these materials to draw clear connections between the nature of the reaction site and its catalytic chemistry.

Now, writing in *Nature Chemistry*[4], Janik, Rioux, and co-workers describe an artful demonstration of the control of reaction-site ensemble size (nuclearity) and geometry in the context of controlling catalytic activity in the semi-hydrogenation of acetylene to ethylene — an industrially relevant reaction. They investigated the catalytic performance

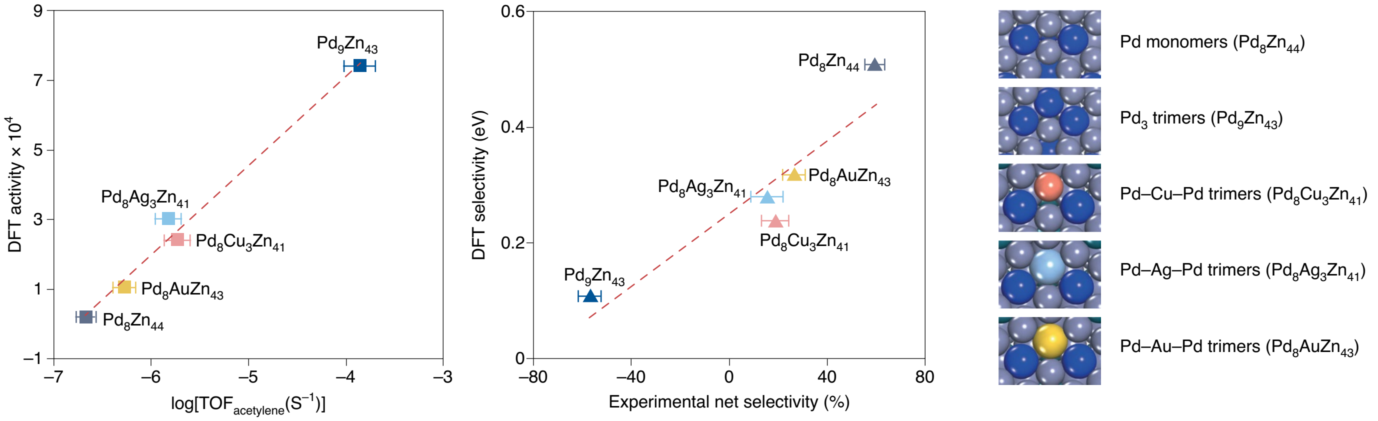

Fig. 1 | Agreement between theory and experimental kinetics for activity and selectivity. The activity (left) and selectivity (right) show strong agreement between experimental kinetics and density functional theory. The agreement shows model catalytic systems can be controlled and their structure–activity relationships understood. Schematic structures of the various reactive sites (materials) studied are shown on the far right. Images reproduced from ref. [4] Models calculated using Density Functional theory (DFT).

of a series of Pd–Zn intermetallic compound catalysts with well-defined, isolated, three-atom Pd–M–Pd active sites. Through careful control of the palladium to zinc ratio and the addition of a tertiary unreactive metal (M = Cu, Ag or Au), Janik, Rioux and co-workers were able to produce palladium monomers (nominally Pd–Zn–Pd), trimers (Pd–Pd–Pd) and Pd–M–Pd ensembles at the surfaces of the crystals (Fig. 1, right). They characterized the materials using a combination of quantum-chemical modelling and experiments (advanced synthesis methods, energy-dispersive X-ray and inductively coupled plasma optical emission spectroscopy, scanning electron microscopy and X-ray diffraction characterization), verifying the production of these specific surface reaction-site ensembles and quantifying how their structure and composition dictated elementary reaction step energetics.

The ability of Janik, Rioux and colleagues to control surface ensembles originates from a considerable understanding of the crystal structure of the γ-brass phase of the Pd–Zn intermetallic compound, element site preference in the crystal structure and surface facet energetics. Their approach illustrates the level of understanding needed to thoroughly control the surface composition of a complex multi-element solid compound and will serve as a model for other investigators in the field. The prominent use of quantum chemical modelling techniques to understand the compositional ordering of elements, surface facets presented and surface reaction energetics nicely illustrates the continued rise and power of theoretical approaches in heterogeneous catalyst design (Fig. 1)[5]. Just a few decades ago, this was assumed by many to be impossible. Now, the rational design of complex catalytic materials is clearly within our grasp.

The catalytic reaction itself acts as a characterization tool and is powered by both well-developed experimental and theoretical techniques to provide intricate molecular insights into the nature of the reaction site. Using these molecular insights, Janik, Rioux and colleagues were able to manipulate the catalytic selectivity for ethylene by systematically presenting palladium monomer and trimer reaction sites, by carefully balancing the palladium to zinc ratio and through the addition of coinage metals (Pd_8Zn_{44}, Pd_9Zn_{43}, $Pd_{10}Zn_{42}$, Pd_8AgZn_{43}, Pd_8CuZn_{43} and Pd_8AuZn_{43}). The highly selective catalyst (Pd_8Zn_{44}) also retained high selectivity towards ethylene up to 100% conversion of acetylene, which is vital for downstream catalytic polymerization processes.

The study from Janik, Rioux and colleagues illustrates what is currently possible in the field of rational catalyst design, but further improvement of well-defined catalyst synthesis and characterization is still needed. For example, the catalysts used were synthesized by the melt method, which provides excellent control over bulk crystal structure and compositional ordering in the intermetallic, but also produces an ingot of material that must be mechanically cleaved into smaller particles to enhance surface area. The processes used to reduce particle size involve high-energy impact events that cleave crystals thus also provide enough energy to readily manipulate surface compositions. To avoid these issues, growth of nanoparticles on high-surface-area supports must be developed. However, the use of more reactive elements such as zinc or post-transition metals that bind strongly to support surfaces can result in slow diffusion and inhibit stoichiometric nanoparticle formation. Ongoing research, including in my group, aims to understand this synthesis approach, as well as supported nanoparticles of several late-transition-metal–post-transition-metal intermetallic compounds with near-phase pure crystal structure.

Equally important to controlling bulk composition of intermetallics is the control and appropriate measurement of surface compositions. Janik, Rioux and colleagues clearly demonstrate the presence of specific reaction-site ensembles and a control of their composition when a tertiary element is included by using catalytic performance as a probe. This approach is appropriate due to the sensitivity of catalytic reactions and the ability to model their reaction energetics with appropriate accuracy. However, the direct measurement of first atomic layer surface composition should be an aim of the heterogeneous catalysis community. X-ray photoelectron spectroscopy is often employed for surface composition analysis, but because of the electron escape depth, the composition measured is actually an average of the first few nanometres of the surface or more. On the other hand, high-sensitivity low-energy ion scattering (HS-LEIS) is a technique that can provide first-atomic-layer surface composition information[6]. There are few HS-LEIS instruments in the world, but they are becoming more common and deployed as user facilities. There are currently two in the US that may be used by the community (at Lehigh University and the University of Colorado, Boulder). If the community embraces characterization of catalytic materials at the level of the first atomic layer, more rapid advancements in catalyst design and structure–activity relationship development are assured.

Overall, Janik, Rioux and colleagues have demonstrated considerable control over the Pd–Zn intermetallic compound catalyst and convincingly connected catalyst performance with the ensemble size (nuclearity) and geometry. However, the intermetallics studied represent a small selection of what is possible with respect to the production of new surface chemistry. Considerable work is still needed to understand the surface chemistry of intermetallic compounds composed of more strongly interacting elements in which wholly new electronic structures are produced and markedly different surface chemistry is present including formulations that are not based on expensive noble metals such as palladium. ❐

Max Mortensen✉ **and Siris Laursen**✉
Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN, USA.
✉*e-mail: mmorten1@vols.utk.edu; slaursen@utk.edu*

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Competing interests

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NANOTUBES

Keeping COFs in the loop

The rational synthesis of organic nanotubes and their hierarchical architectures has remained challenging. Now, one-dimensional hollow covalent organic frameworks have been prepared that can further assemble into toroid-shaped materials.

Gabrielle A. Leith and Natalia B. Shustova

Graphitic materials (such as nanoribbons, graphene, π-bowls and fullerenes) have attracted intense interest — and have been the focus of Nobel prize-winning investigations — owing to their unique carbon-based structural motifs and corresponding physicochemical properties that give rise to the materials' unusual performances[1,2]. These carbon-rich structures serve in a myriad of applications ranging from optoelectronics to photovoltaics to drug delivery systems[3–5]. Such practical versatility explains the sustained interest from the broader scientific and industrial communities in this area of research. Carbon nanotubes (CNTs), which possess one-dimensional (1D) electric and thermal conductivity, as well as high mechanical strength, have found use in particular as components in batteries, sensors, membranes, and nanoprobes[3–7].

A bottom-up approach using synthetically tunable building blocks is a rational pathway to access carbon-rich nanotubes whose properties can be modulated. Specifically, precise control of the nanotubes' height and width is very desirable as these parameters affect the materials' overall performance, yet this has proven to be a persistent challenge, as shown with CNTs[3,5–7]. Among available methods, the self-assembly approach from predesigned building blocks can lead to the facile preparation of nanotubes. This has been demonstrated, for example, with 1D hollow metal–organic frameworks (MOFs)[6,7]. Formation of these tubular MOFs is relatively straightforward through a typical solvothermal synthesis — that is, heating the semirigid organic linkers in the presence of metal salts — with ligands judiciously chosen to promote the MOF growth in one direction. Yet it has remained challenging to synthesize their covalent organic counterparts.

In a transformative work presented in *Nature Chemistry*, Suvendu Karak, Giovanni Pavan, Rahul Banerjee and co-workers have devised a tetratopic tetraamine and a ditopic dialdehyde that assemble into covalent organic nanotubes (CONTs) by imine condensation; the prepared materials in turn serve as precursors for the formation of complex and unique toroids (Fig. 1)[8]. The CONTs were formed through a one-pot synthetic route. The orientation of the amine groups is key to promoting the growth of a well-defined cylindrical structure by imine bond formation; the competitive imidazole formation is minimized by optimizing the reaction conditions. It is easy to imagine that functionalization of the different building blocks may lead to a family of derivatives through synthetic modifications of the linker's core, providing a pathway for CONTs modularity and tailoring of their properties. In fact, the researchers prepared two analogous tubular structures, reacting a tetraamine triptycene with either terephthalaldehyde or its dimethoxy-functionalized derivative (dimethoxybenzene-1,4-dicarboxaldehyde (DMDA); see Fig. 1b).

The resulting CONTs were also determined to be porous materials with surface areas — that is, the area of a nanotube interstitial cavity per unit mass of material — of up to 321 $m^2\ g^{-1}$. This is comparable with single-walled CNTs, whose surface areas typically do not exceed 600 $m^2\ g^{-1}$. The synthesis of the materials is relatively rapid, as formation of nanotubes with a length of 100–200 nm and a diameter of ~5 nm were observed within the first six hours of the reaction. Control of the nanotube length can be achieved relatively easily as longer reaction times lead to longer nanotubes. Indeed, after twelve hours, the CONTs grew to 500–800 nm in length, while their diameter remained unchanged.

After 24–30 hours, the nanotube reached an average length of 1,000 nm and intertwining of the hollow tubes occurred (Fig. 1). This is perhaps an intuitive process: long strands are more flexible, allowing for more interactions between pieces than shorter strands with limited flexibility. The