

Catalysis by clusters with precise numbers of atoms

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Clusters that contain only a small number of atoms can exhibit unique and often unexpected properties. The clusters are of particular interest in catalysis because they can act as individual active sites, and minor changes in size and composition — such as the addition or removal of a single atom — can have a substantial influence on the activity and selectivity of a reaction. Here, we review recent progress in the synthesis and characterization of well-defined subnanometre clusters, and the understanding and exploitation of their catalytic properties. We examine work on size-selected supported clusters in ultrahigh-vacuum environments and under realistic reaction conditions, and explore the use of computational methods to provide a mechanistic understanding of their catalytic properties. We also highlight the potential of size-selected clusters to provide insights into important catalytic processes and their use in the development of novel catalytic systems.

Particles with diameters of a few nanometres or less often have properties that change with the addition of a single atom. Such particles are known as clusters and are of considerable research interest. Clusters can exhibit a range of fascinating reactive, optical, electronic and magnetic properties, which are not observed in the corresponding bulk sample. This distinct behaviour is due to a variety of factors including the very high ratio of surface-to-bulk atoms, electronic shell closings¹ (according to the Jellium model^{2,3}), geometric shell closings⁴, superatomic character^{5–7} in which electrons are shared among atoms differently from bulk materials, and quantum confinement. As a result of this behaviour, the materials are of significant interest in catalysis, where the selectivity and activity of catalytic reactions can potentially be altered through minor changes in the size and composition of a cluster.

Initial investigations of well-defined clusters probed gas-phase ions of only a few atoms⁸. These gas-phase investigations relied on mass spectrometric techniques^{9,10} for the isolation of individual clusters and pioneered techniques for cluster generation^{11–14}. The investigations provided fundamental insights into the reaction mechanisms of O₂ activation¹⁵, C–H bond cleavage¹⁶, C–C bond scission^{17,18}, and oxidation of hydrocarbons^{19,20} with clusters. These gas-phase clusters were also ideal candidates for modelling in early theoretical investigations due to their well-defined composition and limited size. The techniques and fundamental understanding that was established through these gas-phase investigations forms the basis of current investigations of deposited clusters with precise sizes and numbers of atoms.

The deposition of size- and composition-selected clusters on a support material bridges the gap between fundamental gas-phase investigations and the conventional field of heterogeneous catalysis research. It also provides a range of new capabilities to both specialties. The high ratio of surface-to-bulk atoms in the clusters means that they can, for example, provide new reaction pathways and can lower activation barriers. The reduced size of clusters increases the number of under-coordinated atoms compared with larger nanocatalysts, and they can therefore potentially provide catalysts with enhanced activity. As many of the most active catalysts are made from precious metals, the use of clusters could also have a significant economic impact by reducing the amount of precious metal required for a catalytic reaction.

The deposition of clusters on a support material also allows support effects, which are known to be important in many catalytic processes, to be carefully investigated. Because of the reduced size of clusters, and the fact that a considerable fraction of their atoms are located at the cluster/support interface, these effects are likely to be more pronounced in cluster catalysts than typical nanoparticle catalysts, leading to modification of their structural and electronic character. Furthermore, a wide range of techniques including X-ray photoelectron spectroscopy (XPS)^{21,22}, scanning tunnelling microscopy (STM)^{23–25}, (scanning) transmission electron microscopy ((S)TEM)²⁶, atomic force microscopy (AFM)²⁷, and synchrotron methods^{28–30} are available to characterize deposited clusters, and can be used to gain knowledge of their unique properties and interaction with support materials. Moreover, elaborate reactions — Fischer–Tropsch, partial oxidation, polymerization³¹ and dehydrogenation³² processes, for example — that have complex reactants and products, and would be difficult to investigate in the gas phase, can be studied with deposited clusters.

Investigations of deposited, well-defined clusters began with the use of single-crystal surfaces in ultrahigh-vacuum (UHV) conditions³³. (Of particular note is the pioneering work of Cox and Kaldor, in which they deposited monosized metal clusters on Si(100) wafers and compared their electronic structures with XPS³⁴.) These early studies focused on understanding the process of soft-landing a cluster on a support, while also characterizing the electronic and structural properties of the clusters³⁵. During the soft-landing process the ionized clusters lose their charge to the surface becoming neutral species following deposition. Operating under UHV conditions, however, limits the concentration of reactants that can be introduced to the clusters and restricts the reaction studies that can be performed; by bridging the pressure gap, and moving towards more realistic conditions, size-selected clusters have, more recently, been used in a wide range of catalytic processes^{28,36,37}. Furthermore, the transition from single crystals to amorphous supports, which are more realistic and industrially relevant, can provide further advantages, such as providing steric hindrance and stabilizing clusters in wells. These new directions in the application of size- and composition-selected clusters on supports can be used to identify species with high catalytic activity and selectivity, while also probing their applicability for use under both industrially relevant and electrochemical conditions^{38,39}.

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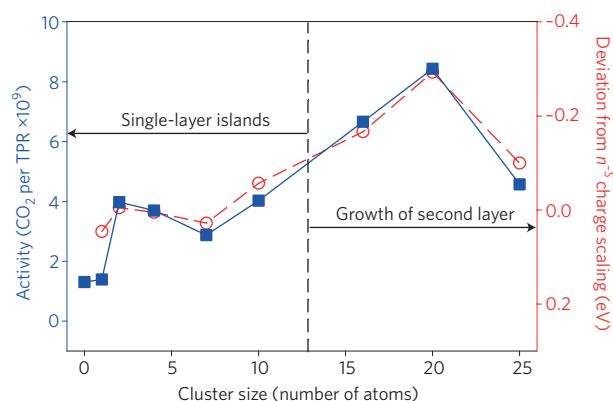


Figure 1 | CO oxidation using Pd atoms and clusters supported on titania.

The graph shows the effect of particle size on CO oxidation activity obtained from temperature-programmed reaction studies (TPR, left axis, solid squares), and correlates the observed activity with the shift in the Pd 3d binding energy relative to expectations from smooth bulk scaling (XPS, right axis, open circles, where n is the number of atoms in the cluster and S is a scaling factor used to fit the electronic binding energies). Clusters with lower binding energy compared with the bulk exhibit enhanced CO oxidation activity. The production of CO₂ from single Pd atoms was equal to that of the rutile TiO₂(110) support, indicating that isolated Pd atoms are not active for CO oxidation. However, the addition of a single atom to the cluster has a dramatic effect: Pd₂ exhibits a twofold enhancement in CO₂ production. The production of CO₂ slightly decreases for Pd₄ and Pd₇, before beginning to increase again for Pd₁₀, with a maximum at Pd₂₀. The fluctuations in binding energy for Pd_{*n*} clusters strongly correlate with CO oxidation results obtained through TPR. Figure reproduced with permission from ref. 21, AAAS.

The advantages of clusters in catalysis

Exerting control over the size of a cluster has proven to be a valuable method for increasing activity and tuning the selectivity in a catalytic process. In addition, multicomponent clusters can be created in which composition is manipulated on the atomic scale, creating mixtures that are not found as stable species in nature. Moreover, support materials can have a significant influence on the character of a cluster via charge transfer, as well as having an effect on cluster mobility. The ability to control each of these characteristics in a well-defined manner provides a powerful method for understanding catalytic processes on the atomic level, and can potentially lead to the development of more efficient and cost-effective processes. Furthermore, well-defined clusters are amenable to treatment with the highest-level density functional theory (DFT) methods, which can deliver molecular-level understanding of catalytic active sites and could potentially be used to lead experiments.

The archetypal cluster with unique catalytic properties is gold deposited on a support. Bulk gold is thought to be largely unreactive, but in the 1980s it was shown that small gold nanoparticles and clusters are active for the oxidation of CO (ref. 40). This discovery led to numerous further studies and the materials have since been shown to be active in a range of catalytic reactions^{41,42}, including the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$)⁴³.

In the subnanometre size regime, every atom can have a substantial influence on catalytic activity. A prime example is Pd_{*n*} ($n \leq 25$) clusters deposited on rutile TiO₂(110) for the oxidation of CO (Fig. 1)²¹. The higher relative activity for samples such as Pd₂/TiO₂ and Pd₃₀/TiO₂ is due to an unstable valence shell. Stability of the valence shell is dependent on cluster size and electron count. A filled valence shell is the most stable, yet the addition of a single atom will greatly decrease stability because weakly bound electrons are being added to the next valence shell. This illustrates how the

alteration of a cluster by a single atom can dramatically change the intrinsic physical and chemical properties.

Catalytic reactions occur primarily on the surface of a nanoparticle, with the core atoms often not directly involved in the process. Core atoms of expensive metals significantly increase the cost of a catalytic reaction without substantially adding to the activity or selectivity; the creation of core-shell particles with cores of a less expensive metal can have a considerable economic impact⁴⁴. As well as the reduction in the use of expensive metals, mixed clusters can also exhibit synergistic enhancement in catalytic activity beyond the corresponding pure clusters⁴⁵. For instance, the Pd₆Ru₆ cluster formed from a solvated carbonylate precursor and encapsulated within the pores of mesoporous silica is highly active in the hydrogenation of alkenes and naphthalene⁴⁶. Specifically, the Pd₆Ru₆ cluster is orders of magnitude more active than monometallic clusters of Pd and Ru in the hydrogenation of hex-1-ene to *n*-hexane with greater conversion and selectivity. The benefits of well-defined, mixed clusters in catalysis are evident and this system is a prime example of developments in synthesis methods to make such species in the solution phase.

Studies of well-defined clusters in catalytic applications have the potential to provide significant fundamental insights into catalytic processes that have so far not been possible due to the complexity of conventional investigations. Methods for synthesizing and depositing clusters are capable of creating samples with a monodisperse size that can range from a few atoms to diameters of more than 10 nm. This capability is paramount in determining the true size of particles responsible for promoting a desired reaction. Solution methods are being developed to create particles with atomic precision, such as size separation based on electrophoresis or chromatography. However, they are not ubiquitous and often require ligands to stabilize particles^{47–49}. When introduced to the same reactant, the terraces of a nanometre-sized particle may promote the production of a different molecule than a subnanometre cluster with more under-coordinated atoms. Therefore, identifying the size of a particle most active for the creation of a desired product may lead to considerable increases in selectivity.

On the molecular level, a catalytic active site encompasses the cluster-like surface chemical bonds involving atoms that directly interact with a reactant molecule and with near neighbours of the catalyst itself. Additionally, if the active site occurs at the interface, atoms of the support contribute to the reaction environment⁵⁰. A cluster of several atoms is an effective model for a surface active site⁵¹ as it is large enough to allow for charge transfer, as well as rearrangement of the adsorbed species. Furthermore, there is evidence that on introduction of reactants such as CO to stepped single-crystal surfaces a major restructuring occurs and nanometre-sized clusters are formed⁵², validating the use of clusters as models for active catalytic sites. Such observations of surface restructuring to form clusters that are the expected active sites, opens a new chapter in materials science for the directed design of catalysts with improved efficiency through the utilization of clusters having appropriate size and composition to form a desired product. Moreover, multifunctional catalysts can be created through the formation of cluster-assembled materials that utilize supports more resourcefully to transport intermediates from active sites, or develop synergistic relationships through deposition of multicomponent clusters or by creating multiple interfaces.

Preparation and characterization of small clusters

Major advances in well-defined cluster studies have relied on the development of novel preparation techniques as well as enhanced characterization capabilities.

Synthesis and mass separation. The limiting factor in all cluster studies is creating a sufficiently high concentration of the desired

species and separating them from the overall distribution formed during cluster generation. Numerous cluster sources have been developed with unique attributes making each suited for different applications^{27,53}. Species created from high-melting-point metals are typically formed through vaporization or sputtering techniques. However, if solvated precursors are available they can be ionized and transferred to the gas phase through electrospray ionization. An important advantage of cluster deposition from ion beams is that the particles can be deposited as bare metal (with the exception of the electrospray technique). This is a huge benefit because most nanoparticles and clusters prepared in solution are covered with ligands, which must be removed by treatment at high temperatures or by, for example, other solution-based processing. This may inevitably destroy the monodispersity of the particles.

Laser vaporization is a highly flexible method for cluster generation in which a laser interacts with a rotating metal rod or disk creating a plasma at the point of contact^{11,54}. A carrier gas aids in cluster formation as well as transporting the atoms and clusters from the plasma to a vacuum region. Vaporization sources can be adapted to create a desired cluster size by adding a nozzle, which will increase collisions before entering the vacuum region. Clusters of mixed composition can also be created through laser vaporization by seeding a gas, such as oxygen or methane, in the carrier gas to form oxides and carbides. Furthermore, mixed clusters can be formed using binary alloy targets⁵⁵ or a dual-rod configuration⁵⁶ to create well-defined clusters containing multiple metals.

Another highly utilized method for cluster formation is magnetron sputtering, which also relies on forming a plasma to sputter a target^{14,26,57}. In this method, a voltage is used to create the plasma, which erodes the target and ejects atoms into a rare gas where atoms aggregate and form clusters. Through operating dual magnetron-sputtering devices independently in a gas-aggregation cell it is also possible to create mixed clusters^{58,59}. The d.c. magnetron sputtering technique is effective for conducting and semiconducting targets, however ferromagnetic materials present difficulties. In response, radiofrequency magnetron sputtering has been developed to be effective in the creation of clusters from insulating materials⁶⁰. A cold or hot reflex discharge ion source (CORDIS, CHORDIS) is another method utilizing sputtering to create ion beams from a wide variety of elements¹².

Clusters can also be formed through arc discharge by eroding a cathode consisting of the material of interest¹³. New adaptations of arc discharge cluster ion sources are increasing the concentration of clusters created⁶¹ as well as providing means for the creation of mixed clusters⁶². Benefits of arc discharge sources are that they do not require an expensive laser to operate and can be used with ferromagnetic materials as well.

Electrospray ionization is another technique for introducing clusters into the gas phase and concomitantly ionizing these species⁶³. A solution of the cluster precursor passes through a small biased capillary and is electrosprayed into a carrier gas forming a molecular beam of ions through supersonic expansion⁶⁴. The precursors can be introduced to the gas phase with ligands still attached⁶⁵ and subsequently fragmented to remove ligands according to the precursor and bias placed on the capillary⁶⁶. Additionally, some aggregation to larger clusters can occur within the molecular beam during supersonic expansion⁶⁷. Important advantages of the electrospray ionization are that it is a relatively inexpensive technique, it can produce intense ion beams, and requires very little operator maintenance in comparison with other molecular beam techniques. However, one limitation is in finding precursors that are stable in solution and can be electrosprayed.

These sources typically produce a wide distribution of sizes; to create samples of well-defined composition, a mass separation (size selection) technique is necessary. A wide range of size-selection techniques have been developed with each suited to the

charge of clusters created, size range of interest, and required mass resolution. Manipulation and size selection of charged clusters is achieved through utilizing principles of electrostatics. Commonly utilized methods for size selection of charged particles are time of flight⁶⁸, radiofrequency quadrupole mass filters^{34,69}, and electrostatic quadrupole mass filters⁷⁰. Detailed reviews have been written comparing the benefits of each size-selection method in different applications^{27,71,72}.

As methods for creation and separation of clusters have developed to suit the unique purposes and research interests, so have the methods to characterize the prepared species. Characterization methods are available for determination of the bonding characteristics, oxidation state, and structure. Recent efforts are focused on utilizing these techniques *in situ* to determine how characteristics of clusters change during catalytic reactions.

Scanning tunnelling microscopy characterization. Clusters can be well defined in the gas phase and subsequently soft-landed on a surface to keep them from shattering on impact. However, after being deposited on a surface it is important to study the clusters to determine if they remain separated or agglomerate. Many factors come into play when considering the mobility of clusters on a surface including the size of the cluster, chemical nature of the cluster and support, defect structure of the support, temperature of the system, pressure of the system, and chemical make-up of the introduced gases. Scanning tunnelling microscopy is a technique utilized to identify the shape, adsorption sites, and size distribution of adsorbed clusters with atomic resolution^{24,73–76}.

New developments in instrument design are resolving these issues so STM images can be acquired while performing catalytic testing to correlate structural morphology with catalytic activity. Imaging by STM has also been utilized to compare the properties of deposited size-selected Ag_n clusters with comparable Ag islands formed through low-temperature deposition of Ag atoms, when on annealing to room temperature, the clusters would decay and penetrate into the support while the Ag islands would reorganize into larger islands²⁵.

The process of depositing a cluster on a support at low energy, known as soft-landing, leaves the species intact without fragmentation or entering the support; however, when temperature is increased or reaction gases are introduced, aggregation or decay often occurs changing the size of the cluster. Increasing the impact energy of deposition, known as pinning, results in the displacement of support atoms with a cluster, leading to a surface-bound species resistant to diffusion at room temperature²³. An STM investigation of Ag₇₅⁺ on a graphite surface determined that a threshold energy of 750 ± 50 eV is required to pin the cluster⁷⁷. Deposition at lower energies of samples with equal atomic loading results in aggregation of clusters. A similar investigation of Pd clusters on a graphite surface determined that an equivalent pinning energy was necessary for comparatively sized clusters to prevent them from sintering under realistic reaction conditions⁷⁸. Moreover, the stability of the clusters can be tailored by adjusting the pinning energy with respect to the threshold energy, forming catalysts with high sintering resistance at relevant reaction conditions.

Comprehensive investigations of cluster dynamics have been performed using STM to determine the three-dimensional structure as well as mobility. Gold atoms deposited on TiO₂(110) are found to have high mobility and form large clusters upon soft landing⁷⁹. In stark contrast, STM images showed Au₂ clusters to be highly isolated and laying flat on the surface. In fact, Au_{2–8} clusters remain isolated when soft landed on the TiO₂(110) surface. Scanning tunnelling microscopy is also useful in probing the height of a cluster. Au_{2–4} was observed to lie flat on the surface while Au_{5–8} presents a layered structure. Revealing the structural dynamics of a cluster on a surface is crucial to understanding catalytic systems. Another example

employs STM to investigate the diffusivity of Au clusters deposited on monolayers of C₆₀ supported by an Au(111) under-layer⁸⁰.

Scanning tunnelling microscopy is also used to determine the structure and density of clusters exposed to a reactive atmosphere, such as the catalytic oxidations of CO (ref. 76) as shown in Fig. 2a.

Atomic force microscopy characterization. Another alternative technique for imaging well-defined clusters that have been deposited is AFM. For example, it has been utilized to investigate the cluster–support interaction and agglomeration of Au_n (with cluster diameters of 1–3 nm) species deposited on a cleaved mica substrate (Fig. 2b)⁸¹. For comparison, identical Au_n clusters deposited on atomically flat Au(111) and Ag(111) films displayed significant differences in morphology. The clusters on Au(111) and Ag(111) remained individual with at most a few clusters aggregating into islands. This investigation demonstrates the importance of cluster–support interactions as the mica surface has a weaker interaction and results in cluster diffusion and aggregation after deposition.

(Scanning) transmission electron microscopy characterization. Transmission electron microscopy is another useful method for imaging deposited clusters to characterize stability on various supports and under diverse conditions. It has been utilized to monitor the agglomeration of individual clusters into islands and can distinguish when the individual clusters have sintered into a single grain²³. A typical TEM image from a study of the coarsening of supported clusters is shown in Fig. 2c (ref. 82).

Aberration-corrected STEM has been utilized to study many systems including a solution-phase method of cluster formation to determine uniformity of size induced through treatment conditions⁸³. STEM images revealed clusters of six Au atoms or less were formed through solution treatment at 318 K. Typical methods for solution-phase cluster generation create a wide range of nanoparticle sizes that can be observed through STEM on the same sample. The reported method created a narrow range of small clusters with evidence of uniformity in the STEM images.

A representative investigation studied size-selected Pt clusters deposited on thin amorphous carbon films⁸⁴. Clusters of 1.34 and 2.3 nm average size were deposited and transferred in vacuum to the TEM chamber for imaging. The stability of the Pt clusters was investigated under relevant reaction conditions by introducing air, water, and diluted acid solutions. Transmission electron microscopy imaging of the clusters after prolonged exposure verified the stability of well-defined clusters prepared in UHV and after introduction to relevant catalytic conditions. Agglomeration of the 2.3 nm Pt clusters due to coverage dependence was also examined on samples prepared with 0.004, 0.02, and 0.05 clusters per nm². The clusters are isolated at low coverage of 0.004 cluster per nm². Amid the mostly well-separated clusters, a few agglomerated clusters appear at coverage of 0.02 cluster per nm². Further increasing the coverage to ~0.05 cluster per nm² results in aggregated Pt clusters in the form of branched structures with nearly no isolated clusters. The TEM investigation provides clear evidence of mobility on a surface and the increasing likelihood for agglomeration with higher cluster coverage.

X-ray photoelectron spectroscopy characterization. The previously discussed methods of investigating well-defined clusters are ideal for imaging and observing variations in size and structure. However, many of the physical and chemical properties of a cluster are related to the electronic characteristics, which are difficult to determine through imaging methods. X-ray photoelectron spectroscopy is a widely used technique for elucidating the electronic character of supported clusters under varying environments. For example, the 3d binding energy of size-selected Ag clusters (3–16 atoms) deposited on sputter-damaged highly ordered pyrolytic graphite

(HOPG) has been compared with Ag ‘islands’ formed through thermal evaporation⁷⁴. Contrary to expectations, no significant shift in 3d level spectra is observed. However, a comparison with Ag islands of similar size created through thermal evaporation shows a significant difference in core-level shift (Fig. 2d) indicating a different chemical environment for the Ag atoms, thus reflecting an effect of the preparation method on cluster properties. The difference in electronic properties may be due to dissimilar isomers being formed as well as distinctive metal–support interactions. Although the two preparation methods create Ag particles of similar size, XPS has shown that mass-selected Ag clusters formed through soft-landing on sputter-damaged HOPG differs significantly with Ag islands created via thermal evaporation.

Utilizing XPS, differences in binding energy have been identified for size-selected Pd_n (n = 1–25) clusters deposited on TiO₂(110) substrates (Fig. 1)²¹. The evolution of the binding energy for Pd_n clusters strongly correlates with the CO oxidation activity of the clusters: clusters exhibiting a higher binding energy were less active in CO oxidation, while the highest activity was observed for the 20-atom cluster, with the lowest binding energy. The core-level electrons probed via XPS indirectly reflect the valence electronic structure. Thus, a stable valence electron shell would tend to increase core-level binding energy. The increased stability of a valence electron shell is likely to be the cause for decreased reactivity for Pd₁ and Pd₇ on TiO₂ samples. As shown here, XPS is a useful tool for investigating the electronic structure of well-defined clusters and provides insights into catalytic mechanisms.

Synchrotron radiation investigations. Owing to the high flux of X-rays available and versatility of beamlines, synchrotron radiation has become a valuable tool for investigating deposited, size-selected clusters. To keep well-defined species from aggregating, coverages are typically less than 15% of an atomic monolayer equivalent. Such low coverages are often difficult to analyse and greatly benefit from the high flux of X-rays provided by synchrotron radiation sources. New techniques utilizing synchrotron radiation are continually being developed to probe clusters under conditions more relevant to catalytic processes. Utilization of synchrotron radiation to perform ambient pressure X-ray photoelectron spectroscopy (AP-XPS) enabled the investigation of Pd_n (n = 4, 10, 17) clusters on amorphous alumina thin-film supports in oxidative and reductive environments (O₂ and CO, respectively)⁸⁵. In comparison to Pd foil, the characteristics of the atoms in the Pd clusters are different having Pd 3d binding energies 1 eV–1.4 eV higher under both oxidative and reductive conditions. Additionally, the AP-XPS spectra for the clusters show a sole Pd component suggesting the conditions affect the atoms equally, indicative of a likely two-dimensional structure, while multiple Pd components are observed for the Pd foil. Investigations utilizing novel techniques for *in situ* characterization (such as AP-XPS) to probe well-defined clusters are essential to develop a fundamental understanding of catalytic materials and will lead to more proficient design of catalytic processes.

The adaptability of synchrotron radiation and beamlines provides the facilities to characterize well-defined clusters through multiple methods. In particular, X-ray absorption spectroscopy (XAS), XPS and Auger electron spectroscopy (AES) were performed at a beamline on Cu₁₉ clusters of 5% and 40% of a monolayer coverage that had been soft-landed on silicon wafers for comparison with bulk Cu (ref. 30). The XAS spectrum of the Cu₁₉ clusters shows distinct differences to the bulk in both absorption edge and multiple scattering fine structure (Fig. 2e). Even at 40% atomic coverage density, the clusters remain primarily isolated. The XPS results show a shift to higher energy as well as widened full-width at half-maximum (FWHM) for the Cu₁₉ clusters compared with bulk Cu. Although the clusters in the 40% coverage sample are isolated, AES analysis provides evidence for interaction between the clusters as a smaller energy shift from the

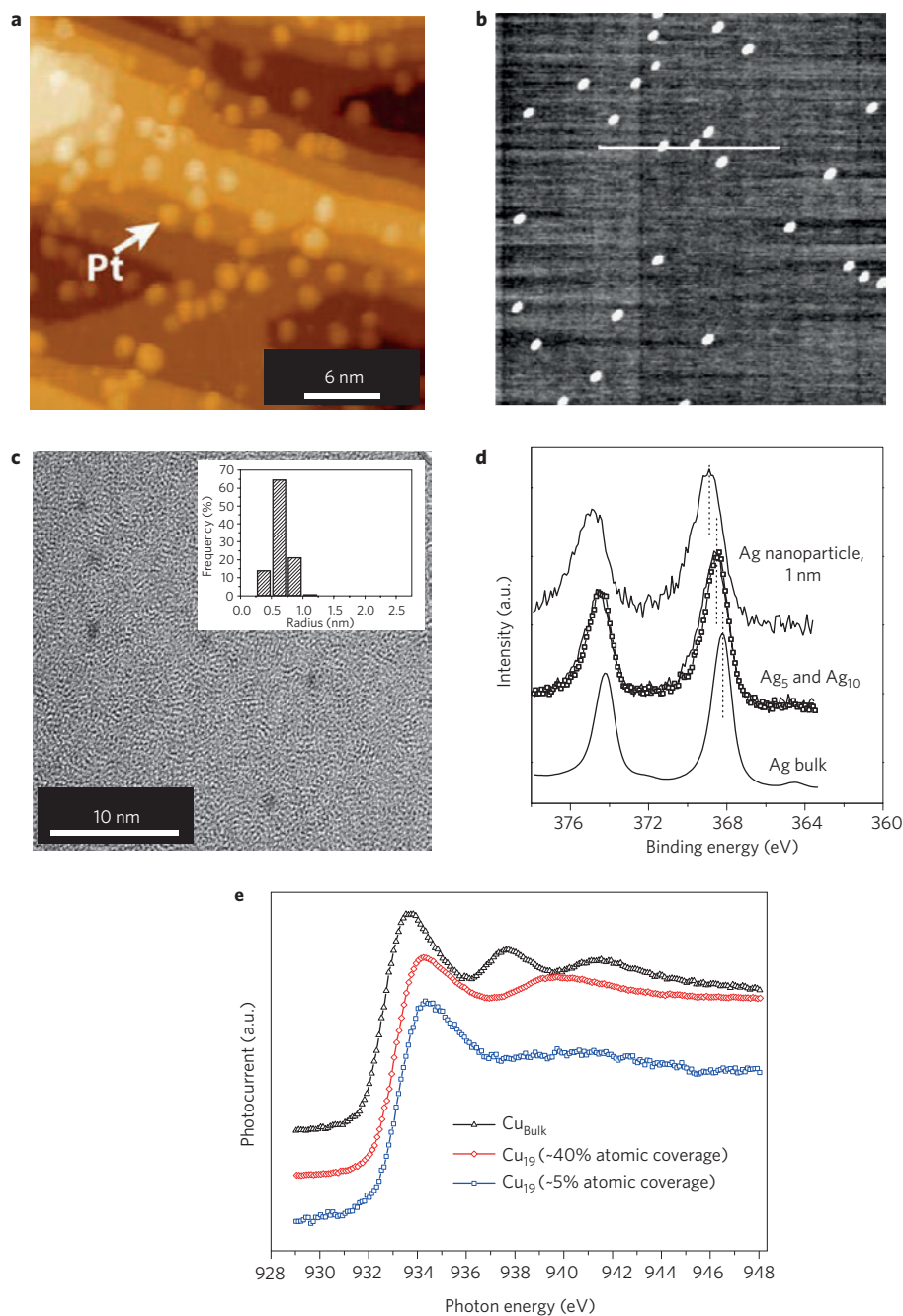


Figure 2 | Techniques suitable for the characterization of small clusters. **a**, STM image after deposition of Pt₇ clusters on TiO₂. The utility of STM is shown by determining the structure and density of size-selected Pt₇ clusters in the catalytic oxidation of CO (ref. 76). At a coverage of 5% monolayer (ML) the Pt clusters are isolated with an average height of 4 Å. **b**, A 5 × 5 μm² (z range, 4 nm) non-contact AFM image of a sample created by depositing Au_n clusters between 1 and 3 nm in size on a cleaved mica substrate⁸¹. A distribution of cluster diameters ranging from 40–140 nm is observed with a mean island height of 1.25 nm, confirming that the deposited clusters diffuse and aggregate on the mica substrate. The white line shows the position of the line scan along which the height and diameter of the islands was determined (data not shown). **c**, TEM of a Au₂₀ cluster-based sample, with a radius of 0.65 nm, 7 days after deposition on amorphous carbon substrates. An investigation into the stability of Au_n clusters ($n = 4, 6, 13, \text{ and } 20$) deposited on amorphous carbon substrates over a 32-month period utilized TEM to analyse the coarsening behaviour of the clusters⁸². Analysis of the clusters 8 months after deposition shows an increase in radius to 0.98 nm with a broader distribution in size indicating significant changes have occurred to the clusters during that time (inset). **d**, Ag 3d level XPS spectra of Ag bulk, Ag₅ and Ag₁₀ clusters deposited on sputter-damaged HOPG, and 1-nm-sized Ag islands prepared using thermal evaporation of Ag atoms on the same substrate are compared⁷⁴. Clusters ranging from Ag₃ to Ag₁₆ were individually soft-landed and exhibited no significant shift in 3d level spectra. However, comparison with Ag islands of similar size created through thermal evaporation onto sputter-damaged HOPG reveals a significant difference in core-level shift indicating that Ag atoms are in different chemical environments due to preparation method. The vertical dashed lines indicate the peak binding energy. **e**, X-ray absorption spectra of supported Cu₁₉ clusters at two different coverage densities (high coverage, red; low coverage, blue) in comparison to a Cu bulk film (black)³⁰. The differences observed between the bulk and both the low- and high-coverage Cu₁₉ samples are due to the non-crystalline character of the isolated clusters. Even at 40% atomic coverage density, the clusters remain primarily isolated. Figure reproduced with permission from: **a**, ref. 76, American Chemical Society; **b**, ref. 81, IOP Publishing; **c**, ref. 82, Elsevier; **d**, ref. 74, Springer; **e**, ref. 30, © AIP Publishing LLC.

bulk spectra is observed. Combinatorial investigations utilizing synchrotron radiation provide the ability to study multiple characteristics of well-defined clusters for the determination of the origin of structure–function relationships.

A combination of *in situ* grazing-incidence small-angle X-ray scattering (GISAXS), *in situ* XPS, and UHV XPS were utilized to investigate the catalytic epoxidation of propylene by Ag₃ clusters deposited on alumina supports to correlate variations in size, structure and oxidation state with reactivity²⁹. At temperatures below 110 °C the clusters remained isolated; at higher temperatures, sintering to 3.5 nm particles occurs. The Ag₃ clusters promote low-temperature formation of propylene oxide and acrolein with combustion (CO₂ formation) occurring above 60 °C. Ultrahigh-vacuum XPS revealed the Ag₃ clusters to be partially oxidized under reaction conditions. The aggregates formed above 110 °C display superior catalytic selectivity for propylene oxide formation under identical reaction conditions with equivalent per surface atom activity to that of the Ag₃ clusters.

UHV studies of supported size-selected clusters

Initial studies involving supported size-selected clusters were performed under UHV conditions to understand the deposition process and determine the influence of support materials on electronic and structural characteristics. Performing these experiments under UHV conditions was necessary to limit the influence of co-adsorbed species. Additionally, considerable technical difficulties arise for many characterization methods at pressures above UHV. Moving forward, studies were conducted to model simple catalytic reactions under UHV conditions by dosing size-selected clusters with a small quantity of reaction gases. Carbon monoxide oxidation⁸⁶ is the model reaction most widely studied due to its simplicity and significance. Subsequently, more complex reactions have been investigated including acetylene cyclotrimerization^{86,87} and hydrazine decomposition⁸⁸. Such model studies are fruitful in elucidating the basic mechanism of a catalytic process and determining the influence of cluster size as well as support interactions leading to enhanced catalytic systems.

Comprehensive studies have been performed to investigate the oxidation of CO using size-selected Au_{*n*} catalysts due to the notoriety of Au_{*n*} clusters and the significance of the target reaction. Au₈ on MgO(001) has been reported⁸⁹ to be the smallest Au cluster active for CO oxidation at temperatures as low as 140 K (Fig. 3). Au₈ clusters supported by defect-rich MgO demonstrated significantly enhanced CO₂ production compared with defect-poor MgO (ref. 86). A distinct redshift for the CO stretch when adsorbed on Au₈ supported by defect-rich MgO indicated a change in the charge state of the cluster. Unmistakably, the electronic character of the Au₈ cluster is influenced by the support in this study, resulting in markedly enhanced CO oxidation. Further evidence for the importance of metal–support interactions in size-selected cluster reactivity is gained through the investigation of Au_{*n*} cluster oxidation and reduction by O and CO, respectively.

When Au_{*n*} (*n* = 2–10) clusters were deposited on silica surfaces, it was found that Au₅ and Au₇ clusters were resistant to oxidation and reduction as determined by XPS, while a range of oxidation states were detected for the remaining clusters⁹⁰. Conversely, Au_{*n*} (*n* = 2–10) clusters deposited on HOPG were unchanged when introduced to atomic oxygen, except for Au₈. Additional peaks at higher binding energies in the XPS spectra for Au₈ on HOPG after introduction to atomic oxygen are evidence for strong oxidation of the cluster⁹¹. Thus, Au_{*n*} clusters of 10 atoms or less possess chemical properties that are strongly size-dependent while also exhibiting strong metal–support interactions.

The reactivity of size-selected Pd clusters is another system that has garnered attention due to significant catalytic differences observed by altering a cluster by a few atoms. A key process in

oxidation reactions is the ability to activate O₂ by a catalytic material. A range of Pd_{*n*} clusters deposited on alumina have been reacted with O₂, all of which become oxidized, except for Pd₄ (ref. 92).

A significantly higher than expected Pd 3*d* binding energy is detected through XPS for Pd₄, which is attributed to the enhanced stability of the valence shell and inertness towards O₂. Pd atoms and clusters deposited under UHV on MgO supports exhibit size-dependent activity and selectivity in the conversion of acetylene to larger molecules⁸⁶ (Fig. 4). Increasing the size of deposited clusters to Pd₄ has a significant influence in product distribution during the polymerization of acetylene as significant quantities of C₄H₆ are detected at low temperature⁸⁷. Such insights can only be obtained via synthesis methods that can precisely control particle size with atomic resolution. Substantial advances in fundamental understanding of catalytic mechanisms as well as development of size-selected deposition techniques have come from UHV investigations.

Clusters on realistic supports and under realistic conditions

Having developed instrumental capabilities for depositing well-defined size-selected clusters and establishing a fundamental understanding of physical and chemical properties through UHV studies, investigations have begun to address the challenges of examining such species under realistic reaction conditions. For instance, an increase in reaction pressure may have a substantial influence on selectivity and activity. Furthermore, many industrially relevant catalytic processes have complex reactant feeds that are difficult to model under UHV conditions. An additional challenge is the deposition of clusters on technologically relevant support materials, which represent superior models for industrial systems. A major goal is to perform *in situ* investigations of size-selected clusters under the aforementioned conditions to develop a fundamental understanding of the nature of active catalytic sites. Investigations under reaction conditions represent formidable challenges on the stability of cluster-based catalysts, to assure the preservation of the size of the particles during extended tests. Suppression of sintering of particles can be achieved for example by using supports that strongly bind the clusters³² or by pinning the clusters into the support⁷⁸. Other methods of stabilization of the particles can be achieved for example by using patterned surfaces or nanopores^{36,46,78,93,94}, or by applying a selective protective overcoat that ‘locks’ the cluster in place²⁸.

The *in situ* investigation of catalytic materials provides a detailed understanding of an active site under working conditions by probing characteristics including size, morphology, oxidation state, electronic character and others while detecting reactivity products. Size-selected clusters present a unique detection challenge during *in situ* investigation as they are typically deposited in a necessarily low concentration to prevent aggregation. Techniques are being developed to overcome these challenges, many of which utilize high-flux synchrotron beamlines for improved results as well as unique analysis methods including studies performed at a grazing incidence that improves detection efficiency⁹⁵. Such state-of-the-art studies are limited, however many new research efforts are underway.

Studies from our own research group illustrate efforts to investigate size-selected clusters under relevant reaction conditions. The oxidative dehydrogenation of propane by Pt_{8–10} clusters deposited on Al₂O₃ (prepared via atomic layer deposition) resulted in turnover frequencies up to two orders of magnitude higher than previously studied platinum catalysts while also maintaining a high selectivity for propylene³⁷. Soft-landed Au₆–Au₁₀ clusters²⁸ and Ag₃ clusters²⁹ were investigated for direct propylene epoxidation utilizing *in situ* GISAXS to monitor structural morphology during reaction. Both systems were effective in formation of propylene oxide at low temperatures (below 200 °C) with the Au_{*n*} clusters remaining subnanometre, while the Ag₃ clusters aggregated to 3.5 nm (Fig. 5). Strikingly high selectivity for propylene oxide was observed from the Ag_{*n*} aggregates. X-ray photoelectron spectroscopy performed on the Ag₃ clusters

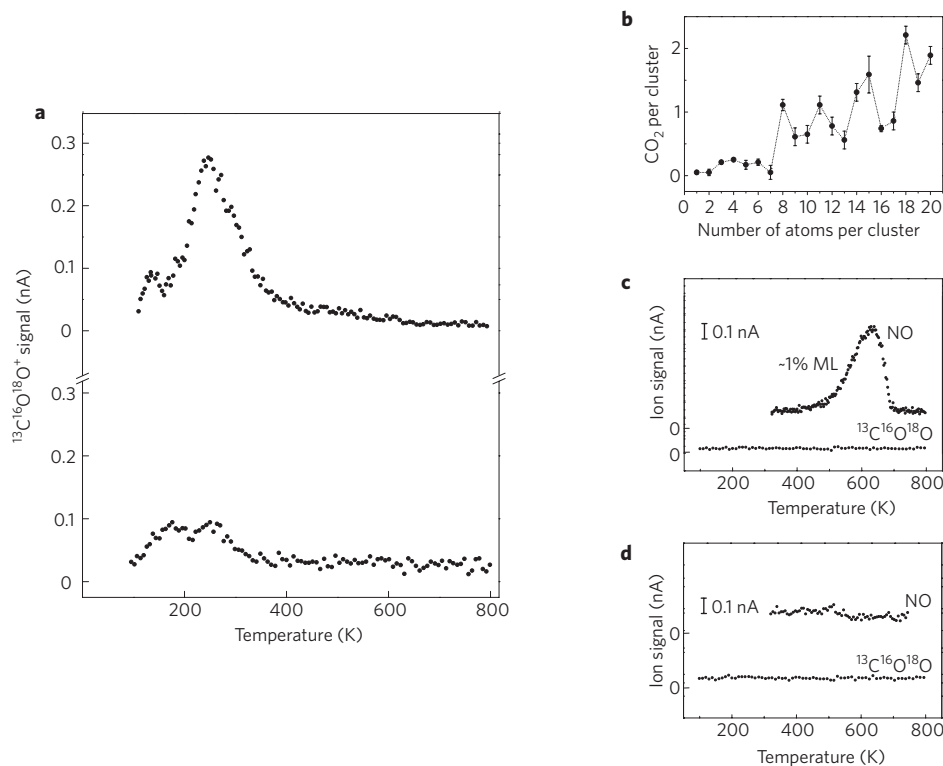


Figure 3 | CO oxidation using MgO-supported Au₈ clusters in UHV. **a**, The Au₈ (0.4% ML) clusters are supported on defect-rich (top) and defect-poor (bottom) MgO(100) films, and the activity is shown by the production of ¹³C¹⁶O¹⁸O obtained by TPR experiments. Au₈/MgO(100) is exposed at 90 K first to an average of 20 molecules of ¹⁸O₂ and subsequently to 20 molecules of ¹³C¹⁶O per deposited Au atom; these exposures correspond to saturation as the CO₂ production did not enhance at higher exposures. **b**, Size-dependent overall reactivity of gold clusters, Au_{*n*}, supported on defect-rich MgO(100) films, expressed as the number of CO₂ molecules per cluster. Note that clusters up to the heptamer are inert (reactivity <0.2). **c,d**, Results of the titration of NO from defect-rich (**c**) and defect-poor MgO films (**d**) (without gold clusters). Note that no CO₂ is formed on both films (lower spectra in each panel) under the same experimental conditions as used for the deposited-clusters experiments. Figure adapted with permission from ref. 89, American Chemical Society.

(*ex situ*) and Ag_{*n*} aggregates (*in situ*) determined the particles are mostly metallic with a small oxidized contribution. Propylene oxide is a prominent industrial precursor currently produced via expensive and environmentally unfriendly methods; thus, identification of a direct catalytic route from propylene is highly desirable and emphasizes the importance of such investigations. The aforementioned sub-nanometre clusters represent a new class of low-temperature catalysts with significant benefits for industrial applications.

Valuable knowledge can also be gained through *ex situ* investigations of well-defined clusters either under model reaction conditions or pre- and post-reaction. The catalytic oxidation of methane was investigated for Pd₅₅ clusters on graphite surfaces to compare particle sintering between pinned and non-pinned clusters⁷⁸. *Ex situ* STM analysis determined the Pd₅₅ clusters pinned at 2 keV to have suppressed sintering versus the soft-landed analogues.

Utilizing size-selected clusters in electrochemical reactions is a novel application^{38,39,96,97} that presents significant difficulty for *in situ* investigation due to the experimental conditions. Pt_{*n*} nanoclusters soft-landed on amorphous carbon supports were treated in a standard electrochemical three-electrode set-up to investigate structural changes that occur under electrochemical conditions⁹⁸. The as-deposited nanoclusters were originally 2.09 ± 0.30 nm and well separated as determined by TEM. On electrochemical treatment, entire nanoclusters migrate and form large branch-like structures viewed with TEM. The Pt_{*n*} nanoclusters were similarly deposited on glassy carbon substrates for electrocatalytic measurements to be performed on the unique species⁸⁴. Comparison of the size-selected nanocatalysts with standard 5 nm and polycrystalline Pt samples displayed significant differences in electrocatalytic activity due to particle size and surface area.

Results from UHV studies can provide intimate and important details about a reaction pathway of a perfectly defined cluster-support system, but such systems can undergo considerable changes as pressures and temperatures increase. For example, defects present on the surface of the support under UHV conditions may not be present at higher pressures or in the presence of traces of contaminants or additives, the crystalline support may reconstruct at elevated pressures and temperatures, and the oxidation state of the catalyst may also change. The pressure gap is being addressed through ambient-pressure studies at increased pressures with respect to UHV conditions and ultimately by studies performed under realistic pressure conditions, especially *in situ/operando*. A central issue here is the stability of the catalysts: in other words, how long they last under stream. To date, model catalysts have typically been tested in a single temperature cycle and over limited time periods (on the order of hours), without monitoring the potential evolution of the size of the particles, especially under UHV, ambient pressure or electrochemical conditions. Recently, however, an increasing number of studies included the characterization of the size of clusters before and after reaction (see, for example, refs 38,76,78,84,98), as well as monitoring the size of the particles *in situ/operando* (in some cases up to ~10 hours or longer, including multiple temperature cycles)^{28,29,32,95}. Furthermore, a handful of studies have reported having the model catalyst exposed to elevated temperatures for periods of time that exceed 24 hours (see refs 36,37). Ways of stabilizing the clusters have also been explored, demonstrating that the aggregation of clusters can be prevented by, for example, pinning of clusters into the supports (see, for example refs 77,78, work on surrounding clusters with an added oxide layer^{28,37} or using nanostructured supports^{36,37}).

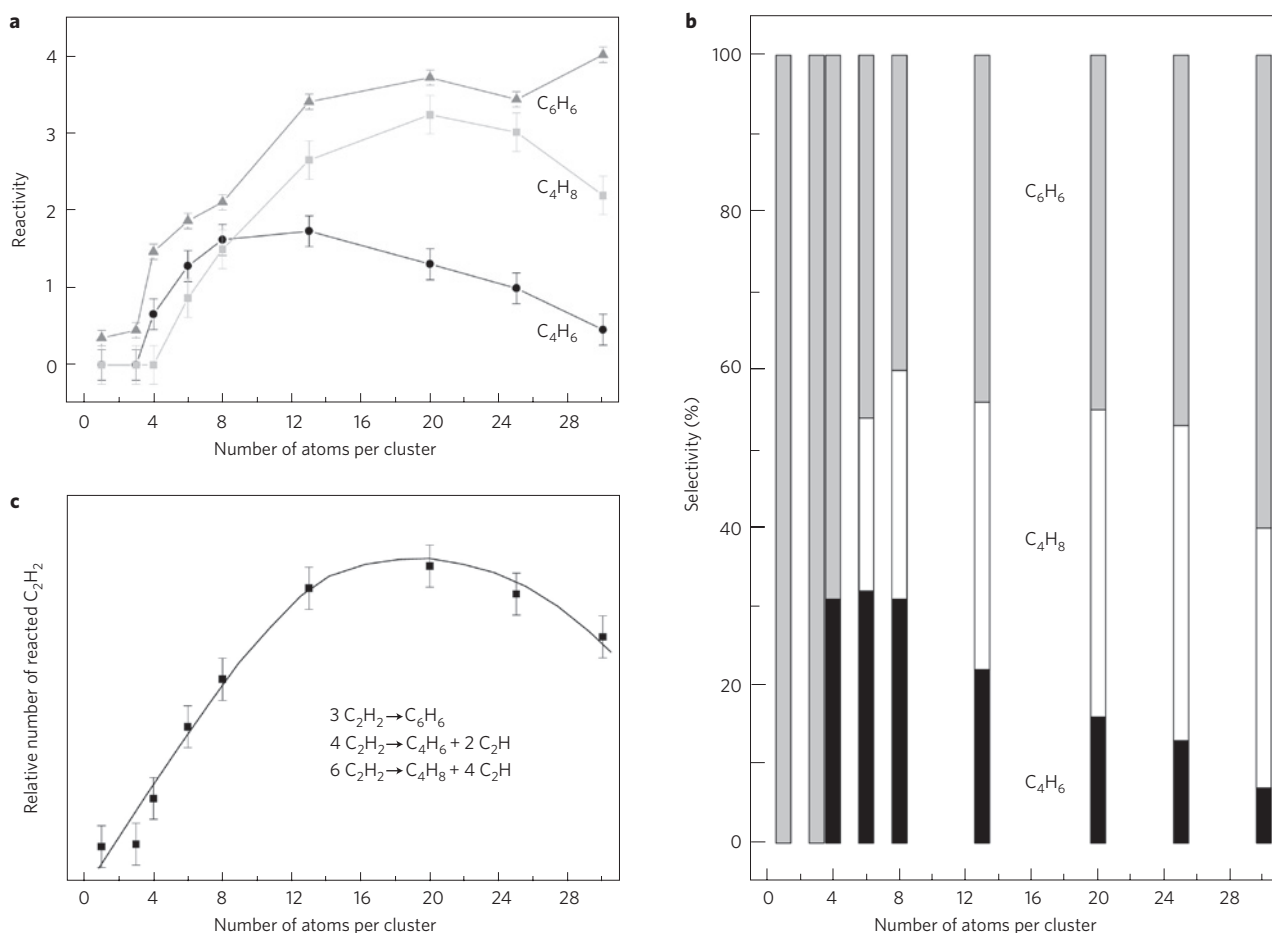


Figure 4 | The size-dependent activity and selectivity of Pd atoms and clusters on MgO in UHV. a,b, Reactivity (**a**; expressed as the number of product molecules per cluster) and selectivity (**b**; expressed as the relative amount in %) of the polymerization of C₂H₂ on size-selected Pd_{*n*} (*n* = 1–30) deposited on defect-rich MgO thin-films. Pd atoms deposited under UHV on MgO supports are observed to be highly selective for creation of benzene on dosing with acetylene. Increasing the size of deposited clusters to Pd₄ has a significant influence in product distribution during the polymerization of acetylene as significant quantities of C₄H₆ are detected at low temperature. Further increase in cluster size to Pd₆ leads to the creation of C₄H₈, showing the significant influence particle size has towards selectivity in a catalytic process. **c**, Also shown is the relative number of reacted C₂H₂ as a function of cluster size. Figure reproduced with permission from ref. 87, © AIP Publishing LLC.

As far as the catalytic testing and interpretation of the results is concerned, a very careful approach needs to be taken when working with such ultrasmall loadings of catalysts. This includes, for example, a careful subtraction of the background signal (that is, products) formed in the reactor with a blank support of identical size and batch as the one the clusters were deposited on, and collected under identical reaction conditions as the cluster-containing sample. (In passing, we note that a notable advantage of the model catalysts is that their loading is known with high accuracy, which allows for a direct and accurate determination of the turnover rates on metal atom basis.) Since the reactors used in these studies are of various designs and different flow conditions, being able to compare the test results obtained on model and/or real catalysts in different reactors could be a valuable addition in the interpretation and validation of results²⁸. Progress has also been made in testing of model catalysts under gas flow conditions that more closely mimic the conditions applied to ‘real’ catalysts, such as catalysts supported on monoliths. Here, the model catalysts are deposited into nanoporous membranes (in some papers dubbed as ‘nanoliths’) and tested in a membrane reactor that eliminates bypass of the reactants potentially present in other types of reactor design^{36,37}.

Computational studies of size-selected clusters

Complementary computational investigations have been enormously valuable in determining the catalytic reaction mechanisms

as well as describing the structural and electronic character of the size-selected clusters. Computational and instrumental investigators have been working together to better understand the fundamental characteristics of catalytic active sites on the atomic scale for a host of reactions^{86,99,100}. Size-selected clusters are well suited for computational modelling due to the systems being well defined and the clusters being relatively small in size. Full DFT treatment can be given to small clusters identifying detailed cluster–support interactions as well as charge localization, which are effects of great importance in catalytic processes.

Computational investigations are also bridging the gap between ideal UHV and realistic reaction conditions. For instance, bare Pd_{*x*} clusters supported on magnesia strongly interact with O₂ to form Pd_{*x*}O_{*y*} clusters that act as oxygen reservoirs for the oxidation of CO (ref. 101). The oxidation of CO is also a system of wide appeal for computational study due to its impact and simplicity. A wide range of catalysts and support combinations have been studied for CO oxidation including Au_{*n*}/TiO₂ (ref. 102), Au_{*n*}/MgO (refs 86,103), Pd_{*n*}/MgO (ref. 101), and Pt_{*n*}/FeO_{*x*} (ref. 104). Such investigations are immensely beneficial in identifying reaction pathways at either metal/support interfaces, under-coordinated sites, or other localized active sites responsible for reactivity with the intention of guiding insightful fabrication of future catalytic materials.

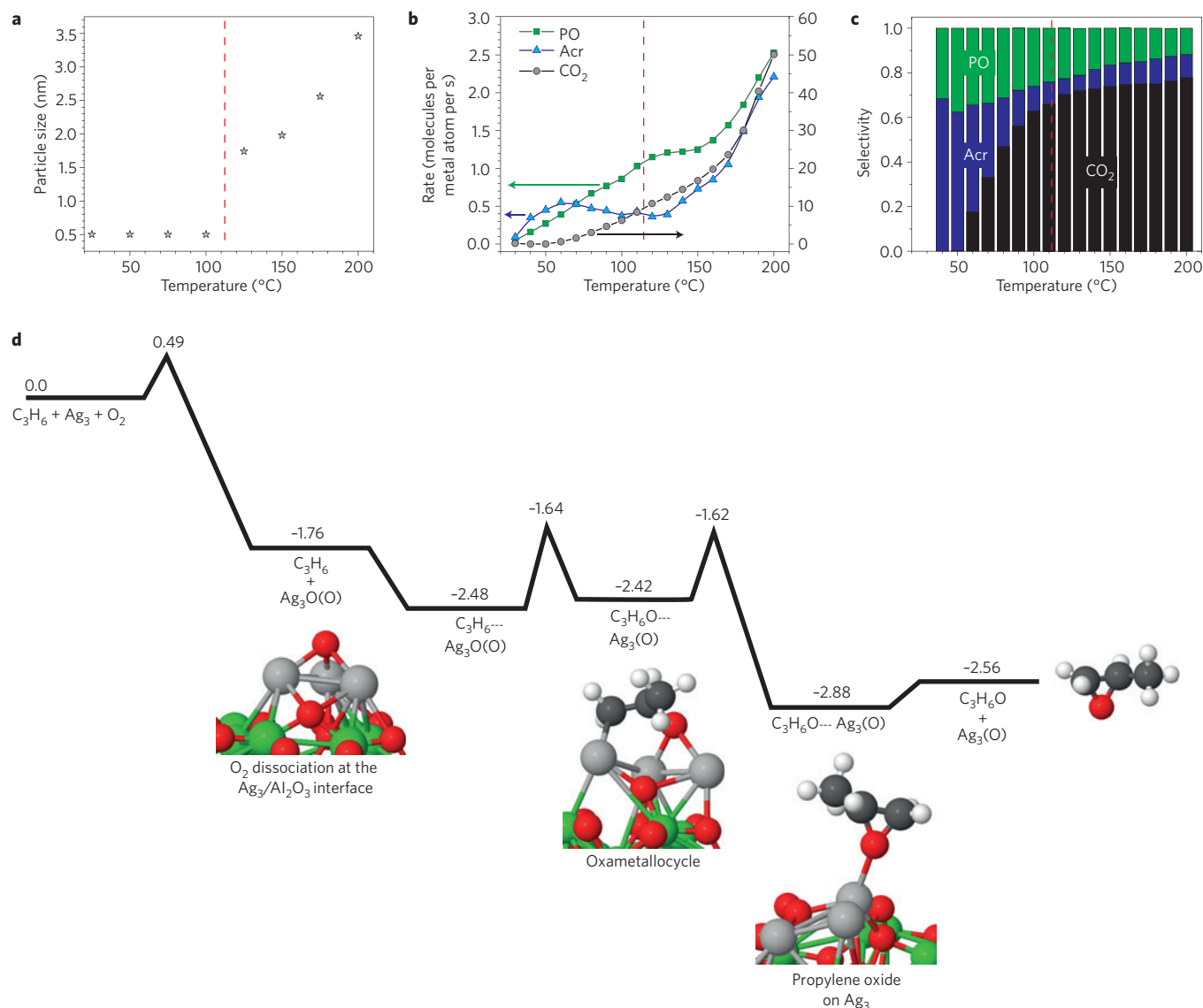


Figure 5 | Propylene oxidation using size-selected Ag₃ clusters on amorphous alumina support. **a**, Temperature-dependent average cluster size from GISAXS, indicating sintering of the clusters above 120 °C. **b**, Rate of propylene oxidation towards propylene oxide (PO), acrolein (Acr), and CO₂ per surface silver atom. (Note the different scale for propylene oxide and acrolein versus CO₂.) **c**, Selectivity of propylene oxide, acrolein, and CO₂ versus temperature showing highest selectivity towards propylene oxide and acrolein at low temperatures. The red vertical dashed lines indicate the temperature at which the sintering of the silver trimers begins. **d**, Energy of intermediates and transition states in the mechanism for epoxidation of propylene from DFT calculations. The apparent barrier for epoxidation is 0.12 eV relative to gas-phase propylene and Ag₃ with dissociated O₂. There are two different oxygen sites resulting from dissociation of O₂ at the trimer/alumina surface interface: (i) the three-fold site on Ag₃, and (ii) alumina at the interface with Ag₃. The latter oxygen is indicated in parentheses. The reaction pathway as shown will result in excess interface oxygen, which can be removed either by migration to the three-fold site (calculated barrier of ~1 eV) or by diffusion and recombination on the alumina surface. Figure reproduced with permission from ref. 29, AAAS.

Further, impactful computational studies have been performed probing industrially significant reactions including propylene epoxidation, propane dehydrogenation, and methanol dehydrogenation. The investigation of Au_n clusters for the epoxidation of propylene has identified the importance of OH and OOH radicals in the reaction mechanism as well as compared the influence of supports including TiO₂ and Al₂O₃ (refs 28,105). Ag₃ clusters supported on Al₂O₃ present high activity and selectivity for propylene epoxidation in comparison to the Ag(111) surface due to a unique open-shell electronic structure possessed by the clusters²⁹ (Fig. 5c). Additionally, vanadium oxide clusters are active in the oxidative dehydrogenation of methanol through a unique mechanism involving the addition of methanol to the double bond in the vanadyl leading to the formation of formaldehyde¹⁰⁰. The aforementioned investigations provide

detailed mechanistic insights into important industrial catalytic processes revealing the unique character of deposited clusters.

Clusters prepared by wet chemistry

The well-defined clusters discussed in this Review, prepared and separated in the gas phase, are ideal systems for identifying the fundamental characteristics of deposited clusters and their unique catalytic properties through changing size of the cluster and support material. However, this fabrication method is not realistic for the production of industrial-scale quantities of catalyst. Owing to the appealing properties of well-defined subnanometre clusters, solution-phase methods are being adapted to create clusters having a narrow size range at significantly larger quantities. Thus, the identification of well-defined clusters active for key catalytic reactions will

direct efforts in solution-phase synthesis to create similar species on equivalent supports.

Synthesis methods of subnanometre clusters in the solution phase began by forming aggregates with various ligands acting as protecting groups to prevent further agglomeration. In some instances these clusters were found to have enhanced catalytic properties^{106,107}, however the ligands are likely to influence the electronic character of the cluster and sizes may be restricted due to synthesis methods. Further developments in synthesis methods are emerging aimed at removing ligands as well as ligand-free preparations for the production of clusters such as Ag_n (ref. 94), Ir_n (ref. 108), and Au_n (ref. 109). For instance, Au atoms that were deposited on a multiwalled carbon nanotube were initially inactive for oxidation of thiophenol. After heating, the Au atoms aggregate to subnanometre clusters that exhibit enhanced catalytic activity. Unfortunately, the aggregation is uncontrolled so a range of clusters are created and continues until the clusters are nanometres in size, which are inactive¹⁰⁹. Currently there are limitations to the controlled solution-phase synthesis of well-defined subnanometre clusters. However, significant efforts are being extended due to the exemplary catalytic properties identified for size-selected clusters.

Future of the field

The application of size-selected clusters in catalysis has made significant progress since early studies on modelling catalytic active sites in the gas phase. Recent experimental developments have led to the investigation of well-defined clusters under realistic reaction conditions and have revealed the remarkable catalytic properties of subnanometre clusters. While important insights have been obtained, such as the identification of a catalytic pathway for the low-temperature production of propylene oxide using Ag_n clusters, significant challenges and opportunities lie ahead for the field.

Catalytic reaction tests, as well as characterization investigations, have so far been hampered by the limited quantities of clusters that can be produced. This problem is, however, being addressed with the development of higher-intensity cluster sources and instrumentation that helps focus ion beams with limited ion loss. Sources are also being developed to fabricate clusters of unique character such as oxides, carbides, and mixed metals with a broad range of composition. Furthermore, the development of *in situ* characterization methods is essential to determine structure–function relationships of well-defined clusters in catalytic processes. Concurrent to instrumental developments, advances in theoretical approaches will enable the modelling of more complex systems, as well as the prediction of clusters with extraordinary catalytic activity.

The continued integration of advances in synthesis, *in situ* characterization, and theoretical modelling can lead to more efficient prediction of advanced catalytic processes. Improved characterization and computational methods are crucial to understanding fundamental aspects of reaction systems including active centres, support interactions, and processes occurring at interfaces. The investigation of size-selected clusters provides an opportunity to build a fundamental understanding of the molecular-scale interactions occurring in catalytic systems, which have until now been unattainable, and can lead to significant advances in many areas of catalysis.

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Competing financial interests

The authors declare no competing financial interests.