

Title: Conquering Catalyst Complexity: Nanoparticle Synthesis And Instrument Development For Molecular And Atomistic Characterisation Under *In Situ* Conditions.

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Abstract: Most heterogeneous, homogeneous and enzyme catalysts are nanoparticles. Conquering the complexity of such materials' mode of operation at the atomic and molecular level necessitates being able to elucidate their structure under operational conditions. Here, we show examples of the crucial interplay of atomic or molecular resolution *in situ* techniques with atomically and molecularly well-defined nanoparticle catalysts to achieve this goal. In particular we focus on mono-dispersed metal nanoparticles in the 0.8 – 10 nm range with precise size distribution provided by modern colloidal synthetic techniques. These have been used in conjunction with a range of *in situ* techniques for understanding the complexity of a number of catalytic phenomena. Drawing on the nanoparticle size discrimination afforded by this approach, most metal nanoparticle catalysed covalent bond making/breaking reactions are identified as being structure sensitive, even when that was previously not thought to be the case. Small nanoparticles, below 2 nm, have been found to have changes of electronic structure that give rise to high oxidation state clusters under reaction conditions. These have been utilized to heterogenize typically homogeneous catalytic reactions using metal nanoclusters in the range of 40 atoms or less to carry out reactions on their heterogenized surfaces that would typically be expected only to occur at the higher oxidation state metal centre of a homogeneous organometallic catalyst. The combination of in-situ techniques and highly controlled metal nanoparticle structure also allows valuable insights to be achieved in understanding the mechanisms of multicomponent catalysts, catalysis occurring in different fluid phases and phenomena occurring at the metal-oxide interface.

Keywords: Heterogeneous catalysis; *in situ* spectroscopy; nanoparticles; particle-size; oxidation state.

Introduction: In Liverpool and Cambridge, UK, Sir David King's work in catalytic surface science, in particular studying adsorption phenomena, was built on combining atomically precisely-controlled single-crystal metal surfaces with the development of the appropriate calorimetry techniques to study these phenomena. It is a pleasure to contribute a paper to honor Sir David King, on his 75th birthday.

Here we highlight the combination of atomically (and molecularly) precisely controlled catalyst systems and the development of the appropriate instrumentation as being highly complementary for studying the molecular level mechanisms of catalysts under *in situ* conditions. While much progress was made through studies on single-crystal metals, modern synthetic techniques provide colloidal nanoparticles of controlled size, shape and/or composition, which can be viewed as a next generation of atomically controlled catalysts. This allow us to build upon studies

made on single-crystals to understand increasingly more complex catalytic phenomena, such as the importance of catalyst size or the metal/oxide interface – not readily studied without access to more complex catalyst structures. However, for employing *in situ* spectroscopic techniques, the homogeneity / simplification of the catalyst afforded by these colloidal nanoparticle syntheses is key – it ensures that the spectroscopic signal reported (an average signal from all particles present in the sample), can be used in conjunction with catalytic data to build up a mechanistic picture of how nanoparticles of a particular size or composition really affect catalytic activity and selectivity.

In this paper we illustrate the use of *in situ* techniques coupled to the deliberate synthesis of highly controlled catalytic nanoparticle structures with a number of recent examples from work in Berkeley. Specifically we show how this combined approach enables demonstration of the structure sensitivity of many metal nanoparticle catalysed reactions; observation of small nanoparticles exhibiting higher oxidation states; elucidation of mechanistic phenomena in multicomponent catalysts; and acid-base type catalysis occurring as a result of the presence of metal-oxide interfaces.

1. Nanoparticle synthesis as a route to catalysts

Many heterogeneous metal catalysts contain small metal particles (with dimensions of a few nm) supported upon large high surface area metal oxides (dimensions often up to microns). Examples of such catalysts are used in many important areas, from automotive catalysis (Pd, Pt, Rh on alumina), to reforming (Ni or other metals on oxide supports), to methanol synthesis (Cu/ZnO/Al₂O₃) to name only a few examples. Such catalysts are conventionally prepared by wet impregnation or precipitation of a metal salt precursor, and subsequent calcination and reduction to yield metal nanoparticles upon the oxide support.[1] Such materials inevitably contain a range of particle sizes, shapes compositions (if more than one active metal). As highlighted in the introduction, in order to study such materials and their mode of operation at the atomic or molecular level, simplifications of the material are of great advantage in order to ensure meaningful correlations between kinetic and spectroscopic data. This is often necessary because signals represent an average of either all the different surface sites available for reactants or all the sites probed by a particular analytical technique, and typical industrial catalysts contain a plethora of different sites resulting from the method of preparation.

Many important discoveries have been made through the use of single crystals as such a simplification – allowing a considerable reduction in the number of variables present as compared to an industrial-type catalyst. An example of such studies is the discovery of the importance of specific atomic arrangements to assist in dissociating N_2 on iron catalysts used for manufacturing ammonia. Experiments were performed on different single crystal facets of iron using auger spectroscopy to determine the relative surface concentration of nitrogen.[2] By preparation of different atomic facets the discrimination using auger spectroscopy, which averaged over all sites in a real catalyst, was made possible. Single crystal studies can be thought of as a first generation of model catalysts, but the recent advances in nanomaterials synthesis now permit a series of more complex or “next generation” models to be prepared, still drawing upon the need for well-defined molecular or atomic structure. These are the focus of this paper. These can be prepared in two dimensions either by further modifications of a single crystal in order to introduce supported nanoparticles,[3-5] or else by separate preparation of 2D nanoparticle samples using wet synthesis protocols and subsequent deposition on a 2D substrate such as a silicon wafer, for instance by Langmuir Blodgett deposition.[6] They can also be applied by deposition of the colloidal nanoparticles on supporting oxide materials to yield 3D structures, directly analogous to industrial type catalysts, but prepared with precise control over the nanoparticle structure independently of the step used to support the nanoparticles on the oxide.[7,8] Figure 1 illustrates these different types of model catalyst system.

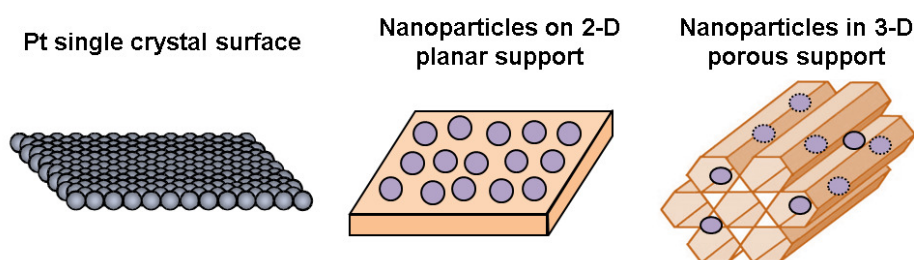
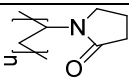
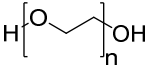
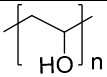
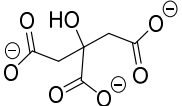
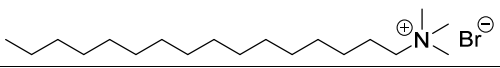
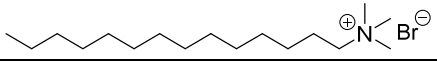
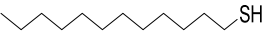
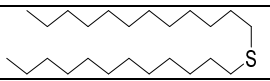
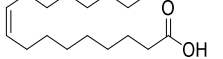
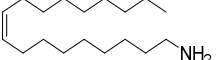
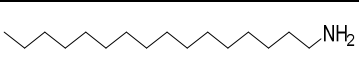


Fig. 1 Schematic showing model catalyst systems from a single crystal metal to colloidal nanoparticles deposited either on a 2-D substrate or in the pores of a 3-D support material

The synthesis of metal nanoparticles, and their synthesis for applications in catalysis has been well reviewed elsewhere.[9,10] In the examples that follow two key techniques are used to prepare the various nanoparticles in solution. Firstly colloidal chemistry using the solution phase reduction of a metal salt (or decomposition of a zero-

valent metal precursor) to produce zero-valent metal atoms in solution, which rapidly nucleate and grow, but are controlled in size using a variety of capping agents. As indicated in Table 1, a large number of capping agents are used in preparing nanoparticles for catalytic studies ranging from polymeric capping agents, such as PVP, to coordinating thiols or long chain acids and amines.

Table 1 Showing the structure of common capping agents used to prepare colloidal nanoparticles for use in catalytic studies

Type of Capping Agent	Examples	Structures	Literature Example
Polymers	Polyvinylpyrrolidone (PVP)		[11]
	Polyethylene glycol (PEG)		[12]
	Polyvinylalcohol (PVA)		[13]
Ionic	Citrate		[14]
	Cetyl Trimethyl Ammonium Bromide (CTAB)		[15]
	Tetradecyl Trimethyl Ammonium Bromide (TTAB)		[16]
Sulfur containing	Dodecanethiol		[17]
	Dodecylsulfide		[18]
Acids and Amines	Oleic Acid (OAc)		[19]
	Oleylamine (OAm)		[19]
	Hexadecylamine (HDA)		[20]

Although initially there was considerable doubt as to the impact on catalysis of such capping agents (in order to function as a capping agent, necessarily a strong interaction with the surface must be present), in many cases we find the reactivity (turn-over frequency) is found to be constant, independent of the capping agent employed.[21] The likely role of residual carbon from this type of synthesis may in fact be little different from residual species from

other catalyst synthesis procedures. The beneficial effects of such capping agents in terms of blocking unselective sites have even been speculated on.[22] In certain instances however the role of the capping agent has been found to play an important role – notably in oxidation reactions where we identify PVP plays an interesting inhibitory role only under oxidising conditions.[23] In general, however, this approach permits the custom synthesis of purposefully designed nanoparticles of controlled size, shape and, for bimetallic systems, composition, which can be used as model catalysts for addressing more complex problems about catalyst mechanism.

The second technique in the examples that follow for preparing well-defined nanoparticles is the use of dendrimer (hyper-branched polymer) templates. This approach is especially important in accessing small nanoparticles with a high degree of size control. The idea here is the dendrimer acts as a ligand able to co-ordinate to a fixed number of metal ions in solution - the uniform structure of the dendrimer determines the number of ions attached to any one dendrimer.[24] The subsequent reduction of the dendrimer then permits small, often < 1 nm particles to be prepared, theoretically with atomic precision based on the number of co-ordination sites available. It should, however, be noted that only under certain conditions does the dendrimer truly appear to control the structure of the nanoparticle as theoretically envisaged.[25] The dendrimer molecule also acts as a capping agent to prevent further aggregation. A number of types of dendrimer have been used to prepare nanoparticles – PAMAM[25] and PPI[26] being most common, but also also triazole “click” dendrimers[27] and metallophosphorous dendrimers.[28] We have shown the PAMAM dendrimer prepared nanoparticles can be deposited on 3D oxide supports as catalysts for typical hydrogenation type reactions (e.g. pyrrole).[29] The reduction process to form nanoparticles and the consequent rearrangement of the dendrimer molecule has been studied using spectroscopy and aberration corrected electron microscopy for Pt – PAMAM dendrimer molecules.[30,31] Interestingly the continued presence of the co-ordinating ligands of the dendrimer allow changes between metallic nanoparticle and oxidised Pt²⁺ like species dependant on the conditions as discussed in Section 4. Again, these metallo-dendrimer systems represent an important model catalyst system for studies attempting to elucidate more complex mechanistic phenomena in catalysis.

2. *In situ* techniques for studying nanoparticle catalysts

Complementary to the availability of well-defined model catalysts is the ability to observe them under working conditions. Recent years have shown the rise of a plethora of techniques for *in situ* or *operando* analysis. The details of such techniques have been well reviewed by us and others.[32,33] The rise in use of *in situ* techniques stems from

a realisation that many catalysts undergo dramatic restructuring in the presence of reactants, pressure and temperature. Accordingly, the working state of the catalyst surface appears very different from that observed before or after reaction, *pre-natal* or *post-mortem* states. A good example of this phenomenon is the restructuring of stepped Pt(557) single crystals in carbon monoxide atmospheres observed by high pressure scanning tunnelling microscopy – small clusters are pulled out of the surface in trimers as the pressure increases to 1 Torr CO, but then returns to a stepped structure when evacuated.[34] Some particular techniques of importance to the examples that follow are optical sum frequency generation spectroscopy, allowing the observation of molecular adsorbates, and synchrotron X-ray absorption and photoelectron spectroscopies, permitting atomic-level, element specific structural characterisation of the catalyst. We have also recently used *in situ* TEM to observe changes to PtCo nanoparticles under H₂ atmospheres[35,36] and *in situ* diffraction to observe the oxidation / reduction of mesoporous ceria supports (indicated by a substantial change in lattice parameter) under reducing and oxidising conditions.[37]

Sum frequency generation (SFG) spectroscopy, developed by Shen and coworkers in the late 1980s,[38] is a technique which lends itself very well to studies of catalyst surfaces, due to its inherent interfacial sensitivity – even for buried interfaces. This arises because SFG, in its most useful form, is a second order optical technique and forbidden in centrosymmetric media (most bulk solids, liquids and gases). This means SFG only gives rise to a signal at interfaces, where a centre of symmetry is broken. This is in contrast to conventional linear optical infrared and Raman spectroscopies where the surface signal is often swamped by contributions from the bulk. SFG spectroscopy is achieved in a typical setup by overlapping two incident lasers beams in time and space at the sample, usually a fixed frequency visible component, ν_{vis} , and a tuneable infrared beam, ν_{ir} . The superposition of the two electromagnetic waves produces a “sum frequency” ($\nu_{\text{ir}} + \nu_{\text{vis}}$) when ν_{ir} coincides with a molecular vibrational mode of a molecule at the interface, allowing highly surface sensitive vibrational spectroscopy to be performed under a wide range of operational conditions.

In recent years a variety of synchrotron X-ray spectroscopic techniques have also become important for the study of catalytic surfaces. Near Edge- and Extended- X-ray Absorption Fine Structure (NEXAFS and EXAFS) spectroscopies are particularly valuable for studying the oxidation state and co-ordination structure of atoms within a catalyst. X-ray absorption processes result from excitation of core levels either into specific conduction band or antibonding orbital levels, the position and electron filling of which is typically very sensitive to oxidation state

(NEXAFS), or into the vacuum where their escape is influenced by co-ordination sphere of the atom from which the electron is generated (EXAFS). These techniques are again valuable for *in situ* studies because in principle they are again photon in – photon (or electron) out techniques that are possible for studies of catalysts in a variety of reaction media. EXAFS particularly benefits from the ability to generate well-defined small nanoparticles which are homogeneous in size and composition.[39,40] Being a bulk technique, EXAFS spectroscopy otherwise quickly becomes dominated by small numbers of larger agglomerates. Catalysis meanwhile is usually a function of surface area and so may be dominated by smaller high surface area parts of an inhomogeneous sample. This point is emphasized in Figure 2 by considering a typical size distributions (by numbers of particles) obtained by TEM for a nanoparticle catalyst with tight size distribution and a typical incipient wetness catalyst – and how this changes when normalised to either surface area or volume (approximating particles to be spherical). This serves only to underline the considerable importance of using nanomaterial-based model catalysts in conjunction with spectroscopy for probing catalytic phenomena.

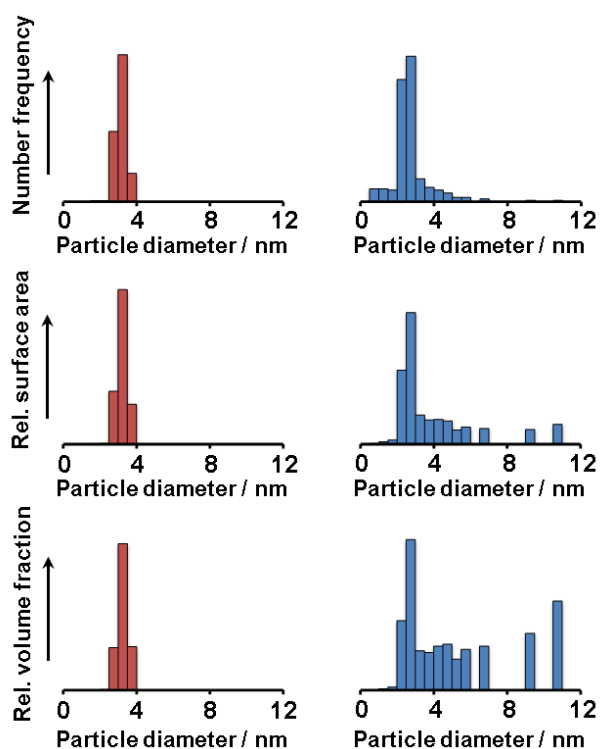


Fig. 2 Showing two particle size distributions obtained from a typical nanoparticle catalyst (left) and a typical incipient wetness catalyst (right); in each case the distribution is plotted weighted by number (top) as might be

typical for counting particles from a TEM image, by surface area (middle) indicative of active site density on different sized particles and by volume (bottom) as would be observed using many spectroscopies (approximating particles to be spherical). In both cases sizes of > 200 individual particles from different areas of the sample were counted.

Another synchrotron X-ray spectroscopy technique we have utilised a great deal for studying nanoparticle catalysts is Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS). Although pioneered for simpler laboratory measurements some time ago,[41,42] the availability of focused bright tunable X-ray sources at synchrotrons has given rise to a large number of studies using this now more sensitive techniques.[43] NAP-XPS, unlike the photon absorption techniques above requires measurement of the energy of the emitted electron. This is achieved by extracting emitted electrons from the sample chamber (containing a gaseous atmosphere in which the mean free path of electrons is short) through a small aperture into a series of differentially pumped chambers for subsequent energy analysis. In this way it is possible to record photoemission spectra of samples under conditions of temperature and up to several Torr of reactive gases, providing compositional and oxidation state information. Although not working at truly “industrial” conditions of pressure, such studies put the catalyst into a fundamentally different regime from studies under high vacuum, since the rate of molecules colliding with the surface typically makes mass transfer in the gas phase prior to adsorption cease to be rate limiting.[44] In conjunction with the tunability of synchrotron X-rays, which permit depth sensitive analysis on the scale of the nanoparticles being studied (of the order of a few nm), this technique has been invaluable in elucidating a number of catalytic phenomena, in particular the rapid restructuring of bimetallic nanoparticles in reactive gases.[44]

3. Metal nanoparticle size dependent covalent bond catalysis

One important catalytic observation enabled by nanoparticles is the structure sensitivity of large numbers of covalent bond breaking/making processes on catalyst surfaces. As indicated in Section 1, model catalysts prepared using nanoparticles and separately deposited on the oxide support now allow much more precise particle size selection than conventional preparation methods, especially in the sub-10 nm region not accessible by other techniques (e.g. lithography). Classical certain reactions, such as ammonia synthesis mentioned previously, have long been identified as structure sensitive,[45] that is the rate of a reaction depends on the particular surface facets present (analogous to one single crystal facet of a single crystal model catalyst). Meanwhile, many other reactions, including many

hydrogenations had been found to occur with a per surface site reaction rate independent of the surface configuration of atomic sites present – a good example of such a reaction being ethylene hydrogenation.[46] One method to test the structure sensitivity of a reaction is to investigate the catalytic behaviour (activity and selectivity) of a series of catalysts containing different particle sizes, small particles having different numbers of corner, edge and terrace sites as compared to larger ones.[47] Clearly, the more precisely nanoparticles size can be controlled, the more sensitive the discrimination of structure sensitivity becomes. An important recent example of this is the observation of size sensitivities in benzene and toluene hydrogenations – reactions widely used and studied as prototypical reactions for those used in petrochemicals processing. In this case the use of Pt nanoparticles allowed the observation that nanoparticles around 3 nm exhibit a maximum in per surface Pt site activity (TOF ~ 3 times enhanced).[48] For catalysts used on a large scale and with lifetimes of many months it is valuable to understand such effects at a fundamental level. While maybe not otherwise obvious in short bench-scale testing of industrial type catalysts, understanding which surface sites are optimal can inform attempts to maximise these sites and improve the catalyst. If the reactions are multipath reactions (containing more than one product) it may also enable an understanding of the reaction selectivity and potential methods to avoid this – for instance certain sites may be selectivity poisoned. (An example of this is selective hydrogenation of acetylene in ethylene using a palladium catalyst where low coordination sites are poisoned with sulfur[49]). Finally understanding the surface site configuration that delivers desirable selectivity or activity may permit the rational investigation of different catalytic materials (for example purposeful alloying of two metals) to try and overcome the present activity or selectivity limitation. In Berkeley we have studied a number of hydrogenation reactions using nanoparticles to provide accurate discrimination of particle size. Results of important examples are summarized in Table 2.

Table 2 Showing important examples of particle size effects in hydrogenation reactions and the change in activity or selectivities obtained with largest versus the smallest particles

Species hydrogenated	Catalyst	Size range studied	Size effect observed	Reference
Cyclohexene	Pt(PVP)/SiO ₂	1.7 – 7.1 nm	For conditions under which both dehydrogenation and hydrogenation occur, smaller particles lead to greater selectivity for benzene formation while larger particles favour cyclohexane formation.	[50]
Furan	Pt (PVP and dendrimer) / SiO ₂	1-7 nm	Nanoparticles produce considerable cracking to propylene, but at low temperature larger nanoparticles exhibit	[51]

			higher selectivities for butanol formation than smaller ones.	
Pyrrrole	Pt (PVP and dendrimer) / SiO ₂	1 -5 nm	Small particles selective for pyrrolidine and butylamine while larger particles form dominantly butylamine.	[52]
Benzene	Pt (PVP and dendrimer) / SiO ₂	1.5 – 5.2 nm	A maximum in activity is observed for 2-3 nm nanoparticles	[48]
Toluene	Pt (PVP and dendrimer) / SiO ₂	1.5 – 5.2 nm	A maximum in activity is observed for 2-3 nm nanoparticles	[48]
Crotonaldehyde	Pt(PVP)/SiO ₂	1.7 – 7.1 nm	Smaller particles dominantly produce butyraldehyde while larger particles produce both butyraldehyde and crotyl alcohol.	[53]
Furfural	Pt(PVP)/SiO ₂	1.5 – 7 nm	Smaller particles favour decarbonylation to furan while large nanoparticles favour the production of furfuryl alcohol.	[54]
Methylcyclopentane	Pt(PVP)/SiO ₂	1.5 – 11 nm	At high temperatures smaller particles favour ring opening and isomerization while larger particles favour ring enlargement and dehydrogenation to form benzene.	[55]
1,3-butadiene	Pt(PVP)/SiO ₂	1.0-6.7 nm	On going from small to large particles the dominant product changes from n-butane to 1-butene	[56]

The results clearly illustrate that in every case (except ethylene), significant structure sensitivity can be observed. Furthermore, in multipath reactions there are significant differences in the extent of structure sensitivity for different reaction pathways, resulting in different reaction selectivities for different particle sizes. From an atomistic and molecular standpoint, of course, the observation that most reactions are in fact structure sensitive is unsurprising, since there is no reason to suppose *a priori* that one particular configuration of metal atoms should catalyse covalent bond making or breaking the same as another. Varying the relative ratios of different surface atom configurations available is therefore bound to change the rate. The key result is that nanoparticles methods now allow us to discriminate when this is occurring and to what extent.

The complementary use of nanoparticles and *in situ* spectroscopy has also offered insight into the origin of such structure sensitivities in terms of different molecular absorption modes. For example, using SFG it has recently been possible to show that during 1,3-butadiene hydrogenation the ratios of different intermediates (resulting from addition of the first hydrogen atom at an internal or terminal position on the carbon chain) vary as a function of

nanoparticle size.[56] The variation in the intermediates observed correlates well with both the final products obtained and DFT calculations for two possible reaction pathways that can occur for this reaction.

Having identified that particle size changes result in significant changes in selectivity and activity, it should be noted that nanoparticles of a fixed size (prior to deposition on an oxide support) can also be used to good effect to study the effect of different supports on catalytic behaviour, independently of the effect of the support on the metal particle synthesis or growth. Recently this has been done for Pt nanoparticles deposited on a large number of different oxide supports[57] – allowing complete separation of the effect of metal particle synthesis from the type of support on which it is subsequently deposited.

It should be noted that hydrogenation reactions are good systems for employing this approach, since many other possible effects can be ignored, such as oxidation state (see Section 4) or possible oxidation / leaching rate of metal into solution phase reactions.

4. Oxidation state based catalytic phenomena in small metal clusters

Conventionally metal catalysts are generally considered in the metallic zero-valent state, especially for precious metals. In a series of studies, however, it can now be identified that significant changes in the observed oxidation state determined via X-ray spectroscopy under reaction conditions occur on going from bulk metal to very small nanoparticles. In particular accessing nanoparticles in the sub 2 nm regime for Pt and Rh has shown large changes in oxidation state (Figure 3).[58,59] This is of great importance since many industrial type catalysts contain a significant proportion of small (< 2 nm) particles.

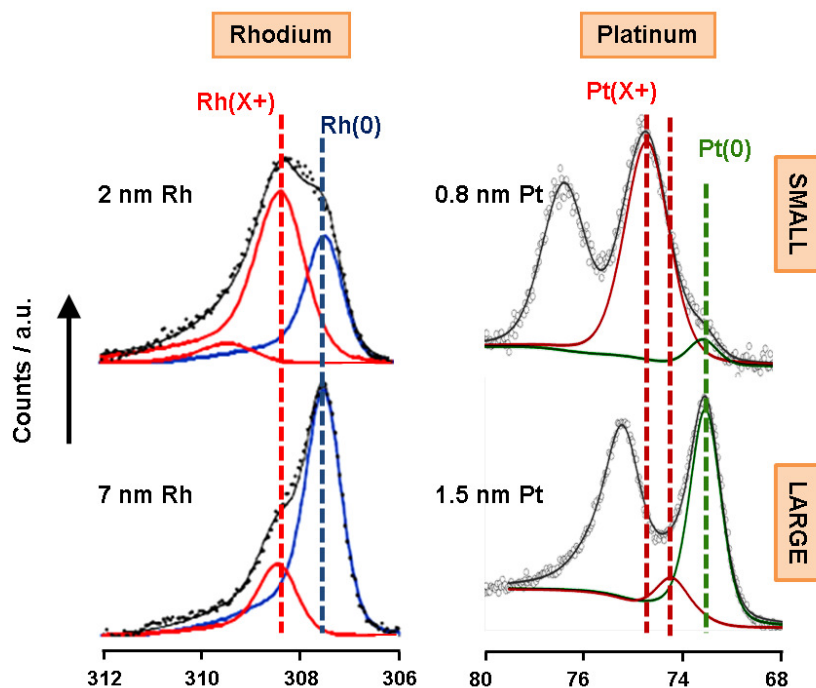


Fig. 3 Typical near ambient pressure XP spectra of small versus large nanoparticles indicating a substantial difference in oxidation state for both Rh[58] and Pt[59] occurs under CO oxidation conditions (200 mTorr CO; 500 mTorr O₂).

These effects were shown to occur for small particles irrespective of whether PVP was used as a capping agent or the nanoparticles were prepared via a dendrimer template.[29,60] The small-size induced oxidation state increase is also seen to have a marked effect on catalytic activity in CO oxidation over Rh catalysts below around 3 nm where a thick oxide shell has formed.[58] Furthermore we have recently demonstrated using PVP capped nanoparticles that similar size effects occurred during Pt nanoparticle catalysed methanol oxidation – 1 nm Pt nanoparticles were by far superior in activity and also considerably more oxidised when studies using XPS.[60] Additionally using CO as a probe molecule for infra-red studies also indicated the presence of a small nanoparticle induced oxidation state increase for 1 nm particles, in contrast to 2, 4 and 6 nm sizes.

The observation of marked differences in activity for nanosized gold particles, for instance in CO oxidation, has been known for some time and in the case of gold attributed to specific quantum size effects resulting from a metal to non-metal transition.[61] Recently, however, Nørskov, Jacobsen and co-workers conducted a theoretical study systematically varying particle size and looking at the strength of CO and O₂ adsorption and the impact of the

adsorption on the metal nanoparticles' electronic structures.[62] In this they discriminate three independent size effects: (1) geometric terrace versus edge and corner site type effects (as seen in Section 3 above); (2) adsorbate induced changes in electronic structure due to small size of terraces; and (3) quantum size effects in very small clusters. These latter two electronic factors result in a much sharper change in catalytic behaviour for very small nanoparticles than expected for just changes in the ratio of sites with different co-ordination numbers. Crucially (2) is also dependant on the presence of catalytic adsorbates, emphasising the importance of *in situ* measurements such as NAP-XPS for observing such phenomena. The size range of their findings is also in good agreement with the examples above where dramatic changes in both catalytic activity and oxidation state occur for nanoparticles < 2 nm. In this sense the combination of nanoparticles of discrete sizes with *in situ* techniques is invaluable to probe how size effects are occurring.

The variation in oxidation state on decreasing size into the < 2 nm regime can be considered to bring heterogeneous catalysts much closer to their homogenous counterparts (typically organometallic metal-centred complexes in which the metal is in a higher oxidation state). In addition to small size induced increases in oxidation state using the dendrimer template approach,[29] the use of dendrimer templates has also afforded a route for the reversible interconversion of the metal between clustered nanoparticles and higher oxidation state dendrimer bound individual metal atoms – a means of heterogenizing homogeneous catalysts. The first example of this was the demonstration that Pt₄₀ – PAMAM dendrimer (see Figure 4a) nanoparticles supported on SBA-15 silica could be oxidised using PhICl₂ to yield electrophilic catalysts capable of a series of intramolecular π -bond functionalization reactions.[63] The presence of higher oxidation state Pt was hypothesized to mimic platinum halide compounds that are typically used for homogeneous catalysis of such reactions. Unlikely larger Pt nanoparticles, the dendrimer bound Pt was found to be able to be recycled (via reoxidation in PhICl₂) and resistant to leaching in non-polar solvents. An analogous Pd₄₀ – PAMAM dendrimer – PhICl₂ system was found to have similar resistance to leaching and high activity, and was demonstrated in a continuous flow mode for one such reaction.[64] Mechanistic studies using *in situ* hard X-ray absorption spectroscopy were able to show co-ordination of the Pt to other Pt atoms and to chlorine atoms following this oxidation process (EXAFS), and also variations in the oxidation state of the Pt (NEXAFS).[65] The co-ordination number of the Pt in the ~ 1 nm clusters is around 5, but on oxidation decreases to below 1 indicating the Pt atoms co-ordinate to the dendrimer but only some Pt atoms co-ordinate to each other. NEXAFS spectroscopy showed this was accompanied by forming a significant fraction of Pt(II) and Pt(IV) as a result of the

oxidation. *In situ* measurements to understand deactivation processes occurring were indicative of Pt(IV) being more active but less stable to reduction under reaction conditions, explaining the previous observation that the catalyst recycle necessitates re-oxidation using PhICl_2 . The general scheme for preparation, oxidation and reaction / regeneration is shown Figure 4b.

More recently, studies using the gold version of the system with two different similar dendrimers (G4-PAMAM-OH as above and a phenyl alanine terminated, less sterically crowded G4 dendrimer) showed that the dendrimer could behave analogously to ligands around a metal centre in a conventional homogeneous catalyst. The sterics of the 'ligand,' in this case the dendrimer, were found to control the diastereoselectivity of a cyclopropane forming reaction.[66] Furthermore the heterogenized nature of this catalyst permitted reactions to be conducted in flow where the residence time of the reactants in the catalyst bed can be used as a further parameter to control the reaction selectivity, in contrast to homogeneous catalysts for the reaction where such control is difficult to achieve. Another advantage of using such catalysts in a flow reactor is the ability to study the reactants and a catalysts as a function of contact time using *in situ* techniques such as infrared and X-ray spectroscopy simply by mapping changes that occur spatially along the length of the reactor. This has recently been done using *in situ* XAS and ir microspectroscopy to study the PhICl_2 oxidized Au₄₀-PAMAM dendrimer system during a dihydropyran synthesis reaction where regions of Au(III) and product formation could be found to correlate.[67]

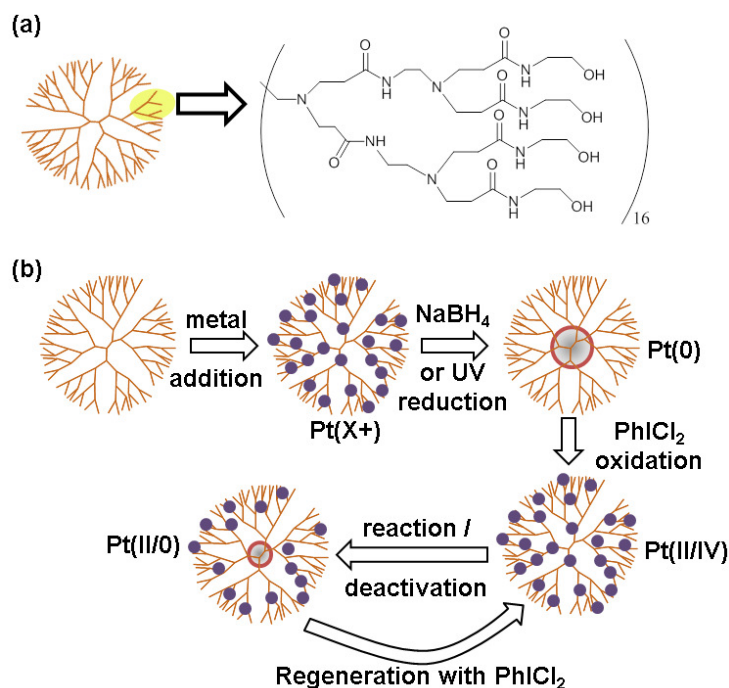


Fig 4. (a) Showing structure of PAMAM type dendrimer (b) Schematic showing metal loading, reduction, PhICl_2 oxidation, reaction and regeneration processes for the case of Pt loaded PAMAM G4OH dendrimer

5. Multicomponent catalysts studied *in situ* with metal nanoparticles

Catalysts containing two metal components have long been known to exhibit catalytic properties not found in their individual constituent metal catalysts. In consequence, they find extensive use in many important chemical processes, such as Pt and Pd for olefin hydrogenation or Pt and Sn for hydrocarbon reforming or dehydrogenation reactions.[68] A basic accepted understanding for the origins of such behaviour was provided by Sachtler in 1981, by introducing the idea that alloys could change selectivity (or activity) of a reaction by either “geometric” or “electronic” surface effects.[69] However, a clear picture of the roles and structure of the two metals in the working catalysts (under reaction conditions) is difficult to obtain, especially as multicomponent catalysts are very often relatively inhomogeneous due to the difficulty of mixing the two metal components during deposition. Again nanoparticles combined with *in situ* spectroscopy can be a valuable route to understanding the working structure of the catalyst present and in turn the mechanism of reaction. One particularly important route to doing this has been to prepare nanoparticle catalysts where each individual nanoparticle contains the same fixed ratio of the two metal components. Synthesis of such nanoparticles has been achieved for a good many systems, which can in turn be

exploited for studying changes in structure under reactions conditions. For instance RhPd and PtPd nanoparticles have been studied in detail using NAP-XPS under oxidising and reducing conditions (including NO and CO relevant to catalysing the decomposition of harmful species in automotive emissions).[70] For RhPd it was observed they formed a reversible core shell structure with a different metal dominant at the surface depending on the gas mixture present. This change occurred reversibly. A number of such systems have now been studied, although it is apparent that a large number of factors are involved in determining the catalyst structure under working conditions and experimental verification of the working structure is still invaluable to understanding the catalytic metal surface actually present under reaction conditions.[44] One catalyst system of interest, which we have studied extensively, is the combination of Pt and Co. This combination is of considerable importance because of applications in reactions such as Fischer-Tropsch Synthesis (used to make synthetic fuels). Analogously to the RhPd example above we have prepared and studied bimetallic PtCo nanoparticles in which each nanoparticle contains equal numbers of Pt and Co atoms. These nanoparticles have been studied using NAP-XPS and NEXAFS spectroscopy under reducing and CO oxidation conditions and the different oxidation states and structures of Co present at the surface correlated with reaction activity (due to both surface segregation of Co during reaction and changes in oxidation states resulting from different partial pressures of the reactants).[71] The same PtCo system has also been studied for CO₂ hydrogenation, where interestingly it is less active than the correspondingly sized pure Co catalyst. NAP-XPS and *in situ* TEM were used to show this was the result of Pt segregation under reaction conditions to form an inert platinum shell over the cobalt, which then prevents the reaction occurring.[36] Since Pt is widely viewed as a reaction promoter in CO hydrogenation, the inertness of the bimetallic PtCo nanoparticles points to the fact the structure of the working catalyst used industrially (in which promotion not inhibition is observed) is likely one in which the two metals are less intimately contacted than in the PtCo bimetallic nanoparticle catalyst studied here. In view of this we subsequently studied the impact of combining separate Pt and Co nanoparticles on reaction (as shown in Figure 5a).[72] When the Co and Pt are present as independent nanoparticles there is indeed a promotional effect. This likely results from the diffusion of dissociatively chemisorbed hydrogen between the Pt and the Co during reaction (Figure 5b) – a fact supported by *in situ* NEXAFS spectroscopy during reduction[72] and the diffusion limited kinetics of the reaction.[73]

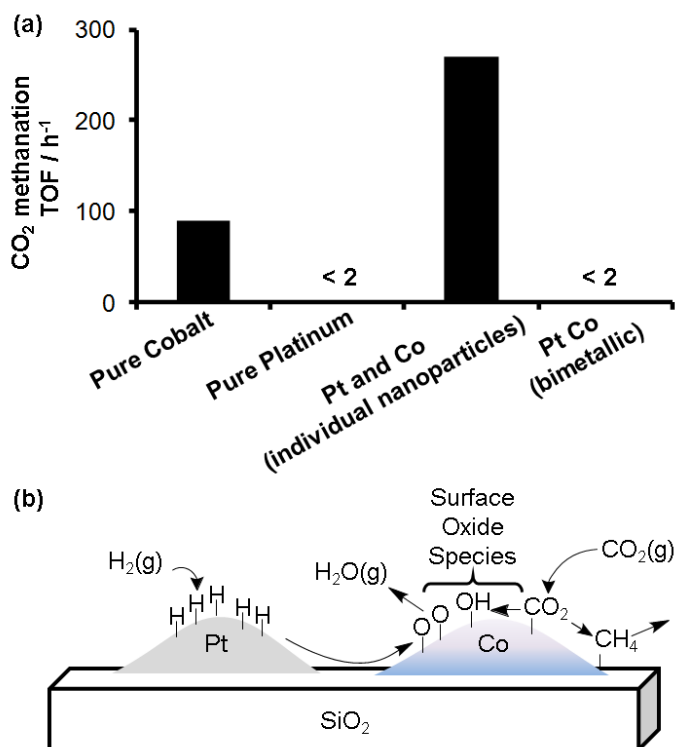


Fig. 5 (a) Showing relative TOFs for CO₂ methanation on different Pt Co catalyst structures (b) Showing postulated mechanism involving surface diffusion of hydrogen species.

6. The oxide metal interface

As discussed in earlier sections, many practical catalysts consist of small metal nanoparticles supported on a metal oxide substrate. A first approximation may be to view this oxide substrate as inert, however numerous examples exist where this is not so and the electronic properties of the support and the metal-support interface play a major part in determining catalytic activity and selectivity. The most prominent form of this is the well studied SMSI effect.[74-78] This may result from partially oxidised states, or oxygen vacancies in the support close to the interface or both,[79-81] but electronic transfer between metal and support has also been postulated for some time to be an important cause of the enhancement effects seen in the presence of certain supports such as TiO₂. [82] In view of the possibility that electronic effects important in catalysis result from a Schottky-like barrier between metal and metal oxide at the interface,[83] and the observation that the oxides exhibiting the greatest promotional effect (TiO_x, TaO_x and NbO_x) all share similar bandgaps of 3.5 - 4.5 eV (which determine the Schottky barrier height),[1] a series investigation have been conducted on catalytic Schottky contacts or “nanodiodes.” Initially these show that for

reactions such as CO oxidation to CO_2 or H_2 oxidation to H_2O , the exothermic heat can be transferred to an electron (the heat capacity of the electron is much smaller than the metal lattice, and so initially the heat is transferred to an electron). This generates a hot electron, which, if the distance of travel to a Schottky interface is less than the mean free path of the electron, can cross the barrier and end up in the conduction band of the oxide (allowing a current to be measured). This has been done with both Pt films[84-88] and colloidal Pt nanoparticles on a Au/TiO₂ nanodiode,[89,90] the latter is depicted in Figure 6.

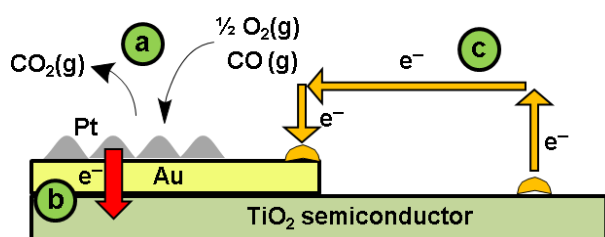


Fig. 6 Illustrating a typical nanodiode setup with colloidal Pt nanoparticles deposited on a Au/TiO₂ nanodiode: (a) exothermic reaction occurs over Pt nanoparticles creating hot electrons; (b) hot electrons have sufficient energy to be injected through Schottky barrier into TiO₂ conduction band; and (c) electrons in conduction band of TiO₂ have higher potential than in Au, causing current to flow so a “chemicurrent” can be measured

More importantly for understanding the electronic origins of promotional effects at the metal-oxide interface, recent studies have shown that the nanodiode can operate in reverse to alter the charge state of the Pt catalyst. This has been achieved by several means. Firstly, using n-type doping with fluorine in TiO₂ to result in conduction band electrons that can migrate into the Pt with enough energy to influence the reaction (it is postulated this occurs by increasing the electron density on chemisorbed oxygen atoms).[91] Reaction rates for CO oxidation have also been controlled simply by biasing the nanodiode or using illumination to change the electronic state of the diode and push electrons into the conduction band.[92] Very recently Pt-CdSe-Pt dumbbell nanostructures have also been used to allow light absorption to promote electrons within the CdSe semiconductor, which migrate to the Pt and enhance the rate of CO oxidation.[93] These examples show very clearly that it is possible to enhance reactions through electronic support-metal interactions. From a fundamental perspective it is also noteworthy that catalysts operating by injection or removal of electrons in this way (rather than through thermal bond breaking or bond making) are similar to acid or base catalysts, where ions are able to provide or remove electronic to a reactant in an analogous

manner. Further work is underway to improve our understanding of the links between acid base catalysis and the electronic effects seen in catalytic promotion at the metal oxide interface.

7. Comparison of liquid and gas phase catalysed reactions using Pt nanoparticles

A final notable use of nanoparticles combined with *in situ* spectroscopy is the study of a reaction at both the solid-liquid and solid-gas interfaces. This has recently been accomplished through the use of Pt nanoparticles (of various sizes from 2 - 8 nm) for the oxidation of isopropyl alcohol to acetone.[94] For all sizes a marked difference in reaction rate (by around 2 orders of magnitude) was observed between gas phase and liquid phase reactions (with similar concentrations of reactants achieved by use of an inert diluent (heptane) in the liquid phase). Combining these kinetic measurements with *in situ* measurement using SFG spectroscopy allowed elucidation of the orientation of the isopropyl group, which was found to be parallel to the surface in the gas phase, but adopts a more upright geometry in the liquid phase. Different apparent activation energies were also observed. Speculatively the different geometries observed plausibly contribute to this by changing the relative ratios of the isopropyl alcohol absorbed in an appropriate conformation to react, although further work is clearly needed to better understand this new observation. Nevertheless, it is a good example of the value of combining *in situ* spectroscopy in conjunction with well-defined, size controlled nanoparticle catalysts to shed light on otherwise difficult to understand catalytic observations. In this particular instance there is a marked activity dependence on particle size in both the gas and liquid phase reactions and so employing nanoparticles of a consistent, well defined size is crucial to be able to conduct such experiments.

Future perspectives and conclusions

In summary, over recent years the improved control afforded by using highly controlled nanoparticles (in terms of size, shape and composition), especially in conjunction with appropriate *in situ* techniques to study the catalyst or catalytic adsorbates under reaction conditions, has permitted a much greater understanding of a number of important catalytic phenomena. For spectroscopies, the sample homogeneity provided by such materials is essential in simplifying data interpretation to a tractable level and ensuring different components of a catalyst are not overwhelmingly dominant in providing active surface area as compared to those dominant in spectroscopic signals, as illustrated for the case of particle size. Examples of using this approach have been shown for studying particle

size effects, both geometric and as a way of elucidating important electronic and oxidation state phenomena. In this context especially, the ability to prepare particles of tuneable sizes has provided an invaluable benchmark for development of advanced theoretical understanding of the different factors that contribute to electronic effects on catalytic rate and selectivity on the nanoscale. Through controlling the composition of nanoparticles such that every single nanoparticle has the same elemental composition, multicomponent systems have been studied and important observations about the restructuring of nanoparticles under reaction conditions have been made possible. Exciting new avenues of research in understanding the relation of electronic effects and hot electron phenomena to acid-base catalysis and also in understanding the role of a condensed liquid phase in contrast to a gas phase reactant streams on adsorbate and catalyst structure have been discussed. It seems clear than highly controlled nanoparticles and nanostructures, especially when used in conjunction with appropriate *in situ* techniques, are likely to continue to make key contributions to our understanding of these and doubtless many other phenomena in the field of catalysis in the future.

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