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## Size-selected Metal Clusters: New Models for Catalysis with Atomic Precision

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**Abstract:** The field of heterogeneous catalysis is built upon the exploitation of materials structured on the nanometre-scale. Supported, size-selected nanoclusters open up new opportunities for research in catalysis as the catalyst functionalities can be explored as a function of cluster size, composition and atomic structure. In this review, we consider as an example, the catalytic oxidation of carbon monoxide by oxidised palladium clusters, coupling vibrational infrared spectroscopy with temperature programmed reaction experiments. The results clearly show that the detailed atomic structure of the clusters plays a crucial role in the catalytic performance. The new generation of aberration-corrected electron microscopes provides a new window on the structure of such nanoparticles, with atomic precision, as illustrated by High-Angle Annular Dark-Field detector-Scanning Transmission Electron Microscopy images of size-selected gold and palladium clusters.

**Key words:** Size-selected clusters, model catalysts, scanning transmission electron microscopy

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### INTRODUCTION

Investigations of the catalytic performance of nanometre-size metal clusters, and development of new methods to design nanocatalysts with distinct reactivity, represent major areas of recent research endeavour (Heiz and Landman, 2006; Henry, 2000; Palmer *et al.*, 2003; Santra and Goodman, 2003; Haruta and Date, 2001; Turner *et al.*, 2008; Harding *et al.*, 2008). To explore size- and structure-dependent reactivity at the atomic scale, appropriate methods of both fabrication and characterisation are required. In this context the development of size-selected cluster beam technology opens up new avenues for atom-by-atom design of nanocatalysts with the potential for tunable chemical activity, specificity and selectivity. The complexity of the cluster-support interaction, however, presents challenges to our understanding of the properties of these new model systems even under UHV conditions. Moreover, little is known about the possible structural variation of metal clusters under realistic reaction conditions (Kuhn *et al.*, 1992; Freund *et al.*, 2001; Vajda *et al.*, 2009).

In model studies of heterogeneous catalysis, supported metal oxide films represent a valuable

compromise between atomically flat, single crystal metal oxide surfaces and high surface area industrial metal oxides. The small thickness (1-100 nm) of the well-defined oxide layers allows for better heat transfer and the transport of electrons to the conductive substrate, avoiding the charging effects, which can otherwise accompany the application of e.g., electron spectroscopies. Particularly important in nanocatalysis is the interaction of the cluster and oxide layer, which can control the morphology, modify the electronic properties and, consequently, affect the reactivity of the model catalysts (Harding *et al.*, 2009; Somorjai *et al.*, 2006; Yoon *et al.*, 2005). Therefore, understanding the cluster-surface interaction and determining the atomic structure are of central importance to the design of a nanocatalyst (Li *et al.*, 2008; Herzing *et al.*, 2008; Young *et al.*, 2008). The interplay between experimental data and theoretical modeling has proved a valuable tool in this task (Hakkinen and Manninen, 1996; Pacchioni and Rosch, 1996; Ricci *et al.*, 2006; Huber *et al.*, 2005).

In this topical review study, we illustrate these issues, and look to the future with the help of some recent research results from the Munich and Birmingham groups. We consider the effects of the annealing (in oxygen) on

the catalytic activity of size-selected palladium clusters supported on magnesia, via a combination of cluster deposition and surface science analysis techniques, and demonstrate how aberration-corrected electron microscopy promises to reveal the atomic-scale structure and electronic properties of such systems with hitherto unsurpassed clarity.

### MATERIALS AND METHODS

The catalysis experiments were performed in a state-of-the-art, ultrahigh vacuum apparatus in Munich consisting of a cluster source (base pressure  $\sim 8 \times 10^{-3}$  mbar), surface analysis chamber (base pressure  $\sim 5 \times 10^{-10}$ ) and micro-calorimeter chamber (base pressure  $\sim 1 \times 10^{-9}$  mbar), Fig. 1a. The analysis chamber was equipped with a manipulator allowing resistive heating to  $\sim 800$  K and liquid nitrogen cooling to  $\sim 100$  K, with the sample temperature being monitored by a W-5%Re/W-26%Re thermocouple. The model catalysts were prepared by depositing size-selected Pd clusters with low kinetic energy ( $< 0.2$  eV/atom) onto well-defined oxide films. For each experiment, the magnesium oxide films were prepared *in situ*, prior to cluster deposition, by epitaxial growth on a Mo(100) single crystal. Thin MgO films ( $\sim 8$ -10 monolayers (ML)) were created by evaporating Mg ( $\sim 0.1$  ML  $\text{min}^{-1}$ ) in a  $^{16}\text{O}_2$  atmosphere ( $\sim 5 \times 10^{-7}$  mbar) at  $\sim 320$  K. Auger electron spectroscopy, metastable helium impact electron spectroscopy and ultraviolet

photoelectron spectroscopy were employed to verify the cleanliness and electronic states of the oxide layer. The metal clusters were produced using a high frequency (120 Hz) laser vaporisation source (Heiz *et al.*, 1997), in which the second harmonic of a Nd:YAG laser (INNOLAS, Spotlight 600) was focussed onto a rotating Pd target. The resultant plasma was cooled by a helium pulse from a piezo-driven pulsed-valve. The clusters were formed upon the supersonic expansion of the metal-gas mixture through a nozzle. Neutral and charged clusters were guided by a set of ion optics through differentially pumped vacuum chambers, (Fig. 1b), positively charged clusters were deflected by a custom-made electrostatic ion bender and focused into the quadrupole mass-selecting unit (ABB-Extrel; mass limit 4000 amu). After propagation through further sets of ion optics, the mass-selected clusters were finally soft-landed onto the prepared supports. The charged clusters are neutralised either by interaction with surface defects or via charge tunnelling through the support at surface (Abbet *et al.*, 2001; Di Valentin *et al.*, 2002). The coverage of clusters was obtained from the integration of the cluster current during deposition. The deposition of less than 1% of a monolayer ( $1 \text{ ML} \approx 2.2 \times 10^{15}$  clusters  $\text{cm}^{-2}$ ) at a substrate temperature of  $\sim 100$  K ensures that the supported clusters are isolated and prevents agglomeration

Vibrational measurements of the adsorbed molecules were accomplished with a commercial Fourier transform

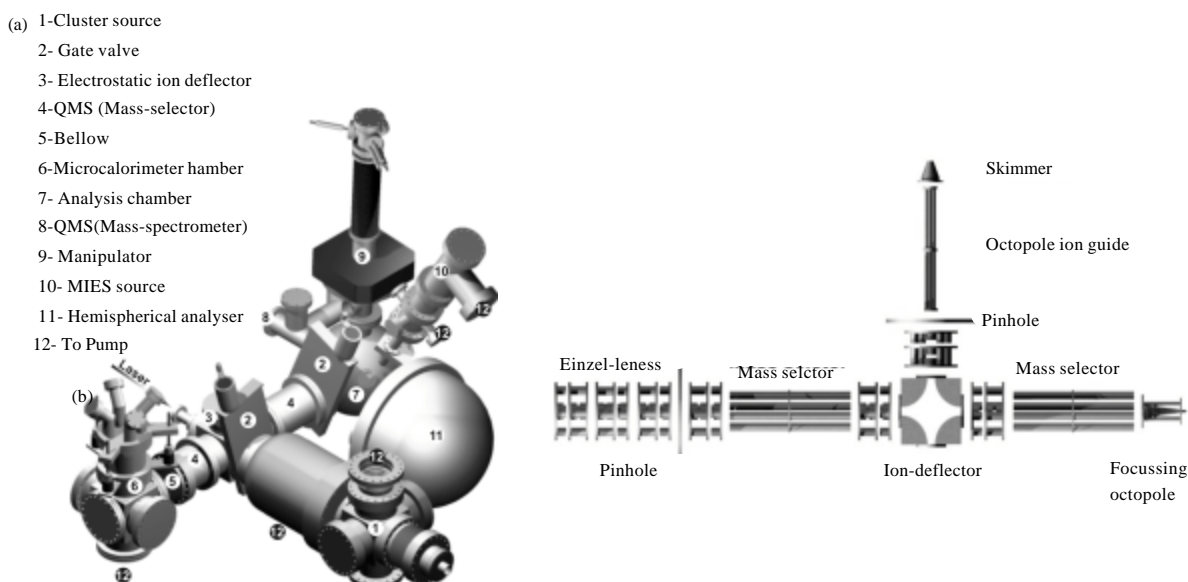


Fig. 1: Schematic 3D view of (a) the multi technique UHV apparatus (see text); (b) cluster ion optics including: skimmer, octopole ion guide, pinholes, Einzel-lenses, quadrupole bender, mass selector units, and focussing octopole

infrared spectroscopy (FTIR) spectrometer (Thermo Nicolet 6700). IR radiation was focussed onto the sample at grazing incidence with the use of an IR-compatible concave mirror. The radiation reflected from the surface was detected with a liquid nitrogen-cooled mercury-cadmium-tellurium detector (EG&G Optoelectronics, MCT-A). The  $^{13}\text{CO}$  isotopomer was used as a probe molecule to enhance the signal-to-noise ratio of the measurements. FTIR spectra were recorded over 512 scans with resolution  $4\text{ cm}^{-1}$  from the cluster sample after CO dosing and also for a reference surface (cluster deposition but no CO dosing).

Temperature Programmed Reaction (TPR) approach is one of the fundamental methods in model catalysis and have been widely used to explore surface reactivity (Bhatia *et al.*, 1990; Lee *et al.*, 2009). A differentially pumped ( $60\text{ sec}^{-1}$ ) quadrupole mass spectrometer (Balzers QMG 421) was used to detect the chemical products generated on the model catalyst while the temperature of the sample was linearly increased at a constant rate ( $\sim 2\text{ K sec}^{-1}$ ). The heating procedure was controlled by a feedback driven temperature controller (RHK Technology, TM 310) via a LabView computer program. At the end of each TPR experiment, the oxide films as well as the deposited clusters were removed from the underlying molybdenum by annealing the sample to  $\sim 1800\text{ K}$  by electron bombardment heating.

## RESULTS

Figure 2a presents FTIR vibrational spectrum at  $\sim 120\text{ K}$  of  $^{13}\text{CO}$  molecules adsorbed on oxidised, size-selected palladium clusters of different stoichiometry; specifically  $\text{Pd}_6\text{O}_x$  ( $2063\text{ cm}^{-1}$ ),  $\text{Pd}_{13}\text{O}_x$  ( $2068\text{ cm}^{-1}$ ) and  $\text{Pd}_{30}\text{O}_x$  ( $2076\text{ cm}^{-1}$ ). These nanocatalyst particles were generated by oxidation at  $\sim 370\text{ K}$  in an oxygen background of  $\sim 5 \times 10^{-7}\text{ mbar}$  for 30 sec then cooled to  $\sim 100\text{ K}$  prior to saturation  $^{13}\text{CO}$  exposure and IR spectral acquisition. The IR spectra of Fig. 2a exhibit dominant vibrational frequencies characteristic of CO adsorbed in an on-top configuration. Interestingly, the oxidised clusters reveal a distinct shift to higher frequencies in comparison with the corresponding metallic palladium clusters; a blue-shift of  $\sim 20\text{ cm}^{-1}$  CO is mainly observed for the on-top bound (Table 1) (Worz *et al.*, 2003). Furthermore, in contrast to the metallic clusters, no bridge bonded CO could be detected on the oxidised clusters (i.e., only one CO adsorption site is manifested). A frequency shift in the opposite directions is observed when oxidised palladium clusters with a range of size ( $\text{Pd}_n\text{O}_x$ ,  $n \geq 30$  atoms) are reduced in a  $^{13}\text{CO}$  atmosphere ( $\sim 5 \times 10^{-7}\text{ mbar}$ ) at  $\sim 370\text{ K}$  for 30 sec, Fig. 2b. The peak

Table 1: Stretching frequencies ( $\text{cm}^{-1}$ ) of adsorbed  $^{13}\text{CO}$  on magnesia supported, size-selected Pd clusters in three different forms (oxidised, reduced and metallic), obtained from the experiments

Cluster	O <sub>2</sub> treated	CO treated	Metallic
Pd <sub>6</sub>	2063	2048	2037, 2014, 1893(Pd <sub>6</sub> )
Pd <sub>13</sub>	2068	2052	----
Pd <sub>30</sub>	2076	2052	2055,1930

frequencies for the on-top and bridging features for the reduced clusters are  $2060$  and  $1956\text{ cm}^{-1}$ , respectively, values substantially red shifted from the  $2081\text{ cm}^{-1}$  observed for the oxidised clusters.

The catalytic activity of the oxidised clusters was explored by TPR experiments. Figure 3a-c demonstrates the oxidation of CO as catalysed by oxidised  $\text{Pd}_{13}$  clusters ( $\text{Pd}_{13}\text{O}_x$ ) that were prepared at several different oxidation temperatures,  $\sim 370$ ,  $\sim 460$  and  $\sim 550\text{ K}$ , respectively. After the oxidation step, the oxygen was pumped out, the sample cooled to  $\sim 120\text{ K}$  and the  $^{13}\text{CO}$  molecules were administered to the surface using a calibrated molecular beam doser; then corresponding TPR spectrum was acquired. The production of carbon dioxide is clearly observed in both the spectra shown in Fig. 3a-b but in Fig. 3c hardly any  $\text{CO}_2$  is detected (no reactivity). This latter result probably indicates that the palladium oxide clusters, prepared by annealing at high temperature are either unstable or that they diffuse on the surface to form large nanoparticles presenting a drastically reduced number of surface reactive sites in comparison with the highly dispersed  $\text{Pd}_{13}$  clusters. Some instability of cluster-based model catalysts has also been observed in other, pulsed molecular beam reactive scattering experiments (Harding *et al.*, 2009), in which the measured turnover frequencies were found to deviate drastically from those calculated by microkinetic models at temperatures around  $\sim 500\text{ K}$ .

The major reactivity peaks detected at  $\sim 200\text{ K}$ ,  $\sim 300\text{ K}$ , and  $\sim 400\text{ K}$  (shoulder) in Fig. 3a and b, which are labelled as  $\alpha$ ,  $\beta$  and  $\gamma$ , respectively, suggest that three different oxygen species (i.e., three reaction mechanisms) are involved in CO combustion, with different thermal stability. The surface atomic species  $\text{O}_\beta$  and  $\text{O}_\gamma$  are thermally stable up to at least  $\sim 460\text{ K}$  otherwise no  $^{13}\text{C}^{16}\text{O}_2$  could be observed in Fig. 3b. The low-temperature formation of  $\text{CO}_2$  ( $\alpha$ -mechanism) is typical of a reaction of carbon monoxide with a highly activated, molecularly bound oxygen species. It is thus not surprising that this weakly bound oxygen species is only observed in Fig. 3a, where the cluster were oxidised at  $\sim 370\text{ K}$  (It would be desorbed at the higher oxidation temperatures.). For the high-temperature  $\gamma$ -mechanism at  $\sim 400\text{ K}$  dissociatively adsorbed oxygen (surface or subsurface) is

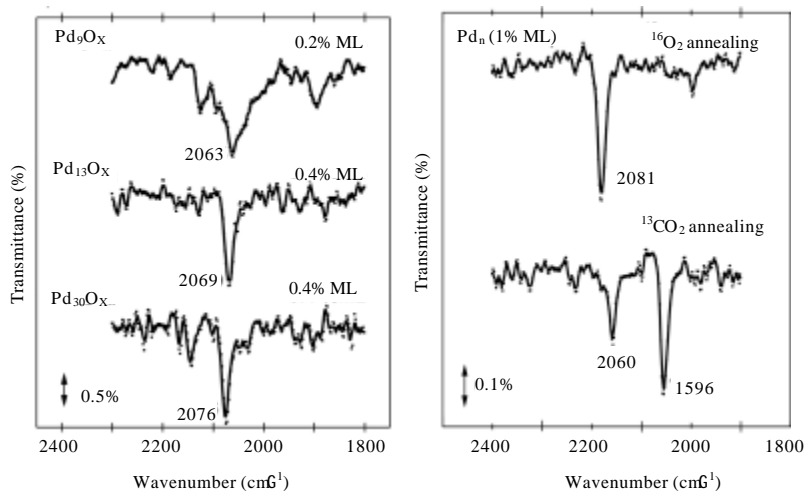


Fig. 2: IR spectra of adsorbed  $^{13}\text{CO}$  on (a) oxidised  $\text{Pd}_9$ ,  $\text{Pd}_{13}$  and  $\text{Pd}_{30}$  and (b) unselected palladium clusters in oxidised and reduced form, supported on  $\text{MgO}$  in each case. For all the measurements presented, a background spectrum ( $\text{CO}$  free) was subtracted

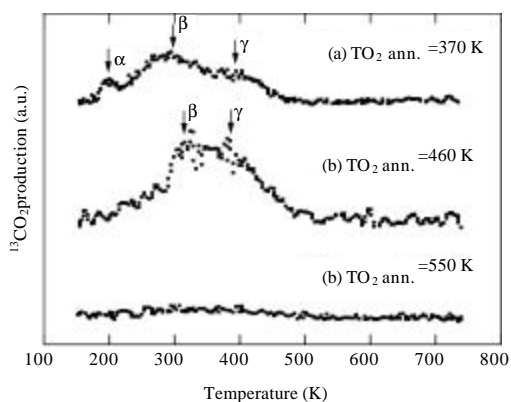


Fig. 3:  $\text{CO}_2$  formation on magnesia supported  $\text{Pd}_{13}\text{O}_x$  clusters, prepared by annealing palladium clusters in an oxygen atmosphere ( $5 \times 10^{-7}$  mbar) at various temperatures; 370, 460 and 550 K, respectively. The temperature ramp was performed after  $\text{CO}$  exposure at  $\sim 120$  K

most likely responsible. This high-temperature reactivity also explains the FTIR data. In other words, the cluster-oxides cannot be completely reduced at  $\sim 370$  K (i.e., they are partially reduced) and, therefore, different  $\text{CO}$  vibrational bands, associated with bonding to metallic clusters, are detected. The same effects have also been observed in TPR measurements for oxidised  $\text{Pd}_9$  and  $\text{Pd}_{30}$  clusters. It is noteworthy that in the case of metallic  $\text{Pd}_8$  and  $\text{Pd}_{13}$  clusters only a single reactivity channel at  $\sim 400$  K was reported, indicating a single reaction channel (Heiz *et al.*, 2000).

The example of cluster catalysis, which we have considered in some detail, demonstrates the activity as well as the tunability of these new and precisely defined model systems. In the future, what one would really like to be able to do is to couple the chemical performance of the clusters with their (3D) structure (and electronic properties) at the atomic scale. While the sensitivity of ultrasmall particles containing only 10 or 20 metal atoms to radiation presents formidable experiment challenges. It is instructive to discuss the new advances that are taking place in one method of characterisation, electron microscopy, which appears to offer at least the potential to address the structure problem. By way of concrete illustration, we consider some new electron microscopy studies, in Birmingham, of the atomic structures of somewhat larger clusters, containing hundreds of atoms; it does not seem impossible that one day a similar approach can be applied to even smaller particles. Scanning Transmission Electron microscopy (STEM) is a powerful technique, which if an aberration-corrected instrument is employed-enables us to determine the size, 3D shape, orientation and atomic arrangement of size-selected clusters. We consider size-selected  $\text{Au}_{923}$  and  $\text{Pd}_{923}$  clusters deposited on carbon grids. The STEM instrument employed (JEM2100F, JEOL) for the electron beam probe operates at 200 kV and features a spherical aberration corrector (CEOS GmbH). Sub-Angstrom resolution can be reached under optimised conditions. The signal was collected by a High-Angle Annular Dark-Field detector (HAADF) with inner and outer collection angles of 62 and 164 mrad in these experiments.

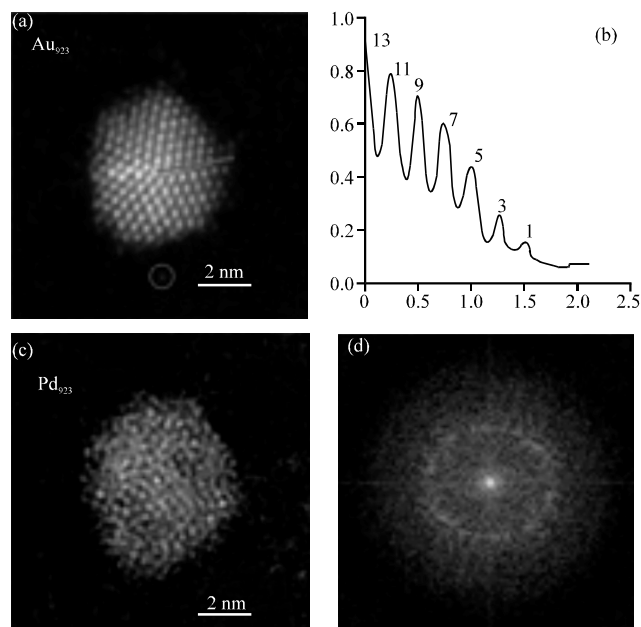


Fig. 4: Aberration-corrected HAADF-STEM investigation of size-selected Au and Pd clusters. (a) High-resolution HAADF image of Au<sub>923</sub>, (b) line profile along the line in (a), (c) high-resolution HAADF image of Pd<sub>923</sub> and (d) power spectrum of (c)

Figure 4a shows a high-resolution STEM-HAADF image taken from soft-landed size-selected Au<sub>923</sub> cluster on carbon. This cluster, projected along its five-fold symmetry axis, shows the hallmark of a Marks-decahedral structure (Mark, 1994). Single atoms are occasionally observed around the cluster, one of which is marked with a circle as an example. The line profile, shown in Fig. 4b reveals the variation in height of the clearly resolved atomic layers from the centre (symmetry axis) to the edge of the cluster. The numbers given on the line profile denote the number of the atoms along the incident beam (Z-) direction, in each column, an assignment, which depends on the incoherent nature of the high angle scattering and previous calibration (Young *et al.*, 2008; Wang *et al.*, 2010). This demonstrates that information about the 3D atomic arrangement of the cluster (specifically, an atom density map) can be acquired in single snapshot with the STEM-HAADF technique. The cluster can be further visualised via the 3D colour surface plot as shown in Fig. 5a.

The STEM-HAADF image of a size-selected Pd<sub>923</sub> cluster on carbon (Fig. 4c) shows significant structural differences when compared with the Au<sub>923</sub> cluster. The atomic arrangement of the Pd cluster appears rather disordered, which can also be confirmed from the power spectrum in Fig. 4d and the 3D colour plot in Fig. 5b. The structural differences between the Au and Pd clusters of the same nuclearity at the atomic-scale presumably manifest difference in their bonding or electronic structures.

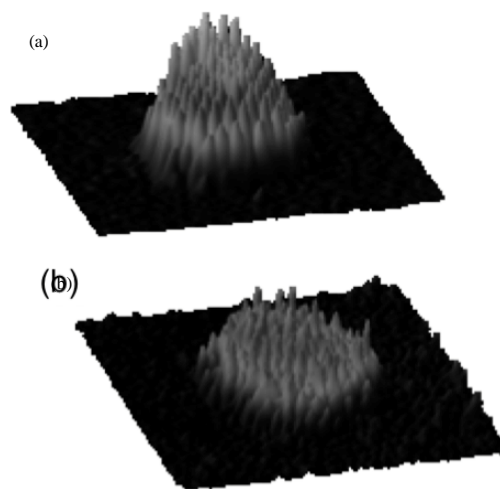


Fig. 5: (a) 3D colour plot of Fig. 4a and (b) 3D colour plot of Fig. 4c

## CONCLUSION

The results we have reviewed illustrate the potential for employing supported, size-selected clusters as model systems in the design of new or refined catalysts. The cluster morphology, surface composition and chemical states and the nature of the support (e.g., the thickness of an oxide film) can be used as design parameters. Exciting future directions in this emerging field of nanocatalysis include attempts to extend the new

3D atomic structure studies containing a few hundred atoms into the ultrasmall regime. The potential of the STEM-HAADF method in the aberration corrected microscope has been demonstrated. One of the biggest challenges in heterogeneous catalysis is enhanced selectivity in multichannel chemical reactions. Here, the distinctive and tunable structural and electronic properties of size-selected clusters may prove of particular value.

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