Mass-selected supported cluster catalysts: Size effects on CO oxidation activity, electronic structure, and thermal stability of Pd_n/alumina ($n \leq 30$) model catalysts

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ABSTRACT

An intense, mass-selected cluster source for preparation of model supported clusters is described, and results are presented for cluster size effects on CO oxidation activity for Pd_n clusters supported on alumina films grown on Re(0001) or Ta(110) single crystals. The electronic structure of the samples was probed by X-ray and UV photoelectron spectroscopy, and low energy ion scattering was used to probe binding morphology. The Pd_n activity was monitored via both steady state and temperature-programmed reaction (TPR) methods. In both cases, the samples appear to be stable in repeated reaction cycles for temperatures up to 600 K. In the TPR experiments, CO oxidation activity *per* Pd atom varied by ~40% between the most and least reactive clusters, while under steady state conditions, the activity varied by ~55%, but with a different pattern of activity vs. size. The difference in the effects of cluster size is attributed to the fact that TPR experiments were done under conditions where the rate-limiting step is oxygen activation, while the steady-state reactivity conditions were most sensitive to the strength of CO binding. Two distinct types of CO binding were observed and characterized by a combination of temperature-programmed desorption (TPD), and temperature-dependent ISS (TD-ISS).

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1. Introduction

Catalysts are important in 35% of the world GDP [1], thus, it is not surprising that there is extensive fundamental and applied research aimed at improving catalytic activity and selectivity [2–18]. Typical supported catalysts are quite complex and difficult to characterize in detail, and an important research thrust uses model catalysts to simplify the problem and allow important properties to be varied and measured in detail, to extract mechanistic insight. Among other approaches to tuning catalyst properties, using bi- or tri-metallic combinations [7,19–22], or varying the size of the catalytic metal particles are common [2,23–28]. Understanding the effects of particle size is complicated by the fact that there is typically a broad distribution of sizes present, and it is generally not possible to vary size independently, without also changing other properties such as metal loading or support structure. Consider gold nanocatalysts, which have received tremendous attention over the past decade, using a wide variety of approaches [17,29–33]. Much of the original work focused on the properties of

Au nanoparticles in the 2–5 nm size range, because these were the obvious species detectable in conventional electron microscopy [34–37]. Planar model catalyst work suggested that smaller gold structures were reactive [38–45], and size-selected cluster deposition experiments similar to those discussed here, showed significant activity for gold clusters as small as seven or eight atoms [15,17,30,46–50]. Development of aberration-corrected scanning transmission electron microscopes has allowed features on the atomic scale to be detected in supported catalysts, and allowed studies showing that clusters in the ~10 atom size range are highly active under realistic conditions [51,52].

Preparation of catalysts by deposition of mass-selected cluster ions on well characterized supports, provides a powerful mechanistic tool, allowing studies where cluster size, composition, density, and impact energy can be varied independently. Cluster deposition has applications in catalysis, magnetic and electronic materials, as well as being useful in studying the fundamental properties of nanostructures. Our group has focused on exploring size-dependent correlations between catalytic activity and physical properties such as cluster electronic structure and morphology, using CO oxidation to probe systems such as Au/TiO₂ [49], Pd/TiO₂ (110) [6,24,53,54], Pd/Al₂O₃ [55,56], and Pt/Al₂O₃ [57]. We also recently observed a very strong size-dependent correlation

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between Pt electronic structure and electrocatalytic activity for Pt/glassy carbon, where some sizes showed the expected Pt redox and oxygen reduction activity, but other sizes efficiently catalyzed electro-oxidation of carbon by water [2]. The Heiz group has reported numerous studies of catalysis with recent work including CO oxidation kinetics over Pd clusters deposited on MgO [13,14,58–61], optical spectroscopy of deposited clusters and adsorbates [62,63], studies of oxide support thickness effects on cluster activity [15,64], Pt_n deposition on CdS nanorod films for photocatalysis studies [65], and STM studies of cluster mobility on graphene/Ru(0001) Moiré supports [66]. In collaboration with Arenz, this group has also reported studies of electrocatalytic activity of supported Pt clusters [67–71]. Harbich and co-workers have carried out STM and reactivity studies of deposited clusters, and recently reported studies focusing on the fundamentals of CO oxidation over Pt_n/TiO₂ [72,73], and of electrocatalysis, using an approach where Pt clusters are deposited directly on a solid electrolyte, allowing electrochemistry to be studied *in vacuo* [7,74]. The Vajda group has an active program where size-selected catalysts are studied in a variety of reactors, recently focusing on *in operando* studies using tools such as X-ray scattering, to probe chemistry under realistic reaction conditions [4,9,10,75–83]. Buratto and co-workers have used cluster deposition in conjunction with STM and theory to examine stability and reactivity of several types of clusters on TiO₂(110), with recent work focusing on vanadia clusters on titania [84]. Ganteför and co-workers developed another instrument combining cluster deposition with STM and used this for a number of studies of Au_n deposited on several supports [85–88]. This work has proceeded in collaboration with Kim and co-workers in Korea, recently focusing on gold chemistry under ambient conditions [32,89–91]. Watanabe and co-workers have an instrument that allows STM, XPS, and high pressure reactivity studies of size-selected model catalysts [92] and have reported studies of CO oxidation over Pt_n/TiO₂(110) [11,93] and correlations with core level binding energies. White and co-workers studied properties and reactivity of Mo₄S₆ deposited on Au(111) [94], and used two photon photoemission to probe charging of several different size and stoichiometry Mo_xS_y clusters on alumina supports [95]. Chorkendorff and co-workers have developed a program using mass-selected cluster deposition to study chemistry and morphology changes under both UHV and high pressure reaction conditions [96–98]. Recently, Bowen and co-workers have reported work on deposited clusters including stability of size-selected Mo nanoparticles on highly ordered pyrolytic graphite (HOPG) [99], and gold clusters supported on TiO₂ showing single atom sensitivity to reactivity for CO oxidation [100].

For the system studied here, CO oxidation over Pd/alumina, there has been a tremendous amount of relevant work that provides valuable mechanistic insight. Briefly, using Pd single crystals and other bulk surfaces, it had been shown that CO and O₂ combine to form CO₂ via a Langmuir–Hinshelwood mechanism that entails adsorbed CO reacting with adsorbed O atoms [101–105]. It was also shown that oxygen and CO compete for the same binding sites such that a 60% saturation dose of CO prevents dissociative binding of O₂ on Pd(110). The kinetics of the CO oxidation reaction over Pd single crystals [103–106] and Pd/alumina nanoparticle catalysts [107–111] have been discussed in detail. Furthermore, it was determined for room temperature experiments, that CO and O₂ have reasonably high sticking coefficients of 0.5 and 0.4, respectively [112]. For Pd(111) it was shown that for greater than ~0.15 ML coverage of oxygen, dissociative adsorption of further oxygen became an activated process [113]. In the temperature-programmed reaction (TPR) experiments discussed below, the samples were exposed to O₂ prior to CO, to avoid CO poisoning. There has also been

considerable previous work on Pd clusters/nanoparticles on alumina films. For example, Goodman and co-workers investigated the Pd cluster size needed to transition from nonmetallic to metallic characteristics, [114] as well as the adsorption and further oxidation of Pd clusters in the size range of 25–70 nm on powdered alumina surfaces [115,116]. The Freund group did similar studies for Pd nanoclusters in the 0.5–14 nm range deposited on alumina films grown on NiAl(110), examining particle growth [117] and CO binding via infrared spectroscopy, to probe charge transfer between the particle and the alumina support [118]. The self-limiting, 0.5 nm thick alumina film that grows on NiAl(110) when heated in O₂ has been used in numerous model catalyst studies. We previously attempted to study CO oxidation over size-selected Pd_n deposited on alumina/NiAl(110), but no reaction was observed [56]. Experiments by Shaikhutdinov et al. on CO oxidation over Pd nanoparticles grown on the same support showed that the problem was that the alumina film was too thin to act as an efficient diffusion barrier, allowing oxygen activated on the Pd clusters to react with the NiAl substrate, in preference to CO [114]. In the experiments below, thicker alumina films are grown by aluminum evaporation in an O₂ atmosphere, following methods developed to produce alumina films on Ta, Re, or Ru single crystals [119–121]. Epitaxial growth of alumina on Ta and Re crystals provides an chemically inert, thermally stable support which is ideal for the size-dependent mechanistic studies discussed below [55,57]. The alumina support isolates the Pd clusters from the underlying metal support, but the oxide also influences the chemistry. For example, as discussed below, both the overall reactivity and its size dependence is substantially different for Pd_n supported on alumina films vs. TiO₂(110), under identical conditions.

2. Experimental

2.1. The apparatus

The experiments were done in the vacuum system shown in Fig. 1, which has been briefly described previously [49,50,55,122], however, a number of changes have been made to improve operation. The system consists of two main sections: a cluster deposition source/beamline (top) and an ultra-high vacuum (UHV) surface preparation/analysis system (bottom). The coaxial laser vaporization cluster ion source is shown in detail in Fig. S1 of the supplementary information. The beam from a frequency-doubled Nd:YAG laser (30 Hz, 30–60 mJ/pulse) is focused on the Pd target through the cluster exit nozzle, creating a Pd-containing plasma. Approximately 300–500 ms before the laser pulse, helium is pulsed into the elliptical source volume using a piezoelectric pulsed valve (4500 Torr through a 1 mm orifice for 1 ms) to help confine and cool the plasma, leading to supersaturation and cluster formation. The cluster size distribution can be controlled to some extent by changing the source residence time, via interchangeable exit tubes of various lengths.

The Pd target is glued to a spring-loaded aluminum block, which is mounted to an X–Y translation stage, allowing the target to be rastered, so that vaporization occurs uniformly over the target area (~1 cm × 2 cm). A target can be used for about 100 deposition experiments before becoming rough enough to seriously degrade source stability. The target is then simply sanded flat and reused until the laser begins to penetrate through to the glue layer. Two targets, each good for >300 depositions, can be fabricated from a single 99.9% Pd one ounce bullion bar, making the target cost negligible. A good seal and low sliding friction between the target and source body is critical, and for this purpose, a 0.1 mm thick Teflon gasket is bonded around the edge of the target. Motion of the X–Y stage is driven by stepping motors,

Fig. 1. Cluster deposition beamline (top), and UHV surface preparation and analysis system (bottom). The beamline is connected to the UHV system at the flange labeled “Ion Beam”.

allowing easy control over the raster pattern. The motors and source body are water-cooled to prevent overheating and enhance clustering.

The cluster-containing helium expands out of the exit nozzle, directly into the first of a series of quadrupole ion guides, which collects the ionized clusters and allows helium to pump away. Pressure in the source chamber is ~ 45 mTorr during deposition, dropping to ~ 5 mTorr in the 1st quadrupole chamber. All potentials on the beamline are referenced to an adjustable common potential, which is varied to set the deposition energy. The source is typically biased at -5 V with respect to this common potential, and the first quadrupole ion guide is biased at 0 V, decelerating the clusters, which exit the source with considerable kinetic energy due to the helium expansion. This ion guide is operated with radio-frequency (RF) amplitude of 200 – 500 V, at a frequency of 1.8 MHz.

The first quadrupole guides the clusters to a split electrode, built into the differential wall between the “Quad1” and “Quad2” vacuum chambers. At this point, the positive ions are deflected by 18° , and enter the second quadrupole guide. The bend eliminates negative ions and neutrals from the beam and allows coaxial injection of the laser into the source. The second quadrupole guides the clusters ions through three additional differential pumping walls, and operates with an RF voltage of 300 – 550 V at 1.8 MHz, with a DC bias potential of approximately 3 V, depending on cluster size. The pressure at the exit of this 2nd quadrupole

(in the “QMS” chamber) is $\sim 2 \times 10^{-6}$ Torr during operation, with base pressure of 2×10^{-8} Torr.

The ions are focused from the 2nd quadrupole guide into a mass selecting quadrupole (QMS) operated at 880 kHz, able to mass-select Pd_n^+ to at least $n = 30$. The QMS is homemade, with 9.5 mm diameter rods and short RF-only pre- and post-filter sections that can be adjusted to optimize transmission, and is driven by commercial electronics (Extrel). The cluster mass spectrum shows no evidence of multiply charged species such as Pd_n^{m+} (n odd), indicating that our operating conditions generate predominantly singly charged cluster ions. The QMS is operated at sufficient resolution to baseline and resolve the spectrum of Pd_n^+ produced in the source, thus the clusters deposited on the substrate are exactly size-selected. The more difficult question is whether the clusters remain intact, or whether they agglomerate or shatter upon impact. The instrument does not have scanning tunneling or other imaging capabilities, thus we rely on indirect evidence on this issue. In particular, we observe that both chemical activity and spectral properties of samples vary significantly with deposited cluster size, thus implying that the model catalysts retain “memory” of the deposited size. At the exit of the QMS, the mass-selected cluster beam passes through a set of four lenses, which also function as a differential pumping wall. A 1 mm thick, pneumatically actuated slide valve is built into one of the lenses, allowing the beamline to be isolated from the UHV section of the

instrument except during cluster deposition. This capability is critical, allowing the source and other beamline components to be serviced without venting the UHV section of the instrument, which must be baked for several days after exposure to atmosphere. After passing through the valve/lens, the clusters enter a final quadrupole ion guide (Quad3), operated with RF voltage of 150–600 V at 2.0 MHz, with DC bias potential of roughly -20 V. The pressure in the Quad3 chamber during deposition is 10^{-8} Torr, and the base pressure is in the mid- 10^{-10} Torr range.

At the exit of the final quadrupole guide, the ions pass through a thin, 2 mm diameter electrode that functions as a lens, exposure mask, and differential pumping aperture. For deposition, the sample substrate is positioned 1 mm behind the exposure mask and grounded via an electrometer, to allow continuous measurement of the current of Pd_n^+ on the sample. For the experiments described below, the cluster deposition energy was set at 1 eV/atom, as determined by retarding potential analysis on the deposition substrate. 1 eV/atom is smaller than typical metal-metal bond energies, as well as typical bond energies of metal atoms to oxide supports, and thus corresponds to soft landing condition, while still allowing high beam intensities to be delivered to the sample. Intensity is critical, even in UHV, to minimize adventitious contamination of the highly dispersed clusters [54,123,124]. The total Pd coverage deposited on each sample was held constant at 1.53×10^{14} Pd atoms/cm², equivalent to 10% of a close-packed Pd monolayer (0.1 ML equivalent). The samples differ, therefore, only in the size of the Pd_n^+ with which the Pd coverage is delivered. Typical deposition currents for various cluster sizes are listed, along with the corresponding deposition times, in Table S1 in the supplementary material. The fact that deposition times are longest for small clusters (~ 30 min deposition times) reflects the fact that the source was optimized for large clusters (~ 5 min deposition times), by using a long exit nozzle to increase the residence time.

The analysis chamber is equipped with tools for surface preparation and analysis, allowing chemical and physical properties of the samples to be probed without air exposure. Tools available include X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and low energy He⁺ ion scattering spectroscopy (ISS) for electronic structure and morphology characterization. In addition, the chamber is equipped with two mass spectrometers for reaction studies. One is a residual gas analyzer (SRS Inc. RGA-100) used to monitor gas doses to the sample. To monitor reactants and products desorbing from the catalyst samples, we use the arrangement shown in Fig. S2 of the Supplementary Material. A UTI 100C quadrupole, driven by 2.1 MHz Extrel electronics, is housed in a separately pumped UHV chamber that views the analysis chamber through a 2.5 mm diameter aperture at the tip of a skimmer cone, which is surrounded by 6 directional gas dosing lines. The dosing lines are fed by three variable leak valves and three pulsed valves, allowing both pulsed and continuous gas exposures. During dosing, the sample is positioned 2 mm from the skimmer orifice, and is typically moved 1 mm from the orifice for desorption studies. The directional dosing tubes provide a ten-fold increase in exposure at the sample surface, relative to the exposure at the chamber walls, thereby minimizing degradation of the chamber vacuum during reactivity studies. The exposure rate from the tubes was calibrated by comparing exposures through the tubes and by backfilling the chamber [53].

The clusters are deposited on an alumina support film, which is grown on a $10 \times 5 \times 1$ mm Re(0001) single crystal (Marketch International), spot welded to a pair of Ta heating wires, which are spot welded to a pair of 1 mm thick Ta support rods that hang from a liquid nitrogen-filled cryostat. The cryostat is mounted on a XYZ/rotation manipulator, which is, in turn, mounted on a 38 cm

diameter homemade rotary platform, with triple, differentially pumped seals. The combination allows the sample to be positioned for deposition, spectroscopy, mass spectral probing, or surface preparation. The sample can be cooled to ~ 125 K and resistively heated to 1200 K. For the higher temperatures required during sample cleaning/annealing, electron bombardment from the back side heats the sample to 2200 K. Temperature is measured by a type C thermocouple spot welded to the back of the Re(0001) single crystal. Commercial type C vacuum feedthroughs use pins made from 405/426 extension alloy, rather than actual type C material (W5% Re and W26% Re), and in our experience, the performance was inadequate at cryogenic sample temperatures, where the type C sensitivity (mV/K) is low. Feedthroughs were, therefore, fabricated using 1 mm pins of type C material, nickel plated and soldered into tubular commercial feedthroughs. The resulting thermocouple system was calibrated against a K type thermocouple attached to the sample, with excellent agreement over the temperature range from 125–1600 K (i.e., $< T_{\text{melt}}$ for K type wire).

A small UHV “load lock” chamber is attached to a port under the analysis chamber, as shown in Fig. 1. When the sample is lowered into this small chamber, it is isolated by another triple differentially pumped seal, allowing the lower chamber to be pressurized up to 1 atm without affecting the analysis chamber pressure. For the experiments here, the lower chamber was used to grow the alumina support film, to avoid exposing the analysis chamber to high $^{16}\text{O}_2$ pressure, which tends to result in elevated water background, presumably due to reaction with hydrogen on the chamber walls. The lower chamber can also be opened for repair of the aluminum vaporization source or sample, as needed.

2.2. Model catalyst preparation

Typical samples consisted of 0.1 ML-equivalent of Pd_n deposited on an alumina support film grown on a Re(0001) single crystal, following procedures developed by Wu et al. [120] and Chen et al. [121]. To clean and prepare the Re crystal for an experiment, the sample was simply heated in vacuum to 1770 K for 25 min. The sample was then probed by XPS to ensure that all of the alumina and Pd from the previous experiments was desorbed, and to check for carbon or other contaminants. Occasionally, particularly if the previous experiment involved an unusually thick alumina film, it was necessary to repeat the cleaning process. According to the literature, heating in this temperature range is also sufficient to anneal the Re crystal, resulting in a sharp LEED pattern [125]. After cleaning, the only contaminant observed was oxygen, present in sub-monolayer concentrations, which is not a problem because the next step in the sample preparation involves heating the Re in oxygen, prior to starting alumina deposition. The alumina film was grown in the lower chamber resistively heating the Re(0001) crystal to 970 K in a background of 5×10^{-6} Torr of ultrahigh purity $^{16}\text{O}_2$, which was further purified by passing the O_2 gas line through an ethanol/liquid nitrogen bath just before leaking into the lower chamber. Aluminum was evaporated onto the Re support in the O_2 atmosphere, using a home-made evaporator consisting of a shrouded, resistively heated alumina crucible filled with 99.999% aluminum. The film growth rate was set to 0.2 ± 0.01 nm/min, as determined from Al and Re XPS peak intensities as a function of deposition time.

Similar alumina films grown using this procedure have been characterized by LEED and ISS [119–121,126]. It was reported that the films grow by coalescence of islands, forming complete, continuous films at ~ 0.6 nm thickness for alumina grown on Ta (110), and at ~ 1.5 nm for alumina grown on Re(0001). Our ISS results show a small, but significant Re signal in ISS, even for films up to 10 nm thick, suggesting that there is diffusion of Re into the alumina, doping the surface layer with $\sim 1\%$ Re [127]. Such doping

of oxide overlayers by diffusion of atoms from the support crystal has been seen in other systems [6,55,128,129], and the dopant atoms may act as anchoring sites for deposited metal clusters [128]. We carried out a detailed study of the thickness dependence of both the physical and chemical properties of the alumina/Re (0001) [127] and alumina/Ta(110) films [55], and as expected, the properties become thickness-independent for films thicker than ~ 2.7 nm and 4.5 nm, respectively. Because of Re doping, the alumina films are reasonably conductive, and signs of charging (e.g., shifts in UPS or XPS peak energies) are observed only for films thicker than ~ 7 nm [127]. To avoid this issue in the present study, all experiments were done on films in the 3–6 nm thick range. The thickness was estimated from the intensity ratios of the Al 2s and Re 4f peaks measured by XPS, using photoemission cross sections and β parameters from the literature [130], and effective attenuation lengths calculated using the NIST Electron Effective-Attenuation-Length Database [131]. The estimation ignores Re mixing into the alumina film, and therefore the thicknesses are slightly underestimated. The estimated absolute uncertainty in film thickness is $\pm 20\%$, however, the relative uncertainty in comparing thicknesses of different films is estimated to be less than 5%.

2.3. Characterization and reactivity measurements

After preparation and characterization of the alumina film, Pd_n was deposited at 300 K with a Pd density of 0.1 ML equivalent in a ~ 2 mm diameter spot. A combination of XPS and UPS was used to probe the sample electronic structure, both as deposited, and after changes due to a sequence of surface reactions. XPS was done using Al K α X-rays from a dual anode source, and UPS was done using He I radiation (21.1 eV) from a differentially pumped discharge lamp [132]. After XPS characterization of the freshly deposited Pd_n/alumina samples, the samples were cooled to ~ 130 K in approximately 25 min, for temperature-programmed reaction (TPR) studies of activity.

The sequence used in the TPR studies is as follows. The samples were first flashed to 560 K to remove any adventitious adsorbates, then cooled quickly to 400 K (~ 2 min), at which point they were exposed to 10 L of $^{18}\text{O}_2$, corresponding to roughly two O₂ molecules impinging *per* surface atom, on average. The oxygen is 99 at.% ^{18}O , and was passed through an ethanol/liquid nitrogen bath (~ 160 K) to remove any condensable contaminants. After oxidation, the sample was cooled to 180 K where it was exposed to 10 L of $^{13}\text{C}^{16}\text{O}$. This CO dose temperature was chosen for comparison to previous studies of CO oxidation over Pd_n/TiO₂. The sample was then cooled to 135 K and centered 1 mm in front of the differentially pumped mass spectrometer, then heated to 560 K at 3 K/s, while the mass spectrometer rapidly cycled between monitoring mass 18 (H₂O or ^{18}O), 20 (H₂ ^{18}O), 36 ($^{18}\text{O}_2$), and all isotopologs of CO and CO₂.

To allow observation of changes in sample chemical properties induced by TPR, each sample was probed by three sequential TPR runs, including oxidation at 400 K and CO exposure at 180 K. After completion of the three TPR runs, the sample was probed by CO temperature-programmed desorption (TPD), using a protocol identical to that used for TPR, with the exception that there was no $^{18}\text{O}_2$ exposure. Because (see Section 3) CO binds to Pd_n, but not to the alumina film, the CO TPD results provide a measure of the Pd binding site density remaining after TPR. Furthermore, measuring CO₂ desorption during this final CO TPD run probes the extent to which any reactive ^{18}O is left on the surface at the conclusion of the TPR runs. It is useful, mechanistically, to convert the ion signals recorded during TPR/TPD to the corresponding number of CO or CO₂ molecules desorbing from the samples. The sensitivity calibration procedure is discussed in the supplementary information, and the molecular fluxes given below are estimated to be

accurate to within a factor of two. For reasons described in the supplementary information, it appears that the estimates may be on the low end of the uncertainty range.

Finally, to probe Pd_n morphology and adsorbate binding, scattering of 1 kV He⁺ (i.e., ISS) was used, with either low (0.15 μA) or high (1.15 μA) He⁺ flux. Raw ISS data consists of kinetic energy (E) spectra for He⁺ scattered from the surface, plotted as a fraction of the incident energy (E_0). Only a small fraction of the incident beam survives to scatter from the surface as He⁺, mostly in events where He⁺ scatters from a single atom in the surface layer [54,122,133]. Such events lead to well defined peaks, with E/E_0 indicating the mass of the surface atom. A broad background results from sub-surface and/or multiple scattering events, and this signal is weak because the He⁺ ion survival probability is low in such trajectories. ISS, therefore, is a probe of the distribution of different elements in the top-most layer of the sample. As such, it is sensitive to cluster morphology, and binding of adsorbates on the cluster surface. Because ISS damages the surface, these experiments were either done at the end of an experimental sequence to generate “post-reaction” results, or using separately prepared samples to generate “as-deposited” results.

3. Results and discussion

3.1. Pd_n size dependent reactivity

Fig. 2 shows typical TPR results, in this case for a Pd₂₅/alumina/Re(0001) sample exposed to 10 L of $^{18}\text{O}_2$ at 400 K, and 10 L of $^{13}\text{C}^{16}\text{O}$ at 180 K. As shown below, results for other cluster sizes are similar. The sample was then cooled to 130 K, and heated at 3 K/s while monitoring all CO, O₂, and CO₂ isotopomers. No desorption signal was observed for $^{18}\text{O}_2$, and the only significant signals for CO and CO₂ were residual, unreacted $^{13}\text{C}^{16}\text{O}$ and the $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ product. It can be concluded, therefore, that ^{18}O bound on the surface does not desorb as $^{18}\text{O}_2$ in this temperature range, and that ^{16}O present in the alumina film is not significantly involved in CO oxidation under these conditions. Data are shown for the three sequential TPR runs, and for the subsequent CO TPD run, where the 400 K $^{18}\text{O}_2$ exposure was omitted. Control experiments on alumina/Re(0001) without deposited Pd show no evidence for CO₂ production, indicating that the active sites are associated with Pd.

One obvious point is that both the CO₂ production and residual CO desorption are consistent from run to run, i.e., the model catalyst, as prepared, is quite stable under these conditions. Further probes of catalyst stability are discussed below. CO₂ is produced in a broad feature that starts at 180 K, and terminates at ~ 500 K. The observation that the CO₂ feature starts at 180 K simply reflects the fact that the CO exposure was done at 180 K, reacting away any adsorbed oxygen capable of reacting at lower temperatures. The CO₂ produced during the CO dose was also measured, and amounts to only 2–3% of the total CO₂ production. Furthermore, the lack of ^{12}CO or $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ desorption during TPR suggests that any adventitious ^{12}CO that might have adsorbed on the sample during deposition, XPS characterization, and cooling, was removed by the combination of the 560 K flash and 400 K O₂ exposure.

Desorption of unreacted CO is bimodal, and the sharp decline in CO₂ production at high temperatures is coincident with growth of the higher temperature CO desorption peak. The most obvious interpretation is that oxygen activated on the clusters is the limiting reactant, and that it is all reacted away by about 500 K, leaving the balance of the CO to desorb unreacted. There may be some oxygen remaining on the clusters, but so stably bound that it is unreactive in the temperature range where CO remains on the surface. If so, this stably bound oxygen can't have any effect on O₂ activation, CO binding, or CO₂ production in the 2nd and 3rd TPR

Fig. 2. (a) Residual CO desorption during three consecutive TPR measurements on $\text{Pd}_{25}/\text{alumina}/\text{Re}(0001)$, followed by a CO TPD measurement. (b) CO_2 production during each of the three TPR measurements, and the CO TPD measurement. For both of these figures the 1st, 2nd, and 3rd TPR measurements are plotted in blue (circles), red (squares), and green (diamonds), respectively. The final CO TPD measurement is plotted in black (triangles). For all TPR measurements, the sample was exposed to 10 L $^{18}\text{O}_2$ at 400 K and 10 L ^{13}CO at 180 K. The final CO TPD measurements were exposed to the same 10 L ^{13}CO at 180 K, with no $^{18}\text{O}_2$ exposure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

experiments, which seems unlikely. Testing for the presence of active oxygen was part of the purpose for the final CO TPD experiment, carried out after the three TPR runs. Production of CO_2 and CO isotopomers was monitored, both during the 180 K ^{13}CO exposure, and during the subsequent heat ramp. No CO_2 was observed, indicating that there is no active oxygen left on the surface at the end of the TPR.

The amount of CO desorbing in this final CO TPD is roughly twice the amount of residual CO desorbing during TPR. There are

two contributing factors. A significant fraction of the CO adsorbed on the pre-oxidized samples is reacted away during TPR. In addition, as shown below, CO and oxygen are expected to compete for binding sites, thus adsorption of oxygen probably blocks sites for subsequent CO adsorption. This competition between CO and oxygen for binding sites is also observed for bulk Pd surfaces or larger Pd nanoparticles [103–105,134].

One question is whether the broad CO_2 desorption temperature dependence is controlled by the energetics for the reaction of $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$ on the surface, or by the desorption energy of the CO_2 product. Typically, CO_2 binds weakly to metal surfaces [135–138], and to see if that is also true here, we ran TPD experiments where $\text{Pd}_n/\text{alumina}/\text{Re}(0001)$ samples were exposed to CO_2 at various temperatures. It is not obvious whether sticking of molecular CO_2 should be an activated process or not, therefore we tried this experiment using CO_2 exposure temperatures ranging from 180 K to 400 K. In no case was there any evidence of CO_2 sticking to the surface. It is conceivable that CO_2 formed on the surface by reaction might have different desorption properties, but we tentatively conclude that the CO_2 temperature dependence during TPR, reflects the energetics of the CO oxidation reaction, rather than CO_2 desorption. In that case, there is clearly a considerable range of activation energies, presumably reflecting the variety of O and CO binding sites possible on these samples.

Fig. 3 shows how the integrated CO_2 production varies with cluster size. Results from each of the three TPR runs are shown as open symbols, and the average of the three runs is shown as a solid symbol. Roughly 0.2 CO_2 molecules are produced *per* deposited Pd atom, thus the number of CO_2 produced *per* cluster increases from ~ 0.8 for Pd_4 to ~ 6 for Pd_{30} , although, as discussed above, these numbers are probably low, by up to a factor of two. As indicated, the results are quite stable from run to run, so that the random error is only $\sim 1\%$. It can be seen that activity is weakly dependent

Fig. 3. The integrated amount of CO_2 produced from the 1st, 2nd, and 3rd TPR measurements are plotted against the left axis, as a function of Pd_n cluster size, along with the average of the three TPR measurements, with error bars representing the standard error. The as-deposited Pd 3d 5/2 binding energy is plotted against the right axis (note inverted scale). The error bar on the point for Pd_{20} is the standard error from a series of measurements on different samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

on cluster size, varying by only $\sim 40\%$. The most reactive samples had Pd₅ and Pd₂₅ deposited.

Fig. S3 shows the variation in integrated CO desorption with cluster size, showing both total CO, and CO associated only with the high temperature (HT) desorption component, in both TPR and TPD experiments. The separation of the HT component was based on simulations of the data, discussed below. The results are shown as CO/Pd atom, and again, could be low by up to a factor of 2. For the TPD measurements, where there is no competition with adsorbed oxygen for binding sites, the coverage of CO is roughly constant at ~ 0.45 CO/Pd atom, with ~ 0.2 CO/Pd desorbing in the HT desorption feature. The observation of weak dependence of CO coverage on cluster size is not surprising, and is consistent with the ISS results discussed below. During TPR, the amount of unreacted CO desorbing is reduced by roughly a factor of two, for both the total and HT CO desorption, due to some combination of CO oxidation to CO₂ and competition between oxygen and CO for binding sites. Comparison of Figs. 3 and S3 shows that roughly equal integrated amounts of CO and CO₂ desorb during TPR, i.e., about half the CO adsorbed during TPR is converted to CO₂ under these conditions. Furthermore, the combined CO and CO₂ desorption during TPR is similar to the CO desorption during the TPD run, suggesting that binding site competition between pre-adsorbed oxygen and CO does not substantially reduce the amount of CO that adsorbs. By comparing the temperature dependence for CO₂ production for different size clusters, shown in Fig. S4 in the supplementary information, it can be seen that Pd₅ and Pd₂₅ have increased reactivity at temperatures above 400 K. This suggests that these two active clusters are able to activate more oxygen, which results in CO₂ production at higher temperatures before the oxygen is depleted.

To further probe the kinetics of O₂ activation on the Pd clusters, and to test the hypothesis that activated oxygen is the limiting reagent under these conditions, additional experiments were performed. If oxygen is limiting, then one might expect that using a larger O₂ exposure might lead to additional adsorption of oxygen, and therefore higher CO oxidation activity. This hypothesis was tested for Pd₅ using a TPR protocol identical to that used above, but increasing the ¹⁸O₂ exposure from 10 L to 50 L (at 400 K). This resulted in no change in either the CO₂ production, or the amount of residual CO desorbing. Evidently, 10 L O₂ exposure at 400 K is sufficient to saturate all sites capable of binding active oxygen, so that additional O₂ exposure has no significant effect. The result is reminiscent of the observation that O₂ dissociative adsorption on Pd(110) becomes an activated process when the coverage exceeds 0.15 ML [113], i.e., O₂ dissociative adsorption is self-limiting. We also examined the possibility that oxygen binding might have an activation barrier by running another series of TPR measurements where the protocol was as above, except that the 10 L ¹⁸O₂ exposures were carried out at 180 K, rather than 400 K. Again, there was no significant change in the CO₂ production, indicating that the kinetics of oxygen binding are still efficient enough at 180 K to saturate the limited number of active oxygen binding sites. The lack of activation energy is consistent with experiments performed on Pd_n/alumina/NiAl, where temperatures as low as 100 K were shown to oxidize Pd, as shown by a shift in the Pd 3d core level [50].

It is interesting to compare CO oxidation over Pd_n/alumina/Re (0001) with results under identical conditions for CO oxidation over Pd_n on different oxide supports. For Pd_n/alumina/Ta(110) [55] the dependence of activity on size is also relatively weak, varying by 30% from the most active (Pd₆) to least active (Pd₁₀ and Pd₂₅) clusters. In contrast, variations by more than a factor of five are seen for Pd_n/TiO₂(110) under similar conditions [24]. To some extent, the weak size dependence for Pd_n/alumina is not surprising, because the activity in both Pd_n/alumina systems is quite high under these conditions, with $\sim 45\%$ of the CO converted

to CO₂, while the Pd_n/TiO₂ conversion is at most $\sim 5\%$. In the case of the Pd_n/alumina systems CO₂ production appears to be limited by availability of active oxygen. In that case, one might suppose that for the much less active Pd_n/TiO₂(110) system, which is also shown to be oxygen-limited [53], increasing the O₂ exposure would increase CO₂ production, however, there is another factor at play. On the TiO₂(110) support, prepared by vacuum annealing, $\sim 8\%$ of the surface unit cells have a vacancy in the bridging oxygen position [50], and at the temperatures reached in the TPR/TPD experiments, interstitial Ti³⁺ is known to diffuse to the surface [129,139,140]. Both provide binding sites for O atoms, and as a result, ¹⁸O initially bound to the Pd clusters can, instead of oxidizing CO, spill over and bind on the TiO₂ support. This issue is discussed further in the next section.

3.2. ISS investigation of cluster morphology and co binding sites

When using ISS to determine cluster morphology, stability or adsorbate binding locations, it is important to be able to disentangle the effects of adventitious background gases. A detailed explanation of the processes used in this study to negate the effects of elemental sensitivity, post reaction adsorbates and the inherent destructive nature of ISS measurements has been proved in the supplementary information.

Fig. 4 summarizes the as-deposited and post-reaction Pd ISS results as a function of cluster size. Because the as-deposited and post-reaction experiments each require a fresh sample, it was not practical to repeat the experiments for every cluster size, and as-deposited ISS was only done for a subset of the clusters. To assess reproducibility, we ran three as-deposited and three post-reaction experiments on six separate Pd₂₀/alumina samples, and the standard errors are shown as error bars on those points. It can be seen that the reproducibility of the as-deposited ISS is quite high, and this has been our experience with previous systems as well. As expected, the reproducibility for the post-reaction analysis is lower, due to the extrapolation required to account for the adsorbates present.

For the as-deposited clusters, the Pd ISS signal decreases by $\sim 30\%$ as the cluster size is increased from Pd₂ to Pd₂₅, indicating that the fraction of Pd atoms in the surface layer of the sample also decreases slowly with increasing size. If we assume that in Pd₂/alumina, the clusters lie flat on the surface, then the trend suggests that Pd₅ also deposits as a single layer island, but that with increasing size, a small fraction of the Pd atoms begin to form a second layer, thereby attenuating scattering from underlying Pd. The transition to multilayer cluster structures is similar to what was observed for Pd_n/TiO₂(110) [24], but unlike that for Au_n/TiO₂

Fig. 4. The Pd/(Al+O) ratio determined in ISS is plotted as a function of Pd_n cluster size both as deposited (circles) and after reaction studies consisting of three TPR measurements and a CO TPD (squares).

(110) [141], Ir_n/TiO₂(110) [142] and Ni_n/TiO₂(110) [143], where the decrease with size is more rapid, indicating formation of more 3-dimensional structures.

More surprisingly, once the attenuation from adsorbates is corrected for, there is little if any difference between the as-deposited and post-reaction Pd ISS intensity. The implication is that while reaction may leave some adsorbates on the surface, the structure of the underlying Pd is not significantly changed. Presumably this is one factor accounting for the high stability of these samples in sequential TPR experiments.

ISS can also be used to probe changes in samples at different stages of the sample preparation and TPR process. When 0.1 ML equivalent of Pd_n is deposited on an alumina film, both O and Al peaks are attenuated, as expected, but the Al attenuation is slightly larger, suggesting a tendency for clusters to deposit such that they cover more aluminum than oxygen sites. The Pd, Al, and O signals are unchanged by the 560 K flash, suggesting that the Pd clusters are stable up to 560 K. After exposure to 10 L ¹⁸O₂ at 400 K, however, there is a ~20% drop in Pd signal, with no change in Al or O signals, including no significant shoulder for ¹⁸O on the ¹⁶O peak. This result implies that there is no significant adsorption of ¹⁸O on the alumina film, but there is ¹⁸O bound to Pd in geometries that attenuate He⁺ scattering. The relationship between oxygen coverage and Pd ISS attenuation depends on the type of oxygen binding site. If O were bound directly atop Pd atoms, then every O atom would block scattering from one Pd atom, thus the O coverage would be ~20% of the Pd coverage (~2% of the surface layer). If, on the other hand, O atoms bind in other sites not directly atop Pd atoms, then the coverage would probably need to be higher in order to attenuate Pd ISS by 20%. In either case, however, the total ¹⁸O coverage would be too small to produce a distinguishable peak at $E/E_0 = 0.44$ given the relatively high multiple scattering background. In contrast to the small effect of O₂ exposure, 10 L exposure to CO results in almost complete attenuation of the Pd signal, with little change in the Al and O signals. This result implies that the Pd clusters are essentially saturated with CO, at least some of which is bound on top of the clusters. As shown above, after the series of three TPR and one TPD experiments, followed by XPS analysis, the Pd ISS intensity initially attenuated by adsorbates, recovering with increasing He⁺ flux, however, there is no significant change in O and Al signals, indicating that the adsorbates remaining on the surface are bound mainly to Pd.

The absence of a post-reaction signal for ¹⁸O, is in contrast to what was observed for Pd_n/TiO₂(110) under identical conditions, where an ¹⁸O feature corresponding to >20% of the total surface layer oxygen was observed [6]. This large ¹⁸O feature implied that ¹⁸O, initially activated and bound on the Pd clusters, spilled over to the TiO₂ support to bind at vacancies or to Ti³⁺ interstitials that diffuse to the surface at high temperatures [129,139,140]. This spillover process is in competition with CO oxidation, and presumably was responsible for the relatively low (<10%) CO oxidation efficiency in the Pd/TiO₂ system. Similarly, oxygen spillover was proposed as an explanation for the negligible CO oxidation activity observed for Pd_n/alumina/NiAl(110), where the alumina film is only 0.5 nm thick [56,144]. Evidently, oxygen spillover is not significant for Pd/alumina/Re(0001), presumably because the film is fully oxidized and thick enough to act as a diffusion barrier. Instead, the adsorbed oxygen remains on the Pd clusters, reacting with high efficiency.

3.3. Correlations with pd electronic properties

XPS was used immediately after Pd_n deposition to characterize the as-deposited Pd. Because the alumina films are thin enough to allow observation of the Re 4f peaks from the Re(0001) support, the XPS energy scale was set to align the Re 4f_{7/2} peak to the

literature value (40.3 eV) for bulk Re. The shift required was only ~0.2 eV, and quite reproducible from day to day. This approach does not compensate for charging of the alumina film, however, no evidence for charging is seen for the alumina film thicknesses used in this study. The Pd 3d peak also has 3d_{5/2} and 3d_{3/2} spin orbit components, and in fitting the spectra, the peak splitting was constrained to the literature value of 5.26 eV [145]. The Pd 3d binding energies discussed below are for the larger 3d_{5/2} peak, and are plotted in red against the secondary axis in Fig. 3. Note that the Pd 3d binding energy scale is inverted to make it easier to compare the binding energies and CO₂ production activities as a function of cluster size. As expected, the Pd 3d_{5/2} binding energies are substantially greater than the value for bulk Pd (335.1 eV) [145], due to factors such as the more limited relaxation and core hole screening possible in small clusters, compared to that in bulk metal [146–149]. For the same reason, it is expected that the binding energy should generally decrease with increasing cluster size, converging to the bulk value for nanoparticles that are large enough to have bulk-like electronic structure [147,150].

In addition to this overall trend, there is a fluctuation, where Pd₅ and Pd₆ show binding energies that are significantly lower than expected from the overall trend. There are other apparent fluctuations, however, only this one is statistically significant. It appears that there is an anticorrelation between Pd 3d binding energy and activity, i.e., samples with high Pd 3d binding energy are relatively unreactive, and vice versa. Clearer anticorrelations of this sort have been observed for CO oxidation over Pd_n/TiO₂ [24] and Pt_n/alumina [57], where the size-dependent fluctuations in both reactivity and XPS binding energies were substantially larger. A strong anticorrelation was also found between activity for carbon oxidation and Pt 4f binding energy in an electrocatalytic study of Pt_n/glassy carbon [2]. Such anticorrelations between binding energy and activity for oxidation catalysis can be rationalized in terms of either initial or final state effects on the binding energies. In an initial state picture, the variation in Pd binding energy with size would be attributed to varying electron density on the Pd clusters, due to electron transfer between the Pd clusters and support. Clusters in an electron rich environment (i.e., with a partial negative charge) tend to have low binding energies, and an electron rich environment might also aid in activating adsorbed oxygen, by electron transfer to the O₂ π* orbitals. Conversely, if the clusters have lost electron density to the support, that would tend to increase the Pd 3d binding energy, and decrease the ability to activate O₂. It has been previously shown that Pd deposited on alumina surfaces, can cause a dipole to form due to electron charge transfer from the alumina support to the Pd clusters [151,152]. From a final state perspective, clusters that have particularly polarizable valence electronic structure would tend to relax and screen the core-hole final state more than clusters with more tightly bound valence electrons, and one would also expect that loosely (tightly) bound valence electrons would be more (less) efficient for O₂ activation. In reality, both initial and final state effects probably contribute to the variations in Pd 3d binding energy.

We also examined the cluster size dependence of the onset of the Pd valence band, as shown in Fig. 5. The zero of the electron binding energy (i.e., the sample Fermi level, E_F) was obtained from the spectrum of silver foil attached to the sample holder. Examples of the near- E_F region of the raw UPS for alumina/Re(0001) and Pd₁₀/alumina/Re(0001) are shown in frame (a) of the figure. The spectra are dominated by the O 2p band from the alumina film, which has an onset at ~4.5 eV below E_F . Fig. 5b shows the near- E_F region on a magnified scale, demonstrating that the signal from Pd₁₀ is easily observed, due to its location in the alumina band gap. The UPS for the clean alumina film shows a weak, featureless background in the 0–4 eV binding energy range. This background

Fig. 5. (a) UPS spectra for a clean alumina film before (solid black) and after Pd₁₀ deposition (dashed red), with energy referenced to the Fermi level of the sample, E_F. Inset (b) shows the near-EF region on a reduced scale. Inset (c) shows the subtracted spectrum (black circles), and the fit to the spectrum used to determine the onset energy of the Pd valence band (solid red). The intersection of the line tangent to the inflection point of the fit is plotted (dashed blue) to indicate the Pd valence band onset energy. Frame (d) shows the Pd valence band onset energy as a function of Pd_n cluster size (black-left axis), and Pd 3d 5/2 core level binding energy (red-right axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

results from a combination of midgap states in the alumina, primarily due to ~1% Re doping in the film, and emission from the Re substrate, strongly attenuated by passage through the alumina. Signal due to deposited Pd₁₀ is much larger than the background, and the background-subtracted spectrum is shown in Fig. 5c. It can also be seen that the addition of Pd to the alumina film shifts the O 2p band closer to E_F, and there is also a shift in the high energy spectral cutoff (not shown) that implies an increase in surface work function. Neither of these shifts has significant dependence on

deposited cluster size. The Pd valence band onset energies vs. cluster size were extracted by first subtracting the alumina background from the spectra for each as-deposited sample. The residual Pd signal was then fit by a Gaussian-convoluted step function, and the onset energy was taken as the horizontal intercept of the line tangent to the inflection point, as depicted in Fig. 5c. This procedure, suggested by Gutmann [153], approximately corrects for instrumental broadening [154].

Fig. 5d shows the shift in the Pd valence band onset energy as a function of cluster size, and compares this indicator of valence structure to the Pd 3d core level binding energy. There is an overall decrease in binding energy with increasing cluster size, expected due to better screening and delocalization of the final state charge, but it is clear that the valence onset energy for Pd₅ is anomalously high relative to E_F, i.e., Pd₅ is less bulk-like than might be expected from the overall trend. It is interesting that the trends of electronic stability with cluster size appear to be opposite for core and valence electrons. Pd₅ has an anomalously low 3d binding energy, and anomalously high valence band onset energy. It is not clear why this might be true, or how this connects with activity as measured in TPR.

3.4. The nature of co binding

To better understand the reaction mechanism, it is instructive to examine the CO desorption behavior in more detail. Fig. 6a shows the results of a CO TPD experiment, taken after three TPR measurements and was exposed to 10 L CO at 180 K, then heated, without any O₂ exposure. The open black circles are experimental data while the solid red and blue lines show a fit to the temperature dependence (bottom axis) of the CO intensity. The dashed black curve shows the sum of the two components, which have been adjusted to give a fit to the experimental signal. The temperature dependence was simulated using the Polanyi–Wigner rate expression, as discussed by Redhead [155], assuming first order desorption, as expected for a molecular adsorbate like CO. The desorption signal I(t) can be written:

$$I(t) \propto \frac{-d\theta}{dt} = (\theta \times \nu) \times e^{\frac{-E_{\text{desorption}}}{k_b T}} \quad (1)$$

where θ is the coverage, ν is a prefactor, $E_{\text{desorption}}$ is the desorption energy, and T is the temperature at time t . Ideally, the prefactor should be determined from a series of experiments, however, given the difficulties and significant time inherent to preparing these samples, this approach is impractical. We have assumed ν to be 10^{14} s^{-1} , in the middle of the range typically seen for CO desorption [54], and have tested the sensitivity of the extracted desorption energy distributions to the value of ν . The extracted $E_{\text{desorption}}$ distribution shifts by ~7% for an order of magnitude change in ν , providing an estimate for the systematic uncertainty in the $E_{\text{desorption}}$ and relative intensities [54]. The figure also shows the $E_{\text{desorption}}$ distribution, plotted against the top axis, which has been constructed so that the temperature and $E_{\text{desorption}}$ distributions are roughly superimposed. It can be seen that the low temperature desorption feature corresponds to $E_{\text{desorption}}$ peaking near 0.6 eV, while the high temperature desorption feature corresponds to $E_{\text{desorption}}$ peaking near 1.4 eV.

Fig. 6b shows the intensity of the high temperature CO desorption peak, as a percent of the total CO desorption intensity, determined from the integrated intensities of the TPD simulation components. It can be seen that for both the residual CO desorbing during TPR, and the CO desorbing during the final CO TPD experiment, the fraction of the CO in the high temperature desorption feature increases with increasing cluster size, and accordingly, the fraction desorbing in the low temperature feature decreases. Since CO is not observed to bind to the alumina film in

Fig. 6. (a) CO desorption during CO TPD from Pd₂₅. The open black circles are the raw CO desorption while the solid red and dashed blue lines are fits to the low and high temperature components, based on a simulation of the desorption kinetics. The dashed black line is the simulated TPD, i.e., the sum of the two features. By referring the simulated TPD curve to the $E_{\text{desorption}}$ axis plotted across the top of the figure, the distribution of desorption energies can be seen. (b) The intensities of the high temperature desorption feature, as a percent of total CO desorption, for CO TPD (solid red) and residual CO in TPR (open blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

this temperature range, both CO desorption features are clearly associated in some way with the Pd clusters, and the obvious question is how the CO is bound. We might, for example, expect CO to bind on top of the Pd clusters, but there might also be sites where CO is bound to the alumina at the cluster periphery, or at the cluster-support interface.

The nature of the CO binding sites associated with the two desorption features was probed by temperature-dependent ISS (TD-ISS), as shown in Fig. 7. These data are for Pd₂₀ (a representative large cluster) deposited on a alumina film grown on Ta(110), and similar results were obtained for Pd₂/alumina (a representative small cluster). Furthermore, the behavior for Pd_n/alumina is quite similar to that observed for CO binding to Pd_n/TiO₂ (110) [6]. The figure shows a CO TPD spectrum, taken using the protocol described above, showing the two CO desorption features. A curve is also shown that gives the fraction of the total CO desorption that has occurred at each temperature. The results of two different ISS experiments are also shown, done on two freshly prepared samples. One simply measured the as-deposited ISS intensities, using the same procedure that was used for Fig. S5. The result is the data point at 0.42 on the left hand axis, which is the Pd ISS intensity normalized to the sum of the Al and O intensities. All other points in the TD-ISS data set were taken using low flux scans

Fig. 7. CO TD-ISS for Pd₂₀/alumina/Ta(110). See text for explanation.

on a separately prepared sample, in order to minimize the effects of He⁺ sputtering. The point at ~0.03, directly below the as-deposited point, shows the Pd intensity measured after exposure to 10 L CO at 180 K, followed by cooling to 130 K. The subsequent points in the TD-ISS curve were obtained by heating the sample to the indicated temperatures, then taking a low flux ISS scan as the sample cooled. We did not measure ISS while the sample was being heated because we wanted to monitor the He⁺ flux, which required the heating connections to be broken temporarily.

As noted, intensity in ISS peaks mostly results from single scattering events, primarily involving atoms in the top-most sample layer. The >90% drop in Pd signal resulting from the 10 L CO exposure indicates that CO is binding to the Pd clusters in such a way as to almost completely attenuate He⁺ scattering from Pd. In our ISS geometry (45° angle of incidence, detection along the surface normal), CO binding on top of the clusters is expected to strongly attenuate scattering from Pd, while CO binding around the cluster periphery would attenuate scattering from Pd only if the CO extended high enough off the surface to cast a scattering shadow cone [133] intersecting Pd atoms in the cluster. The near-total attenuation observed is additional support for the idea that the absolute coverage estimated above (Figs. 3 and S3) is probably on the low side of our factor-of-two uncertainty window.

Note that as the sample is heated, the Pd ISS signal gradually increases. Two effects contribute. As CO is thermally desorbed, underlying Pd is exposed to the He⁺ scattering, however, it is also important to take into account the increase in Pd ISS signal that occurs due to CO loss by He⁺ sputtering [54]. The line labeled “CO sputter rate” was measured by preparing an identical CO-saturated sample, then running a series of low flux ISS measurements while keeping the sample at 130 K, so that sputtering is the only CO loss mechanism. Of course, He⁺ sputtering also removes Pd, and the “Pd sputter rate” line was measured by preparing yet another sample, and then simply probing it repeatedly with low flux ISS. It can be seen that the Pd intensity loss rate from sputtering is much lower than the rate of Pd ISS recovery from sputtering of overlying CO.

From the TPD results, it can be seen that heating to 300 K results in desorption of 50% of the total CO coverage, but the Pd ISS signal only recovers to a small extent. By 420 K, 75% of the CO has desorbed, with ~50% recovery of the Pd ISS signal. In the temperature above 420 K, the rate of Pd ISS recovery increases sharply, leading to about half the total Pd ISS recovery, despite the fact that only 25% of the total CO desorbs above 420 K. As expected, the Pd ISS plateaus as the CO desorption goes to completion. The implication of these results is that the most strongly bound CO is in sites on top of the clusters, where its desorption leads to a strong recovery of He⁺ scattering from the underlying Pd. The less efficient

attenuation from the more weakly bound sites indicates that this component of the CO is bound in geometries that do not efficiently shadow or block He^+ scattering from Pd, such as sites around the cluster periphery. Similar behavior was seen for Pd_2 on this same support as well as for $\text{Pd}_n/\text{TiO}_2(110)$ [54], which also shows bimodal CO desorption, and for that system Liu [156] showed via DFT that the strongest CO binding sites are bridging sites on the cluster surface, but that there are also sites, with only about half the binding energy, where CO is bound around the cluster periphery, in geometries that would not lead to significant attenuation of He^+ scattering from Pd.

The notion that the stronger binding sites are on the cluster surface, while the weaker sites are around the cluster periphery suggests that the relative population of CO in the stronger binding sites should increase with increasing cluster size. For example, if the Pd_n clusters deposited as circular, single layer thick islands, then the surface area *per* cluster would vary like n , while the perimeter length would vary like $n^{1/2}$. Since the number of clusters deposited varies like n^{-1} , the total number of “on-top” sites on the samples would be n -independent, while the total number of perimeter sites would decrease like $n^{-1/2}$. For non-circular structures, the details would be different, but as long as the morphology is not strongly size-dependent, as suggested by Fig. 4, then we would expect the ratio of “on-top” to peripheral sites to increase with cluster size. Just such an increase in the fraction of high temperature CO desorption is observed, as shown in Fig. 6b.

One final aspect of the TD-ISS results merits comment. The Pd ISS intensity at the end of the experiment is $\sim 12\%$ lower than what would be expected from the as-deposited intensity, taking the Pd sputter rate into account. As shown in Fig. S5, in the supplementary information, there is an attenuation after the TPR/TPD sequence, which, however, is largely reversed by light He^+ sputtering. The explanation proposed above was partial coverage by adsorbates on the clusters, however, it is also possible that TPR and TPD lead to restructuring of the clusters to more compact geometries, where a smaller fraction of Pd atoms is in the surface layer. Such restructuring could involve sintering to form larger clusters, or simply isomerization to more multilayer cluster structures. The difficulty with the restructuring scenario is that it would be difficult to explain the restoration of the Pd ISS intensity, essentially to the as-deposited values (Fig. 4) by light He^+ sputtering. On this evidence, molecular adsorbates appear to be the more likely explanation for the post-reaction drop in Pd ISS. The nature of the adsorbates is unclear. The chamber background pressure does increase during TPR and TPD due to the gas doses and desorbing molecules, and there may be some readsorption during the 20 min when the sample was probed by XPS, prior to the ISS measurements. There may also be some CO or O left on the surface at the end of the TPR/TPD experiments, although we did not observe any additional CO desorption in test experiments carried out to 610 K, nor is there any active oxygen left on the samples at the conclusion of TPR, as shown by absence of CO_2 production in subsequent CO exposure and heating (Fig. 2b).

3.5. Steady state reactivity

TPR is a probe of activity under unrealistic conditions, where O_2 is allowed to interact with the samples prior to CO exposure. For selected sizes we also examined CO oxidation activity under constant flows of both reactants, as the temperature was stepped from 340 K to 600 K. The sizes studied were Pd_5 , Pd_{20} , and Pd_{25} , representing the two most reactive (5, 25), and one of the least reactive (20) samples under TPR conditions. These experiments were done by exposing the samples to CO and O_2 flows from the dosing tubes (Fig. S2) that resulted in increases in chamber pressure of 5×10^{-9} Torr and 1×10^{-7} Torr, respectively, for ^{13}CO and $^{18}\text{O}_2$. The fluxes at the sample

position were equivalent to local pressures roughly an order of magnitude higher, and still in a 1:20 ratio.

The experiments began with growth of the alumina film, deposition of 0.1 ML equivalent of Pd_n , and characterization by XPS, just as in the TPR experiments. The sample was then exposed to 50 L of $^{18}\text{O}_2$ at 340 K to generate an initial concentration of adsorbed oxygen. The sample was next exposed to a constant flow of CO, generating a spike of CO_2 product, which decayed to baseline within 50 s, as the CO removed the initial oxygen coverage. At that point, the $^{18}\text{O}_2$ flow was resumed (leaving the CO flowing as well), resulting in a small steady-state flux of CO_2 product. The CO flow was started first in order to get its flow rate stabilized before starting the much larger O_2 flow. The initial CO_2 steady state production rate is quite small, because, as well established [20,61,103,157], CO binds efficiently to sites on the Pd, poisoning them for O_2 activation until the sample temperature becomes large enough to result in significant CO desorption rate. In our protocol, where the O_2 flow was 20 times larger than the CO flow, a small but significant CO_2 production rate was observed even at 340 K.

Once steady flows of CO and O_2 were established, the sample temperature was increased in 20° steps, with each temperature held constant until the CO_2 production rate became constant, signaling that a steady-state coverage of reactants had developed. In Fig. 8a, each black vertical line with a temperature above it indicates the time when the sample temperature controller was set to that temperature. The sample then took roughly 40 s to ramp to the set temperature, and then further time was allowed for the CO oxidation kinetics to reach steady state. For example, at 525 s the set point was changed to 400 K, the sample reached 400 K at 565 s, and then the kinetics took another ~ 10 –15 s to reach the new steady state, at which point the set point was raised to 420 K. The 20 K temperature steps continued up to 600 K. After ~ 200 s at 600 K, the heat was shut off, allowing the temperature to drop slowly back to 340 K, and it can be seen that the CO_2 production during cooling qualitatively retraced the behavior during heating, as might be expected from the high stability that these samples showed during repeated TPR measurements over the same temperature range. The fact that the temperature and intensity of the peak CO_2 production were slightly different in the heating and cool-down phases of the experiment, probably just reflects the faster cooling rate, which did not allow time for steady state to be achieved. At 2000 s (340 K sample temperature), the CO flow was turned off, resulting in no significant change in CO_2 production. 100 s later, the O_2 flow was turned off, resulting in an essentially immediate cessation of CO_2 production. Clearly, at this temperature, activated, adsorbed oxygen is the limiting reagent.

Several points should be noted. It can be seen that the time width of the temperature steps initially decreased as the temperature was stepped to ~ 500 K, and then got wider again as the temperature increased to 600 K. Over the same temperature range, the CO_2 production rate increased, peaking at ~ 460 K, then decreased by 60% by the time the temperature reached 600 K. The time widths of the temperature steps were determined by the combination of the time needed to reach the new set temperature, and the time it took the CO_2 signal to stabilize. Changes in the time widths, therefore, reflect changes in the time it took to for the kinetics to reach steady state.

In the temperature range of these experiments, the kinetically important processes are adsorption of oxygen, adsorption of CO, desorption of CO, and reaction of adsorbed CO and oxygen to form CO_2 , which is assumed to desorb as it forms. O_2 desorption is not expected in this temperature range, nor was any observed in our TPR experiments. At low temperatures, stable CO binding tends to poison the surface, so that CO_2 production is limited by the availability of binding sites for oxygen adsorption and activation. As the temperature is raised through the range where the CO begins to desorb, (see TPD spectrum in Fig. 6), additional sites for

Fig. 8. (a) Raw CO_2 production from $\text{Pd}_{25}/\text{alumina}/\text{Re}(0001)$ under steady state flow conditions, as described in the text. (b) Comparison of steady state CO oxidation activity for Pd_{25} (blue circles), Pd_{20} (red squares), and Pd_5 (green diamonds) showing both total CO_2 per second (solid lines, left axis) and CO_2 produced per Pd_n cluster per second (dashed lines, right axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

oxygen activation become available, increasing the reaction rate on the surface, which both increases the CO_2 production and shortens the time to reach steady state coverage of the reactants. At temperatures above 500 K, the CO lifetime on the surface becomes so short that the CO_2 production rate is limited by the low surface concentration of CO (the CO pressure is 20 times lower than the O_2 pressure). One interesting point is that TPD shows that our samples clearly have two types of CO binding sites. At the temperatures probed in these experiments, the sites responsible for the low temperature CO desorption component, which TD-ISS suggests are largely around the cluster periphery, would be largely empty, even at the 340 K starting temperature. The fact that the samples are still

CO-poisoned at 340 K suggests that oxygen activation is not efficient in peripheral sites. On the other hand, the fact that the CO_2 production rate peaks in the temperature range where the high temperature CO TPD feature also peaks, suggests that it is these sites, identified as being on-top of the Pd clusters, that are responsible for the oxygen activation and CO_2 production.

Fig. 8b compares the CO_2 production temperature dependence measured for Pd_5 , Pd_{20} and Pd_{25} , where each data point is the steady state CO_2 signal at the indicated temperatures. The CO_2 ion signal has been converted to CO_2 molecules per second, and given the total of 4.59×10^{12} Pd atoms deposited in the form of different clusters in the 2 mm cluster spot, we also give the signal in terms of CO_2 molecules per cluster per second. The corresponding peak turnover frequencies on a per Pd atom basis are $\sim 5.1 \times 10^{-3}$ CO_2 per Pd atom per second for Pd_5 , $\sim 7.4 \times 10^{-3}$ for Pd_{20} , and $\sim 8.5 \times 10^{-3}$ for Pd_{25} . Note also that the order of activity on a per atom basis is different under steady state conditions ($\text{Pd}_{25} > \text{Pd}_{20} > \text{Pd}_5$), compared to TPR ($\text{Pd}_5 \gtrsim \text{Pd}_{25} > \text{Pd}_{20}$), presumably reflecting subtle cluster size effects on the energetics and kinetics for CO desorption and oxygen activation. Under TPR conditions, where the samples were oxidized prior to CO exposure, but with a relatively small O_2 exposure, the activity appears to be primarily correlated with the ability of the clusters to binding and activate oxygen. In the steady state measurements, activity is more obviously related to CO desorption kinetics, i.e., by the need to free up suitable sites for O_2 adsorption and activation.

4. Conclusions

It has been shown that size selected Pd_n clusters can be efficiently deposited on a thin, conductive alumina films for both chemical and physical investigation as model catalysts. Through a combination of CO TD-ISS coupled with CO TPD, it is found that $\text{Pd}_n/\text{Al}_2\text{O}_3$ has two types of CO binding sites, with more weakly bound CO in sites around the cluster periphery, and the more strongly bound CO in sites on top of the clusters. Steady state CO oxidation experiments suggest that the high temperature CO binding site is important for both oxygen activation and binding of reactive CO, leading to CO_2 production. Under TPR experimental conditions used here, the CO_2 production appears to be limited by the amount of activated oxygen, which varies as a function of cluster size. For the steady state reaction conditions, competition between CO and O_2 for binding sites determines the reactivity, particularly at low temperatures. Interestingly, the total amount of CO_2 produced during TPR only varies by only about 40% between the most and least active clusters, while in the steady state study the CO_2 turnover frequency varies by nearly a factor of two for Pd_5 and Pd_{25} , even though these are the two most active cluster sizes under TPR conditions. Presumably the difference is related to the size- and temperature-dependent affinities for different size clusters for CO and O_2 .

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ijms.2014.06.018>.

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