Relating Adatom Emission to Improved Durability of Pt-Pd Diesel Oxidation Catalysts

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Abstract: Sintering of nanoparticles is an important contributor to loss of activity in heterogeneous catalysts, such as those used for controlling harmful emissions from automobiles. But mechanistic details, such as the rates of atom emission or the nature of the mobile species, remain poorly understood. Herein we report a novel approach that allows direct measurement of atom emission from nanoparticles. We use model catalyst samples that can be heated in air under conditions relevant to diesel oxidation catalysts, and a novel reactor that allows the same region of the sample to be observed after short term heat treatments (seconds). Monometallic Pd is very stable and does not sinter when heated in air ($T \leq 800$ °C). However, the presence of Pt keeps the Pd metallic allowing mobile species to be emitted, causing Ostwald ripening. Pt sinters readily in air and at high temperatures (~ 800 °C) mobile Pt species emitted to the vapor phase lead to the formation of large, faceted particles. DFT calculations show that the barrier for atom emission to the vapor phase is much greater than the barrier for emitting atoms to the support. Hence vapor phase transport becomes significant at high temperatures while diffusion of adatoms on the support dominates at lower temperatures (~ 650 °C). Pd slows the rate of emission of atoms to

the vapor phase, helping prevent the formation of abnormally large particles in Pt-Pd catalysts. In summary, the role of Pd in Pt DOCs is quite complex: at low temperatures Pt enhances the rate of Pd sintering which otherwise would be stable as an oxide, while at higher temperature Pd helps to slow the rate of Pt sintering.

Keywords: Adatom emission, Ostwald ripening, Catalyst sintering, Pt-Pd, Diesel oxidation, Exhaust treatment

Introduction

Low-temperature after-treatment catalysts are increasingly important due to a tighter regulatory environment in recent years and the demand for more efficient advanced combustion engine technologies [1]. Specifically, Pt and Pd are the precious metals used in diesel oxidation catalysts (DOCs) for hydrocarbon (HC), carbon monoxide (CO), and nitrogen oxide (NO) oxidation in engine exhaust. Previous reports in the literature indicate that Pt sinters and has poor durability under oxidizing conditions [2, 3]. After high temperature aging in air ($>700^{\circ}\text{C}$), Pt can grow to form particles greater than 200 nm in diameter and approaching microns [4] which is detrimental to low temperature reactivity, and a considerable economic loss in view of the high price of Pt. Adding Pd prevents the formation of large Pt particles, leading to improved durability and performance [4-6]. There is, however, limited understanding of how Pd modifies the behavior of Pt. Learning how Pd helps Pt catalysts can have significant payoffs in the design of more robust catalysts for this and other high temperature catalytic processes.

Previous work shows that Ostwald ripening – inter particle transport of mobile species emitted from small particles – plays an important role in the sintering of supported metal

catalysts [7, 8]. When metal nanoparticles are heated in air, volatile metal oxides can be formed, but these are easily trapped within the pore structure of an industrial catalyst. Hence role of vapor phase processes in interparticle transport is not well understood. In this work we have used planar model catalysts which allow measurements of the rate of emission to the vapor phase. By redirecting the emitted atoms back to the surface we are able to simulate what might happen within a porous catalyst support. Besides being able to observe the same region of the sample before and after treatment, model catalysts allow studies via in-situ TEM where the sample can be observed in real time or after short term treatments. But many of the in-situ TEM studies are performed at low pressures which can sometimes result in different sintering behavior. In a recent study Behafarid et al. [9] report that Pt is quite stable in O₂ up to 800 °C when studied via in-situ TEM at 1 Torr total pressure showing negligible growth in particle size over 30 minutes. In contrast, Chen and Schmidt [10] found rapid sintering and also documented a loss in Pt content when model catalysts were heated in air at atmospheric pressure. Using similar model catalysts, Simonsen et al.[8] found no loss of Pt when studying the samples via in-situ TEM, but at low pressures. It is clear that oxygen pressure is important, since the formation of a metal oxides of Pt is first order in O₂ pressure [11].

Accelerated aging of Pt catalysts is generally carried out in air at atmospheric pressure where we see rapid sintering at elevated temperatures [12] [13]. Furthermore air-aging leads to similar catalyst deactivation as that seen in vehicle aging [14]. Therefore to allow comparison with supported catalysts, we performed our experiments at atmospheric pressure. To preserve the benefits of model catalysts while allowing heating in air at elevated temperatures, we used custom made Si TEM grids with Si₃N₄ windows [15, 16]. Rapid heating was made possible by using a heating device [17] that provides heating and cooling rates over 100°C s⁻¹. This set up

allowed us to perform short term aging of the model catalysts, so that we could capture the disappearance of individual nanoparticles which can occur on the time scale of seconds [18]. Such short term observations cannot be performed in a tube furnace due to long heating and cooling times.

A notable feature of Pt is the high vapor pressure of Pt oxide which can cause a loss of weight in Pt crucibles, and cause massive restructuring of Pt foils heated in air [19, 20]. But Pd on the other hand forms a stable oxide (PdO) in air that has negligible vapor pressure (~3 orders of magnitude less than that of Pd metal) [21]. If PtO_2 were the only mobile species, we would expect that Pt-Pd nanoparticles would slowly lose Pt, leaving behind the Pd and causing phase segregation of the catalyst. However, in supported catalysts rather than seeing segregation we find that even a physical mixture of Pt/alumina and Pd/alumina leads to Pt-Pd alloy formation after aging in air [3]. This apparent ‘self-assembly’ of Pt and Pd into bimetallic Pt-Pd particles occurs because PdO acts as a trap for the mobile Pt species. Therefore, metallic Pt-Pd particles are formed under conditions where Pd by itself would transform into stable PdO, and this is why the working state of a Pt-Pd diesel oxidation catalysts consists of metallic Pt-Pd alloy particles [12]. What is not understood is how the presence of Pd slows the rates of sintering in these catalysts. Another unknown is the relative importance of vapor phase and surface processes in these catalysts. As we show here, vapor phase processes become increasingly important at elevated temperatures. At 650 °C, sintering appears to be largely occurring via surface migration of mobile species emitted from the particles, but at 800 °C it is the vapor phase processes that become significant. This shift in mechanisms causes profound changes in the observed particle size distributions, and the vapor phase processes appear to be responsible for the formation of

abnormally large Pt particles. We conclude that the primary role of Pd is to slow the rates of emission of mobile Pt species from bimetallic nanoparticles.

Materials and Methods

Imaging Methods

The TEM grids were custom-made using a design developed in previous work at TU Eindhoven [16]. They have a 100 μm x 100 μm silicon nitride membrane window with a thickness of 15 nm. The top and bottom 3 nm have been transformed into a surface oxide layer through calcination in air at 750°C for 24 hours. High purity (99.999%) metals (platinum and palladium) purchased from Materion Corporation were used to fabricate these samples. The metals were deposited directly onto the 2 mm x 2 mm SiO₂ TEM grid surface using a 10kV Temescal electron beam evaporator. This high vacuum cryo-pumped system was pumped to a base pressure of 1×10^{-7} Torr prior to deposition. The film thickness was controlled by a quartz crystal microbalance (QCM), while the deposition rate was controlled to 0.03 Å s⁻¹. This system as configured is capable of controlling the film thickness to 0.1 Å. These noble metals are non-wetting on oxide surfaces so a continuous film is not formed during deposition at these very low loadings. All films were deposited to a thickness equivalent to 5 Å (500 pm). The as-prepared samples were treated for 10 minutes at 700 °C in flowing 7% H₂/N₂ (140 sccm) in a SabreTubeTM furnace manufactured by Absolute Nano to allow the deposited films to dewet and form nanoparticles (an image of the furnace is provided in Figure S1 in the supporting information). The furnace allows for a 100°C s⁻¹ heating rate over a 1 cm wide substrate. Temperatures up to 1000°C are possible with the SabreTubeTM. The short, up to two-minute, aging treatments were performed in the SabreTubeTM in flowing air at 140 sccm. The 1.5 hour

aging treatments were done with the sample placed in a ceramic boat within in a quartz tube furnace in flowing air at 100 sccm. The quartz tubes have an inner diameter of 2 cm. The ramp rate of the furnace was $20^{\circ}\text{C min}^{-1}$, and the temperature was held for 1.5 hours and then decreased to room temperature in the flowing air. In some of the experiments we covered the ceramic boat with a smaller boat inverted on the sample to trap the emitted species – helping us simulate the conditions encountered in a porous catalyst structure. Figure 1 shows a schematic diagram of the three configurations used for aging the model catalyst samples. The major difference in these three arrangements is the mass transfer to the flowing air. The Sabre tube being open allows the flowing air to sweep away any volatile oxides emitted to the vapor phase. The rate of emission is slower in the tube furnace since the sample sits within a ceramic boat. The least rate of emission is seen with the covered sample. As we will discuss later, the differences in rate of emission from a pure Pt samples are related directly to the rate of mass transfer since the concentration of the vapor rapidly approaches equilibrium with the metal nanoparticles. A similar approach used by Alcock and Hooper to study the emission of volatile metal oxides from Pt and Pt-Pd alloys [11].

For each experiment, we imaged the sample after initial reduction and then after heat treatment. For brevity, we only show image of one the samples in its initial state. Additional information is presented in the supplementary information that provides statistics and comparison of the initial and final state of each sample. Since the shapes of the particles can change after pretreatment, the volume of each particle is difficult to obtain from the projected views. Hence, we determined the rate of atom emission via elemental analysis using EDS (see Experimental section for further details on the methods used).

Transmission electron microscopy (TEM) as well as scanning transmission electron microscopy (STEM) were used for imaging the samples after reduction and after the aging treatment under oxidizing conditions. A JEOL 2010F 200kV FASTEM FEG (field emission gun) TEM/STEM was used to acquire all STEM images. This microscope has a point-to-point resolution of 0.194 nm and a minimum spot size in STEM mode of 0.14 nm. It has a GATAN GIF 2000 Energy Filter, JEOL bright and dark field STEM detectors, GATAN bright and dark field STEM detectors, and an Oxford Instruments ISIS/INCA energy dispersive x-ray spectroscopy (EDS) system with an Oxford Pentafet Ultrathin Window (UTW) Detector. EDS was used to obtain compositions as well as gather information on loss of metal. Gatan Digital Micrograph was used for all image processing, and INCA was used for the analysis of all EDS data. Diameters of nanoparticles were determined by manual measurement within the Digital Micrograph software. To determine the loss of metal on each sample, either the ratios of the metal to silicon or the absolute counts of the metal were compared before and after aging in air at the specific temperature. This was using the L lines of Pt and Pd as described in the next section.

Determination of Particle Size Distributions and Rates of Adatom Emission

Gatan Digital Micrograph was used for all image processing, and INCA software from Oxford Instruments was used for the analysis of all EDS data. Diameters of nanoparticles were determined by manual measurement within the Digital Micrograph software. EDS was used to obtain compositions as well as gather information on loss of metal. Pt and Pd L lines were used in the EDS analysis. Each time EDS was performed on a model catalyst sample, it was done in at least ten areas around the sample. The electron transparent region of each sample was a 100 μm x 100 μm square. One area in each of the four corners and one area along each of the four

edges were analyzed. Then, at least two random areas in the center of the square were analyzed. Two different techniques were used to quantify emission on these model catalysts. One technique compares the ratio of the atomic percentage of metal to the atomic percentage of silicon before aging and after aging. The SiO₂ membrane can be assumed to remain constant in mass during the aging treatments. If, however, a volatile silica species (SiO_x) caused the loss of Si, using the ratio technique would not provide accurate loss of metal. For this reason, we also considered the absolute counts of the metal before and after aging. To correctly use this approach, all instrumental parameters had to be kept constant. Every time a sample had EDS performed on it, the sample holder had to be tilted to the same degree, and the magnification, spot size, apertures, process time, and live time had to be kept the same. The beam current was measured using the built in pico-ammeter on the phosphor screen. There was some fluctuation of the current density so this was noted every time EDS was performed so that the Pt counts could be normalized. The ratio technique and the method of using absolute counts provided very similar emission results. They were always within the experimental error of EDS ($\pm 5\%$).

DFT Computations

We augmented our experiments with first-principle calculations that are based on density-functional-theory [22] as implemented in the periodic structure software package VASP.[23-25] Electronic exchange and correlations were treated at the GGA level within the parameterization of Perdew and Wang [26]. The interactions between electrons and nuclei were described within the PAW formalism [27, 28]. The electronic configurations (core radii in atomic units, 1 a_B=0.529 Å, in parentheses) were 5s²4p⁶3d⁸ (2.300 a_B), 5d⁹6s¹ (2.500 a_B), 2s²2p⁴ (1.900 a_B), for Pd, Pt, and O, respectively. The Fermi-level was slightly broadened Gaussian

broadening ($\sigma=0.1$ eV). All calculations were performed using a cutoff energy of $E_{\text{cut}}=500$ eV which was found to be sufficient to obtain converged results. The equilibrium fcc-Pd and fcc-Pt structures were computed in the conventional unit cell with the same energy cutoff and $16 \times 16 \times 16$ k-point grid. The optimized fcc-lattice parameters are 3.956 Å and 3.985 Å for Pd and Pt, respectively. These lattice parameters compare favorably with experiments, Pd: 3.8907 Å and Pt: 3.9239 Å [29]. The extended (111) surface structures were derived from the computed bulk equilibrium lattice parameters. All slabs consisted of 4 layers and consisted of a total of 64 atoms for the (111) surface and 72 atoms for the (100) and (110) surfaces. Similar to previous work, the shape of the simulation cell and the atoms in the lower two layers remained fixed at their equilibrium values while the top two layers were allowed to relax. The modeled slab and its periodic images perpendicular to the surface were separated by a 14 Å vacuum layer and residual artificial interactions were reduced by introducing a compensating dipole layer. Properties of the slabs were computed using a Γ -centered $3 \times 3 \times 1$ k-point mesh. The energies of isolated PdO dimers, PtO₂ trimers, and O₂ were computed in an orthorhombic simulation cell of dimensions 10 Å x 11 Å x 12 Å using a single k-point (Γ -point).

Results

Short term (≤ 2 minutes) aging studies in the Sabre tube furnace

Figure 2 shows HAADF STEM images of the Pd-only sample in its initial state and after aging in air at 650 °C for 2 minutes and at 800 °C for 1.5 hours. Very little sintering occurs on this sample even after aging for 1.5 hours at 800 °C. We also confirmed via EDS that there was no loss of Pd to the vapor phase. Most of the sintering occurred during the initial heating (650°C, 2 minutes) when the Pd is transforming to PdO (leading to a drop in the number of

particles per unit area). Once PdO has formed, it is a very stable oxide, and no further particle growth occurs even after heating to 800°C for 1.5 hours. This is confirmed by counting the total number of particles per unit area, which decreases slightly after the initial aging, but then is relatively constant. Particle size distributions for the Pd-only catalyst sample are also included in Figure 1, showing that the increase in size occurs within 2 minutes. The increase in size of the particles is caused by the volume increase upon oxidation (68% for Pd→PdO), which leads to an increase in the projected area of the nanoparticles, due in part also to a change in shape due to altered contact angle. Table 1 lists the changes in particle size, numbers of particles and the fraction of area occupied by the particles. Additional statistics and error bars are included in Table S1 in the SI. HRTEM images of these samples are provided in Figure 2 to confirm that the Pd transforms into PdO, which is the final state of the catalyst in the samples heated to 800 °C in air.

Fig. 4 shows the results of aging Pt and Pt-Pd (38 at% Pt) samples in air for 2 minutes at 650°C and 750°C. It can be seen that the Pt metal particles grow rapidly in air at 750°C in just 2 minutes with a twenty fold decrease in the number of particles per unit area (see Table 2 and additional statistics in Table S2 and S3). In contrast, we see only a three-fold decrease in the number of particles for the Pt-Pd sample. The particle size distribution (PSD) shifts to larger sizes with increasing treatment temperature, accompanied by a drop in the number of particles. What is striking is the presence of particles smaller than 2 nm for the Pt-only sample heated at 750°C, which is not seen in the case of the Pt-Pd samples. As we will show later in this manuscript, the presence of such small particles is evidence of condensation of the vapor phase oxide of Pt.

To gain mechanistic insight into the role of Pd, we also captured images of the same region of the sample before and after short term aging (15 s) as shown in Fig. 5 for both the Pt and Pt-Pd samples. By tracking distances between nanoparticles and their relative positions we concluded there was minimal movement of the particles relative to each other; however, some particles had grown in size and others had shrunk or completely disappeared. The particle in the black rectangle (Fig. 4a) that disappeared over 15s (Fig. 4b) was initially 3.5 nm in diameter. It is important to know whether such rapid disappearance could be caused by emission to the vapor phase, or whether it is due to the transport of mobile species over the surface to neighboring particles (ie Ostwald ripening) and our preliminary analysis (presented in the discussion section) suggests that surface diffusion of the mobile species is responsible for the changes in particle size seen at low temperatures and over the short aging times. While Pt is known to form a volatile oxide, we have already shown in figure 1 that Pd forms a stable oxide (PdO) in air (Fig. 1) and it is known that PdO has negligible vapor pressure (~3 orders of magnitude less than that of Pd metal) [21]. Therefore, the total disappearance of the smallest particles in the bimetallic Pt-Pd sample (Fig. 6d) is very surprising.

The similarity in the observed phenomenon – ie disappearance of some particles and the growth of others, suggests Ostwald ripening is the mechanism responsible for the growth of particle size in both samples. If PtO_2 were the only mobile species, we would expect that Pt-Pd nanoparticles would slowly lose Pt, leaving behind the PdO and causing phase segregation of the catalyst. Such phase segregation was not seen and the compositions of the Pt-Pd particles in the aged catalysts, even after a fourfold increase in particle size, were similar to that of the initial catalyst suggesting that the rates of atom transport of Pt and Pd must be similar. To demonstrate this aspect we present EDS analysis of a region of the Pt-Pd sample after aging in air at 750 C for

2 minutes where the number of particles per unit area had dropped by a factor of three. Analysis of individual particles was not possible with our microscope due to sample drift, so we performed EDS analysis of smaller regions of this sample. The compositions of the Pt-Pd particles of these regions on the model catalysts are included in Figure 5, and the observations are similar to those reported by us previously on a supported catalyst,[12] where EXAFS, XRD, and STEM-EDS confirmed that the composition of the individual particles in the aged catalyst mirrors that of the initial catalyst. The results show clearly that Pt and Pd mobile species are emitted from these nanoparticles and the rates of their transport are similar, leading to similar compositions of the larger particles that are formed.

Longer term (1.5 hours) aging studies in a tube furnace

The results of longer term aging at 750 °C and at 800 °C in air in the tube furnace are shown in Fig. 7 and Fig. 8. At these temperatures we start to see significant emission of Pt to the vapor phase, leading to a decrease in the number of particles. Hence, the evolution of the particle size distribution is caused in part by evaporation and in part due to Ostwald ripening. Therefore the measurements of mass loss need to be considered before the results can be interpreted. We measured the rates of Pt emission using two independent methods based on the metal signal derived from x-ray fluorescence in the microscope. We derived the metal loading through the absolute counts of Pt as well as the ratio of Pt/Si. The results on these experiments are summarized Table 3. The initial sample loading was 5 Å (500 pm) of metal. The metal is present in the form of nanoparticles, as shown in figures 2-5, but we present the loading in terms of the effective thickness of the metal if it were present as a thin film on the surface. As seen

from Table 3, the major effect of added Pd is to lower the rates of Pt emission. The loss of Pt leads to a change in the composition of the sample as already shown in Figure 6.

The particle size distributions are presented as the absolute counts of the number of particles per unit surface area, providing an indication of the loss of metal upon heating in flowing air. The effect of added Pd can be seen clearly in the particle size distribution and the extent of metal evaporation during aging as seen in Figure 7 and 8 and Table 4. After 1.5 hr of aging at 800 °C, this sample has lost over 65% of the Pt to the gas phase (Table 4). The significant loss of Pt is evident also in the decrease in the number of particles per unit area (see Fig. 7b). The particle size distribution for the initial state of the catalyst is indicated in red in Fig. 7c with a mean diameter of 3.1 nm (see figure 3). Detailed statistics on the numbers of particles in these samples are reported in the supplementary information (Tables S2 and S3). After aging in air for 1.5 hours at 800 °C the average particle size has increased to 5.5 nm (Table 4). Surprisingly this increase in particle size is smaller than that seen when the same sample was aged for 2min at 750 °C, where it had already grown to 7.7 nm (Table 4).

We wanted to simulate what might happen in a supported catalyst where the emitted Pt would be captured in other parts of the sample. Therefore we placed an inverted ceramic boat on the TEM sample, helping to cut the loss of Pt to 40% (Table 4) after the 1.5 hour aging. Redirecting the Pt back to the surface caused significant changes in the morphology and size of the resulting Pt particles. We now see a very broad size distribution, with particles as large as 145 nm (figure 9). The average particle size of 14.3 nm does not capture the state of this sample since the size distribution is so broad that we have to use two plots to show it clearly (the green curve in figure 9c and 9d). The comparison of images in figure 7a and 9a shows that when vapor phase transport occurs, we start to see large faceted particles of Pt. There are also numerous

small particles of Pt, smaller than those in the initial catalyst, as shown in figure 9b where the background was changed to blue to make it easier to see these particles. We suspect that these small particles are caused by the nucleation of the mobile Pt oxide present in the vapor phase around the specimen when the sample is rapidly cooled down.

While Pt is lost very rapidly from these samples when aged in air, we find that the addition of Pd leads to a significant decrease in the rates of metal emission (Table 4). The particles size distribution of the Pt-Pd sample is much narrower with a mean size of 12.4 nm but the maximum particle size is only 29 nm, unlike the 145 nm seen on the Pt only sample (see Fig. 7 and 8 and Table 4). Furthermore, the Pt-Pd sample lost only 10% of the metal originally present, even after aging for 1.5 hrs at 800 °C. While the majority of the metal particles in the Pt-Pd samples are spherical and appear to be single phase, we do see a few biphasic Pt-Pd/PdO particles where the oxide has segregated to one side of the particle (Fig. S2 in the SI). However, the metallic Pt-Pd particles are free of any surface oxide as shown by us previously [12].

DFT Computations of Adatom Emission Energetics

First-principle density-functional-theory (DFT) calculations were carried out to explore the energetics of atom emission from monometallic (Pd, Pt), and bimetallic (PtPd) surfaces (An example for the computational geometry is shown in Fig. 10). The high emission energies for reduced metallic particles (Table 5) show that emission in the vapor phase is unlikely. In contrast, the emission of the oxidized species requires much less energy and is generally the thermodynamically preferable emission pathway. Furthermore, emission energies of PtO₂ are lower than any emission energies into the vapor phase for Pd or PdO which suggests that PtO₂ is likely the mobile species responsible for Pt sintering.

Extending the results to bimetallic alloys is not trivial due to the large number of different configurations. For example for a slab containing 64 atoms of composition Pd50Pt50, $\sim 10^{19}$ configurations would need to be sampled, out of reach for first-principle simulations. Therefore we tested five different arrangements with different Pd and Pt distributions and obtained 10 emission energies (5 for Pd and 5 for Pt). An example of the model system is shown in Fig. S13. The results (Table 6) show that the emission energies scatter about the value for the particle emissions for the monometallic surfaces. These results are consistent with a small degree of non-ideality in the PdPt system and suggest that it is mainly a diluting effect rather than a chemical or electronic effect that accounts for the changing properties of bimetallic PdPt catalysts.

In order to understand the energetics of the complete sintering process in this catalyst, it is necessary to consider the detachment of the mobile species onto the support, as well as the activation barriers for surface diffusion. With the present results it is possible to estimate the detachment energies by considering the emission into the vapor phase and subsequent condensation onto the support. For the binding energy to the support we find 2.1 eV and 3.5 eV for Pd and Pt, respectively in excellent agreement with previous work [30, 31]. For the binding energies of PdO and PtO₂ to a γ -Al₂O₃(100) surface we find 2.9 eV and 0.8 eV, respectively. Using the average emission energies from Table 6, we obtain detachment energies of 1.3 eV (4.2 – 2.9) and 0.8 eV (1.6 – 0.8) for the oxidized species of Pd and Pt. The similarity of these values may indicate similar energetics for emission from metallic nanoparticles onto the support and suggests that the mobile species most likely are PdO and PtO₂. These estimates are for alumina supports but we expect similar trends for the silica support we used, suggesting that the detachment of Pt and Pd from bimetallic particles is feasible, which provides an explanation for the similar composition of the bimetallic particles before and after aging.

These computations presented here are also in agreement with the reported bulk thermodynamics of these metal oxides. Using the results of Alcock and Hooper [11], we find that ΔH for formation of PtO_2 vapor as estimated from vapor pressure measurements to be 39.3 kcal/mole which is 1.7 eV. The calculated value of emission energy for PdO is also in reasonable agreement with the $\Delta H_{298\text{K}}$ for formation of PdO of 83.4 kcal/mole which is 3.6 eV [21].

Discussion

Sintering of monometallic Pd/SiO₂ and Pt/SiO₂ in air

The results in Fig. 2 show that Pd rapidly transforms into PdO and then does not sinter during atmospheric pressure aging at temperatures up to 800 °C. The number of particles per unit area dropped only by 10%, consistent with the low rate of sintering of Pd. The limited amount of sintering occurred while the Pd was still metallic, ie at the early stages of oxidation. The results of the DFT calculations are presented in schematic form in Figure 12. The computed barrier for emission of PdO to the support from a metallic surface is 1.3 eV. However, if bulk PdO is formed, it is very stable and does not emit adatoms. This is exactly what is seen in a supported catalyst. When we heated Pd/alumina and Pd/La-alumina in air at 750 °C for 10 hours it was found that the PdO peaks were barely detectable via XRD, indicating very small crystallite sizes[12].

In contrast, the Pt/SiO₂ exhibits rapid growth in particle size on the model catalysts. As seen in Fig. 4 and Table 2, heating at 650 °C for only 2 minutes causes the number of Pt particles per unit area to decrease by 78%, with a corresponding growth in particle size. Heating at 750 °C for 2 minutes causes the number of particles to drop by 95% compared to the initial state of

the catalyst. The results are consistent with those seen previously [12] on supported catalysts where heating in air at 750 °C for 10 hours caused the crystallite size to grow to 18 nm on Pt/Al₂O₃ and 34 nm on Pt/La-Al₂O₃. Emission of Pt as PtO₂ to the vapor phase has a much lower barrier (1.6 eV) compared to that of emission of PdO to the vapor phase (4.2 eV). While these calculations are for bimetallic Pt-Pd, the results for monometallic Pt and Pd will be similar since these metals form a nearly ideal solution [32]. It is clear that the rates of sintering of monometallic Pd and Pt under oxidizing conditions are very different. But under reducing conditions, *metallic* Pd sinters more readily *metallic* Pt, as is consistent with the differences in the barrier for emission of atoms from the metal surfaces (Table 5).

The observed emission of Pt to the vapor phase (Table 3) is not surprising due to its high vapor pressure in the presence of air. The loss of Pt in a flowing stream of air was used Alcock and Hooper [11] to derive the vapor pressure of Pt oxide and to conclude that the stoichiometry of the emitted species was PtO₂. Using a similar approach, Darby and Miles [32] showed that the vapor pressure of Pt was lowered by the addition of Pd and the Pt-Pd system exhibited only a small degree of deviation from ideal solution behavior. In these measurements, it was found that the equilibrium between the metal and vapor phase was established rapidly and the rate of Pt loss was directly proportional to the flow rate of the carrier gas. The observations on model catalysts reported in the literature are consistent with this picture for atom emission. In the in-situ TEM study of Simonsen et al. [8] there was negligible loss of Pt from a model catalyst, since the flow rates in an ETEM are very low, to prevent sample drift and mobility. But when a similar sample was analyzed in an ambient pressure XPS chamber, Porsgaard et al. [33] found rapid loss of Pt due to the higher flow of gases over the sample. The rate of Pt loss is clearly related to the nature of the gas flow over the sample surface. It is not surprising then that in a supported

catalyst we see negligible net loss of metal to the vapor phase since the metal is located in a porous structure and no sweep gas is present. The experiments performed here demonstrate that a volatile oxide of Pt is present in the vapor phase in equilibrium with the nanoparticles in a supported catalyst, but the vapor may not leave the sample unless it is swept away. The Sabre tube reactor provides a flow of gas over the catalyst surface and therefore allows us to study the role of vapor phase processes. In the next section, we divide our results into two regimes on the basis of whether or not we see significant loss of metal to the vapor phase. We estimate our measurement error for metal emission to be $< 5\%$ based on replicate measurements for the evaporation of Pt.

Sintering of Pt and Pt-Pd under conditions of negligible emission to the vapor phase

Figure 5 shows that dramatic changes in particle size occur when Pt and Pt-Pd samples are heated for only 15s at 650 °C in air. However, under these conditions, at short heating times (≤ 2 minutes) and low temperatures (≤ 750 °C) we found the net rate of emission to the vapor phase to be below our detection limits. We made use of the net emission rates in the longer term experiments to derive an estimate of the relative contribution of vapor phase processes to the changes in particle size shown in Fig. 5. Based on the dependence of vapor pressure of PtO₂ [11] on temperature we concluded (see calculations in Tables S5-S8) that the total emission in 15s at 650 °C would lead to a change in particle size of only 0.05 pm and about 2.9 pm at 750 °C in 2 minutes. Both of these changes are below the detection limits of TEM. The fact that individual particles as large as 3 nm in size disappear in 15s at 650 °C implies that an alternate path, surface diffusion, must be responsible for the inter particle transport.

The results of DFT calculations (Fig. 12) show that the detachment energy for the emission of PtO_2 to the support is less uphill (0.9 eV) than emission to the vapor phase (1.7 eV). Therefore, we would expect that adatom emission to the support followed by diffusion of these atoms as the dominant path for sintering of these catalysts at 650°C. Similar results are seen for the Pt-Pd catalysts. The detachment energy for Pt is only slightly altered in the bimetallic (Table 6), consistent with the nearly ideal solution behavior for the Pt-Pd system.[32] While we would not expect PdO to be emitted to the vapor phase due to the higher detachment energy for emission (4.2 eV), DFT calculations (Fig. 12) show that the emission of PdO from Pd metal to the support is feasible (1.3 eV). Furthermore, once Pt is emitted from a bimetallic particle, we leave behind a severely under-coordinated Pd, making it even easier to be emitted. The similar rates of emission of Pt and Pd are reflected in the similar growth in particle size for Pt and Pt-Pd during low temperature aging in the model catalysts (Figure 5, 650°C) and also in supported catalysts [3]. Hence Pd does not stop the process of particle growth that occurs through atom emission and migration over the support.

The behavior of the Pt-Pd sample (Fig. 4 and 5) can be contrasted with that of monometallic Pd in Fig. 2 and 3. While the Pd particle size hardly changes even after heating to 800 °C in air (Fig. 3), the Pt-Pd samples show rapid growth in particle size (Fig. 4). The difference is caused by the oxidation of monometallic Pd to PdO which has negligible vapor pressure. But the bimetallic Pt-Pd stays metallic as also seen previously via XAS on an aged supported Pt-Pd/alumina [12]. We therefore come to the conclusion that the presence of Pt enhances the rate of Pd sintering by keeping the Pd in a metallic state. However as we show next, the role of Pd is very different when vapor phase transport starts to become significant, at elevated temperatures.

Sintering of Pt and Pt-Pd when significant emission occurs to the vapor phase

When the Pt/SiO₂ model catalyst is heated for 1.5 hours in a tube furnace at 750 °C and 800 °C (Fig. 7) we see rapid loss of Pt metal caused by evaporation. This is evident from a decrease in the number of Pt particles per unit area (Table 4), and also the loss of Pt as detected by EDS (Table 3). The mean particle diameter is also reported in Table 4 but it does not provide an indication of the extent of sintering of Pt since so much of it is lost to the vapor phase. And we see a surprising trend, that the maximum detected particle size is larger after the 750 °C treatment than after 800 °C. One might conclude that sintering is more rapid at 750 °C than 800 °C, but these results are distorted by the loss of Pt, which causes the large particles to disappear.

The role of the vapor phase processes becomes more apparent when we compare the results of heating at 800 °C for a covered sample (Fig. 9). Here we allowed some of the vapor phase to linger over the sample surface, causing the growth of larger particles and a distinctly bimodal distribution. Since the sample was not hermetically sealed, we did see loss of Pt, but much less than seen in an open sample. The net result of covering the sample was to allow some of the emitted Pt to deposit back to the sample surface. This covered sample of Pt/SiO₂ retained 60% of the initial Pt even after aging in air at 800C for 1.5 hours, (Table 3). STEM HAADF images of the covered Pt sample are shown in figure 9. The Pt that was redirected back to the support caused the formation of large faceted particles and numerous smaller particles, leading to a broad particle size distribution. Some of the large faceted particles show lower contrast, which we conclude to be due to their shapes being very different, since they were clearly formed due to vapor phase growth. We investigated the possible formation of Pt silicides, but the electron diffraction (Figure S4) showed only fcc Pt. Previous work shows that Pt silicides tend to form

when the samples are heated in H_2 [9]. We conclude that the presence of Pt particles smaller than those in the initial catalyst is likely due to condensation of the vapor phase of Pt present in equilibrium with the metal particles. The results obtained so far show that vapor phase processes become important at elevated temperatures and the large faceted particles likely arise from such a vapor phase mediated growth of Pt.

The presence of Pd causes a definite decrease in the rate of Pt emission as shown in Table 3. Since PdO is not volatile, a shell of PdO surrounding the bimetallic nanoparticles could impede Pt volatilization and could shut down the emission of Pt to the vapor phase. No shell of PdO was seen in any of our images (Fig. 4, 5 and 8) or on a supported catalyst reported previously (reproduced in Figure S3); therefore, there must be an alternative explanation for the reduced emission of Pt to the vapor phase. Since Pt and Pd are miscible and exhibit only a small degree of non-ideality, we would expect a decrease in vapor pressure due to the lower atomic concentration of Pt in the bimetallic particles [32]. At 800 °C, the emission of adatoms dropped 84% when the sample contained 68 atom % Pd (loss of 323 pm for Pt and 51 pm for the bimetallic, Table 4). The change in emission does not appear to be linearly related to concentration but there are major differences in the particle sizes of these samples, which would also need to be considered. Nonetheless, the results demonstrate the important role of Pd (which does not form a volatile oxide) in slowing the emission of Pt to the vapor phase. The major effect of Pd is seen on the catalysts heated at 800 °C for 1.5 hours. The particle size distributions do not show the bimodal distributions seen on the Pt only catalyst, there are no large faceted particles and we lose less Pt to the vapor phase. Since the compositions of individual particles are similar to the initial catalyst, accounting for the small loss of Pt, we infer that the sintering occurs via surface diffusion as seen clearly in the results of 15s heating at 650 °C in Fig. 5.

Therefore, we find that Pd has only a minimal effect on the overall particle size distributions for catalysts heated under conditions where vapor phase transport is not significant, and this was noted also on supported catalysts in our previous work[12].

Conclusions

The model catalyst approach described here presents a platform for unraveling atomic scale details during the evolution of metal nanoparticles relevant to heterogeneous catalysis. Rapid heating under conditions similar to those used in industrial practice and at atmospheric pressure, and observation of the same region of the sample before and after treatment allowed us to derive insights into the emission of atoms and the nature of mobile species. The simple geometry of the model catalyst (a single square transparent window) allows us to image the identical region of the sample before and after aging.

We show that the oxides of Pt and Pd play an important role in the sintering seen under oxidizing conditions in automotive exhaust catalysts. Pd hardly sinters under these conditions because the formation of PdO shuts down the emission of adatoms. Pt helps keep Pd in metallic form allowing the emission of both Pt and Pd oxides to continue from the bimetallic nanoparticles. At elevated temperatures, the mechanism switches to vapor phase transport. The high vapor pressure of Pt in the presence of O₂ can lead to significant transport of Pt which results in the formation of abnormally large particles seen previously in industrial catalysts. Pd helps slow the emission of Pt to the vapor phase, preventing the abnormal growth patterns seen on Pt-only catalysts. Furthermore, since Pt keeps Pd in metallic form at the surface, it leads to improved catalytic reactivity of the bimetallic for hydrocarbon oxidation [34].

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Table 1**Characteristics of the Pd/SiO₂ model catalyst shown in Figure 2**

Pd/SiO₂	Initial	Aged 650°C, 2min	Aged 800°C, 1.5hr
Mean Diameter (nm)	3.7(Pd)	4.2	4.8 (PdO)
Particles/mm²	8700	7800	7900
Projected Area (%)	10	12	15

Table 2**Characteristics of the Pt/SiO₂ and Pt-Pd/SiO₂ model catalysts shown in Figure 3**

	Initial		Aged 650°C, 2min		Aged 750°C, 2min	
	Pt	Pt-Pd	Pt	Pt-Pd	Pt	Pt-Pd
Mean Diameter (nm)	3.4	3.7	5.1	4.8	7.7	5.2
Particles/mm²	20,000	13,600	4,300	7,000	920	4,530
Projected Area (%)	20	16	10	13	6	11

Table 3**Effective thickness of the metal (in picometers) after aging in air in a tube furnace**

	Pt (open boat)	Pt-Pd (open boat)	Pt (covered boat)
Initial	500	500	500
Aged 750 °C for 1.5 h	315	429	-
Aged 800 °C for 1.5 hr	177	448	298

Table 4**Characteristics of the Pt/SiO₂ and Pt-Pd/SiO₂ subjected to longer term aging**

	Aged 750 °C, 1.5 hr		Aged 800 °C, 1.5 hr		Aged 800 °C, 1.5 hr
	Open boat		Open boat		Covered boat
	Pt	Pt-Pd	Pt	Pt-Pd	Pt
Mean Diameter (nm)	19.4	4.5	5.5	12.4	14.3
Maximum Diameter (nm)	97	8.2	31	29	145
Particles/mm ²	121	7000	1270	290	830

Table 5.**Emission energies from DFT from monometallic (111),(100), and (110) surfaces.**

	Emitted Gas phase Particle			
Surface	PdO(g)	PtO ₂ (g)	Pd(g)	Pt(g)
(111)	4.1	1.7	4.6	6.6
(100)	3.7	0.9	4.3	5.9
(110)	3.4	0.5	3.9	5.5
<p>The emission energies (eV) were computed as (TM=Pd, Pt; n=64 for (111) surface and n=72 for (100) and (110) surfaces): $TM_n + xO_2 \rightleftharpoons TM_{n-1} + TMO_{2x}$ for the emission of the oxidized species (x=1/2 and 1 for PdO(g) and PtO₂(g) emission, respectively). The emission of the reduced metallic species is computed as $TM_n \rightleftharpoons TM_{n-1} + TM(g)$.</p>				

Table 6.**Emission energies (eV) for PdO and PtO₂ from bimetallic PdPt(111) model surfaces.**

Configuration	Number of Pd atoms	Number of Pt atoms	PdO(g)	PtO ₂ (g)
1	1	63	4.3	1.6
2	3	61	3.9	1.9
3	3	61	4.3	1.5
4	4	60	4.4	1.7
5	4	60	4.1	1.5
Average			4.2	1.6

Figure 1. Schematic diagram showing the nature of air flow over the TEM specimen for the three heating arrangements (with nanoparticles shown in red).

Figure 2. HAADF STEM images of Pd/SiO₂ in its (a) initial state (b) aged 650°C for 2 min and (c) aged 800°C, 1.5 hr.

Figure 3. HRTEM images of Pd/SiO₂ (a,b) aged 650°C, 2 min and HAADF-STEM image of Pd/SiO₂ (c) aged 650°C, 2 min. These images show that Pd is not fully oxidized since some particles retain their spherical shapes, while a surface oxide is evident in (b); HRTEM image of Pd/SiO₂ (d) aged 800°C, 1.5 hr shows that Pd is now fully oxidized. The lattice spacing of the particles is consistent with that of PdO.

Figure 4. HAADF images of Pt/SiO₂ after short term aging in the Sabre tube reactor (a) initial and (b) after aging in air at 650°C, 2 min and (c) 750°C, 2 min; Pt-Pd/SiO₂ (d) initial and after aging in air (e) 650°C, 2 min and (f) 750°C, 2 min. The particle size distributions are shown in (g) for Pt and (h) for Pt-Pd.

Figure 5. Bright field TEM images of the same area of the sample in the Sabre tube reactor before and after aging in 21% O₂/Ar at 650°C for Pt (a) initial (b) aged for 15s and Pt-Pd (d) initial and (e) aged for 15s. There is very little particle mobility so that the sintering can be seen to be mainly caused by Ostwald ripening. The disappearance of particles is seen for both the Pt as well as the Pt-Pd sample indicating the emission of mobile Pt and Pd species from these particles.

Figure 6. HRTEM images of Pt-Pd/SiO₂ sample aged 750 °C for 1.5 hr in a tube furnace. The initial sample had 38% Pt and 62% Pd. EDS analysis of a large region and several smaller regions shows the range of compositions, but clearly showing a loss of Pt due to emission to the vapor phase.

Figure 7. HAADF images of Pt/SiO₂ after long term air aging in a tube furnace at (a) 750°C, 1.5 hr (b) 800°C, 1.5 hr. All samples started with 500 pm of metal with particle size distributions as shown in figure 4. The particle size distributions become very broad hence are shown in two parts (a) up to 20 nm and (d) up to 100 nm. The PSDs have been scaled (x10 or x300) since the numbers of particles have decreased significantly after aging.

Figure 8. HAADF images showing the results of longer term aging of Pt-Pd (initial composition was 38% Pt 62% Pd) under conditions where significant emission of the metal is observed for the Pt sample (see figure 7). Pt-Pd/SiO₂ aged in air (a) 750 °C, 1.5 hr (composition 32% Pt) and (b) 800 °C, 1.5 hr (composition 28% Pt). The PSD has broadened with a significant decrease in the number of particles after aging at 800 °C.

Figure 9. HAADF images of the samples after aging the Pt/SiO₂ in air in a tube furnace with the sample boat covered to reduce the rate of Pt emission to the vapor phase. The sample started with 500 pm of metal with particle size distribution as shown in Figure 4. The low magnification image (a) shows large faceted particles, some with a lower contrast indicating a flattened profile and (b) higher magnification view showing the presence of very small Pt particles, much smaller than those seen in the initial sample (with a blue background to make it easier to see the small Pt

particles). The particle size distribution is very broad and is shown in two parts (a) <20 nm and (b) up to 200 nm.

Figure 10. Example model system for the computations of emission energies from extended surfaces. Left: defect free Pt(111) surface; Right: One Pt atom has been removed. The location of the removed atom is indicated by the circle.

Fig. 11. Example model system to explore emission energetics from an extended (111) surface. The surface is derived from the corresponding Pt(111) surface by Pt => Pd doping. (Light color: Pt; dark color: Pd): Left: before emission; middle: after Pd emission; right: after Pt emission. The location of the removed/emitted atom is indicated by the black circle.

Figure 12. A schematic diagram summarizing the results of DFT calculations and the results of aging in air at 800 C in the panel on the right. It is seen that Pt emission can occur to the vapor phase as well as to the support. A similar process occurs with Pt-Pd particles, with small changes in the barrier due to alloying of the Pt-Pd. The emission of Pd in the form of PdO is also possible from the metallic Pt-Pd particles, but once bulk PdO forms it is stable and does not undergo Ostwald ripening. These computational results are confirmed by the observations summarized in the panel on the right after aging at 800 °C in air.

Sabre Tube Reactor

Air flow

Tube furnace with open boat

Tube furnace with covered boat

figure 2

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figure 3

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figure 4
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