Size-controlled nanocrystals reveal spatial dependence and severity of nanoparticle coalescence and Ostwald ripening in sintering phenomena†

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A major aim in the synthesis of nanomaterials is the development of stable materials for high-temperature applications. Although the thermal coarsening of small and active nanocrystals into less active aggregates is universal in material deactivation, the atomic mechanisms governing nanocrystal growth remain elusive. By utilizing colloidally synthesized Pd/SiO2 powder nanocomposites with controlled nanocrystal sizes and spatial arrangements, we unravel the competing contributions of particle coalescence and atomic ripening processes in nanocrystal growth. Through the study of size-controlled nanocrystals, we can uniquely identify the presence of either nanocrystal dimers or smaller nanoclusters, which indicate the relative contributions of these two processes. By controlling and tracking the nanocrystal density, we demonstrate the spatial dependence of nanocrystal coalescence and the spatial independence of Ostwald (atomic) ripening. Overall, we prove that the most significant loss of the nanocrystal surface area is due to high-temperature atomic ripening. This observation is in quantitative agreement with changes in the nanocrystal density produced by simulations of atomic exchange. Using well-defined colloidal materials, we extend our analysis to explain the unusual high-temperature stability of Au/SiO2 materials up to 800 °C.

Introduction

Structural stability is critically important in the development of industrially relevant materials, yet it is underemphasized in academic research.1 In many applications involving polycrystalline solid or powder composites, high-temperature nanocrystal coarsening leads to deteriorated properties; in catalysis, for example, it decreases the activity, changes the selectivity, and leads to overall loss of productivity due to the downtime associated with catalyst reactivation or replacement.2,3 When reactivation is not possible, catalyst deactivation results in the utilization of a large quantity of the catalytic material to ensure effective catalysis throughout the material’s application.4

In powder catalysts especially, one of the most common and severe causes of deactivation is the loss of reactive surface area caused by particle growth. This process is known as sintering. Two mechanisms have been proposed: Ostwald (atomic) ripening, or the exchange of atoms between stationary nanocrystals (NCs), and particle migration and coalescence, or the collision and fusion of entire nanocrystals.3,5 In the literature, there is a lack of experimental methods to distinguish between these mechanisms. In situ microscopy offers a promising approach, but has low throughput, requires controlled conditions, and demands extreme care to avoid spurious effects of the high-energy electron beam.6 Additionally, the study of evolving particle size distributions in polydisperse catalysts has been identified as fruitless.7 Approaches involving kinetic modeling may provide insight, but incorrect assumptions can create significant errors.8 Overall, it has been challenging to identify and therefore suppress the coarsening mechanisms in composite nanomaterials.

To combat any potential coarsening mechanism, researchers have been continuously developing novel nanostructures in attempts to enhance material stability. Common nanostructured motifs include encapsulation, nanocrystal embedding in nanochannels, and nanocrystal entrenchment into
nanobowls or other high-surface-area supports.9–18 Nanostructured geometries aim to physically separate particles to minimize interparticle interactions and maximize particle stability. However, such schemes often result in decreased overall activity due to mass-transfer limitations or reduced reactive surface area. A description of the specific sintering processes would allow for the intelligent design of nanostructures that target a specific deactivation mechanism.

In this work, by combining colloidally synthesized powder nanomaterials and quantitative simulation studies, we provide new fundamental insights into material stability. By precisely controlling the nanocrystal size (3.0, 9.1, and 15.8 nm) and nanocrystal density (from 2 NC μm−2 to 367 NC μm−2), we uncover the unique size and density dependences of particle growth processes. At lower temperatures, a density-dependent nanoparticle coalescence occurs, which is evidenced by the direct observation of a bimodal particle size distribution. However, at higher temperatures, the nanocrystal growth is dominated by density-independent Ostwald ripening, which is directly observed via the emergence of small nanoclusters. The latter process represents the most severe loss of the nanocrystal surface area, and it was found to be in quantitative agreement with the simulations of a metallic vapor-phase sintering process. By observing nanocrystal growth to be independent of the nanocrystal spatial distribution, we identify atomic emission as the critical process controlling nanocrystal growth and, therefore, sintering processes. Finally, we demonstrate that simulations of vapor-phase atomic exchange also predict the behavior of Au/SiO2 composites, which maintain unusually remarkable stability up to 800 °C.

Results and discussion

Synthesis and characterization of well-defined nanocrystal ensembles

To disentangle the effects of the nanocrystal size and spatial distribution on material stability, we used a colloidal assembly approach where pre-formed Pd or Au nanocrystals were deposited onto pre-formed SiO2 spheres. The key advantages of this building-block approach are as follows: (1) a highly uniform active phase, which allows probing of size-dependent sintering properties; (2) well-defined initial particle sizes, which allow particle size measurements to indicate the sintering mechanism (vide infra); and (3) independent control of the size and spatial distribution of NCs, to study the effect of spatial parameters on material stability. Here, we synthesized size-controlled 3.0 ± 0.3 nm, 9.1 ± 0.5 nm, and 15.8 ± 1.3 nm Pd nanocrystals as active phases (Fig. 1a–c), and monodisperse 232 nm Stober SiO2 spheres as the supporting oxide phase. Controlled assembly of Pd nanocrystals onto colloidal SiO2 was performed by impregnation in solution, such that Pd was well dispersed on the surface of each SiO2 sphere (Fig. 1d–f and ESI Fig. S1–S3†). Although transmission electron microscopy (TEM) measurements may show an overlap between Pd NCs, this effect is due to the 2D projection nature of microscopy images for particles lying on opposite sides of the SiO2 spheres. High-angular annular dark field scanning electron microscopy (HAADF-STEM) tomography demonstrates the random distribution of Pd NCs on the overall SiO2 surface (ESI Fig. S4†). The measurements of the Pd nanocrystal size, as-synthesized and after assembly onto the SiO2 surface confirm the uniformity of the Pd phase, although a slight decrease in size is observed due to different wetting properties of Pd on carbon with respect to silica (Fig. 1g–i). Pd loading and additional characterization for each nanocomposite are presented in ESI Table S1.†

Additionally, for some materials, various NC loadings were synthesized to investigate the effects of nanoparticle proximity. These materials are labeled N–Pd/SiO2, where N represents the average number of Pd NCs per SiO2 sphere. Representative TEM images of the four materials are shown in ESI Fig. S5,† where we observe different NC spatial distributions but the NC size was maintained. The NC loadings are quantified by tallying the number of Pd NCs per SiO2 sphere over many Pd/SiO2 structures within a sample, and these statistics are shown in ESI Fig. S5.† Consequently, the four materials are labelled as 0.3-Pd/SiO2, 4.0-Pd/SiO2, 17-Pd/SiO2, and 62-Pd/SiO2, after the average number of Pd NCs per SiO2 sphere. By computationally simulating this random NC deposition process and modeling a large number of spheres with a given number of Pd NCs on their surface, we can calculate the distribution of the nearest neighbor distances for each sample, a parameter crucial to processes where interparticle diffusion governs the material stability (ESI Fig. S6†).16 As the average nearest neighbor distance between NCs varies from 26 nm to 173 nm along the sample series, we expect these materials to possess different stability properties if surface diffusion processes dominate. Additionally, these Pd/SiO2 nanocomposites represent localized support surfaces where particles may sinter, as there are significant barriers to atomic transfer between spheres.19

Thermal stability studies

The prepared materials were used to study the size-dependent Pd stability after calcination in air. The SiO2 support spheres were stable in air up to at least 925 °C and therefore remained stable under the conditions investigated in this work. For each nanocomposite, we measured the mean nanocrystal diameter after aging at increasing temperature (Fig. 2). Between room temperature and 800 °C, we observed a slight increase in the nanocrystal size for all three materials, which we identified as density-dependent oxidative particle coalescence (vide infra).

However, between 888 °C and 900 °C, the mean diameter of the 3.0 nm and 8.8 nm samples increased dramatically to ~30 nm. The fact that these samples show particle growth at approximately the same temperature (within 15 °C) is surprising given that smaller particles are usually considered to have a much higher driving force to sinter due to their higher surface energy.20 Once the 3.0 nm Pd sample began to sinter, the number of NCs per SiO2 sphere dramatically decreased, and very few yet large Pd aggregates were observable. Although the 14.7 nm sample also produced numerous larger aggregates
between 888 °C and 900 °C, the mean particle diameter slightly decreased, giving fundamental insight into the mechanism of particle growth (vide infra). Overall, all NC sizes produced very large sintered aggregates at 888 °C, and this temperature represents a critical turning point in the stability of Pd/SiO<sub>2</sub> materials.

To understand the increase in the NC size between 25 °C and 800 °C, we studied nanocrystal projected areas before and after aging at 800 °C for the 8.8 nm 62-Pd/SiO<sub>2</sub> nanocomposite (Fig. 3). Interestingly, we observed that the originally monodisperse distribution centered around 64 nm<sup>2</sup> (≈9.0 nm diameter) of the NC areas transitioned to a bimodal distribution with peaks at 80 nm<sup>2</sup> (≈10.1 nm diameter) and 161 nm<sup>2</sup> (≈14.3 nm diameter). The fact that the second peak in the bimodal area distribution is centered at two times the larger peak suggests the formation of dimers due to entire particle coalescence, which would result in peak distributions located at integer values of the original NC size. This phenomenon is only observable with highly uniform nanocrystals, as polydisperse catalysts would reveal smooth monomodal particle size distributions regardless of the growth mechanism. Furthermore, various NC densities were studied in a similar manner, and particle coalescence was found to be most severe in the catalyst with the highest NC density (62 NCs/SiO<sub>2</sub>), where ~35% (ESI Fig. S7†) of the original NCs coalesced to form dimers (and even some trimers). Given the well-defined particle densities and support surface areas, Monte Carlo simulations suggested that these fusion percentages were achievable if each particle translated on the support at most 8 nm from its original starting location (ESI Fig. S7†). The fact that we did not observe extensive particle coalescence in the 3.0 nm Pd/SiO<sub>2</sub> materials suggests the occurrence of simultaneous nanocrystal oxidation and coalescence, rather than multiple steps of NC diffusion, as the main particle coalescence mechanism. These materials are broadly stable above their Tamman temperatures, which suggests that this measure of bulk mobility is not a sufficient predictor to anticipate when significant nanocrystal growth may occur on a support.2

Fig. 1 Size-controlled nanocomposites. Transmission electron microscopy (TEM) images of three sizes of (a–c) the as-synthesized colloidal Pd nanocrystals and (d–f) the corresponding SiO<sub>2</sub>-supported Pd nanocrystals. Particle size distributions (g–i) of the as-synthesized nanocrystals (open bars) and SiO<sub>2</sub>-supported nanocrystals (closed bars). Mean values and standard deviations shown for the as-synthesized nanocrystals (μ<sub>NCs</sub>) and SiO<sub>2</sub>-supported nanocrystals (μ<sub>Cat</sub>).
Next, bulk characterization techniques were used on the 8.8 nm Pd/SiO$_2$ sample to understand the onset of rapid sintering at 888 °C. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) measurements were performed on the Pd/SiO$_2$ samples to understand whether the SiO$_2$ chemistry governed the stability of the Pd/SiO$_2$ nanocomposites (ESI Fig. S8†). However, no obvious changes were observed in the surface chemistry of SiO$_2$ upon reaching 875 °C, suggesting that changes in the surface chemistry of the support do not determine the observed stability behavior.

We therefore studied changes in the Pd oxidation state in order to understand its contribution to the observed sintering behavior. According to procedures developed to preserve the oxidation state in Pd materials, the 8.8 nm Pd/SiO$_2$ sample was heated to either 875 °C or 900 °C for 5 h in static air, and rapidly cooled down for analysis to freeze the state of the Pd particles.$^{21}$ High resolution TEM (HRTEM) analysis was performed to understand the oxidation state of the material during the sintering process (ESI Fig. 9†). While at 875 °C we observed mostly PdO, after aging at 900 °C we observed the emergence of metallic Pd in the sintered aggregates with the diameter greater than 25 nm. An additional proof of the relationship between the oxidation state and stability was obtained via X-ray diffraction analysis (ESI Fig. 9†). Like TEM analysis, while we only observed PdO after aging at 875 °C, we found the emergence of metallic Pd after aging at 900 °C. The fact that metallic Pd was observed only when sintering had occurred indicates that metallic Pd is necessary for high-temperature nanocrystal sintering. Further proof was obtained by performing in situ temperature programmed reduction experiments, where particle growth was observed only after PdO was reduced to Pd (ESI Fig. 10†).

Although we implicate the metallic Pd state in the sintering mechanism above 888 °C, at this stage, it remains unclear whether Ostwald ripening or further particle coalescence leads to this severe nanocrystal sintering. To answer this question, a detailed particle size analysis was performed after different aging treatments for the 14.7 nm Pd/SiO$_2$ sample. After aging at 800 °C or 900 °C for 5 hours in static air, 200 particles were measured along the maximum chord as observed via TEM (Fig. 4 and ESI Fig. S11†), but the analysis of the projected nanocrystal area yielded the same conclusions (ESI Fig. S12†). Overall, a shift of the center of the distribution from ~19 nm to ~16 nm was observed, and a compensatory evolution of much larger 40–80 nm aggregates appeared. Most importantly, after aging at 900 °C we observed the emergence of NCs with an average size of less than 10 nm, smaller than the smallest

![Fig. 2 Size-dependent stability of Pd/SiO$_2$ materials. Mean NC diameter versus aging temperature for 3.0 nm, 8.8 nm, and 14.7 nm Pd/SiO$_2$ nanocomposites.](image)

![Fig. 3 Particle size distribution analysis reveals particle coalescence. (a) Distribution of particle projected areas for 62-Pd/SiO$_2$ as-synthesized and after aging at 800 °C for 5 h in static air (N > 200). (b) Representative TEM image of 62-Pd/SiO$_2$ after aging at 800 °C for 5 h in static air. Red arrows indicate the formation of NC dimers.](image)
particles present in the 800 °C aged sample, and smaller than the original Pd NCs. The emergence of small NCs is conclusive evidence of Ostwald ripening, where the particle size decrease is due to atomic emission and recapture by larger particles, and is uniquely demonstrated by using size-controlled nanocrystal composites. On the other hand, particle coalescence processes could only generate nanocrystals larger than the original nanocrystal building blocks, and would lead to a bimodal size distribution as we saw earlier. However, we cannot exclude that after an initial OR phase, some level of PMC may occur with the formed smaller nanocrystals, while OR continues to proceed. Furthermore, the emergence of smaller nanocrystals, without the complete disappearance of nanocrystals, explains the decrease in the NC diameter observed in Fig. 2 for the sample containing large nanocrystals between 800 °C and 900 °C. The schematic inset in Fig. 4a illustrates how atomic exchange between nanocrystals leads to smaller nanocrystals.

An additional quantitative particle density analysis was performed for different densities of 8.8 nm Pd/SiO2 nanocomposites at temperatures up to 900 °C, where the change in the NC density is represented as the post-treatment nanocrystal density divided by the original nanocrystal density \( \frac{N_{\text{Aged}}}{N_0} \) (Fig. 6a). The choice of aging conditions was motivated by the fact that palladium emissions control catalysts and their stability are typically studied under oxidizing conditions at temperatures up to 900 °C. The nanocrystal density decreased slightly between 25 °C and 800 °C due to nanocrystal coalescence \( \text{vide supra} \). Nevertheless, as observed in Fig. 2, the materials maintained a high nanocrystal density until ~875 °C, at which point the nanocrystal density rapidly decreased. Similar stability results were achieved for Pd/SiO2 nanocomposites synthesized with commercial Davisol SiO2, suggesting that this remarkable stability is not a unique function of impurities in the SiO2 prepared with our method, but is instead a more general phenomenon of SiO2-supported catalysts (ESI Fig. S13 and S14†). Surprisingly, aside from the early oxidative coalescence of nearby crystallites between room temperature and 800 °C, there was no obvious trend observed relating how the initial NC density, controllably varied in these four materials, affected the aged NC density. Instead the samples followed the same trend independent of the initial NC density, and all the nanocomposites fell onto the same curve. The density independence of NC growth means that the distance between NCs is not the most important factor for NC stability, suggesting that the atomic diffusion of Pd is rapid and Pd atomic emission is the rate-determining step in the Pd sintering process. A similar emission-limited process was recently observed in the case of atomic redispersion for Pd/Al2O3 and has been theorized in other works.6,24 The fact that the 0.3-Pd/SiO2 sample containing a very low density of particles sintered to such a great extent, leaving behind many empty SiO2 spheres to form large Pd aggregates, demonstrates the large distances Pd rapidly traveled (ESI Fig. S15†). It was extremely challenging to find Pd aggregates in the 0.3-Pd/SiO2 sample, with an average ratio of 1 Pd aggregate per 300 SiO2 spheres, suggesting that Pd traversed up to 1 micron in the prolonged sintering process.

Given the remarkable high-temperature stability of Pd/SiO2 nanocomposites, and the atomic nature of the sintering process across SiO2 spheres, a vapor-phase sintering process was hypothesized. Although only few quantitative analyses of vapor-phase sintering exist in the experimental literature, significant efforts to analyze these processes have been pursued \textit{via} simulations and modeling.25 By implementing recently developed simulations for vapor-phase sintering processes, we modeled changes in the nanocrystal density due to the vapor-phase sintering process of metallic Pd as a function of temperature, in the absence of any contributions from surface atomic processes or particle migration and coalescence pro-
cesses. Vapor-phase ripening simulations were performed using a mean-field model for Ostwald ripening, which assumes a constant background pressure of the migrating species. These vapor-phase simulations are represented as a dashed line in Fig. 5. It is important to note that the developed vapor-phase simulation is independent of the nanocrystal spatial distribution due to the assumption that Pd diffusion in the gas phase is more rapid than emission into the gas phase; this assumption is consistent with our experimental observations showing that the change in the nanocrystal density is independent of the initial state. Theoretical works often study atomic processes in a similar emission-limited regime, even for the surface OR process. Furthermore, we assume that there are no strong adsorbates on the mobile metallic Pd atoms for this analysis, as stable PdO moieties have not been posited and experimentally verified.

The sensitivity of this vapor-phase simulation to slight variations in the nanocrystal surface energy is plotted in ESI Fig. S16. In these simulations, the Gibbs-Thompson equation is used to model the size-dependent nanocrystal energies, and adhesion energies, while important in general, are neglected due to the known weak interactions of SiO₂ supports. Overall, the experimentally measured changes in the nanocrystal density matched well with the nanocrystal density loss simulated via a vapor-phase sintering mechanism. Vapor pressure calculations of metallic Pd at 900 °C revealed that each NC emitted 4 times its total volume of atoms within a 5 hour aging experiment, with each NC emitting 5 atoms each second. The emitted gas-phase Pd atoms would have a root mean square velocity of 524 m s⁻¹ at 900 °C, suggesting that it would take a Pd atom 442 picoseconds (ps) to travel 232 nm between SiO₂ spheres. Compared to an atomic emission rate of 5 atoms per s, it is clear that atomic emission, rather than vapor-phase or surface diffusion, is the rate-determining sintering step. However, as we did not experimentally analyse gaseous Pd atoms, we therefore cannot confirm whether the process is purely vapor-phase or with some contribution from the surface process. However, this analysis shows that any surface atomic processes occurring are either (1) occurring at low rates or (2) governed by emission kinetics very similar to that of emitting a Pd atom directly into the gas phase. Either way, the results demonstrate a sintering process governed at high temperatures by emission-limited atomic ripening processes.

Surprisingly, the vapor-phase sintering model predicts nanocrystal growth at 700–800 °C for the 3.0 nm Pd sample (ESI Fig. S16†), yet experimentally we observe stability until 875 °C (Fig. 2). Although these smallest nanocrystals seem to achieve stability past the vapor-phase limit, this unexpected result can be explained by understanding the role of the oxidation state in the sintering process. At temperatures between 700 °C and 875 °C, particles are still oxidized as PdO and therefore do not exhibit a sintering behavior governed by the vapor phase processes of metallic Pd. However, when these particles reduce to metallic Pd at 888 °C, we observe rapid loss of almost all the particle density, at which point the sintering is dominated by atomic processes. At this point, it becomes extremely challenging to observe Pd aggregates, and only 1–3 Pd aggregates were found after aging at 900 °C, although the aggregates were at least 20 nm in size. Given the satisfactory agreement between the experimental and simulation results, the data suggest that atomic surface processes are unlikely to occur to an extent as to dominate the nanocrystal growth process.

Au/SiO₂ nanocomposites

To probe the generality of the vapor-phase sintering mechanism, we also studied particle growth in Au/SiO₂ materials. Au
catalysts have been heavily investigated for several applications, although material stability is a well-established issue. Previous works, despite identifying the higher stability of Au/SiO$_2$ catalysts compared to other supports, did report a noticeable growth of 2.5 nm Au particles to 6.5 nm when treated in air at 700 °C. Numerous nanostructured support motifs have been developed to increase the stability of Au catalysts. Here, similar temperature-dependent stability studies were performed on colloidally synthesized Au/SiO$_2$ nanostructures, where the nanocrystal density was tracked against the aging temperature. The average number of Au NCs per SiO$_2$ sphere was 2.2 in the as-synthesized material. Surprisingly, the Au NC density remained constant up to 800 °C, at which point the nanocrystal density dropped by a factor of five as the temperature approached 900 °C. These data indicate that Au/SiO$_2$ materials are stable until at least 800 °C and then they begin to undergo particle growth processes similar to that described for Pd. Note that at low temperatures we did not observe any loss of density, as no particle coalescence would occur at these low NP densities. Representative TEM images of the Au/SiO$_2$ as-synthesized (Fig. 6a) and aged at 800 °C (Fig. 6b) demonstrate that the small size of the Au NCs was maintained even when multiple NCs coexisted on the same SiO$_2$ sphere. Quantitatively, the average size changed minimally, from 7.8 nm for the Au starting material to 7.5 nm for the Au after aging (ESI Fig. S18†). The stability was quantitatively predicted via the simulation of the vapor-phase sintering mechanism, and it is plotted in Fig. 6c. Au does not form a stable oxide but remains metallic up to high temperatures, and thus the vapor-phase mechanism in this case very well explains the behavior.

The high-temperature stability of the Au nanocomposite, which can be explained by vapor-phase sintering processes, is surprising given the vast efforts made to design nanostructured Au catalysts which would produce barriers to surface processes but not necessarily vapor processes. We attribute previous works showing drastic sintering of Au-based catalysts to different supports or the presence of byproducts from the synthesis that could undermine the Au stability with temperature. Furthermore, in many studies showing Au sintering at lower temperatures, Au NCs may be separated by trivially small distances of ~1–2 nm where processes such as directed migration of adjacent particles within such small proximities may occur. In literature examples where control catalysts are compared to encapsulated materials, it is likely that the control material does not contain the exact same nanocrystal size distribution as that of the encapsulated sample, which may lead to confounding effects in understanding catalyst stability. Nevertheless, there still exist many studies discussing the encapsulation of Au for enhanced stability under static calcination conditions. Here we demonstrate that ‘unencapsulated’ Au NCs on SiO$_2$ maintain their stability up to 800 °C in static furnace calcination, at which point they sinter in a process quantitatively consistent with a vapor-phase atomic mechanism. This method can therefore be generalized and extended to several other systems to understand their deactivation behavior.

Conclusions

In this work, we demonstrated how to synthesize powder nanocomposites with precise and independent control of the nanocrystal size and nanocrystal spatial distribution. These materials are not only highly stable but are important tools in providing fundamental understanding and atomistic insight into nanocrystal sintering mechanisms. By using size-controlled nanocrystal materials, we can deconvolute the spatial extents and severity of entire nanocrystal coalescence from atomic Ostwald ripening processes. These processes are uniquely observed in size-controlled NC composites through changing particle size distributions. Particle coalescence is demonstrated through the formation of a bimodal particle size distribution, while Ostwald ripening is demonstrated via the emergence of small nanocrystals. Nanocrystal densities are
controlled and tracked throughout the aging process, and the experimentally measured nanoparticle densities are in quantitative agreement with simulations based on the vapor pressure of Pd and Au metals. This work also demonstrates that appropriate conditions can stabilize metals well beyond what is reported in the literature.

Materials and methods

Material synthesis

Pd NCs were synthesized according to a prior work.24 ~18 g of SiO2 spheres were synthesized in a scaled up batch synthesis, according to the following procedure: 72 mL of MilliQ H2O was mixed with 400 mL of EtOH (Gold Shield), which was heated to 75 °C and maintained at that temperature for 15 min. Next, 67 mL of NH3OH (28–30%) was added, following which the temperature quickly fell to 65 °C, at which point 60 mL of tetraethyl orthosilicate (TEOS, 98% Aldrich) was quickly added under vigorous stirring. The solution immediately turned pearly white, and the reaction was completed after 10 minutes. SiO2 spheres were stored in solution and only isolated as a solid directly prior to use.

Extensive effort was made to synthesize composite materials with controlled NC size and spatial distribution. In short, 1.52 mL (50 mg) of colloidal SiO2 from the mother solution (H2O/EtOH/NH3) was isolated by centrifugation at 8000 rpm for 10 min. The recovered powder was dried in a centrifuge vial upside down for 10 min, and then redispersed in 15 mL of toluene via sonication and vortexing. At this point, the SiO2 spheres dispersed poorly in toluene and quickly precipitated. The powder was isolated again at 8000 rpm for 3 min and redispersed in 35 mL of a 15 vol% EtOH/toluene solution, which dispersed the SiO2 well. The desired amount of Pd NPs, precipitated once with EtOH and isopropanol (IPA), was redispersed in 5 mL of toluene and added dropwise to the stirring SiO2 solution over a period of 5 minutes. This dark mixture was allowed to stir for 30 min, at which point the composite materials were isolated by centrifugation at 8000 rpm for 3 min and dried overnight at 80 °C. These materials were sieved through an 80 µm mesh prior to thermal stability testing.

Thermal aging experiments and statistics

Typically, four small ceramic crucibles (each with ~5 mg of catalyst) were placed near the center of a box furnace, and all were heated simultaneously. The samples were subjected to a 3 °C min⁻¹ ramp rate up to the calcination temperature, followed by a five hour isothermal treatment, and finally ramped back down at 3 °C min⁻¹ to room temperature. Without further treatment, the samples were dry-loaded onto a C/Cu TEM grid for analysis. In cases where rapid cool-down was used (i.e. Fig. 3), the furnace was carefully opened, and the crucible was extracted directly with large tongs and cooled by keeping in ambient air. Control experiments demonstrated that this rapid isolation was crucial, as slow cool-down at 3 °C min⁻¹ would lead to a sample that is completely oxidized. The cooling rates only affected the nanocrystal oxidation states, and similar sintered particle sizes were observed with either fast or slow cooling rates. Unless noted, at least 100 SiO2 spheres were analyzed to obtain the density statistics, and at least 100 NCs were studied to obtain the NC size statistics. For area statistics, the ImageJ outline function was used which calculates enclosed areas in designated polygons. 100 NCs could not be analysed for the 3.3 nm Pd/SiO2 sample aged at 900 °C due to the low density of NCs on the surface after sintering.

Monte Carlo simulations of nearest neighbor nanoparticle distances (ESI Fig. S8†) and particle per bead distribution (ESI Fig. S13†)

Monte Carlo simulations were performed using standard MATLAB functions. To calculate the nearest neighbor distances, an ensemble of at least one thousand SiO2 was populated with randomly distributed nanoparticles (i.e. 4, 17, or 62 per bead), according to a known algorithm (http://mathworld.wolfram.com/SpherePointPicking.html). Next, a two-dimensional matrix of all interparticle distances (greater circle distances) across the spherical surface was calculated. For each nanoparticle, the smallest nearest neighbor distance was selected. By collecting these nearest neighbor distances for thousands of nanoparticles on thousands of spheres, a histogram of nearest neighbor distances was compiled.

Vapor-phase simulations

Vapor-phase ripening simulations were performed using a mean-field model for Ostwald ripening, which assumes a constant background pressure of the migrating species.25,42 Particle-size dependent vapor pressures were calculated using the Gibbs–Thomson equation with experimental values for both the surface free energies of Pd and Au and their temperature-dependent bulk vapor pressures (see Table S3 in the ESI†). The sticking coefficient of the atoms on the metallic surfaces is assumed to be 1. The simulations were initialized with a discretized particle distribution according to a normal distribution, which is centered at the mean diameter and is cut off at values greater than 3 times the standard deviation. Experimental mean diameters and standard deviations of the SiO2-supported nanocrystals, as shown in Fig. 1, were used. The discretization is based on 1000 bins to ensure a smooth particle size distribution. The simulated time is 5 h with a time step that is restricted to be below 0.027 s.

Author contributions

E. D. G. and M. C. conceived the idea for the study. E. D. G. prepared the samples with contribution from E. Z. C., N. T., A. J. and T. N. T. E. D. G. and A. A. performed the XPS and TEM characterization. E. M. D. performed the vapor-phase simulation with supervision from P. N. P. M. C. supervised the entire project. E. D. G. wrote the manuscript with contribution from all authors.

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Conflicts of interest

The authors declare no competing financial interest or conflicts of interest.

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