



## Priority Communication

# Revealing particle growth mechanisms by combining high-surface-area catalysts made with monodisperse particles and electron microscopy conducted at atmospheric pressure



Shuyi Zhang<sup>a,b</sup>, Matteo Cargnello<sup>c,d</sup>, Wei Cai<sup>a</sup>, Christopher B. Murray<sup>c,e</sup>, George W. Graham<sup>a,\*</sup>, Xiaoping Pan<sup>a,b,f,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA

<sup>b</sup> Department of Chemical Engineering and Materials Science, University of California – Irvine, Irvine, CA 92697, USA

<sup>c</sup> Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA

<sup>d</sup> Department of Chemical Engineering and SUNCAT Center for Interface Science and Catalysis, Stanford University, Stanford, CA 94305, USA

<sup>e</sup> Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

<sup>f</sup> Department of Physics and Astronomy, University of California – Irvine, Irvine, CA 92697, USA

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## ABSTRACT

*In situ* aberration-corrected transmission electron microscopy, conducted in forming gas (5% H<sub>2</sub>/N<sub>2</sub>) at atmospheric pressure and elevated temperatures (up to 800 °C), was used to follow the growth of Pt nanoparticles dispersed on a high-surface-area Al<sub>2</sub>O<sub>3</sub> support. These direct observations, facilitated by the use of monodisperse Pt nanoparticles, allowed for an unambiguous separation of the relative contributions of Ostwald ripening and particle migration/coalescence to the overall growth process and made possible the estimation of corresponding energetic and kinetic parameters. Whereas the parameters describing Ostwald ripening were as expected, the diffusion coefficient characterizing particle migration was surprisingly small. Size-selection methods were thus shown to have significant potential for suppressing Ostwald ripening, the dominant growth process, in practical catalysts.

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## 1. Introduction

Supported transition metal nanoparticles (NPs) find widespread applications in catalysts [1–5], sensors [6,7], fuel cells [8–10], and several other energy conversion devices [11,12]. In many of these applications, stable materials that sustain high temperatures without losing active surface area are required. This need is particularly important when precious metals are used, due to their dwindling supply and increasing demand that requires NP growth over time to be mitigated as much as possible. The understanding of mechanisms involved in the growth of supported metal NPs is thus crucial, and despite the large body of work, still not complete. In particular, a detailed atomistic description of the processes taking place under conditions that are closest to the final applications is still missing.

The ability to clearly differentiate between the two most commonly mentioned deactivation phenomena, Ostwald ripening (OR) and particle migration and coalescence (PMC), is important to the design of more stable catalysts. Difficulty arises from the fact that samples in which particle size distributions are broad do not easily allow for discrimination between the two mechanisms, in which on the one side single atom species participate in the particle growth (OR), and on the other the entire particles merge to produce larger ones (PMC).

Various observation techniques have been exploited in this sense. Indirect techniques, such as chemisorption or X-ray diffraction, typically applied to large ensembles of NPs, provide only averaged information about particle size distributions (PSDs). Direct measurement of PSDs by transmission electron microscopy (TEM), on the other hand, is plagued by the uncertainty of conclusions drawn from severely limited sample size in highly heterogeneous samples. Further, the validity of using the shape of the PSD to discriminate between the two main growth processes, has been questioned because similar log-normal distributions can satisfactorily fit both mechanisms of growth [13]. Efforts to characterize these processes on model supports using the environmental TEM,

\* Corresponding authors at: Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA (G.W. Graham and X. Pan).

E-mail addresses: [gwgraham@umich.edu](mailto:gwgraham@umich.edu) (G.W. Graham), [xiaoping.pan@uci.edu](mailto:xiaoping.pan@uci.edu) (X. Pan).

which allows for real-time observation, have been reported and greatly advanced the fundamental understanding [14–18], but the material and pressure gaps inherent in such work still raise questions about whether the results hold true for conditions closer to realistic applications.

In the present study, we employ a recently developed *in situ* TEM technique [19–21], which can be used at atmospheric pressure, to identify the separate contributions of OR and PMC to the growth of monodispersed Pt NPs in high-surface-area Pt/Al<sub>2</sub>O<sub>3</sub> catalysts under reducing conditions. The use of this technique on realistic samples eliminates both pressure and material gaps, thus allowing us to directly observe both processes separately in real time. Further, the use of monodispersed Pt NPs not only allows for the suppression of OR, as recently shown on a model planar support [22], but also demonstrates the utility of this approach for controlling growth rates of supported metal NPs for potentially realistic applications.

## 2. Experimental

### 2.1. Preparation of Pt/Al<sub>2</sub>O<sub>3</sub> samples

Pt nanocrystals were synthesized by following established procedure with minor modifications [5]. All syntheses were performed using standard Schlenk techniques. Pt(acac)<sub>2</sub> (98%, Acros Organics) was used as metal precursor. Trioctylamine (TOA, 97%) was purchased from Acros. Oleylamine (OLAM, 70%), trioctylphosphine (TOP, 97%) and oleic acid (OLAC, 90%) were purchased from Sigma–Aldrich and used as received. 0.2 mmol of Pt(acac)<sub>2</sub> was mixed with oleylamine (2 mmol) and oleic acid (8 mmol) in TOA (10 mL) and evacuated at RT for 5 min. Trioctylphosphine (0.1 mmol for smaller particles, 0.5 mmol for larger ones) was then added and the mixture evacuated further and heated to 120 °C for 30 min. The flask was flushed with nitrogen and heated very quickly (~40 °C min<sup>-1</sup>) to 250 °C (smaller particles) or 350 °C (larger particles). After 30 min of reaction under continuous stirring, the solution was cooled to room temperature. The particles were isolated by addition of isopropanol and centrifugation (8000 rpm, 3 min). No size selection procedures were employed. The particles were soluble in low-polar solvents (hexanes, toluene, chloroform, THF) and were finally dissolved in toluene or hexanes for further analysis. It was found that a small volume of OLAM (50 µL) was generally needed to ensure the complete redissolution of the particles.

The high surface area alumina (Sasol TH100-150) was calcined to 900 °C for 24 h, and therefore stable under the condition utilized in our study. Stock solutions at known concentrations of Pt were prepared in hexanes and slowly added to a mixture of 200 mg of calcined alumina powder well dispersed in toluene (15 mL) by sonication. Adsorption of the particles occurs instantaneously, and the powder is isolated by centrifugation and dried at 120 °C overnight. Samples were prepared with final nominal Pt loading of 0.5 wt% (0.25 wt% for each size in the mixed-size sample). Removal of the ligands was performed on the dried samples by following a fast thermal treatment at 700 °C for 30 s as recently reported [23].

### 2.2. Microscopy characterization

*In situ* observations were carried out with a double spherical aberration-corrected microscope (JEOL JEM-3100R05) operated at 300 kV in combination with a closed gas cell system (Protochips Atmosphere™), as recently adopted in another *in situ* study [20]. Further experimental details, including the procedure used for measuring NP areal densities, are in the Supporting Information (SI).

## 3. Results and discussion

Pt NPs, either 2.2 ± 0.4 nm (referred to as “small”) or 4.4 ± 0.2 nm (referred to as “large”) in diameter, or a mixture thereof (referred to as “mixed”) were prepared and supported on high-surface-area alumina. Based on alumina surface area and the nominal Pt loading, the expected NP areal density was ~10<sup>-3</sup> nm<sup>-2</sup> in the small and mixed samples and roughly ten times smaller in the large sample, though local variations in particle density were found in some regions of the sample. For the purposes of this study, regions with comparable densities were selected for detailed observation. The measured average areal density of NPs for the small, large and mixed samples analyzed below was 12.6 × 10<sup>-4</sup> nm<sup>-2</sup>, 6.9 × 10<sup>-4</sup> nm<sup>-2</sup> and 10.6 × 10<sup>-4</sup> nm<sup>-2</sup> (7.9 × 10<sup>-4</sup> nm<sup>-2</sup> for NPs smaller than 3 nm), respectively. A low-magnification high-angle annular dark field (HAADF) image of the as-synthesized mixed NP sample is shown in Fig. 1(a). (Corresponding images of small and large NP samples are shown in the Fig. S3.) Atomic resolution HAADF images of individual large and small Pt NPs are shown in Fig. 1(b) and (c). These images were taken *ex situ*, with the mixed NP sample supported on a carbon grid.

Samples were heated under 760 Torr of forming gas (5 vol% H<sub>2</sub> in N<sub>2</sub>) at 600 °C, 700 °C, and 800 °C, for 5 h at each temperature, inside the gas cell in the microscope. Sequential images of 6–10 different areas in each sample were taken 4–5 times at each temperature. These images were taken with an electron beam diameter about 0.1 nm and a probe current of 10 pA (the spreading of the probe due to the SiN window is not accounted), and the beam was valved off between image acquisitions, in order to avoid possible beam effects, as detailed in SI. Histograms of PSDs measured from such images at the conclusion of the treatments at 700 and 800 °C are shown in Fig. 2, together with the initial PSDs that were measured at 300 °C. As shown in Fig. 2(a), no significant change occurred in the PSD of the small NP sample until 800 °C, after which the mean particle size had increased by 0.5 nm, ~23%. By contrast, the PSD of the large NP sample remained basically unaffected throughout the entire experiment, as shown in Fig. 2(b). The largest change in PSD, by far, occurred in the mixed NP sample, where most of the small NPs disappeared during the 5 h at 800 °C, as shown in Fig. 2(c). It is important to emphasize that our initial (and final, when stationary) PSDs are truly representative of the entire sample due to the high uniformity of the particles, a situation which has been exploited in previous work [5]. The large change between the initial and final PSDs in the mixed NP sample, compared with the others, thus strongly suggests that OR has been drastically limited through size selection. Dynamic observation in real time, however, is needed for undisputable evidence of the NP growth mechanisms.

A video (shown in SI) and sequential HAADF images, such as those shown in Fig. 3, provide direct evidence of the disappearance of the small NPs in the mixed sample. The artifact induced by high dose electron beam and the procedures to avoid them are detailed in SI. An example of the disappearance of a NP is indicated by the red arrow in Fig. 3, and an example of the shrinking of another NP is indicated by the yellow arrow. It is important to note that the shrinking particles in Fig. 3 and video in SI are representative of the small particles in the mixed sample. A plot showing the changes in the particle size (radius) as a function of time for four NPs, two shrinking and two disappearing, is shown in the bottom left panel of Fig. 3. Even though particle migration was also observed in the case of some small NPs (but not in the case of larger ones shown in the video in SI), at the current particle densities the distance between particles ensures that PMC is almost completely suppressed. Thus, OR has to be the dominant mechanism of NP growth in the mixed NP sample under our conditions of NP density and environment.

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