Aggregation of CeO₂ particles with aligned grains drives sintering of Pt single atoms in Pt/CeO₂ catalysts†

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Understanding the sintering mechanism of platinum-group-metals (PGMs) supported on reducible oxides, such as CeO₂, is of fundamental and practical importance for the development of durable catalysts. It has been reported that the sintering of PGM nanoparticles occurs simultaneously with the aggregation of CeO₂ nanostructures during high temperature thermal treatment. However, mechanistic insights into the coupled sintering processes are insufficient, due to the lack of direct in situ observations of the atomic scale reconstruction processes. Here, we utilize in situ and ex situ transmission electron microscopy measurements to examine the processes of Pt and CeO₂ sintering in model catalytic materials consisting of Pt on isolated CeO₂ particles and Pt on aggregated CeO₂ particles with varying grain boundary alignment. CeO₂ particle aggregation is observed to occur most facilely at particle contacts with well aligned grain boundaries and in turn these contacts serve as locations of the most significant Pt sintering. Our results suggest that the surface reconstruction during CeO₂ aggregation provides the driving force for Pt sintering and provides new understanding of the sintering mechanism of PGM catalysts.

Introduction

Platinum-group-metals (PGMs) on oxide supports serve as active sites in heterogeneous catalysts with applications ranging from three-way catalysts to oil refining.1–8 The cost and scarcity of PGMs require that the metals should be finely dispersed on oxide supports to maximize metal utilization efficiency. CeO₂ is a widely used support material,9 because PGM dispersions of 100% can be obtained on CeO₂.4,10–32 However, CeO₂-supported PGMs suffer from sintering under reducing conditions at high temperature,33–34 which can be detrimental to their catalytic activity. The sintering of Pt is often described by the enhanced mobility of Pt single atoms (SAs) resulting in the formation of Pt nanoparticles (NPs) at high temperature.35–37 In addition, DFT calculations predict that hydroxylation of the CeO₂ surface promotes Pt mobility and sintering.38 However, high-surface-area CeO₂ is also prone to severe aggregation at elevated temperatures (>600 °C, Fig. S1†), which can influence the mobility of supported Pt, and potentially, the sintering of Pt. Therefore, the mechanism of Pt sintering on CeO₂ surfaces must consider both Pt mobility and CeO₂ aggregation, and the microscopic origin of how these processes may be coupled.

The mobility of Pt SAs supported on reducible oxides has been mainly investigated by spectroscopic methods such as CO-Fourier-transform infrared (CO-FTIR) spectroscopy and X-ray absorption spectroscopy (XAS). While these techniques provide valuable information on Pt SAs, they are mainly focused on identifying the oxidation state or the coordination number of Pt. In addition, the inability of Pt SAs on the CeO₂ surface to bind CO probe molecules and the presence of a CeO₂ overlayer covering Pt NPs at high temperature further make it difficult to study how Pt sintering is spatially correlated with CeO₂ aggregation.10,14

Transmission electron microscopy (TEM) is an appropriate technique for examining the spatial correlation between Pt sintering and CeO₂ aggregation. Previous TEM observations demonstrate that the mobility and the sintering behavior of Pt SAs can depend on various factors, such as support materials and support surface facets, by simultaneously observing both the Pt SAs and Pt NPs.29,38–40 However, possible changes in the
surface structure of the CeO₂ support during catalysis and their effects on Pt sintering are still unclear. TEM observations of Pt/CeO₂ subjected to a high temperature pretreatment would unravel the spatial correlation between Pt sintering and CeO₂ aggregation, with the knowledge of the precise locations where Pt sintering and CeO₂ aggregation are initiated.

Here, we investigate the thermally driven restructuring of Pt/CeO₂ samples using atomically resolved TEM. Observations of Pt-containing (in the form of NPs and SAs) CeO₂ particles with controlled spatial separation (isolated and aggregated with varying grain boundary alignment) reveal that Pt sintering occurs primarily at the interface between aggregated CeO₂ particles, while Pt sintering is suppressed on isolated CeO₂ particles. In addition, we found that the degree of Pt sintering depends on the relative orientations of CeO₂ particles with respect to each other; Pt sintering primarily occurs at the interface of CeO₂ particles with grain boundaries in close alignment. It is hypothesized that reconstruction and diffusion of CeO₂ surfaces, which occur preferentially at well-aligned CeO₂ grain boundary interfaces, facilitate Pt mobility and provide the primary pathway for Pt sintering in aggregated CeO₂ support particles. This finding would provide useful information to understand the mobility of Pt SAs supported on the high-surface area CeO₂ support.

**Experimental**

**Sample preparation**

Pt was loaded on ceria (Rhodia, surface area, 135 m² g⁻¹, average particle size, 8.5 nm) by the incipient wetness impregnation method with aqueous Pt(NH₃)₄(NO₃)₂ (Sigma-Aldrich, 99.99% grade, metal basis) solution as a metal precursor at room temperature. After impregnation, the samples were dried in an oven at 100 °C for 24 h. The dried samples were further treated by using 15 vol% O₂/N₂ or 10 vol% H₂/N₂ or N₂ at the selected temperature for 2 h. The oxidation at X °C, the reduction at Y °C or the N₂ treatment at Z °C are represented by XC, YR and ZNC, respectively. For example, Pt/CeO₂ 500°C–250°C–800°C was prepared by (i) oxidizing dried Pt/CeO₂ at 500 °C for 2 h, (ii) reducing Pt/CeO₂ 500°C at 250 °C for 2 h, and finally (iii) N₂ treating Pt/CeO₂ 500°C–250°C at 800 °C for 2 h. The flow rate was always kept at 100 mL min⁻¹.

**H₂-temperature programmed reduction (H₂-TPR)**

The H₂-TPR curve was collected using a BEL-CAT-II (BEL Japan Inc.) equipped with a thermal conductivity detector. 0.05 g of the sample was pretreated under a 20 vol% O₂/Ar flow at 500 °C for 1 h. After cooling down to −90 °C under an Ar flow by using a cryo-device, the sample was exposed to 5 vol% H₂/Ar for 30 min to stabilize the TCD signal. Afterwards, the H₂-TPR curve was obtained by increasing the temperature from −90 to 900 °C with a ramping rate of 10 °C min⁻¹. The flow rate was 50 mL min⁻¹.

**X-ray diffraction (XRD)**

XRD patterns were obtained at a voltage of 40 kV and a current of 30 mA with Cu-Kα radiation (λ = 0.1542 nm) using a Mode 1 Smartlab diffractometer (Rigaku, Japan). A scanning-step size of 0.02° at a speed of 2.5° min⁻¹ was used.

**Raman spectroscopy**

40 mg of Pt/CeO₂ was spread on a sample holder inside the environmental cell (LinkamCCR1000) to collect in situ Raman spectra. The spectra were collected with a Bay Spec Nomadic™ Raman spectrometer equipped with a confocal microscope (Olympus BX-51 upright microscope), volume phase gratings, and a dichroic filter. The sample was excited with a 532 nm laser. The scattered photons were focused onto a CCD detector (2048 × 64 pixels) with a spectral resolution of 4 cm⁻¹. After pretreatment at 350 °C in 3 vol% O₂/Ar for 30 min, Pt/CeO₂ was reduced by using 3 vol% H₂/Ar at 50 or 250 °C for 20 min. The Raman spectra were collected after cooling down the sample temperature to 50 °C under a He flow. The spectra were recorded by averaging 5 scans (100 s per scan). The flow rate was 30 mL min⁻¹.

**Surface area measurement**

N₂ adsorption/desorption isotherms were measured on a Micromeritics ASAP 2010 apparatus at a liquid N₂ temperature of −196 °C. Before analysis, all the catalysts were pretreated at 300 °C for 4 h under evacuation conditions.

**Transmission electron microscopy**

For high-angle annular dark-field (HAADF) scanning TEM (STEM) images and energy dispersive X-ray spectroscopy (EDS), powders of Pt/CeO₂ were diluted in ethanol and a drop of the sample solution was placed onto a lacey carbon TEM grid or a SiN₃ film (Super-thin film, Balzers) for 30 s. The sample was then removed and the grid or film was dried under vacuum overnight at room temperature. All images were obtained using a JEOL-JEM-ARM200F transmission electron microscope (JEOL, Japan) operated at 200 kV and installed at the National Center for Inter-University Research Facility in Seoul National University. The microscope was equipped with a spherical aberration corrector in the condenser lens (probe corrector). The convergence semi-angle was 19 mrad and the collection semi-angle spanned from 68 mrad to 280 mrad. For EDS, an Oxford Instruments X-Max SDD equipped with an active area of 100 mm and a solid angle of 0.9 sr, equipped in the microscope was used. For in situ heating TEM of Pt/CeO₂ 500°C–250°C, a JEM-2100F transmission electron microscope (JEOL) and a DENSsolutions Smartlab diffractometer (Rigaku, Japan). A scanning-step size of 0.02° at a speed of 2.5° min⁻¹ was used.

**Results and discussion**

A model catalyst consisting of 2% by weight of Pt loaded on CeO₂ that was oxidized at 500 °C (500°C treatment) was used for our analyses unless stated otherwise. With the starting hypothesis that CeO₂ sintering is a critical process coupled to Pt sintering, we started by identifying conditions that induce CeO₂ sintering using a combination of Raman spectroscopy and H₂ temperature programmed reduction (H₂-TPR).
The surface and bulk reduction of Pt/CeO₂ occurs in a H₂ environment below 250 °C and above 600 °C, respectively, as seen in the H₂-TPR curve (Fig. S2†). The reduction of the surface of Pt/CeO₂ causes the cleavage of Pt–O–Ce bonds in addition to Ce–O bonds, as shown in the in situ Raman spectra (Fig. S3†). To investigate the effect of Ce–O and Pt–O–Ce bond activation on CeO₂ sintering, we performed three types of thermal treatments on the Pt/CeO₂ 500C sample: (i) 800C (oxidation at 800 °C), (ii) 800NC (N₂ treatment at 800 °C), and (iii) 250R → 800NC (reduction at 250 °C followed by N₂ treatment at 800 °C). (i) and (ii) represent the thermal treatment without the reductive activation of Ce–O or Pt–O–Ce bonds, while (iii) is the thermal treatment following the reductive activation of Ce–O or Pt–O–Ce bonds. The average crystallite size of CeO₂ in Pt/CeO₂, estimated from XRD, increases from 8.6 to 9.8 nm both after (i) 800C and (ii) 800NC treatments, while it increases to 31.1 nm after (iii) (Fig. 1a). These results clearly indicate that the crystallite size of CeO₂ in Pt/CeO₂ becomes larger after high temperature treatment following reductive activation of Ce–O or Pt–O–Ce bonds. It should be noted that the crystallite sizes of Pt-free CeO₂ particles, measured from XRD, after the three types of the thermal treatment are similar to 17.2 nm (Fig. S4†). This is because thermal energy at 250 °C is insufficient to activate Ce–O bonds on CeO₂; the surface reduction of CeO₂ can occur below 250 °C in the presence of Pt (Fig. S2†).

The effect of various high-temperature treatments on the sizes of CeO₂ particles and Pt species in Pt/CeO₂ was studied by HAADF-STEM. CeO₂ particles smaller than 10 nm are observed in Pt/CeO₂ 500C–250R (Fig. 1b and c), while CeO₂ particles larger than 30 nm are observed in Pt/CeO₂ 500C–250R–800NC (Fig. 1e and f), consistent with the XRD measurements. On the other hand, abundant Pt SAs, along with Pt clusters as small as 1 nm are observed in Pt/CeO₂ 500C–250R (Fig. 1c, d and S5†), while many Pt NPs larger than 1 nm and fewer Pt SAs are observed in Pt/CeO₂ 500C–250R–800NC (Fig. 1e–g and S6–S8†). These results demonstrate that high-temperature treatment at 800 °C induces Pt sintering as well as CeO₂ aggregation on Pt/CeO₂ 500C–250R.

These results are consistent with the recent study by Alcala et al., where they suggested that the presence of Pt and other transition metal SAs reduces the surface mobility of CeO₂, helping to slow CeO₂ aggregation. Once the Pt atoms become mobile on a CeO₂ surface through the activation of Pt–O–Ce bonds, the mobility of surface Ce atoms will subsequently be enhanced, leading to CeO₂ aggregation. However, the other scenario is also possible that the mobility of Pt SAs can be enhanced by the movements of surface atoms in CeO₂ during the process of CeO₂ aggregation. Investigating the casual relationship between the two situations – (i) CeO₂ aggregation promoted by Pt sintering and (ii) Pt sintering promoted by CeO₂ aggregation – is challenging because Pt sintering and CeO₂ aggregation occur simultaneously. This requires controlling the extent of CeO₂ aggregation, which can be accomplished by adjusting the interparticle distances of CeO₂ particles.

We analyzed the progress of Pt sintering that occurs at high temperatures via in situ and ex situ (S)TEM of the samples in which the interparticle distances of CeO₂ are controlled. We prepared Pt/CeO₂ particles on silicon nitride (SiN₃) TEM grids at low particle densities to deposit Pt/CeO₂ particles with diverse interparticle distances in a field of view. The SiN₃ TEM grid plays dual roles as a thermally stable substrate for the high-

Fig. 1 CeO₂ aggregation and Pt sintering of surface-reduced Pt/CeO₂. (a) XRD patterns of Pt/CeO₂ 500C (black), 500C–800NC (purple), 500C–800NC (red), and CeO₂ crystallite sizes of the corresponding samples calculated by using the Scherrer equation (inset). (b and c) Low-magnification (b) and high-resolution (c) HAADF-STEM image of Pt/CeO₂ 500C–250R. (d) Low-pass filtered, magnified view of the region marked in (c) (upper panel) and the intensity profile along the line (lower panel). (e and f) HAADF-STEM image of Pt/CeO₂ 500C–250R–800NC (e), and EDS elemental maps of Pt and Ce (f). (g) Histogram showing the diameter of Pt NPs in Pt/CeO₂ 500C–250R–800NC.
temperature treatment and an electron-transparent window for direct, high-resolution (S)TEM without further handling (Fig. S9 and ESI Discussion II†). While controlling the interparticle distances of CeO$_2$ particles would be difficult for powder samples, we could make the variations in the interparticle distances by dispersing the samples on the TEM grids.

When Pt/CeO$_2$ 500C–250R is dispersed on a SiN$_x$ TEM grid and subsequently 800NC-treated, regions with densely packed CeO$_2$ particles and sparsely distributed CeO$_2$ particles are randomly formed (Fig. 2a). After 800NC treatment, CeO$_2$ aggregation and Pt sintering occur simultaneously in regions with high initial density of CeO$_2$ particles (Fig. 2b and c), with more significant particle growth occurring in the more aggregated areas; Fig. 2c compared to 2b. Alternatively, CeO$_2$ aggregation and Pt sintering are suppressed in regions with low initial density of CeO$_2$ particles (Fig. 2d). For example, isolated Pt/CeO$_2$ particles maintain their initial size of ~10 nm without aggregation during 800NC treatment (Fig. 2d). Furthermore, Pt SAs with high concentrations are clearly observed in the HAADF-STEM images of the isolated Pt/CeO$_2$ particles (Fig. 2e, f and S10†). If Pt sintering had occurred irrespective of CeO$_2$ aggregation, then Pt sintering should have occurred even on the isolated CeO$_2$ particles. Therefore, the observation of the maintained existence of Pt SAs on isolated CeO$_2$ particles, and significant Pt sintering in aggregated CeO$_2$ particles, demonstrates that thermal energy alone is not sufficient to drive Pt sintering and instead that Pt sintering is coupled to CeO$_2$ aggregation.

The mechanism of how CeO$_2$ aggregation induces Pt sintering was investigated by in situ heating TEM of Pt/CeO$_2$ 500C–250R (Fig. S11, S12 and ESI Discussion II†). Pt/CeO$_2$ particles are dispersed with random orientations on a SiN$_x$ grid at 600 °C (Fig. 3a). As the temperature increases further, CeO$_2$ particles rotate, and grain growth begins to occur, as evidenced by the temperature dependent appearance of lattice fringes in the in situ TEM images and the CeO$_2$ (111) peaks in fast-Fourier transforms (FFT) of the images (Fig. 3a and b). The rotation of crystalline NPs before aggregation is considered energetically favorable, as it can preclude the formation of grain boundaries with high mismatch and interfacial energy.$^{44-46}$ Grain boundaries with better orientations between the grains provide lower energy pathways for the diffusion of Ce and O atoms on the nanocrystal surfaces, which are required for the reconstruction and densification of aggregated CeO$_2$ particles.$^{46-48}$ Significant Ce and O diffusion, along with CeO$_2$ surface reconstruction, must accompany the aggregation of irregularly shaped CeO$_2$ particles (Fig. 2d). Notably, in situ heating TEM (Fig. 3a) and following STEM (Fig. 3b) clearly confirm that the formation of Pt NPs by Pt sintering at an elevated temperature progresses along with the aggregation of CeO$_2$ particles.

The sintering behavior of Pt atoms depending on the relative orientation of CeO$_2$ particles can be further investigated by observing the Pt/CeO$_2$ particles dispersed on a substrate with an appropriate density. Under these conditions the relative orientation of the grains of individual CeO$_2$ particles at interfacial junctions can be resolved by HAADF-STEM after 800NC treatment (Fig. 3c). On examining a grain boundary with a significantly mismatched angle of ~53° between (022) planes of contacting CeO$_2$ particles (Fig. 3d), abundant Pt SAs are found (Fig. 3e and f). On the other hand, in a grain boundary with a small mismatch angle of ~12° between (111) planes of contacting CeO$_2$ particles (Fig. 3g), individual Pt SAs cannot be clearly identified (Fig. 3h). Instead, Pt NPs are observed at the edge of the grain boundary of aggregating CeO$_2$ particles (Fig. 3g). This indicates that the mobility of Pt SAs increases during the aggregation of relatively well-aligned CeO$_2$ particles,
where surface reconstruction through surface diffusion of Ce and O species is kinetically more facile than in boundaries between mismatched grains.

As discussed previously, CeO$_2$ aggregation must accompany the surface reconstruction of CeO$_2$ particles, because (i) the O atoms on the O-terminated CeO$_2$ surface should be removed for the densification of the aggregating CeO$_2$ particles and (ii) each of the CeO$_2$ particles before aggregation is irregularly shaped (Fig. 2d) so that they can change their shape to aggregate to larger particles. During the surface reconstruction of CeO$_2$, Pt is likely to obtain mobility and eventually sinter into the larger particle at the edge of the aggregating particles (Fig. 3j). On the other hand, for CeO$_2$ particles with high misorientation angles, more energy would be required to align the particles, and therefore, the reconstruction of the interface and the diffusion of Pt SAs would be hindered (Fig. 3j).

We conducted additional experiments to investigate if CeO$_2$ aggregation can promote Pt sintering at a lower temperature. XRD patterns show that aggregation of CeO$_2$ particles into the larger crystals marginally occurs by 500°C treatment (Fig. S13†), while sintered Pt is observed in HAADF-STEM (Fig. S14†). Interestingly, HAADF-STEM shows the alignment of CeO$_2$ lattices and the partial aggregation of the neighboring CeO$_2$ particles (Fig. S14†). This indicates that even the partial aggregation of CeO$_2$ particles by lattice alignment at a low temperature may provide a sufficient driving force for Pt sintering.

Although the simultaneous occurrence of Pt sintering and CeO$_2$ aggregation is confirmed with both bulk characterization (XRD) and microscopic characterization (TEM), it should be noted that the promotion of Pt sintering by CeO$_2$ aggregation could be identified only with TEM. Thus, we have mainly
focused on TEM characterization that can unravel the spatial correlation between Pt sintering and CeO₂ aggregation. While we observed this correlation in multiple regions of the sample with TEM to give statistical meaningfulness to our finding, the evidences from bulk characterization tools will further supplement our understanding of the correlation between Pt sintering and CeO₂ aggregation. In this study, CeO₂ from Rhodia is used. The observed event, promoting Pt sintering by CeO₂ aggregation, presumably occurs universally on a CeO₂ support, regardless of its source or the synthesis method, because aggregation of CeO₂ with a high surface area commonly occurs at high temperature.

While the sintering of Pt SA on the CeO₂ surface has been studied for decades, it should be emphasized that the effect of CeO₂ aggregation on Pt sintering has not been fully understood. This would partly originate from the different models used to study Pt/CeO₂. For example, in most DFT models of Pt/CeO₂ or model Pt/CeO₂ systems in surface science, CeO₂ aggregation does not occur because the CeO₂ surface is infinitely expanded or the CeO₂ particles are spatially isolated. However, in high-surface-area powder samples, high temperature treatment would promote CeO₂ aggregation. Therefore, we believe that understanding how CeO₂ aggregation in high-surface-area powder samples promotes Pt sintering would be vital to develop thermally stable SA catalysts.

Conclusions

In this work, we show that the aggregation of the catalyst support, CeO₂, can induce the sintering of Pt atoms supported on surface-reduced CeO₂ particles. XRD and TEM show that Pt sintering and CeO₂ aggregation occur simultaneously. In order to unravel how CeO₂ aggregation influences Pt sintering, the extent of CeO₂ aggregation was controlled by changing the interparticle distance of CeO₂ particles by dispersing them on TEM grids. TEM of Pt/CeO₂ particles with different extents of CeO₂ aggregation shows that Pt sintering is promoted in the regions with severe CeO₂ aggregation, while abundant Pt SAs are found on spatially isolated CeO₂ particles where their aggregation is suppressed even at 800 °C. In addition, in situ TEM and high-resolution TEM indicate that Pt sintering is promoted at the low-angle grain boundary, indicating that the surface reconstruction of CeO₂ supports during their aggregation facilitates the migration of Pt SAs and Pt sintering. Our results uncover the unexplored sintering mechanism of supported Pt catalysts which should be considered to develop thermally stable catalysts with the high metal dispersion.

Author contributions

J. L. and D. H. K. designed the research. J. L. and E. L. synthesized and characterized the Pt/CeO₂ catalysts. S. K. conducted the STEM experiments. J. L., S. K., M. K., and J. S. performed in situ TEM. J. L. and S. K. performed analysis and interpretation of experimental results. J. L. and T. J. K. performed in situ Raman spectroscopy. P. C., J. P., and D. H. K. supervised the research effort. All the authors contributed to the writing of the manuscript and to the discussion of the results.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean Government (MSIT) (NRF-2016R1A5A1009592) [D. H. K.] (NRF-2019M3E6A1064877 and NRF-2021M3H4A1A02049904) [J. P.]; the Institute for Basic Science (IBS-R006-D1) [J. P.]; the Science Research Center [NRF-2017R1A5A1015365] [J. P.]. This work was also supported by a Postdoctoral Fellowship program granted by NRF [2020R1A6A3A03039683] (J. L.).

Notes and references
