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Tuning single-atom Pt\textsubscript{1}-CeO\textsubscript{2} catalyst for efficient CO and C\textsubscript{3}H\textsubscript{6} oxidation: Size effect of ceria on Pt structural evolution

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Abstract: To reveal the effect of ceria particle size on dispersion and structure of supported Pt catalysts during preparation, activation, and reaction testing, a unique CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} support (CA-c) with smaller CeO\textsubscript{2} particle size and more surface defects was prepared using a colloidal CeO\textsubscript{2} precursor, comparing with a conventional CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} support (CA-n) using cerium nitrate as precursor. More atomically dispersed Pt and abundant Pt-O-Ce structures were observed in the Pt/CA-c Catalyst than in the Pt/CA-n Catalyst. Both parent catalysts received significant enhancement on their catalytic CO oxidation activities if activated by 10% hydrogen at 400 °C before reaction. Between the two representative catalysts, the extent of activity enhancement upon activation was more pronounced for Pt/CA-c. We found that smaller Pt clusters with more active ionic Pt sites were generated on the activated Pt/CA-c catalyst, while agglomerated larger Pt particles with more metallic sites were formed on the activated Pt/CA-n catalyst. The facile formation of Ce\textsuperscript{3+} was also indicative of more active metal-support interfaces in the activated Pt/CA-c catalyst. These results highlight the importance of regulating ceria support particles to enable a controlled anchoring and subsequent activation of Pt single atoms for low-temperature CO oxidation reaction.

Introduction

With the increasing environmental awareness and adoption of more stringent regulations for automotive emissions, designing highly efficient catalysts for vehicle exhaust emission control at low temperatures is a topical research area. Generations of emissions control catalysts have been developed and implemented for real-world applications since the late 1970s\textsuperscript{[1]}. The supported platinum group metals (PGMs), especially Pd and Rh, remain to be the central components catalyzing the emission control reactions, albeit the increasingly high prices and supply deficits of these scarce elements\textsuperscript{[2]}. While also being a PGM as Pd and Rh, the promising catalytic activity, lower price, and higher abundance in earth of platinum enabled Pt-based catalysts to become attractive alternatives. Of course, improved low-temperature activity and thermal stability of Pt catalysts must be achieved to allow Pt being seriously considered as a replacement for Pd or Rh.

As one of the most intensively investigated and widely used rare earth oxides, CeO\textsubscript{2} shows good ability to store and release oxygen dynamically, which promotes the formation of strong metal-support interaction (SMSI) with supported metals\textsuperscript{[3]}. Therefore, as a catalyst support, CeO\textsubscript{2} is beneficial for precious metal dispersion and stabilization\textsuperscript{[4]}. In the last few years, a number of Pt/CeO\textsubscript{2} single-atom catalysts have been developed and studied, where the Pt species can ultimately be stabilized through the Pt-O-Ce linkages in the catalyst as isolated atoms to maximize the atom efficiency (not necessarily reactivity) for Pt. Dvořák et al. reported that the surface defects on CeO\textsubscript{2} supports contributed to the formation and stabilization of single-atom Pt catalysts\textsuperscript{[5]}. Jones et al. found that single-atom Pt tends to locate at the step sites of CeO\textsubscript{2}. Kunwar et al. supported the view that stable Pt single atoms preferred to locate at steps sites on CeO\textsubscript{2}, and CeO\textsubscript{2} with rich step sites could help to increase the loading amount of Pt single atoms\textsuperscript{[6]}. Chen et al. developed a novel surface engineering protocol by creating abundant Ce\textsuperscript{3+} sites to anchor Pt single atoms\textsuperscript{[7]}. As known from above, the dispersion and location of Pt are highly dependent on the defects (e.g. step sites and/or surface Ce\textsuperscript{3+} sites) of CeO\textsubscript{2} supports, and these properties are intrinsically associated with the particle size, crystallinity, and exposed crystal facets of CeO\textsubscript{2}. It has been anticipated that CeO\textsubscript{2} particles with smaller sizes and higher surface areas could provide more step and defect sites to anchor Pt single atoms\textsuperscript{[8]}. Therefore, one of the objectives in this work is to develop CeO\textsubscript{2} particles with smaller sizes and more defects to better host the single atom Pt species, and we measure such a material against its conventional industrial counterpart.

While single-atom catalysts deliver excellent performance in reactions such as hydrogenation, water-gas shift, selective oxidation, reforming, etc.\textsuperscript{[9]}, the Pt single atoms are inferior to small Pt clusters for CO and HC oxidation\textsuperscript{[10, 11, 12, 13]}. As a natural next step, new efforts are devoted to control the evolution of single atom Pt to the more efficient Pt clusters or ensembles where new chemistry may happen when Pt atoms are no longer isolated. For example, Pereira-Hernández et al. prepared a thermally stable Pt single atom catalysts on CeO\textsubscript{2} using high temperature vapor phase trapping method, in which the limited CO oxidation activity of this single-atom catalyst witnessed a great improvement after the formation of Pt clusters by an activation in CO flow at 275 °C\textsuperscript{[14]}. Using Pt single atom catalyst as a parent platform, Wang et al. created Pt-O-Pt ensembles on CeO\textsubscript{2}, which exhibited superior CO oxidation activity at low temperature\textsuperscript{[15]}. Although the authors found that a similar type of highly active Pt clusters can be produced on several different types of ceria\textsuperscript{[16, 17, 18]}, the actual population of the desired Pt species was heavily influenced by the ceria properties. In this work, we plan to further investigate the effect of CeO\textsubscript{2} size on Pt structural evolution from its single-atom
to cluster forms, and to validate their catalytic performance for CO and C₂H₄ oxidations, both of which relate to vehicle emission control applications.

With the goal of surviving high-temperature spikes encountered in automotive exhaust, a promising Pt/CeO₂ catalyst must show excellent thermal stability at elevated temperatures. Pure CeO₂ support is less stable than widely used Al₂O₃ for the typical application temperature window [11]. γ-Al₂O₃ has been used to support some metal oxides such as CeO₂ and TiO₂ to improve the thermal stability of the latter [12]. After harsh aging treatment, the overall surface area of these metal oxides can be better maintained in such a fashion [12]. However, this largely remains a statistically averaged result. The morphology and size of CeO₂-loaded on γ-Al₂O₃ were difficult to control by traditional impregnation method. Alternatively, hydrothermal method and surfactant-template method are well established approaches to prepare stand-alone CeO₂ species with small particle size and higher surface area. Besides the often complex and laborious synthesis [13], perhaps the most significant roadblock for such methods is that the CeO₂ particles obtained were difficult to be redispersed and loaded with high amount onto thermally stable Al₂O₃ supports. Hence, we explore the possibility of preparing a new CeO₂/Al₂O₃ support with well controlled particle size through a facile method. The new support is hoped to be utilized as an effective host for the highly dispersed Pt species to realize the intended catalytic functions.

In this work, a novel CeO₂/Al₂O₃ support with uniform and small CeO₂ particles dispersed on Al₂O₃ was obtained using a commercial colloidal CeO₂ as precursor (CA-c as the resulted support). Compared with a conventional CeO₂/Al₂O₃ support prepared using a cerium nitrate precursor (CA-n as the resulted support), Pt deposited on this new support (as Pt/CA-c catalyst) showed higher metal dispersion in the form of single-atom Pt. The Pt/CA-c with small CeO₂ size showed advantages such as catalytic oxidation activity. Through analyses including XRD, Raman spectroscopy, HR-TEM, in situ DRIFTS, H₂-TPR, XPS, etc., we discuss the reasons behind the superior catalytic performance on activated Pt/CA-c. The small CeO₂ particles enriched with surface defects and dispersed Pt clusters with more active ionic Pt sites are the key enablers for the excellent catalytic performance from activated Pt/CA-c catalyst.

Results and Discussion

The details of sample preparation and characterizations have been listed in Experimental Section.

The CO oxidation activities of the as-prepared (fresh) and aged supports were measured and shown in Figure 1a. CA-c performed much higher CO oxidation activity than CA-n before and after aging treatment (800 °C in air, 12 h). A slight decline in the catalytic activity was detected on CA-c-800A, while CA-n-800A suffered from significant deactivation after aging treatment. That is to say, CA-c exhibited better oxidation activity and thermal stability than CA-n. With the loading of Pt, great enhancement on CO oxidation activity was observed over Pt/CA-c and Pt/CA-n (Figure 1b). After the activation by 10% hydrogen at 400 °C, the catalytic activity of Pt/CA-c-ACT and Pt/CA-n-ACT was improved significantly (Figure 1c), with the Tₕ₀ (where the CO conversion reached 50%) decreasing from ca. 170 °C to 112 °C and 137 °C, respectively. It should be noted that, Pt/CA-c-ACT performed much higher CO oxidation activity than Pt/CA-n-ACT. As illustrated in Figure S1a, the CO oxidation activity of Pt/Al₂O₃-ACT was boosted after the modification by CeO₂, which suggested that Pt-CeO₂ interfaces were more favorable than Pt-Al₂O₃ interfaces for CO oxidation in general.

To evaluate the thermal stability of Pt/CA-c and Pt/CA-n, the samples were aged in air at 800 for 12 h, and subsequently tested for CO oxidation. As shown in Figure 1d, aged Pt/CA-c-ACT performed much better CO oxidation activity than Pt/CA-n-ACT. Also, after the modification by colloidal CeO₂, the thermal stability of Pt/Al₂O₃ was greatly improved, which should relate to the creation of desired Pt-CeO₂ interaction (Figure S1a). The oxidation of C₂H₄, one of the main hydrocarbons (HCs) in vehicle exhaust, was also chosen to evaluate the thermal stability of developed catalysts (Figure S1b). Similar to the CO oxidation results, Pt/CA-c-800A-ACT performed much better C₂H₄ oxidation activity than Pt/CA-n-800A-ACT. In summary, Pt/CA-c-ACT using colloidal CeO₂ as ceria precursor is an efficient catalyst with high catalytic oxidation activity and thermal stability.

XRD was performed to explore the crystal structure of Pt/CA-c and Pt/CA-n, and the results are shown in Figure 2. The crystallite size of CeO₂ was calculated by Scherrer equation and listed in Table 1. The XRD patterns of CA-c and CA-n mainly exhibited a typical cubic fluorite structure of CeO₂ [14] in addition to γ-Al₂O₃ phase. The intensity of the CeO₂ peaks for CA-c was much lower than that for CA-n, and the peaks for CA-c were broader, which meant that the crystallite size of CeO₂ on CA-c was smaller than that on CA-n. With the deposition of Pt on CA-c and CA-n, no obvious difference in XRD patterns was observed, indicating that Pt was highly dispersed on both CA-c and CA-n. The XRD patterns of aged samples were also collected (Figure S2). Compared with the as-prepared samples, an increase in the intensity of CeO₂ diffraction peaks was detected on both Pt/CA-c-800A and Pt/CA-n-800A. Meanwhile a new diffraction peak attributed to bulk Pt phase was observed in the aged samples. These findings implied the growth of CeO₂ and Pt particle size during the aging process [15].

Figure 1. a) CO oxidation activity of fresh and aged CA-c and CA-n. b) Pt/CA-c-ACT, Pt/CA-n-ACT, CA-c and CA-n. c) Pt/CA-c and Pt/CA-n before and after activation treatment; d) CO oxidation activity of activated Pt/CA-c and Pt/CA-n before and after aging treatment (800 or 1000 °C for 12 h in air).
The specific surface areas of the samples were also measured (Table 1). The CA-c exhibited a much higher specific surface area than the CA-n (131.3 m²/g vs. 97.2 m²/g). Considering that both CA-c and CA-n used the same γ-Al₂O₃ as support (140 m²/g) and followed the same calcination process, we inferred that CeO₂ in CA-c was well dispersed and exposed larger surface area in the as-prepared catalysts. By depositing the commercial colloidal CeO₂ with controlled size onto γ-Al₂O₃ to produce the CA-c support, small CeO₂ particles were successfully prepared with uniform size (~10 nm), higher specific area, and better versatility for catalytic applications.

Notably, the overall advantage of the CA-c as a support for Pt catalysts in low-temperature CO and C₃H₈ oxidation reactions was retained after aging, when measured against the more conventional CA-n. As reflected by the extent of change in crystallite size and specific surface area before and after aging (Table 1), Pt/CA-n was perhaps more structurally stable than Pt/CA-c due to the much larger crystallite size of ceria in the former sample in as-prepared state. The sintering of both CeO₂ and Pt are apparently the main reasons for the decline in CO oxidation activity after the aging treatment. Nevertheless, even with shrinking advantages in terms of catalyst texture, Pt/CA-c-800A still exhibited much better catalytic activity than that of Pt/CA-n-800A, and those reasons behind this more favorable catalytic chemistry will be discussed in later sections.

Table 1. Crystallite size, specific surface area and concentration of surface defects of prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>Specific area (m²/g)</th>
<th>%S/14eV20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CA-c</td>
<td>6.9</td>
<td>128.2</td>
<td>0.07</td>
</tr>
<tr>
<td>Pt/CA-n</td>
<td>11.2</td>
<td>93.4</td>
<td>0.03</td>
</tr>
<tr>
<td>Pt/CA-c-800A</td>
<td>10.9</td>
<td>79.6</td>
<td>/</td>
</tr>
<tr>
<td>Pt/CA-n-800A</td>
<td>12.4</td>
<td>62.6</td>
<td>/</td>
</tr>
<tr>
<td>CA-c</td>
<td>6.7</td>
<td>131.3</td>
<td>/</td>
</tr>
<tr>
<td>CA-n</td>
<td>10.0</td>
<td>97.2</td>
<td>/</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>/</td>
<td>140.9</td>
<td>/</td>
</tr>
</tbody>
</table>

[a] The crystallite size was calculated by Scherrer equation, using CeO₂ (111).
[b] The specific areas of prepared samples were measured by N₂ physisorption at -196°C.
[c] Concentration of surface defects. T was the peak area of the band in Raman spectra at corresponding wavenumber.

HR-TEM technique was employed first to reveal the size and morphology of Pt/CA-c and Pt/CA-n (Figure 3). Small CeO₂ particles with uniform size (ca.10 nm) were found on Pt/CA-c, while no obvious Pt species were observed. For Pt/CA-n, large CeO₂ particles (~ 20 nm) with irregular shapes were observed on Al₂O₃, which was in good accordance with the XRD results. For CeO₂ particles on both CA-c and CA-n, CeO₂ (111) was the main facet that was exposed. HR-TEM images of Pt/CA-c-800A and Pt/CA-n-800A were also collected (Figure S3). Although the sintering of CeO₂ was observed, the dispersion of the ceria in Pt/CA-c-800A were still better than that of the Pt/CA-n-800A sample, which is in consistency with the findings from the XRD patterns of the aged catalysts (Figure S2).

Figure 2. XRD patterns of a) CA-c, CA-n, Pt/CA-c and Pt/CA-n, b) Pt/CA-c and Pt/CA-n (from 25 to 42.5°).

Figure 3. HR-TEM images of a, b) Pt/CA-c and c, d) Pt/CA-n. Note: Small CeO₂ particles on Pt/CA-c are marked in red circles.

Figure 4. CO adsorption as well as the reaction between O₂ and adsorbed CO monitored by in situ DRIFTS on a) Pt/CA-c; b) Pt/CA-n at 60 °C.
Acknowledging that HR-TEM cannot detect highly dispersed Pt single atoms on ceria, we performed in situ DRIFTS of CO adsorption on Pt/CA-c and Pt/CA-n to probe the states of Pt in these samples. As illustrated in Figure 4, for Pt/CA-c, two distinctive bands could be observed. The band at ca. 2172 cm⁻¹ was assigned to gaseous CO, while the band at ca. 2096 cm⁻¹ with high symmetry was attributed to CO linearly adsorbed on Pt sites. According to literature, the Pt species could be assigned to singly dispersed Pt (CO-Pt=O@Pt)ₙ [19, 110, 115]. In other words, Pt in Pt/CA-c were present in single-atom form. However, for Pt/CA-n, other than the bands ascribed to gaseous CO and Pt adsorbed on ionic Pt, another band was detected at ca. 2068 cm⁻¹, which could be assigned to CO adsorbed on Pt clusters (CO-Pt@clusters) [116]. This result suggests that the Pt on Pt/CA-n exhibited a mixed form of single dispersed Pt and Pt clusters.

After the activation treatment by 10% hydrogen at 400 °C, no obvious change occurred in the overall morphology of the corresponding Pt/CA-c-ACT sample (Figure 5, Figure S4). Pt might be present in the form of single atom and/or small clusters (< 2 nm) in the Pt/CA-c-ACT, while Pt particles (2 ~ 5 nm) formed in the Pt/CA-n-ACT (Figure 5, Figure S4, Figure S5). This indicated the better dispersion of Pt species on Pt/CA-c-ACT than on Pt/CA-n-ACT. The higher dispersion of Pt species on Pt/CA-c-ACT can directly contributed to availability of catalytically active sites, which in turn led to the superior CO oxidation activity.

Raman spectra were collected to further investigate the detailed structure of Pt/CA-c and Pt/CA-n. The intensive band at 462 cm⁻¹ could be assigned to the CeO₂ F₉r mode vibration, and the band at 595 cm⁻¹ could be assigned to the defect-induced mode, which was related to the existence of oxygen vacancies in CeO₂. The concentration of surface defects was calculated from 1606/1652 (I' means the peak area of the band at corresponding wavenumber) [115]. As illustrated in Figure 6a and Table 1, more surface defects were present on CA-c than on CA-n (0.07 to 0.03). After the deposition of Pt, two new bands at 557 cm⁻¹ and 658 cm⁻¹ emerged, which could be attributed to Pt-O-Ce and Pt-O (in Pt-O- Ce) structure, respectively. Higher intensity of bands at 557 cm⁻¹ and 658 cm⁻¹ on Pt/CA-c indicated that more Pt-O-Ce linkages were formed on Pt/CA-c, which might relate to the higher dispersion of Pt on CA-c. As reported by Dvořák et al. [89] and Kunwar et al., more step sites on CeO₂ could help to anchor the Pt single atoms. As illustrated in the XRD patterns and HR-TEM images from this work, smaller CeO₂ particles with fruitful step and corner sites were formed on CA-c, which would be beneficial for higher Pt dispersion. This result was in good agreement with the Raman spectra showing that more surface defects were formed on CA-c than on CA-n and more Pt-O-Ce species were generated on Pt/CA-c. After H₂ activation before reaction test, the intensity of the two bands assigned to Pt-O-Ce and Pt-O declined dramatically, which could be attributed to the depletion of Pt-O bonds and the formation of metallic Pt clusters (Figure 6b). The formation of non-isolated Pt species on Pt/CA-c-ACT and Pt/CA-n-ACT should have contributed to the enhancement of catalytic performance, since it has been reported that Pt clusters or ensembles on CeO₂ were more active than Pt single sites for CO oxidation [30, 39].

To further demonstrate the structural evolution of Pt/CA-c and Pt/CA-n catalysts in the process of reductive activation treatment, H₂-TPR experiment was performed and the H₂-TPR profiles are illustrated in Figure 7. Specifically, reduction peaks with higher intensity were observed on CA-c comparing to CA-n. Furthermore, the peak assigned to the reduction of surface Ce₄+ on CA-c was observed at lower temperature (544 °C) than that on CA-n (580 °C) [116]. The lower reduction temperature for Pt/CA-c compared to CA-n helps in the higher CO oxidation activity on CA-c (Figure 1a). After loading Pt onto CA-c or CA-n, several new reduction peaks were detected (Figure 7b), where the peak at ca. 150 °C was attributed to the reduction of Pt-O and Pt-O-Ce[20]. The low reduction temperature for Pt-O and Pt-O-Ce (< 300 °C) explains the disappearance of Pt-O-Ce and Pt-O bands in the Raman spectra on the activated samples. The peak centered at ca. 340 °C could be assigned to the reduction of CeO₂ around Pt[21]. The bands at ca. 450 °C and ca. 720 °C are attributed to the reduction of surface Ce₄+ and bulk CeO₂, respectively.

Figure 5. HR-TEM images of a, b, c) Pt/CA-c-ACT and d, e, f) Pt/CA-n-ACT. Notes: Small CeO₂ particles on Pt/CA-c-ACT are marked in red circles; Pt clusters on Pt/CA-n-ACT are marked in yellow circles.

Figure 6. Raman spectra of a) CA-c, CA-n, Pt/CA-c and Pt/CA-n, b) fresh and activated Pt/CA-c and Pt/CA-n. Note: The height of CeO₂ F₉r band for various samples was normalized.
The Ce 3d XPS of prepared samples are shown in Figure 8b-d, and all the spectra could be fitted into ten peaks. In detail, u', u, v and v0 are assigned to surface Ce(IV), while the rest are attributed to surface Ce(III). The surface concentration of Ce(III) could be obtained by the following equation:

\[
\text{Ce}(\text{III}) = \frac{(S_u + S_u' + S_v + S_v')}{(S_u + S_v)} \times 100
\]

\((S_u \text{ and } S_v \text{ are the peak areas of peaks labelled as } u \text{ and } v)\)

The fitting results were listed in Table 2.

Figure 7. H:\textsubscript{2}-TPR profiles of a) CA-c and CA-n; b) Pt/CA-c and Pt/CA-n.

Figure 6. XPS spectra in the a) Pt 4d core level of fresh and activated Pt/CA-c and Pt/CA-n; b) Ca-c and CA-n; c) fresh and activated Pt/CA-c; d) fresh and activated Pt/CA-n.

The H\textsubscript{2} consumptions, which was calculated by the integration of peak areas on H\textsubscript{2}-TPR profiles for Pt/CA-c and Pt/CA-n, were listed in Table S1. Significantly higher H\textsubscript{2} consumption by Pt-O reduction was observed on Pt/CA-n than Pt/CA-c, which might be due to the formation of PtO\textsubscript{2} clusters/particles that has limited contact with CeO\textsubscript{2} on Pt/CA-n. Differently, it was found that the H\textsubscript{2} consumption by Pt-O Ce reduction on Pt/CA-c was much higher than that on Pt/CA-n, indicating the higher dispersion of Pt and more Pt-O-Ce linkages on Pt/CA-c. The higher reduction intensity of CeO\textsubscript{2} at 366 and 457 \text{ \textdegree}C might be resulted from the higher reduction degree of CeO\textsubscript{2} on Pt/CA-c with smaller CeO\textsubscript{2} particle size.

Raman spectroscopy and H\textsubscript{2}-TPR experiments suggested that the intensity of interaction between Pt and CeO\textsubscript{2} (Pt-O-Ce) was distinguishable, which might have caused the different states of Pt and CeO\textsubscript{2} before and after activation treatment.

XPS experiments were conducted to further reveal the surface chemical state of CA-c, CA-n, Pt/CA-c and Pt/CA-n. The concentration of Pt/CA-c, higher surface concentration of Pt was detected on Pt/CA-c, which indicated a higher dispersion of Pt on CA-c than on CA-n. After activation, the concentration of Pt on Pt/CA-c and Pt/CA-n decreased, which was due to the formation of Pt clusters, in accordance with what HR-TEM images have demonstrated. Obviously, the decrease in surface concentration of Pt on Pt/CA-n-ACT was much sharper (from 0.20 to 0.12\%) than that on Pt/CA-c-ACT (from 0.23 to 0.18\%), indicating larger Pt clusters formed on Pt/CA-n-ACT. The Pt 4d XPS of fresh and activated samples are shown in Figure 8a. For both Pt/CA-c and Pt/CA-n, Pt species mainly existed in the form of Pt\textsubscript{2+}. After activation, the peaks assigned to Pt 4d\textsubscript{5/2} and Pt 4d\textsubscript{3/2} shifted to lower binding energy, accounting for the formation of metallic Pt species[23].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface atomic concentration (%)</th>
<th>Ce(III)/ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CA-c</td>
<td>O 56.7  Al 41.4  Ce 1.68  Pt 0.23</td>
<td>17.9</td>
</tr>
<tr>
<td>Pt/CA-n</td>
<td>O 57.2  Al 42.1  Ce 0.54  Pt 0.20</td>
<td>19.6</td>
</tr>
<tr>
<td>Pt/CA-c-ACT</td>
<td>O 56.5  Al 41.4  Ce 1.94  Pt 0.18</td>
<td>28.1</td>
</tr>
<tr>
<td>Pt/CA-n-ACT</td>
<td>O 55.9  Al 43.4  Ce 0.56  Pt 0.12</td>
<td>24.1</td>
</tr>
<tr>
<td>CA-c</td>
<td>O 59.4  Al 37.6  Ce 3.03  Pt /</td>
<td>24.3</td>
</tr>
<tr>
<td>CA-n</td>
<td>O 58.5  Al 40.9  Ce 0.63  Pt /</td>
<td>23.2</td>
</tr>
</tbody>
</table>

It was observed that higher concentration of Ce was observed on CA-c comparing to CA-n, indicating that CeO\textsubscript{2} in CA-C showed higher dispersion due to the smaller CeO\textsubscript{2} size. Furthermore, more Ce\textsuperscript{2+} species were observed on CA-c than on CA-n (24.3 \% vs. 23.2 \%). The higher concentration of Ce\textsuperscript{2+} was potentially related to rich surface defects, as demonstrated in Raman spectra (Figure 6). After the deposition of Pt, the concentration of surface Ce\textsuperscript{2+} decreased dramatically, which could be resulted from the reaction between PtO\textsubscript{2} and Ce\textsuperscript{3+} (PtO\textsubscript{2} + 2Ce\textsuperscript{3+} → Ce\textsuperscript{4+} - Pt\textsubscript{2+} - O\textsubscript{2+} - Ce\textsuperscript{2+}). Interestingly, contrary to the result that CA-c possessed more Ce\textsuperscript{2+} than CA-n, Pt/CA-c showed lower Ce\textsuperscript{2+} concentration (decreased from 24.3 \% to 17.9 \%), comparing to Pt/CA/n (decreased from 23.2 \% to 19.6 \%). These results imply that Ce\textsuperscript{2+} on CA-c was more active than that on CA-n regarding to the reaction with PtO\textsubscript{2}, and more Pt-O-Ce species could be formed on Pt/CA-c, matching the conclusion from Raman spectra. After
H₂ activation, the concentration of surface Ce³⁺ on both Pt/CA-c-ACT and Pt/CA-n-ACT greatly increased. According to H₂-TPR results, Pt-O-Ce structure and surface Ce³⁺ could be reduced below 400 °C, which would result in the formation of reduced Pt species and surface Ce³⁺. As demonstrated in Figure 7 and Table S1, more intensive reduction of Pt-O-Ce and surface Ce³⁺ was observed on Pt/CA-c than on Pt/CA-n, which well explained why more surface Ce³⁺ was formed on Pt/CA-c-ACT. The higher concentration of surface Ce³⁺ on Pt/CA-c-ACT related to more active sites at Pt-CeO₂ interfaces, accounting for the high catalytic oxidation activity of Pt/CA-c-ACT.

From the results of CO adsorption (DRIFTS), Raman spectroscopy, H₂-TPR and XPS, it can be seen that Pt was highly dispersed on CA-c in single-atom form, and induced strong interaction between Pt and Ce (rich Pt-O-Ce species). Moreover, as shown in Figure 4, the adsorbed CO on ionic Pt almost showed no change after being purged by O₂ for 15 min at 60 °C, which would cause CO poisoning effect on ionic Pt due to the lack of properly activate O₂ to react with the adsorbed Pt⁶⁺. Such CO poisoning effect on Pt single sites would account for the lower CO oxidation activity of as-prepared Pt/CA-c and Pt/CA-n comparing to Pt/CA-c-ACT and Pt/CA-n-ACT.

![Figure 9](image_url)  
**Figure 9.** CO adsorption and reaction between O₂ and adsorbed CO monitored by in situ DRIFTS on a) Pt/CA-c-ACT, b) Pt/CA-n-ACT (40 °C).

**In situ** DRIFTS of CO adsorption and subsequent oxidation was performed for Pt/CA-c-ACT and Pt/CA-n-ACT to identify the active sites on these two activated catalysts. After the activation, in addition to the bands at ca. 2100 cm⁻¹ (CO on Pt single sites), two distinctive bands were observed on both catalysts, which could be assigned to CO adsorbed on ionic Pt at the interface between Pt clusters and CeO₂ (CO-Pt@clusters, ca. 2083 cm⁻¹), and CO on metallic Pt sites of Pt clusters (CO-Pt@clusters, ca. 2066 cm⁻¹) [25] (Figure 9). These two bands were consumed gradually with the introduction of O₂ and experienced minimal further change after 10 min on stream, indicating that both sites were active (though may at different extents) in CO oxidation. Despite the overall similarity, the bands at ca. 2083 cm⁻¹ for Pt/CA-c-ACT were more distinguishable than that for Pt/CA-n-ACT. The amount of the ionic Pt species (Pt-CeO₂ interfacial sites) are normally dependent on the size of Pt clusters. A catalyst with smaller Pt cluster size possesses more active Pt-CeO₂ interfacial sites, which may account for the improved CO oxidation activity [25]. In order to further determine the reactivity of CO adsorbed on catalyst, the spectrum at which the band would experience minimal further change in O₂ flow (O₂ purge 630 s) was subtracted from a series of spectra from Ar purge 15 min to O₂ purge 600 s (Figure S6). The two distinct species (CO-Pt@clusters and CO-Pt@clusters) were confirmed. The peak areas of these two bands in the first 50 s of O₂ purge (as shown in Figure S6) were further calculated by integrating the peak intensities. According to the results shown in Figure 10, a comparatively higher portion of CO adsorbs as CO-Pt@clusters on Pt/CA-c-ACT, while higher portion of CO adsorbs as CO-Pt@clusters on Pt/CA-n-ACT. Due to the confirmed higher CO oxidation activity from Pt/CA-c-ACT, we believe the ionic Pt species on those small Pt clusters is mainly responsible for the more efficient CO oxidation. Although the peak intensity and its decreasing rate for the adsorption as CO-Pt@clusters is indeed prominent, the quantified results exclude the Pt@clusters as the actual working catalytic centers that lead to the much-enhanced activity found in this work.

![Figure 10](image_url)  
**Figure 10.** Integral results of peak intensities (peak area) for the bands assigned to CO adsorbed on ionic Pt sites at Pt-CeO₂ interface and metallic Pt sites of Pt clusters on Pt/CA-c-ACT and Pt/CA-n-ACT in the first 50 s after O₂ introduction.

The oxygen storage capacity (OSC) is one of the important indices for evaluating the redox properties of catalysts for vehicle exhaust purification. The dynamic OSC of as-prepared and aged Pt/CA-c and Pt/CA-n samples after activation were tested under alternating pulses of 2% CO/4% O₂ in 30 s, and presented in Figure S7 and Figure 11a. CA-c was a better OSC material than CA-n, with a higher OSC value of 100 μmol O₂/gcat. at 300 °C when
comparing to that of CA-n (30 µmol O/g-w.). After the loading of Pt, the OSC values of CA-c and CA-n significantly improved, and Pt/CA-c-ACT always exhibited higher OSC values than Pt/CA-n-ACT at different temperatures before or after aging treatment. It was found that the variation trend of OSC values was similar to that of CO oxidation activity. The relationship between the OSC values and CO conversions of as-prepared and aged samples at 120 and 140 °C is shown in Figure 11b. An approximately linear relationship between OSC and CO conversions was observed, which suggests that the storage and activation of oxygen was vital for the catalytic oxidation of CO.

This activity enhancement is the consequence of more active ionic Pt sites at the interface of smaller Pt clusters and CeO$_2$ formed on Pt/CA-c-ACT, which contribute to its superior catalytic oxidation activity and OSC values. Our work provides a new strategy to design a thermally stable Pt single atom catalyst, not directly as an active catalyst, but as a platform for a controlled formation of small Pt clusters and a creation of more active sites at Pt-CeO$_2$ interfaces, which are critical in achieving high activity for CO and HC oxidation at low temperatures.

![Figure 11](image.png)

Figure 11. Results of OSC measurement. a) OSC values of Pt/CA-c-ACT, Pt/CA-c-800A-ACT and Pt/CA-n-ACT and Pt/CA-n-800A-ACT; b) The relationship between CO conversion and OSC values (at 120/140 °C) of Pt/CA-c-ACT, Pt/CA-c-800A-ACT and Pt/CA-n-ACT and Pt/CA-n-800A-ACT.

In previous research, it has been widely recognized that CO oxidation reaction on Pt/CeO$_2$ catalysts mainly followed a Mars-van Krevelen (MVK) mechanism, wherein CO adsorbed on Pt sites reacted with activated lattice oxygen, while the activation of oxygen on oxygen vacancies was the rate-determining step.[3] The results of OSC testing confirmed that the CO oxidation reaction on Pt/CeO$_2$/Al$_2$O$_3$ catalysts also proceeded in MVK mechanism. As discussed above, CeO$_2$ particles on CA-c were much smaller than those on CA-n and possessed more surface oxygen defects and superior redox ability. Pt on CA-c was well dispersed and more active ionic Pt-CeO$_2$ interfacial sites were formed on Pt/CA-c-ACT after activation. Therefore, Pt/CA-c-ACT showed much higher OSC than Pt/CA-n-ACT owing to the rich Pt-CeO$_2$ interfaces.

Conclusion

In summary, by loading Pt on a novel CeO$_2$/Al$_2$O$_3$ support (CA-c) with uniform distribution of small CeO$_2$ particles (~10 nm), high specific surface area and abundant surface defects, a Pt single atom catalyst was successfully synthesized. Comparing with the Pt catalyst on traditional CeO$_2$/Al$_2$O$_3$ support (CA-n), the singly dispersed Pt on CA-c resulted in the formation of more abundant Pt-CeO$_2$ interfaces. A significant improvement of catalytic activity for CO and C$_3$H$_8$ oxidation was observed for both Pt/CA-c and Pt/CA-n catalysts after being activated in a hydrogen treatment, and the improvement is particularly pronounced for the Pt/CA-c.

Experimental Section

1. Samples preparation

30 wt.% CeO$_2$ (Ce(NO$_3$)$_3$·6H$_2$O or colloidal CeO$_2$ as precursor was loaded onto commercial γ-Al$_2$O$_3$ provided by Sasol by an incipient wetness impregnation (IWI) method. The mass ratio of CeO$_2$ to γ-Al$_2$O$_3$ was fixed to be 3:7. The colloidal CeO$_2$ with a uniform diameter of 20 nm was purchased from Nyacol Nano Technologies, Inc. Typically, the Ce(NO$_3$)$_3$·6H$_2$O solution or colloidal CeO$_2$ with designated concentration was added dropwise to the γ-Al$_2$O$_3$ powder; when the amount of the added solution was about to exceed the pore volume of the support, the mixture would be dried at 120 °C for 30 min. After all solution of CeO$_2$ precursor has been added to the support, the obtained powders were calcined at 550 °C for 2 h with a ramping rate of 2 °C/min. These two types of CeO$_2$/Al$_2$O$_3$ supports obtained from Ce(NO$_3$)$_3$·6H$_2$O and colloidal CeO$_2$ were denoted as CA-n and CA-c, respectively. 1 wt.% Pt (Pt(NO$_3$)$_3$ as precursor) was subsequently loaded onto the CA-n and CA-c by the IWI method. The samples were obtained after calcination at 550 °C for 2 h with a ramping rate of 5 °C/min and were denoted as Pt/CA-n and Pt/CA-c, respectively. 1 wt.% Pt loaded on stand-alone γ-Al$_2$O$_3$ and CeO$_2$ obtained by calcination of Ce(NO$_3$)$_3$·6H$_2$O in air at 550 °C for 2 h) were also prepared by IWI method as references, denoted as Pt/Al$_2$O$_3$ and Pt/CeO$_2$, respectively. To evaluate their thermal stability, the prepared samples were treated in air condition at 800 or 1000 °C for 12 h, and the obtained samples were denoted as S-800A or S-1000A, where S presented the name of as-prepared samples. Before testing, all the samples were pretreated in air at 300 °C or 10 °C H$_2$ (30 ml/min) at 400 °C for 1 h. The samples activated by H$_2$ were denoted with "-ACT".

2. Characterizations

A Philips X’pert Pro diffractometer with Ni filtered Cu Kα1 radiation (0.15408 nm) was used to collect the X-ray powder diffraction (XRD) patterns. The X-ray tube was operated at 40 kV and 40 mA. The average crystallite size of prepared samples was calculated by Scherrer equation.

The specific areas of prepared samples were measured by N$_2$ physisorption at -196 °C on a Micromeritics ASAP-2020 analyzer. Before each test, the samples were degassed at 300 °C for 3 h.

Raman spectra were collected on a Spex 1877 D triplemate spectograph with 2 cm$^{-1}$ resolution at room temperature. The wave number of the laser was 532 nm with a power output of 5 mW.

The high-resolution transmission electron microscopy (HR-TEM) images of prepared samples were taken by a JEM-2100 instrument, operated at 200 kV.

Hi-temperature programmed reduction of prepared samples was conducted on a Quantachrome Autosorb-1C instrument. In each test, sample (ca. 30 mg) was first treated with air at 400 °C for 1 h. Then the sample was cooled down to room temperature in air. After switching the purging gas to H$_2$ (10 % H$_2$/Ar, 30 ml/min), the temperature was linearly
raised from 30 to 900 °C with a ramping rate of 10 °C/min. The signal of H₂ consumption was collected by a thermal conductivity detector (TCD).

X-ray photoelectron spectra (XPS) of prepared samples were collected on a PHI 5000 VersaProbe system, with monochromatic Kr radiation (1486.6 eV) operated at an accelerating power of 15 kV. To compensate the sample charging effects, all binding energies of prepared samples were calibrated with the adventitious C1s peak at 284.6 eV.

The oxygen storage capacity (OSC) values were obtained from a multi-pulse experiment under alternating pulses of 2% CO/4% O₂ (the total flow rate was 100 ml/min). The OSC values at 60, 80, 120, and 160 °C were measured. For each temperature point, the testing duration was 30 min. A single cycle lasted 1 min (30 s / 30 s cycling switch control by MFC systems). The OSC value was calculated from the average CO₂ formation detected by an online mass spectrometer.

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) experiments were conducted on Nicolet iSSO FT-IR spectrometer equipped with an MCT detector cooled by liquid N₂. In each test, ca.28 mg sample was loaded on the Si/SiO₂ substrate. The samples were pre-heated by air at 500 °C or 10% H₂ (30 ml/min) at 400 °C for 1 h. After that, the samples were cooled to room temperature. The background spectra of the catalysts were collected in air at the specific temperature during the cooling process. For CO adsorption/oxidation experiments, the feed gas was set at a flowing rate of 83.33 ml/min (1% CO when needed, 1% O₂ when needed, N₂ in balance). The spectra were collected from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ for 100 scans. The DRIFTS spectra were presented in the form of absorbance.

3. Activity testing method
The CO oxidation and propylene oxidation activities of the samples were evaluated in a fixed-bed reactor. For each test, 25 mg sample (40-60 mesh) was pre-mixed with 250 mg SiC. For CO oxidation activity test, the reactant consisted of 1.0% CO and 1.0% O₂ (Ar in balance) and the reaction was performed under steady conditions. While for CO₂ oxidation test, the reactant consists of 2000 ppm CO and 2% O₂. The reaction was performed under transient conditions with a ramping rate of 2 °C/min. The total flow rate was 83.33 scm with a weight hourly space velocity (WHSV) of 6 and 350, respectively.

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Keywords: Pt single atom • activation treatment • CeO₂ particle size • exhaust emission control


Entry for the Table of Contents

Highly dispersed Pt single atoms were created on a novel CeO$_2$/Al$_2$O$_3$ support (CA-c) with small CeO$_2$ particle size. After activation treatment, excellent catalytic oxidation performance was achieved on Pt/CA-c-ACT, resulted from the smaller Pt clusters with more active ionic Pt sites at the interface of Pt-CeO$_2$. 

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