Activation of Pt Nanoclusters on TiO$_2$ via Tuning the Metallic Sites to Promote Low-Temperature CO Oxidation

Kailin He $^{1,2}$ and Qingyue Wang $^{3,4,*}$

Abstract: Metallic Pt sites are imperative in the CO oxidation reaction. Herein, we demonstrate the tuning of Pt sites by treating a Pt catalyst in various reductive atmospheres, influencing the catalyst activities in low-temperature CO oxidation. The H$_2$ pretreatment of Pt clusters at 200 °C decreases the T$\text{50}$ from 208 °C to 183 °C in the 0.1 wt % Pt/TiO$_2$ catalyst. The T$\text{50}$ shows a remarkable improvement using a CO pretreatment, which decreases the T$\text{50}$ further to 135 °C. A comprehensive characterization study reveals the integrated reasons behind this phenomenon: (i) the extent of PIsO transition to metallic Pt sites, (ii) the ample surface active oxygen triggered by metallic Pt, (iii) the CO selectively adsorbs on metallic Pt sites which participate in low-temperature CO oxidation, and (iv) the formation of the unstable intermediate such as bicarbonate, contributes together to the enhanced activity of CO pretreated Pt/TiO$_2$.

Keywords: reduction pretreatment; metallic Pt sites; CO adsorption; CO oxidation; reactive intermediate

1. Introduction

Low-temperature CO oxidation is one of the most investigated model reactions in the field of heterogeneous catalysis [1]. The CO oxidation is not only important in practical applications (e.g., automotive emission control [2,3] and remediation of flue gas [4,5]) but also acts as a probe reaction guiding the design of catalysts’ surface properties [6]. The adsorption of CO on active sites of catalyst surface is a crucial step that controls CO oxidation reaction rates, and it is especially true for noble metal catalysts [7]. The linear CO adsorbed on metallic Pt sites that can facilely react with atmospheric O$_2$ is responsible for the high activity in the low-temperature CO oxidation [8]. The ionic Pt reacts with linear CO when the temperature is higher than 100 °C. This required reduction pretreatment of Pt/TiO$_2$ to obtain high activity in the low-temperature CO oxidation. On the other hand, the pretreatment conditions influence the peroxide and superoxide generated by O$_2$ adsorption at the metal-support interface that determines the catalytic performance [9,10]. As a critical step of CO oxidation, pretreatment can modify the chemical properties of catalyst and alter the reaction pathway [11,12]. Maldonado-Hodar’s group [13] studied the influence of treatments in the reductive atmosphere (i.e., H$_2$) and inert atmosphere (i.e., He) on the performance of Pt/TiO$_2$. They found that the reduction pretreatment by H$_2$ favored the formation of oxygen vacancies and facilitated the diffusion of Pt species into the TiO$_2$. The Pt–TiO$_2$ interface and the active surface sites were suppressed by He pretreatment, leading to unsatisfactory activity in the selective citral hydrogenation. Reduction pretreatment in CO also promotes the activity, as evidenced by the CO oxidation over Pt/CoO$_2$-Al$_2$O$_3$ catalyst. The CO pretreatment induces a more reduced Pt with a low Pt-O coordination number than the catalysts pretreated in H$_2$ or C$_3$H$_6$, leading to
enhanced activity in diesel oxidation reaction [14]. Moreover, investigations on Au/CeO₂ catalyst pretreated in O₂, N₂, CO, and H₂ suggest that the long-term activity is dominated by the reducibility of the support and the particle size [15]. It is generally accepted that the reductive atmosphere has a significant impact on both the chemical status and morphology of noble metal and thus varies the activity of the catalysts. However, the difference of the reductant atmospheres (e.g., CO and H₂) on the transition of active sites (e.g., Pt⁰, Pt⁺ sites) and surface oxygen species (e.g., O₂⁻ ads, O⁻ ads) and roles they play in the reaction are still unclear and require detailed investigations.

In this work, the tuning of Pt sites in Pt/TiO₂ was carried out by a mild reduction in the atmospheres of H₂ and CO, respectively. The influences on the chemical and surface properties of Pt/TiO₂ catalyst were investigated by a combination of surface characterization (e.g., X-ray photoelectron spectroscopy (XPS)), H₂ temperature-programmed reduction (H₂-TPR), O₂ temperature-programmed desorption (O₂-TPD)). The impact of reduction pretreatment on the structural characters of Pt/TiO₂ was studied by the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The transition of Pt active adsorption sites and the reactive intermediates were investigated by the CO adsorption using an in situ diffuse reflectance infrared Fourier transform spectroscopy (In situ DRIFTS). Furthermore, the catalytic performance of Pt/TiO₂ catalysts was studied by both in situ and ex situ CO oxidation to identify the influence of pretreatments on catalyst surface species.

2. Results

2.1. Chemical and Structural Modifications

The Pt/TiO₂-H₂ and Pt/TiO₂-CO catalysts have XRD patterns similar to that of Pt/TiO₂ (Figure 1a), showing primarily anatase TiO₂ (JCPDS No. 21-1272) with crystal planes (101) (004), (200), (105), (211), (204), (116), (220), and (215). The characteristic peak at 27.34° is assigned to TiO₂ rutile (110) (JCPDS No. 21-1276). The absence of Pt characteristic peak in the XRD patterns indicates a good dispersion of Pt nanoclusters [16,17]. A slight shift of anatase TiO₂ (101) from 25.30° to 25.34° is detected on Pt/TiO₂-H₂, implying a distortion of TiO₂ lattice caused by the interaction of Pt species [18,19]. The crystal sizes of TiO₂ for Pt/TiO₂ catalysts are 17.1 ± 0.3 nm, as calculated in Table S1 by the Debye–Scherrer equation from the XRD patterns in Figure 1a.

![Figure 1](image_url)

**Figure 1.** (a) XRD patterns, (b) micro-Raman spectra, and (c) N₂ adsorption–desorption isotherm of Pt/TiO₂, Pt/TiO₂-H₂, and Pt/TiO₂-CO catalysts.

The micro-Raman spectra of Pt/TiO₂, Pt/TiO₂-H₂, and Pt/TiO₂-CO catalysts in Figure 1b are characterized by the vibrational modes of 144 cm⁻¹ (E₉(1)), 197 cm⁻¹ (E₉(2)), 396 cm⁻¹ (B₁g), 516 cm⁻¹ (A₁g), and 639 cm⁻¹ (E₉(3)) of TiO₂ anatase phase, and 453 cm⁻¹ (E₉(3)) of TiO₂ rutile phase (Figure 1b) [20]. The blue shifts of E₉(1) modes at 144 cm⁻¹ are observed for Pt/TiO₂-H₂ and Pt/TiO₂-CO that shift to 146 cm⁻¹ and 148 cm⁻¹, respectively. Meanwhile, peak broadening is found for both the Pt/TiO₂-H₂ and Pt/TiO₂-CO catalysts. This is determined by a full width at half maximum (FWHM) of E₉(1) modes of 14 cm⁻¹ and 16 cm⁻¹ for Pt/TiO₂-H₂ and Pt/TiO₂-CO catalysts, respectively, in comparison to an FWHM of 12 cm⁻¹ for Pt/TiO₂ (Table S2). The peak shift and broadening indicate the
lattice distortion and the defect formation [16] trigger by reduction pretreatments [21]. Additionally, the porous structure of the three Pt/TiO₂ catalysts is comparable with a surface area of 64.0 ± 1.8 m²/g and a pore volume of 0.30 ± 0.02 cm³/g (Figure 1c and Table 1).

Table 1. Surface species concentrations (based on XPS peak area) and porous properties of Pt/TiO₂, Pt/TiO₂-H₂, and Pt/TiO₂-CO catalysts.

| Catalysts     | BET Surface Area (m²/g) | Pore Volume (cm³/g) | Pore Size (nm) | Pt⁰/(Pt⁰ + Pt²⁺) | O_ads/(O_latt + O_ads) | Ti³⁺/(Ti³⁺ + Ti⁴⁺) |
|---------------|--------------------------|---------------------|----------------|------------------|------------------------|---------------------|
| Pt/TiO₂       | 62.2                     | 0.3                 | 14.2           | 16.7%            | 12.5%                  | 4.5%                |
| Pt/TiO₂-H₂    | 65.8                     | 0.3                 | 13.6           | 23.7%            | 16.5%                  | 3.8%                |
| Pt/TiO₂-CO    | 65.0                     | 0.3                 | 14.9           | 46.9%            | 17.0%                  | 4.5%                |

The chemical status of Pt and surface composition of Pt/TiO₂ catalysts are characterized by the X-ray photoelectron spectroscopy (XPS) spectra with Pt 4f, O 1s, and Ti 2p narrow scan spectra in Figure 2a–c. The influence of air exposure on a sample before the XPS test is negligible for it happened at room temperature (ca., 25 °C), which is much lower than the reduction pretreatment temperature of 200 °C. In the presence of an overlapping Ti loss peak at around 75 eV [22], the Pt 4f spectra of Pt/TiO₂ catalysts exhibit Pt⁰ at 71.00 eV, 74.35 eV [23] and Pt²⁺ at 72.40 eV, 75.75 eV [24]. Though the signal-to-noise ratio (S/N) problem occurs for the catalyst with a low loading ratio of Pt on TiO₂ (i.e., 0.1 w.t.% [22], the tendency of Pt valence state change over reduction pretreatments can be recognized. The ratio of metallic Pt⁰ of Pt/TiO₂ catalyst without pretreatment is 16.7% (Table 1), which is lower than the H₂-pretreated (i.e., 23.7%) and CO-pretreated catalysts (46.9%). Almost a half of Pt in Pt/TiO₂-CO being metallic Pt suggests that CO reduced Pt effectively. Meanwhile, the O 1s spectra in Figure S1 exhibits two peaks belonging to lattice oxygen (O_latt) at 529.78 eV and oxygen species adjacent to oxygen vacancies (O_ads) at 531.44 eV [25,26]. The ratio O_ads/(O_latt + O_ads) of reduced Pt/TiO₂ catalysts in Table 1 is close to 17.0%, which is higher than that of un-pretreated Pt/TiO₂ (i.e., 12.5%). This indicates that the reduction pretreatment facilitates the adsorption of oxygen on the catalyst surface by producing metallic Pt, as schemed in Figure 2 [27,28].

The structural modifications of Pt/TiO₂ catalysts are studied using high-resolution, high-angle annular dark-field (HAADF) scanning transmission electron microscopy. All three catalysts present a spherical morphology with a TiO₂ particle size of 20 ± 2 nm that is similar to the P25 TiO₂ support. The bright points of 2 nm in the dark-field STEM micrographs and elemental map of Pt in Figure 2d–f indicate the existence of Pt nanoclusters in all the Pt/TiO₂ catalysts. A slight aggregation of Pt nanoparticles is observed on the Pt/TiO₂ pretreated by H₂ in Figure 2e. This might be due to the particle migration and coalescence in H₂ during heating treatment [29].
Figure 2. Up: Schematic diagram of the Pt/TiO\textsubscript{2} pretreated in H\textsubscript{2} and CO; Down: (a–c) XPS narrow spectra of Pt 4f for (a) Pt/TiO\textsubscript{2}, (b) Pt/TiO\textsubscript{2}-H\textsubscript{2}, and (c) Pt/TiO\textsubscript{2}-CO catalysts; and (d–f) high-resolution, high-angle annular dark-field (HAADF) STEM images, EDS-mapping and size distribution of (d) Pt/TiO\textsubscript{2}, (e) Pt/TiO\textsubscript{2}-H\textsubscript{2}, and (f) Pt/TiO\textsubscript{2}-CO catalysts.

2.2. Surface Reduction Properties

The temperature-programmed studies (i.e., O\textsubscript{2}-TPD, H\textsubscript{2}-TPR) are performed to analyze the surface properties of the Pt/TiO\textsubscript{2} catalysts prior to and after the reduction pretreatments. The surface adsorbed oxygen is determined by the O\textsubscript{2}-TPD, and the desorption profiles for the three Pt/TiO\textsubscript{2} catalysts are shown in Figure 3a. The desorption peak at 120 °C to 250 °C is attributed to the superoxide O\textsuperscript{2−}\textsubscript{ads} [30]. The amount of O\textsuperscript{2−}\textsubscript{ads} is improved after the reduction pretreatment in CO and H\textsubscript{2}, and the desorption temperatures of O\textsuperscript{2−}\textsubscript{ads} on Pt/TiO\textsubscript{2}-CO (i.e., 187 °C) and Pt/TiO\textsubscript{2}-H\textsubscript{2} (i.e., 190 °C) are lower than the one of unpretreated Pt/TiO\textsubscript{2} (i.e., 202 °C). The desorption peak from 350 °C to 550 °C is assigned to the dissociatively adsorbed peroxide O\textsuperscript{2−}\textsubscript{ads} [30] on Pt/TiO\textsubscript{2} catalysts that participate in low-temperature CO oxidation [31]. The O\textsuperscript{2−}\textsubscript{ads} peak area of the Pt/TiO\textsubscript{2}-CO at 350 °C to 550 °C is the largest, followed by Pt/TiO\textsubscript{2}-H\textsubscript{2}, and Pt/TiO\textsubscript{2} shows the smallest O\textsuperscript{2−} area, similar to pristine TiO\textsubscript{2}. The superoxide and peroxide in Pt/TiO\textsubscript{2}-CO facilitate the oxidation of CO at low temperatures, indicating an elevated activity of the catalyst.
The redox property of the Pt/TiO$_2$, Pt/TiO$_2$-CO, and Pt/TiO$_2$-H$_2$ catalysts is evaluated by H$_2$-TPR profiles shown in Figure 3b, and the H$_2$ consumption summarized in Table S3. The reduction peak at 119 °C that is only observed on the Pt/TiO$_2$ catalyst is ascribed to the reduction of PtO$_x$ to metallic Pt [32]. The absence of PtO$_x$ reduction on Pt/TiO$_2$-CO, and Pt/TiO$_2$-H$_2$ suggests that the majority of Pt on the catalyst surface are in the form of metallic Pt. The reduction that occurs at 314 °C is assigned to the partial reduction of surface oxygen, as induced by hydrogen spillover from Pt to the TiO$_2$ surface [21,32,33]. The pure TiO$_2$ only presents a reduction of lattice oxygen at a temperature higher than 600 °C [33]. These results show that the reduction peak of surface oxygen only presents in the presence of Pt, which is indicative of a strong Pt-TiO$_2$ interaction that produces oxygen vacancy for the dissociative oxygen adsorption. Furthermore, Pt/TiO$_2$ consumes more H$_2$ (i.e., 0.40 mmol/g) during H$_2$-TPR than the H$_2$ required by Pt/TiO$_2$-CO (i.e., 0.32 mmol/g) and Pt/TiO$_2$-H$_2$ (i.e., 0.29 mmol/g). The suppression of PtO$_x$ reduction peak and low H$_2$ consumption for Pt/TiO$_2$-H$_2$ and Pt/TiO$_2$-CO catalysts confirm the transition from ionic Pt to metallic Pt by H$_2$ or CO pretreatment, which is in line with XPS results (Figure 2).

2.3. Catalytic Performance

The catalytic performance of un-pretreated Pt/TiO$_2$ and the two pretreated Pt/TiO$_2$ catalysts in H$_2$ (i.e., Pt/TiO$_2$-H$_2$) and CO (i.e., Pt/TiO$_2$-CO) are evaluated by the CO oxidation in Figure 4. It is noteworthy that the Pt/TiO$_2$-CO exhibits a significantly enhanced activity, with a much lower temperature for 50% conversion (i.e., $T_{50}$) of 135 °C, as compared to 184 °C of Pt/TiO$_2$-H$_2$ and to 203 °C of the catalyst without pretreatment. Complete oxidation of CO is achieved at 150 °C (i.e., $T_{100}$) by Pt/TiO$_2$-CO, while the Pt/TiO$_2$ and Pt/TiO$_2$-H$_2$ require high temperatures of 210 °C and 190 °C, respectively. Figure 4b presents the Arrhenius plots of the three Pt/TiO$_2$ catalysts. The apparent activation energies calculated from the slopes of the fitting lines are 63.4 kJ/mol, 56.1 kJ/mol, 41.2 kJ/mol for Pt/TiO$_2$, Pt/TiO$_2$-H$_2$, and Pt/TiO$_2$-CO, respectively. It is found that the CO reduction pretreatment produces a high ratio of metallic Pt sites over ionic Pt sites (i.e., 46.9%) as indicated by the XPS spectra in Figure 2, and abundant surface oxygen species (e.g., O$_{2-}$,ads) as suggested by the temperature-programmed studies in Figure 3, which promotes the oxidation at low-temperatures [34]. The related mechanism is discussed in Section 2.4 by in situ DRIFTs that explore the adsorbed intermediates of CO adsorption and the reaction pathway of CO oxidation.
2.3. In Situ CO Adsorption–Desorption–Oxidation

Figure 5 plots in situ DRIFT spectra of CO + O₂ at 200 °C, where the CO adsorption is carried out in 2 vol.% CO/N₂ for 10 min, followed by purging in N₂ for 15 min, and the oxidation is carried out by introducing O₂ for 6 min. The CO exhibits four types of IR vibrations that centered at 2171 cm⁻¹ for gaseous CO [32,34,35], at 2117 cm⁻¹ for CO adsorbed on Pt sites (Pt⁰-CO) [34–36], at 2090 cm⁻¹ for CO adsorbed on metallic Pt with Ptₐ₉) neighbor (Pt⁷⁺-CO) [32,34,35,37], and at 2078 cm⁻¹ for linear CO adsorbed on Pt sites (Pt⁶⁺-CO) [34–36,38] (Table S1). CO adsorbed on Pt species is barely observed on unpretreated Pt/TiO₂ catalyst at 1 min (Figure 5a), implying that CO adsorption on predominant Pt²⁺ sites takes place slowly at 200 °C. A fast CO adsorption occurred on the pretreated catalysts that have Pt⁰ sites. Both Pt/TiO₂-H₂ and Pt/TiO₂-CO exhibit the adsorbed CO at 1 min, with Pt⁰-CO and Pt²⁺-CO on Pt/TiO₂-H₂ (Figure 5b), and only Pt⁰-CO on Pt/TiO₂-CO (Figure 5c). The absence of Pt²⁺-CO on Pt/TiO₂-CO at 1 min demonstrates that CO pretreatment converted the surface Pt species to Pt⁰ more effectively than H₂ pretreatment, and Pt⁰ adsorbed CO faster than Pt²⁺. When the adsorption is launched for 2 min, the CO is adsorbed on unpretreated Pt/TiO₂ primarily in the form of Pt²⁺-CO, followed by Pt⁷⁺-CO and Pt⁶⁺-CO (Figure 5a). The CO adsorbed on Pt⁰ sites accumulates on the surface of Pt/TiO₂ catalyst for 2 min, and the intensity of Pt²⁺-CO declines simultaneously (Figure 5a,d). This indicates that the fed CO in the CO adsorption triggers the reduction of the unpretreated Pt/TiO₂ [24,34].
N\textsubscript{2} is purged at 200 °C from 10 min to 25 min to remove the weakly adsorbed CO. The CO adsorbed on Pt\textsuperscript{0} of unpretreated Pt/TiO\textsubscript{2} starts to drop at 10 min with the increasing Pt\textsuperscript{2+}-CO in N\textsubscript{2} flow (Figure 5a,d), indicating that the Pt\textsuperscript{0} sites created by the CO adsorption for only 10 min are unstable that facilely transfer to Pt\textsuperscript{2+}. In contrast, a transition from Pt\textsuperscript{0} to Pt\textsuperscript{2+} is not observed on the pretreated samples (Figure 5b,c,e,f), instead, the intensity of Pt\textsuperscript{2+}-CO decreases because of the desorption of CO in N\textsubscript{2}. In the spectra obtained after CO adsorption and N\textsubscript{2} purging (Figure S2), the ratio of the CO on metallic Pt peak area of Pt/TiO\textsubscript{2}-H\textsubscript{2} and Pt/TiO\textsubscript{2}-CO are 99% and 93%, respectively, both higher than that of Pt/TiO\textsubscript{2} (i.e., 72%), indicating that H\textsubscript{2} and CO reduction triggers the transition of Pt\textsuperscript{2+} to Pt\textsuperscript{b+} and Pt\textsuperscript{0}, which is consistent with the XPS (Figure 2) and H\textsubscript{2}-TPR (Figure 4b) analysis.

The CO adsorbed on metallic Pt (i.e., Pt\textsuperscript{0}-CO and Pt\textsuperscript{b+}-CO) for all the three catalysts is completely disappeared after feeding O\textsubscript{2} for 6 min, as shown in Figure 5. The CO adsorbed on ionic Pt accumulates on the catalyst surface of unpretreated Pt/TiO\textsubscript{2} (Figure 5d) and H\textsubscript{2} pretreated Pt/TiO\textsubscript{2} (Figure 5e), especially on the unpretreated Pt/TiO\textsubscript{2}, which is in line with its low activity in Figure 4. This confirms that the metallic Pt sites act as the active sites for the low-temperature CO oxidation [34]. When introducing oxygen at 25 min after the saturation adsorption of CO on the catalysts, a change of CO\textsubscript{2} intensity is observed for the three catalysts (Figure S4). The Pt/TiO\textsubscript{2}-H\textsubscript{2} and Pt/TiO\textsubscript{2}-CO produced more CO\textsubscript{2} than Pt/TiO\textsubscript{2} as their CO\textsubscript{2} intensities increase more than Pt/TiO\textsubscript{2}. The weaker CO\textsubscript{2} peak intensity of Pt/TiO\textsubscript{2} at 31 min indicates that not all CO adsorbed on Pt\textsuperscript{0} converts to CO\textsubscript{2}, but also transfers to Pt\textsuperscript{2+} to form Pt\textsuperscript{2+}-CO, where the Pt\textsuperscript{2+} is originated from the re-oxidation of Pt\textsuperscript{0} under the oxidative condition. The disappearance of adsorbed CO is monitored on Pt/TiO\textsubscript{2}-CO when introducing O\textsubscript{2} only for 2 min (Figure 5f). The high activity of Pt/TiO\textsubscript{2}-CO in CO oxidation in Figure 4 is due to the plentiful metallic Pt sites (Figure 2) created by CO pretreatment, which promotes both CO adsorption and CO oxidation at low
temperature [34,35]. Furthermore, studies of Pt catalysts pretreated in CO have shown that CO assists the transition of higher coordination number of Pt at larger wavenumber to lower coordination number of metallic Pt (i.e., Pt\(^0\)-CO) at smaller wavenumber more effectively than H\(_2\) [14]. It provides active sites for CO adsorption and low-temperature oxidation [39], considering that the Pt\(^{2+}\) sites are less active in low-temperature CO oxidation and the oxygen-surrounding Pt\(^{6+}\) partially deactivates the sites [34].

The species that formed during the CO adsorption, desorption and oxidation are presented in Figure 6 for Pt/TiO\(_2\), Pt/TiO\(_2\)-H\(_2\), and Pt/TiO\(_2\)-CO catalysts. Carboxylate, which has the structure of -CO\(_2\)\(^-\), with C atom or C and O atoms binding on the support, is found on all the three Pt/TiO\(_2\) catalysts with characteristic IR vibrations of asymmetric stretching mode at 1542 cm\(^{-1}\) and symmetric stretching mode at 1361 cm\(^{-1}\) [40]. Carbonate species at 1438 cm\(^{-1}\) [41] is only observed on unpretreated Pt/TiO\(_2\) after the CO adsorption (Figure 6a). The carboxylate requires a lower energy barrier to be reacted to CO than that of carbonate species [42]. Moreover, the bidentate carbonate at 1315 cm\(^{-1}\) [41] is produced at 31 min on Pt/TiO\(_2\) (Figure 6a) and Pt/TiO\(_2\)-H\(_2\) (Figure 6b), along with the partial oxidation of Pt\(^0\) to Pt\(^{2+}\) (Figure 5a,b). It implies that adsorbed CO is transformed to bidentate carbonates in O\(_2\). No carbonates species are found on in situ DRIFT spectra of Pt/TiO\(_2\)-CO in Figure 6c for the whole CO adsorption–desorption–oxidation process, which is in line with its high activity in the CO oxidation in Figure 4.

![Figure 6](image-url)

**Figure 6.** The carbonaceous species presented on in situ DRIFT spectra in the CO adsorption–desorption–oxidation for (a) Pt/TiO\(_2\), (b) Pt/TiO\(_2\)-H\(_2\), and (c) Pt/TiO\(_2\)-CO catalysts at 200 °C. (Note: In situ DRIFT study was carried in 2 vol.%CO for 10 min, in N\(_2\) for 15 min, and in O\(_2\) for 6 min.)

### 2.4.2. In Situ CO Oxidation

In situ DRIFT spectra of the CO oxidation (i.e., CO/O\(_2\) condition) in Figure 7 are obtained in an atmosphere containing 0.7 vol.% CO and 16 vol.% O\(_2\). The temperature program with an interval of 15 °C is set up for each catalyst according to the corresponding light-off curve in Figure 5. The unpretreated Pt/TiO\(_2\) in Figure 7a displays both Pt\(^{2+}\)-CO at 2117 cm\(^{-1}\) and Pt\(^0\)-CO at 2071 cm\(^{-1}\) at 150 °C, and consumption of the Pt\(^0\)-CO occurs when the temperature is higher than 180 °C, implying that CO oxidation takes place at the metallic Pt sites with CO adsorbed. The Pt\(^0\)-CO disappears as it is fully converted to CO\(_2\), leaving CO adsorbed on Pt\(^{2+}\) participates in the high-temperature oxidation. Similarly, it is also true for the pretreated Pt/TiO\(_2\) catalysts in Figure 7b,c that the ratio of Pt\(^{2+}\)-CO...
to Pt\(^0\)-CO becomes predominant along with increasing temperatures. Bicarbonates at 1608 cm\(^{-1}\) (\(\nu_{as}\)) and 1627 cm\(^{-1}\) (\(\nu_s\)) are reactive intermediates in the CO oxidation for Pt/TiO\(_2\) catalysts, implying a reaction pathway that CO converted to bicarbonates before transiting to CO\(_2\) (Figure S5) [40].

**Figure 7.** In situ DRIFT spectra in the CO oxidation for (a) Pt/TiO\(_2\), (b) Pt/TiO\(_2\)-H\(_2\), and (c) Pt/TiO\(_2\)-CO catalysts; and IR intensity of (d) Pt\(^0\)-CO and (e) Pt\(^2+\)-CO as a function of temperatures.

Figure 7d,e summarizes the IR intensity of Pt\(^0\)-CO and Pt\(^2+\)-CO as a function of reaction temperature. The Pt\(^0\)-CO peak intensity of Pt/TiO\(_2\), Pt/TiO\(_2\)-H\(_2\), and Pt/TiO\(_2\)-CO reaches their summit at 180 °C, 180 °C, and 150 °C, respectively, which correspond with their activity tests in Figure 4a (i.e., the T\(_{100}\) of 210 °C, 190 °C, 150 °C, respectively). The Pt\(^0\)-CO peak intensity of Pt/TiO\(_2\)-CO at low temperature is higher than those of the Pt/TiO\(_2\)-H\(_2\) and Pt/TiO\(_2\)-CO, indicating that Pt/TiO\(_2\)-CO owns high CO adsorption capacity. The Pt\(^2+\)-CO accumulates up to a temperature of 255 °C in Figure 7e, which is much higher than Pt\(^0\)-CO, implying that CO is adsorbed more strongly on Pt\(^2+\) than Pt\(^0\)-CO [35,36] upon exposure to the reactant gases. These results are consistent with the literature [35,43] that linear CO adsorbed on metallic Pt is responsible for reacting in the low-temperature CO oxidation, while the CO adsorbed on ionic Pt participates in the CO oxidation along with the increasing temperature. The abundant metallic Pt sites introduced by the reduction pretreatment, especially the CO pretreatment, are responsible for the high activity in the low-temperature CO oxidation.
3. Discussion

The reduction assists the formation of the metallic Pt, which is responsible for the oxygen activation at the metal–support interface. This is related to the electron transfer from platinum to titanium, forming Pt–O–Ti$^{3+}$ sites, leading to more oxygen vacancy for the dissociative oxygen adsorption (Figure 3) [27]. The abundant adsorbed superoxide and peroxide produced on the catalyst surface participate in the Langmuir–Hinshelwood (L–H) mechanism at low temperatures. The oxygen activation capacity of Pt/TiO$_2$ is elevated by the CO and H$_2$ pretreatment. Moreover, in the reaction gas, the adsorbed oxygen on the catalyst surface assists the direct transition of bicarbonate intermediates to CO$_2$ instead of forming carbonate, which could inhibit CO oxidation [44]. On the basis of the above considerations, the reductive pretreatment of Pt/TiO$_2$ catalyst by H$_2$ and CO enhances the catalytic performance over CO oxidation reaction.

CO adsorption is also influenced by the factors such as dispersion of Pt on TiO$_2$ support and the coordination number of Pt sites to O [34]. The reductive pretreatment at 200 $^\circ$C in CO can not trigger the particle migration and coalescence that enlarge the particle size [14,29]. The Pt/TiO$_2$ after CO and H$_2$ pretreatment varies from pristine Pt/TiO$_2$ in valence state, presenting more metallic Pt sites. The reduction extent of H$_2$ and CO in this work is consistent with the results reported on Pt/CeO$_2$–Al$_2$O$_3$ catalyst [14]. CO pretreatment generates more metallic Pt with a low Pt-O coordination number than H$_2$ pretreatment. The strength of CO adsorption on metallic Pt is weaker than ionic Pt [36], and thus the CO on metallic Pt reacts with oxygen at lower temperatures [34], leading to a remarkable CO oxidation activity.

4. Materials and Methods

4.1. Materials

The PtCl$_4$ (99%) and TiO$_2$ (P25, 20 nm, 99%) were purchased from Macklin Inc. (Shanghai, China). All chemicals were used as received without further purification. The deionized water was generated from a Master-Q (Hitech, Shanghai, China) water purification system.

4.2. Catalyst Preparation

The 0.1 wt.% Pt/TiO$_2$ catalyst was synthesized by an incipient wetness impregnation method. The P25 TiO$_2$ powder (0.1 mol, 8 g) was dispersed in 5.5 mL deionized water by stirring to obtain a homogenous slurry. The slurry was dried at 120 $^\circ$C for 6 h, then calcined in a programmable furnace at 450 $^\circ$C for 4 h with a heating rate of 5 $^\circ$C/min. The TiO$_2$ was crushed and sieved to make 40–60 mesh granules. The 1.75 g/L platinum precursor solution was prepared by dissolving 5.25 mg PtCl$_4$ in 3 mL deionized water, and it was dropwise absorbed by 2.625 g TiO$_2$ granules under continuous stirring. The wet granules were dried at 120 $^\circ$C for 6 h and then calcined at 400 $^\circ$C for 4 h with a ramping rate of 5 $^\circ$C/min to obtain 0.1 wt.% Pt/TiO$_2$ catalyst.

Reductive pretreatment of Pt/TiO$_2$ catalyst was performed in a tube furnace in 2 vol.% H$_2$/Ar and in 2 vol.% CO/N$_2$ at 200 $^\circ$C for 2 h to obtain Pt/TiO$_2$-H$_2$ and Pt/TiO$_2$-CO catalysts, respectively. After pretreatments, the catalysts were swept by N$_2$ for 15 min to remove the physically adsorbed gas molecules.

4.3. Catalysts Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 X-ray diffractometer (XRD) using Cu Ka radiation ($\lambda = 1.54178$ Å). Micro-Raman spectra of catalysts were generated by a LabRAM ARAMIS micro-Raman spectrometer (HORIBA Scientifics, Kyoto, Japan) with an excitation laser of 532 nm. N$_2$ physisorption of the granular samples was conducted on a V-sorb 2800 P surface area and porosimetry analyzer (Gold APP Instruments), before which the samples were outgassed in vacuum at 120 $^\circ$C for 2 h. High-resolution transmission electron microscopy (HRTEM) patterns were collected on an FEI (Hillsboro, OR, USA) Talos F200S and analyzed by the Gatan Digital Micrograph program.
X-ray photoelectron spectra (XPS) were analyzed by a Thermo Fisher Scientific (Waltham, MA, USA) K-alpha, with the binding energy calibrated to C 1s at 284.8 eV.

The O$_2$ temperature-programmed desorption (O$_2$-TPD), H$_2$ temperature-programmed reduction (H$_2$-TPR), and CO pulse chemisorption were performed on an AutoChem II 2920 automated chemisorption analyzer equipped with a thermal conductivity detector (TCD) detector. A total of 0.1 g granular catalyst was packed into the reactor of the chemisorption analyzer. The pretreatment was performed in a He atmosphere at 200 °C for 60 min for the O$_2$-TPD, H$_2$-TPR, and the CO pulse chemisorption measurements. The O$_2$ adsorption was conducted at 50 °C for 60 min in 10 vol.% O$_2$/He flow at a rate of 50 mL/min, and then the temperature program was carried out in He flow from 50 °C to 600 °C at a heating rate of 10 °C/min. A total of 10 vol.% H$_2$/Ar was used in H$_2$-TPR experiment, with a temperature ramping rate of 10 °C/min from 50 °C to 450 °C. The CO pulse chemisorption was carried out at room temperature to estimate the Pt diameter of the Pt/TiO$_2$ catalyst, and prior to the CO chemisorption, the sample was reduced by H$_2$/Ar at 450 °C for 30 min.

The in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) for CO adsorption (i.e., CO + O$_2$) and CO oxidation (i.e., CO/O$_2$) was performed using a Thermo Fisher Nicolet iS20 Fourier transform infrared (FTIR) spectrometer equipped with a Mercury–Cadmium–Telluride (MCT) detector. Each spectrum was recorded for 8 scans at a resolution of 8 cm$^{-1}$. The sample was loaded into the Harrick reaction cell with ZnSe windows and purged at 200 °C in 50 mL/min N$_2$ for 30 min. A background spectrum was recorded at 200 °C before in situ DRIFTS measurements of the CO adsorption. A total of 2 vol.% CO/N$_2$ was passed through the catalyst bed for 10 min, followed by N$_2$ purging for 15 min, and by O$_2$ feeding for 6 min. In the CO oxidation DRIFTS measurements, the background spectra of Pt/TiO$_2$, Pt/TiO$_2$-H$_2$, and Pt/TiO$_2$-CO under N$_2$ flow were recorded at 150 °C, 135 °C, and 90 °C, respectively. As the reaction gas (0.7 vol.% CO, 16 vol.% O$_2$, balanced with N$_2$) passed through the catalyst bed, the spectra were recorded at a temperature interval of 15 °C. For each temperature, 5 min was maintained to reach the equilibrium.

4.4. Catalytic Performance Tests

The CO oxidation was carried out in a stainless-steel tubular reactor (ID = 15 mm) encased by a tubular furnace with a thermocouple inserted in the reactor above the catalyst bed. A total of 2.5 g catalyst (40–60 mesh) was packed into the fixed bed reactor to generate a 17 mm-high catalyst bed. The gas hourly space velocity (GHSV) was 32,000/h as the flow rate of the reaction gases was 1600 mL/min. The large GHSV rules out the mass transfer limitation. Typically, the components of the reaction gases were 0.7 vol.% CO, 16 vol.% O$_2$, 0 vol.% NO, and N$_2$ for balance. The reactant gases were modulated by the mass flow controller and pre-mixed in a chamber before feeding into the reactor. The catalytic performance was evaluated by analyzing the exhaust gases using a GASMET, DX4000 FTIR gas analyzer.

5. Conclusions

The Pt/TiO$_2$ surface composition and textural properties were significantly modified after the reduction treatment in H$_2$ and CO at 200 °C. Reduction pretreatment improved the catalytic performance of Pt/TiO$_2$ in low-temperature oxidation by facilitating the formation of metallic Pt sites that can adsorb CO effectively. The unpretreated Pt/TiO$_2$ with insufficient metallic Pt sites adsorbed CO on Pt$^{2+}$, which participate in the oxidation reaction at elevated temperatures. The carbonate species on the unpretreated catalyst is hard to convert to CO$_2$, leading to low activity. CO pretreatment is more effective than H$_2$ pretreatment to trigger the reduction of Pt$^{2+}$ to Pt$^0$ with low coordination numbers, which exhibits the most remarkable CO adsorption and oxidation property at low temperatures. The metallic Pt sites triggered by the CO reduction are more stable upon oxygen exposure than H$_2$, without transiting to Pt$^{2+}$. The copious metallic Pt sites on the CO-pretreated Pt catalyst facilitate the production of active oxygen species (e.g., O$_2^{-}$ads). The CO adsorbed
on metallic Pt sites participate in low-temperature CO oxidation with the surface oxygen species via the L–H mechanism, presenting bicarbonate as reactive intermediates. As a result, the Pt/TiO2-CO catalyst exhibited high activity with complete oxidation of CO at 150 °C. Thus, it is tentatively concluded that Pt on TiO2 is more activated with thermal pretreatment in an atmosphere of CO than H2.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11111280/s1, Figure S1: XPS narrow spectra of (a) O 1s and (b) Ti 2p of Pt/TiO2, Pt/TiO2-H2 and Pt/TiO2-CO catalysts. Figure S2: The deconvoluted peaks of the IR spectra obtained after CO adsorption and N2 purging at 24 min for (a) Pt/TiO2, (b) Pt/TiO2-H2 and (c) Pt/TiO2-CO. Figure S3: The plots of CO-Ptδ and CO-Ptδ+ peaks intensity to time in CO adsorption–desorption–oxidation. Figure S4. The peak intensity of CO2 in the in situ DRIFT spectra of the CO adsorption–desorption–oxidation for Pt/TiO2, Pt/TiO2-H2, and Pt/TiO2-CO catalysts at 200 °C. Figure S5. The peak intensity of CO2, the integrated peak area of carboxylate and bicarbonate as a function of temperature for (a) Pt/TiO2, (b) Pt/TiO2-H2, and (c) Pt/TiO2-CO. Figure S6: (a) Influence of NO on CO conversion as a function of reaction temperatures, and (b) apparent activation energy (Ea) calculated by the Arrhenius equation of Pt/TiO2, Pt/TiO2-H2, and Pt/TiO2-CO catalysts (R = 8.314 × 10**-3** kJ/(mol K)).

Table S1: Crystal sizes of TiO2 calculated by the Debye–Scherrer equation from the XRD patterns of Pt/TiO2, Pt/TiO2-H2, and Pt/TiO2-CO catalysts. Table S2: Raman shift and full width at half maximum (FWHM) of TiO2 Eg vibration mode obtained from the Raman spectra of Pt/TiO2, Pt/TiO2-H2 and Pt/TiO2-CO catalysts. Table S3: Desorption temperature during O2-TPD of oxygen species and H2 consumption in H2-TPR experiment. Table S4: Vibration mode assignments of IR bands on DRIFTS of Pt/TiO2, Pt/TiO2-H2 and Pt/TiO2-CO catalysts. Table S5: The T100 and T50 in the CO oxidation experiment over Pt/TiO2-CO and Pt/TiO2-CO oxidized in 2 vol. % O2/N2 for 2 h at 200 °C.

Author Contributions: Conceptualization, K.H.; Formal analysis, Q.W., K.H.; Funding acquisition, K.H., Q.W.; Investigation, K.H.; Methodology, K.H., Q.W.; Visualization, Q.W.; Writing—original draft, K.H.; Writing—review and editing, Q.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Changsha science and technology program project funds, grant number kh2005005, the Hunan Special funds for the innovative province construction, grant number 2020GK4055, the Research Start-up Grants-Institute of Zhejiang University-Quzhou, and the Key R&D Program of Hunan province, grant number 2022SK2065.

Data Availability Statement: The data presented in this study are available within the article or supplementary material.

Acknowledgments: The authors thank the China Minmetals Corporation for the financial support from Sci-Tech Innovation project.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References
1. Nan, B.; Fu, Q.; Yu, J.; Shu, M.; Zhou, L.-L.; Li, J.; Wang, W.-W.; Jia, C.-J.; Ma, C.; Chen, J.-X.; et al. Unique structure of active platinum-bismuth site for oxidation of carbon monoxide. *Nat. Commun.* 2021, 12, 3342. [CrossRef]
2. Wang, H.; Liu, J.-X.; Allard, L.F.; Lee, S.; Liu, J.; Li, H.; Wang, J.; Wang, J.; Oh, S.H.; Li, W.; et al. Surpassing the single-atom catalytic activity limit through paired Pt-O-Pt ensemble built from isolated Pt1 atoms. *Nat. Commun.* 2019, 10, 1–12. [CrossRef]
3. Nie, L.; Mei, D.; Xiong, H.; Peng, B.; Ren, Z.; Hernandez, X.I.P.; DeLaRiva, A.; Wang, M.; Engelhard, M.H.; Kovarik, L.; et al. Activation of surface lattice oxygen in single-atom Pt/CoO2 for low-temperature CO oxidation. *Science* 2017, 358, 1419–1423. [CrossRef]
4. Feng, C.; Liu, X.; Zhu, T.; Tian, M. Catalytic oxidation of CO on noble metal-based catalysts. *Environ. Sci. Pollut. Res.* 2021, 28, 24847–24871. [CrossRef]
5. Tripathi, A.; Haresh, C.; Sinthika, S.; Andersson, G.; Thapa, R. CO oxidation on Pt based binary and ternary alloy nanocatalysts: Reaction pathways and electronic descriptor. *Appl. Surf. Sci.* 2020, 528, 146964. [CrossRef]
6. Lin, J.; Wang, X.; Zhang, T. Recent progress in CO oxidation over Pt-group-metal catalysts at low temperatures. *Cuihua Xuebao/Chin. J. Catal.* 2016, 37, 1805–1813. [CrossRef]
7. Newton, M.A.; Ferri, D.; Smolentsev, G.; Marchionni, V.; Nachtegaal, M. Room-temperature carbon monoxide oxidation by oxygen over Pt/Al₂O₃ mediated by reactive platinum carbonates. Nat. Commun. 2015, 6, 1–7. [CrossRef]

8. Beniya, A.; Higashi, S.; Ohba, N.; Jimmouchi, R.; Hirata, H.; Watanabe, Y. CO oxidation activity of non-reducible oxide-supported mass-selected few-atom Pt single-clusters. Nat. Commun. 2020, 11, 1–10. [CrossRef]

9. Guzman, J.; Carrettin, S.; Fierro-Gonzalez, J.C.; Hao, Y.; Gates, B.C.; Corma, A. CO oxidation catalyzed by supported gold: Cooperation between gold and nanocrystalline rare-earth supports forms reactive surface superoxide and peroxide species. Angew. Chem.-Int. Ed. 2005, 44, 4778–4781. [CrossRef]

10. Gerrard, A.L.; Weaver, J.F. Kinetics of CO oxidation on high-concentration phases of atomic oxygen on Pt(111). J. Chem. Phys. 2005, 123, 224703. [CrossRef]

11. Jan, A.; Shin, J.; Ahn, J.; Yang, S.; Yoon, K.J.; Son, J.-W.; Kim, H.; Lee, J.-H.; Ji, H.-I. Promotion of Pt/CeO₂ catalyst by hydrogen treatment for low-temperature CO oxidation. RSC Adv. 2019, 9, 27002–27012. [CrossRef]

12. DeRita, L.; Rasosco, J.; Dai, S.; Bobnov, A.; Thang, H.V.; Hoffman, A.S.; Ro, I.; Graham, G.W.; Bare, S.R.; Pacchioni, G.; et al. Structural evolution of atomically dispersed Pt catalysts dictates reactivity. Nat. Mater. 2019, 18, 746–751. [CrossRef]

13. Bailón-García, E.; Carrasco-Marín, F.; Pérez-Cadenas, A.F.; Maldonado-Hódar, F.J. Influence of the pretreatment conditions on the development and performance of active sites of Pt/TiO₂ catalysts used for the selective citral hydrogenation. J. Catal. 2015, 327, 86–95. [CrossRef]

14. Gänzler, A.M.; Casapu, M.; Vennouix, P.; Loridant, S.; Aires, F.J.C.S.; Epicier, T.; Betz, B.; Hoyer, R.; Grunwaldt, J.D. Tuning the Structure of Platinum Particles on Ceria In Situ for Enhancing the Catalytic Performance of Exhaust Gas Catalysts. Angew. Chem.-Int. Ed. 2017, 56, 13078–13082. [CrossRef] [PubMed]

15. Abd El-Moemen, A.; Abdel-Mageed, A.M.; Bansmann, J.; Parlinska-Wojtan, M.; Behm, R.J.; Kučerová, G. Deactivation of Au/CoO₂ catalysts during CO oxidation: Influence of pretreatment and reaction conditions. J. Catal. 2016, 341, 160–179. [CrossRef]

16. Oh, S.; Ha, H.; Choi, H.; Jo, C.; Cho, J.; Choi, H.; Ryoo, R.; Kim, H.Y.; Park, J.Y. Oxygen activation on the interface between Pt nanoparticles and mesoporous defective TiO₂ during CO oxidation. J. Chem. Phys. 2019, 151, 234716. [CrossRef]

17. Chen, X.; Su, X.; Duan, H.; Liang, B.; Huang, Y.; Zhang, T. Catalytic performance of the Pt/TiO₂ catalysts in reverse water gas shift reaction: Controlled product selectivity and a mechanism study. Catal. Today 2017, 281, 312–318. [CrossRef]

18. Wang, Q.; Li, Z.; Bañeres, M.A.; Weng, L.-T.; Gu, Q.; Price, J.; Han, W.; Yeung, K.L. A Novel Approach to High-Performance Alloyed-Substituted Catalysts—2D Bimetallic MOF-Derived CeCuOₓ Microsheets. Small 2019, 15, 1903525. [CrossRef]

19. Kępiński, Ł.; Wołczyr, M. Microstructure of Pd/CoO₂ catalyst: Effect of high temperature reduction in hydrogen. Appl. Catal. A Gen. 1997, 150, 197–220. [CrossRef]

20. Apopei, P.; Catrinescu, C.; Teodosiu, C.; Roier, S. Mixed-phase TiO₂ photocatalysts: Crystalline phase isolation and reconstruction, characterization and photocatalytic activity in the oxidation of 4-chlorophenol from aqueous effluents. Appl. Catal. B Environ. 2014, 160–161, 374–382. [CrossRef]

21. Wang, Z.; Huang, L.; Su, B.; Xu, J.; Ding, Z.; Wang, S. Unravelling the Promotional Effect of La₂O₃ in Pt/La-TiO₂ Catalysts for CO₂ Hydrogenation. Chem.-A Eur. J. 2020, 26, 517–523. [CrossRef]

22. Macino, M.; Barnes, A.J.; Althabban, S.M.; Qu, R.; Gibson, E.K.; Morgan, D.J.; Freakley, S.J.; Dimitratos, N.; Kiely, C.J.; Gao, X.; et al. Tuning of catalytic sites in Pt/TiO₂ catalysts for the chemoselective hydrogenation of 3-nitrostyrene. Nat. Catal. 2019, 2, 873–881. [CrossRef]

23. Motin, A.M.; Haunold, T.; Bukhitiyarov, A.V.; Bera, A.; Rameshan, C.; Rupperchter, G. Surface science approach to Pt/carbon model catalysts: XPS, STM and microreactor studies. Appl. Surf. Sci. 2018, 440, 680–687. [CrossRef]

24. Li, N.; Chen, Q.-Y.; Luo, L.-F.; Huang, W.-X.; Luo, M.-F.; Hu, G.-S.; Lu, J.-Q. Kinetic study and the effect of particle size on low temperature CO oxidation over Pt/TiO₂ catalysts. Appl. Catal. B Environ. 2013, 142–143, 523–532. [CrossRef]

25. Benkoulà, S.; Sublemonnier, O.; Patanen, M.; Nicolas, C.; Strotti, F.; Naitabdi, A.; Gaié-Lefrel, V.; Antonsson, E.; Aureau, D.; Ouf, F.-X.; et al. Water adsorption on TiO₂ surfaces probed by soft X-ray spectroscopies: Bulk materials vs. isolated nanoparticles. Sci. Rep. 2015, 5, 15088. [CrossRef] [PubMed]

26. Chen, K.; Li, W.; Zhou, Z.; Huang, Q.; Liu, Y.; Duan, Q. Hydroxyl groups attached to Co²⁺ on the surface of Co₃O₄: A promising structure for propanol catalytic oxidation. Catal. Sci. Technol. 2020, 10, 2573–2582. [CrossRef]

27. Kim, G.J.; Lee, S.M.; Hong, S.C.; Kim, S.S. Active oxygen species adsorbed on the catalyst surface and its effect on formaldehyde oxidation over Pt/TiO₂ catalysts at room temperature; Role of the Pt valence state on this reaction? RSC Adv. 2018, 8, 3626–3636. [CrossRef]

28. Huang, H.; Leung, D.Y.C. Complete elimination of indoor formaldehyde over supported Pt catalysts with extremely low Pt content at ambient temperature. J. Catal. 2011, 280, 60–67. [CrossRef]

29. Simonsen, S.B.; Wang, Y.; Jensen, J.O.; Zhang, W. Coarsening of carbon black supported Pt nanoparticles in hydrogen. Nanotechnology 2017, 28, 475710. [CrossRef] [PubMed]

30. Liang, W.; Du, X.; Zhu, Y.; Ren, S.; Li, J. Catalytic oxidation of chlorobenzene over Pd-TiO₂/Pd-Ce/TiO₂ catalysts. Catalysts 2020, 10, 347. [CrossRef]

31. Neumann, S.; Gutmann, T.; Buntkowsky, G.; Paul, S.; Thiele, G.; Sievers, H.; Bäumer, M.; Kunz, S. Insights into the reaction mechanism and particle size effects of CO oxidation over supported Pt nanoparticle catalysts. J. Catal. 2019, 377, 662–672. [CrossRef]
32. Hoang, S.; Guo, Y.; Binder, A.J.; Tang, W.; Wang, S.; Liu, J. (Jimmy); Liu, H.; Lu, X.; Wang, Y.; Ding, Y.; et al. Activating low-temperature diesel oxidation by single-atom Pt on TiO$_2$ nanowire array. *Nat. Commun.* 2020, **11**, 1–10. [CrossRef]

33. Zhang, C.; He, H.; Tanaka, K. Catalytic performance and mechanism of a Pt/TiO$_2$ catalyst for the oxidation of formaldehyde at room temperature. *Appl. Catal. B Environ.* 2006, **65**, 37–43. [CrossRef]

34. Ke, J.; Zhu, W.; Jiang, Y.; Si, R.; Wang, Y.J.; Li, S.C.; Jin, C.; Liu, H.; Song, W.G.; Yan, C.H.; et al. Strong Local Coordination Structure Effects on Subnanometer PtO$_x$ Clusters over CeO$_2$ Nanowires Probed by Low-Temperature CO Oxidation. *ACS Catal.* 2015, **5**, 5164–5173. [CrossRef]

35. Lee, S.M.; Kim, G.J.; Lee, S.H.; Hwang, I.H.; Hong, S.C.; Kim, S.S. Catalytic Performance of Ce$_{0.6}$Y$_{0.4}$O$_2$-Supported Platinum Catalyst for Low-Temperature Water-Gas Shift Reaction. *ACS Omega* 2018, **3**, 3156–3163. [CrossRef]

36. DeRita, L.; Dai, S.; Lopez-Zepeda, K.; Pham, N.; Graham, G.W.; Pan, X.; Christopher, P. Catalyst Architecture for Stable Single Atom Dispersion Enables Site-Specific Spectroscopic and Reactivity Measurements of CO Adsorbed to Pt Atoms, Oxidized Pt Clusters, and Metallic Pt Clusters on TiO$_2$. *J. Am. Chem. Soc.* 2017, **139**, 14150–14165. [CrossRef]

37. Qiao, B.; Wang, A.; Yang, X.; Allard, L.F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt$_1$/FeO$_x$. *Nat. Chem.* 2011, **3**, 634–641. [CrossRef] [PubMed]

38. Cao, S.; Zhao, Y.; Lee, S.; Yang, S.; Liu, J.; Giannakakis, G.; Li, M.; Ouyang, M.; Wang, D.; Sykes, E.C.H.; et al. High-loading single Pt atom sites [Pt-O(OH)$_x$]$_x$ catalyze the CO PROX reaction with high activity and selectivity at mild conditions. *Sci. Adv.* 2020, **6**, eaaba3809. [CrossRef]

39. Liu, A.; Liu, X.; Liu, L.; Pu, Y.; Guo, K.; Tan, W.; Gao, S.; Luo, Y.; Yu, S.; Si, R.; et al. Getting Insights into the Temperature-Specific Active Sites on Platinum Nanoparticles for CO Oxidation: A Combined in Situ Spectroscopic and ab Initio Density Functional Theory Study. *ACS Catal.* 2019, **9**, 7759–7768. [CrossRef]

40. Chernyshova, I.V.; Somasundaran, P.; Ponnurangam, S. On the origin of the elusive first intermediate of CO$_2$ electroreduction. *Proc. Natl. Acad. Sci. USA* 2018, **115**, E9261–E9270. [CrossRef]

41. Chen, S.; Cao, T.; Gao, Y.; Li, D.; Xiong, F.; Huang, W. Probing surface structures of CeO$_2$, TiO$_2$, and Cu$_2$O nanocrystals with CO and CO$_2$ chemisorption. *J. Phys. Chem. C* 2016, **120**, 21472–21485. [CrossRef]

42. Li, J.-J.; Zhu, B.-L.; Wang, G.-C.; Liu, Z.-F.; Huang, W.-P.; Zhang, S.-M. Enhanced CO catalytic oxidation over an Au–Pt alloy supported on TiO$_2$ nanotubes: Investigation of the hydroxyl and Au/Pt ratio influences. *Catal. Sci. Technol.* 2018, **8**, 6109–6122. [CrossRef]

43. Kim, G.J.; Kwon, D.W.; Hong, S.C. Effect of Pt Particle Size and Valence State on the Performance of Pt/TiO$_2$ Catalysts for CO Oxidation at Room Temperature. *J. Phys. Chem. C* 2016, **120**, 17996–18004. [CrossRef]

44. Fujitani, T.; Nakamura, I.; Haruta, M. Role of water in CO oxidation on gold catalysts. *Catal. Lett.* 2014, **144**, 1475–1486. [CrossRef]