

Tuning Metal–Support Interaction of Pt-CeO₂ Catalysts for Enhanced Oxidation Reactivity

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MSI, which is able to balance each step in the catalytic cycle over Pt and $Pt-CeO_2$ interface domains, displays the highest activity for CO/HCHO oxidation under ambient conditions.

KEYWORDS: Pt-CeO₂ catalysts, metal-support interaction, removal of CO and HCHO, catalytic oxidation, mechanistic study

1. INTRODUCTION

Carbon monoxide (CO) and formaldehyde (HCHO) are both indoor air pollutants. Indoor CO is usually produced from incomplete combustion during daily activities,¹ such as cooking and supply heating, while HCHO is commonly emitted from various building and decorative materials.² These two pollutants may even coexist in some special spaces, e.g., storage rooms for vegetables and in submarines.³ Since longterm exposure to CO and HCHO may impose detrimental effects on human health, vast efforts have been devoted to the development of effective approaches for removal of indoor CO and HCHO. Among the developed approaches, catalytic oxidation under ambient conditions without heat/electricity/ light input has been recognized as the most promising. Oxidation of CO and HCHO has been explored over numerous catalysts, including supported noble metals (e.g., Pt,^{4,5} Pd,^{6,7} Au^{8,9}) and base metal oxides (e.g., MnO_2 , 10,1110,11 Co_3O_4 , 12,1312,13 CuO,¹⁴ and their hybrids¹⁵). Most of the developed catalysts target one particular compound but show a much lower activity on the oxidation of the other one. It is more desirable to employ one catalyst that is able to efficiently catalyze the oxidation of a mixture of multipollutants, especially for CO and HCHO, under ambient conditions.

Pt-based catalysts have shown promising performance for the oxidation of CO or HCHO in various studies. High reactivity could be preserved over different supports,¹⁶

extremely low loading,¹⁷ a wide range of relative humidities (RH),¹⁸ etc. CeO₂ is commonly used in three-way catalysts for the removal of CO, hydrocarbon, and nitrogen oxides in exhaust converters of automobiles, and its interaction with supported metal, or the so-called metal-support interaction (MSI), has been generally accepted as one of the key factors influencing the reactivity.¹⁹ In this context, the Pt-CeO₂ catalyst is promising for the efficient oxidation of a CO and HCHO mixture. While the Pt-CeO₂ catalyst has been extensively studied for CO oxidation, its activity under ambient conditions varies distinctly in different literature. For example, Pt-CeO₂ (1.7 wt % Pt) prepared by Jan et al.²⁰ showed no reactivity at 25 °C, as evidenced by the infrared spectra, while Song et al.²¹ observed a decent activity of Pt-CeO₂ for CO oxidation at 25 °C. Boronin et al. recently reported a CO oxidation reactivity below 0 °C over 20 wt % Pt supported on CeO₂; however, the catalyst became inactive below 100 °C if the amount of Pt was decreased to 1 wt %.²² As for HCHO

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oxidation, a rare study has been reported with a mechanistic understanding of HCHO oxidation on $Pt-CeO_2$ catalysts.

The oxidation of CO and HCHO involves a stream of catalytic steps including CO/HCHO adsorption, O2 adsorption and activation, and oxidation of adsorbed molecules/ intermediates, which may happen on the same site and compete with other steps to slow down the whole process. One prominent example is the "CO self-poisoning" phenomenon of Pt-based catalysts (i.e., strong CO adsorption blocks Pt sites, which are thus not accessible for oxygen adsorption and activation). Therefore, the highest reactivity is usually achieved when all of the reaction steps are well coordinated to reach the optimal compromise. MSI has been widely reported to affect the reactivity by regulating the local electronic structures of supported metal particle and metal-support interfaces.¹⁹ Recent studies of MSI over Pt-CeO₂ catalysts for CO oxidation have reported the appropriate local coordination structure of the Pt site with high activity,²³ enhanced reactivity by elongation of the Pt–O bond,²⁴ particle size effect of Pt in the activation of ceria redox chemistry,²⁵ etc. Besides an understanding of the chemical/physical structure of active sites at the atomic level, several studies have focused on the investigation of several particular catalytic steps, such as synergy of active sites for CO adsorption and O supply,²⁶ lattice and interfacial oxygen activation,²⁷ etc. However, it still remains elusive about how MSI affects each catalytic step during the oxidation of CO, as well as HCHO. Moreover, enhancing MSI has been usually reported to be beneficial for the promotion of catalytic performance for a variety of reactions.^{24,25,28} It brings another question: whether this enhancement of MSI is always a benefit?

MSI could be regulated by a variety of approaches, such as crystal plane effect,¹⁴ reduction–oxidation–reduction treatments,²⁹ controlling the particle size of the support³⁰ and metal,³¹ etc., among which tuning the reduction temperature is facile and the most well-known.³⁰ Given that carbon deposition may also influence the reactivity of Pt,³² hydrogen is a more appropriate reductant to tune the MSI than CO and other carbon-containing molecules. Moreover, Pereira-Hernández et al.²⁷ reported that using atom trapping synthesis at 800 °C to prepare the Pt-CeO₂ catalyst precursor showed a superior reactivity than the conventional impregnation method.²⁷ This enhancement was ascribed to the improved reducibility of lattice oxygen led by atom trapping synthesis.

In the present study, we employed the single-atom Pt on CeO₂ obtained by atom trapping synthesis³³ as the catalyst precursor, which shows a strong MSI, and gradually decreased the degree of MSI by applying different activation conditions. We report tuning the MSI of the Pt-CeO₂ catalyst to boost the activity for the oxidation of the CO and HCHO mixture under ambient conditions without the input of energy. A combination of complementary characterization techniques including Raman spectroscopy, scanning transmission electron microscopy (STEM), and X-ray photoelectron spectroscopy (XPS), together with a study of simulated redox cycles using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and in situ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), revealed that a moderate degree of MSI is optimal for this catalytic process. In contrast to stronger or weaker MSI intensifying either CO adsorption/ activation and the following oxidation of adsorbed CO or oxygen adsorption/activation under the sacrifice of the other, the moderate MSI balances each catalytic step to facilitate the

whole redox process. As a result, the catalyst with moderate MSI displayed the highest activity and completely removed the coexisting CO and HCHO under ambient conditions (i.e., 25 °C and 35% relative humidity in air).

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. A total of 10.0 g of $Ce(NO_3)_2$. $6H_2O$ (Sigma Aldrich) was thermally decomposed at 350 °C for 2 h. The obtained CeO_2 powder was used as a support to prepare the Pt/CeO₂ catalyst (1 wt % Pt) by incipient wetness impregnation with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Sigma Aldrich). The wet mixture was stirred for 10 min and then dried at 80 °C overnight followed by calcination in air at 800 °C for 2 h to improve the reducibility of lattice oxygen.²⁷ Thereafter, the sample was reduced in 10 vol % H_2/N_2 at 125, 250, and 350 °C and in 30 vol % H_2/N_2 at 450 and 550 °C. The obtained catalysts are denoted Pt-Ce(*X*)H, where (*X*) is the temperature for reduction.

2.2. Characterization. Raman spectra of the catalysts were recorded at room temperature on a UV resonance Raman spectrometer (UVRDLPC–DL-03) equipped with a 532 nm (Ventus LP 532) laser source. X-ray diffraction (XRD) analyses were performed with a Bruker D8 ADVANCE X-ray powder diffraction meter with a Cu K α radiation ($\lambda = 0.154056$ nm) operated at 40 kV and 40 mA. The diffraction was recorded from 20 to 80° with a scan step of 0.01°. XPS was performed using an ESCALAB250Xi system, equipped with an X-ray anode operated at 225 W and 15 kV (Al K $_{\alpha}$ radiation, $h\nu = 1486.6$ eV). The C 1s peak (284.8 eV) was used to calibrate the binding energy values.

The study of the redox property was carried out on a chemisorption analyzer (Micromeritics AutoChem 2920) equipped with a mass spectrometer. Specifically, 0.08 g of sample was loaded into a U-type quartz tube and pretreated with 10 vol % H₂/Ar (50 mL/min) at 125 °C for 20 min, followed by switching to ultra-high purity (UHP) He (50 mL/ min) to remove the dissociated H on the sample. Then, there were two routes to conduct the experiment. In route #1, the sample was cooled down to 25 °C. After stabilizing the system for 30 min, 0.5 mL (at 110 °C) of 10 vol % O₂/He was dosed into the He carrier gas and repeated 10 times. Thereafter, the sample was further cooled down to -50 °C and maintained for 10 min. After switching to 10 vol % CO/He (50 mL/min) and waiting for 20 min, the temperature was ramped to 200 °C (20 $^{\circ}C/min$). In route #2, the temperature dropped to -40 $^{\circ}C$ followed by switching the gas to 10 vol % CO/He (50 mL/ min). After 20 min, the gas CO was evacuated for 30 min using UHP He and the gas flow was switched to 10 vol % O₂/He (temperature-programmed oxidation, O₂-TPO). After stabilizing the system for 20 min, the temperature was ramped to 200 $^{\circ}$ C (20 $^{\circ}$ C/min).

In situ DRIFTS experiments were performed with a Thermo Fisher iS 50 spectrometer coupled with a Praying Mantis Diffuse Reflection Accessory from Harrick. In each test, the sample was purged with UHP N₂ (50 mL/min) for 100 min before recording the background. For the study of surface turnover in CO oxidation, 1 mL of 10 vol % CO/He was then dosed into the carrier gas (UHP N₂) followed by several dosages of 0.1 mL of UHP O₂. This process was repeated several times with the recording of spectra. For CO desorption, after one dosage of 1 mL of 10 vol % CO/He, the sample was purged with UHP N₂ (50 mL/min) where the recording of spectra started. For the study of HCHO oxidation, 300 ppm of



Figure 1. Different regions (a and b) in Raman spectra and XRD patterns (c) of the Pt-CeO₂ catalysts. (A) Pt-Ce125H; (B) Pt-Ce250H; (C) Pt-Ce350H; (D) Pt-Ce450H; and (E) Pt-Ce550H.



Figure 2. Catalytic performances of Pt-CeO₂ catalysts for oxidation of CO and HCHO in air. (a) TOF of CO oxidation over Pt-CeO₂ catalysts at 25 °C. Reaction condition: 300 ppm CO, 35% RH, GHSV = 750 000 mL/(g_{cat} ·h). (b) TOF of HCHO oxidation over Pt-CeO₂ catalysts. Reaction condition: 300 ppm HCHO, 35% RH, GHSV = 750 000 mL/(g_{cat} ·h). (c) Conversion of mixed CO (150 ppm) and HCHO (150 ppm) over Pt-Ce450H at 25 °C and 35% RH, GHSV = 20 000 mL/(g_{cat} ·h). For kinetic measurement, the conversion was controlled below 20%.

HCHO continuously flew through the sample for 60 min; then, 10 dosages of 0.1 mL of O_2 were consecutively injected into the carrier gas (UHP N_2).

2.3. Evaluation of Catalytic Performance. The activities of Pt-CeO₂ samples for catalytic oxidation of CO and HCHO were evaluated in a fixed-bed plug flow reactor with a gas mixture containing 300 ppm of pollutant(s) (CO, HCHO, or CO/HCHO 1:1 mixture), 35% relative humidity (RH), and 20% O_2 and N_2 balance at a total flow rate of 125 cm³/min. Also, 35% RH was selected since it is a common value of indoor humidity in the winters of Northern China that enforces the indoor airtight condition. While CO was directly obtained by dilution of compressed CO, gaseous HCHO was obtained by flowing UHP He through a paraformaldehyde container in a water bath, and the concentration of inlet HCHO was controlled by adjusting the temperature of the water bath. To measure the intrinsic activity within the kinetic region, the gas hourly space velocity (GHSV) was adjusted to 750 000 mL/(g_{cat} ·h). Water vapor was generated by flowing helium through a water bubbler at 25 °C, and the RH in the reaction atmosphere was controlled by adjusting the flow rate of the purging helium and measured by a hygrometer. The

inlet and outlet gases were monitored with an infrared spectrometer equipped with a gas cell and a deuterated triglycine sulfate (DTGS) detector, as shown in our previous study.⁵

3. RESULTS AND DISCUSSION

3.1. Structural Characterization. Raman spectroscopy was first employed to investigate the interaction between Pt and CeO₂ (Figure 1a,b). A main peak appears at 452–455 cm⁻¹ (Figure 1a), which can be attributed to the F_{2g} symmetry of the CeO₂ support.³⁴ The peak position gradually shifts from 452 cm⁻¹ for Pt-Ce125H to 455 cm⁻¹ for Pt-Ce550H, and this blue shift implies a stronger Ce–O interaction.³⁵ Another two peaks in the spectrum of Pt-Ce125H show up at around 548 and 656 cm⁻¹, which can be attributed to the bridging Pt–O–Ce vibration and the Pt–O vibration,^{27,36} respectively. The precursor of all of the catalysts (i.e., Pt-CeO₂ calcined at 800 °C in air) displays a comparable spectrum as Pt-Ce125H (Figure S1). While the peak intensities of both Pt–O–Ce and Pt–O decrease with the increase of reducing temperature of catalysts, the peak position for Pt–O–Ce gradually shifts to a lower wavenumber (Figure 1b). This red shift can be

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Figure 3. (a, b), Pt 4f line (a) and O 1s line (b) of XPS analysis. (c) Calculated valence of Pt over each $Pt-CeO_2$ catalyst. (d) Correlation of reactivity and surface O species.

attributed to the elongation of Pt-O-Ce and a decrease in binding strength,^{35,37} together with the decreased peak intensity, indicating that the Pt-Ce125H and precursor of all catalysts have the strongest MSI and the activation with H₂ at different temperatures is able to finely tune down the degree of MSI between Pt and CeO₂. It is consistent with the blue shift of the Ce–O peak in Figure 1a since the weakening Pt–CeO₂ interaction should lead to less perturbation to CeO₂ by Pt and regain the strong Ce-O binding strength, which is further supported by the XPS study discussed below. The catalysts were then characterized with XRD, as shown in Figure 1c. The patterns of all catalysts display exclusively the diffraction of cubic ceria. No crystallized Pt species was detected, indicating the high dispersion of Pt on all of the catalysts. A recent study reported that the variation of particle size of the support was able to change the MSI and the performance of the catalyst.³⁰ Therefore, the crystallite size of CeO₂ particles was determined by Scherrer's equation using the peak located at 28.5° (Table S1). All of the catalysts were in the range of 22-24 nm, suggesting that the variation of MSI in the catalysts was not caused by the size difference of the support.

3.2. Catalytic Performance. The as-synthesized catalysts were evaluated by CO and HCHO oxidation at 25 °C without other pretreatments. CO_2 was the exclusively detected product in the activity test. The mean particle size was determined with high-resolution microscopy (Figures S2, S3 and Table S1). The turnover frequency (TOF) is calculated based on the amount of exposed Pt sites (see the Supporting Information). As shown in Figure 2a, the TOF of CO oxidation gradually increases from 0 to ~0.7 min⁻¹ as the reducing temperature ramps to 450 °C, while further increasing the reduction

temperature decreases the reactivity. A similar behavior is also observed in the oxidation of HCHO over these catalysts that Pt-Ce450H displays the highest reactivity, as shown in Figure 2b. To gain an understanding about the active site, the apparent activation energies (E_a) of three representative catalysts (i.e., Pt-Ce125H, Pt-Ce450H, and Pt-Ce550H) were determined with Arrhenius plots (Figure S4). The E_a of catalysts shows a reverse volcano behavior that Pt-Ce125H exhibits the highest E_a of 46 kJ/mol, while increasing the reduction temperature decreases the E_a to 37 kJ/mol as the lowest over Pt-Ce450H. It suggests that the finely tuned MSI also modifies the active site to decrease the reaction barrier. Pt-Ce450H was also tested for the removal of the CO/HCHO mixture at 35% RH, and the catalyst displayed a complete oxidation of both CO and HCHO to CO₂ at room temperature (Figure 2c). In contrast, the majority of the developed catalyst system may be highly effective for one compound but showed a much lower activity on the oxidation of the other one (Table S2). The performance of Pt-Ce450H was tested at a higher GHSV (Figure S5), and a slow deactivation was observed, which is possibly due to the deposition of carbonaceous species.³⁸ The Pt-CeO₂ interface has also been proposed to be the possible active site in the CO oxidation;³⁹ we calculated the ratio between the conversion rate and the length of the Pt-CeO₂ interface (Figure S6 and notation). The inconstant values in both Figures 2 and S6 suggest that the alternation of reactivity cannot be simply attributed to the change in amounts of active sites (exposed Pt or Pt-CeO₂ interface). Size effect is well-known to affect the catalytic reactivity.⁴⁰ However, the previous study of Pt-CeO₂ catalysts showed a monotonous increase of intrinsic reactivity



Figure 4. Investigation of the redox properties of Pt-CeO₂ catalysts. (a) Schematic illustration of routes and the surface dynamics in redox analysis. (b) O_2 pulse adsorption of Pt-CeO₂ catalysts. (c) Linear regression of peak areas in (b) to study the O_2 adsorption/activation property of Pt-CeO₂ catalysts. (d) CO-TPR after O_2 adsorption. (e) O_2 -TPO after CO adsorption over Pt-CeO₂ catalysts.

for CO oxidation with the increment of Pt particle size in the range of 1-8 nm,⁴¹ which is not consistent with the present volcano-type relationship. In another study, the Pt-CeO₂ catalysts with comparable particle size but different reducibility of lattice oxygen showed distinct CO oxidation activities at low temperatures.²⁷ Therefore, besides the so-called size effect, other factors that also impact the degree of MSI must be significantly regulating the reactivity. Gatla et al.²⁴ ascribed the low-temperature catalytic activity of reduced Pt-CeO₂ to a strong MSI with the elongated Pt-O bond compared with that of PtO₂, as determined by in situ extended X-ray absorption fine structure. Similarly, Gänzler et al.²⁵ attributed the superior activity of Pt-CeO₂ for the oxidation of CO, compared with Pt supported on Al₂O₃, to the stronger MSI that perturbs the electronic properties of Pt. However, our result suggests that the benefit of enhancing MSI only shows up in a particular range of MSI strength, while a negative impact appears in the rest. As a result, the moderate MSI is optimal in terms of catalytic performance. It implies that most studies were possibly conducted in a narrow range of MSI strengths, and this necessitates a comprehensive mechanistic study to understand this volcano-type relationship.

3.3. Mechanistic Study. Tuning MSI usually changes the electronic perturbation in the domain of supported metal and charge transfer between the metal and support.⁴² The electronic property was then investigated with XPS, as shown in Figure 3a,b. The spectra for the Pt 4f region of Pt-CeO₂ catalysts (Figure 3a) show that Pt peaks gradually shift

to a lower binding energy (metallic state) from Pt-Ce125H to Pt-Ce550H. However, the shoulder peaks at higher binding energies suggest that a certain proportion of Pt species remains in the oxidized state. Deconvolution was performed to quantify the distribution of different Pt species (Figures 3a and S7). Pt^{2+} species (89.6%, located at 72.6 eV for the $4f_{7/2}$ line and at 76.0 eV for the $4f_{5/2}$ line⁴³) dominates in Pt-Ce125H, while the rest shows +4 valence. After reduction and activation at a higher temperature (e.g., 550 °C), the content of Pt²⁺ decreased to 35.6% over Pt-Ce550H and the rest were present as a metallic state (Pt⁰, 71.1 eV for the $4f_{7/2}$ line and 74.4 eV for the $4f_{5/2}$ line⁴⁴). Based on the deconvolution results shown in Table S1, the average valence of platinum was derived and correlated with the intrinsic reactivity for the oxidation of CO and HCHO. As shown in Figure 3c, neither strong nor weak electronic perturbation is associated with the highest reactivity; in fact, the moderate MSI with +1.2 average valence of Pt presents the optimal catalytic performance. This is in stark contrast to previous literature reporting that the increase in percentage of metallic Pt is always beneficial to reactivity⁴⁵ but consistent with a recent report that the coexistence of metallic and oxidized Pt (average valence is around +1.4) contributes to the high reactivity.²⁶ The spectra for the O 1s region (Figure 3b) display two bands located at 531.5 and 529.3-529.6 eV. The shoulder peak at 531.5 eV can be attributed to the surface active oxygen species (O_{surf}) with a lower electron density,⁴⁶ while the main peak at 529.3-529.6 eV can be attributed to lattice oxygen.⁴⁷ As the activation temperature increases, the



Figure 5. In situ DRIFTS study of CO oxidation on the Pt-CeO₂ catalyst. (a) Time-on-stream intensity of the main CO peak during desorption over different Pt-CeO₂ catalysts at 25 °C. (b) DRIFTS spectra of CO adsorption and CO₂ formation over Pt-Ce450H. (c) DRIFTS spectra of ¹³CO adsorption and oxidation over Pt-Ce450H that was preadsorbed with ¹²CO. In all of the DRIFTS spectra, unless specified, the C in CO is ¹²C. (d) Time-on-stream absorbance at 2073 cm⁻¹ in the spectra of Pt-Ce450H during cycles of CO injection and O₂ injection. (e) Time-on-stream absorbance at 2070 cm⁻¹ in the spectra of Pt-Ce250H during cycles of CO injection and O₂ injections.

peak associated with lattice oxygen shifts to a lower binding energy, which suggests that the lattice oxygen becomes more electron-rich. Given that Ce has a much lower electronegativity (1.05 in Pauling's scale) than that of Pt (2.1 in Pauling's scale),⁴⁸ the more electron-rich state of oxygen suggests a decrease of coordination with Pt and an increase of that with Ce, which leads to alternation of hybridization of the electronic structure in the Pt and Pt-CeO₂ interface domains. This is consistent with the results of Raman spectra (Figure 1a,b) showing the enhanced Ce-O and weakened Pt-CeO₂ interactions, i.e., the H₂ at higher temperatures is able to finely tune down the degree of MSI between Pt and CeO₂. Oxygen vacancy has been proposed to facilitate the oxidation reaction in numerous studies,^{20,28} and it should be proportionally associated with Ce³⁺ species.⁴⁹ However, a deconvolution analysis of Ce XPS spectra shows no definitive correlation between Ce³⁺ and reactivity for the tested catalysts (Figure S8 and notation). It suggests that oxygen vacancy may not play a determining role in this reaction system. The area of the O_{surf} peak after deconvolution (Figures 3b and S9) was normalized by the area of the Ce $3d_{5/2}$ line (Figure S8), and it gradually increases from Pt-Ce125H to Pt-Ce450H and then decreases over Pt-Ce550H. This sequence well correlates with the oxidation reactivity of the catalysts (Figure 3d), suggesting

abundant active oxygen species on the surface, which may be determined by the degree of MSI, contributing to the enhancement of catalytic performance since the enriched surface active oxygen facilitates the oxygen supply for the oxidation reaction.

The variation of electronic perturbation may eventually regulate the redox dynamics on the catalyst surface, which is studied by applying two routes, as illustrated in Figure 4a. In the first route, O₂ pulses consecutively passed through the catalyst that was in situ pretreated in H2 at 125 °C, and the adsorption profile of each catalyst is displayed in Figure 4b. While Pt-Ce125H showed barely any adsorption of O2, significant O₂ consumptions were observed over other catalysts. The highest O2 consumption appeared on Pt-Ce250H, and the calculated O/Pt molar ratio (based on a nominal amount of Pt) is about 4.3:1 (Table S1), which suggests that the H₂ activation and spillover facilitate the consumption of O atoms in the adjacent region of Pt sites during the H₂ treatment. The O/Pt molar ratio gradually decreases with the increase of reduction temperature (Table S1) and reaches 2.8:1 for Pt-Ce550H, which is likely due to the lower dispersion of Pt. The more remarkable difference lies in the efficiency of O₂ adsorption, i.e., Pt-Ce250H shows a mild adsorption behavior with a gradual increase of the O₂ pulse intensity, while a steep rise of the O_2 pulse peaks appears over both Pt-Ce450H and Pt-Ce550H. The area of each peak is calculated, and the regression is then performed to quantitatively compare the rising rate of O₂ peaks. As displayed in Figure 4c, the slope increased from 0.02 for Pt-Ce125H to around 0.4 for Pt-Ce450H and Pt-Ce550H. If the sticking probability of O_2 to a clean surface of the catalyst is high, the surface with a high coverage of dissociated O will still be able to efficiently adsorb/dissociate O2 before the surface is saturated,^{50,51} which presents the steep rise of intensity of O₂ pulse peaks as the cases of Pt-Ce450H and Pt-Ce550H. In contrast, the much lower sticking probability leads to the mild growth for Pt-Ce125H and Pt-Ce250H. After the saturation of O on Pt-CeO₂, CO-temperature-programmed reduction (TPR) was performed to investigate the intrinsic activity of CO oxidation by adsorbed O on the catalyst surface (Figure 4d). Likely due to the low activity to dissociate O₂, the Pt-Ce125H presents CO₂ formation only when the temperature is above 35 °C. In contrast, CO oxidation occurs at -23 °C over Pt-Ce250H, and a slight increase of the ignition temperature appears with the increment of the H₂ activation temperature for other catalysts. The above results suggest that weakening MSI may enhance the O₂ activation while attenuating the activity for CO adsorption and activation when the Pt domain is saturated with dissociated O. Moreover, the CO₂ formation amount is comparable to that of adsorbed O for Pt-Ce250H, Pt-Ce350H, Pt-Ce450H, and Pt-Ce550H (Table S1), implying that the adsorbed O_2 in Figure 4b was subsequently activated (i.e., all of the adsorbed O_2 participated in the CO oxidation reaction over these catalysts).^{20,28,49} Pt-Ce125H displays completely different amounts of O consumption with CO2 formation, which may be ascribed to the strong interaction preserving O of the support during the reduction pretreatment, leading to the low O adsorption amount during O₂ injections. In route #2, the CO first adsorbed on Pt, followed by an O_2 -TPO process shown in Figure 4e. The preadsorbed CO also displayed a gradual increase of the ignition temperature for oxidation, suggesting that the weakened MSI abates the activity of oxidation of adsorbed CO. Note that the CO-TPR in route #1 shows a much higher amount of CO_2 formation than O_2 -TPO in route #2 (the ratio approaches 5:1 over Pt-Ce450H for #1 and #2, Figure S10). Since the CO_2 formation amount is determined by the amount of less abundant reactants (activated O over both Pt and the adjacent region for route #1 and CO over Pt for route #2), the much higher CO_2 formation amount in route #1 suggests that the activated O to oxidize CO is mainly from the adjacent region of Pt through the reversed O spillover from CeO_2 .

In situ DRIFTS was employed to further reveal the surface chemistry of CO adsorption/activation and oxidation. The Pt– CO binding strength was studied by CO desorption at 25 °C with N₂ purging (Figure S11), and the changes in intensity of the main peak are shown in Figure 5a. Pt-Ce125H shows only a barely detectable decrease of the CO band intensity, while CO on Pt is completely desorbed over Pt-Ce550H in 300 s. It should be noted that the CO in the adsorption process prior to desorption is excessive, and it consumes all of the active oxygen species on the Pt domain and the Pt-CeO₂ interface.⁴⁹ The removal of CO in Figure 5a should exclusively be ascribed to desorption of CO, other than oxidation. The desorption rate follows the following order: Pt-Ce125H < Pt-Ce250H < Pt-Ce350H < Pt-Ce450H < Pt-Ce550H, which correlates well with the MSI intensity and the CO oxidation activity in Figure 4d,e. The above results suggest that the stronger the MSI, the more intense the electronic perturbation of the Pt species, enabling a stronger interaction between Pt and CO for CO activation, and vice versa. Figure 5b shows the spectra of Pt-Ce450H obtained after exposing to different reactants successively. After dosing one pulse of CO, one main peak shows up at 2073 cm⁻¹, which is attributed to the linearly adsorbed CO on the Pt particle.⁵² Two shoulders emerge at around 2099 and 2017 cm⁻¹, which are attributed to the CO on cationic single-atom $Pt^{27,53}$ and the CO on the interface of Pt and CeO_2 , respectively. The gas-phase CO peaks, typically located at 2172 and 2126 cm⁻¹, also show up, while the one at 2126 cm⁻¹ should be overlapped with the adsorption of CO on the catalyst surface. Besides the adsorption associated with CO, the gas-phase CO₂ peaks located at 2300-2400 cm⁻¹ increase presumably due to CO oxidation by the O2-saturated catalyst surface. Following one dosage of CO, one dosage of O2 was subsequently injected, which led to the significant decrease of IR absorption by CO on-top Pt particle (2073 cm⁻¹) and over the Pt-CeO₂ interface $(\sim 2017 \text{ cm}^{-1})$.⁵⁵ The peak intensity of gas-phase CO₂ was maintained, indicating that the CO was oxidized by dissociated O. The second dosage of O_2 further oxidized the CO on Pt forming CO₂ and consuming the majority of the rest of the CO. Therefore, the spectrum for the third O_2 dosage shows little change of CO adsorption and an obvious decrease of gasphase CO₂ concentration. In contrast to the significant change in the region of linearly adsorbed CO on the Pt particle, the intensity of 2099 cm⁻¹ remained unchanged, suggesting that the CO on the cationic single atom is not active under such a condition. This is further corroborated by the CO/O_2 dosage experiments of Pt-Ce125H with single-atom Pt, which shows the nearly unchanged CO absorption peak at 2099 cm⁻¹ after O_2 dosages (Figure S12). Figure 5c shows the adsorption of isotopically labeled ¹³CO after preadsorption of ¹²CO. Although the Pt surface is presaturated with ¹²CO, rapid change of the peak shape in the spectrum is observed once one dosage of ¹³CO is injected, suggesting that CO adsorption on Pt species is dynamic so that a part of ¹²CO is rapidly exchanged with ¹³CO. The appearance of absorption at around 1950 cm⁻¹ implies that, besides the on-top site, ¹³CO is also over the $Pt-CeO_2$ interface. The peaks that are attributed to $^{13}\mathrm{CO}$ and $^{12}\mathrm{CO}$ decrease proportionally after the O_2 injections, suggesting that ¹³CO and ¹²CO are proportionally distributed on the active site.

After the first turnover of the catalyst surface, four more cycles were repeated, and the intensity of the 2073 cm⁻¹ peak as a function of time-on-stream is shown in Figure 5d. The periodic injection of CO and O₂ leads to the rapid increase or decrease of the absorption band for CO on the Pt particle, indicating the active turnover of Pt site under this condition and the CO oxidation reaction happens on the site associated with the Pt particle. The turnover cycles of other Pt-CeO₂ catalysts were also investigated and are shown in Figure 5e for Pt-Ce250H, Figure S12 for Pt-Ce125H, and Figure S13 for Pt-Ce550H catalysts. Unlike the instant response of Pt-Ce450H to the O₂ injection, the CO adsorption of Pt-Ce250H remains unchanged after the first O2 pulse. The second O2 pulse slightly decreases the CO absorption bands, while the third one decreases more. It suggests that Pt-Ce250H undergoes severe CO self-poisoning, and the strongly adsorbed CO spatially inhibits the adsorption/activation of O₂ on Pt.^{26,52} When there are more exposed Pt sites, more O2 can be



Figure 6. In situ DRIFTS study of HCHO oxidation on Pt-CeO₂ catalysts at 25 °C. (a) Spectra of HCHO adsorption and O₂ pulse injection over Pt-Ce450H. (b) Spectra of HCHO adsorption and O₂ pulse injection over Pt-Ce250H.

adsorbed and activated to react with CO, which leads to the gradual increase of the CO elimination rate in the first three O_2 injections. This implies that, besides the O transfer from the CeO_2 support as indicated in Figure 4 and other literature,⁵⁶ O activated by Pt also significantly contributes to CO oxidation at 25 °C. The CO self-poisoning is even much more severe for Pt-Ce125H that almost no decrease of the CO band is detected after introducing O₂, while Pt-Ce550H (Figure S13) shows a similar behavior with Pt-Ce450H. However, the lower intensity of CO₂ bands (~2350 cm⁻¹) in the spectra suggests that the rapid decrease of the CO peak is mainly contributed by desorption of CO. This is further supported by similar CO band consumption rates under different conditions: bare desorption in N_2 (Figure 5a) versus oxidation + desorption (Figure S13), as shown in Figure S14, indicates that the CO band consumption led by oxidation is limited. The lower CO₂ formation rate is presumably ascribed to the overly weakened interaction with CO, which leads to the less efficient CO activation and the following oxidation.

The surface chemistry for HCHO oxidation was also investigated by *in situ* DRIFTS. Figure 6a displays the spectra of HCHO adsorption after evacuation of gas-phase HCHO and the following HCHO oxidation by O_2 dosage over Pt-Ce450H. The spectrum of HCHO adsorption shows peaks in the C–H stretching region at 2936, 2838, and 2718 cm⁻¹, of

CO at 2067 cm^{-1} , in the stretching region of COO species at 1595, 1551 (asymmetric) and 1370 (symmetric) cm^{-1,15,18} and in the C–O stretching region at 1064 $\text{cm}^{-1,57}$ indicating the formation of formate, dioxymethylene (DOM), and CO species on the surface. Compared with the one led by directly dosing CO (2073 cm⁻¹), the CO band of HCHO adsorption slightly shifts to a lower wavenumber, indicating a weakening of the C–O bond. This red shift may be caused by the electron transfer from the second adsorbate (e.g., other intermediates from HCHO conversion) toward Pt, which increases the electron density of Pt and thus the extent of Pt-CO backdonation.⁵⁸ A negative peak also shows up at 3660 cm⁻¹ (O-H stretching), which is attributed to the consumption of the hydroxyl group by reacting with HCHO and forming the intermediates.⁵⁹ After the first dosage of O₂, the peaks associated with CO, DOM, and formate and the negative peak of hydroxyl decay with the growth of gas-phase CO₂ $(2400-2280 \text{ cm}^{-1})$ and molecular H₂O $(3500-3200 \text{ cm}^{-1})$, suggesting the conversion of surface intermediates to CO₂ and H_2O . The second O_2 dosage further intensifies this behavior that only small CO and DOM remain in the spectrum. However, formate species (COO and C-H) still maintain a strong absorption even when they are exposed to more O2 dosages, which suggests that these remaining formate species are likely not close to the active site and thus act as spectators.

The nearly complete disappearance of CO and DOM implies that these species only form on the active sites (i.e., Pt domains) and participate in the catalytic process. In contrast to the rapid turnover of the Pt-Ce450H surface, the Pt-Ce250H exhibits a much milder change, as shown in Figure 6b. The absorptions of all of the peaks merely show a slight decrease after seven dosages of O_2 , indicating the low reactivity of the Pt domain on Pt- Ce250H. No change of spectra is observed for Pt-Ce125H (Figure S15), which has the lowest activity in HCHO oxidation (Figure 2b).

4. DISCUSSION

The variation of Pt-O-Ce and Ce-O binding strengths as suggested by Raman spectra indicates that increasing the temperature for H₂ reduction of Pt-CeO₂ with strong MSI is able to tune down the MSI between Pt and CeO₂. The finely tuned MSI, which controls the electronic perturbation of both Pt and O as suggested by XPS, elaborately regulates the local surface chemistry (e.g., electron density of Pt, sufficiency of active oxygen species, binding strength with reactants, etc.) in the Pt and Pt-CeO₂ interface domains. The typical Langmuir-Hinshelwood or Mars-van-Krevelen reaction models for CO oxidation basically involve CO adsorption/activation, O₂ adsorption/activation, and oxidation of adsorbed CO. Our study demonstrates that tuning down the degree of MSI between Pt and CeO₂ results in enhanced O₂ adsorption/ activation with abated activity of CO adsorption/activation and oxidation of adsorbed CO. As a result, the overly strong MSI makes Pt intensely bind to CO with a low activity to adsorb/dissociate O₂, which leads to the CO self-poisoning effect, while the overly weak MSI results in rapid desorption of CO from Pt and degradation of the oxidation activity of adsorbed CO. Due to this trade-off between O₂ adsorption/ activation activity with CO adsorption/activation and oxidation of adsorbed CO, Pt-Ce450H with a moderate MSI, which is able to balance each step in the catalytic cycle, displays the highest activity for CO oxidation at ambient conditions.

The NAP-XPS study (Figures S16-S19 and the notation) shows the coexistence of metallic and oxidized Pt during the reaction, which is consistent with a previous report.²⁶ In that work, the synergy of the two Pt species was proposed, i.e., metallic Pt provides strong adsorption sites for CO, while oxidized Pt supplies the reactive oxygen.²⁶ However, the Pt-Ce250H containing a high amount of oxidized Pt in our study still shows a low rate to oxidize the adsorbed CO on metallic Pt, as indicated by DRIFTS. Thus, a simple attribution of the synergy between metallic and oxidized Pt cannot completely explain our experimental observation. It implies that, together with the synergy of metallic and oxidized Pt, the electronic perturbation/modification of Pt and the Pt-CeO₂ interface domain by MSI may also play a pivotal role in regulating the reactivity, i.e., the hybridization of the electronic structure in the domain of Pt and the Pt-CeO₂ interface needs to be finely tuned to achieve the nature of the active site that possesses the highest activity.

The above results also suggest that it may not be appropriate to claim the active site as metallic or oxidized since the turnover in the catalytic reaction makes the valence of the active site dynamic and likely dependent on the concentration of reactants. As for the site to activate O_2 , while the CO-TPR demonstrates that the O in the support is able to participate in the reaction, the DRIFTS of Pt-Ce250H shows an enhanced CO oxidation activity after a part of CO is removed and Pt sites are exposed. It suggests that Pt is also one possible site for O_2 activation under ambient conditions. The mechanistic study supports two possible reaction routes, as illustrated in Figure S20. One is that Pt activates oxygen and transfers it to the metallic Pt site that adsorbs CO for the following oxidation, as supported by the increase in the CO oxidation rate when Pt-Ce250H exposes more Pt sites (less bonding with CO), as shown in Figure 5e. The other is oxidation of CO with the O supplied by the Pt-CeO₂ interface, as supported by the excessive formation of CO₂ during CO-TPR (Figure 4d and Table S1).

CO has been demonstrated as an important and downstream intermediate from formate and DOM in HCHO oxidation,⁶⁰ and similar peak intensities associated with CO, formate, and DOM during HCHO adsorption for Pt-Ce450H and Pt-Ce250H indicate their similar activities for catalyzing the upstream steps prior to forming CO. Therefore, the different rates of intermediate consumption in the DRIFTS spectra and of HCHO oxidation in the activity test are mainly due to the distinct reactivities of CO oxidation, i.e., CO oxidation is the main rate-limiting step in HCHO oxidation. This is also supported by the same reactivity sequence of Pt-CeO₂ catalysts for HCHO and CO oxidation. Since the moderate MSI of Pt-Ce450H balances CO adsorption, surface oxidation, and O2 adsorption/activation and results in the optimal reactivity for CO oxidation over Pt-Ce450H, the HCHO oxidation reactivity is also optimized.

In summary, the MSI of the Pt-CeO₂ catalyst, which leads to the hybridization of the electronic structure, was finely tuned to achieve the nature of the most active site by regulating the condition for catalyst activation, aiming at boosting the activity for the oxidation of CO and HCHO under ambient conditions. It was found that activation of Pt-CeO₂ having strong MSI at increased temperatures gradually decreases the degree of MSI, which is accompanied by enhanced oxygen adsorption/ activation and weakened CO adsorption and oxidation of adsorbed CO. This mitigates the competitive adsorption of CO that inhibits the O_2 activation, i.e., the CO self-poisoning effect. However, overly weakening the MSI results in the decrease of reactivity since the weakening of interaction between Pt and CO leads to less efficient CO activation and oxidation of adsorbed CO. The optimal reactivity is attained over the catalyst with moderate MSI (i.e., Pt-Ce450H) that balances capacities of oxygen adsorption/activation, CO adsorption/activation, and oxidation of adsorbed CO to facilitate the whole catalytic redox process. The catalytic performance for oxidation of HCHO is highly dependent on the activity of CO oxidation as the rate-limiting step. Due to the high reactivity and versatility, Pt-Ce450H completely removed coexisting CO and HCHO under ambient conditions (i.e., 25 °C and 35% relative humidity in air).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c06400.

Raman spectra of $Pt-CeO_2$ catalysts; microscopic characterization of $Pt-CeO_2$ catalysts; Pt particle size distributions over Pt/CeO_2 catalysts; calculated ratio between the conversion rate and the length of the Pt- CeO_2 interface in CO oxidation and HCHO oxidation; fitting lines of the XPS pattern of Pt 4f, Ce 3d, and O 1s regions; CO₂ formation profile in routes #1 and #2 using Pt-Ce450H; spectra for CO desorption in N₂ at 25 °C; DRIFTS spectra of CO adsorption and CO₂ formation; *in situ* DRIFTS study of HCHO adsorption and O₂ exposure over the Pt-Ce125H catalyst; lines of the Pt 4f region in the *in situ* NAP-XPS pattern; size of CeO₂ and Pt particles, distribution of Pt species, ratio of O₂ adsorption and CO₂ formation to Pt; comparison of reported catalysts for oxidation of CO and HCHO at 25 °C (PDF)

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Notes

The authors declare no competing financial interest.

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