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

Annai Liu^{‡†}, Xiao Liu^{⊥†}, Lichen Liu[§], Yu Pu[‡], Kai Guo[‡], Wei Tan[‡], Song Gao[‡], Yidan Luo[‡], Shuohan Yu[‡], Rui Si^{//}, Bin Shan[¶], Fei Gao^{‡△*}, Lin Dong^{‡△}

[‡]Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering Nanjing University, Nanjing, 210093, Jiangsu, P. R. China

[△]Jiangsu Key Laboratory of Vehicle Emissions Control, School of Environment, Center of Modern Analysis, Nanjing University, Nanjing, 210093, Jiangsu, P. R. China

[⊥]State Key Laboratory of Digital Manufacturing Equipment and Technology and School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, P. R. China

[§]Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Av. de los Naranjos s/n, 46022 Valencia, Spain.

^{//} Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, P. R. China.

[¶]State Key Laboratory of Materials Processing and Die and Mould Technology and School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, Hubei, P. R. China

KEYWORDS. Active sites, CO oxidation, Pt Nanoparticles, *in situ* IR spectroscopy, Temperature

Abstract

The geometrical structure of metal nanoparticles has been found to be a critical factor that can influence the catalytic behaviour significantly. For typical metal nanoparticles, the exposed surface atoms usually exhibit different coordination environment among different surface sites. By *in situ* diffuse reflectance Fourier transform infrared spectroscopy, kinetic measurements and DFT calculations, it has been found that, for Pt catalyzed CO oxidation at different temperatures, CO reacts preferentially on different surface sites of Pt nanoparticles. At low temperatures, Pt species with higher coordination numbers (≥ 7 -fold coordinated) present higher catalytic activities due to the lower CO adsorption energy. While at high temperatures, especially beyond ignition temperature, Pt species with lower coordination numbers (≤ 6 -fold coordinated) play a predominant role because of their better capability for O₂ activation.

Introduction

Metal catalysts are widely used in various industrial processes like the production of fuels, chemicals, raw materials, and environmental remediation.^{1, 2} Understanding the catalytic behavior of metal catalysts has always been one of the core interests among heterogeneous catalysis community. It is now well recognized that two general factors, known as geometric and electronic factors, can influence the catalytic properties of heterogeneous metal catalysts.^{3, 4} These two aspects are usually associated with the atomic arrangement on the surface and the chemical states of a metal catalyst.

Numerous fundamental researches have been carried out to clarify how geometric structures affect the catalytic behavior of different metal catalysts. For instance, Pt catalyst, as one of the critical active component in the three-way catalyst, has been intensively studied for the CO oxidation reaction.⁵ Investigation on different facets of Pt single crystals has been thoroughly performed during the last decades, leading to comprehensive understandings of the adsorption and reaction of CO on different Pt surface structures.⁶⁻¹³ For example, it is found that, on most single Pt crystal surfaces, this reaction most likely proceeds under a Langmuir-Hinshelwood mechanism,¹¹ while the oscillatory behaviors are quite different among Pt(110), Pt(100) and Pt(111)

surfaces.^{6, 13} These results imply that the surface structures of Pt nanoparticles can govern the performance of Pt catalysts.^{14, 15}

Studies have been brought to shed light on the effect of coordination numbers of metals on the CO catalytic oxidation reactions.^{16, 17} Well-coordinated Pt (WC, 9-fold coordinated) sites on the alumina supported Pt nanoparticles have been designated as the active sites for this reaction by CO-IR spectroscopy.¹⁶ However, the activity of specific active sites comes from the balance among the adsorption/desorption equilibrium, surface diffusion, surface reaction, etc. As a result, factors other than the structure of the catalyst *per se*, such as reaction temperature, are also considered to influence the catalytic performance significantly. It is worth mentioning that, much as the *in situ* spectroscopic method has been developed, limited studies have been carried out with *in situ* infrared characterizations at high temperatures (typically > 400 K),^{16, 18} at which the apparent conversion of the CO would have emerged. This situation is most likely because of the drastic reaction between the adsorbed CO and the continuous flow of O₂, making it challenging to capture the surface species by conventional IR spectroscopy. Further evidence with *in situ* characterizations on this topic has shown that, during the reaction, active gas molecules such as CO, O₂ or H₂ may induce the surface reconstruction or the change of particle size at various temperatures.¹⁹⁻²¹ This discovery has indicated that, for Pt nanoparticles, distinct active sites may be present at different reaction temperatures. It has been found that single atoms, to which plenty of attention has been paid in recent years,²²⁻²⁶ do not always serve as efficient catalysts as particles for this reaction for their strong adsorption strength at 373 K; yet as the temperature elevates, the CO adsorbed on the single atoms also reacts with oxygen.¹⁸ These understandings, especially the variation of active sites caused by the reaction conditions, could pave more explicit ways for the design of better catalysts. At this point, to characterize the catalytic process at various temperatures, especially beyond ignition temperature (>400 K)²⁷, is indispensable to the full perception of this reaction.

In this work, by *in situ* pulsed IR spectroscopic, kinetic studies and computational research, it will be demonstrated that, at different temperatures, different Pt surface sites dominate this catalytic reaction. At low-temperature region, Pt surface sites with higher

coordination numbers (≥ 7 -fold coordinated) are the active sites. While at a higher temperature (beyond ignition temperature), highly under-coordinated (H-UC, ≤ 6 -fold coordinated) Pt sites are the active sites. In both theoretical and experimental ways, we have proved that CO adsorption and O₂ activation synergistically regulate the activity of different Pt surface sites for this reaction at different temperatures.

Experimental Section

Pt nanoparticles supported on two different sized faujasite (FAU) zeolites,²⁸ which have been widely used as catalyst supports because of their catalytic inertness, highly ordered structures and narrow tunnels that could confine the growth of metal particles,^{23, 29} have been prepared. There are, nevertheless, drawbacks like poor stabilities under electron beam, leading to difficulties acquiring high-resolution transmission electron microscopy (HR-TEM) images. Fortunately, this problem can be overcome by specific skills such as taking images quickly within seconds with computational reconstruction during TEM imaging.^{18, 30, 31}

Synthesis of Catalysts. The zeolites were prepared hydrothermally as previously reported.²⁸ The nano-sized Y zeolites were synthesized by controlling the hydrothermal time and temperature, which is labeled as NanoY and Y, respectively. The Si/Al ratio (by ICP) of NanoY and Y are 1.6 and 2.3, respectively. Pt was introduced by ion exchange followed by calcination at 623 K. In a typical synthesis of the catalyst, 1 g Y zeolite was stirred for 1 h after ultrasonically dispersed in 200 mL DI water, followed by adding 19.80 mg Pt(NH₃)₄(NO₃)₂ dissolved in 50 mL DI water dropwise. The suspension was then stirred vigorously for 3 h before filtered. The sample collected was washed with water three times and acetone once. After dried at 403 K overnight, the as-prepared sample was calcined in the presence of flowing 20% O₂ in Ar in a once-through glass tubular flow reactor. The stream of the gas flowed at a rate of 200 mL/min as the temperature was ramped to 623 K at a rate of 1 K/min. The temperature of the reactor was held at 623 K for 4 h, and then it was cooled to room temperature with the continuous gas flow. Samples calcined in O₂/Ar were re-calcined in 7% H₂/Ar flow at 623 K for another 2 h at a ramp of 5 K/min. These samples were designated as Pt/NanoY

and Pt/Y respectively. Pt loading and Si/Al ratio of the catalysts were tested by ICP-AES.

CO Oxidation Catalysis. Catalysts were pretreated for 30 min at 573 K under Ar flow at a rate of 25 mL/min. The reaction was carried out in a fixed-bed reactor, where the data was collected by an online gas chromatograph equipped with two columns, a flame ionization detector (FID) and a thermal conductivity detector (TCD) used for analyzing the production. The feed was 1.6% CO and 20% O₂ in Ar with a total flow rate of 25 mL/min at atmospheric pressure. 50 mg catalyst was used for the test of the light-off curve, corresponding to a space velocity of 30,000 cm³(STP)/(g·h). For the kinetic test, aside from the confirmation of the kinetic regime (Figure S1), only 10 mg catalyst diluted with 90 mg of inert γ -Al₂O₃ was used, corresponding to a space velocity of 150,000 cm³(STP)/(g_{catal}·h). To eliminate the influence of heat and mass transfer on the kinetic measurements, we performed the test of TOF at 403 K with Pt/Y catalyst with different dilution ratio of catalyst vs. inert alumina from 1:4 to 1:24.^{32, 33} At the dilution ratio of 1:9, the diluted pellets were also mixed with SiO₂ grains to examine the effect of external mass/heat transfer. At the dilution ratio of 1:24, a test at a different space velocity was also performed. All TOF tests for the confirmation of kinetic regime mentioned above show very similar results (See Figure S1), indicating that our test is at kinetic regime. The dilution of the catalyst is achieved by grinding the catalyst powder and the inert alumina with a mortar for at least seven times. All conversions, for the kinetic study, are kept below 20%.

CO conversion is calculated by

$$\text{CO conversion} = \left(1 - \frac{[\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}}\right) \times 100\%$$

TOF is calculated by

$$\text{TOF} = \frac{(\text{CO conversion}) \times 1.6\% \times 0.025\text{L/min} \times 60\text{s/min}}{22.4\text{L/mol} \times \frac{m_{\text{Pt}}}{195\text{g/mol}} \times D_{\text{Pt}}}$$

Characterization. X-ray diffraction (XRD) measurement patterns were recorded on a Philips X'pert Pro diffractometer using Ni-filtered Cu K α radiation ($\lambda = 0.15$ nm). The X-ray tube was operated at 40 kV and 40 mA.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) was carried out on a Nicolet 5700 FT-IR spectrometer equipped with an MCT detector. The cup, in which ca. 20 mg sample was pressed and mounted, was pretreated with pure He at 573 K for 30 min to eliminate the adsorbed impurities before cooled down to a specific temperature chosen from 363 K to 433 K. 10 % CO in He was introduced at a rate of 30 mL/min to the sample to achieve the adsorption equilibrium. Pure He was applied to purge the gas phase as well as the weakly adsorbed CO for 20 min after the adsorption of CO. For the O₂-pulse test, a home-made valve was applied to pulse 1 mL O₂ every minute, while FT-IR spectra were collected simultaneously with the pulses. The spectra were collected from 400 to 4000 cm⁻¹ at a spectral resolution of 4 cm⁻¹ for 32 scans. It is pointed out by the report³⁴ that from the quantitatively analytic point of view, the DRIFTs data presented in the form of Kubelka-Munk and of (pseudo)absorbance should be chosen under the consideration of surface concentrations. We compared the different presentations of our results of the CO_{ad} spectra after different pulses (see Figure S2 and S3). The data in different forms give no effect to the understanding of CO adsorption. For quantitative purpose, we present the IR data in Kubelka-Munk form in this study. For the temperature-programmed desorption (TPD) test, CO was introduced to achieve the adsorption equilibrium, followed by the He purging. The ramp rate of temperature is $\beta = 10$ K/min, allowing the redhead analysis³⁵ by the equation:

$$\frac{E}{RT_p} = \ln\left(\frac{\nu T_p}{\beta}\right) - 3.64$$

E is the desorption energy. T_p is the peak desorption temperature. The rate constant is previously justified as $\nu = 10^{15} \text{ s}^{-1}$.^{35, 36} For the temperature-programmed oxidation (TPO) test, 1 % O₂/He was introduced after the CO adsorption. The ramp rate of temperature is $\beta = 10$ K/min, with a spectrum collected every 5 K.

The microscopic measurements were performed on an FEI Tecnai F20 transmission electronic microscope operating at 200 kV in scanning-transmission mode (STEM) and in transmission mode (TEM). STEM images were obtained using a high-angle annular dark-field detector (HAADF), which allows Z-contrast imaging. All images except

those for the beam-damage test were focused recorded in 1 minute to eliminate the beam induced corruption or agglomeration to the sample.

The X-ray Absorption Fine Structures (XAFS) were collected at Shanghai Synchrotron Radiation Facility (SSRF), using the beamline BL14W1 in fluorescent mode with a Lytle collector.³⁷ The after-reaction samples were pretreated with reaction gas feed at 443 K for 2 h in a U-shaped tube with valves on each end. The samples were then sealed with Kapton tapes in a glove box under N₂ protection. Pt foil and PtO₂ were used for calibration and standards. The XAFS data were processed with IFEFFIT package.³⁸

Computational methods. Vienna Ab Initio Simulation Program (VASP) was applied to calculate the adsorption/desorption behaviors of CO and O₂, and CO oxidation pathways on Pt clusters based on density function theory (DFT).^{39, 40} The exchange-correlation functional was described by the Perdew-Burke-Ernzerhof (PBE)⁴¹ approximation. The cutoff energy was set to 400 eV. All calculated energies were converged to within 10⁻⁴ eV and forces were converged to within 0.05 eV/Å. Two Pt clusters were built with respectively 43 and 92 atoms in cubic box of 25 Å and 30 Å, respectively, which represented the Pt particles in Pt/NanoY and Pt/Y. Only Γ point was considered in the Brillouin zone. The adsorption energies were calculated by

$$E_{\text{ads}} = E_{\text{CO-Pt cluster}} - E_{\text{CO(g)}} - E_{\text{Pt cluster}}$$

where E_{ads} , $E_{\text{CO-Pt cluster}}$, $E_{\text{CO(g)}}$, $E_{\text{Pt cluster}}$ were the adsorption energy, the energy of CO adsorbed on Pt cluster, the energy of gas-phase CO and the energy of Pt cluster, respectively. For the adsorption of CO, fully-CO covered structures were constructed on both clusters. While for the adsorption and dissociation of O₂, the CO molecule with minimum desorption energy was considered to desorb from the Pt cluster. The O₂ molecule was then located on the very Pt site. Both Eley-Rideal (E-R) and Langmuir-Hinshelwood (L-H) mechanisms are considered to calculate the CO oxidation pathway. For the E-R theory, a gas phase CO was adsorbed on the adsorbed O₂ to formulate CO₂. For the L-H theory, CO₂ was formed by a CO adsorbed near the O₂ adsorbed Pt site reacted with the oxygen species. The transition state of the CO oxidation was searched

by the climbing image nudged elastic band method by considering six intermediate images.

Results and Discussion

Figure 1. a and b) STEM-HAADF images of Pt/Y(a) and Pt/NanoY(b) The average sizes of Pt particles of Pt/Y(c) and Pt/NanoY(d) were estimated from particle counts in STEM-HAADF images with more than 1000 particles. (scale bar: 50 nm)

Catalyst synthesis and structure. To generate Pt nanoparticles with different surface structures as model catalysts, we have utilized zeolite Y with different sizes (10-30 nm, NanoY, and >200 nm, Y) as relatively inert support.⁴² By the conventional ion-exchange method, Pt species can be introduced to zeolite Y crystallites. The structural characterizations of both supports and catalysts can be found in Figure S4-S8. It is found from STEM-HAADF images (see Figure 1a, 1b, Table 1) that Pt is well dispersed in both samples with narrow distributions. For Pt/NanoY sample, the average size of Pt

particles is ~1.0 nm, while for Pt/Y, Pt particles show a larger average size of ~2.1 nm. From a structural point of view, for a metal nanoparticle with face-center cubic (fcc) crystallographic structure, the percentage of exposed surface atoms will increase when decreasing the particle size. Furthermore, the exposed surface atoms within the smaller particles will exhibit a lower average metal-metal coordination number (CN_{M-M}) compared to those larger ones. Therefore, in the Pt/NanoY sample, it is expected that a higher amount of highly under-coordinated Pt atoms will be present on the surface of Pt nanoparticles than those in the Pt/Y sample. Besides, synchrotron-based X-ray Absorption Fine Spectroscopy (XAFS, Figure S9) could also indicate the structural properties of supported Pt particles. It can be inferred from the first Pt-Pt shell from the Extended X-ray Absorption Fine Spectra (EXAFS) of Pt/Y sample that this sample contains larger Pt clusters than that of Pt/NanoY.

Table 1. Synthesis and catalytic performance of Pt/Y and Pt/NanoY

Catalyst	Pt (wt%) ^a	Particle size (nm) ^b	Dispersion ^c	TOF $\times 10^2$ (s ⁻¹) at 403/363 K ^d	Ignition temperature (K)
Pt/Y	0.6	2.13 $\pm$ 0.56	0.47	6.30/1.14	433
Pt/NanoY	0.6	1.03 $\pm$ 0.25	0.79	9.85/1.05	403

^aLoading was calculated from ICP-AES. ^bEstimated from particle counts in STEM-HAADF images with more than 1000 particles. ^cThe Pt dispersion was calculated by $D = 1.483 \frac{\langle d^2 \rangle}{\langle d^3 \rangle} - 0.733 \frac{\langle d \rangle}{\langle d^3 \rangle} + \frac{0.121}{\langle d^3 \rangle}$, d is average particle size. TOFs were measured by normalizing the molecular reaction rate (moleCO/molePt·s) to the dispersion measured by STEM (D). ^dNote that kinetic measurement could be affected by intra-pellet heat transfer caused by the exothermic reaction per se³². This effect is eliminated by the confirmation of the kinetic regime (See Figure S1).

The surface coordination state of the exposed Pt atoms in Pt nanoparticles can be investigated with the relative intensities of different absorption bands of adsorbed CO in the IR spectra in a semi-quantitative way.¹⁶ The attribution of those peaks in the spectrum has been thoroughly studied in earlier reports.^{16, 19, 43} As shown in Figure 2, in a typical CO-IR spectrum of Pt nanoparticles, two absorption band can be observed. The one at higher frequency (2080-2060 cm⁻¹) is assigned to be the collective oscillation of CO molecules linearly adsorbed on the under-coordinated (UC, 7-8-fold coordinated)

Pt sites; while the other at lower frequency (2055-2000 cm^{-1}) is assigned to the collective oscillation of CO linearly adsorbed on highly under-coordinated (H-UC, ≤ 6 -fold coordinated) Pt sites. CO adsorbed on WC Pt sites (usually at ca. 2098 cm^{-1}) was detected on neither of the samples, due to the small sizes of the Pt particles present in higher amount of H-UC Pt sites is formed in the Pt/NanoY sample, which is in line with the smaller particle size.

Figure 2. Normalized DRIFT spectra of CO adsorption at 363 K for Pt/Y (orange) and Pt/NanoY (green).

Catalytic performance in CO oxidation and the change of active sites. We have tested the catalytic performance of Pt/Y and Pt/NanoY for CO oxidation reaction in a fix-bed reactor. The light-off curve provides vital information such as ignition temperature (See Figure S10 for the light-off curve). Nevertheless, the light-off curve can be affected by other factors such as the mass/heat transfers or the total Pt surface area.²⁷ To study the intrinsic activity of Pt surface atoms, the turnover frequency (TOF) was also tested. Table 1 has summarized the ignition temperatures and the TOF values at different reaction temperatures of two catalysts. At low-temperature (e.g., 363 K), both catalysts exhibit low TOFs. Pt/Y gives a slightly higher TOF, implying that Pt

nanoparticles with larger particle size are more active than the small ones in this situation. It is noted that there would be an ignition process for Pt catalyzed CO oxidation. The ignition temperature is believed to be important for the design of practical exhaust catalyst for emission control. As the temperature increases, Pt/NanoY transcends the Pt/Y sample with a higher TOF (see Figure 3), which is accompanied by the ignition progress (Figure S10).

Figure 3. CO oxidation of TOFs of both catalysts at 363 K and 403 K.

This change of relative catalytic activities at different temperatures implies a change in the reaction pathways or type of active sites. Pt/NanoY with more H-UC Pt sites is found to exhibit a lower ignition temperature (Table 1, Figure S10), indicating a better potential for smaller Pt particles with more H-UC Pt sites as low-temperature emission-control catalyst. Moreover, the catalytic stabilization of both samples was tested with the under working conditions for more than 10 hours as shown in Figure 3. No deactivation has been observed during the stability test, and the distribution of Pt sites with different coordination states in both samples also remains stable, which is confirmed CO-IR adsorption spectra (Figure S11 and S12).⁴⁴ The average sizes of both

samples does not change up to the reaction at 443 K, which also suggests the unchanged site distribution. (Figure S13-S14)

Figure 4. (a)IR spectra recorded for CO adsorbed on Pt/Y after every two pulses of O₂ at 363 K. Before the introduction of O₂, full CO adsorption was achieved. (b)Percentages of integrated area of CO adsorbed on UC Pt sites (2180-2160 cm⁻¹) and H-UC Pt sites (< 2055 cm⁻¹) after O₂ pulses at 363 K.

Identification of the active sites at low temperatures (before ignition temperature). In order to identify the active sites of Pt/zeolite catalysts, we adopted a modified *in situ* DRIFT spectroscopic method from an early report¹⁶ by injecting O₂ into the cell to react with the CO adsorbed on the surface of Pt/zeolite catalysts every minute, whereas a DRIFT spectrum is collected simultaneously. In a typical experiment, CO was introduced to achieve saturated adsorption, followed by He purging to remove CO in the gas phase (see Figure S16 for the spectra of last five minutes of He purge), and then O₂ pulses were injected while the spectra were collected. According to the DRIFT spectra of Pt/Y at 363 K (see Figure 4a), the intensity of the IR band at 2075 cm⁻¹, corresponding to CO adsorbed on UC Pt sites, decreased after the introduction of

oxygen to the sample, while the IR bands the peak at $< 2050\text{ cm}^{-1}$, corresponding to H-UC Pt sites, almost remained unchanged. Figure 4b shows the percentage of the integrated area of two peaks as a function of pulses indicating that CO adsorbed on UC Pt sites react faster with O_2 , which is consistent with early reports that, at a relatively low temperature (before ignition), UC Pt sites play a predominant role for CO oxidation rather than H-UC Pt sites.¹⁶ Also, for Pt/NanoY with mainly H-UC Pt sites, adsorbed CO barely reacted with O_2 pulses (Figure S17a).

Figure 5. TPD profiles of Pt/Y (a, c) and Pt/NanoY (b, d). He was introduced after the full CO adsorption on the sample at room temperature, after which the temperature was elevated with a ramp of 10 K/min, with the collection of spectra every 5 K.

The low activity of Pt catalysts at low temperatures is proposed to be related to the strong adsorption of CO on surface Pt sites, which blocks the Pt sites for O₂ activation.¹¹ The difference of activities at low temperatures is supposedly related to the difference of CO-adsorption/desorption behavior between UC and H-UC Pt sites. To clarify the CO adsorption behavior over different Pt species, a TPD test was performed by DRIFTS, as shown in Figure 5a-5d. As mentioned above and shown in Figure 5a, for Pt/Y, two peaks of adsorbed CO indicate two different kind of Pt sites. Figure 5c shows the profile of spectroscopic intensities of CO adsorbed on both UC and H-UC Pt sites as the temperature rises. When increasing the temperature, CO adsorbed on UC sites (peak at 2070-2080 cm⁻¹) declined first, reaching the fastest desorption at ~ 420 K. CO adsorbed on H-UC sites (peak at 2040-2050 cm⁻¹) desorbed most extensively at ~ 540 K. For Pt/NanoY (Figure 5b, 5d), only one peak of CO adsorbed on H-UC Pt sites was present, which desorbed most rapidly at ~ 520 K. A redhead analysis³⁶ was also performed to compute the desorption energies of CO on different Pt sites (Table 2, Table S1). For Pt/Y, the desorption energy of CO is 1.42 eV on UC Pt sites and is 1.83 eV on H-UC sites, proving adsorption on H-UC Pt sites is stronger. For Pt/NanoY, the desorption energy is 1.76 eV for H-UC Pt sites. It is noted that, from the CO-TPD profiles, at elevated temperatures, a slight shift of the peak position is observed as well as the desorption, which indicates a minor surface reconstruction¹⁹, especially at ca. 520 K.

Table 2. Experimentally derived and DFT-calculated desorption energy of CO on UC and H-UC Pt Sites.

		Desorption Energy (eV)	
		UC Pt sites	H-UC Pt sites
Experimental	Pt/Y	1.42	1.83
Results	Pt/NanoY	--	1.76
Computational	Pt ₉₂ cluster	1.40 (site 1) ^a	1.52 (site 2) ^a
Results	Pt ₄₃ cluster	--	1.78 (site 1) ^b

Note: Computational desorption energies are calculated on sites labeled on ^a Figure 6a and ^b Figure 6b.

Figure 6. Atomic structures and average CO adsorption energies of CO fully-covered Pt₉₂(a) and Pt₄₃(b) clusters. Yellow and green colors indicate UC Pt sites and H-UC Pt sites, respectively. Numbers in the Pt clusters show the calculated sites for CO desorption. (see Table S2 and S3 for detailed results).

Density functional theory (DFT) calculations were performed to study the adsorption behavior of CO on both UC and H-UC sites. According to the IR results, two Pt clusters (Pt₉₂ and Pt₄₃) were constructed to simulate the surface coordination states of Pt/Y and Pt/NanoY, respectively. The Pt₉₂ cluster was constructed with the surface sites of a combination of mainly UC sites (CN_{M-M}=7-8) and a minority of H-UC sites (CN_{M-M}=5), while the surface of the Pt₄₃ cluster was totally consisted by the H-UC Pt sites with the main CN_{M-M} of 6. It is reported⁴⁵ that CO diffusing from step to terrace sites is more facile than desorption from the step site directly. We calculated both direct desorption and diffusion-assisted desorption of CO molecules from H-UC site at Pt₉₂ cluster. As shown in Figure S18, the diffusion-assisted desorption process is more suitable than the direct desorption process with lower desorption energy, which is also consistent to the previous reference.⁴⁵ The DFT calculation results of adsorption of CO on both clusters (Figure 6a, 6b) show that CO exhibits stronger adsorption on H-UC Pt sites, which explains the reason for its low activity at this temperature, and the calculated desorption energies are 1.40 eV for UC Pt sites and 1.52-1.78 eV for H-UC Pt sites, which are consistent with those derived from the IR-TPD data (Table 2, Table S2-S3), confirming that CO holds a stronger adsorption on H-UC Pt sites than UC Pt sites, which according to the Sabatier Principle could inhibit the catalytic process, making UC Pt sites the active sites at low temperatures.

Figure 7. IR spectra recorded for CO adsorbed on Pt/Y after every two pulses of O₂ at 403 K(a) and 433 K(c); Percentages of integrated area of UC sites (2180-2160 cm⁻¹) and H-UC sites (< 2055 cm⁻¹) after O₂ pulses at 403 K(b) and 433 K(d).

Identification of the active sites at high temperatures (beyond ignition temperature). As mentioned before, the relative activity of Pt particles with different sizes for CO oxidation can change with the temperature (Figure 3). In the literature, for Pt catalysts supported on irreducible supports, a typical ignition behavior can be observed mostly at above 400 K.⁴⁶ As shown in Figure 7a and Figure 7c, a series of spectra were recorded at elevated temperatures after the injection of O₂ to the CO adsorbed Pt/Y sample. At 403 K, both of the peaks decreased after the O₂ was injected, indicating that CO adsorbed on both types of Pt sites can react with O₂ at this temperature. To eliminate the surface reconstruction effect on the observation of the reaction between CO and pulsed O₂, we also performed a CO-adsorption test with both samples at different CO concentrations (see Figure S19). As shown in Figure S19, it can be deduced from the identical spectra that, for both samples, there is nearly no change of the CO adsorption patterns at different CO partial pressures, which could rule out the possibility of surface reconstructions. The CO adsorbed on H-UC sites decreased even faster after O₂ was introduced than CO adsorbed on UC sites at 433 K,

suggesting that, at this temperature where ignition (see Figure S10) took place, the H-UC Pt sites excelled the UC sites to be the most active sites in this catalyst. Figure 7b and 7d summarize the trends of CO consumed on both sites at different temperatures. These trends demonstrate that at elevated temperature, H-UC Pt sites are the most active sites in this system. (See Figure S17b, S17c for IR results for Pt/NanoY at 403 K and 433 K.)

Figure 8. TPO profiles of Pt/Y(a). 1% O₂/He was introduced after He purge of the gas phase CO among the CO-adsorbed catalyst surface. (b) Intensities of CO adsorbed on different Pt sites of Pt/Y and their relative intensity (blue line).

The change of the most active sites is also verified by the temperature-programmed oxidation (TPO) test. To study the reaction of CO adsorbed on different Pt sites at different temperatures, after the adsorption of CO at room temperature, O₂ was introduced during the increase of the temperature. Figure 8a shows the TPO profiles of

Pt/Y, the peak intensities of adsorbed CO on both UC Pt sites and H-UC Pt sites declined with the peak reaction rate at different temperatures, suggesting that the adsorbed CO had reacted with the oxygen as the temperature increased. It should be mentioned that, due to the different extinction coefficient factors of different CO-adsorbing Pt sites for the IR peaks,⁴³ the absolute intensities of different IR peaks do not necessarily demonstrate the quantitative reaction behavior directly. The comparison of the relative intensities of different IR peaks, however, can illustrate the relative activities of different Pt sites at different temperatures semi-quantitatively. The absolute intensities of adsorbed CO peaks are plotted in Figure 8b. The ratio of the intensities of CO adsorbed on UC Pt sites versus that of H-UC Pt sites is also depicted as a function of the temperature. At low temperatures (below 393 K), this ratio decreases as the temperature rises, indicating that CO adsorbed on UC Pt sites react faster with O₂ than CO adsorbed on H-UC Pt sites, which proves that, at low temperatures, UC Pt sites are the active sites. However, as the temperature increases up to 400 K, especially higher than 420 K, the change of the ratio has become a mounting pattern along the raise of the temperature, proving that, at high temperatures, H-UC Pt sites are the most active sites (See Figure S20 for TPO profiles of Pt/NanoY). Additionally, there is no peak shift observed during the TPO test like it can be seen in the TPD test (Figure 5), indicating that, once O₂ is introduced in the system, the reconstruction of Pt surfaces would not affect the observation of active sites.

The above results from DRIFT experiments have shown that the active sites have shifted from UC to H-UC Pt sites when increasing the reaction temperature. It is believed that the reaction of O₂ with CO adsorbed Pt surfaces is the rate-limiting step since the strongly absorbed CO species will block the surface of Pt nanoparticles.^{32, 47, 48} In other words, at higher temperatures where CO started to desorb from the fully adsorbed Pt surface (Figure 5), the activity of a Pt site to catalyze this reaction might depend on its ability to activate O₂. This proposed reason for the elevated activity of H-UC sites at above ignition temperature is also supported by kinetic studies (Figure 9).⁴⁹ We studied the kinetic behavior of both catalysts at a relatively high temperature (403

K), where higher turnover frequency is observed. At 403 K, the kinetic equation could be calculated to be:

$$r_{\text{Pt/Y}} = k_{\text{Pt/Y}}[\text{CO}]^{-0.46}[\text{O}_2]^{0.68}$$

$$r_{\text{Pt/NanoY}} = k_{\text{Pt/NanoY}}[\text{CO}]^{-0.62}[\text{O}_2]^{0.92}$$

Figure 9. Reaction orders for CO and O₂ of Pt/Y and Pt/NanoY. The rate of CO reaction can be described as $r = k[\text{CO}]^x[\text{O}_2]^y$ with x, y being constants.⁴⁹

The negative reaction order of CO further confirms the inhibition of oxygen activation from the CO adsorption.^{32, 49} The high reaction order of CO in Pt/NanoY also implies that the CO adsorption on H-UC sites is stronger than that of UC sites. Besides, TOFs are proportional to O₂ pressure, indicating that the O₂ activation limits the rate of this reaction.³² It can also be concluded that the activation of O₂ affects H-UC Pt sites in a more significant manner due to the higher reaction order for O₂. It should be noted that, according to previous report,³³ at even higher temperatures (700-800 K), O₂ dissociation might block the surface from further reaction, leading to a different situation. It is, however, very unlikely for O₂ to poison the surface at temperatures in this work due to the positive reaction order of O₂.³² At this point, however, CO does not

necessarily poison the surface of Pt particles, providing positions to bind oxygen species, allowing continuous and rapid catalytic reaction to occur. The better ability to activate O_2 further accounts for the higher activity of H-UC Pt sites at high temperatures.

Figure 10. Atomic structures of O_2 adsorbed on CO saturated Pt_{43} (a) and Pt_{92} (b) clusters after one CO molecule desorption and the corresponding O_2 adsorption energies are labelled. Yellow and green colors indicate UC Pt sites and H-UC Pt sites, respectively. Numbers in the Pt clusters show the calculated sites for O_2 activation. (see Table S4 for detailed results). Gray, black, red, purple balls indicate Pt, C, O (in CO molecules), O (in O_2 molecules) atoms, respectively. Electronic and bond length analysis of adsorbed O_2 on Pt_{43} (c) and Pt_{92} (d) clusters.

The above kinetic results of reaction orders confirm the vital role of O_2 activation on CO saturated Pt sites. According to the CO desorption energies on UC and H-UC sites (spectroscopic) and different sites of Pt_{43} and Pt_{92} clusters, we considered the first CO desorption sites on Pt_{43} and Pt_{92} clusters with the increase of reaction temperature. We then calculated the adsorption behavior of O_2 on the CO-free Pt sites as shown in Figure 10 and Table S4. It turns out that Pt_{43} cluster with a majority of H-UC Pt sites can adsorb O_2 with an adsorption energy of -0.54 eV (Figure 10a), while for the Pt_{92} cluster with

more UC Pt sites, O₂ is weakly adsorbed with an adsorption energy of +0.01 eV (Figure 10b). A more efficient charge transfer between Pt₄₃ and O₂ is also confirmed by the theoretical calculations (see Figure 10c, 10d), which may further contribute a higher capability for O₂ activation on smaller Pt nanoparticles. The higher capability O₂ under the CO adsorption equilibrium on Pt may lead to a better activity for CO oxidation, especially above ignition temperature where the activation could progress.

Figure 11. Proposed reaction pathways of CO oxidation for both catalysts within Langmuir-Hinshelwood or Eley-Rideal mechanisms. Insets show the corresponding atomic structures of transition states.

The whole CO oxidation reaction mechanism was also calculated under either Langmuir-Hinshelwood or Eley-Rideal pathways (Figure 11). For either reaction pathways, smaller Pt clusters with more H-UC sites can catalyze this process more rapidly provided that O₂ can activate the adsorbed CO, confirming the higher activity at high temperatures.

Conclusion

In the current work, we have identified the temperature-dependent active sites of Pt/zeolite catalysts for CO oxidation reaction by combining spectroscopic, kinetic and theoretical studies. At low temperatures where the CO conversion is low, Pt surface sites with higher coordination numbers are more active than those with lower coordination numbers. As the temperature rises to the ignition point, Pt sites with lower

coordination numbers become more active, which emphasizes the significance of creating more defects in the Pt catalysts to improve the overall activity, considering the significant turnover at this temperature. Strong adsorption of CO on the surface of Pt nanoparticles limits the activity at low temperatures. The activation of O₂ is more favorable on UC Pt sites due to a lower CO adsorption energy on these Pt sites at low temperature (typically lower than 370 K). At high reaction temperature, the situation changes. The inhibition effect of CO adsorption is overcome and the higher capability to activate O₂ leads to a better CO oxidation activity on H-UC Pt sites, leading to a better overall activity and lower ignition temperature. As a result, we should consider the working temperature when designing practical catalysts with different purposes. For example, the U. S. Department of Energy has proposed a request for catalysts that convert over 90 % all pollutants at 150°C,⁵⁰ making the catalysts with more H-UC sites more practically potential. These findings could contribute to the design of low-temperature three-way catalysts, and emphasize the importance to re-examine the active sites of different catalysts under the consideration of reaction temperature.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

More STEM images, CO oxidation, more DRIFT spectra and detailed DFT analysis.

AUTHOR INFORMATION

Corresponding Author

* gaofei@nju.edu.cn

Author Contributions

† These authors contribute equally in this work.

Funding Sources

The financial supports of National Natural Science Foundation of China (No. 21573105), Natural Science Foundation of Jiangsu Province (BK20161392) are gratefully acknowledged.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Beamline BL14W1 (Shanghai Synchrotron Radiation Facility) is thanked for the beam time.

Prof. Peng Wang and Dr. Shaojie Fu at National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, P. R. China are thanked for the help with the STEM imaging and relevant data processing.

References

1. Thomas, J. M.; Thomas, W. J., *Principles and practice of heterogeneous catalysis*. John Wiley & Sons: 2014.
2. Somorjai, G. A.; Li, Y., *Introduction to surface chemistry and catalysis*. John Wiley & Sons: 2010.
3. Newton, M. A.; van Beek, W., Combining synchrotron-based X-ray techniques with vibrational spectroscopies for the in situ study of heterogeneous catalysts: a view from a bridge. *Chem. Soc. Rev.* **2010**, *39*, 4845-4863.
4. Liu, L.; Corma, A., Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chem. Rev.* **2018**, *118*, 4981-5079.
5. van Spronsen, M. A.; Frenken, J. W. M.; Groot, I. M. N., Surface science under reaction conditions: CO oxidation on Pt and Pd model catalysts. *Chem. Soc. Rev.* **2017**, *46*, 4347-4374.
6. Eiswirth, M.; Moller, P.; Wetzl, K.; Imbihl, R.; Ertl, G., Mechanisms of spatial self-organization in isothermal kinetic oscillations during the catalytic CO oxidation on Pt single crystal surfaces. *J. Chem. Phys.* **1989**, *90*, 510-521.
7. Sander, M.; Imbihl, R.; Ertl, G., The mechanism of kinetic oscillations in catalytic oxidation of CO on Pt (210). *J. Chem. Phys.* **1991**, *95*, 6162-6170.
8. Sander, M.; Imbihl, R.; Ertl, G., Kinetic oscillations in catalytic CO oxidation on a cylindrical Pt single crystal surface. *J. Chem. Phys.* **1992**, *97*, 5193-5204.
9. Ertl, G.; Neumann, M.; Streit, K. M., Chemisorption of CO on the Pt (111) surface. *Surf. Sci.* **1977**, *64*, 393-410.
10. Tao, F.; Dag, S.; Wang, L.-W.; Liu, Z.; Butcher, D. R.; Bluhm, H.; Salmeron, M.; Somorjai, G. A., Break-up of stepped platinum catalyst surfaces by high CO coverage. *Science* **2010**, *327*, 850-853.
11. Engel, T.; Ertl, G., Elementary steps in the catalytic oxidation of carbon monoxide on platinum metals. *Advances in Catalysis* **1979**, *28*, 1-78.
12. Neugebahren, J.; Borodin, D.; Hahn, H. W.; Altschäffel, J.; Kandratsenka, A.; Auerbach, D. J.; Campbell, C. T.; Schwarzer, D.; Harding, D. J.; Wodtke, A. M., Velocity-resolved kinetics of site-specific carbon monoxide oxidation on platinum surfaces. *Nature* **2018**, *558*, 280.
13. Yeates, R.; Turner, J.; Gellman, A.; Somorjai, G. A., The oscillatory behavior of the CO oxidation reaction at atmospheric pressure over platinum single crystals: Surface analysis and pressure dependent mechanisms. *Surf. Sci.* **1985**, *149*, 175-190.
14. Liu, X.; Zhu, Q.; Lang, Y.; Cao, K.; Chu, S.; Shan, B.; Chen, R., Oxide-Nanotrap-Anchored Platinum Nanoparticles with High Activity and Sintering Resistance by Area-Selective Atomic Layer Deposition. *Angew. Chem.* **2017**, *129*, 1670-1674.
15. Vendelbo, S.; Elkjær, C. F.; Falsig, H.; Puspitasari, I.; Dona, P.; Mele, L.; Morana, B.; Nelissen, B.; Van Rijn, R.; Creemer, J., Visualization of oscillatory behaviour of Pt nanoparticles catalysing CO oxidation. *Nature materials* **2014**, *13*, 884.
16. Kale, M. J.; Christopher, P., Utilizing Quantitative in Situ FTIR Spectroscopy To Identify Well-Coordinated Pt Atoms as the Active Site for CO Oxidation on Al₂O₃-Supported Pt Catalysts. *ACS Catalysis* **2016**, *6*, 5599-5609.
17. Yoshida, H.; Kuwauchi, Y.; Jinschek, J. R.; Sun, K.; Tanaka, S.; Kohyama, M.; Shimada, S.; Haruta, M.; Takeda, S., Visualizing gas molecules interacting with supported nanoparticulate catalysts at reaction conditions. *Science* **2012**, *335*, 317-319.

18. Ding, K.; Gulec, A.; Johnson, A. M.; Schweitzer, N. M.; Stucky, G. D.; Marks, L. D.; Stair, P. C., Identification of active sites in CO oxidation and water-gas shift over supported Pt catalysts. *Science* **2015**, *350*, 189-92.
19. Avanesian, T.; Dai, S.; Kale, M. J.; Graham, G. W.; Pan, X.; Christopher, P., Quantitative and Atomic-Scale View of CO-Induced Pt Nanoparticle Surface Reconstruction at Saturation Coverage via DFT Calculations Coupled with in Situ TEM and IR. *J. Am. Chem. Soc.* **2017**, *139*, 4551-4558.
20. Liu, L.; Zakharov, D. N.; Arenal, R.; Concepcion, P.; Stach, E. A.; Corma, A., Evolution and stabilization of subnanometric metal species in confined space by in situ TEM. *Nat Commun* **2018**, *9*, 574.
21. Moliner, M.; Gabay, J. E.; Kliewer, C. E.; Carr, R. T.; Guzman, J.; Casty, G. L.; Serna, P.; Corma, A., Reversible Transformation of Pt Nanoparticles into Single Atoms inside High-Silica Chabazite Zeolite. *J. Am. Chem. Soc.* **2016**, *138*, 15743-15750.
22. 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 Pt1/FeOx. *Nat Chem* **2011**, *3*, 634-41.
23. Kistler, J. D.; Chotighrai, N.; Xu, P.; Enderle, B.; Praserttham, P.; Chen, C. Y.; Browning, N. D.; Gates, B. C., A single-site platinum CO oxidation catalyst in zeolite KLTL: microscopic and spectroscopic determination of the locations of the platinum atoms. *Angew. Chem. Int. Ed.* **2014**, *53*, 8904-7.
24. Liu, J., Catalysis by Supported Single Metal Atoms. *ACS Catalysis* **2017**, *7*, 34-59.
25. Nie, L.; Mei, D.; Xiong, H.; Peng, B.; Ren, Z.; Hernandez, X. I. P.; DeLaRiva, A.; Wang, M.; Engelhard, M. H.; Kovarik, L., Activation of surface lattice oxygen in single-atom Pt/CeO2 for low-temperature CO oxidation. *Science* **2017**, *358*, 1419-1423.
26. Therrien, A. J.; Hensley, A. J. R.; Marcinkowski, M. D.; Zhang, R.; Lucci, F. R.; Coughlin, B.; Schilling, A. C.; McEwen, J.-S.; Sykes, E. C. H., An atomic-scale view of single-site Pt catalysis for low-temperature CO oxidation. *Nature Catalysis* **2018**, *1*, 192-198.
27. Casapu, M.; Fischer, A.; Gänzler, A. M.; Popescu, R.; Crone, M.; Gerthsen, D.; Türk, M.; Grunwaldt, J.-D., Origin of the Normal and Inverse Hysteresis Behavior during CO Oxidation over Pt/Al2O3. *ACS Catalysis* **2017**, *7*, 343-355.
28. Awala, H.; Gilson, J.-P.; Retoux, R.; Boullay, P.; Goupil, J.-M.; Valtchev, V.; Mintova, S., Template-free nanosized faujasite-type zeolites. *Nature materials* **2015**, *14*, 447-451.
29. de Graaf, J.; van Dillen, A. J.; de Jong, K. P.; Koningsberger, D. C., Preparation of Highly Dispersed Pt Particles in Zeolite Y with a Narrow Particle Size Distribution: Characterization by Hydrogen Chemisorption, TEM, EXAFS Spectroscopy, and Particle Modeling. *J. Catal.* **2001**, *203*, 307-321.
30. Lu, J.; Aydin, C.; Browning, N. D.; Gates, B. C., Imaging isolated gold atom catalytic sites in zeolite NaY. *Angew. Chem. Int. Ed.* **2012**, *51*, 5842-6.
31. Ortalan, V.; Uzun, A.; Gates, B. C.; Browning, N. D., Direct imaging of single metal atoms and clusters in the pores of dealuminated HY zeolite. *Nat Nanotechnol* **2010**, *5*, 506-10.
32. Allian, A. D.; Takanabe, K.; Fajdala, K. L.; Hao, X.; Truex, T. J.; Cai, J.; Buda, C.; Neurock, M.; Iglesia, E., Chemisorption of CO and mechanism of CO oxidation on supported platinum nanoclusters. *J. Am. Chem. Soc.* **2011**, *133*, 4498-517.
33. García-Diéguez, M.; Iglesia, E., Structure sensitivity via decoration of low-coordination exposed metal atoms: CO oxidation catalysis on Pt clusters. *J. Catal.* **2013**, *301*, 198-209.
34. Sirita, J.; Phanichphant, S.; Meunier, F. C., Quantitative Analysis of Adsorbate Concentrations by

Diffuse Reflectance FT-IR. *Anal. Chem.* **2007**, *79*, 3912-3918.

35. Redhead, P., Thermal desorption of gases. *Vacuum* **1962**, *12*, 203-211.
36. Thang, H. V.; Pacchioni, G.; DeRita, L.; Christopher, P., Nature of stable single atom Pt catalysts dispersed on anatase TiO₂. *J. Catal.* **2018**, *367*, 104-114.
37. YU Hai-Sheng, W. X.-J., LI Jiong, GU Song-Qi, ZHANG Shuo., The XAFS beamline of SSRF. *Nuclear Science and Techniques* **2015**, *26*, 50102-050102.
38. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of synchrotron radiation* **2005**, *12*, 537-541.
39. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical review B* **1996**, *54*, 11169.
40. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational materials science* **1996**, *6*, 15-50.
41. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
42. Zhang, J.; Wang, L.; Zhang, B.; Zhao, H.; Kolb, U.; Zhu, Y.; Liu, L.; Han, Y.; Wang, G.; Wang, C.; Su, D. S.; Gates, B. C.; Xiao, F.-S., Sinter-resistant metal nanoparticle catalysts achieved by immobilization within zeolite crystals via seed-directed growth. *Nature Catalysis* **2018**, *1*, 540-546.
43. Yoshinobu, J.; Tsukahara, N.; Yasui, F.; Mukai, K.; Yamashita, Y., Lateral Displacement by Transient Mobility in Chemisorption of CO on Pt(997). *Phys. Rev. Lett.* **2003**, *90*, 248301.
44. Cao, K.; Liu, X.; Zhu, Q.; Shan, B.; Chen, R., Atomically Controllable Pd@Pt Core-Shell Nanoparticles towards Preferential Oxidation of CO in Hydrogen Reactions Modulated by Platinum Shell Thickness. *ChemCatChem* **2016**, *8*, 326-330.
45. Golibrzuch, K.; Shirhatti, P. R.; Geweke, J.; Werdecker, J.; Kandratsenka, A.; Auerbach, D. J.; Wodtke, A. M.; Bartels, C., CO Desorption from a Catalytic Surface: Elucidation of the Role of Steps by Velocity-Selected Residence Time Measurements. *J. Am. Chem. Soc.* **2015**, *137*, 1465-1475.
46. Singh, J.; Alayon, E. M.; Tromp, M.; Safonova, O. V.; Glatzel, P.; Nachttegaal, M.; Frahm, R.; van Bokhoven, J. A., Generating highly active partially oxidized platinum during oxidation of carbon monoxide over Pt/Al₂O₃: in situ, time-resolved, and high-energy-resolution X-ray absorption spectroscopy. *Angew. Chem. Int. Ed.* **2008**, *47*, 9260-4.
47. Liu, X.; Tang, Y.; Shen, M.; Li, W.; Chu, S.; Shan, B.; Chen, R., Bifunctional CO oxidation over Mn-mullite anchored Pt sub-nanoclusters via atomic layer deposition. *Chemical science* **2018**, *9*, 2469-2473.
48. Mu, R.; Fu, Q.; Xu, H.; Zhang, H.; Huang, Y.; Jiang, Z.; Zhang, S.; Tan, D.; Bao, X., Synergetic effect of surface and subsurface Ni species at Pt-Ni bimetallic catalysts for CO oxidation. *J. Am. Chem. Soc.* **2011**, *133*, 1978-86.
49. Cargnello, M.; Doan-Nguyen, V.; Gordon, T. R.; Diaz, R. E.; Stach, E. A.; Gorte, R. J.; Fornasiero, P.; Murray, C. B., Control of metal nanocrystal size reveals metal-support interface role for ceria catalysts. *Science* **2013**, 1240148.
50. Zammit, M.; DiMaggio, C. L.; Kim, C. H.; Lambert, C.; Muntean, G. G.; Peden, C. H.; Parks, J. E.; Howden, K. *Future automotive aftertreatment solutions: The 150° C challenge workshop report*; Pacific Northwest National Lab.(PNNL), Richland, WA (United States): 2013.

Figures and Tables

Figure Captions

Figure 1. a and b) STEM-HAADF images of Pt/Y(a) and Pt/NanoY(b) The average sizes of Pt particles of Pt/Y(c) and Pt/NanoY(d) were estimated from particle counts in STEM-HAADF images with more than 1000 particles. (scale bar: 50 nm)

Figure 2. Normalized DRIFT spectra of CO adsorption at 363 K for Pt/Y(orange) and Pt/NanoY(green).

Figure 3. CO oxidation of TOFs of both catalysts at 363 K and 403 K.

Figure 4. (a)IR spectra recorded for CO adsorbed on Pt/Y after every two pulses of O₂ at 363 K. Before the introduction of O₂, full CO adsorption was achieved. (b)Percentages of integrated area of CO adsorbed on UC Pt sites (2180-2160 cm⁻¹) and H-UC Pt sites (< 2055 cm⁻¹) after O₂ pulses at 363 K.

Figure 5. TPD profiles of Pt/Y (a, c) and Pt/NanoY (b, d). He was introduced after the full CO adsorption on the sample at room temperature, after which the temperature was elevated with a ramp of 10 K/min, with the collection of spectra every 5 K.

Figure 6. Atomic structures and average CO adsorption energies of CO fully-covered Pt₉₂(a) and Pt₄₃(b) clusters. Yellow and green colors indicate UC Pt sites and H-UC Pt sites, respectively. Numbers in the Pt clusters show the calculated sites for CO desorption. (see Table S2 and S3 for detailed results).

Figure 7. IR spectra recorded for CO adsorbed on Pt/Y after every two pulses of O₂ at 403 K(a) and 433 K(c); Percentages of integrated area of UC sites (2180-2160 cm⁻¹) and H-UC sites (< 2055 cm⁻¹) after O₂ pulses at 403 K(b) and 433 K(d).

Figure 8. TPO profiles of Pt/Y(a). 1% O₂/He was introduced after He purge of the gas phase CO among the CO-adsorbed catalyst surface. (b) Intensities of CO adsorbed on different Pt sites of Pt/Y and their relative intensity (blue line).

Figure 9. Reaction orders for CO and O₂ of Pt/Y and Pt/NanoY. The rate of CO reaction can be described as $r = k[\text{CO}]^x[\text{O}_2]^y$ with x, y being constants.⁴⁹

Figure 10. Atomic structures of O₂ adsorbed on CO saturated Pt₄₃(a) and Pt₉₂(b) clusters after one CO molecule desorption and the corresponding O₂ adsorption energies are labelled. Yellow and green colors indicate UC Pt sites and H-UC Pt sites, respectively. Numbers in the Pt clusters show the calculated sites for O₂ activation. (see Table S4 for detailed results). Gray, black, red, purple balls indicate Pt, C, O (in CO molecules), O (in O₂ molecules) atoms, respectively. Electronic and bond length analysis of adsorbed O₂ on Pt₄₃(c) and Pt₉₂(d) clusters.

Figure 11. Proposed reaction pathways of CO oxidation for both catalysts within Langmuir-Hinshelwood or Eley-Rideal mechanisms. Insets show the corresponding atomic structures of transition states.

Table Titles

Table 1. Synthesis and catalytic performance of Pt/Y and Pt/NanoY

Table 2. Experimentally derived and DFT-calculated desorption energy of CO on UC and H-UC Pt Sites.

Table of Content