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11, 3578**Pt₁-O₄ as active sites boosting CO oxidation via a non-classical Mars–van Krevelen mechanism†**Yang Lou, ^{*ab} Yongping Zheng,^{*c} Wenyi Guo^b and Jingyue Liu ^{*a}

Single-atom catalysts (SACs) exhibit excellent performance for various catalytic reactions but it is still challenging to have adequate total activity for practical applications. Here we report the high-valence, square planar Pt₁-O₄ as an active site that enables significantly to increase the total activity of the Pt₁/Fe₂O₃ SAC with a Pt loading of only ~30 ppm, which is similar to that of a 1.0 wt% nano-Pt/Fe₂O₃, for CO oxidation at 350 °C. Density functional theory calculations reveal that Pt₁-O₄ catalyzes CO oxidation through a non-classical Mars–van Krevelen mechanism. The adsorbed O₂ on Pt₁ atoms activates the coordination oxygen in the Pt₁-O₄ configuration, and then a barrierless O₂ dissociation occurs on the Pt₁-Fe₂ triangle to replenish the consumed coordination oxygen by the cooperative action of Pt 5d and Fe 3d electrons. This work provides a new fundamental understanding of oxidation catalysis on stable and active SACs, providing guidance for rationally designing future heterogeneous catalysts.

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rsc.li/catalysis**1. Introduction**

Noble metal-based catalysts have been widely utilized in various important chemical transformations.^{1–3} However, most of the noble metal-based catalysts have low atom efficiency since their dispersion is much less than 100%, especially for larger nanoparticles (NPs), which significantly increases the usage of noble metal and unavoidably increases the cost of supported noble metal catalysts. The recently developed single-atom catalysts (SACs) have the potential of increasing the atom efficiency to 100% and thus significantly decrease the cost of supported noble metal catalysts,^{4–8} which also demonstrate excellent performance for various important catalytic reactions.^{9–19} However, the major issues for practical applications of SACs are the low total activity (defined as the catalytic activity based on the total weight of the catalyst including both the active metal component and the support) due to the low levels of metal loading and, in some cases, the sintering during catalytic reactions, especially at high reaction

temperatures.^{20–23} Progress toward stabilizing single metal atoms and significantly increasing the total activity of SACs is critical to advancing SACs for commercial applications. One approach to solve this problem is to anchor high-number-density single metal atoms on the support surfaces so that the total activity of the synthesized SACs can be significantly increased.¹¹ Another approach is to make each catalytic site super active so that even with low levels of isolated metal atoms, the total activity of the fabricated SACs is high enough for practical applications.

The term of highly active catalysts has been defined based on the activity of supported Au catalysts for CO oxidation,²⁴ which corresponds to 20 mmol_{CO} g_{cat}^{−1} h^{−1} for a 1 wt% Au loading. Although the specific reaction rate (calculated on the basis of active metal species) of single metal atoms may be higher than that of their NP counterparts, the total activity of a stable SAC can barely satisfy the definition of highly active catalysts due to the low-number-density of the active metal atoms. When the catalytic activity of each single metal atom is significantly increased, the total catalytic activity of a SAC can be comparable to their NP counterparts, which usually require high levels of metal loading. We define such SACs as super active, in analogy to super active Ziegler–Natta catalysts used in polymer synthesis such as olefin polymerization.^{25–28} These super active polymerization catalysts have achieved important production process innovations,²⁹ which have influenced our daily life in countless beneficial ways.

In this work, we report that by constructing a unique Pt₁-O₄ structural configuration as the active site, single Pt (Pt₁) atoms supported on reducible metal oxides (*e.g.*, Fe₂O₃ and CeO₂) can

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become super active for CO oxidation at elevated temperatures. For CO oxidation at 350 °C, the specific activity of the Pt₁/Fe₂O₃ SAC with a Pt loading of only ~30 ppm is similar to that of the nano-Pt/Fe₂O₃ catalyst with a Pt loading of ~1.0 wt%. To our knowledge, this is the first time that such a super active behavior of a SAC under relatively high temperature reaction conditions is reported. Density functional theory (DFT) calculations reveal that the high-valence Pt₁-O₄ active site efficiently catalyzes CO oxidation through a non-classical Mars–van Krevelen (MvK) reaction pathway.

2. Experimental section

2.1 Catalyst preparation

Fe₂O₃ and CeO₂ nanocrystallites are synthesized by a precipitation method. Iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Sigma-Aldrich) and sodium carbonate (Na₂CO₃, Sigma-Aldrich) are used as a precursor salt and a precipitant, respectively. The obtained precipitates are dried at 60 °C for 12 h in air. The Fe₂O₃ and CeO₂ precipitates are calcined at 350 °C for 4 h and 400 °C for 5 h in air, respectively. γ-Al₂O₃ is purchased from Inframat Advanced Materials.

Single Pt atoms are dispersed onto the surfaces of Fe₂O₃, CeO₂ and γ-Al₂O₃ by a strong adsorption method.^{13,14,30} A corresponding amount of Pt (H₂PtCl₄·6H₂O, Sigma-Aldrich) is firstly dispersed onto the Fe₂O₃, γ-Al₂O₃, and CeO₂ surfaces. The pH values of the Pt-containing solutions are finely controlled for each support material. Typically, a pH value of 2.3 is used for Fe₂O₃ and 3.0 is used for γ-Al₂O₃ and CeO₂. After being aged at room temperature for 2 hours and filtered, the solid powders are dried at 60 °C for 12 h in air. The Pt/Fe₂O₃, Pt/γ-Al₂O₃, and Pt/CeO₂ catalysts are calcined at 300 °C for 2 h in air. The actual loadings of Pt measured by inductively coupled plasma mass spectrometry (ICP-MS) on Fe₂O₃, γ-Al₂O₃, and CeO₂ are 0.029 wt%, 0.034 wt%, and 0.013 wt%, respectively.

A corresponding amount of Pd (PdCl₂, Sigma-Aldrich) is firstly deposited onto the surfaces of Fe₂O₃. The pH of the Pd-containing solutions is finely tuned to 3.8. After being aged at room temperature for 2 hours and filtered, the Pd/Fe₂O₃ powders are dried at (60 °C/12 h) and calcined at 300 °C for 2 h in air. The Pd actual loading on Fe₂O₃ is 0.17 wt% as measured by ICP-MS.

Pt particles over Fe₂O₃ and CeO₂ are synthesized by a colloidal method.⁵ Typically, NaOH (2.32 mmol) and H₂-PtCl₆·6H₂O (5.16 μmol) are added into 13.3 ml glycol solution with stirring for 1 h at room temperature and then the resulting solution is heated at 140 °C for 4 h to obtain the brown colloidal solution. Then, 100 mg Fe₂O₃ (CeO₂) is dispersed in the obtained colloidal solution under stirring at room temperature. After stirring for 2 h, the precipitate is filtered and washed thoroughly with distilled water until free of chloride ions (tested using saturated AgNO₃ solution). The obtained precipitate is dried at (60 °C/12 h) and calcined at 350 °C for 4 h in air. Thorough washing with DI water and

air calcination ensure that organic residues on the Pt surfaces are eliminated.

The synthesized SACs are denoted as Pd₁/Fe₂O₃, Pt₁/Fe₂O₃, and Pt₁/γ-Al₂O₃ and the catalysts of Pt nanoparticles supported on Fe₂O₃ and CeO₂ are denoted as nano-Pt/Fe₂O₃ and nano-Pt/CeO₂, respectively.

2.2 Catalyst characterization

The loadings of Pt species are measured using a Thermo Finnigan iCAP Q quadrupole ICP-MS with collision cell technology (CCT), which are run in kinetic energy discrimination mode by taking in-line aspiration as the internal standard of multiple elements.

HAADF-STEM images are acquired on a JEM-ARM200F TEM/STEM instrument with a resolution of 0.08 nm. Before collecting data, the catalysts are dispersed in ethanol using an ultrasonic machine. Then a droplet of dispersed catalyst solution is dropped onto a copper grid coated with lacey carbon film. Low-magnification images are extensively screened to make sure that Pt nanoparticles are not present in the as-synthesized or used SACs. Atomic resolution images are used to screen the presence of individual Pt atoms and the absence of Pt clusters in both the fresh and the used SACs.

Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) of CO adsorption on Pt₁ and nano-Pt catalysts is conducted using an FT-IR spectrometer (Nicolet 6700) with a MCT detector (cooled by liquid nitrogen). The sample cell is provided with CaF₂ windows. DRIFT spectra are acquired with a resolution of 4 cm⁻¹ and 64 scans in Kubelka–Munk units. When collecting the data of CO-DRIFTS on Pt₁ and nano-Pt, the samples are firstly heated at 120 °C for 40 min to remove H₂O and other possible impurities on the surface. Then the samples are cooled to 25 °C and 50 °C, respectively, and the background is acquired until the background is stable. Then, CO (1 vol% CO/He) molecules are allowed to adsorb on the catalyst surfaces until the catalyst surfaces are saturated with adsorbed gaseous CO (~15 min). Then, pure He is used to purge out the gaseous CO from the sample cell so that the chemically adsorbed/bound CO species can be observed. After collecting the background signal, the whole procedure was recorded by FTIR including the processes of CO adsorption and He purging.

The X-ray absorption fine structure spectra of the Pt₁/Fe₂O₃ SAC, nano-Pt/Fe₂O₃, Pt₁/CeO₂ SAC, nano-Pt/CeO₂ and Pt foil experiments are collected at the Advanced Photon Source (APS) on beamline 10-BM (MRCAT) with an electron energy of 7 GeV and an average current of 100 mA. The XAFS spectra are collected in fluorescence mode. Data reduction, data analysis, and EXAFS fitting are performed using the Athena and Artemis software packages. The energy calibration of the catalysts is conducted through a standard Pt foil and PtO₂.

2.3 Kinetic measurements

The specific reaction rate (calculated based on eqn (1)) of all the synthesized nano-Pt/Fe₂O₃, Pt₁/Fe₂O₃ SAC, Pt₁/γ-Al₂O₃

SAC, Pd₁/Fe₂O₃ SAC and the corresponding supports (Fe₂O₃, and γ -Al₂O₃) is measured under typical reaction conditions of 1.0 vol% CO, 4.0 vol% O₂ and He balance. Feed gas compositions of 2.5 vol% CO, 2.5 vol% O₂ and He balance and 2.5 vol% CO, 1.25 vol% O₂ and He balance are also used for measuring the specific reaction rate of Fe₂O₃, nano-Pt/Fe₂O₃ and Pt₁/Fe₂O₃ SAC as well as the CeO₂, nano-Pt/CeO₂ and Pt₁/CeO₂ SAC catalysts. To eliminate the internal and external diffusion effects, the CO conversion rates are adjusted to below 20% when conducting the kinetic measurements by adjusting the hourly gas space velocity to calculate the reaction rates. The concentrations of CO and CO₂ in the outlet stream are measured using an on-line gas chromatograph (Agilent 7890A equipped with a thermal conductivity detector).

Since the three different supports also exhibit catalytic activity for CO oxidation at elevated temperatures, we subtract the contribution of the support surfaces when we compare the catalytic behavior of the Pt₁ atoms supported on different supports and the supports are treated following the same procedures as done on catalysts. Since the Pt loading is extremely low we can assume that the reaction rates originate from the Pt₁ atoms by subtracting the reaction rates of the supports from the reaction rates of the corresponding SACs. This treatment is justifiable as long as the total number of the supported Pt₁ atoms is much less than the total number of the surface atoms of the support material and the activity of the SACs is much higher than that of the support.

The TOF is defined, in this case, as the amount of CO molecules converted over one Pt atom in one second and calculated based on eqn (2).

$$r = \frac{C_{\text{CO}} \cdot X_{\text{CO}} \cdot V \cdot P_{\text{atm}}}{m_{\text{cat}} \cdot R \cdot T} \quad (\text{mol s}^{-1} \text{ g}_{\text{cat}}^{-1}) \quad (1)$$

$$\text{TOF} = \frac{(r_{\text{catalyst}} - r_{\text{support}}) \cdot N_{\text{A}}}{N_{\text{Pt}}} \quad (\text{s}^{-1}) \quad (2)$$

where r_{catalyst} and r_{support} : the reaction rates of catalysts and supports, respectively; m_{cat} : mass of catalyst in the reactor bed (g); C_{CO} : concentration of CO in the feed gas; V : total flow rate of the inlet gas mixture (m³ s⁻¹); X_{CO} : conversion rate of CO; R : molar gas constant (8.314 Pa m³ mol⁻¹ K⁻¹); T : reaction temperature (K); P_{atm} : atmospheric pressure (101.3 KPa); N_{A} : Avogadro constant (6.02×10^{23} mol⁻¹); and N_{Pt} : the number of Pt atoms per gram of catalyst.

2.4 DFT calculation methods

Computational studies are performed through spin-polarized density functional theory with Hubbard- U correction (DFT+ U) ($U_{\text{eff}} = 5$ eV)³¹ implemented in the Vienna *Ab initio* Simulation Package (VASP).³² The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional (PBE-GGA)³³ is adopted for the exchange correlation interactions. The projector augmented wave (PAW)³⁴ method and the plane-wave

basis with an energy cutoff of 450 eV are used for efficient electronic calculations. The pseudopotential valence-electron configurations used in the calculations are Pt 5d⁹6s¹, Fe 3d⁶4s², O 2s²2p⁴, and C 2s²2p². The structural calculations are relaxed to a force convergence of 0.01 eV Å⁻¹ for each ionic step and an energy convergence of 10⁻⁵ eV for each electronic step. The k -space sampling is done using the Monkhorst–Pack grid with a k spacing of less than 0.03 Å⁻¹. To obtain more reliable free energies, the spin ordering of the simulated hematite α -Fe₂O₃ is considered and relaxed in its most preferable experimental antiferromagnetic configuration, *i.e.*, spin-up and -down Fe ions are antiferromagnetically aligned along the [001] direction and ferromagnetically ordered in each (001) FeO plane. This magnetic ordering is preserved in the slab calculation for the modeling of the (001) surface. Additionally, the top and bottom surfaces in the slab supercell are spaced to more than 10 Å distance in vacuum to prevent any periodic image interaction. The DFT-PBE calculated over-binding energies of O₂, CO and CO₂ are corrected according to a previous report.³¹

3. Results and discussions

3.1 Synthesis and identification of Pt₁ SACs

Pt₁ atoms were dispersed onto the surfaces of Fe₂O₃ and CeO₂ nanocrystallites with a loading level of 0.029 wt% and 0.013 wt%, respectively, determined by inductively coupled plasma mass spectrometry (ICP-MS). By examining numerous low- and high-magnification HAADF-STEM images of both the fresh and the used Pt₁/Fe₂O₃ SACs (Fig. 1a and b, S1 and S2†) and Pt₁/CeO₂ SACs (Fig. 1c and d, S3 and S4†), we

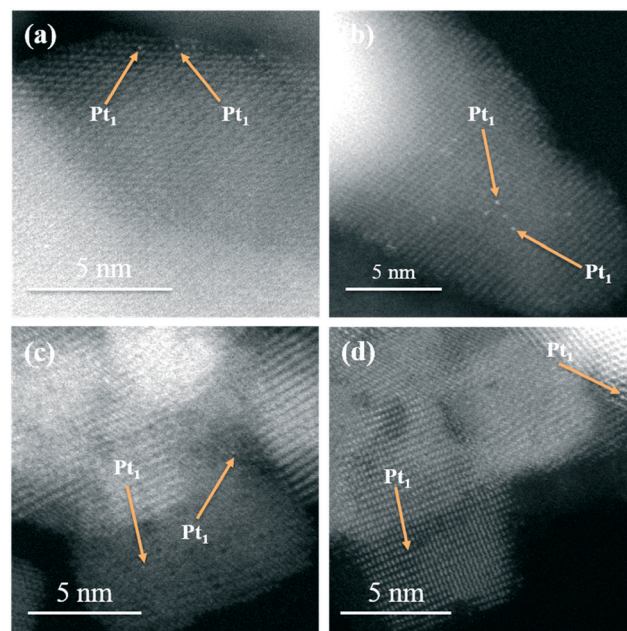


Fig. 1 Atomic resolution HAADF-STEM images of used (a) and fresh (b) Pt₁/Fe₂O₃ SAC and used (c) and fresh (d) Pt₁/CeO₂ SAC, clearly revealing the Pt₁ atoms in both the fresh and the used SACs.

concluded that the as-synthesized and used $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs contained no Pt clusters/particles but only isolated Pt_1 atoms.

3.2 Super active behaviors of Pt_1 SAC for CO oxidation

Our experimental results show that the specific reaction rate of Pt_1 atoms supported on reducible metal oxides (Fe_2O_3 and CeO_2) for CO oxidation dramatically increased when the reaction temperature is higher than 260 °C (Fig. 2). The $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs became super active for CO oxidation at temperatures of around 350 °C with a specific reaction rate as high as 7.34 $\text{mol}_{\text{CO}} \text{ g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ (1432.7 CO molecules per Pt atom per s) and 3.91 $\text{mol}_{\text{CO}} \text{ g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ (762.1 CO molecules per Pt atom per s) with a feed gas mixture of 1.0 vol% CO, 4.0 vol% O_2 and He balance. After the CO oxidation reaction at 350 °C, the Pt_1 atoms were still in the form of isolated single atoms (Fig. 1a and c), suggesting that the Pt_1 atoms did not sinter during the relatively high temperature CO oxidation process. More aberration-corrected HAADF-STEM images of the used $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs are displayed in Fig. S2 and S4,[†] respectively, showing the presence of only Pt_1 atoms without any Pt clusters or NPs.

Fe_2O_3 -supported Pt NPs (denoted as nano-Pt/ Fe_2O_3) and CeO_2 -supported Pt NPs (denoted as nano-Pt/ CeO_2) with 0.62 wt% Pt and 0.55 wt% Pt (determined by ICP-MS), respectively, were synthesized as reference samples using a colloidal method reported in the literature.³⁵ By analyzing numerous low- and high-magnification HAADF-STEM images of the nano-Pt/ Fe_2O_3 (Fig. S5[†]) and nano-Pt/ CeO_2 (Fig. S6[†]) catalysts, we concluded that the Pt NPs are uniformly distributed on the Fe_2O_3 and CeO_2 powders with an average size of 1.3 ± 0.1 nm and 4.0 ± 0.1 nm, respectively. The

colloidal Pt NPs are thoroughly washed and calcined to ensure the elimination of organic residues on the synthesized catalysts. Although the majority of the Pt species were in the form of nanometer-sized particles, Pt_1 atoms were still detected (Fig. S5(b–d) and S6(d and e)[†]) in these catalysts.

The specific reaction rates (per gram of Pt) at 350 °C under the same reaction conditions were estimated to be 0.04 $\text{mol}_{\text{CO}} \text{ g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ and 0.08 $\text{mol}_{\text{CO}} \text{ g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ over the nano-Pt/ Fe_2O_3 and nano-Pt/ CeO_2 , which are ~ 190 and ~ 50 times lower than that on the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ SAC and Pt_1/CeO_2 SAC, respectively. These catalytic evaluation results suggest that compared to reducible metal oxide Fe_2O_3 - and CeO_2 -supported Pt NPs, the supported Pt_1 atoms are super active for CO oxidation at elevated temperatures (260 °C to 350 °C).

To demonstrate the importance of the metal oxide supports in facilitating the super activity of supported Pt_1 atoms, we further tested the performance of Pt_1 atoms supported on irreducible $\gamma\text{-Al}_2\text{O}_3$ support. The CO oxidation activity over the as-synthesized $\text{Pt}_1/\gamma\text{-Al}_2\text{O}_3$ SAC (HAADF-STEM images of fresh and used $\text{Pt}_1/\gamma\text{-Al}_2\text{O}_3$ SAC are shown in Fig. S7 and S8,[†] respectively) is much lower, with a specific reaction rate of only 0.41 $\text{mol}_{\text{CO}} \text{ g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ at 350 °C (feed gas of 1.0 vol% CO, 4.0 vol% O_2 and He balance). These comparative studies unambiguously demonstrate that the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs are super active for CO oxidation at elevated temperatures and that the reducible metal oxide support plays a major role in controlling the super active property of the Pt_1 atoms at elevated temperatures.

We further evaluated the effect of the O_2/CO ratio on the total activity of the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs at the temperatures that these SACs yield super active properties

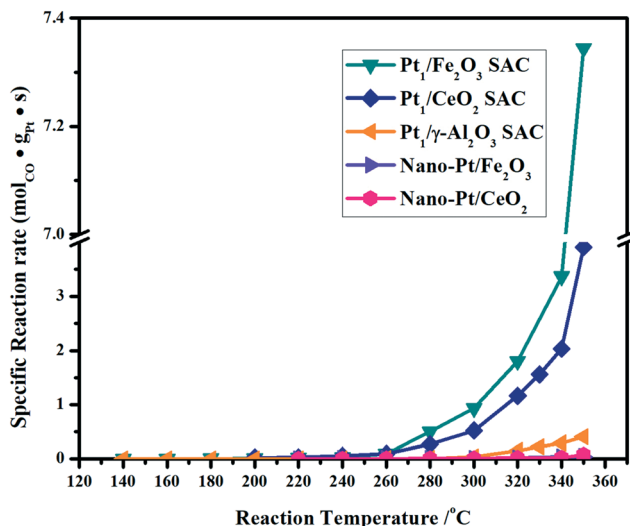


Fig. 2 The specific reaction rate (per gram of Pt) for CO oxidation vs. reaction temperature over $\text{Pt}_1/\text{Fe}_2\text{O}_3$ SAC, Pt_1/CeO_2 SAC, $\text{Pt}_1/\gamma\text{-Al}_2\text{O}_3$ SAC, nano-Pt/ CeO_2 and nano-Pt/ Fe_2O_3 . Feed gas composition: 1 vol% CO, 4 vol% O_2 and He balance; space velocity: 9000–45 000 $\text{l g}^{-1} \text{ h}^{-1}$; and pressure: 0.1 MPa.

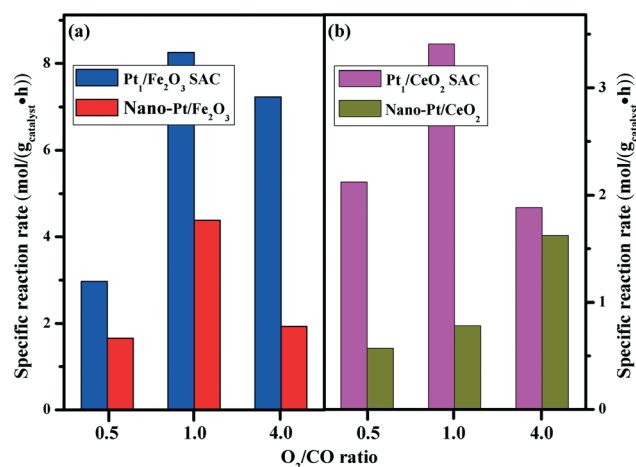


Fig. 3 The total specific rate (per gram of catalyst) of the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ SAC and nano-Pt/ Fe_2O_3 (a) and Pt_1/CeO_2 SAC and nano-Pt/ CeO_2 (b) catalysts for CO oxidation at 350 °C with different O_2/CO ratios. Three different feed gas compositions were used to measure the total specific rate of Pt_1 SACs and Pt nanoparticle catalysts for CO oxidation at 350 °C: (1) 1.0 vol% CO, 4.0 vol% O_2 and He balance ($\text{O}_2/\text{CO} = 4.0$); (2) 2.5 vol% CO, 2.5 vol% O_2 and He balance ($\text{O}_2/\text{CO} = 1.0$); and (3) 2.5 vol% CO, 1.25 vol% O_2 and He balance ($\text{O}_2/\text{CO} = 0.5$). The space velocity varied from 17 400 $\text{l g}^{-1} \text{ h}^{-1}$ to 45 000 $\text{l g}^{-1} \text{ h}^{-1}$ with pressure = 0.1 MPa.

(Fig. 3). The total activity of the Pt₁/Fe₂O₃ and Pt₁/CeO₂ SAC was as high as 8.26 mol_{CO} g_{catalyst}⁻¹ h and 3.41 mol_{CO} g_{catalyst}⁻¹ h, respectively, at 350 °C when the O₂/CO volume ratio is adjusted to ~1 (feed gas of 2.5 vol% CO, 2.5 vol% O₂ and He balance). When the O₂/CO ratio is increased to 4 (1.0 vol% CO, 4.0 vol% O₂ and He balance) or decreased to 0.5 (2.5 vol% CO, 1.25 vol% O₂ and He balance), the total activity changed to 7.23 mol_{CO} g_{catalyst}⁻¹ h and 2.97 mol_{CO} g_{catalyst}⁻¹ h (over Pt₁/Fe₂O₃ SAC), and 1.88 mol_{CO} g_{catalyst}⁻¹ h and 2.12 mol_{CO} g_{catalyst}⁻¹ h (over Pt₁/CeO₂ SAC), respectively. These results clearly demonstrate that the super activity of CO oxidation on the Pt₁ atoms is also influenced by the reactant gas composition. The nature of the metal oxide support plays an important role as well since the specific rate of Fe₂O₃-supported Pt₁ is different from that of CeO₂-supported Pt₁. When the O₂/CO ratio is close to reaction stoichiometry, the difference in reaction rate between the two different metal oxides supports is much smaller.

For CO oxidation at 350 °C, the total activity of the Pt₁/Fe₂O₃ SAC is about 1.5 to 5 times higher than that of the nano-Pt/Fe₂O₃ catalyst for different reactant gas compositions (Fig. 3) even though the Pt loading of the nano-Pt/Fe₂O₃ catalyst is ~21 times higher than that of the Pt₁/Fe₂O₃ SAC. Moreover, after subtracting the activity contribution from the Fe₂O₃ nanocrystallites, the specific reaction rate of the Pt NPs was about 34 to 188 times lower than that of the Pt₁ atoms (Table S1†). Similarly, the total activity of the Pt₁/CeO₂ SAC is 1.2 to 4.4 times higher than that of the nano-Pt/CeO₂ catalyst (Fig. 3) even though the Pt loading of the nano-Pt/CeO₂ catalyst is ~42 times higher than that of the Pt₁/CeO₂ SAC. After subtracting the activity contribution from the CeO₂ nanocrystallites, the specific reaction rate of CeO₂-supported Pt NPs is about 49 to 199 times lower than that of the CeO₂-supported Pt₁ atoms (Table S1†). From these analyses, one can unambiguously conclude that for CO oxidation at 350 °C our as-prepared Pt₁/Fe₂O₃ SAC with a Pt loading of only ~30 ppm exhibits a performance similar to or better than that of the nano-Pt/Fe₂O₃ catalyst with a Pt loading of ~1.0 wt%. For CO oxidation in the temperature range of 260–350 °C, the 0.03 wt% Pt₁/Fe₂O₃ and Pt₁/CeO₂ SAC can be used for practical applications.

For CO oxidation on reducible metal oxide-supported metal NP catalysts, the metal atoms located along the perimeters between the metal NPs and the support are often considered as the main active sites.^{36–38} If we assume that only the perimeter Pt atoms act as the active centers for CO oxidation over the nano-Pt/Fe₂O₃ and nano-Pt/CeO₂ catalysts, then we can estimate their TOF values based on the average sizes of the Pt particles. The average sizes of the Pt particles supported on the Fe₂O₃ and CeO₂ (Fig. S5 and S6†) were measured to be 1.3 ± 0.1 nm and 4.0 ± 0.1 nm, respectively. Therefore, for CO oxidation over the nano-Pt/Fe₂O₃ catalyst the TOFs on the perimeter Pt atoms are estimated to be 28.0, 63.3 and 12.9 s⁻¹ (Fig. S9a†) with an O₂/CO ratio of 0.5, 1.0 and 4.0, respectively, about 20 to 111 times lower than those on the isolated Pt₁ atoms in the Pt₁/Fe₂O₃ SAC. Similarly, we

estimated that the perimeter Pt TOFs in the nano-Pt/CeO₂ catalyst are 12.0, 17.0 and 37.8 s⁻¹ (Fig. S9a†) with an O₂/CO ratio of 0.5, 1.0 and 4.0, respectively, about 20 to 82 times lower than those of the Pt₁ atoms in the Pt₁/CeO₂ SAC.

The above analyses and discussion unambiguously demonstrate that in comparison to that of the nano-Pt/Fe₂O₃ and nano-Pt/CeO₂ catalysts, the Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs possess super active properties with extremely high TOF values. Our catalytic testing results imply that the Pt₁ atoms are intrinsically much more active than the perimeter atoms of Pt NPs for CO oxidation at elevated temperatures. The experimentally observed high specific reaction rate of the Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs originates not only from the 100% dispersion but also from the significantly higher intrinsic activity of each Pt₁ atom, which is further confirmed by the different apparent activation energies as shown in Fig. S10†.

3.3 The unique behavior of super active Pt₁ SAC for CO oxidation

Single-crystal Pd metal has been reported to possess hyperactivity for CO oxidation under ultra-high vacuum (UHV) conditions and the TOF (CO₂ formation rate) is reported to be as high as 40 000 site⁻¹ s⁻¹ at 525 K in 0.5 torr CO and 9.5 torr O₂.³⁹ In order to compare with the UHV single-crystal results, a single Pd₁/Fe₂O₃ SAC with a Pd loading of 0.17 wt% (by ICP-MS) is synthesized. As confirmed by the HAADF-STEM imaging method (Fig. S11†), the Pd₁ atoms were still in the form of isolated atoms after CO oxidation, which ensures that the measured catalytic activity originated from the Pd₁ atoms rather than Pd clusters or NPs. The maximum TOF (32.6 s⁻¹) on the Pd₁/Fe₂O₃ SAC occurred at 340 °C (Fig. S12†), ~50 times lower than that of the Pt₁/Fe₂O₃ SAC. Furthermore, the TOF decreased to 22.6 s⁻¹ at 350 °C, ~63 times lower than that of the Pt₁/Fe₂O₃ SAC. At lower reaction temperatures (40 °C to 120 °C), the Pd₁/Fe₂O₃ SAC, however, yielded much higher activity than the Pt₁/Fe₂O₃ SAC (Fig. S13a†). When the reaction temperature was >140 °C (Fig. S13b and c†), the catalytic activity of the Pt₁/Fe₂O₃ SAC became higher than that of the Pd₁/Fe₂O₃ SAC and was much higher at reaction temperatures >260 °C. These results indicate that unlike the behavior of the single-crystal Pd under ultra-high vacuum conditions, the Pd₁/Fe₂O₃ SAC does not show significant super activity behavior for CO oxidation at elevated temperatures. Hence, the super active property of the Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs may originate from factors that are different from the previously reported hyperactivity of single crystals under UHV conditions.

At elevated temperatures, ignition of CO molecules on Pt single-crystal systems has been reported.^{40–42} Based on our experimental data for CO oxidation on Fe₂O₃- and CeO₂-supported Pt NPs at high reaction temperatures, it is justifiable to conclude that no super activity behavior would be observable on Pt NPs. Furthermore, Pt₁ atoms on γ-Al₂O₃ did not demonstrate any super activity behavior either. All

these results unambiguously show that the observed super activity of Fe_2O_3 - and CeO_2 -supported Pt_1 is unique to only Pt_1 atoms supported on highly reducible metal oxides such as Fe_2O_3 and CeO_2 . Furthermore, as we have discussed earlier, Fe_2O_3 -supported Pd_1 atoms did not show super active behavior for CO oxidation at elevated temperatures. Therefore, the experimentally observed super active property of the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs must be related to the intrinsic nature of Pt atoms and how they interact with the support surfaces.

3.4 Local coordination and electronic structure of Pt_1 SACs

To identify the unique nature of the Pt_1 atoms in the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs, X-ray absorption experiments have

been conducted to probe the local structure and electronic states of the Pt_1 species. Extended X-ray absorption fine structure (EXAFS) spectroscopy data provided further evidence on the atomic dispersion and local geometric configuration of the Pt species supported on the Fe_2O_3 and CeO_2 powders.^{43–45} The EXAFS functions and fitting details of the Pt L_3 -edge filtered k^2 -weighted $\chi(k)$ obtained on the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs are listed in Table S2.† As shown in Fig. S14,† both the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and the Pt_1/CeO_2 SACs predominantly exhibit Pt–O bonds located at approximately $2.0 \text{ \AA}$,⁴⁶ suggesting that the Pt species are mainly in the form of Pt_1 atoms dispersed on the surfaces of Fe_2O_3 and CeO_2 powders, corroborating the conclusion from the STEM imaging results. For the nano-Pt/ Fe_2O_3 and nano-Pt/ CeO_2 catalysts, they both exhibit weak Pt–O bonds (approximate

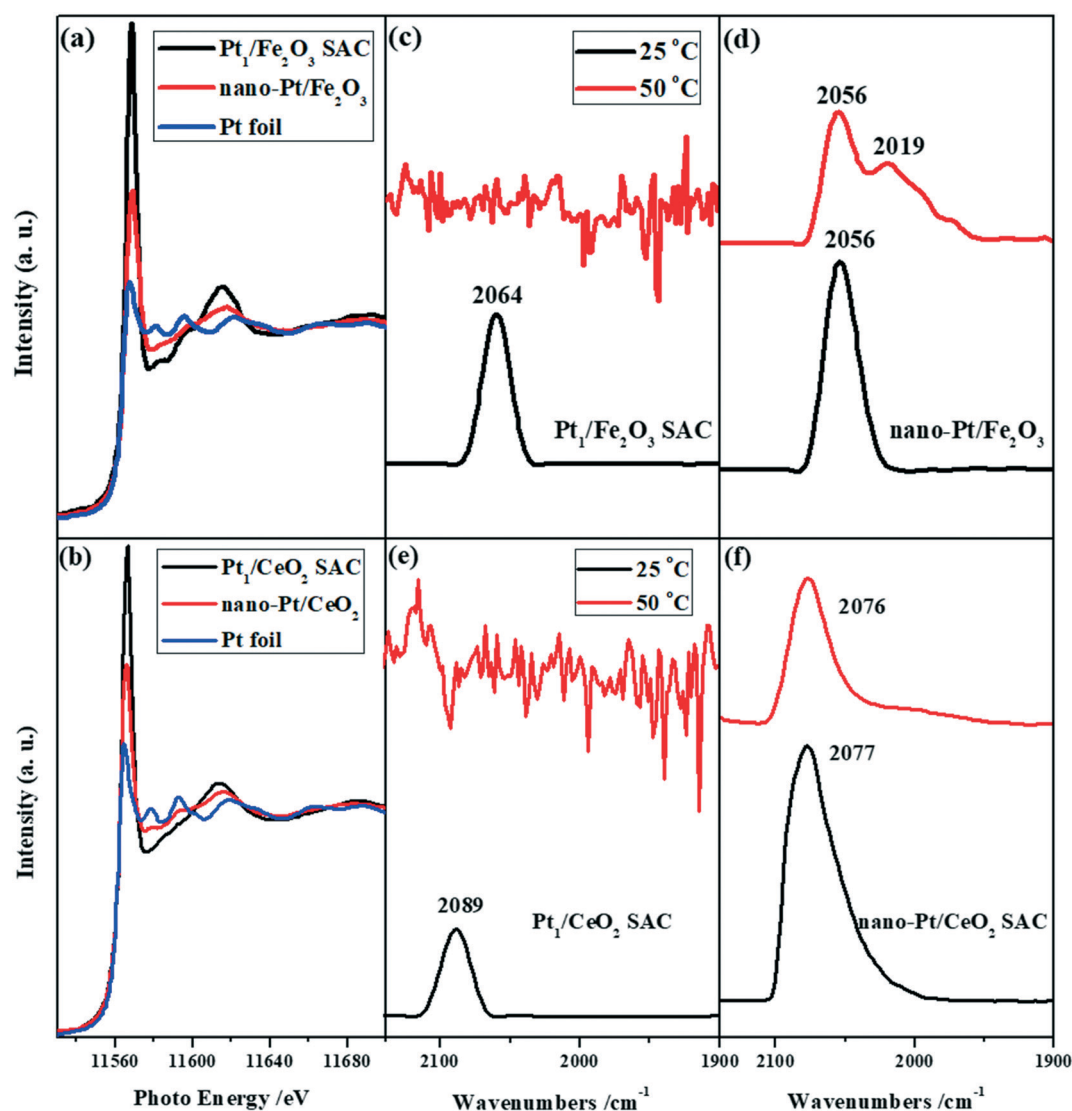


Fig. 4 XANES spectra at the Pt L_3 -edge of Pt_1 atoms and Pt particles of $\text{Pt}_1/\text{Fe}_2\text{O}_3$ SAC and nano-Pt/ Fe_2O_3 (a) and Pt_1/CeO_2 SAC and nano-Pt/ CeO_2 (b); *in situ* CO-DRIFTS of $\text{Pt}_1/\text{Fe}_2\text{O}_3$ SAC (c) and nano-Pt/ Fe_2O_3 (d), Pt_1/CeO_2 SAC (e) and nano-Pt/ CeO_2 (f) at 25 and 50 °C. The XANES spectra reveal a decreasing trend in the intensity of the Pt L_3 white line: $\text{Pt}_1/\text{Fe}_2\text{O}_3$ SAC (2.57) > nano-Pt/ Fe_2O_3 (1.70) > Pt foil (1.23) and Pt_1/CeO_2 SAC (2.14) > nano-Pt/ CeO_2 (1.63) > Pt foil (1.29). The numbers in parentheses refer to the normalized absorption height for different samples. The peak intensities of the CO-DRIFTS are normalized.

bond length of 2.0 Å) and relatively strong Pt–Pt bonds (approximate bond length of 2.7 Å). The first shell coordination number (CN), bond length, and the corresponding standard deviations are extracted by curve-fitting based on the two main peaks in the R range of 0–3.0 Å (Table S2†). On average, each Pt atom is coordinated with three oxygen atoms (CN = 2.8 for nano-Pt/Fe₂O₃ and CN = 3.0 for nano-Pt/CeO₂), which agrees well with the reported coordination structure of oxide-supported Pt catalysts (CN = 2 and 3) in the literature.^{46–48} On the other hand, each Pt₁ atom in the Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs is coordinated with four O atoms (CN = 4.4 for Fe₂O₃-supported Pt₁ and CN = 4.0 for CeO₂-supported Pt₁), which indicates that the isolated Pt₁ atoms in the Pt₁/Fe₂O₃ SAC and Pt₁/CeO₂ SAC possess a Pt₁–O₄ configuration. These results suggest that the local coordination environments of the Pt₁ atoms are totally different from those of the small Pt NPs.

To unravel the electronic structures of the Pt₁ atoms and Pt NPs supported on reducible Fe₂O₃ and CeO₂, X-ray absorption near-edge structure (XANES) analysis was conducted. As shown in Fig. 4a, the Pt white-line intensity of the Pt₁/Fe₂O₃ SAC and nano-Pt/Fe₂O₃ (11 568 eV) is significantly higher than that of the Pt foil, confirming that both the Pt₁ atoms and the small Pt nanoparticles are oxidized, probably *via* electron transfer from the Pt species to the metal oxide support.⁵ Furthermore, the white-line intensity of the Pt₁/Fe₂O₃ SAC is considerably higher than that of the nano-Pt/Fe₂O₃, indicating that the Pt₁ atoms possess much higher oxidation states compared to that of the Pt NPs. These conclusions apply to the Pt₁/CeO₂ SAC and nano-Pt/CeO₂ catalyst as well (Fig. 4b).

The peak area of the normalized XANES spectra at the Pt L₃-edge is proportional to the amount of unoccupied Pt 5d orbitals.^{49,50} By applying a simplified formula (see details in Table S2†), the total amount of unoccupied Pt 5d orbitals in both the Pt₁/Fe₂O₃ SAC and the Pt₁/CeO₂ SAC is estimated to be ~1.1 times higher than that in the nano-Pt/Fe₂O₃ and nano-Pt/CeO₂ catalysts, respectively, implying that more electrons might have been transferred from the Pt₁ to the metal oxides, leading to a stronger electronic metal–support interaction (EMSI) for Pt₁ SACs.^{5,51} A higher number of unoccupied Pt 5d orbitals enables weakening of the CO adsorption strength since the back-donation interaction between the Pt species and the CO molecules is reduced due to the fewer available electrons in the Pt 5d orbitals.⁵² By using Bader charge analysis, and calibrating with common Pt oxides PtO, Pt₃O₄ and PtO₂ as listed in Fig. S15,† we identify the oxidation state of Pt in SCAs close to Pt₃O₄, *i.e.*, Pt^{2.67+}, which is in line with the DRIFTS and XANES data.

The *in situ* CO-DRIFTS results further corroborate that the CO adsorption strength on Pt atoms is significantly weaker than that on Pt NPs (Fig. 4c–f). The linear CO adsorption species, centered at 2064 cm^{−1} and 2056 cm^{−1} on Pt₁/Fe₂O₃ SAC and nano-Pt/Fe₂O₃ (Fig. 4c and d), respectively, were detected at 25 °C. When the sample temperature increased from 25 °C to 50 °C the CO adsorption species were barely

observable on the Pt₁/Fe₂O₃ but they were clearly detected on the nano-Pt/Fe₂O₃. The significant blue-shift of the CO absorption peak indicates that the valence of the Pt₁ atoms is higher than that of the Pt NPs, in agreement with the XANES results. The *in situ* CO-DRIFTS data show a similar conclusion for the Pt₁/CeO₂ and nano-Pt/CeO₂ systems (Fig. 4e and f). The DRIFTS results corroborate those of the XANES and Bader charge analysis data that a higher number of unoccupied Pt 5d orbitals significantly weakens the CO adsorption strength. The less strongly bonded CO molecules to the Pt₁ atoms facilitate the CO oxidation process, leading to significantly enhanced catalytic activity.^{5,53}

3.5 Proposed catalytic mechanism *via* DFT calculations

To uncover the fundamental mechanism that governs the ultra-high activity and stability of the Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs, we take Pt₁/Fe₂O₃ SAC as a representative example to explore the potential catalytic mechanisms on these two catalysts *via* density functional theory (DFT) calculations. We firstly performed DFT calculations on the synthesis processes. The local coordination environment of the atomically dispersed Pt atoms on the Fe₂O₃ (001) surface underpins the catalytic activity and stability; therefore, an appropriate physical model of the as-prepared SACs is critical. Fig. 5 shows the detailed structural evolution of the Fe₂O₃ (001) surface with and without the presence of Pt₁ atom. The modelling of structure evolution starts from an oxygen-rich (001) surface (step I), a hexagonal surface geometry comprising six edge-shared FeO₆ octahedra. One third of the topmost surface oxygen of the FeO₆ unit could easily desorb to form a six edge-shared FeO₅ square pyramid and 1/3 monolayer (ML) surface oxygen vacancies (step II). This process is extremely exothermic (−4.40 eV) under synthesis conditions, which can even take place at room temperature. Without Pt atom loading, the surface will be stabilized in 1/2 ML surface oxygen vacancies (step III) with the removal of another two oxygen atoms, resulting in a squeezed hexagonal geometry comprising four point-shared tetrahedra and two edge-shared square pyramids, while the Pt₁ atom can stabilize the surface at 5/12 ML surface oxygen vacancies with the formation of square planar Pt₁–O₄ (step VI), which agrees well with our EXAFS data. The binding energy of the Pt₁ is about −1.41 eV, against Pt agglomeration into bulk at high temperatures.

The four-oxygen coordination of Pt₁–O₄ yields a high-valence Pt site as confirmed by the XANES and CO-DRIFTS measurements. DFT results show that both O₂ and CO molecules can be adsorbed on the high-valence Pt site with around −0.5 eV and −0.8 eV binding energies, respectively. These adsorption energies are relatively weak compared to that on the Pt surface, avoiding CO poisoning on the Pt₁ atom, but also leading to the difficulty in O₂ activation because of the deep Pt 5d band of Pt₁–O₄. Indeed, that is the reason why high-valence Pt sites are not considered catalytically active for CO oxidation.⁵⁴ However, it is found

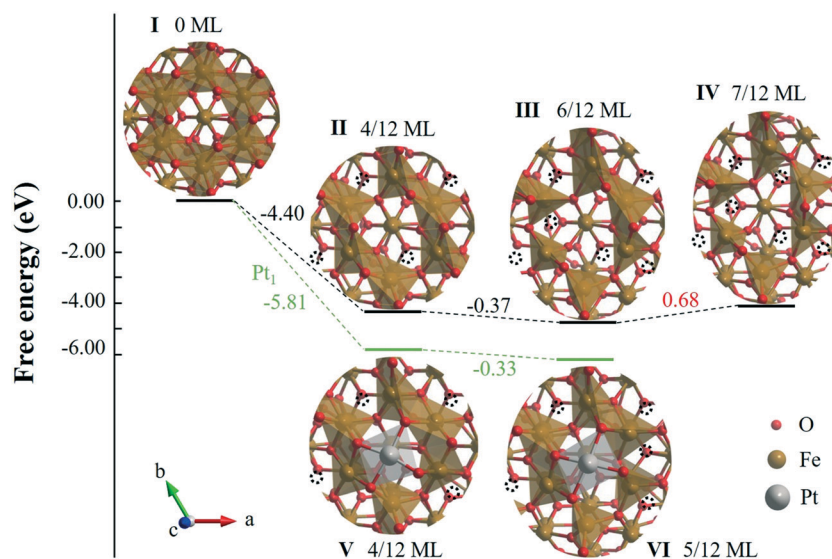


Fig. 5 Evolution of the Fe_2O_3 (001) surface under synthesis conditions (300 °C in air, 0.05 MPa O_2 partial pressure). The dotted black circles represent surface oxygen vacancies, and its coverage is in units of monolayer (ML). The calculated free energies are referenced to gas phase O_2 and bulk Pt.

that an unusual catalytic mechanism exists to change the catalytic behavior of our stable Pt SACs. Fig. 6 displays a non-classical MvK catalytic cycle for CO oxidation on $\text{Pt}_1/\text{Fe}_2\text{O}_3$. Although the four-oxygen coordinated Pt_1 atom cannot directly activate O_2 , the adsorbed O_2 , however, facilitates the movement of the coordination oxygen atoms with a small barrier (0.55 eV). Upon O_2 adsorption, one of the coordination oxygen atoms can readily break the Pt–O bond and migrate into a nearby surface oxygen vacancy site. Meanwhile, the adsorbed end-on O_2 will bridge the Pt and Fe site by forming a Pt–OO–Fe configuration (steps ii to iii). The migrated coordination oxygen atom can then directly

combine with the adsorbed CO to form a CO_2 molecule which readily desorbs, recovering the oxygen vacancy site (step iv). The subsequent O_2 dissociation process becomes barrierless through O_2 adsorption on the Pt– Fe_2 triangle (step iv to v), which can dissociate the O_2 molecule with zero activation energy. The side-view images of O_2 adsorption configurations are presented in Fig. S16† to better demonstrate the process of O_2 activation. Thereafter, one of the split oxygen atoms replenishes the consumed coordination oxygen in the $\text{Pt}_1\text{–O}_4$ configuration, while the other one fills the nearby surface oxygen vacancy again and can directly oxidize CO into CO_2 to recover the initial catalyst surface (step i). Overall, the CO oxidation can be efficiently catalyzed by the high-valence Pt site with four-oxygen coordination through a non-classical MvK reaction pathway, indicating a promising design strategy for stable and active SACs. The detailed change in free energy (ΔG) of each elementary step during CO oxidation by a non-classical MvK mechanism is listed in Table S3.†

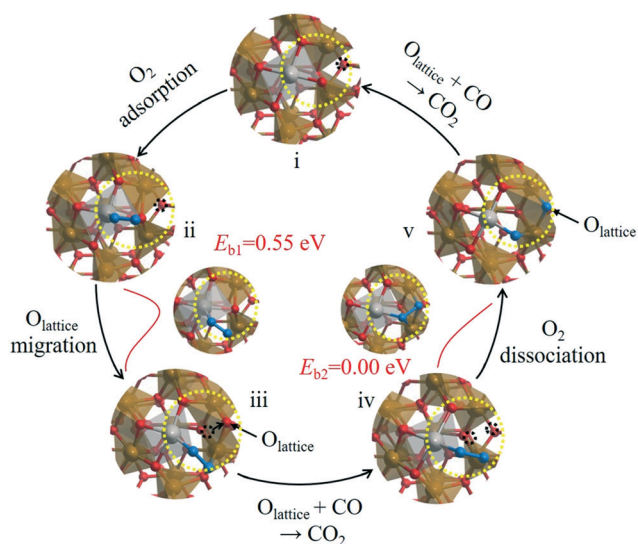


Fig. 6 Non-classical MvK CO oxidation mechanism with lattice oxygen migration and activation under gas-phase O_2 adsorption on four-fold coordinated single Pt atoms. The blue balls represent adsorbed oxygen. The active region is highlighted by bright yellow circles.

3.6 Potential practical applications of super active Pt_1 SACs

Platinum plays a crucial role in three-way catalysts (TWCs) that have been widely used in automobiles for emission control, primarily due to its excellent oxidation and reduction ability in the removal of CO,^{55,56} hydrocarbons (HCs)⁵⁷ and NO_x .^{58–60} However, the expensive Pt with limited resources will not be sustainable. Therefore, development of abundant alternatives to significantly minimize the usage of Pt becomes crucial.⁶¹ The work reported in this paper clearly demonstrates that by using atomically dispersed Pt atoms the Pt specific reaction rates of the $\text{Pt}_1/\text{Fe}_2\text{O}_3$ and Pt_1/CeO_2 SACs are more than 2 orders of magnitude higher than that of commercial TWCs (0.5 wt% Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 0.5 wt% Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$).

Al₂O₃) for CO oxidation at 350 °C (Table S1†).⁶² The total catalytic activity (calculated based on the total catalyst weight that includes both the noble metal and the oxide support) of the synthesized Pt₁/CeO₂ and Pt₁/Fe₂O₃ SACs is more than 185 and 452 times higher than that of the commercial 0.5 wt% Pt/CeO₂/γ-Al₂O₃ at 350 °C. Therefore, the super active Pt₁-based SAC may be an excellent candidate to replace the Pt NPs in the TWCs, leading to the significant reduction of the usage of the costly Pt. The practical applications of such extremely low levels (10–50 ppm) of Pt to emission controls may have a major societal impact and significantly enhance the sustainability of rare and expensive resources.

4. Conclusions

We have reported the unique super activity behavior for high-temperature CO oxidation on extremely low Pt loading and stable Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs. The total activity of the as-synthesized Pt₁/Fe₂O₃ SAC with a Pt loading of only ~30 ppm is comparable to that of the 1.0 wt% nano-Pt/Fe₂O₃ for CO oxidation at 350 °C. DFT calculations reveal that the Pt₁-O₄ configuration not only catalyzes CO oxidation through a non-classical MvK reaction pathway but also stabilizes the Pt₁ atoms. The super active and stable Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs may become a potential candidate to replace the Pt NPs that are used in the current commercial TWCs, leading to significant reduction in cost and sustainable use of expensive and rare resources. Although this work only explored the super activity nature of Pt₁/Fe₂O₃ and Pt₁/CeO₂ SACs, it is expected that other types of metal and support combinations may provide similar behavior. The discovery of super active and stable SACs that operate at elevated reaction temperatures provides an alternative route to practical applications of SACs that can significantly reduce the cost of goods.

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Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Y. L. synthesized the catalysts, designed and tested the experiments, analyzed the data, and drafted and revised the manuscript. W. G. assisted in synthesizing catalysts and testing the experiments. Y. Z. conducted the DFT work and revised the manuscript. J. L. conducted the STEM work, discussed the results and revised the manuscript.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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