Surpassing the single-atom catalytic activity limit through paired Pt-O-Pt ensemble built from isolated Pt₁ atoms

Hui Wang¹¹, Jin-Xun Liu²³¹, Lawrence F. Allard⁴, Sungsik Lee⁵, Jilei Liu⁶, Hang Li¹, Jianqiang Wang¹, Jun Wang¹, Se H. Oh⁷, Wei Li⁷, Maria Flytzani-Stephanopoulos⁶, Meiqing Shen¹⁸⁹, Bryan R. Goldsmith²³ & Ming Yang⁷

Despite the maximized metal dispersion offered by single-atom catalysts, further improvement of intrinsic activity can be hindered by the lack of neighboring metal atoms in these systems. Here we report the use of isolated Pt₁ atoms on ceria as “seeds” to develop a Pt-O-Pt ensemble, which is well-represented by a Pt₈O₁₄ model cluster that retains 100% metal dispersion. The Pt atom in the ensemble is 100–1000 times more active than their single-atom Pt₁/CeO₂ parent in catalyzing the low-temperature CO oxidation under oxygen-rich conditions. Rather than the Pt-O-Ce interfacial catalysis, the stable catalytic unit is the Pt-O-Pt site itself without participation of oxygen from the 10–30 nm-size ceria support. Similar Pt-O-Pt sites can be built on various ceria and even alumina, distinguishable by facile activation of oxygen through the paired Pt-O-Pt atoms. Extending this design to other reaction systems is a likely outcome of the findings reported here.
An ideal supported metal catalyst will simultaneously maximize dispersion of the metal and display optimal intrinsic activity per metal atom. Recently, advanced techniques for synthesizing many heterogeneous catalysts as single atoms have addressed the former issue. Single-atom catalysis dramatically reduces the usage requirements of expensive and rare metals by stabilizing the supported metal atoms in a fully dispersed state as isolated bonded species that serve as active sites\(^1-^6\). A general question regarding single-atom metal catalysts, despite the nearly 100% material efficiency of the supported metals, is whether a catalytic center designed in the form of one metal atom substituted or anchored on a support represents the optimal structure to deliver the highest intrinsic catalytic activity. Previous work answered this question for platinum and gold catalysts for the water–gas shift reaction, where the optimal catalytic center is the single-atom Pt\(_1\) (or Au\(_1\))-O(OH)\(_x\) species on a variety of catalyst supports\(^1-^6\). Nonetheless, for other important reactions such as the low-temperature CO oxidation, these configurations as isolated atomic active sites may lack neighboring metal centers and the reactivities associated with the latter. This fundamental question remains unanswered and industrial needs for more active catalysts await.

The catalytic oxidation of CO to CO\(_2\) involves classic molecular rearrangements with oxygen intermediates that make it an attractive probe reaction in catalytic systems to gain better mechanistic understanding, such as the identity of metal catalytic centers and the importance of metal–support interaction. The low-temperature CO oxidation is also important in the purification of vehicle emissions. To meet latest fuel-efficient engine designs and to reduce vehicle exhaust emissions, platinum group metals (PGMs) dispersed on ceria supports are needed to be much more active in eliminating CO emissions below 150 °C during the engine cold start\(^7\). A group of Pt single-atom catalysts using CeO\(_2\), Al\(_2\)O\(_3\), and KLTLE zeolite\(^12\) supports were developed and probed for CO oxidation. Compared with the conventional Pt nanoparticles where most of the metal atoms are buried inside the particle bulk without catalyzing the surface reaction, these single-atom catalysts certainly facilitate the full utilization of scarce platinum metal\(^4-^6,^8,^9\). However, the properties of the Pt\(_1\) may be suboptimal for certain reactions. Indeed, a closer examination of the activity per Pt atom shows that such Pt\(_1\) catalysts are often similar to (or even worse than)\(^3\) the conventional Pt nanoparticles and clusters under comparable reaction conditions and catalyst formulations (Supplementary Table 1). In the context of oxygen-rich reaction conditions (oxygen in excess to fully oxidize all the reductants), which reflects the implementation of emerging fuel saving technologies such as lean-burn engines, hybrid powertrains, and dynamic fuel management, the known benefit of creating oxygen vacancies on ceria surfaces to promote CO oxidation under near stoichiometric oxygen concentrations\(^13-^15\) cannot be sustained because the surface oxygen vacancies associated with Ce(III) heal in seconds\(^16,^17\). Consequently, the natural question arises whether a properly paired multi-atom catalytic site (ensemble of the single-atom M\(_1\)-O\(_x\) species) will increase the catalytic performance over Pt\(_1\)/CeO\(_2\) under oxygen-rich conditions, and how we can build such a site with an appreciable loading amount on a given support surface. In this work, by extending the concept of isolated atoms to the paired ensembles, we show that the paired Pt-O-Pt catalytic units can achieve higher activity through an oxygen migration mechanism.

Here we report a general approach—reassembling isolated Pt\(_1\) atoms as the precursor to create a one-layer multi-atom o xo site (Pt-O-Pt) while keeping ~100% Pt utilization. We use a variety of experimental and computational techniques (grand canonical Monte Carlo (GCMC) simulations combined with density functional theory (DFT) calculations (GCMC-DFT))\(^18\) to elucidate the catalyst active site structure and the CO oxidation reaction mechanism that is responsible for the dramatically enhanced reactivity of this multi-atom o xo site. The Pt-O-Pt ensemble is shown to be the base unit in the high-performance catalyst, where the well-known Pt-CeO\(_2\) metal–support interfacial catalysis no longer ranks as the favorable reaction path for this highly active low-temperature CO oxidation catalyst under oxygen-rich reaction conditions.

**Results**

**Dramatic change of catalytic performance.** We began this work by synthesizing a variety of single-atom Pt\(_1\)/CeO\(_2\) to serve as the baseline for catalytic performance. Next, the isolated Pt atoms in the Pt\(_1\)/CeO\(_2\) were used as seeds to generate a much more active Pt site through a facile activation treatment, where a mild H\(_2\) reduction was followed with a CO plus O\(_2\) treatment to trigger the restructuring of the platinum (see optimization of the activation treatment and the stable, high reactivity rates in Supplementary Figs. 1–3). The optimized samples are labeled as Pt-O-Pt/CeO\(_2\), see Table 1). The potential alternative activity contributors, such as creating persistent oxygen vacancies and additional –OH species on the catalyst surface during the activation treatment, have been excluded (Supplementary Figs. 4 and 5).

Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images show that the single Pt atoms are the majority species in the various Pt\(_1\)/CeO\(_2\) samples prepared in this work (see Fig. 1a and Supplementary Figs. 6–8 for Pt\(_1\)/CeO\(_2\)-a, Pt\(_1\)/CeO\(_2\)-b, and Pt\(_1\)/CeO\(_2\)-c samples), where Pt loadings of 0.27, 0.16, and 0.11 wt.% and ceria supports with diverse amounts of reducible oxygen species were used (Supplementary Figs. 9 and 10). A few pseudoclusters of platinum might be found in these single-atom catalyst samples, where these pseudo-clusters are composed of several nearby single-atom Pt\(_1\) species embedded in the cerium columns. In the activated catalysts, namely the Pt-O-Pt/CeO\(_2\) samples, the Pt atoms are fully transformed into another structure with a narrow size distribution of 1 ± 0.1 nm on the ceria surface (see Fig. 1b and Supplementary Figs. 11–13 for Pt-O-Pt/CeO\(_2\)-a, Pt-O-Pt/CeO\(_2\)-b, and Pt-O-Pt/CeO\(_2\)-c samples). We measure the Pt dispersion of Pt-O-Pt/CeO\(_2\) samples to be nearly 100% (Table 1). Additional STEM images and discussion of the representative Pt\(_1\)/CeO\(_2\)-a and Pt-O-Pt/CeO\(_2\)-a samples can be found in Supplementary Figs. 14 and 15 and their accompanying text. None of the crystal patterns for platinum metal or oxides were detected in the Pt-O-Pt/CeO\(_2\) catalysts by either STEM imaging or X-ray diffraction (Fig. 1b and Supplementary Figs. 11–13, 15, and 16), meaning that only the highly dispersed platinum species reside on the predominant CeO\(_2\)(111) surfaces (Supplementary Fig. 17) with ceria nanoparticle sizes of 10–30 nm. There are some rounded edges, steps, and kinks on these rather typical industrial CeO\(_2\) support particles, but no clear evidence of these locations as the preferred anchoring sites for the platinum species is found (Supplementary Fig. 18). Therefore, we selected CeO\(_2\)(111) to model the stable geometry and CO oxidation reaction path for Pt\(_1\)/CeO\(_2\) and Pt-O-Pt/CeO\(_2\).

Despite the apparently low conversion values on the Pt\(_1\)/CeO\(_2\) catalysts (Fig. 1c and Supplementary Fig. 19), which are due to the high gas flow rate compared to catalyst weight, the absolute (or intrinsic) activities of our single-atom Pt for low-temperature CO oxidation per Pt site (turnover frequencies, TOFs) are within the same order of magnitude as the activities reported recently for other single-atom Pt catalysts\(^8-^12,^19-^24\), particularly when reducible oxide supports such as titania and ceria were used (Supplementary Table 1). Under the same reaction conditions,
however, the Pt-O-Pt/CeO$_2$ catalysts have 2–3 orders of magnitude higher intrinsic activity than their Pt$_1$/CeO$_2$ counterparts from 80 to 150 °C. The reaction rates on the Pt$_1$/CeO$_2$-a catalyst are $1.7 \times 10^{-9}$ and $2.2 \times 10^{-7}$ mol CO$_2$/(g$_{cat}$·s) at 80 and 150 °C, respectively. In contrast, at the same total platinum loading, the reaction rates on the Pt-O-Pt/CeO$_2$-a catalyst are $2.6 \times 10^{-6}$ and $2.5 \times 10^{-5}$ mol/(g$_{cat}$·s) at 80 and 150 °C. Kinetic measurements (Fig. 1d) further reveal that the Pt-O-Pt/CeO$_2$ and Pt$_1$/CeO$_2$ catalysts are also distinguishable from differences between their catalytic centers and reaction mechanisms. Specifically, the CO oxidation reaction catalyzed by the Pt-O-Pt/CeO$_2$ catalysts has a smaller measured apparent activation energy ($E_{app} = 40 \pm 2$ kJ/mol) compared with the Pt$_1$/CeO$_2$ catalysts ($E_{app} = 86 \pm 3$ kJ/mol).

### Table 1 Key metrics of the Pt$_1$/CeO$_2$ and the Pt-O-Pt/CeO$_2$ catalysts

| Samples       | Pt material efficiency (%) | Active sites                                                                 | Relative activity | $E_{app}$ (kJ/mol) | Rate-determining step                                                                 |
|---------------|-----------------------------|------------------------------------------------------------------------------|-------------------|-------------------|--------------------------------------------------------------------------------------|
| Pt$_1$/CeO$_2$| 100                         | Isolated Pt$_1$ atoms embedded in CeO$_2$ surface by substitution of surface Ce atoms | 1$^b$             | $86 \pm 3$ (Exp.) | O$_2$ dissociation at Pt$_1$/CeO$_2$; CeO$_2$ is involved in the catalytic cycle    |
| Pt-O-Pt/CeO$_2$ | 100                         | Pt-O-Pt ensemble. Pt atoms are separated but bridged by four oxygen atoms | $10^2 - 10^3$ higher$^c$ | 40 $\pm$ 2 (Exp.) | Oxygen atom migration at the Pt-O-Pt ensemble; CeO$_2$ is not involved in the catalytic cycle |

$^a$Based on spectroscopic observations from HAADF-STEM images and the chemical titrations of CO chemisorption

$^b$The catalyst activity is similar with many recently reported single-atom Pt$_1$/CeO$_2$ catalysts (see Supplementary Table 1)

$^c$Reaction in the window of 80–150 °C

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**Fig. 1** Direct measurements of the Pt$_1$/CeO$_2$ and Pt-O-Pt/CeO$_2$ catalysts. **a**, **b** Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images for the Pt$_1$/CeO$_2$-a and Pt-O-Pt/CeO$_2$-a catalysts (shown images were recorded at $\times10$ M and $\times6$ M original magnifications, respectively). Yellow circles and squares are used to highlight the single-atom Pt$_1$ and the Pt-O-Pt ensemble, respectively. **c** CO oxidation light-off performance ([CO] = 1000 ppm, [O$_2$] = 5%, balanced with N$_2$ at a contact time of 2,400,000 mL/g$_{cat}$/h). **d** Arrhenius-type plot of CO oxidation rates at different temperatures with apparent activation energies ($E_{app}$) shown.
Atomic-level structural analyses. Our DFT calculations identified the stable Pt structures for the Pt1/CeO2 and Pt-O-Pt/CeO2 catalysts. We find that the isolated Pt1 atom prefers to substitute the Ce atom rather than anchor on the CeO2(111) surface (the dominant facet on which ~70% counts of the experimental Pt1 and ~1 nm Pt-O-Pt species were anchored, Supplementary Fig. 17). This Pt1 anchoring site was proposed in a prior experimental study.27 The Pt1 anchored on top of the CeO2(111) is thermodynamically unstable due to a highly unsaturated coordination environment (Supplementary Fig. 23a). In the identified Pt1/CeO2 structure (Fig. 2a and Supplementary Figs. 23b and 24), the Pt1 substitutes the Ce atom on the ceria surface and is surrounded by up to six nearby oxygen atoms. In line with the recent findings from surface science and DFT calculations studies,28,29 we noticed that four of the oxygen atoms prefer to bind directly to the Pt center to form a square-planar Pt1−O4 structure, which is the starting structure of the Pt1/CeO2 catalysts used here to model the CO oxidation reaction.

Computationally intensive GCMC-DFT simulations were performed to search the structure and composition of Pt8O14 in the presence of oxygen (pO2 = 0.05 atm) at 350 K, which is consistent with the experimental reaction conditions. The computationally tractable Pt8 cluster was selected here because the experimental Pt-O-Pt/CeO2 sample has a similar platinum diameter of ~1 nm on the CeO2(111) surfaces (Supplementary Fig. 25a). When exposed to an oxygen atmosphere as in our reaction tests, the Pt8/CeO2 rearranges into Pt8O14 (~0.92 nm), which contains solely Pt-O-Pt as the catalytic base unit and is only one layer thick (Fig. 2b and Supplementary Fig. 26b). Our GCMC simulation is similar with the experimental activation procedure in that the reduced Pt1 clusters, formed by assembling Pt1 species under the first step of H2 treatment, can be oxidized to the Pt-O-Pt ensemble by the introduction of an O2-rich environment. The Pt8O13 cluster model identified by the GCMC algorithm is regarded as a representative structure of our experimental system, as in reality some experimental heterogeneity does exist. Nevertheless, as we show below it captures many of the salient features of this rather clean experimental catalytic system, as indicated by the overall agreement of experimental observations and computational predictions.

Since our synthesis of the Pt1/CeO2 and Pt-O-Pt/CeO2 catalysts yields almost exclusively either single-atom Pt1 species or the ~1 nm Pt-O-Pt structure on the different ceria supports, the representative Pt8O14 structure predicted by GCMC-DFT can be vetted by our experimental analysis. The x-ray absorption near-edge structure (XANES) and the x-ray photoelectron spectroscopy (XPS) results (Fig. 2c–d and Supplementary Figs. 26 and 27) confirm the cationic nature of the Pt atoms in both groups of catalysts. The Pt chemical valence in Pt1/CeO2 is Pt(IV) and is slightly more positive than the Pt in the Pt-O-Pt/CeO2 samples. Bader charge analysis of the predicted catalyst structures shows the same trend (Supplementary Table 2). Extended X-ray absorption fine structure (EXAFS) measurements (Fig. 2e, Supplementary Fig. 28, and Supplementary Table 3) show the typical exclusive Pt-O coordination environment (up to six nearby O atoms) for Pt1/CeO2. For the Pt-O-Pt/CeO2 samples, unlike the prevalent three-dimensional platinum (oxide) clusters that possess more than one Pt layer, the Pt8O14 model is consistent with the experimental Pt-O-Pt/CeO2 (Supplementary Fig. 20), but the large activity gap between the Pt-O-Pt/CeO2 and Pt1/CeO2 catalysts is observed after adding 3% H2O into the CO oxidation feed stream (Supplementary Fig. 26 and Table 3). Consistent with the EXAFS measurements, the GCMC-predicted Pt8O14 structure is composed of eight fully separated Pt cations, each bound to four nearby oxygen atoms with the average Pt-O distance of 1.99 Å. The lack of long-distance Pt-Pt and second shell Pt-O information for the Pt-O-Pt/CeO2 catalysts at higher radial distances (R > 3 Å) is the result of experimental signal dampening by the one-layer platinum structure, dilute platinum concentrations, and inherent signal attenuation in EXAFS analyses. These factors are discussed in the Supplementary Information accompanying Supplementary Fig. 29.

Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) studies under the CO oxidation conditions (Fig. 2f and Supplementary Fig. 30) reveal one dominant vibrational mode at 2095 cm−1 for the Pt1/CeO2 samples, as reported in the literature.9 A Pt1 anchored on CeO2(111) can be ruled out because of its highly endothermic formation energy (Supplementary Fig. 23a) and its strong CO adsorption (ECO = −313 kJ/mol) with a calculated CO wavenumber of 2070 cm−1, which is not observed in our DRIFTS measurement. The structure of Pt1 substituted in the CeO2(111) surface is more stable and the calculated CO wavenumber of 2095 cm−1 on Pt1/CeO2−y(111) with one oxygen vacancy nearby is in line with our experimental measurement. The two sets of experimentally measured CO adsorption bands centered at 2107 and 2081 cm−1 for the Pt-O-Pt/CeO2 samples correspond to CO chemisorption at the top and bridge sites of an undercoordinated Pt-O-Pt ensemble, according to our representative Pt8O13/CeO2(111) model system (identified after examination of all possible CO adsorption sites on Pt8O14 (x = 13–14) involved in the CO oxidation cycle). On Pt8O13/CeO2(111), CO chemisorption is −146 and −153 kJ/mol at the top and bridge site, respectively (Fig. 2f and Supplementary Figs. 30 and 31). Adsorbed CO can interchange between the bridge site and the top site. This evidence does not necessarily corroborate that these CO adsorption modes must belong to the reaction intermediates of the most energy-favored reaction pathways. Also, although the calculated frequencies of adsorbed CO on Pt8O13/CeO2 have similar values compared with the experimental peak centers, we cannot exclude the other possible CO adsorption modes on any heteronuclear PtO2 species in the Pt-O-Pt/CeO2 catalyst. This limitation is also evidenced and discussed from the perspective of experimental DRIFTS results (Supplementary Fig. 30). We emphasize that the C-O vibrational frequency cannot be used to definitively identify the Pt adsorption site,32 and a combined analysis approach of HAADF-STEM, XPS, XANES, and EXAFS must be used to corroborate the theory.
predicted representative structure, as these characterization results together set the context of platinum species size, chemical valence, and coordination environment.

Identification of oxygen migration reaction mechanism. To understand how the Pt1/CeO2 and Pt-O-Pt/CeO2 catalysts catalyze CO oxidation so differently, DFT calculations combined with mean-field microkinetic simulations were conducted to study the CO oxidation mechanism (the partial pressure for CO and O2 are 0.001 and 0.05 bar, respectively, consistent with our reaction studies). The schemes for the CO oxidation cycles and geometric and energetic information are shown in Fig. 3, Supplementary Figs. 32, 33, and Supplementary Table 4. On Pt1/CeO2(111) and PtO2, the preferred pathway involves adsorbed CO...
Fig. 3 Potential energy diagrams and configurations for CO oxidation cycle. CO oxidation proceeds on a the Pt1/CeO2 and b at the Pt-O-Pt catalytic unit in Pt8O14/CeO2. CO adsorption energies and reaction barriers are indicated in kJ/mol in the potential energy diagram. The bond distance between the two fragments at the transition state (TS) is given in angstrom (Å) in the configurations of CO oxidation. Beige, red, and blue spheres are Ce, O, and Pt atoms, respectively. The small gray and green spheres are C and O atoms involved in CO oxidation. Corresponding energetics are given in Supplementary Table 4.
on the Pt site during the CO oxidation cycle due to stronger adsorption of CO compared with O₂ at the same Pt site (Supplementary Table 5). CO oxidation is predicted to follow the Mars–van Krevelen (MvK) mechanism \(^{33-35}\) at the square-planar Pt₁-O₄ unit in Pt₁/CeO₂ (Fig. 3a and Supplementary Table 4), where adsorbed CO on the Pt atom (CO\(_{\text{Pt}}\)) reacts with surface lattice oxygen (O\(_{\text{Ce}}\)) in CeO₂ with a moderate activation barrier (\(E_a < 105 \text{ kJ/mol}\)). O₂ dissociation (\(E_a = 150 \text{ kJ/mol}\)) will heal the oxygen vacancy sites to complete the catalytic cycle on Pt₁/CeO₂.

For the Pt-O-Pt/CeO₂ samples, we have considered three potential catalytic cycles in the Pt₈O₁₄/CeO₂ system, namely: (1) at the platinum–ceria interface of Pt₈O₁₄/CeO₂, (2) at the edge of Pt₈O₁₄, and (3) at the Pt-O-Pt site in Pt₈O₁₄. The first step for CO oxidation in scenario 1 is the removal of one oxygen atom in Pt₈O₁₄ by CO\(_{\text{Pt}}\) with an activation barrier of 26 kJ/mol (Supplementary Fig. 32 and Supplementary Table 4). Afterwards, CO oxidation may take place at the interface of Pt₈O₁₄/CeO₂ obeying the MvK mechanism and involving O\(_{\text{Ce}}\) removal and O₂ dissociation. The reaction of CO\(_{\text{Pt}}\) with O\(_{\text{Ce}}\) to form CO₂ has the highest activation barrier for CO oxidation (\(E_a = 151 \text{ kJ/mol}\)), followed by O₂ dissociation (\(E_a = 72 \text{ kJ/mol}\)). The predicted apparent activation energy is 176 kJ/mol at the metal–support interface of Pt₈O₁₄/CeO₂, which results in a much too low CO oxidation rate compared with the experimental measurements (Fig. 4). The lower activity of the Pt₈O₁₄/CeO₂ interface compared with Pt₁/CeO₂ originates from the weak CO adsorption on Pt₈O₁₄/CeO₂ (\(E_a = 27 \text{ kJ/mol}\)), resulting in low CO coverage (Supplementary Figs. 34b and 35b). Although the platinum–ceria interface is accepted as the catalytic center for CO oxidation catalyzed by either single-atom Pt₁/CeO₂ catalysts or classic nanoparticles/clusters supported on ceria\(^{36,37}\), the active site at the interface of our Pt₈O₁₄/CeO₂ system cannot rationalize the observed high activity of the Pt-O-Pt/CeO₂ catalysts under these oxygen-rich conditions at low temperatures.

Alternatively, we probed the possible reaction route where CO oxidation proceeds solely on the Pt₈O₁₄ and the CeO₂ support is a spectator (scenarios 2 and 3). At the Pt₈O₁₄ edge atoms, O₂ physisorbs (\(E_d = 1 \text{ kJ/mol}\)) after CO adsorption (Supplementary Fig. 33 and Supplementary Table 4). The RDS for CO oxidation is \(CO + O_{\text{Pt}} \rightarrow CO_2 + O_{\text{Pt}}\) with an activation barrier of 117 kJ/mol (Supplementary Figs. 34c, 35c and Supplementary Table 4). Consequently, the CO oxidation rate is still too slow at the Pt₈O₁₄ edge atoms with an apparent activation energy of 258 kJ/mol (Fig. 4) due to the weak adsorption of O₂ and high barrier for CO\(_{\text{Pt}}\) reacting with O₂. Surprisingly, this work finds that the Pt-O-Pt ensemble in the Pt₈O₁₄ (scenario 3) can facilitate an O migration mechanism to rapidly catalyze CO oxidation (Fig. 3b and Supplementary Table 4). One O atom from the adsorbed O₂ can migrate to a neighboring O atom in the Pt₈O₁₄ to form O₂V with an \(E_d = 103 \text{ kJ/mol}\), followed by O₈P removal and O₂V dissociation. The activation barriers for the O₈P atom reacting with O₈P and O₂V dissociation are predicted to be at least 26 kJ/mol lower than the O atom migration step; thus, O migration is the RDS for this mechanism (Supplementary Figs. 34d, 35d and Supplementary Table 4). The microkinetic simulations predict \(E_{\text{app}}\) for the Pt-O-Pt/CeO₂ catalysts of 54 kJ/mol, which is close to our experimentally measured result of 40 ± 2 kJ/mol (Fig. 4).

The next H₂ consumption peak in the temperature range of 160–200 °C is related to the further depletion of the ceria lattice oxygen that can migrate to the Pt₁-CeO₂ interfaces. In contrast, the Pt-O-Pt/CeO₂ catalysts may not display active [O] supply from the ceria to initiate the low-temperature oxidation. A trace amount of [O] reduction takes place in the temperature range of 40–60 °C for all three Pt-O-Pt/CeO₂ catalysts. To examine the impact of the ceria supports, the three types of ceria, a, b, and c, were first probed with the CO oxidation reaction as bare
The catalyst surface [O] reducibility and site-specific turnover frequencies (TOFs) for CO oxidation reaction. a H₂ temperature programmed reduction (TPR) profiles and integrated amounts of reducible [O] for the Pt₁/CeO₂ and Pt-O-Pt/CeO₂ catalysts. The labeled values in a are the integrated amount of reducible oxygen with the default unit of μmol [O]/g.cat. b Identical TOFs were found for the Pt-O-Pt/CeO₂ catalysts and different TOFs were found for the Pt-free ceria supports (inset).

Discussion

It is worth noting that the concept of “maximized atom efficiency” is different from “maximized activity per atom.” Our results highlight that Pt₁ indeed has maximized its material utilization efficiency, but there is large room to improve the activity per Pt atom. The solution from this work is to tackle the issue of lacking neighboring Pt atoms in the typical Pt₁/CeO₂ system. By forming the Pt-O-Pt catalytic unit in representative one-layer Pt₆O₁₄ cluster, the Pt atoms can now effectively activate and utilize the oxygen intermediates to catalyze the low-temperature CO oxidation. A recent work adjusted the Pt-O coordination number between 2 and 3 in Pt₆O clusters by either reductive or oxidative treatment at 350 °C to modify the catalytic activity of PtOₓ/CeO₂ nanowire catalysts within one order of magnitude for the CO oxidation under oxygen-rich conditions. Despite that the platinum was not fully exposed in this prior work, as the dispersion ranged from 10 to 83% (Supplementary Table 1), the authors may have created a portion of similar sites as we did in this work (best-performing catalysts from the current work are on average six times more active by incorporating the possible impact of different reactant concentrations). Here, by maintaining 100% platinum dispersion, which means that all the Pt atoms are accountable for surface catalysis and there is a minimal amount of spectator Pt species to distort the averaged characterization results, we found that the coordination number of Pt-O may not be the most decisive factor for the much more dramatic change of the CO oxidation activity, because both our Pt₁ and Pt-O-Pt structures have four oxygen atoms directly bonded to the platinum center at the starting point of each catalytic cycle. More importantly, the synergistic effect of the two, paired, platinum atoms in the Pt-O-Pt ensemble provides an alternative oxygen supply route independent of ceria substrates. This intrinsic catalytic difference between the isolated Pt₁ and the paired Pt-O-Pt structure could likely not be overcome by merely changing the Pt-O coordination numbers and considering each Pt atom as an independent unit. The mechanistic importance of the Pt-O-Pt interaction is highlighted in this work, where most of the attention was on the Pt-O-Ce interaction in previous studies. As shown in Fig. 6, the rate-determining steps of the CO oxidation reaction by Pt₁/CeO₂ and Pt-O-Pt/CeO₂ catalysts involve different sites and mechanisms for oxygen activation. The CO oxidation reaction proceeds through the MvK mechanism at the Pt₁-O-Ce interface in the Pt₁/CeO₂ catalyst, while the reaction is more efficiently catalyzed by the Pt-O-Pt/CeO₂ catalyst at its Pt-O-Pt unit with the bridge -O- participating. The similar feature might be shared with other oxide clusters having high metal dispersion and abundant undercoordinated metal sites.

The findings from this work should only be cautiously extended to a general type of clusters that retain a layered three-dimensional structure, where the lower dispersion and more saturated coordination environment of platinum bring more uncertainties. However, we infer that the Pt-O-Pt catalytic unit defined in this work is a prototype that illustrates an important advantage of catalysts with neighboring metal centers for efficient oxygen activation. Several recent reports are now indicating a general sense of agreement about the concept of using PGMs to create PGM-O-PGM catalytic units. Recent work by Zhao et al.
report a synthesis of a Ir-O-Ir structure on α-Fe2O3, and the synergistic effects between the two nearby iridium atoms were inferred to explain the 2.6 times higher activity of the dinuclear structure from its single-Ir atom counterpart for solar water oxidation. Jeong et al.39 reported that the Rh1/CeO2 catalyst has low activity for C3H6 and C3H8 oxidation, but another speculated Rh ensemble catalyst is highly active for C3H6 and C3H8 oxidation. The elusive Rh ensembles cannot be observed in HAADF-STEM images, and the k3-weighted EXAFS radial distribution indicates two sets of Rh-O-Rh bonds with coordination numbers near 0.6 (means not even a dinuclear structure—instrumental signal limitations). More recently, Dessal et al.40 confirmed an enhancement of CO oxidation activity of the Pt/γ-Al2O3 catalysts when the Pt atoms were agglomerated into platinum oxide clusters with a Gaussian distribution of cluster sizes from 0.5 to 1.5 nm. These studies are using different PGM species, supports, PGM domain sizes, and different reactions, but the formation of the paired PGM-O-PGM bond is the common variable behind the improved catalytic performance. We believe this is where the general implication of this material development and mechanistic investigation work resides.

One should also avoid oversimplifying this work as any dinuclear Pt-O-Pt structures can be more active than the single-atom Pt species in activating [O] intermediates. Notably, one of the platinum atoms in this highly active Pt-O-Pt catalytic unit does not have any direct -O- linkages to the ceria support, and it is in fact the enabler for facile O migration and fast CO oxidation. Indeed, the lattice oxygen of ceria is critical for the formation of stable Pt-O bonds according to our XAS analyses. However, the ceria is also shown to be largely a spectator species in the low-temperature CO oxidation reaction catalyzed by the Pt-O-Pt/ CeO2 systems. We envision that, if the Pt-O-Pt unit can be stabilized through similar oxygen linkages, a similar catalytic species may be created on various support substrates other than ceria. The formation of a Pt-O-Pt structure on activated Pt/La2O3 supports this hypothesis (Supplementary Figs. 37–39), but developing alternative preparation methods to build the exclusive catalytic sites on the alumina support needs further effort that is outside the scope of this work.

The exception from the general assessment of the present work is most likely to happen when quantum-size effects become evident in small ceria nanoclusters (especially <5 nm). Elegant studies showed that the oxygen vacancy formation in CeO2 nanoclusters exposing small O-terminated (111) and (100) facets is more probable compared to the extended CeO2 surfaces41–44. Theoretical evidence shows that the oxygen reverse spillover from these small ceria nanoparticles to the supported Pt species can generally be a more favorable process compared with Pt species supported on larger ceria particles, the latter of which is typically represented by slab computational models45,46. Such an unusual high oxygen mobility from the ceria have been predicted by modeling studies on CeO2 nanoclusters comprising from about 60 to over 200 atoms, where the largest Ce14O180 has an approximate size of ~2.4 nm47,48. The supporting experimental evidence was provided by carefully growing small Pt/CeO2 nanoparticles on a CeO2(111) film under ultrahigh vacuum—these grown ceria nanoclusters are only about ~3 nm in diameter and 0.4 nm in height49,50. We emphasize that the these CeO2 nanoclusters (up to ~3–4 nm) with extraordinary capability for generating mobile oxygen species are intrinsically different from the 10–30 nm ceria particles (homemade and commercial) used in this work. For example, small ceria nanoparticles of 3–4 nm were shown to improve the catalytic activity of gold species for CO oxidation by about two magnitudes49,50, but this highly active oxygen supply disappears quickly for regular ceria nanoparticles that are larger than 10 nm in automotive applications51–53. Theoretical calculation treatment from 300 to 1000 °C to fully decompose cerium precursors and to form stable ceria structures usually leads to the CeO2 particle size from 10 to 30 nm51,52.

These ceria particles have abundant stable CeO2(111) facets54,55. These differences lead to the observation that our single-atom Pt1(IV)-O5 is mostly observed on the stable CeO2(111) surfaces of a 10–30 nm ceria particle, although a sinter-resistant single-atom structure Pt1(II)-O4 sits at the less stable CeO2(100) facets of the small ceria nanoclusters (e.g., 1–3 nm)29,56. Of course, the small fraction of rounded edges, steps and kinks in our 10–30 nm ceria particles may well have led to the presence of a tiny portion of active sites as Pt-O-Pt plus active ceria substrates. These nonuniformities could be part of the reason for the deviations of kinetics between the computational results and experimental measurements. A success of synthesizing and stabilizing tiny ceria nanoclusters and anchoring an appreciable amount of the targeted platinum structure (e.g., the Pt-O-Pt) onto them bodes the ultimate solution of best using both the platinum and ceria substrate.

However, the bottom line is, when widely available ceria particles with larger size (>10 nm) and mediocre oxygen mobility are being adopted as an industrial catalyst support, activating the single-atom Pt to form the paired Pt-O-Pt ensemble is an effective way to create an alternative oxidative reaction pathway to benefit the low-temperature reactions. These tunable catalytic systems, either at a single-atom form or a Pt-O-Pt structure, may serve as powerful platforms for future studies of many other reactions.

Methods
Catalyst preparation. Platinum was loaded onto the ceria supports by a strong electrostatic adsorption method29,18. H2PtCl6 was chosen as the platinum precursor, because oxygen ligands complex anions can easily adsorb on the positively charged – Ce-OH2+ surface sites on ceria as single-atom layers when the pH of the solution is below the point of zero charge of ceria. To begin, the pH value of the H2PtCl6 solution was adjusted to pH = 9 by ammonia. The transparent solution was stirred at 70 °C overnight to allow the substitution of –Cl in [PtCl6]2– by –OH in solution. The as-prepared ceria powder was then added into the solution to adsorb the preformed [Pt(OH)6]2– as a single-atom Pt layer. The concentrations of the platinum precursor and the amount of ceria were varied to keep the same solid-liquid contact interface of 500 m2/L. We washed the filtration cake (filtered catalyst) with a total of 2 L distilled water at 80 °C during each sample filtration. The obtained samples were dried at 100 °C overnight, then calcined in air at 500 °C for 3 h, followed by H2 reduction at 250 °C for 0.5 h to further remove any possible residual –Cl and finally calcined in air at 500 °C for 1 h. These Pt/CeO2 samples are hereafter referred to as the “as-prepared” catalysts, and designated as “Pt1/CeO2-a, Pt2/CeO2-b, and Pt1/CeO2-c.” None of the Pt-containing components were detected as crystallized structures (Supplementary Figs. 6–8, 11–16), and limited changes happened to the BET surface areas, that is, they changed to 74, 60, and 44 m2/g from 80, 64, and 51 m2/g, respectively. Our Pt1/CeO2 samples were

Fig. 6 Different transition states for oxygen activation by the Pt1-O-Ce and the Pt-O-Pt ensembles. The detailed configurations for the CO oxidation cycles of the two groups of catalysts are illustrated in Fig. 3. The Pt1 single atoms are assembled into the more active Pt-O-Pt ensembles during the activation protocol. Color legend of atoms: Ce = yellow; Pt = blue; O = red; O atoms in the transition states for O2 activation are green. MvK = Mars-van Krevelen.
calculated at 500 °C, so the bulk diffusion of the Pt into CeO₂ that usually occurs above 700 °C is limited18,19. The nearly 100% Pt dispersion (measured at room temperature by a CO chemisorption method that passes the ceria support in directly contributing to CO adsorption19,20,61) and the measured catalytic activity in line with published data (Supplementary Table 1) confirm that the Pt₈ sites are accessible to the reactants.

After mild reduction at 500 °C in 5% H₂ and subsequent exposure of these Pt/CeO₂ (Pt₈) to CO plus O₂ feed stream ([CO]=1000 ppm, [O₂]=5%, balanced with N₂) at ambient temperature, we saw a notable enhancement of catalytic activity due to the restructuring of the platinum species. The reason for using diluted H₂ at mild temperatures is to adequately break the Pt-O bond that holds the single-atom Pt in place while avoiding extensive metal Pt sintering30,31,32. Our optimizations for reduction temperature and time are shown in Supplementary Fig. 1. Here, mild H₂ reduction at 200 °C breaks the Pt-O-Ce bond in the Pt₁-O₈ single-atom structure, because all the reducible oxygen species near Pt-terminated surface are consumed below 200 °C according to H₂-TPR for the Pt₁/CeO₂ catalysts (Fig. 5a). During the optimized H₂ reduction phase, we expect the single-atom Pt₁/CeO₂ catalysts to generate abundant oxygen vacancies on the Pt surface, which will mask the activity of CO adsorption33,62. A Pt₈/CeO₂(111) surface with one O-Ce-O layer was used as the support model without geometry relaxation to improve the calculation efficiency. We did not include the presence of persistent oxygen vacancies on CeO₂(111) surfaces during our CO oxidation mechanistic studies, as their rapid healing has been demonstrated by both theory and experiments14–16. The low-temperature CO oxidation conditions17. The plug wave cutoff energy was set to 300 eV and the convergence threshold for geometry optimizations was specified to 10⁻⁶ eV for both GA and GCMC calculations.

A Pt₄(4×4)-CeO₂(111) surface with two O-Ce-O layers was used as the support for simulating the CO oxidation catalytic cycle on both the Pt₄/CeO₂(111) and Pt₈/CeO₂(111) systems. To analyze the impact of the exposed ceria facet on CO oxidation, the representative Pt₄O₄ structure searched by GCMC simulations on CeO₂(111) was deposited on two O-Ce-O-layered (110) and (100) surfaces with each Pt atom binding four oxygen atoms according to our XPS and EXAFS data. Experimental observations14,22 suggest that the (100) surface is terminated by 0.5 nm of Pt, thus, we used a 65 cm⁻¹ rigid shift to all the calculated CO vibrational frequencies on Pt₁/CeO₂ and Pt₈/CeO₂ catalysts to compare with our experimental DRIFTS spectra. The zero-point energy correction was not considered. Details on GA and GCMC simulations as well as the mean-field microkinetic simulations approach are presented in the Supplementary Information.

Data availability

The data that support the findings of this study are available from the corresponding authors upon request.

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Author contributions
H.W. conceived the research concept with M.Y., and performed catalyst synthesis, 
reaction tests, and participated in most of the experimental characterizations. J.-X.L. 
designed and performed the DFT, GCMC, and microkinetic calculations with input 
from B.R.G. L.F.A. performed the microscopic studies. S.L. and J.L. performed the 
XAS measurements and data analysis. J.W., H.L., and J.W. participated in the reaction 
tests and DRIFTS data interpretation. S.H.O. and W.L. designed reaction studies and 
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experimental results and implications. M.Y., M.S., and B.R.G. supervised and led the 
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