Gold Decorated Hydroxyapatite–CeO$_2$ Enabled Surface Frustrated Lewis Pairs for CO Oxidation

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1. Introduction

Carbon monoxide (CO) detection and elimination have been frequently described as significant technical routes for environmental protection and human health.[1–3] Among all technologies envisaged by far, the chemical oxidation of CO by oxygen (O$_2$) is the earliest and most frequently investigated approach. Numerous publications have been dedicated to their development and study, but the activation of molecular O$_2$ and the detailed CO oxidation mechanism remains mysterious.[4,5]

Surface frustrated Lewis pairs (SFLPs) were first discovered via the heterolytic dissociation of H$_2$ molecules over Lewis acidic boron and Lewis basic phosphorus sites.[6] Since then, owing to the steric hindrance between Lewis acid–base pairs and their electronically unquenched nature, SFLPs have shown great potential to activate a wide range of small molecules in homogeneous catalysis.[7–10]

The activation of molecular oxygen (O$_2$) holds the fundamental step for reaction mechanism of carbon monoxide oxidation. Surface frustrated Lewis pairs (SFLPs) with sterically hindered Lewis acid–base pairs are proven to activate small molecules, such as hydrogen. However, the activation of molecular O$_2$ on SFLPs remains unexplored. Herein, the construction of SFLPs in Au decorated hydroxyapatite (HAP)–CeO$_2$ heterojunction is reported. The coordinately unsaturated Lewis acidic Ce$^{3+}$ and the Lewis basic OH/C$^0$ group in HAP enable the activation of O$_2$ molecules to O$_2$–Ce$^{3+}$ species for carbon monoxide (CO) oxidation. The active site is identified based on the comprehensive in situ electron paramagnetic resonance, in situ diffuse reflectance infrared Fourier transform spectroscopy, X-Ray absorption spectroscopy, and theoretical simulation. The results provide a new strategy to construct SFLPs sites for O$_2$ molecule activation and the subsequent CO oxidation.

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However, a limited number of SFLPs were developed to activate small molecules in the field of heterogeneous catalysis, and most studies focused on the activation of the hydrogen molecule.\cite{11,12} A knowledge gap has been shown in the activation of O2 molecules via SFLPs, where O2 represents the simplest and most abundant oxidant for combustion, oxidation, and electrochemical reactions.\cite{13–15}

The CO oxidation reaction could be regarded as one of the most important heterogeneous catalysis reactions,\cite{1–5,15} and it is therefore of major technologic importance to develop SFLPs that could facilitate such reaction. Hydroxyapatite (HAP) has been widely used as a support material for CO oxidation with its unique surface basicity, excellent stability, and sintering resistance property.\cite{14,16–19} The exclusive abundance, low cost, non-toxicity, and tunable acid-base active sites make HAP an excellent candidate for the construction of SFLPs.\cite{2,20–24} Thus, the presence of other cocatalysts like Au may function as the active center for oxygen activation and CO oxidation in SFLPs.\cite{25–27}

Described herein, we developed a strategy using hydrothermal and deposition–precipitation methods to construct SFLPs via the Lewis acidic Ce\(^{3+}\) and Lewis basic OH\(^-\) in the HAP lattice of the HAP–CeO\(_2\) heterojunction. Unlike traditional activated O2 molecule, the resulting SFLPs could activate the O2 molecule to form the O\(_2^-\)/Ce\(^{3+}\) species and subsequently conduct CO oxidation with the presence of Au nanoparticles. In situ electron paramagnetic resonance (EPR) measurements, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-Ray absorption spectroscopy (XAS), and density functional theory (DFT) calculations confirmed the proposed reaction mechanism.

2. Experimental Section

2.1. Catalyst Preparations

2.1.1. Materials

Cerium nitrate tetrahydrate, Ce(NO\(_3\))\(_2\)·4H\(_2\)O (ACS Reagent, 99.5%), and polyvinylpyrrolidone (PVP) (ACS Reagent, average molecular weight: 58 000, K30) were purchased from Macklin. Chlorauric acid tetrahydrate, HAuCl\(_4\)·3H\(_2\)O (Analytical grade, ≥47.8%), was purchased from Shanghai trial (Sinopharm Chemical Reagent Co., Ltd.). Ammonium hydroxide, NH\(_4\)OH (Analytical grade, 25%–28%), was purchased from Macklin. Deionized water and absolute ethanol were of laboratory grade. All reagents and solvents were purchased commercially and used without further purification.

2.1.2. Preparation of Heterojunction HAP–CeO\(_2\) Support

HAP–CeO\(_2\) support was prepared through the hydrothermal method. In a typical synthesis, 8 mmol of Ce(NO\(_3\))\(_2\)·6H\(_2\)O and 20 wt% of HAP (the mass ratio of HAP:CeO\(_2\) = 20%) was added to a solution under vigorous stirring for 20 min to form a homogeneous solution, adjusted to a pH of 11–12 using about 8.0 mL of ammonium hydroxide solution (25%), and stirred for 15 min. The obtained homogeneous solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and then heated at 180 °C for 12 h in thermostat water bath cauldron under normal pressure, centrifuged, washed alternately with distilled water and ethanol until neutral, dried, and calcined at 500 °C for 5 h. CeO\(_2\) was synthesized by a similar method without adding HAP.

2.1.3. Preparation of Gold Catalysts

The HAP–CeO\(_2\)-supported gold catalyst was synthesized through a deposition–precipitation method. HAP–CeO\(_2\) (0.4 g) and a certain amount of 0.01 mol L\(^{-1}\) HAuCl\(_4\) (Au: 0.1 wt%) solution were dissolved in 100 mL of distilled water. The reaction mixture was then stirred at room temperature for 12 h and refixed at 100 °C for 4 h. The final product was centrifuged and the precipitate was washed for several times until no Cl\(^-\) was detected. Collected precipitate was dried at 80 °C and calcined at 300 °C for 2 h in air. Similar procedures were used for preparing Au/HAP and Au/CeO\(_2\) catalysts with HAP and CeO\(_2\) as the supports, respectively.

2.2. Characterization

ICP-OES results were recorded on an Agilent ICPOES730 Instrument. Brunauer–Emmett–Teller (BET) adsorption isotherms were obtained on a Micromeritics ASAP2020M + c apparatus at liquid N\(_2\) temperatures (77 K). X-Ray diffraction (XRD) was performed using Rigaku D/Max-2500 X-Ray diffractometer (Cu K\(_\alpha\), \(\lambda = 0.154 	ext{ nm}\)). Fourier transform infrared (FT-IR) transmission measurements were performed using a Thermo Scientific IS50 Series spectrometer over a range of 400–4000 nm. The morpholoy was characterized on a Tecnai G2F20 transmission electron microscopy (TEM) working at 200 kV. X-Ray photoelectron spectroscopy (XPS) was collected by a ThermoFischer ESCALAB 250Xi spectrometer with a pressure of 6 × 10\(^{-10}\) Torr in an ultrahigh vacuum chamber, using Al K\(_\alpha\) radiation (1486.6 eV) operating at 15 kV and 27 A. A passing energy of 40 eV and step size of 0.1 eV were used for photoelectron detection, and all results were calibrated to C 1s 284.5 eV. UV-vis spectra were measured on a SHIMADZU UV-3600 spectrophotometer. Temperature-programmed desorption of O\(_2\)/CO (O\(_2\)/CO-TPD) was performed on the quartzchrome chemBET TPD. About 40 mg of sample was pretreated in He gas to 300 °C for 1 h, cooled down, and then exposed to O\(_2\)/CO gas for adsorption until saturated. O\(_2\)/CO desorption was measured in 15 mL min\(^{-1}\) He with a heating ramp of 5 °C min\(^{-1}\) from 50 to 600 °C. In situ DRIFTS experiments were performed using a thermo IS10 with a detector cooling by liquid nitrogen. Samples were first pretreated for 2 h at 100 °C in He and the background spectrum was recorded when cooling to 80 °C. CO adsorption experiments were conducted under CO/He for 30 min, following exposure to CO/O\(_2\)/He for CO–O\(_2\) coadsorption to carry on for 30 min. Spectra were recorded at 1, 5, 10, 15, 20, 25, and 30 min and collected with a resolution of 4 cm\(^{-1}\) and 64 scans. In situ EPR spectra were recorded by a Bruker A300. Samples for in situ EPR were evacuated at room temperature for 10 min, and then pretreated at 80 °C for 2 h after introducing 2 mbar O\(_2\) into the cell. The spectra were collected after 30 min cooling at 77 K. In situ Raman spectroscopy was performed using...
a HJY EnvolutionHR instrument. The excitation laser has a wavelength of 532 nm. The measurements were carried out using a long focal length lens with a magnification of 4 ×. Samples for in situ Raman were evacuated at room temperature for 10 min, and then pretreated at 80 °C for 2 h after introducing 2 mbar O2 into the cell.

The obtained X-ray absorption fine structure spectroscopy (XAFS) data were processed in Athena (version 0.9.26) for background, preedge line, and postedge line calibrations. Then, Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k2 weighting, k-range of 3–10 Å–1, and R range of 1 to ≈3 Å were used for the fitting of CeO2; k-range of 3–20 Å–1 and R range of 1.5 to ≈4 Å were used for the fitting of samples. The four parameters, coordination number, bond length, Debye–Waller factor, and E0 shift (CN, R, ΔE0), were fitted without anyone was fixed; the σr was set. For Wavelet transform analysis, the χ(k) exported from Athena was imported into the Hama Fortran code. The parameters were listed as follows: R range, 1–4 Å, k range, 0–20 Å–1; k, weight, 3; and Morlet function with χ = 10; σ = 1 was used as the mother wavelet to provide the overall distribution.

A spin-polarized periodic DFT calculation was carried out on Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation with Perdew–Burke–Emzerh functional (GGA + PBE) was used to describe exchange–correlation interactions. The ion cores and valence electrons interactions were described by expanding a plane wave basis set with a kinetic energy cutoff of 400 eV, using a projector augmented wave method. DFT + U methods incorporated Hubbard U term was used as an on-site Coulombic interaction for strongly localized character of Ce 4f electrons. In present study, a value of U = 4.5 eV was adopted to Ce 4f electrons according to previous reports. In addition, the long-range dispersion corrections were employed by DFT-D3 approach. The Brillouin zone integration was sampling by a 3 × 3 × 4 and 6 × 6 × 6 Monkhorst–Pack k-points mesh for HAP and CeO2 bulk geometry optimization, respectively, and a 2 × 2 × 1 k-points grids was used for all slab model calculations. To investigate O2 activation mechanism on metal oxide FLP sites, a heterostructure HAP (211)/CeO2 (110) model was built by cleaving (211) and (110) crystal plane from optimized of HAP and CeO2 bulk crystal. A vacuum thickness of 15 Å was applied to avoid the neighboring interaction. The bottom three layers were fixed at their bulk position and the top three layers and adsorbate were allowed to relax until the total energy and force were lowered than 10−6 eV and 0.05 eV Å−1, respectively.

The molecular adsorption energy, E_{ads}, was calculated by using the following equation

$$\Delta E_{ads}(M) = E_{slab + M} - E_{slab} - E_M$$

where the $E_{slab + M}$ and $E_{slab}$ are the total energy of with and without adsorbate, and $E_M$ is the total energy of molecules at gas phase. To search for the location of transition state structure of O2 dissociation intermediate species, a climb image nudged elastic band method (CI–NEB) combining with dimer method was adopted and the transition state was further verified by vibrational frequency analysis.

2.3. CO Oxidation Measurements

CO oxidation reaction measurements were carried out in a fixed-bed flow millireactor under atmospheric pressure. The reactor housing was a stainless steel tube with an inner diameter of 8 mm. ≈200 mg sample was packed into the stainless steel tube and was diluted by quartz sand (chemically inert). Reactant gases CO (10 vol%) and air for balance were flowed through the reactor at a total flow rate of 36.3 mL min−1. A GC-508A gas chromatography equipped with a GDX-502 column was used to analyze product gases on line using a thermal conductivity detector (TCD) with every 17 min interval at one temperature, with a ramping rate of 5 °C min−1. CO conversion was calculated using the Equation (2)

$$\text{CO Conversion} = \frac{[\text{CO}]}{[\text{CO}] + [\text{CO}_2]}$$

where [CO] and [CO2] are the concentration of CO and CO2 produced. The specific reaction rates normalized by Au mass at different temperatures were calculated using the Equation (3) and (4)

$$\text{CO rate (mmol CO g}^{-1}\text{Au s}^{-1}) = \frac{\text{Total moles (mmol)} \times \text{CO conversion (%)} \times \text{Reaction time (s)}}{\text{Au mass (g)} \times \text{Reaction time (s)}}$$

Total moles (mmol) = Reactor pressure (Pa) × Total flow rate (mL min−1) × Reaction time (min) × 10% \[ R \times \text{Reactor temperature (K)} \]

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

3. Results and Discussion

3.1. Material Synthesis and Structure

The materials investigated in this study included hydroxyapatite, pristine ceria, hydroxyapatite–ceria, hydroxyapatite-supported Au, ceria-supported Au, and hydroxyapatite–ceria-supported Au, denoted as HAP, CeO2, HAP–CeO2, Au/HAP, Au/CeO2, and Au/HAP–CeO2, respectively. As shown in Figure 1a and S1a, Supporting Information, the representative powder X-Ray diffraction (PXRD) patterns of the synthesized samples revealed the formation of phase-pure cubic CeO2 (JCPDS No. 34-0394) and hexagonal HAP (JCPDS No. 09-0432). Significant differences can be observed between the XRD patterns from HAP–CeO2 and CeO2, except the weak HAP peak at 32.9° due to the low concentration of HAP (Figure S1a, Supporting Information). The profile of the XRD pattern of the Au/HAP–CeO2 catalyst remained very similar compared to that of Au/CeO2 (Figure 1a), and no evidence of any gold species was observed, suggesting the low loading of gold. The average grain
size of HAP–CeO₂ support is estimated to be 8.0 nm, smaller than those of HAP (33.7 nm) and CeO₂ (12.1 nm). This small grain size of 8.0 nm may possibly be associated with the formation of the HAP–CeO₂ heterojunctions (Table S1, Supporting Information). This suggestion can be further corroborated from FT-IR spectra (Figure S1b, Supporting Information), where OH⁻/C₀ and PO₄³⁻/C₀ deformational modes expounded the strong coupling between HAP and CeO₂ in HAP–CeO₂ and Au/HAP–CeO₂.

### 3.2. Catalytic CO Oxidation

When Au was not introduced into the material system, no CO₂ production could be observed for HAP, CeO₂, and HAP–CeO₂ up to 200 °C (Figure S2a, Supporting Information). As shown in Figure 2a, Au/HAP–CeO₂ showed the best catalytic activity with 90% CO conversion at 80 °C. In contrast, Au/CeO₂ exhibited 90% CO conversion at 190 °C, and Au/HAP exhibited only 4% CO conversion at the maximum measurable temperature of 200 °C. It can be noted that the conversion of CO was significantly increased when the temperature increased from 70 to 80 °C on Au/HAP–CeO₂, which was not observed on Au/HAP and Au/CeO₂. This is probably due to the instantaneous growth in activated oxygen species (such as superoxide O₂⁻ species) concentration on Au/HAP–CeO₂ at such a temperature range, which will be discussed later. Additionally, to understand the catalytic activity, the specific reaction rates normalized by Au mass at different temperatures were calculated (Figure 2b). Au/HAP–CeO₂ exhibited a reaction rate of 9.76 molCO g⁻¹Au⁻¹ s⁻¹ at 100 °C, value that is around 31.5 and 1.4 orders activity enhancement of the CO oxidation reaction compared to the Au/HAP (0.31 molCO g⁻¹Au⁻¹ s⁻¹) and Au/CeO₂ (7.18 molCO g⁻¹Au⁻¹ s⁻¹) even at 200 °C, respectively. Such a reaction rate of CO oxidation to CO₂ is also superior to many other catalytic systems conducted under similar conditions (Table S2, Supporting Information). The surface-area-normalized reaction rates of the samples showed a similar trend to those normalized by Au mass (Table S3, Supporting Information), ruling out the geometric effect on catalytic activity.[20]

Furthermore, a 20 h continuous test at 180 °C has been performed to simulate the treatment process of automobile exhaust with the excellent stability (Figure S2b, Supporting Information), and this could be attributed to HAP, which prevents the high-temperature sintering of the active phase. This finding implies that the detrimental effect of high-temperature sintering may be improved in this way. To confirm this hypothesis, Au/CeO₂ and Au/HAP–CeO₂ were calcined at 500 and 600 °C for 2 h to study their thermal stability. As a result, after calcination from 500 to 600 °C, the Au/CeO₂ exhibited a significantly decreased CO conversion from 96.8% to 53.1% at 200 °C (Figure 2c), which may be caused by the sintering of Au nanoparticles. In comparison, the treated Au/HAP–CeO₂ sample exhibited a minor change in its activity with a T₁₀₀ (the temperature at which 100% CO conversion is achieved) of 140 and 150 °C, respectively (Figure 2d). TEM images of the two samples supported the improved sintering.
resistance of Au nanoparticles on Au/HAP–CeO₂ (Figure S3, Supporting Information). However, to fully understand this impressive catalytic performance, extensive characterization of the material is necessary.

3.3. Structure Characterizations

The gold loadings in Au/HAP, Au/CeO₂, and Au/HAP–CeO₂ were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) to be 0.071, 0.087, and 0.12 wt%, respectively. The BET specific surface areas of HAP, CeO₂, HAP–CeO₂, Au/HAP, Au/CeO₂, and Au/HAP–CeO₂ registered at 31, 30, 87, 50, 92, and 89 cm² g⁻¹ by N₂ adsorption measurements, respectively (Figure S4 and Table S3, Supporting Information). Notably, HAP–CeO₂ had a higher specific surface area than HAP and CeO₂, which could be associated with the formation of a HAP–CeO₂ heterojunction, as discussed in more detail below. The specific surface area of CeO₂ loaded with Au increased by 3 times, probably due to the smaller size of hexagonal plate-like CeO₂ structure (see Figure S9, Supporting Information).

Survey and Au 4f XPS spectra (Figure S5, Supporting Information) of Au/HAP, Au/CeO₂, and Au/HAP–CeO₂ exhibited the weak peak of Au 4f due to the gold concentration falling below the detection limit. As illustrated in the O 1s XPS spectra of Au/CeO₂ and Au/HAP–CeO₂ (Figure 1b), two distinct peaks at around 529.1 and 531.3 eV could be assigned as lattice oxygen and oxygen vacancies, respectively. It is further shown that Au/HAP–CeO₂ had a larger oxygen vacancy peak area (63%) as compared to that of Au/CeO₂ (59%). The new peak at 527.4 eV was attributed to the lattice oxygen of HAP, which can be assigned to the strong interaction between HAP and CeO₂ (Figure S6, Supporting Information).

The high-resolution Ce 3d XPS spectra (Figure S7, Supporting Information) provided vital cerium valence states on the surface of CeO₂, HAP–CeO₂, Au/CeO₂, and Au/HAP–CeO₂. The peaks marked as υ, υ”, and υ”’ arise from Ce⁴⁺ 3d₅/₂, and the one marked as ω can be due to Ce⁴⁺ 3d₃/₂. Those labeled as υ’, ω’ in CeO₂, HAP–CeO₂, Au/CeO₂, and Au/HAP–CeO₂ confirmed the formation of Ce³⁺ species. The fitting of the Ce L₃-edge X-ray absorption near-edge structure (XANES) spectra in Figure 3a confirmed the presence of Ce³⁺. Linear combination fit (LCF) analysis collected on Au/HAP–CeO₂ provided reliable results of 0.137 and 0.862 fractions for Ce³⁺ and Ce⁴⁺, respectively (Figure 3b and Table S4, Supporting Information). Coordination number (CN) and bond length values were further obtained by fitting the extended X-ray absorption fine structure spectroscopy (EXAFS) spectra of Au/HAP–CeO₂. The fitted spectra (Figure S8, Supporting Information), wavelet transform analysis (Figure 3c,d), and tabulated parameter values (Table S5, Supporting Information) were also presented. The Ce–O CN
of 4.8 could be caused by the larger ionic radius of Ce$^{3+}$ than that of Ce$^{4+}$.[45] This can be explained in terms of the enhanced oxidizing capability of CeO$_2$ with introduced HAP and Au. To this end, one can surmise that HAP could promote the reduction of tetravalent cerium to trivalent cerium, which would be compensated by the formation of more oxygen vacancies in Au/HAP–CeO$_2$. These results indicate the existence of synergistic interactions between Au and HAP–CeO$_2$, which play a positive role in the CO oxidation performance.[46]

TEM images of HAP nanorods and hexagonal plate-like CeO$_2$ structures with a diameter of about 15–20 nm were present in Figure S9, Supporting Information. Figure S9e–h, Supporting Information shows a heterostructure of HAP–CeO$_2$, where the hexagonal CeO$_2$ nanostructures nucleated and grew on the surface of rod-like HAP crystals. High resolution transmission electron microscopy (HRTEM) images of Au/HAP–CeO$_2$ demonstrated that Au nanoparticles (≈5 nm) were distributed over the HAP–CeO$_2$ (Figure 1c). The high-angle annular dark-field imaging-scanning transmission electron microscopy (HAADF-STEM) was conducted on Au/HAP–CeO$_2$ (Figure 1d and S10, Supporting Information). In the dark field images, the contrast between HAP and CeO$_2$ was sufficiently high, where CeO$_2$ appeared as bright spots with a size of around 5–10 nm. The distribution of the different components was confirmed by energy-dispersive X-ray spectroscopy (EDS) results. According to TEM-selected area electron diffraction (SAED) images (Figure S11, Supporting Information) and gold particle size distributions (Figure S12, Supporting Information), the mean size of gold nanoparticles decorated on HAP (11.4 nm) and CeO$_2$ (8.75 nm) was larger than that on HAP–CeO$_2$ (4.75 nm), which can be attributed to the HAP–CeO$_2$ synergy for CO oxidation catalysis. The corresponding elemental mapping confirmed the existence of different compositions (Figure S13 and S14, Supporting Information). Furthermore, UV–vis measurements also confirmed the smaller gold nanoparticle size on Au/HAP–CeO$_2$ (Figure S15, Supporting Information).[47]

3.4. Reaction Mechanism

To obtain insight into the reaction pathways, in situ DRIFTS was conducted for Au/HAP–CeO$_2$ at 80 °C. As shown in Figure S16, Supporting Information, the peak located at 2171 cm$^{-1}$ is associated with the overlap of gaseous CO and CO adsorption on a metallic Au surface. Then peak at 2122 cm$^{-1}$ can be assigned to the CO adsorption on a metallic Au surface.[19,26] The peak intensity relating to CO–Au$^0$ decreased with the introduction of oxygen, demonstrating the CO oxidation reaction. In Figure 4, the peaks between 3500 and 3800 cm$^{-1}$ could be assigned to gaseous CO$_2$ fingerprint modes, and the peak at 2366 cm$^{-1}$ represented gas-phase CO$_2$. The peaks located at 1669, 1610, 1577, 1427, 1394, and 1319 cm$^{-1}$ could be attributed to carbonate species,[19] indicating that CO was adsorbed in the form of carbonate species. The production of these carbonate species followed by CO–O$_2$ coadsorption was much more efficient here as compared to that in the absence of O$_2$ as shown in Figure S16, Supporting Information. Thus, it was deduced that CO is oxidized on Au/HAP–CeO$_2$ via an intermediate carbonate species due to its migration from the Au surface to the support.[48,49]
Traditionally, the O2 molecule is believed to be activated over Au or oxygen vacancy and the activated O2 molecule could react with absorbed CO subsequently.\cite{50,51} The superoxide O$_2^\cdot$ species were detected here in this work by the increase of the peak intensity around 1000 cm$^{-1}$ in DRIFTS measurements of Au/HAP–CeO$_2$ followed by O$_2$ adsorption (Figure S16b, Supporting Information).\cite{52} Furthermore, the in situ EPR was employed to study the in-depth O$_2$ activation mechanism (Figure 5a). Surprisingly, unlike the traditional activated O$_2$ molecules from Au/CeO$_2$,\cite{53–55} a unique reaction immediate, Ce$_3$$^+$–O$_2^\cdot$ at $g = 2.032$ and $g = 2.034$,\cite{52,56} was observed, which implies that a different activation mechanism occurred as compared to previous studies. In situ Raman also revealed the formation of superoxide O$_2^\cdot$ species on Au/HAP–CeO$_2$ followed by O$_2$ adsorption, in which the Au/CeO$_2$ showed nothing (Figure 5b).\cite{57}

To confirm the presence of the superoxide O$_2^\cdot$ species on the Au/HAP–CeO$_2$ surface, O$_2$ temperature-programmed desorption (O$_2$-TPD) was performed on Au/HAP–CeO$_2$, HAP–CeO$_2$, HAP, and CeO$_2$ (Figure S17, Supporting Information). The signal around 300°C confirmed the presence of superoxide O$_2^\cdot$ species in Au/HAP–CeO$_2$ and HAP–CeO$_2$ samples, whereas HAP and CeO$_2$ showed negligible signals.\cite{58} The peak located at 237°C for HAP–CeO$_2$ could be diagnostic of the desorption of O$_2$ weakly adsorbed on the surface, and the disappearance of such a peak after introducing Au showed that the addition of Au promoted the formation of superoxide O$_2^\cdot$ bound to Ce$_3$$^+$ on Au/HAP–CeO$_2$.\cite{58,59} The desorption peaks observed at 400 and 580°C for Au/HAP–CeO$_2$ could represent oxygen adsorbed on the metal–support interfacial sites and strongly absorbed surface oxygen, respectively.\cite{59,60} Furthermore, CO-TPD measurements for the above samples at 50–450°C (Figure S18, Supporting Information) confirmed that the CO absorption is mainly attributed to the presence of Au.\cite{61} 

DFT calculations were conducted based on the presence of a unique O$_2$–Ce$_3$$^+$ reaction intermediate to simulate the O$_2$ activation mechanism. CeO$_2$ (110) and HAP (211) surfaces were selected due to their excellent thermodynamical stability (Figure S19, Supporting Information).\cite{7,62} Due to the existence of oxygen vacancies (Figure S20, Supporting Information), the Ce4–O49 pair was chosen to investigate O$_2$ adsorption and dissociation (Figure S24, Supporting Information), and are well supported by analogous studies on Ru/CeO$_2$ materials.\cite{63} In addition, Ce4 and O49 pairs with an atomic distance of 4.186 Å included atomic local charges of

![Figure 4. a,c) CO adsorption and b,d) CO–O$_2$ coadsorption spectra acquired over the range of (a,b) 4000 to 2300 cm$^{-1}$ and (c,d) 1750 to 1200 cm$^{-1}$ on the surface of Au/HAP–CeO$_2$ at 80°C.](image-url)
+2.18 $e^{-}$ and $-1.39$ $e^{-}$ (Table S6, Supporting Information), falling in the domain of solid SFLPs.[7,64]

The optimized initial state (IS), transition state (TS), and final state (FS) of O$_2$ dissociation on CeO$_2$ (110) with the reaction intermediate of activated O$_2$ molecule and Ce$^{4-}$O$_4$ SFLPs site in HAP (211)/CeO$_2$ (110) heterojunction are shown in Figure 6. In the IS, the O$_2$ molecule could be adsorbed on CeO$_2$ (110) with an adsorption energy of $-5.29$ eV and an O─O bond length of 1.245 Å (Figure S25a, Supporting Information), and then surpasses an activation barrier of 4.28 eV to reach the TS, leading the formation of a more stable FS. In contrast, for HAP (211)/CeO$_2$ (110), O$_2$ can be adsorbed on Ce$^{4-}$O$_4$ SFLPs with a lower adsorption energy of $-4.50$ eV and an elongated O─O bond length of 1.467 Å (Figure S25b, Supporting Information), which would be consistent with the presence of superoxide O$_2$ species.[51] As a result, it starts from the IS and continues into the TS with a much lower activation barrier of 0.89 eV, and to FS finally by the breaking of Ce─O68 bond, indicating the easier activation of O$_2$ molecules at the Ce$^{4-}$O$_4$ site than CeO$_2$ (110). These considerations can conclusively explain the higher CO oxidation activity of Au/HAP–CeO$_2$.[62]

In light of the CO adsorption on the Au surface and superoxide O$_2$$^{\cdot-}$ produced by the SFLPs Ce$^{3+}$/OH$^-$ (Figure 7), the reaction pathway could be summarized as follows. The activated O$_2$ molecules could form superoxide intermediate O$_2$$^{\cdot-}$Ce$^{3+}$ species, which then reacted with absorbed CO on Au sites to form the stable carbonate intermediates and thus produce CO$_2$ and Ce$^{3+}$-O$^*$. The produced Ce$^{3+}$-O$^*$ intermediate could oxidize the second absorbed CO molecule to complete the whole CO oxidation catalytic cycle.

4. Conclusion

In summary, SFLPs (Ce$^{3+}$/OH pairs) have been successfully constructed over HAP–CeO$_2$ heterostructures for O$_2$ activation to facilitate CO oxidation with the presence of Au. As a result, the threshold temperature for 100% CO conversion could be decreased from 200 to 100 °C with excellent stability at low and high temperatures. The utilization of SFLPs for O$_2$ activation unleashes the potential of SFLPs in oxidation processes, such as...
Figure 7. Schematic illustration of the possible reaction mechanism for CO oxidation by Au/HAP–CeO$_2$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
