Supporting Information

Distinct Role of Surface Hydroxyls in Single-Atom Pt1/CeO2 Catalyst for Room-Temperature Formaldehyde Oxidation: Acid–Base Versus Redox

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EXPERIMENTAL SECTION

Catalyst preparation

Cerium (III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, ≥ 99.99 %) was purchased from Alfa Aesar. Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O, Pt ≥ 37.5%) was purchased from Sinopharm Chemical Reagent Limited corporation. All the reagents were used without further pretreatment. 1 g of Chloroplatinic acid hexahydrate powder was dissolved in 10 mL of deionized water to prepare a chloroplatinic acid solution. Ce(NO$_3$)$_3$·6H$_2$O was calcined in air at 623 K for 2 h to obtain CeO$_2$, which was used as the support to prepare Pt$_x$/CeO$_2$ catalyst.

The catalyst was prepared using the method previously reported.$^1$ A 0.6 wt% Pt$_x$/CeO$_2$ catalyst was synthesized by the incipient wetness impregnation method. An appropriate amount of chloroplatinic acid solution was added drop-wise to the CeO$_2$ while being kept grinding in a mortar and pestle. Then the obtained mixture was dried at 353 K for 12 h in the static air, and ramped to 1073 K at 10 K·min$^{-1}$ in a muffle furnace and hold for 12 h.

The Pt$_x$/CeO$_2$ catalyst is further treated with steam, which is denoted as Pt$_x$/CeO$_2$-S. The Pt$_x$/CeO$_2$ powder was first sieved to 40-60 mesh, subsequently placed in a quartz reactor, and treated with 10% H$_2$O/Ar steam at 1023 K for 9 h, typically with a space velocity of 10,000 mL·g$^{-1}$·h$^{-1}$. The sample was then cooled down to 573 K and the water vapor was discontinued. Afterward, the sample was purged in the same carrier gas for 1 h before cooling down to room temperature. 10 vol% of water was injected into the flowing gas stream by a calibrated syringe pump (LSP02-1B, Longer Pump) and was vaporized in the heated gas line (473 K) before entering the reactor. The pumping rate of water was 2.45 μL·min$^{-1}$ and the total flow rate was 33.3 mL·min$^{-1}$, corresponding to the space velocity of 10,000 mL·g$^{-1}$·h$^{-1}$.

Similarly, the bare CeO$_2$ powder with the same steam treatment by 10% H$_2$O/Ar at 1023 K for 9 h, is denoted as CeO$_2$-S. As a comparison, the Pt$_x$/CeO$_2$ catalyst subjected to 10% H$_2$/Ar (50 mL·min$^{-1}$) reduction at 573 K for 30 min, is denoted as Pt/CeO$_2$-R.
Catalyst characterization

X-ray diffraction (XRD) patterns of catalysts were recorded on Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (40 kV and 30 mA) at a scanning speed of $2\theta = 10.0 \, \text{°/min}$ from 20° to 80°. The surface areas and pore volumes of the calcined catalysts were measured using N2 physisorption on a Micromeritics ASAP 2020 Plus instrument. Pt loading of catalysts was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. X-ray photoelectron spectra (XPS) were recorded with a Quantum 2000 Scanning ESCA Microprobe instrument (Physical Electronics) using Al Kα radiation. The binding energy was calibrated by using the C1s photoelectron peak at 284.8 eV. Raman spectra were obtained using a Labram Aramis micro Raman spectrometer system equipped with a holographic notch filter, a He-Ne laser (632.8 nm), and a CCD detector. Scanning electron microscopy (SEM) images were performed on a Zeiss Gemini 500 field emission scanning electron microscope with an electron high tension (EHT) voltage of 3.0 kV.

The surface oxygen was determined by CO temperature programmed reduction (CO-TPR). CO-TPR was carried out on a homemade instrument, where 100 mg catalyst (40-60 mesh) was typically used in each test. First, the catalyst was oxidized in a 10% O2/He (30 mL·min$^{-1}$) at 573 K for 60 min, then cooled down to room temperature in the He atmosphere. Next, 5% CO/He (30 mL·min$^{-1}$) was introduced. After the gas flow was stabilized, the temperature was ramped at 5 K·min$^{-1}$ from room temperature to 773 K. The evolved CO$_2$ and H$_2$ were analyzed by a mass spectrometer (Pfeiffer Omni Star GSD 320).

HCHO temperature programmed surface reaction (HCHO-TPSR) experiments were performed to explore the possible reaction route. Typically, 100 mg of catalyst (40 - 60 mesh) was loaded in a quartz reactor and pretreated at 573 K for 30 min under 10% O2/He (30 mL·min$^{-1}$) and purged with He for 30 min (30 mL·min$^{-1}$) at the same temperature. The reactor was then cooled down to room temperature. Gaseous HCHO was generated by passing He (15 mL·min$^{-1}$) through a paraformaldehyde container in a thermostatic water bath (313 K). The HCHO flowed through the reactor for 60 min, allowing the substances involved to adsorb on
the catalyst. Next, He was introduced into the reactor to remove the unabsorbed substances, and the temperature was ramped at 10 K·min⁻¹ from room temperature to 773 K in a flow of 2% O₂/He (30 mL·min⁻¹). The CO₂, CO, H₂, and HCHO production were analyzed online by the mass spectrum (Hiden QGA Gas Analysis system).

*In situ* Diffuse Reflectance Infrared Fourier Transformed Spectroscopy (DRIFTS) analysis was employed to investigate the adsorption behavior of CO molecules on Pt species of the catalyst, as well as to monitor the dynamic change of the catalyst surface species on the catalysis during the reaction process. DRIFTS spectra were recorded using a ThermoFisher IS50 instrument quipped with a smart collector and a liquid N₂ cooled MCT detector, coupled with a Praying Mantis™ Diffuse Reflection accessory from Harrick. The spectra and backgrounds taken were averaged from 64 scans with a resolution of 4 cm⁻¹. The procedure for DRIFTS during the CO adsorption was as follows: the catalyst was pretreated at 573 K for 30 min under 10% O₂/He (40 mL·min⁻¹) and purged with He for 30 min (40 mL·min⁻¹) at the same temperature. The temperature was then decreased to 453 K and a background spectrum was taken. Afterward, IR spectra were recorded every minute. 1% CO and 6% O₂-balanced with He was first introduced into the cell with a flow rate of 40 mL·min⁻¹ for 30 min. Subsequently, the flow of CO was discontinued while 10% O₂/He was kept flowing for 15 min.

The procedure for DRIFTS during the HCHO oxidation reaction was as follows: the catalyst was pretreated with N₂ (40 mL·min⁻¹) at 573 K for 60 min. After cooling to room temperature, the background spectrum was collected. The gas of 400 ppm HCHO/N₂ or 400 ppm HCHO/20% O₂/N₂ (a total flow rate of 100 mL·min⁻¹) was then introduced into the reaction cell for the adsorption experiments. Pure N₂ was used as degassing gas and IR spectra were recorded every minute. All the spectra were analyzed by subtracting the background.

**The catalytic performance in HCHO oxidation**

The activity measurement for the catalytic oxidation of HCHO over the catalysts was
performed in a fixed-bed quartz flow reactor (inner diameter = 7.0 mm) under atmospheric pressure. Typically, 60 mg catalyst (40-60 mesh) was mixed with quartz sand and loaded into a straight quartz tube, which was replaced by a U-type quartz tubular placed in an ice bath upon the investigation of the low-temperature (273 - 293 K) activity. The feed gas composition for the activity tests was 400 ppm HCHO/20% O₂/N₂ and 25% relative humidity (total flow 100 mL·min⁻¹) at a weight hourly space velocity of 100,000 mL·g⁻¹·h⁻¹. Gaseous HCHO was generated by passing N₂ through a paraformaldehyde container in a thermostatic water bath, where HCHO concentration can be changed by manipulating temperature and flow rate. Water vapor was generated by introducing liquid water into the vaporizer using a Core Parmer 74900 syringe pump and carried into the reactor by N₂. To investigate the moisture effect, relative humidity was varied from 0 to 75% by adjusting the injection speed of the pump. The oxidation products in the effluent gas were analyzed by an online gas chromatograph (GC2060, Shanghai Ruimin GC Instruments Inc.) equipped with a hydrogen flame ionization detector (FID) and Ni catalyst converter that was used for converting carbon oxides quantitatively into methane before the detector. The concentration of HCHO was calculated by the external standardization through the calibrated curve of CO₂.

Since no other carbonaceous compounds except CO₂ were detected in the effluents over all catalysts, the HCHO conversion was expressed as Equation (1) below:

\[ X_{\text{HCHO}} = \frac{[\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{total}}} \times 100\% \quad (1) \]

where \([\text{CO}_2]_{\text{out}}\) was the concentration of CO₂ produced at a certain temperature and \([\text{CO}_2]_{\text{total}}\) represented the concentration of CO₂ in the outlet gas when HCHO was totally oxidized into CO₂.

For kinetic measurements, the feed gas composition of 1400 ppm HCHO/20% O₂/N₂ and 25% relative humidity (total flow 100 mL·min⁻¹) was applied and the reactor was operated in a differential mode by keeping the HCHO conversion below 15%.

The reaction \(r_{\text{HCHO}}\) rate of HCHO (in a unit of \(\mu\text{mol·gPt}^{-1}·\text{s}^{-1}\)) was calculated by Equation (2):

\[ r_{\text{HCHO}} = \frac{X_{\text{HCHO}} \times f_{\text{HCHO}}}{m_{\text{cat}} \times \eta} \quad (2) \]
where $f_{\text{HCHO}}$ refers to the flow rate of HCHO (in a unit of $\mu\text{mol} \cdot \text{s}^{-1}$), and $m_{\text{cat}}$ refers to the mass of catalyst (in a unit of g) in the fixed bed and $n$ is the weight percentage of the Pt catalysts.

Turnover frequency (TOF) (in a unit of s$^{-1}$) was the number of reactant molecules converted on a single active site per unit of time. It was calculated by Equation (3):

$$\text{TOF} = \frac{r_{\text{HCHO}} \cdot M_{\text{Pt}}}{D}$$  \hspace{1cm} (3)

where the $M_{\text{Pt}}$ refers to the molar weight of Pt (in a unit of g·mol$^{-1}$), and $D$ refers to the dispersion. It has been proved that the catalyst is a single atom when the loading is less than 3%, and the dispersion of Pt is 100%.\textsuperscript{1-3}

The activation energies ($E_a$) were calculated by Equation (4):

$$\ln r_{\text{HCHO}} = -\frac{E_a}{RT} + \ln A$$  \hspace{1cm} (4)

where $E_a$ refers to the apparent activation energy (in a unit of J·mol$^{-1}$), $R$ refers to the universal gas constant (in a unit of J·mol$^{-1}$·K$^{-1}$), and $T$ refers to the reactor temperature (in a unit of K).

**Density functional theory calculations**

All spin polarized calculations were performed using the CP2K package with the gradient-corrected Perdew, Burke, and Ernzerhof (PBE) functional.\textsuperscript{4-5} The effective cores were described by the norm-conserving Goedecker-Teter-Hutter pseudopotentials.\textsuperscript{6-8} The wavefunctions of valence electrons were expanded in the double-$\zeta$ Gaussian basis sets with an energy cutoff of 500 Ry.\textsuperscript{9} Only gamma point was used for Brillouin-zone integration.

DFT+U correction was used for the description of Ce 4f-orbitals with the value of $U = 5$ eV.\textsuperscript{10} Test calculations showed that the total energy change of the reactive system was negligible (<0.01 eV) when the maximum force convergence criteria of 0.001 hartree/bohr was used.

Each reaction state configuration was optimized with the Broyden-Fletcher-Goldfarb-Shanno (BGFS) algorithm with SCF convergence criteria of $1.0 \times 10^{-8}$ au. To compensate for the long-range van der Waals (vdW) dispersion interaction, the DFT-D3 scheme\textsuperscript{11} with an empirical damped potential term was added to the energies obtained from exchange-correlation
functional in all calculations.

The adsorption energy \( (E_{\text{ad}}) \) of formaldehyde (HCHO) on the CeO\(_2\)(111) and Pt\(_1/\)CeO\(_2\)(111) catalyst surfaces was calculated using the following definition

\[
E_{\text{ad}} = E_{\text{adsorbate+surface}} - (E_{\text{surface}} + E_{\text{adsorbate}}) \quad (5)
\]

where \( E_{\text{adsorbate+surface}} \) is the total energy of the HCHO interacting with the catalyst surface slab; \( E_{\text{surface}} \) is the total energy of the optimized catalyst surface slab; and \( E_{\text{adsorbate}} \) is the energy of an HCHO molecule in a vacuum. A negative \( E_{\text{ad}} \) value indicates the favorable (exothermic) adsorption of formaldehyde.

The transition states of elementary reaction steps in the HCHO oxidation over were located using the climbing image nudged elastic band (CI-NEB) method\(^{12-13}\) with five intermediate images along reaction pathways between initial and final states. Each identified transition state was further confirmed by the vibrational frequency analysis. The reaction energy is calculated as the total energy difference between the final state and the initial state. The forward and reverse activation barriers for each reaction are defined as the total energy difference between the initial state and the transition state, and between the final state and the transition state, respectively.

The CeO\(_2\)(111) surface was modeled as a periodic \( p(3 \times 3) \) super cell slab consisting of 12 atomic layers. A vacuum gap of 20 Å in the z direction was used to minimize the interaction between CeO\(_2\)(111) surface slabs. During the geometry optimization, six outermost atomic layers of the CeO\(_2\)(111) surface was allowed to relax while the rest of the atoms in the CeO\(_2\)(111) surface slab was kept fixed to their optimized surface positions. The Pt\(_1/\)CeO\(_2\)(111) surface was modeled by replacing one surface Ce with a single Pt atom. Finally, two surface hydroxyl groups (2OH) were made by directly arranging two hydrogen atoms over the surface oxygen atoms, generating CeO\(_2\)(111)-2OH and Pt\(_1/\)CeO\(_2\)(111)-2OH surfaces. All four surface structures used in this work are given in Table S4 in the supporting information.
Table S1. Characterization of the catalysts

| Catalyst          | Pt weight loading\(^a\) [wt%] | Crystal size\(^b\) [nm] | Surface area [m\(^2\)·g\(^{-1}\)] | Pore volume\(^d\) [cm\(^3\)·g\(^{-1}\)] | Average Pore size\(^e\) [nm] |
|-------------------|-------------------------------|-------------------------|-------------------------------------|----------------------------------------|-----------------------------|
| CeO\(_2\)         | 0                             | 9                       | 80                                  | 0.22                                   | 11                          |
| CeO\(_2\)-S\(^c\) | 0                             | 28                      | 12                                  | 0.05                                   | 16                          |
| Pt\(_1\)/CeO\(_2\) | 0.61                          | 28                      | 21                                  | 0.12                                   | 19                          |
| Pt\(_1\)/CeO\(_2\)-S | 0.61                        | 28                      | 19                                  | 0.11                                   | 24                          |

\(^a\) Determined by the ICP-OES technique.

\(^b\) Determined by the XRD results according to Scherrer equation using FWHM of the (111) peak of CeO\(_2\).

\(^c\) Steam treated in 10% H\(_2\)O/Ar at 1023 K.

\(^d\) Total pore volume at a P/P\(_o\) ratio of 0.99.

\(^e\) Average pore size obtained from desorption curve.

Figure S1. XRD patterns for CeO\(_2\), CeO\(_2\)-S, Pt\(_1\)/CeO\(_2\), and Pt\(_1\)/CeO\(_2\)-S catalysts.
Figure S2. Pt (4f) XPS spectra for Pt₁/CeO₂ and Pt₁/CeO₂-S catalysts.

Figure S3. Raman spectra profiles of CeO₂, Pt₁/CeO₂, and Pt₁/CeO₂-S catalysts.
Figure S4. CO-DRIFTS of the Pt₁/CeO₂ (blue) and Pt₁/CeO₂-S (red) catalysts at 453 K. (Step1: CO/O₂/He was first introduced into the cell for 30 min, Step 2: the flow of CO was discontinued while O₂/He was kept flowing for 15 min.)
Figure S5. HCHO conversions over CeO$_2$, CeO$_2$-S, and Pt/CeO$_2$-R catalysts at various temperatures. Reaction condition: 400 ppm HCHO, 20 vol% O$_2$, and N$_2$ as balance gas, total flow rate: 100 mL·min$^{-1}$, WHSV: 100,000 mL·g$^{-1}$·h$^{-1}$. 
Table S2. Comparison of the performance of Pt/CeO$_2$-S with other single-atom catalysts and Pt-based catalysts reported in the literature in HCHO oxidation.

| Catalyst     | Metal loading [wt%] | Pretreatment | Condition                          | WHSV$^c$ [mL·g$_{cat}$⁻¹·h⁻¹] | $T_{90}$$^d$ [K] | $r$ [μmol·g$_{metal}$⁻¹·s⁻¹] | TOF [s⁻¹] | Ref.          |
|--------------|---------------------|--------------|------------------------------------|-------------------------------|----------------|-----------------------------|-----------|---------------|
| Pt/CeO$_2$-S | 0.61                | None         | 400 ppm HCHO, 20% O$_2$/N$_2$, 100 mL·min⁻¹ RH 50% | 100,000                      | 285           | 290                         | 0.056     | This work     |
| Ag/HMO$^a$-A | 9.7                 | None         | 400 ppm HCHO, 10% O$_2$/N$_2$, 100 mL·min⁻¹ | 30,000                       | 373           | -                           | 0.005     | (333 K)       |
| Ag/HMO$^a$-I | 9.8                 | None         | 400 ppm HCHO, 10% O$_2$/N$_2$, 100 mL·min⁻¹ | 30,000                       | 383           | -                           | 0.004     | (333 K)       |
| Na/HMO$^a$   | 4.5                 | None         | 140 ppm HCHO, 10% O$_2$/N$_2$, 100 mL·min⁻¹ | 120,000                      | 383           | -                           | -         |               |
| K/HMO$^a$    | 4.8                 | None         | 140 ppm HCHO, 10% O$_2$/N$_2$, 100 mL·min⁻¹ | 120,000                      | 383           | -                           | -         |               |
| Rb/HMO$^a$   | 10.4                | None         | 140 ppm HCHO, 10% O$_2$/N$_2$, 100 mL·min⁻¹ | 120,000                      | 383           | -                           | -         |               |
| Au/$\alpha$-MnO | 0.25              | None         | 500 ppm HCHO, Air, 66.6 mL·min⁻¹       | 60,000                       | 349           | -                           | -         |               |
| Au/CeO$_2$   | 0.40                | None         | 100 ppm HCHO, Air, 66.6 mL·min⁻¹, RH 50% | 60,000                       | 348           | -                           | 0.0028    |               |
| Na-Pt/TiO$_2$ | 1.0                 | Reduction    | 600 ppm HCHO, 20% O$_2$/N$_2$, 50 mL·min⁻¹ | 60,000                       | $T_{100}$$^a$ | 2                           | 98        |               |
| Mn-Pt/TiO$_2$ | 0.47                | Reduction    | 100 ppm HCHO, Air, 66.6 mL·min⁻¹, RH 50% | 60,000                       | $T_{100}$$^a$ | 2                           | 88        |               |
| Pt/TiO$_2$   | 0.01                | Reduction    | 160 ppm HCHO, 20% O$_2$/N$_2$, 50 mL·min⁻¹ | 30,000                       | > 353         | 2.5                         | 0.0005    |               |
| Pt-FeO$_x$/Al$_2$O$_3$ | 2.0          | None         | 300 ppm HCHO, 20% O$_2$/N$_2$, 100 mL·min⁻¹ RH 30% | 60,000                       | $T_{100}$$^a$ | 4.3                         | 0.0022    |               |
| Pt/AlOOH     | 0.3                 | None         | 139 ppm HCHO, 21% O$_2$/N$_2$, RH 25% | -                             | $T_{100}$$^a$ | 14.89                       | 0.012     |               |
| Pt/ZrO$_2$   | 0.88                | NaBH$_4$     | 100 ppm HCHO, 20% O$_2$/N$_2$, 100 mL·min⁻¹ | 60,000                       | -300          | 23.08                       | 0.0088    |               |
| Pt/TiO$_2$   | 1.0                 | Reduction    | 24 ppm HCHO, 21% O$_2$/N$_2$, 500 mL·min⁻¹ RH 54% | 120,000                      | $T_{100}$$^a$ | 0.66                        | 0.0004    |               |

$^a$ HMO: Hollandite manganese oxide

$^b$ RH: Relative humidity

$^c$ WHSV: Weight hourly space velocity

$^d$ $T_{90}$: The temperatures at 90% conversion of HCHO
Figure S6. Relative humidity effect on the activity of Pt₁/CeO₂ catalyst at 298 K. Reaction conditions: 400 ppm HCHO, 20 vol% O₂, and N₂ as balance gas, total flow rate: 100 mL·min⁻¹, WHSV: 222,000 mL·g⁻¹·h⁻¹.
Figure S7. SEM images for Pt/CeO$_2$-S catalysts fresh (a) and after the reaction test 60 h (b).
Figure S8. HCHO-TPSR profiles of Pt$_1$/CeO$_2$ and Pt$_1$/CeO$_2$-S catalysts.

Figure S9. HCHO-TPSR profiles of O$_2$ consumption over Pt$_1$/CeO$_2$ and Pt$_1$/CeO$_2$-S catalysts.
Table S3. IR bands after the adsorption of HCHO/N₂ on the different catalysts.

| Species       | Vibrational modes | IR bands wavenumber/cm⁻¹ |
|---------------|-------------------|--------------------------|
|               |                   | Pt₁/ CeO₂²⁸-³⁰ | Pt₁/ CeO₂⁻²⁻⁻S²⁸-³¹ | CeO₂⁻²⁻⁻S²⁸-³⁰ | CeO₂⁻²⁻⁻S²⁸-³⁰ | Al₂O₃²⁹-³²-³³ |
| DOMᵃ          | ν(OCO)            | 1101, 1126,    | 1168               | 1071           | 1081, 1119,   | 1084, 1124,   | -             |
|               |                   | 945            | 949                | 941            | 938            | 938            | -             |
| HCOOᵇ         | ν₅(OCO)           | 1575           | 1577               | 1562           | 1562           | 1574           | 1590          |
|               | δ(CH)             | 1373           | 1375               | 1375           | 1375           | 1373           | 1390          |
|               | ν₆(OCO)           | 1354           | 1356               | 1366           | 1357           | 1366           | 1372          |
| C-H (HCOO.DOM) | ν(OCO)⁺           | 2714, 2737,    | 2712, 2736,       | 2712, 2736,    | 2712, 2736,    | 2712, 2736,    | 2710, 2748,   |
|               | δ(CH)             | 2751, 2851,    | 2757, 2852,       | 2757, 2852,    | 2757, 2852,    | 2757, 2852,    | 2757, 2852,   |
|               | ν(CH)             | 2837, 2870,    | 2873, 2926,       | 2873, 2926,    | 2873, 2926,    | 2873, 2926,    | 2873, 2926,   |
|               |                   | 2898, 2942     | 2948               | 2948           | 2948           | 2948           | 2948          |
| OH (Ⅰ)ᵈ       | ν(OH)             | -              | -                  | -              | -              | -              | 3700          |
| OH (Ⅱ)ᵈ       | ν(OH)             | -              | 3660               | -              | -              | -              | 3738          |

ᵃ DOM = dioxymethylene
ᵇ HCOO = formate species
ᶜ OH (Ⅰ) = one-coordinated OH species
ᵈ OH (Ⅱ) = two-coordinated OH species³¹

Figure S10. The structures of intermediates of the key elementary steps in the oxidation of formaldehyde.
Figure S11. In situ HCHO-DRIFTS of the Pt/CeO$_2$ catalyst as a function of time in a flow of HCHO/N$_2$ at 303 K (a) and 453 K (c); and after exposure to a flow of HCHO/N$_2$ for 30 min (step 1), followed by O$_2$/N$_2$ degassing for 30 min (step 2) at 303 K (b) and 453 K (d).
Figure S12. In situ HCHO-DRIFTS of the Pt/CeO$_2$-S catalyst after exposure to a flow of HCHO/N$_2$ for 30 min (step 1), followed by N$_2$ degassing for 20 min (step 2), and followed by O$_2$/N$_2$ degassing for 30 min (step 3) at 303 K.
**Figure S13.** In situ HCHO-DRIFTS of the CeO$_2$ (a), CeO$_2$-S (b), Pt$_{1}$/CeO$_2$ (c), Al$_2$O$_3$ (d), and Pt$_{1}$/CeO$_2$-S (e) catalysts as a function of time in a flow of HCHO/N$_2$ at 303 K; (f) in situ HCHO-DRIFTS of the different catalysts after exposure to a flow of HCHO/N$_2$ for 30 min at 303 K.
**Supplementary Note 1.** The interactions of formaldehyde with the CeO$_2$ (111), CeO$_2$ (111)-2OH, Pt$_1$/CeO$_2$ (111), and Pt$_1$/CeO$_2$ (111)-2OH at the Pt$_1$ and Ce sites on the surfaces.

**Table S4.** Calculated adsorption energies ($E_{ad}$) of formaldehyde over CeO$_2$ (111), CeO$_2$ (111)-2OH, Pt$_1$/CeO$_2$ (111) and Pt$_1$/CeO$_2$ (111)-2OH surfaces.

| Model                      | Configurations and sites and its adsorption energies ($E_{ad}$) | CeO$_2$ (111) | CeO$_2$ (111)-2OH | Pt$_1$/CeO$_2$ (111) Ce Site | Pt$_1$/CeO$_2$ (111) Pt Site |
|----------------------------|-----------------------------------------------------------------|----------------|------------------|-------------------------------|-------------------------------|
|                            | Monodentate H$_2$CO at the Ce or Pt site                       | -57.0          | -38.6            | -5.9                          | -147.9                       |
|                            | Bidentate H$_2$CO at the Ce or Pt site                         | -113.7         | -78.6            | -30.0                         | -209.4                       |

![Diagram of CeO$_2$ (111) model](image1)

![Diagram of CeO$_2$ (111)-2OH model](image2)

![Diagram of Pt$_1$/CeO$_2$ (111) Ce Site model](image3)

![Diagram of Pt$_1$/CeO$_2$ (111) Pt Site model](image4)
We first calculated the interactions of formaldehyde with the CeO$_2$ (111), CeO$_2$ (111)-2OH, Pt$_1$/CeO$_2$ (111), and Pt$_1$/CeO$_2$ (111)-2OH surfaces using DFT. The calculated adsorption energies and vibrational frequencies of formaldehyde are given in Table S4. For each catalyst surface, both monodentate and bidentate configurations of formaldehyde at the Pt$_1$ and the Ce sites were considered. On the pristine CeO$_2$ (111) surface, the adsorption of formaldehyde in the bidentate configuration ($-113.7$ kJ·mol$^{-1}$) is stronger than it in the monodentate configuration ($-57.0$ kJ·mol$^{-1}$). With the two hydroxyl groups existing on the CeO$_2$ (111) surface, the interaction of formaldehyde with the CeO$_2$ (111) surface becomes weaker. The calculated adsorption energies of formaldehyde in the monodentate and bidentate configurations over the CeO$_2$ (111)-2OH surface are $-38.6$ and $-78.6$ kJ·mol$^{-1}$, respectively. This is consistent with the phenomenon observed in the HCHO-DRIFTS experiment, the DOM adsorption peak intensity on CeO$_2$ is stronger than on CeO$_2$-S (Figure S13 f). Interestingly,
the effect of surface hydroxyl groups on the formaldehyde adsorption at the Ce site over the Pt$_1$/CeO$_2$ (111) surface was found oppositely. In the presence of two surface hydroxyl groups, formaldehyde adsorption on the Pt$_1$/CeO$_2$ (111) surface becomes stronger. The calculated adsorption energies of formaldehyde in the monodentate and bidentate configurations at the Ce site over the Pt$_1$/CeO$_2$ (111)-2OH surface are -82.7 and -241.2 kJ·mol$^{-1}$, respectively, which are much stronger than the corresponding formaldehyde adsorption (-5.9 and -30.0 kJ·mol$^{-1}$) over the Pt$_1$/CeO$_2$ (111) surface. Compared with the CeO$_2$ (111)-2OH surface, the presence of the single-atom Pt$_1$ site enhances the formaldehyde adsorption at the Ce site. However, it is also found that the formaldehyde adsorption at the Ce site over the Pt$_1$/CeO$_2$ (111)-2OH surface in the bidentate configuration is too strong to react with the neighboring surface hydroxyl group leading to the formation of H$_2$COOH. This is confirmed by the DFT calculated activation barrier of ~250 kJ·mol$^{-1}$ for this elementary reaction step. Except for the Ce site, formaldehyde could also adsorb at the Pt$_1$ site over the Pt$_1$/CeO$_2$ (111) and Pt$_1$/CeO$_2$ (111)-2OH surfaces. As shown in Table S4, the calculated adsorption energies of formaldehyde in the monodentate and bidentate configurations at the Pt$_1$ site over the Pt$_1$/CeO$_2$ (111)-2OH surface are -46.6 and -189.2 kJ·mol$^{-1}$, respectively, which are weaker than the corresponding formaldehyde adsorption (-147.9 and -209.4 kJ·mol$^{-1}$) over the Pt$_1$/CeO$_2$ (111) surface. Our DFT calculations show that only the adsorbed formaldehyde at the Pt$_1$ site in the monodentate configuration with the proper adsorption energy is practically reactive for the oxidation reaction. The complete formaldehyde oxidation reaction at the Pt$_1$ site over the Pt$_1$/CeO$_2$ (111)-2OH surface is given in Figure 4. Since the catalyst is a single-
atom catalyst, the model is highly reliable. These results strongly support our analyses of the reaction intermediates, it can explain why in the *in situ* HCHO-DRIFTS spectra of the Pt$_1$/CeO$_2$-S catalyst (Figure 3), there are still unreacted DOM species on Pt$_1$/CeO$_2$-S. The formaldehyde adsorbed by Ce acts as a spectator and does not react with surface hydroxyl groups. Combining experiments confirmed that the steam treatment can activate the catalyst surface, weaken the HCHO adsorption energy on Pt, and can carry out subsequent reactions. This behavior is related to Sabatier’s principle, which states that for reaction intermediates, the best catalytic activity can be achieved on a catalytic surface with intermediate binding energy (or free energy of adsorption).

**Figure S14.** Proposed reaction mechanism for HCHO oxidation on Pt$_1$/CeO$_2$(111) surface and the inset shows the calculated energy profiles in kJ·mol$^{-1}$. 

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![Energy Profile Diagram](image-url)
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