The design strategy integrates three components into the catalyst: (1) a robust, high-surface-area support (for example, SiO₂, Al₂O₃), (2) metal oxide nanoglue clusters (for example, CeO₂, TiO₂) anchored stably to the support as isolated islands, and (3) single metal atoms (M₁) localized on these islands. The nanoglue selection criteria include their stability in dispersed form on the support, their much stronger affinity for the active metal atoms than the support, and their interactions with the active metal to enhance catalytic properties.

Silica is an irreducible, inexpensive and widely used catalyst support with high surface area, structural stability and commercial availability. Because metal atoms anchor to reducible metal oxides (for example, CeO₂, TiO₂) at defect sites, often through strong M₁–O bonds, and because CeO₂ has valuable redox and oxygen-storage properties, we chose CeO₂ nanoclusters as prototype nanoglues to localize Pt atoms for CO oxidation.

Previous metal stabilization strategies focused on incorporating additives in supports to enhance metal nanoparticle (NP)-support interactions, encapsulating metal NPs in oxides, and using large oxide NPs (greater than 5 nm) to stabilize metal ensembles and clusters (see discussion in Methods). To stabilize isolated metal atoms with high and practical M₁ loadings, the CeO₂ nanoislands must be ultrasmall (less than 2 nm), isolated and densely populated on high-surface-area supports, and M₁ should be selectively deposited onto them. Thus, CeO₂ nanoislands were synthesized by strong electrostatic adsorption of charged species from aqueous solution (Fig. 1). The point of zero charge of SiO₂ (278 m²g⁻¹) is 3–4 (refs. 18,19), so that in an alkaline solution its zeta potential is negative. Control of solution OH⁻ concentration and adsorption time yielded adsorption of [Ce(OH)₅]⁺ species on the SiO₂, leading after calcination to uniformly dispersed, isolated CeO₂ nanoislands (Fig. 2a and Extended Data Fig. 1a,b). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images showed uniform Ce species decorating the mesoporous SiO₂ (Extended Data Fig. 1c–e). Calcination at 600 °C produced isolated, stable crystalline CeO₂ nanoislands (approximately 12 wt% CeO₂) with
produced in situ from Ce\(^{3+}\) reacting with OH\(^{−}\) species in a weak alkaline solution. Positively charged Ce-containing species electrostatically adsorb temperature calcination, atomically dispersed Ce species self-assemble into surfaces are positively charged nanoclusters but not the SiO\(_2\) support (Fig. 1), because CeO\(_2\) (point of zero charge of approximately 8.1)\(^{24}\) is much more facile than that of CeO\(_2\) NPs. Harsh H\(_2\) reduction of CeO\(_2\) (Extended Data Fig. 2j), implying that reduction of CeO\(_2\) to Ce\(_{3+}\) sites in CeO\(_2\)/SiO\(_2\) supports Pt 1 nanoclusters to give Ce\(_{3+}\) species\(^{23}\) consistent with the XANES and EXAFS results.

X-ray photoelectron spectra (XPS) (Fig. 2d and Extended Data Fig. 2i) show 28.7%, 10.9% and 8.4% Ce\(_{3+}\) species in CeO\(_2\)/SiO\(_2\), CeO\(_2\) and CeO\(_2\) NPs/SiO\(_2\), respectively\(^{21}\). The greater density of Ce\(_{3+}\) sites in CeO\(_2\)/ SiO\(_2\) implies more anchoring sites on CeO\(_2\) nanoclusters for metal atoms\(^{22}\). The locations of isolated metal atoms on supports determine their catalytic properties\(^{4}\). Individual Pt atoms on well crystallized CeO\(_2\) NPs have been observed by HAADF-STEM\(^{15}\), but unambiguous identification of Pt atoms on ultrasmall CeO\(_2\) nanoclusters is beyond the capability of this technique (Extended Data Fig. 4a–c and Methods). However, an extensive HAADF-STEM investigation of Pt atoms and clusters on the CeO\(_2\)/SiO\(_2\) can firmly identify Pt clusters with sizes greater than 0.4 nm if present on the samples (Extended Data Fig. 4d). Analysis of numerous atomic-resolution images of the 0.4 wt% Pt/CeO\(_2\)/SiO\(_2\) catalyst gave no evidence of Pt atoms or clusters on the SiO\(_2\) surfaces, confirming that the deposited Pt species were restricted to CeO\(_2\) islands—either as single atoms or clusters with sizes less than 0.4 nm.

X-ray absorption spectra provided further insights into the nature of the Pt species. Pt\(_{L_{3}}\)-edge X-ray absorption near-edge structure (XANES) data (Fig. 3a) characterizing the calcined 0.4 wt% Pt/CeO\(_2\)/SiO\(_2\) show that the Pt was cationic, with an oxidation state close to that in bulk PtO\(_2\) (ref. \(^{26}\)). Extended X-ray absorption fine structure (EXAFS) spectra (Fig. 3b) indicate atomically dispersed Pt, with no evidence of a Pt–Pt scattering path in the spectra of the 0.4 wt% Pt/CeO\(_2\)/SiO\(_2\) (Fig. 3b and Extended Data Fig. 4e–j). A Pt–O shell indicating Pt–Ce bonding was found with a coordination number of 4.5 ± 0.5 and a bonding distance of 1.97 ± 0.02 Å (error bounds defined in Extended Data Fig. 4), consistent with EXAFS data for site-isolated platinum on cerium dioxide or iron oxide\(^{25}\). Diffuse-reflectance infrared Fourier-transform spectra (DRIFTS) of the 0.4 wt% Pt/CeO\(_2\)/SiO\(_2\), after CO adsorption, show a sharp single peak near 2,103 cm\(^{-1}\) with a full-width at half-maximum of 12.8 cm\(^{-1}\) (Fig. 3c), assigned to CO adsorbed on isolated cationic Pt\(^{25}\), consistent with the XANES and EXAFS results.

In summary, the as-synthesized CeO\(_2\) nanoclusters are ultrasmall, isolated on the SiO\(_2\) support, and characterized by a high number density of defect sites, making them well suited as hosts for strongly bonded and isolated Pt atoms\(^{22}\).

Strong electrostatic adsorption deposited Pt atoms on the CeO\(_2\) nanoclusters but not the SiO\(_2\) support (Fig. 1), because CeO\(_2\) (point of zero charge of approximately 8.1)\(^{24}\) surfaces are positively charged when in contact with acidic Pt precursor solutions of pH 3–5, so that PtCl\(_2\)\(^{−}\) is attracted to the CeO\(_2\) nanoclusters (Extended Data Fig. 3a). To synthesize CeO\(_2\)-supported Pt single-atom catalysts, the Pt loading was controlled at less than or equal to 0.4 wt% (with respect to the CeO\(_2\)) such that, on average, each CeO\(_2\) nanocluster contained less than one Pt atom (Extended Data Fig. 3b, c). High Pt loadings, which are industrially desirable (for example, up to 1 wt% Pt), can be realized by increasing the SiO\(_2\) surface area and/or the number density of isolated CeO\(_2\) nanoclusters (Extended Data Fig. 3d–f).

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To further understand the stability of the atomically dispersed Pt, the behaviour of Pt atoms on other supports under various conditions was compared. The data include those obtained for Pt atoms on SiO2 and on CeO2. Under reducing or oxidizing environments at temperatures greater than 300 °C, Pt atoms on SiO2 sintered considerably (Extended Data Fig. 5a–f), demonstrating weak Pt–SiO2 interactions. Single Pt atoms on CeO2 NPs did not sinter during calcination, even at high temperatures (Extended Data Fig. 5g–h). Exposure to H2 at 300 °C for 1 h, however, caused breaking of Pt–O bonds, migration of Pt atoms on CeO2 NPs and sintering of Pt atoms to form clusters and NPs (Extended Data Fig. 5i–k). After similar treatment, the Pt NPs formed on CeO2 were smaller than those formed on SiO2 (Extended Data Fig. 5). Sintering by Pt–CeO2 interactions is stronger than the Pt–SiO2 interaction during the H2-reduction treatment. Investigations of Pt sandwiched between hetero-structured CeO2–SiO2 core–shell model systems confirmed the stronger interaction of Pt atoms with CeO2 than with SiO2, excluding the suppression of Pt diffusion from CeO2 onto SiO2 (Extended Data Fig. 6 and Methods).

The stability of the CeO2-supported Pt single-atom catalyst (Pt/CeO2) was investigated under reducing conditions. CeO2-NP-supported Pt atoms became mobile at temperatures greater than 300 °C for 1 h in H2, but Pt atoms, confined to the isolated CeO2 islands, did not sinter, even after H2 reduction at 300 °C for 10 h, as shown by DRIFTS and HAADF-STEM data (Fig. 3d and Extended Data Fig. 7a). The minimal difference in the CO absorption bands characterizing Pt atoms in the reduced versus the as-synthesized catalysts is evidence that the CO probe molecules used in the DRIFTS experiments reduced the Pt atoms in the as-synthesized Pt/CeO2/SiO2, as expected. To further probe the stability of Pt atoms localized on the CeO2 islands, samples were exposed to H2 at temperatures of 400–600 °C. Even under these harsh reducing conditions, the Pt remained as isolated single atoms (Extended Data Fig. 7b–d). The infrared absorption bands characterizing CO on Pt atoms were shifted after reduction in H2 at temperatures greater than 500 °C, suggesting modifications of the Pt–CeO2 interactions, which were corroborated by density functional theory calculations (Extended Data Fig. 7e). Because the DRIFTS experiments were conducted under oxygen-free environments, formation of Pt clusters was excluded (Extended Data Fig. 7f–h,k–p and Methods section 'Extended results and discussions'). Both Ce XPS and Pt XAS data show that formation of Pt clusters or Pt–Ce alloy species under the reduction conditions did not occur (Extended Data Figs. 7i, 9i–p). Thus, notwithstanding changes in the catalysts, the Pt remained site-isolated, with the changes restricted to the host CeO2 islands. By contrast, decreasing Pt atom number density on CeO2 supports (with loadings lower than that of the 0.4 wt% Pt/CeO2) did not prevent Pt atoms from forming clusters and NPs after reduction in H2 at 400 °C (Extended Data Fig. 7j).

To confirm that during H2 reduction the Pt confinement on SiO2-supported CeO2 islands also applies to SiO2-supported CeO2 NPs, a sample containing Pt atoms dispersed on SiO2-supported 8-nm CeO2 NPs (0.4 wt% Pt/CeO2 NPs/SiO2) was exposed to H2 at 300 °C for 1 h. The data (Extended Data Fig. 8a–c) show that the Pt atoms did not migrate onto SiO2, but they did sinter to form small Pt clusters, because larger CeO2 NPs on average, contained more than one Pt atom, further confirming the conclusion that under reduction conditions Pt atoms sinter on CeO2 surfaces. The CO DRIFTS data (Extended Data Fig. 8d–f) correspondingly show evidence of CO adsorbed on Pt clusters and NPs. In sharp contrast to the narrow DRIFTS peak characterizing the reduced
0.4 wt% Pt/CeO₂/SiO₂ (Fig. 3d), the broad overlapping DRIFTS peaks characterizing the reduced 0.4 wt% Pt/CeO₂ NPs/SiO₂ demonstrate the presence of Pt species with a wide range of nuclearities and/or oxidation states. Both the ultrasmall size and isolation of the CeO₂ nanoglue islands by SiO₂ are critical to confining Pt species to prevent sintering.

Further experiments were conducted with high loadings of Pt (4 wt%) on SiO₂-supported CeO₂ nanoislands to investigate synthesis and confinement of uniform Pt clusters on them. After reduction in H₂ at 300 °C for 3 h, Pt clusters were detected by CO DRIFTS (Extended Data Fig. 8g). HAADF-STEM images show uniform Pt clusters (an average size of approximately 0.9 nm) attached to the isolated CeO₂ islands when the reduction temperature increased to 400 °C (Extended Data Fig. 8h). After reduction at 500 °C for 12 h, the CeO₂ islands became amorphous, but the Pt clusters nonetheless retained their sizes and were still attached to the islands (Extended Data Fig. 8i–j). The absence of Pt NPs with sizes greater than 1 nm in these severely reduced catalysts with high Pt loading highlights the effectiveness of the CeO₂ nanoglue strategy for stable localization of Pt species (from isolated metal atoms to subnanometre clusters) and for preventing the formation of larger Pt NPs, thus expanding their potential for practical applications.

We note that the active phase in many catalysts is pre-formed by reduction, and that H₂ treatment at temperatures greater than 200 °C usually causes sintering of atomically dispersed noble metals. In addition to limiting applications, this restructuring also hinders fundamental investigations of single-atom catalyst performance and structure–property relationships. The robustness of the 0.4 wt% Pt/CeO₂/SiO₂ under both oxidizing and reducing environments offers new opportunities in this regard.

Ceria-supported single Pt atoms were reported to be less active for CO oxidation than CeO₂-supported Pt clusters, and our data verify this pattern (Extended Data Fig. 9a–c). Because our CeO₂ nanoglue islands-confined Pt single-atom catalysts remain stable after reductive activation, we could explore CO oxidation performances and show (Fig. 4) that the temperature for 50% CO conversion is 133 °C for the H₂-activated Pt/CeO₂/SiO₂ and 226 °C for the non-activated Pt/CeO₂/SiO₂. This result demonstrates that H₂ activation increases the CO oxidation rate by two orders of magnitude and decreases the apparent activation energy (Extended Data Fig. 9q). The XANES and EXAFS data indicate that H₂ reduction removes oxygen ligands, reduces the coordination number of the first Pt–O shell from 4.5 ± 0.5 to 3.2 ± 0.3 and reduces Pt⁴⁺ to Pt⁰ (refs. 2,27,38) without sintering the isolated Pt atoms (Extended Data Fig. 9i–p). Comparison against catalysts prepared on other CeO₂ supports or by impregnation of CeO₂/SiO₂ and SiO₂ with Pt salt solutions shows that the H₂-activated 0.4 wt% Pt/CeO₂/SiO₂ is much more stable and active for CO oxidation (Extended Data Fig. 9d–h, r–t).

These observations illustrate the value of the CeO₂ nanoglue design strategy, implemented with our scalable strong electrostatic adsorption process for dispersing CeO₂ (ν = 1.86) nanoglue islands with an average dimension of 2 nm or smaller onto a robust, high-surface-area SiO₂ support and then selectively localizing Pt atoms on these islands. The CeO₂ nanoglue islands incorporate abundant Ce³⁺ that strongly anchors Pt atoms and small clusters under either O₂ or H₂ environments, even at elevated temperatures. Challenges for practical applications remain, however, such as the partial and reversible oxidation of the Pt₃ atoms and associated lowering of catalytic activity seen at higher temperatures (for example, 300 °C) under oxidizing conditions (Methods section ‘Extended results and discussions’ and Extended Data Fig. 9i–p). But with our strategy for confining metal atoms by functional nanoglues applicable to metals other than Pt (including Pd and Rh; see Extended Data Fig. 10) and in principle able to produce a wide range of robust...
The Carbon Dioxide Oxidation Reaction (CO oxidation) is a key reaction in catalysis, with applications ranging from industrial processes to automotive exhaust systems. The goal of this research is to develop and evaluate single-atom catalysts for CO oxidation. These catalysts are expected to offer improved performance and selectivity compared to traditional heterogeneous catalysts.

**Article**

**Fig. 4** Evaluation of low-temperature CO oxidation activity and stability. CO conversion during a temperature ramp at a rate of 1 °C min⁻¹, catalysed by the as-synthesized and H₂-activated 0.4 wt% Pt/CeO₂/SiO₂ single-atom catalyst (CO oxidation on the CeO₂/SiO₂ control catalyst is also shown). Activation of the 0.4 wt% Pt/CeO₂/SiO₂ by H₂ reduction at 300 °C for 1 h greatly increased its activity for CO oxidation. The cycling test was conducted with a temperature ramp to 200 °C.

**Online content**

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Methods

Preparation of nanoglues and support materials

**SiO$_2$-supported CeO$_2$.** In general, OH ions in alkaline solutions act as strong coordination agents for Ce$^{3+}$ ions to form cationic complexes, but excessive OH results in precipitation of Ce(OH)$_2$ (solubility product constant $K_{sp} = 1.6 \times 10^{-32}$). To avoid the formation of Ce(OH)$_2$, precipitates from the solution phase, the concentration of the OH was carefully controlled to maintain a relatively stable aqueous solution containing soluble [Ce(OH)$_{2+}$] and [Ce(OH)$_{3+}$] complexes. Dissolved O$_2$ in the aqueous solution slowly oxidizes Ce$^{2+}$ into Ce$^{4+}$, the concentration of which grows with time to reach the precipitation limit of Ce(OH)$_4$ ($K_{sp} = 2 \times 10^{-20}$). Under well-controlled synthesis conditions, the strong electrostatic adsorption (SEA) of [Ce(OH)$_{2+}$] and [Ce(OH)$_{3+}$] occurs within minutes, a much shorter time than that needed for precipitating Ce(OH)$_2$. Such a time difference in the dynamic adsorption and precipitation processes allows efficient, facile production of uniformly decorated high-surface-area SiO$_2$ with Ce species via the SEA process.

In a typical procedure for synthesizing 12 wt% CeO$_2$ nanoglue islands on SiO$_2$, 360 mg of fumed SiO$_2$ powder (Alfa Aesar, total Brunauer–Emmett–Teller (BET) surface area 278 m$^2$·g$^{-1}$) was mixed with 100 ml of deionized (DI) water, and the resultant aqueous solution was sonicated to produce a uniform mixture. Under vigorous stirring, 0.4 mmol of Ce(NO$_3$)$_3$·6H$_2$O was dissolved in the above solution, and 0.8 ml of NH$_3$·H$_2$O (2 M) was quickly injected into the solution with further stirring for 3 min prior to vacuum filtration. The final solution pH was about 8.7. The resultant precipitates were removed for air drying overnight at room temperature. The dried powders were ground to smaller particles and then calcined in a muffle furnace at 500 or 600 °C (with a temperature ramp of 5 °C·min$^{-1}$) for 12 h. This facile synthesis protocol was easily scaled up to routinely produce 10 times more of the final product.

**SiO$_2$-supported CeO$_2$ NPs (IMP) by impregnation.** The SiO$_2$-supported CeO$_2$ NPs were prepared using the same precursors as described above. The pure volume of the SiO$_2$ was determined to be ~2.1 ml·g$^{-1}$. Therefore, 0.8 mmol of Ce(NO$_3$)$_3$·6H$_2$O was dissolved in 2.1 ml of DI water. As the sample was stirred, 2.1 ml of precursor solution was slowly added to 1 g of SiO$_2$ powder to ensure complete wetting of the support by the Ce-containing solution. The final mixture was air-dried overnight prior to oven drying at 60 °C for 12 h. The dried powders were ground and then calcined at 600 °C (the temperature was ramped at a rate of 5 °C·min$^{-1}$) in a muffle furnace.

**Pure CeO$_2$ powders.** To synthesize pure CeO$_2$, 2 g of Ce(NO$_3$)$_3$·6H$_2$O was dissolved in 100 ml of DI water. With the sample vigorously stirred, 2 ml of 15% ammonia solution was slowly injected into the above solution to form a suspension. The product was continuously stirred overnight in open air. Vacuum filtration was used to repeatedly wash the precipitates with DI water. The final light-yellow powders were ground and then calcined at 500 °C for 4 h.

**Selective deposition of Pt atoms and preparation of Pt catalysts Pt/CoO/SiO$_2$, Pt/CoO NPs/SiO$_2$, and Pt/CoO$_2$.** In a typical synthesis protocol, 300 mg of support (500 °C-calcined CeO$_2$/SiO$_2$ CeO$_2$ NPs/SiO$_2$) was immersed in 70 ml of DI water and sonicated. The pH of the solution was adjusted to ~3 by addition of HCl. Simultaneously, 3.0 μmol of H$_2$PtCl$_6$·6H$_2$O was diluted in 50 ml of aqueous solution (pH of ~3 by addition of HCl). With the sample vigorously stirred and within 5 h, the Pt precursor solution was slowly pumped to the aqueous solution containing the corresponding support powders. After being stirred for another 5 h, the final mixture was filtered via vacuum filtration to obtain the precipitates, which were washed several times with DI water to remove residual Pt ions and other species. After the final catalyst precursor powders were dried in air, they were calcined at 600 °C for 12 h to obtain the as-synthesized catalysts. 0.3 wt% Pt/CeO$_2$ catalyst was synthesized by using 30 μmol of H$_2$PtCl$_6$·6H$_2$O and 300 mg of CeO$_2$ powder. The high Pt loading (4 wt% Pt with respect to CeO$_2$) Pt/CoO/SiO$_2$ catalyst was synthesized by using 61 μmol of H$_2$PtCl$_6$ in the above process. After calcination, 4 wt% Pt/CoO/SiO$_2$ catalyst was reduced in H$_2$ at 400 °C to produce Pt clusters. The Pt/CoO/SiO$_2$ samples were produced by mildly calcining the CeO$_2$/SiO$_2$ supported Pt cluster catalysts at 100 °C. For Pd/CoO/SiO$_2$ and Rh/CoO/SiO$_2$, 14 μmol of PdCl$_2$ and 5.8 μmol of RhCl$_3$ were used in the synthesis process, respectively.

**Pt/CoO$_2$/SiO$_2$ (IMP) by impregnation.** The pore volume of the as-synthesized CeO$_2$/SiO$_2$ was determined to be 1.8 ml·g$^{-1}$. With stirring, 0.54 ml of aqueous solution containing H$_2$PtCl$_6$ precursor salt was slowly added to 300 mg of CeO$_2$/SiO$_2$ powder to ensure complete wetting of the support surfaces by the precursor salt solution. The mixture was then dried at 60 °C for 12 h in an oven. The resultant 0.4 wt% Pt/CoO$_2$/SiO$_2$ (IMP) powders were ground and then calcined at 300 °C for 3 h in a muffle furnace. The high-loading Pt/CoO$_2$/SiO$_2$ (IMP) powders were directly reduced in H$_2$ at 300 °C for STEM examination.

**Pt/CoO$_2$ (SEA).** In a typical synthesis process, Pt(NH$_3$)$_4$Cl$_2$ was used as precursor to adsorb Pt(NH$_3$)$_4$Cl$_2$ onto negatively charged SiO$_2$ surfaces in the presence of alkaline solution. Commercial SiO$_2$ powders (180 mg) were dispersed in 50 ml of DI water and the solution was kept alkaline by adding 0.2 ml of 2-M ammonium solution. Then 1 ml of aqueous solution containing 3.2 mg of Pt(NH$_3$)$_4$Cl$_2$ was injected into the SiO$_2$ suspension that was vigorously stirred for 3 h. The as-prepared Pt/CoO$_2$ catalysts, without calcination, contained both Pt single atoms and Pt clusters (Extended Data Fig. 5a,b). The Pt loading on commercial SiO$_2$ powders was determined to be 0.5 wt% by inductively coupled plasma mass spectrometry (ICP-MS) measurements.

**Preparation of core–shell samples SiO$_2$ spheres.** SiO$_2$ spheres were produced by the Stöber method: 30 ml of DI water, 150 ml of ethanol, and 18 ml of ammonia (~25%–28%) were mixed in a flask. Then 12 ml of tetraethyl orthosilicate (TEOS) was added to the solution, which was heated to 58 °C and stirred for 2 h. Then the solvent was removed by evaporation at 100 °C, and the resultant powder was calcined for 2 h at 500 °C.

**Pt/CoO$_2$ spheres.** 500 mg of SiO$_2$ spheres were dispersed in 100 ml of DI water while 1 ml of 2-M ammonia solution was added. Then 50 ml of solution containing 20 mg of Pt(NH$_3$)$_4$NO$_3$ was pumped into the suspension within 1 h. After stirring for another half an hour, the mixture was filtered. The Pt loading on SiO$_2$ spheres was determined to be 0.2 wt% by ICP measurement.

**Porous SiO$_2$ shell.** The Pt/CoO$_2$@SiO$_2$ (Extended Data Fig. 6) was prepared by a modified Stöber method: 500 mg of the as-prepared Pt/CoO$_2$ was dispersed in 300 ml of ethanol by ultrasonication. Then 2.5 ml of TEOS was added, and the solution was stirred for 4 h. Then 5 ml of ammonia (~25%–28%) and 20 ml of DI water were added to the slurry, which was stirred for another 4 h. Finally, the product was washed with ethanol and dried at 100 °C. For Pt/CoO$_2$@SiO$_2$, 150 mg of 0.2 wt% Pt/SiO$_2$ spheres and 1.5 ml of TEOS were used in the synthesis.

**Cu nanoparticles.** A specified amount of Pt/CoO$_2$@SiO$_2$ or Pt/CoO$_2$@SiO$_2$ was added to 25 ml of DI water. The pH value of the solution was...
kept at 9 by adding Na\(\text{CO}_3\) solution. Then Cu(\(\text{NO}_3\))\(\text{aq}\) solution was added dropwise to the above suspension. The target loading of Cu was 2 wt% in each sample. After ageing for 1 h, the products were filtered and dried at 70 °C overnight. The final products, denoted as Cu\((\text{Pt}/\text{CeO}_2)@\text{SiO}_2\) or Cu\((\text{Pt}/\text{SiO}_2)@\text{SiO}_2\), were in situ reduced in \(20 \text{ ml min}^{-1}\) of \(10 \% \text{H}_2/\text{Ar}\) at 400 °C for 3 h in preparation for DRIFTS and HAADF-STEM characterizations.

**Catalytic testing of the prepared catalysts**

The CO oxidation reaction was conducted in a fixed-bed, plug-flow reactor at atmospheric pressure. Typically, 30 mg of 0.4 wt\% Pt/\(\text{CeO}_2/\text{SiO}_2\) catalyst was packed between two quartz wool plugs inside a quartz tube (inner diameter of 4 mm) for each test. Prior to catalytic reaction, the \(\text{H}_2\)-activated catalysts were pretreated with \(10 \text{ ml min}^{-1}\) of \(5 \% \text{H}_2/\text{He}\) at 300 °C for 1 h. After cooling to room temperature, the reaction temperature was ramped up at a rate of 1 °C min\(^{-1}\). The feed gas, containing 1 vol.\% CO and 4 vol.\% O\(_2\) balanced in He, passed through the catalyst bed at a flow rate of 10.0 ml min\(^{-1}\) (corresponding to a weight hourly space velocity (WHSV) of 20,000 ml (g\(_\text{cat}\))\(^{-1}\)). The outlet gas composition was measured with an online gas chromatograph (7890A, Agilent) equipped with a thermal conductivity detector (TCD).

The specific reaction rate and apparent activation energy were measured as the catalyst was exposed to the gas composition stated above. During the kinetics experiments, the CO conversion was controlled to be less than 15\% by adjustment of the feed flow rate or catalyst mass.

**Characterization instruments**

HAADF-STEM images were collected with a JEOL ARM-200F microscope equipped with a probe-forming aberration corrector operated at 200 kV to achieve a nominal image resolution of 0.08 nm. The back-scattered electron images were obtained on a JEOL JXA-8530F electron microprobe. Transmission electron microscopy (TEM) images were taken on a Hitachi HT7700 transmission electron microscope operating at an acceleration voltage of 100 kV. All reported electron microscopy images were raw images. X-ray photoelectron spectroscopy (XPS) analysis was carried out with an ESCALAB 250 X-ray photoelectron spectrometer with Al Ka as the excitation source. The loadings of Pt and Ce were determined with a ThermoFinnigan ICAP Q quadrupole ICP-MS with CCT (Collison Cell Technology), and Pt and Rh were determined with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Atomicscan Advantage, Thermo Jarrell Ash). Samples were run in KED (kinetic energy discrimination) mode, with in-line aspiration of a multi-element internal standard. The BET surface areas were measured by the nitrogen adsorption-desorption method on a surface area and porosity analyser (Quantachrome NOVA 4000e apparatus). Before measurements, the samples were degassed at 180 °C for 6 h under vacuum. The X-ray diffraction (XRD) patterns were recorded on a Rigaku TR III theta-theta rotating anode X-ray diffractometer using Cu Ka radiation (40 kV and 200 mA) with a step size of 0.02°. Raman spectra were collected with a JYLABRAM-HR spectrometer equipped with an integral microscope. DRIFTS experiments were carried out with samples in a diffuse reflectance reaction chamber (Harrick Scientific) equipped with ZnSe windows, mounted in a Praey Mantis diffuse reflection accessory (Harrick Scientific), and coupled to a Thermo Scientific Nicolet IS50 FTIR spectrometer with a liquid-nitrogen-cooled HgCdTe (MCT-A) detector. Hydrogen temperature-programmed reduction (H\(_2\)-TPR) measurements were conducted on a Micromeritics Autochem II 2920 with a thermal conductivity detector (TCD). X-ray absorption spectroscopy (XAS) experiments were carried out at beamlines 4-1 and 9-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) and at the TPS 44A beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The storage ring energies and currents were 3 GeV and 500 mA, respectively. Photon energy selection was achieved with double-crystal Si(220) monochromators at SSRL. A Si (111) channel-cut crystal was used as the quick-scanning monochromator at NSRRC.

**Characterization methods**

ICP. ICP-MS measurements were performed to quantify the loadings (loading levels) of metal species on \(\text{SiO}_2\). For a particular weight of Pt/\(\text{CeO}_2/\text{SiO}_2\) catalyst, Pt and Ce atoms were dissolved in freshly prepared aqua regia solution. Then the insoluble SiO\(_2\) was washed and centrifuged three times with all the solution in a volumetric flask. The final concentrations of Pt and Ce were diluted to meet the calibration standards. The loading of CeO\(_2\) was calculated in terms of CeO\(_2\) units. To verify that Pt atoms were selectively adsorbed by CeO\(_2\) nanogluces, the CeO\(_2\)/\(\text{SiO}_2\) support was replaced by pure SiO\(_2\) in a typical synthesis procedure. Because the loading of Pt on the pure SiO\(_2\) was expected to be much lower than that on the CeO\(_2\)/\(\text{SiO}_2\), larger amount of samples of Pt/SiO\(_2\) were used for the ICP-MS measurement to assure that the concentration of Pt was in the range of the reference standards. The results are summarized in Extended Data Fig. 3a.

**XPS.** For XPS investigations of the high-temperature reduced 0.4 wt\% Pt/\(\text{CeO}_2/\text{SiO}_2\), as-synthesized powder samples were reduced in 10\% \(\text{H}_2/\text{Ar}\) at 300 °C for 1 h. The reactor vessel was then tightly sealed and transferred to a glove box. The catalyst powders were then transferred into the XPS sample holder within the glove box. The XPS sample holder was tightly sealed in the glove box to protect the catalysts from oxidation by air during transfer. After the sample preparation procedure, the XPS sample holder was placed in a vacuum transfer chamber and transferred to the XPS apparatus without sample exposure to air.

**HAADF imaging of CeO\(_2\)/\(\text{SiO}_2\) and Pt/\(\text{CeO}_2/\text{SiO}_2\).** The mesoporous SiO\(_2\) support has interconnected 3D pores and underwent considerable charging under electron beam illumination, making imaging of such materials challenging. In the HAADF images shown in Extended Data Fig. 1d,e, the adjacent regions could not be simultaneously imaged because atomic-resolution HAADF imaging is sensitive to height modulations of the mesoporous SiO\(_2\) support: CeO\(_2\) clusters located at different sample heights would not be clearly revealed in the same HAADF image. Through-focus images were needed to observe clear features of the adjacent regions. Prior to calcination, the conforming coating of Ce species on the mesoporous SiO\(_2\) support made the SiO\(_2\) powders less susceptible to electron beam charging effects. After high-temperature calcination, however, the mesoporous SiO\(_2\) became charged under the influence of the electron beam, owing to the fact that the crystalline CeO\(_2\) nanoclusters were isolated from each other. Because of the sample charging and electron-beam-induced effects, crystalline CeO\(_2\) nanoclusters would usually be transformed quickly into amorphous species. For this reason, a low-dose STEM method was used to acquire STEM images of the sensitive CeO\(_2\) nanoclusters. In some cases, a thin layer (~2 nm) of continuous carbon coating of the CeO\(_2)/\text{SiO}_2\) or Pt/CeO\(_2)/\text{SiO}_2\) powders was used to reduce the sample charging and other electron-beam-induced effects.

The HAADF imaging is sensitive to the atomic number of the atoms in the sample and the sample thickness. For Pt atoms supported on well faceted CeO\(_2\), it is possible to distinguish a Pt atom from columns of Ce atoms, because the image contrast can be considered to be proportional to

\[
\frac{1}{N_{\text{Ce}}} \left( \frac{Z_{\text{Pt}}}{Z_{\text{Ce}}} \right)^2 = \frac{1.8}{N_{\text{Ce}}}
\]

where \(N_{\text{Ce}}\) represents the number of Ce atoms along the electron beam direction. Therefore, even if a single Pt atom is located on top of a 30-Ce-atom-thick CeO\(_2\) column, the image contrast would still be greater than 5\% and reliably detectable in digital HAADF images. However, in this special case, even when a thin layer of carbon coating...
was used to reduce electron-beam-induced effects and sample charging, low-dose STEM imaging conditions and fast image acquisition were needed to preserve the crystallinity of the electron-beam-sensitive CeO\(_2\) nanoclusters. Such a low-dose approach greatly reduced the visibility of single Pt atoms. Furthermore, because the CeO\(_2\) nanoclusters were extremely small and their surfaces were characterized by many steps or other types of surface defects, it became extremely difficult to reliably distinguish the contrast between a supported Pt atom from that of a supported Ce atom (or two Ce atoms). Depending on the specific location of the Pt atom, distinguishing the image contrast of a Pt atom from that of two or more Ce atoms is an impossible task with the currently available technology. All these complications made it impossible to unambiguously identify the presence of Pt single atoms on the CeO\(_2\) clusters by the STEM-HAADF imaging technique. Nor did EDXS (energy-dispersive X-ray spectroscopy) and EELS (electron energy-loss spectroscopy) techniques provide useful results, primarily owing to the electron-beam-induced effects.

**CO DRIFTS.** In a typical experiment, the infrared cell was partly filled with inert KBr powder, followed by catalyst packed onto the KBr support. All the gases that flowed through the cell flowed downward through the catalyst bed. For fresh catalysts, a pretreatment at 300 °C with 10% O\(_2\)/Ar was conducted for 30 min. The flowing gas was then switched to He, and the background spectra were recorded at 50 °C characterizing the as-synthesized 0.4 wt% Pt/CeO\(_2\)/SiO\(_2\) catalyst. CO adsorption was conducted by flowing 15 ml min\(^{-1}\) of 10% CO/Ar and 30 ml min\(^{-1}\) of He for 20 min. The CO desorption spectra were recorded following a He purge at a flow rate of 30 ml min\(^{-1}\) to remove gas-phase CO from the cell. When the sample to be characterized was PtO\(_x\)/CeO\(_2\)/SiO\(_2\), no further oxidative pretreatment was carried out. The CO adsorption experiment was conducted at 100 °C by flowing 10 ml min\(^{-1}\) of 10% CO/Ar, 10 ml min\(^{-1}\) of 10% O\(_2\)/Ar, and 20 ml min\(^{-1}\) of He. Then the O\(_2\) flow was stopped to allow investigation of the CO adsorption behaviour on PtO\(_x\) clusters.

The in situ H\(_2\) reduction treatments were conducted with the sample in the cell—fresh catalyst samples were loaded. The catalysts were heated to the target temperatures in flowing 10% O\(_2\)/Ar, and then the gas was switched to 10% H\(_2\)/Ar. During the reduction treatment at 300–600 °C, 20 ml min\(^{-1}\) of 10% H\(_2\)/Ar flowed through the cell for various periods. The cell was then cooled down to the desired temperatures with the sample in the H\(_2\) environment. The flowing gas was then switched to He and backgrounds of the Pt-containing, Pd-containing, and Rh-containing catalysts were recorded at 100 °C, 25 °C and 180 °C, respectively. CO adsorption was investigated as the sample was exposed to 10% CO/Ar flowing at 15 ml min\(^{-1}\) and He flowing at 30 ml min\(^{-1}\) for 20 min. The CO desorption spectra were recorded following a He purge at a flow rate of 30 ml min\(^{-1}\) to remove gas-phase CO from the cell. The measurement process was conducted in such a way to avoid oxidation of Pt species.

**Simulation of CO IR spectra.** To predict possible adsorption configurations and vibrational frequencies of CO on harshly reduced (above 500 °C) Pt/CeO\(_2\)/SiO\(_2\), spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code\(^{44}\). The projector augmented-wave method (PAW) and the Perdew–Burke–Ernzerhof (PBE) functional were used to deal with the electron–ion interactions and exchange correlation, respectively\(^{45,46}\). DFT+U correction (U\(_{\text{eff}}\) = 5 eV for Ce) was considered to treat the strongly correlated 4f electron\(^{22}\). The van der Waals interactions were described using the empirical DFT+D3 method to improve the accuracy of representation of CO adsorption\(^{28}\). The gamma point was set for the total energy calculations together with a cut-off energy of 400 eV for the plane-wave basis. A vacuum space larger than 10 Å was added in each direction to avoid the interactions between each cluster model. During the structure optimization and frequency analysis, all the atoms were relaxed until the force on each ion was less than 0.02 eVÅ\(^{-1}\).

To obtain plausible structures of harshly reduced Pt/CeO\(_2\)/SiO\(_2\), ab initio molecular dynamics (AIMD) simulations were performed. First, a Pt-doped model cluster (Pt(Ce\(_{15}\)O\(_{30}\)) with local coordination environment consistent with the EXAFS results of the as-synthesized Pt/CeO\(_2\) (crystalline) was established. Then the canonical ensemble (NVT) with the Nosé–Hoover thermostat was implemented in the AIMD simulations for a period of 2 ps at 873 K to give relatively stable structures. The generated configurations were further optimized using standard DFT calculations. The reduced Pt/CeO\(_2\) was represented by a model (Pt/Ce\(_{15}\)O\(_{30}\)) constructed by removing five outermost low-coordinated O atoms from Pt/Ce\(_{15}\)O\(_{30}\). AIMD simulation was further performed for a more stable structure. The Pt single atoms coordinated with 2–3 oxygen ligands are probably located atop the reduced CeO\(_2\) cluster.

The calculated vibrational frequency of gaseous CO was 2,127 cm\(^{-1}\), which is 47 cm\(^{-1}\) lower than our experimental value (2,174 cm\(^{-1}\)). The agreement is satisfactory, but to keep the theoretical values more nearly comparable to our experimental results, we applied a shift of 47 cm\(^{-1}\) to the calculated vibrational frequencies of adsorbed CO on Pt/Ce\(_{15}\)O\(_{30}\) cluster and Pt/Ce\(_{25}\)O\(_{30}\) (ref.\(^{42}\)).

**XAS measurements.** Ex situ EXAFS spectra were used to characterize the Pt-containing sample supported on CeO\(_2\)/SiO\(_2\) at the Pt L\(_{\text{III}}\)-edge. We used a highly sensitive fluorescence detection technique\(^{39,40}\), carried out with a 30-element solid-state Ge detector at SSRF beamline 4-1 and with a 100-element solid-state Ge detector at beamline 9-3 with each sample pressed into a pellet at 23 °C. In situ XANES spectra were collected at beamline 9-3 at SSRF by using the 100-element solid-state Ge detector at the Pt L\(_{\text{III}}\)-edge. Approximately 50 mg of catalyst sample was loaded into a flow-through cell and held in place with quartz wool; a Kapton capillary cell (inside diameter = 2.8 mm), connected to a treatment gas line\(^{39}\), was used to collect in situ XANES spectra during treatment of the as-synthesized Pt/CeO\(_2\)-SiO\(_2\) in 10% H\(_2\)/He flowing at a rate of 20 ml min\(^{-1}\) as the cell temperature was ramped from 25 to 300 °C at a rate of 5 °C min\(^{-1}\) followed by a dwell of 60 min at 300 °C. The PtO\(_x\)/CeO\(_2\)/SiO\(_2\) catalyst was also investigated at the TPS 44A beamline of the NSRRC. The data were collected in fluorescence mode by using a seven-element silicon drift detector, and a standard Pt foil was used as reference for the energy calibration.

Analysis of the EXAFS data was carried out with Athena and XDAP. Athena, part of the Demeter package, was used to merge and deglitch the data, and XDAP was used for background subtraction, normalization and conversion of the data into an EXAFS function file. Reference backscattering phase shifts were calculated from crystallographic data determined with FEFF7. The Pt–O, Pt–O\(_{\text{long}}\), and Pt–O–Pt contributions were calculated on the basis of the structural parameters of PtO\(_2\); the Pt–Ce contribution was calculated on the basis of the structural parameters of the PtCe alloy\(^{41}\). The number of parameters used in the fitting was less than the statistically justified number, computed with the Nyquist theorem, \(n = 2\Delta k/\pi + 2\) (where \(\Delta k\) and \(\Delta\rho\), respectively, are the wavevector range and distance interval in the real space range used in the fitting).

Data fitting was based on an iterative process with a difference-file technique to determine a model comparing the overall fits and fits of individual shells as well. The model was chosen as the best-fitting model when the \(k^2\)- and \(k\)-weighted EXAFS data, Fourier-transformed data, and Fourier-transformed data characterizing each shell contribution were overall in best agreement with the calculated fits. Quality of fits was evaluated by the value of ‘goodness of fit’, defined below:

\[
\text{Goodness of fit} = \frac{\sum_{i=1}^{NPTS} \left( \frac{\sigma_{\text{exp},i}^2}{NPTS} - \frac{\sigma_{\text{model},i}^2}{NPTS} \right)^2}{NPTS(NPTS - N_{\text{free}})}
\]
Determination of physical property parameters of catalysts

Estimated surface area of CeO₂. According to the average sizes of CeO₂ nanoclusters determined from the HAADF images, loadings of Pt and Ce from ICP-MS results, and the BET surface area of Pt/CeO₂ SiO₂, we calculated various parameters characterizing the nanostructured CeO₂/SiO₂. We use a cuboidal model here for CeO₂ nanoclusters. The average dimension of these CeO₂ clusters was taken to be 2 nm with a volume (V(n,ceo)) of 8 nm³. The loading (L(m)) of Ce atoms was taken to be 10 wt%. The surface area (SA) of Pt/CeO₂/SiO₂ was measured to be 267 m² g⁻¹. Each unit cell of the CeO₂ contains four cerium atoms. The mass of one CeO₂ cluster is estimated by

\[ m_{\text{CeO}_2} = \left( \frac{4}{V_{\text{cell}}} \right) \left( \frac{M_{\text{CeO}_2}}{N_A} \right) = 5.8 \times 10^{-20} \text{ g}. \]

Where the molar mass \( M_{\text{CeO}_2} = 172 \text{ g mol}^{-1} \), \( V_{\text{cell}} = 0.157 \text{ nm}^3 \) and \( N_A = 6.02 \times 10^{23} \) is the Avogadro constant.

Estimated surface area of CeO₂ in CeO₂ NPs/SiO₂. The shape of the CeO₂ NPs can be roughly regarded as cuboidal with a dimension of 8 nm. The volume of one CeO₂ NP is thus calculated to be \( V_{\text{ceo}} = 512 \text{ nm}^3 \); the mass of one CeO₂ NP is \( m_{\text{CeO}_2} = 3.7 \times 10^{-18} \text{ g} \); the CeO₂ NPs are loosely positioned on SiO₂ so that their contact area with the support can be ignored. Surface area of one CeO₂ NP is \( S_{\text{CeO}_2} = 384 \text{ nm}^2 \); specific surface area of CeO₂ NPs is \( S_{\text{CeO}_2} / N_{\text{CeO}_2} = 103 \text{ m}^2 \text{ g}^{-1} \).

Estimated Pt atom number density on CeO₂ species. For the 0.4 wt% Pt/CeO₂, the Pt atom number density on CeO₂ is estimated by \( \rho = \frac{N_p}{M_p} \frac{S_{\text{CeO}_2}}{M_{\text{CeO}_2}} = 0.036 \text{ nm}^{-2} \), where the Pt molar mass \( M_p = 195 \text{ g mol}^{-1} \) and \( N_p \) is the wt% of Pt loading. The Pt atom number density characterizing the 0.4 wt% Pt/CeO₂ NPs/SiO₂ is estimated to be \( -0.12 \text{ nm}^{-2} \). The Pt atom number density characterizing the 0.3 wt% Pt/CeO₂ is \(-0.11 \text{ nm}^{-2} \). These calculated results are summarized in Extended Data Fig. 3d.

Extended results and discussions

Stabilization strategies. The most critical challenge to practical applications of single-atom catalysts is to prevent sintering of metal atoms (that is, formation of clusters and nanoparticles) during a desired catalytic reaction, especially under reducing environments at elevated temperatures. Substantial efforts have been made to anchor supported single metal atoms, for example, by filling cation vacancies to form chemical bonds, step trapping, edge anchoring, engineering of support defects to form strong bonds, use of surface functional groups and introduction of strong metal–support interactions. All of these approaches have focused on manipulating the support structure or chemistry to anchor isolated single metal atoms through strong metal–support interactions or interactions between the supported single metal atoms and surface functional groups. These anchoring strategies, however, may not be effective for reactions taking place under strongly reducing and/or oxidizing environments at elevated temperatures. For example, H₂ reduction of metal oxide-supported metal atoms at temperatures >200 °C may cause sintering of metal species regardless of the nature of the metal oxide supports (whether they are reducible or nonreducible). Although H₂ activation is frequently used for supported metal particle catalysts, the heretofore unavoidable sintering of supported metal atoms during H₂ activation makes it difficult to evaluate the true catalytic performance of supported metal atoms.

The strategies for stabilization of supported metal particles and clusters, illustrated, for example, by formation of chemical bonds at metal–support interfaces, encapsulation by porous structures, and...
incorporation of additives on supports with strong metal–additive interactions, are not readily transferred to stabilizing isolated single metal atoms. Alternative approaches are needed to mitigate or confine the movement of metal atoms during a targeted catalytic reaction.

Extended Data Fig. 1c–e shows HAADF images of the Ce–SiO₂ precursor. The Ce-containing species formed large agglomerates. In pure CeO₂ powders, well-crystallized CeO₂ NPs (~17 nm from XRD, determined by the Scherrer equation) connected together to form large agglomerates. The CeO₂(111) lattice spacing was used as an internal calibration standard for measuring the CeO₂(111) spacings (Extended Data Fig. 2h). To increase the measurement precision and to obtain statistically meaningful data, many sets of [111] lattice fringes were evaluated. Intensity line-scan profiles were used to calculate the corresponding lattice spacings. The average interplanar spacing of the [111] planes in the CeO₂ nanoclusters was measured to be 0.33 nm, a value markedly greater than the 0.31 nm characterizing the large CeO₂ nanoparticles—indicating a considerable lattice expansion of the [111] planes in the CeO₂ nanoclusters. Because of their small sizes, strong lattice distortion, and high concentrations of oxygen vacancies, the ultrasmall (~2 nm) CeO₂ nanoclusters were much more easily reduced than the larger CeO₂ NPs (Extended Data Fig. 2g).

Extended Data Fig. 3a shows the ICP-MS results of Pt loadings in the final catalysts. The same SEA procedure and synthesis conditions were used for adsorbing Pt atoms onto CeO₂/SiO₂ and pure SiO₂ supports. The Pt contents of the final catalysts suggest that the as-synthesized Pt/SiO₂ catalyst contained a negligible (0.0006 wt%) amount of Pt and that ~99% of all the Pt atoms adsorbed on the CeO₂ nanoclusters in the CeO₂/SiO₂ catalysts. The ICP-MS data unambiguously demonstrate that there was a negligible loading of Pt atoms on the bare SiO₂ surfaces, corroborating the design strategy. Extended Data Fig. 3c shows estimates of the loading levels of Pt (relative to the CeO₂ nanoclusters) on the CeO₂/SiO₂. The average volume of one CeO₂ cluster is approximately 2 nm × 2 nm × 2 nm = 8 nm³. The lattice parameter of CeO₂ is 0.54 nm, and each unit cell contains four Ce atoms. One CeO₂ cluster contains approximately 203 Ce atoms. The relationship between Pt loading level (y) and the average number of Pt atoms (x) on each CeO₂ nanocluster can be estimated by: y = m_{Pt}/m_{CeO2} × 100% = (100/203) × 100% = 0.56%. This estimate suggests that if each CeO₂ nanocluster hosts only one Pt atom then the Pt loading level (with respect to CeO₂) would be approximately 0.56 wt%. From this perspective, each CeO₂ nanocluster in the as-synthesized 0.4 wt% Pt/CeO₂/SiO₂ contains, on average, ~0.7 Pt atoms. Extended Data Fig. 3e,f show plots of attainable wt% Pt loading (with respect to SiO₂) versus the specific surface area of SiO₂, assuming that each CeO₂ nanocluster hosts only one Pt atom. Small and densely populated CeO₂ nanoclusters and high-surface-area SiO₂ (or other types of supports) are critical to developing stable single-atom or cluster catalysts for practical applications. Extended Data Fig. 3g, i show XPS data characterizing the as-synthesized 0.4 wt% Pt/CeO₂/SiO₂ catalyst. The survey spectra show all the elements present in the as-synthesized catalyst. Platinum was not detectable owing to the low loading level (~0.05 wt% with respect to the total weight of the catalyst). The Cl2p peak (~199 eV) was not detectable either in the survey or in the local scan spectrum, suggesting that the vigorous washing and high-temperature calcination eliminated the Cl residues. The selective Pt adsorption and the subsequent processes did not appreciably change the nature and amounts of defects in the CeO₂ nanoclusters.

Extended Data Fig. 4a–c show HAADF images of the as-synthesized 0.4 wt% Pt/CeO₂/SiO₂ catalyst, confirming the absence of detectable Pt clusters. Considering the relatively high atomic number of Ce and rapid changes in thickness across ultrasmall CeO₂ nanoclusters, it is not possible to unambiguously distinguish Pt single atoms from Ce atoms in low-dose HAADF images. High-current electron probes damage the crystallinity of the CeO₂ nanoclusters. Extended Data Fig. 4d shows an HAADF image of a Pt/CeO₂/SiO₂ sample by the impregnation method. The Pt loading level was controlled to be ~1.5 wt% with respect to the total support (CeO₂ plus SiO₂). This particular catalyst contained various Pt species: NPs (red square), clusters (white square) linked to the CeO₂ nanoclusters, and subnanometre clusters (white circle) attached to the CeO₂ nanoclusters. Although Pt single atoms could not be reliably identified, subnanometre Pt clusters are easily distinguishable from the CeO₂ nanoclusters. The insets show Pt clusters (~0.4 nm) attached to CeO₂ nanoclusters. By analysing numerous such atomic-resolution HAADF images, we concluded that Pt clusters with sizes of ~0.4 nm or larger could be unambiguously identified. Single Pt atoms or tiny, weakly bonded Pt clusters (for example, with sizes <0.3 nm) would not be reliably identified in low-dose atomic-resolution HAADF images of Pt/CeO₂/SiO₂ catalysts.

Extended Data Fig. 6 reports data characterizing the dynamic behaviour of Pt atoms on CeO₂ or SiO₂ during reduction in H₂. A model core–shell structure consisting of Cu[(Pt/CeO₂)@SiO₂] was fabricated to allow tracking of Pt atoms diffusing through the porous SiO₂ shell—the strategy involves incorporating Cu NPs on the outer shell surface to trap (scavenge) Pt atoms that might migrate from the CeO₂ in the interior to—and through—the SiO₂ shell to reach the Cu NPs, where they would form Cu–Pt alloy NPs (Extended Data Fig. 6a,c). In control samples, Cu[(Pt/CeO₂)@SiO₂] was reduced by the same treatment process, Cu[(Pt/SiO₂)@SiO₂]. Pt atoms were observed to form Cu–Pt alloy NPs, having migrated during the H₂-reduction process (400 °C for 3 h) through the porous SiO₂ shell (Extended Data Fig. 6d–h). By contrast, when the Cu[(Pt/CeO₂)@SiO₂] sample was reduced by the same treatment process, Pt atoms were not associated with the Cu NPs (Extended Data Fig. 6i–l), confirming that a much stronger interaction of Pt atoms with CeO₂ than with SiO₂ suppressed their diffusion through the porous SiO₂ shell. The results of this set of experiments demonstrate that, when the interaction strength of Pt atoms with CeO₂ (CeO₂) is much stronger than that with SiO₂, the migration of Pt atoms onto the SiO₂ surfaces is greatly mitigated, even under conditions of H₂ activation processes, although the Pt atoms still sinter on the CeO₂/(CeO₂) surfaces.
characterizing highly reduced Pt single atoms supported on reduced CeO2 nanoclusters.

Extended Data Fig. 7f–h show redox properties of PtOx species. Reducing high-Pt-loading Pt/ CeO2/SiO2 (for example, 4 wt% Pt with respect to CeO2) formed Pt clusters (Extended Data Fig. 8h), whereas mild oxidation at 100 °C yielded PtOx clusters. During a CO-DRIFTS experiment, PtOx clusters were stable when enough O2 was present in the cell (Extended Data Fig. 7g). Under reducing conditions, PtOx clusters were reduced to metallic Pt clusters. After the O2 flow was stopped, the PtOx peak at 2.111 cm−1 rapidly decreased, and a new peak arose at 2.075 cm−1, ascribed to metallic Pt clusters, indicating that the PtOx clusters were reduced by CO at 100 °C. This set of experiments clearly demonstrates how to spectroscopically distinguish small PtOx clusters from isolated cationic Pt atoms by performing such a redox cycle. If there had been PtOx clusters in the as-synthesized 0.4 wt% Pt/ CeO2/SiO2 catalyst, we would easily have observed metallic Pt clusters in the DRIFTS spectra—because such PtOx clusters are not stable either under conditions of CO adsorption or conditions of high-temperature H2 reduction. This facile redox behaviour of PtOx clusters was used to distinguish DRIFTS spectra of isolated Pt/ CeO2, from those of supported PtOx clusters. The CO-DRIFTS spectra of the as-synthesized and reduced 0.4 wt% Pt/ CeO2/SiO2 catalysts confirmed that this catalyst did not contain either Pt clusters or PtOx species. Furthermore, EXAFS data characterizing the 0.4 wt% Pt/ CeO2/SiO2 catalyst did not give evidence of a Pt–O–Pt shell, which, by contrast, was evident in the PtOx/ CeO2/SiO2 spectra (Extended Data Fig. 7k–p). Extended Data Fig. 7j shows that Pt clusters were observed on the reduced 0.02 wt% Pt/ CeO2 (synthesized by SEAA method). The number density of Pt atoms in this 0.02 wt% Pt/ CeO2 sample was estimated to be ~0.007 nm−2, much lower than that of the 0.4 wt% Pt/ CeO2/SiO2 catalyst (0.036 nm−2 on CeO2). Even with such a low number density of Pt atoms, Pt clusters/NPs were still formed during the reduction process. These experimental results confirm that ultrasmall size and isolation of the CeO2 nanoglue islands are critical to confining the movement of Pt atoms.

Extended Data Fig. 8a–c show HAADF images of the 0.4 wt% Pt/ CeO2 NPs/SiO2 treated in H2 at 300 °C for 1 h. This catalyst had a Pt loading level similar to that of the 0.4 wt% Pt/ CeO2/SiO2, but the sizes of the CeO2 crystals were markedly greater (~8 nm from HAADF images). Extended Data Fig. 8a,b show the same sample region but was obtained with a different electron beam defocus value to illustrate that each CeO2 NP is associated with at least one Pt cluster. In examinations of numerous HAADF images, no Pt clusters were found on the bare SiO2 support surfaces, indicating that all the Pt atoms were associated with the CeO2 crystals. The results of this set of experiments clearly demonstrate that during the H2-activation process Pt single atoms on each individual CeO2 NP sintered to form small clusters but did not migrate away from their own CeO2 NPs to form large Pt NPs.

Extended Data Fig. 8g–j show Pt clusters on CeO2/SiO2. When the Pt loading level was increased to 4 wt%, a majority of the CeO2 nanoglue islands contained several Pt atoms, and during the H2-reduction process these Pt clusters sintered to form small clusters. The fact that the sizes of the Pt clusters are similar (average size ~0.9 nm) suggests that (1) the Pt atoms on each CeO2 nanocluster sintered after treatment in H2 at 400 °C for 5 h and (2) even after H2 reduction at 500 °C for 12 h, the Pt atoms were still confined to their own CeO2 nanoclusters. The results of this set of experiments unambiguously demonstrate that the CeO2 nanoglu units strongly localized the Pt atoms even under harsh reduction conditions. Our design strategy of localizing Pt atoms or clusters by confining their movement during a catalyst activation process or a desired catalytic reaction thus proves to be successful. Such a strategy enhances both the catalyst’s stability and activity and/or selectivity. The selection of an appropriate functional nanoglu is critical to enhancing both the catalyst’s performance and stability.

Extended Data Fig. 9i–p show that the H2-reduction treatment at 300 °C not only reduced the oxidation state of the Pt atoms but also modified the local bonding environment of the platinum species. In CO oxidation under lean conditions (O2 partial pressures in excess of the stoichiometric O2:CO ratio of 0.5), the probe reaction reported in this work, the H2-activated 0.4 wt% Pt/ CeO2/SiO2 was active and stable at low temperatures (<200 °C), but at higher temperatures (for example, 300 °C) partial oxidation of the Pt atoms can occur and reduce the catalyst’s activity. This process is reversible: the activity is recovered by H2 reduction. Nonetheless, it remains a considerable challenge to maintain the Pt in a reduced state over a wider temperature window (>200 °C) for lean oxidation applications. Further work is needed to overcome this limitation.

Extended Data Fig. 10 shows results of a CO-DRIFTS investigation of Pd and Rh atoms supported on CeO2/SiO2 and CeO2. Although the CO adsorption experiment was conducted at 25 °C, CeO2-supported Pd atoms were rapidly reduced by CO and aggregated into Pd clusters/NPs (Extended Data Fig. 10b). The very small amount of bridge-bonded COx (characterized by the band at ~1.978 cm−1) in the as-synthesized Pd/CeO2/SiO2 might be evidence of sintering of Pd atoms on their own CeO2 nanoglue islands (Extended Data Fig. 10a). Compared with the notable sintering of Pd atoms on the Pd/CeO2 (Extended Data Fig. 10d), the Pd atoms on CeO2/SiO2 were extremely stable after reduction in H2 (Extended Data Fig. 10c). The CO-DRIFTS experiments characterizing the RH-containing catalysts were conducted at 180 °C to avoid oxidative fragmentation in which exposure of Rh NPs/clusters to CO at temperatures lower than 150 °C leads to oxidation and fragmentation (assisted by support OH groups) that constitutes redisperation of Rh NPs/clusters into cationic single-atom Rh (ref. 46). After the reduction treatment, the Rh atoms remained atomically dispersed on the CeO2/SiO2 support (Extended Data Fig. 10e). On the other hand, after the reduction treatment, the presence of the 2.040 cm−1 peak characterizing the reduced Rh/CeO2 catalyst could be assigned to CO adsorbed on Rh NPs47 (Extended Data Fig. 10f). Although more investigations of the intrinsic structure and catalytic properties of the Pd/ CeO2/SiO2 and Rh/CeO2/SiO2 catalysts are recommended, this set of experimental results clearly demonstrates that the use of functional nanoglu to localize metal atoms and/or clusters works equally well for atomically dispersed Pd and Rh as for Pt. Our metal-atom localization strategy involving grafted ultrasmall functional nanoglu islands on high-surface-area, robust supports is general and can be extended to a plethora of catalyst systems for chemical transformations of important molecules.

### Data availability

All data that led us to understand the results presented here are available with the Article or from corresponding author J.L. upon reasonable request. Source data are provided with this paper.

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Author contributions J.L. conceived the concept, designed the studies and conducted the STEM experiments. X.L. designed the synthesis methods, conducted synthesis work, catalytic tests, DRIFTS experiments and other characterizations. X.I.P.-H. and Y.W. carried out CO DRIFTS experiments during the early stages of this project. Y.C., C.-W.P., C.-Y.F. and B.C.G. performed XAS experiments and analysed XANES and EXAFS data. J.X. conducted relevant experiments. X.L. and J.L. wrote the manuscript. B.C.G., Y.W. and J.Z. revised the manuscript, and all authors acknowledge the use of facilities within the Eyring Materials Center and the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University and thank the Stanford Synchrotron Radiation Lightsource (beamlines 4-1, 9-3) for providing beam time.

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Correspondence and requests for materials should be addressed to Jie Zeng, Yong Wang, Bruce C. Gates or Jingyu Liu.

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Extended Data Fig. 1 | Synthesis of CeO$_2$ nanoglue islands. a, b, SEM backscattered electron images of the CeO$_2$/SiO$_2$ after solution reaction for 3 min (a) and 1 h (b). Bright features in b represent large agglomerates of CeO$_2$ particles produced by Ce(OH)$_4$ precipitation during the prolonged 1 h adsorption process. There were no CeO$_2$ particles detectable in a, either at low or high image magnifications. The inset to a shows a photograph of the as-synthesized CeO$_2$/SiO$_2$ powders. c, d, e, High-resolution HAADF images of the Ce–SiO$_2$ (prior to calcination) at various magnifications and defocus values. f, g, HAADF images show distribution and crystallite structure of the CeO$_2$ nanoglue islands after 600 °C calcination for 12 h. h, i, Size distribution of the as-synthesized CeO$_2$ nanoclusters along two perpendicular directions.
Extended Data Fig. 2 | Characterizations of CeO$_x$/SiO$_2$, CeO$_2$ NPs/SiO$_2$, and CeO$_2$. 

**a.** XRD pattern of 12 wt% CeO$_2$ NPs/SiO$_2$ synthesized by impregnation method. 

**b, c.** HAADF images of 12 wt% CeO$_2$ NPs/SiO$_2$ in separate regions. The inset to **b** shows a photograph of the as-synthesized CeO$_2$ NPs/SiO$_2$ powders. 

**d.** Size distribution of CeO$_2$ NPs in CeO$_2$ NPs/SiO$_2$ from HAADF images. 

**e, f.** HAADF images of pure CeO$_2$ powders, which were fabricated by precipitation and calcination. 

**g.** Normalized Raman spectra of the as-synthesized CeO$_x$/SiO$_2$ and pure CeO$_2$. 

**h.** High-resolution HAADF images of, and intensity linescans across, a crystalline CeO$_x$ nanocluster and a CeO$_2$ nanoparticle. 

**i.** Ce 3d XPS data obtained for the 12 wt% CeO$_2$ NPs/SiO$_2$. Circles and black lines represent the data and the fit, respectively. 

**j.** H$_2$-TPR profiles obtained on the CeO$_x$/SiO$_2$ and pure CeO$_2$. TCD, thermal conductivity detector. 

**k.** XRD patterns of CeO$_x$/SiO$_2$ support after various treatments. Treatment conditions: black, calcined in air at 600 °C for 12 h; red, reduced in H$_2$ at 600 °C for 24 h; blue, re-calcined in air at 600 °C for 12 h after reduction; and orange, calcined in air at 800 °C for 4 h. Prolonged H$_2$ reduction at 600 °C modified the crystallinity of the CeO$_x$ nanoclusters, whereas re-calcination at 600 °C recovered the original structure of the CeO$_2$ nanoclusters.
Extended Data Fig. 3 | Characterization of Pt/CeO$_x$/SiO$_2$.  

**a**, ICP-MS measurements of Pt concentrations in the final catalysts. **b**, BET surface areas of various supports and the 0.4 wt% Pt/CeO$_x$/SiO$_2$ catalyst. The BET surface area of the SiO$_2$ support did not change significantly after deposition of CeO$_x$ and Pt. **c**, Estimate of Pt loading levels (relative to the CeO$_x$ nanoclusters) in the CeO$_x$/SiO$_2$. **d**, Estimated specific surface area of CeO$_x$ in CeO$_x$/SiO$_2$ and CeO$_2$ in CeO$_2$ NPs/SiO$_2$, and number density of Pt atoms on CeO$_x$/CeO$_2$ component. **e**, Plots of attainable wt% Pt loading (with respect to SiO$_2$) versus the specific surface area of SiO$_2$ for various sizes of CeO$_x$ nanoclusters and the distance between them, assuming that each CeO$_x$ nanocluster hosts only one Pt atom. **f**, Plots of attainable wt% Pt loading (with respect to SiO$_2$) versus specific surface area of SiO$_2$ for CeO$_x$ nanoclusters ($D = 2$ nm, $L = 9$ nm) reported in this work. **g, h, i**, XPS data characterizing the as-synthesized 0.4 wt% Pt/CeO$_x$/SiO$_2$ catalyst.
Extended Data Fig. 4 | Nature of Pt species in Pt/CeO$_x$/SiO$_2$ catalyst. 

a, b, c. HAADF images of the as-synthesized 0.4 wt% Pt/CeO$_x$/SiO$_2$ catalyst. 
d. HAADF image of a high-loading Pt/CeO$_x$/SiO$_2$ catalyst, which was fabricated by impregnation and reduced in H$_2$ at 300 °C for 1 h, shows presence of small Pt clusters. 
e–j. EXAFS results characterizing the as-synthesized 0.4 wt% Pt/CeO$_x$/SiO$_2$. 

e, k$^1$-weighted experimental EXAFS function (black solid line) and the sum of the calculated Pt–O, Pt–O$_{long}$ and Pt–O–Ce contributions (red dashed line). 
f, Imaginary part and the magnitude of Fourier transform (k$^1$-weighted) of the experimental EXAFS results (black solid line) and sum of the calculated Pt–O, Pt–O$_{long}$ and Pt–O–Ce contributions (red dashed line). 
g, i, Imaginary part and magnitude of Fourier transform (phase- and amplitude-corrected) of the experimental results (black solid line) and the calculated contributions (red dashed line) of the Pt–O shell (k$^1$-weighted) (g), the Pt–O$_{long}$ shell (k$^1$-weighted) (h), and the Pt–O–Ce shell (k$^3$-weighted) (i). 

j, Summary of the EXAFS parameters. CN, coordination number; $R$, distance between absorber and backscatterer atoms; $\Delta \sigma^2$, disorder term; $\Delta E_0$, inner potential correction. Error bounds (accuracies) characterizing the structural parameters obtained by EXAFS spectroscopy are estimated to be CN, ±10%; $R$, ±0.02 Å; $\Delta \sigma^2$, ±20%; $\Delta E_0$, ±20%.
Extended Data Fig. 5 | Changes of Pt atoms on SiO\textsubscript{2} or CeO\textsubscript{2} supports under various treatment conditions. \textbf{a, b}, Single Pt atoms (yellow circles) and small Pt clusters (yellow squares) were present in the as-synthesized Pt/SiO\textsubscript{2} (synthesized by the SEA method using Pt(NH\textsubscript{3})\textsubscript{4}\textsuperscript{2+} ions in alkaline solution). \textbf{c, d}, After H\textsubscript{2} reduction of the as-synthesized Pt/SiO\textsubscript{2} at 300 °C for 1 h, Pt sintered to form various sizes of nanoparticles (c) although some small Pt clusters were observable (d). \textbf{e, f}, After calcination of the as-synthesized Pt/SiO\textsubscript{2} at 500 °C for 1 h, larger Pt agglomerates (e) and many Pt nanoparticles (e, f) were formed. \textbf{g, h}, Atomic-resolution HAADF images of a 0.3 wt% Pt/CeO\textsubscript{2} catalyst prepared by the SEA method. The Pt single atoms (yellow circles) on flat facets of CeO\textsubscript{2} nanoparticles are clearly distinguishable. \textbf{i, j}, HAADF images of a 0.3 wt% Pt/CeO\textsubscript{2} after reduction treatment (10 ml min\textsuperscript{-1} of H\textsubscript{2}/He at 300 °C for 1 h), clearly reveal formation of small Pt nanoparticles. During the H\textsubscript{2}-activation process, Pt atoms became mobile on CeO\textsubscript{2} surfaces and sintered to form Pt clusters/nanoparticles (yellow squares). \textbf{k}, CO-DRIFTS spectrum of the reduced 0.3 wt% Pt/CeO\textsubscript{2} indicates presence of Pt clusters/nanoparticles.
Extended Data Fig. 6 | Design and characterization of model catalysts.

a, CO-DRIFTS spectra of 0.3 wt% Pt/SiO₂, 4 wt% Cu/SiO₂, and Cu-Pt/SiO₂. b, TEM image of the reduced Cu-Pt/SiO₂ catalyst. c, HAADF image of Cu nanoparticles in reduced Cu-Pt/SiO₂, revealing Pt single atoms/clusters on/within Cu nanoparticles. d, Schematic diagram showing synthesis and formation of Pt-Cu species in Cu[(Pt/SiO₂)@SiO₂] sample. Platinum atoms migrated through the porous SiO₂ shell to interact with Cu nanoparticles. e, TEM image of Cu[(Pt/SiO₂)@SiO₂] shows the CeO₂ nanoparticles as markers between the SiO₂ core and the coated porous SiO₂ shell. The thickness of the porous SiO₂ shell was estimated to be ~10 nm. f, HAADF image of the Cu[(Pt/SiO₂)@SiO₂] catalyst.

g, CO DRIFTS spectrum and h, HAADF image of Cu nanoparticles in the reduced Cu[(Pt/SiO₂)@SiO₂] catalyst (reduction conditions: 10% H₂, 400 °C for 3 h) clearly revealing Pt atoms on/within Cu nanoparticles. i, Schematic diagram showing synthesis and reduction processes of Cu[(Pt/CeO₂)@SiO₂] model catalyst. j, TEM images of Cu[(Pt/CeO₂)@SiO₂] and (Pt/CeO₂)@SiO₂ (inset). The Pt and Cu loadings were 0.3 wt% and 2 wt%, respectively. The thickness of the porous SiO₂ shell was estimated to be ~6 nm. CO adsorption DRIFTS spectrum (k) and HAADF images (l) of Cu nanoparticles in the reduced Cu[(Pt/SiO₂)@SiO₂] catalyst (reduction conditions: 10% H₂, 400 °C for 3 h) confirming the absence of Pt-Cu species.
Extended Data Fig. 7 | Reduction of Pt/CeO$_x$/SiO$_2$ catalysts and investigation of Pt$_x$O$_y$ clusters. 

a. HAADF image of the 0.4 wt% Pt/CeO$_x$/SiO$_2$ after 300 °C reduction in H$_2$ for 10 h shows the absence of detectable Pt clusters. b, c, d. CO adsorption DRIFTS spectra (recorded at 100 °C) characterize the reduced 0.4 wt% Pt/CeO$_x$/SiO$_2$ (H$_2$ at 400 °C for 3 h, 500 °C for 1 h or 600 °C for 1 h, respectively). e, DFT-predicted CO adsorption modes on Pt single atoms supported on CeO$_x$ clusters. f–h. CO-DRIFTS spectra characterizing the Pt$_x$O$_y$/CeO$_x$/SiO$_2$ sample at 100 °C (f), after cessation of O$_2$ flow (g) and reduced Pt$_x$O$_y$ sample (10% H$_2$/Ar, 300 °C, 1 h) (h), reveal transformation of the Pt$_x$O$_y$ species into metallic Pt clusters (2075 cm$^{-1}$). i. Ce 3d XPS data characterizing the 0.4 wt% Pt/CeO$_x$/SiO$_2$ after reduction in 10% H$_2$ at 500 °C for 1 h. The percentage of Ce$^{3+}$ was ~49% and no metallic Ce was observed. j. CO adsorption DRIFTS spectrum characterizing the 0.02 wt% Pt/CeO$_2$ powder after reduction in H$_2$ at 400 °C for 1 h. k–p. EXAFS results characterizing Pt$_x$O$_y$ supported on CeO$_x$/SiO$_2$. k, l. Weighted experimental EXAFS function (black solid line) and the sum of the calculated Pt–O, Pt–O–Pt, and Pt–O–Ce contributions (red dashed line). i. Imaginary part and magnitude of Fourier transform (k$^1$-weighted) of the EXAFS data (black solid line) and sum of the calculated Pt–O, Pt–O–Pt, and Pt–O–Ce contributions (red dashed line). m, n, o. Imaginary part and magnitude of Fourier transform (phase- and amplitude-corrected) of the experimental results (black solid line) and the calculated contribution (fit; red dashed line) of the Pt–O shell (k$^2$-weighted) (m), the Pt–O–Pt shell (k$^3$-weighted) (n), and the Pt–O–Ce shell (k$^3$-weighted) (o). p. Summary of the EXAFS parameters. CN, coordination number; $R$, distance between absorber and backscatterer atoms; $\Delta \sigma^2$, disorder term; $\Delta E_0$, inner potential correction. Error bounds (accuracies) characterizing the structural parameters obtained by EXAFS spectroscopy are as stated in legend of Extended Data Fig. 4.
Extended Data Fig. 8 | Pt clusters on CeO$_2$ NPs/SiO$_2$ and CeO$_x$/SiO$_2$.

a, b, c, HAADF images of the reduced 0.4 wt% Pt/CeO$_2$ NPs/SiO$_2$ (treated in H$_2$ at 300 °C for 1 h) show Pt clusters. Images a and b were obtained from the same region with different electron beam defocus value. d, Comparison of CO-DRIFTS spectra characterizing the as-synthesized 0.4 wt% Pt/CeO$_2$ NPs/SiO$_2$ and CeO$_2$ NPs/SiO$_2$. The CeO$_2$ NPs and SiO$_2$ support did not adsorb CO, and only the two CO gas-phase peaks were observed. e, CO-DRIFTS spectra characterizing the reduced (reduction in H$_2$ at 300 °C for 1 h) 0.4 wt% Pt/CeO$_2$ NPs/SiO$_2$. The peak at 2,086 cm$^{-1}$ is assigned to CO adsorbed on Pt nanoclusters/nanoparticles. f, Schematic diagrams illustrate sintering of Pt atoms on CeO$_2$ NPs under conditions of H$_2$ activation treatment; Ce, O, Pt atoms and SiO$_2$ support are shown in yellow, blue, red and grey, respectively.

g, CO-DRIFTS spectra characterizing the 4 wt% Pt/CeO$_x$/SiO$_2$ catalyst after reduction in H$_2$ at 300 °C for 3 h. h, i, HAADF images of the 4 wt% Pt/CeO$_x$/SiO$_2$ after reduction in H$_2$ at 400 °C for 5 h and 500 °C for 12 h, respectively. j, Schematic diagrams illustrate movement of Pt atoms on each individual CeO$_x$ nanoclusters during the H$_2$ activation process; Ce, O, Pt and SiO$_2$ support are shown in yellow, blue, red and grey, respectively.
Extended Data Fig. 9 | Characterization and CO oxidation performance of the as-synthesized and activated catalysts. a, b, CO oxidation catalysis: light-off curves characterizing 0.3 wt% Pt/CeO$_2$ (5 mg of catalyst mixed with 25 mg of SiO$_2$) (a) and 0.4 wt% Pt/CeO$_2$ NPs/SiO$_2$ (30 mg) (b). Activation conditions: H$_2$ at 300 °C for 1 h. c, Light-off curves of 4 wt% Pt/CeO$_x$/SiO$_2$ (3 mg of catalyst mixed with 27 mg of SiO$_2$ pretreated in H$_2$ at 400 °C for 3 h to form Pt clusters). d–g, CO oxidation light-off data and CO-DRIFTS spectra characterizing 0.4 wt% Pt/CeO$_x$/SiO$_2$ (IMP) (d, e) and Pt/SiO$_2$ (IMP) catalyst (f, g).

h, Light-off temperatures $T_{50}$ (50% CO conversion) of various catalysts: as-synthesized 0.4 wt% Pt/CeO$_x$/SiO$_2$ (A), activated 0.4 wt% Pt/CeO$_x$/SiO$_2$ (B), activated Pt/CeO$_x$ (C), activated Pt/CeO$_2$ NPs/SiO$_2$ (D), activated 4 wt% Pt/CeO$_x$/SiO$_2$ (E), activated Pt/CeO$_x$/SiO$_2$ by impregnation (F), and activated Pt/SiO$_2$ by impregnation (G).

i–l, In situ Pt LIII XANES spectra of 0.4 wt% Pt/CeO$_x$/SiO$_2$ catalyst during activation in 10% H$_2$/He, and Pt foil are included for comparison. k–o, EXAFS results characterizing the activated 0.4 wt% Pt/CeO$_x$/SiO$_2$ catalyst. k, $k^1$-weighted experimental EXAFS function (black solid line) and the sum of the calculated Pt–O, Pt–O$_{\text{long}}$, and Pt–O–Ce contributions (red dashed line). l, Imaginary part and magnitude of Fourier transform ($k^1$-weighted) of the experimental EXAFS results (black solid line) and sum of the calculated Pt–O, Pt–O$_{\text{long}}$, and Pt–O–Ce contributions (red dashed line).

m–o, Imaginary part and magnitude of Fourier transform (phase- and amplitude-corrected) of the data (black solid line) and the calculated contribution (red dashed line) of the Pt–O shell ($k^1$-weighted) (m), the Pt–O$_{\text{long}}$ shell ($k^1$-weighted) (n), and the Pt–O–Ce shell ($k^3$-weighted) (o). p, Summary of the EXAFS parameters. CN, coordination number; $R$, distance between absorber and backscatterer atoms; $\Delta \sigma^2$, disorder term; $\Delta E_0$, inner potential correction. q, Apparent activation energy ($E_a$) for CO oxidation characterizing the as-synthesized and reduced 0.4 wt% Pt/CeO$_x$/SiO$_2$. r, Long-term stability test of the activated 0.4 wt% Pt/CeO$_x$/SiO$_2$ at a reaction temperature of 140 °C. s, HAADF image of the 0.4 wt% Pt/CeO$_x$/SiO$_2$ after stability test. t, Long-term stability test of the activated 0.3 wt% Pt/CeO$_2$ at 140 °C.
Extended Data Fig. 10 | CO-DRIFTS investigation of Pd and Rh atoms supported on CeO<sub>x</sub>/SiO<sub>2</sub> and on CeO<sub>2</sub>. a, As-synthesized 1.4 wt% Pd/CeO<sub>x</sub>/SiO<sub>2</sub> and b, 0.4 wt% Pd/CeO<sub>2</sub>. c, Reduced Pd/CeO<sub>x</sub>/SiO<sub>2</sub> and d, reduced Pd/CeO<sub>2</sub>. CO adsorption temperature, 25 °C. e, f, CO-DRIFTS of reduced 0.6 wt% Rh/CeO<sub>x</sub>/SiO<sub>2</sub> (e) and 0.3 wt% Rh/CeO<sub>2</sub> (f). Reduction conditions: 20 ml min<sup>-1</sup> of 10% H<sub>2</sub> at 400 °C for 1 h. The loadings of Pd and of Rh are reported with respect to the CeO<sub>x</sub> species.