Supplementary Materials
for
Carbon Monoxide Promotes the Catalytic Hydrogenation on Metal Cluster Catalysts

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Materials
Palladium chloride (PdCl₂, 59.8%), disodium tetrachloropalladate (Na₂PdCl₄) and palladium(II) acetate [Pd(OAc)₂] were purchased from Kunming Institute of Precious Metals. Titanium tetrachloride (TiCl₄), and 5% Pd/C were purchased from Alfa Aesar. Hydrochloric Acid (HCl ~35%), ethylene glycol (EG), tetrahydrofuran (THF), styrene, ethanol (EtOH), acetone, poly(vinylpyrrolidone) (PVP, MW= 55 000), L-ascorbic acid, dimethyl formamide (DMF), KBr 2-ethyl anthraquinone (2-eAQ), phosphoric acid, trioctyl phosphate (TOP), sulfuric acid and potassium permanganate were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Al₂O₃ was purchased from Hangzhou Wanjing New Materials Co. Ltd. (Hangzhou, Zhejiang, China) H₂ (99.99%), D₂ (99.99%), CO (99.95%) C₂H₄ (99.5%) and 5% CO/Ar were purchased from Linde Gas. The water was deionized water. All the chemicals were used without further purification (The commercial 5% Pd/C was reduced in 5% H₂/Ar at 100 °C for 1h before using).

Methods
Preparation of TiO₂-EG and TiO₂
Ultrathin TiO₂-EG nanosheets were synthesized corresponding to the reported method.[1] 2 mL TiCl₄ was carefully introduced into 60 mL EG and stirred under ultrasonic until homogeneous light yellow solution was obtained, then the solution was transferred into 100 mL Teflon-lined stainless-steel autoclave and heated at 150 °C for 4h. The obtained white colloids were centrifuged and washed with water for 3 times.

The EG-free TiO₂ that was obtained by heating TiO₂-EG at 350 °C for 2 h under air atmosphere in muffle with a ramp rate of 1 °C/min.

Preparation of Pd₂CO/TiO₂, Pd₂/TiO₂-cal, Pd₂CO/Al₂O₃.
10 μL H₂PdCl₄ (1 M) was introduced into 1 mL THF in a glass bottle, and the solution was kept stirred under 0.2 MPa CO at room temperature till the color of the solution turned into bright yellow. Then the solution was introduced dropwise into 20 mL THF dispersions of the supports (500 mg TiO₂ or Al₂O₃) under stirring, then the solvent was removed by centrifuge and dried under vacuum at room temperature, the as-obtained catalysts were denoted as Pd₂CO/TiO₂ and Pd₂CO/Al₂O₃.

The releasing of CO₂ upon introducing TiO₂ into the solution of H₂[Pd₂(µ-CO)₂Cl₄] was recorded by MX6 iBrid Gas Detector (Industrial Scientific) equipped with a CO₂ detector. The UV-vis spectrum of
the H₂[Pd₂(μ-CO)₂Cl₄]/THF solution and as-obtained Pd₂CO/TiO₂ were performed in dilute and recorded by Shimadzu UV2600 instrument.

In order to remove the adsorbed CO, Pd₂/TiO₂-cal was obtained by heating Pd₂CO/TiO₂ at 350 °C for 1h (ramp rate, 2 °C/min) under static air atmosphere. Before applying in catalysis, Pd₂/TiO₂-cal was treated with H₂ at room temperature for 15 min.

**Preparation of Pd₁/TiO₂-EG and Pd₁/TiO₂-cal**

The single-atom dispersed Pd catalysts were synthesized following the procedures reported in our group previously.[2, 3] Typically, 200 mg TiO₂-EG nanosheets and 4 μL H₂PdCl₄ (1 M) were added in 20 mL H₂O and stirred at room temperature for 30 min. The colloidal solution was then irradiated under 365 nm filter equipped Xe-lamp (100 W) for 15 min. The colloids were centrifuged and washed with water for 2 times, then dried overnight under vacuum at room temperature. The obtained catalyst was denoted as Pd₁/TiO₂-EG. The EG-free single-atom dispersed Pd catalyst, Pd₁/TiO₂-cal was obtained by calcination of Pd₁/TiO₂-EG and at 350 °C for 4h (ramp rate, 1 °C/min) under static air atmosphere.

**Preparation of Pd nanosheets and Pd nanocubes**

The colloidal Pd nanosheets (Pd NSs) and Pd nanocubes (Pd NCs) with preferential (111) and (100) exposed surface respectively were prepared following the procedures reported previously in our group.[4, 5] For Pd nanosheets, 30 μL 1 M H₂PdCl₄ was added into 10 mL DMF and stirred under 0.1 MPa CO atmosphere at room temperature for 15 min, then 1 mL H₂O was introduced and stirred for another 15 min without CO. The colloidal Pd nanosheets were centrifuged and washed with EtOH and acetone for 3 times. For Pd nanocubes, 8 mL aqueous solution containing poly(vinylpyrrolidone) (PVP, MW= 55,000, 105 mg), L-ascorbic acid (60 mg), KBr (200 mg) were placed in a 20 mL vial, and pre-heated in air under magnetic stirring at 80 °C for 10 min. Then the aqueous solution of Na₂PdCl₄ (57 mg in 3 mL H₂O) was added into the vial and kept at 80 °C for another 3 h before it was cooled down to room temperature. The product was collected by centrifugation and washed with water-acetone mixture.

**Preparation of 0.5 wt% Pd/Al₂O₃**

200 mg Al₂O₃ was dispersed in 6 mL acetone, then Pd(OAc)₂/Acetone solution was introduced, the Pd mass loading was controlled to be 0.5 wt%. The samples dried at 40 °C overnight, the obtained
powders were then calcined (ramp rate, 2 °C/min) in static air at 300 °C for 2h. The catalysts were reduced in H2 at 100 °C for 1 h before applied in hydrogenation.

**Catalysis tests**

For styrene hydrogenation, a proper amount of catalyst was introduced in 10 mL EtOH and stirred at 30 °C and 0.1 MPa H2 atmosphere for 10 min, then 0.55 mL (5 mmol) styrene was added and started to measure the conversion of styrene on a KB-WAX chromatographic column equipped gas chromatograph (GC). The ratio of substrate to catalyst (S/C) was controlled, for 0.2 wt% Pd2CO/TiO2 Pd2/TiO2-cal, Pd1/TiO2, Pd1/TiO2-cal and Pd nanosheets S/C=50,000. The activation energy was measured by adjusting the temperature to 20 °C, 30 °C, 40 °C and 50 °C. In order to evaluate the effect of the different amount of CO on Pd2/TiO2-cal, Pd1/TiO2-EG and Pd1/TiO2-cal, different amount of dilute CO was introduced to the bottle before styrene hydrogenation was carried out. The effect of CO on the colloid Pd NSs and Pd NCs was evaluated by soaking them in 5% CO/Ar in EtOH for 15 min and then flushing with H2 for 15 min, then styrene was introduced. The mass specific activity was calculated based on the total amount of Pd in the corresponding catalyst as a conversion level lower than 20%.

For the gas-powder phase ethylene hydrogenation. 2 mg 0.5 wt% Pd/Al2O3 diluted with 20 mg Al2O3 was loaded in a glass tube (8 mm diameter). The sample was reduced at 100 °C with 30 mL/min H2 for 30 min before cooled down to 30 °C. Then, the catalytic hydrogenation was carried out with the feed gas flow of 25 mL/min C2H4 and 75 mL/min H2, the conversion of C2H4 was determined by on-line GC. For CO adsorption, the catalyst was treated with 5% CO/Ar (30 mL/min) at 30 °C for 15 min, then flushed with the feed gas at 60 °C for 30 min before cooled down to 30 °C. For CO desorption, the catalyst was treated with feed gas at 150 °C for 30 min, then cooled down to 30 °C again.

The production of H2O2 was performed following the procedure reported in the literature.[6] Typically, 100 mg 0.2 wt% Pd3CO/Al2O3 were dispersed in 10 mL TOP and then 2.4 g 2-eAQ diluted in 10 mL toluene were added. The hydrogenation of 2-eAQ was performed under 0.2 MPa H2 at 30 °C. 1 mL of the solution was taken out and introduced into 10 mL of 1 M H3PO4 every 30 min, the obtained liquid was stirred in air for 30 min at room temperature. 5 mL of 20 % H2SO4 was added before the amount of H2O2 was titrated by 0.02 M KMnO4.
Characterizations

Transmission Electron Microscope (TEM) characterization

For TEM characterization, the samples were dispersed in EtOH and dropping onto 300-mesh carbon-coated copper grids and the solvent was evaporated in air subsequently. TEM characterization and energy dispersive X-ray spectroscopy (EDX) was carried out on a TECNAI F30 transmission electron microscope operating at 300 kV.

HAADF-STEM characterizations

High-resolution transmission electron micrographs (HRTEM) were performed on JEOL 200F transmission electron microscope operated at 200 keV. Both annular-bright-field (ABF) and high-angle annular-dark-field (HAADF) images were acquired with the illumination semi-angle of 25 mrad and probe current of 100 pA. The dwell time for image acquisition was set at 10 micro second per pixel to ensure desirable signal to noise ratio. The attainable spatial resolution of microscope was 78 pm with a probe spherical-aberration corrector. The collection angles for the ABF and HAADF images were fixed at 12-25 mrad and 90-250 mrad, respectively.

Powder X-ray diffraction (XRD) characterizations

The XRD experiments were carried out on Rigaku Ultima IV using Cu Kα radiation. The operation voltage was set at 40 kV, the current was set at 30 mA. The scan speed was set at 10 °/min

Zeta-potential characterizations

Zeta-potential experiments were tested on Nano-ZS zetasizer (Malvern Instruments, UK). 2.0 mg TiO₂ was dispersed into 10 mL water with varied pH value (2 – 12) and 3 times tests were repeated for every pH point.

N₂ adsorption and desorption experiments.

The BET (Brunauer-Emmett-Teller) surface area of oxides was measured by N₂ adsorption-desorption experiments on Micromeritics ASAP2020 at liquid nitrogen temperature. The samples were degassed at 200 °C for 3h.

Temperature Programmed Desorption-mass spectrometry (TPD-MS) characterization

The TPD-MS experiment was performed on a home-made TPD-TOF analyzer. 3 mg of 1 wt% Pd₂CO/TiO₂ was added into a small tube which will be heated by the surrounded heating coil. A K-
type thermocouple was put inside the sample tube, and insulated from samples to measure the
temperature. The heating coil was powered by a precise electric source, and adjusted at interval of 10
mV. The temperature of sample tube was ramping from room temperature to 450 °C with a rate of 5
K/min. The desorbed spices were ionized by a UV lamp at position very close to the sample tube, with
phonon energy of 10.6 eV, and then transferred to TOF analyzer by an ion optical system. The TOF
analyzer had a resolution of more than 5000, and the sensitivity of ppb level. All those steps were
processed in high vacuum of about 3×10⁻⁵ Pa. The mass spectrum and sample temperature were
acquired and recorded every second. Each spectrum was an accumulation of 10000 spectra gathered at
interval of 100 µs.

X-ray absorption spectroscopy (XAS) measurements and data processing
The X-ray absorption experiments were carried out at the XAS station (BL14W1) of the Shanghai
Synchrotron Radiation Facility (SSRF). The electron storage ring was operated at 3.5 GeV. Si(311)
double-crystal was used as the monochromator, and the data was collected using solid-state detector
under ambient conditions. The beam size was limited by the horizontal and vertical slits with the area
of 1 ×4 mm² during XAS measurements. The X-ray absorption of Pd foil at Pd K-edge of was
measured for energy calibration. All the samples were sealed in N₂ atmosphere before taking to the
station, and the data was recorded under air atmosphere. The obtained XAFS data was processed in
Athena (version 0.9.25) for background, pre-edge line and post-edge line calibrations. Then Fourier
transformed fitting was carried out in Artemis (version 0.9.25).[7] The k² weighting, k-range of ~3 -
12 Å⁻¹ and R range of 1-3 Å were used. The model of bulk Pd and PdO were used to calculate the
simulated scattering paths. The coordination number of Pd-Pd for Pd foil was fixed at 12 to determine
the amplitude reduction factor (S₀²=0.87). Then the four parameters, coordination number, bond
length, Debye-Waller factor and E₀ shift (CN, R, σ², ΔE₀) were fitted without anyone was fixed,
constrained, or correlated.

Pd dispersion determination
Pd dispersion was measured by CO titration carried out on a Micromeritics Auto Chem II 2920
chemical adsorption instrument equipped with a TCD detector. The samples were reduced at 100 °C
in H₂ for 1h before cooled down to 50 °C. Then flashed with He for 1h and CO titration was
performed with 5% CO/He. The Pd dispersion was calculated based on the consumed CO molecules
and ratio between Pd and CO was 2:1.
Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS was carried out on ThermoFisher IS50 Fourier Transform Infrared spectrometer equipped with MCT detector. For Pd_{2}CO/TiO_{2}, the spectrum was recorded under ambient condition, and KBr powder was used as the background. For 0.5 wt% Pd/Al_{2}O_{3}, the sample were loaded in an in-situ chamber (Harrick) and treated with 5% H_{2}/Ar (30 mL/min) at 100 °C for 1 h, then cooled down to room temperature and the background spectrum was collected before treated with 5% CO/Ar for 20 min. The chamber was flushed with Ar for 20 min. The chamber was heated up to 30, 60 and 100 °C with 25 mL/min C_{2}H_{4} and 75 mL/min H_{2} for ~10 min, then cooled down to room temperature and flushed with Ar for 10 min before recording. For Pd_{2}/TiO_{2}-cal, after flushing with Ar and recording the background spectrum, the sample was treated with 5% CO/Ar for 20 min and then flushing with Ar before recording the spectrum.

Electron Paramagnetic Resonance (EPR)

X-band EPR spectra were recorded by a Bruker EMX-10/12 microspectrometer at 90 K, with an operation frequency of 9.45 GHz and a microwave power of 19.9 mW. In a typical measurement, 50 mg sample was used.

Temperature programed desorption

AutoChem 2920 II equipped with TCD detector was used to perform these measurements. For H_{2}-TPD, 0.5 wt% Pd/Al_{2}O_{3} was first reduced with 5% H_{2}/Ar at 100 °C for 1h after calcined in static air. The sample was pretreated under 200 °C with Ar flow for 1 h before cooling down to 50 °C. The sample was further treated with 5% H_{2}/Ar and Ar for 30 min before the recording, respectively. CO-TPD was performed following a similar procedure except 5% CO/Ar was applied after cooling down to 50 °C. For the H_{2}-TPD with pre-adsorbed CO, the sample treated with 5% CO/Ar and 5% H_{2}/Ar for 30 min stepwise before flushing with Ar and recording.

Computational details

Spin-polarized calculations were carried out with the Vienna ab initio simulation package (VASP).[8, 9] The electron exchange and correlation were treated with the generalized gradient approximation using PBE functional.[10] The valence electrons were described by plane wave basis sets with a cut-off energy of 400 eV, and the core electrons were replaced by the projector augmented wave pseudopotential.[11, 12] Geometries of minima and transition states (TSs) were converged to a
residual force smaller than 0.03 eV/Å. The TSs were determined using the nudged elastic band (NEB) approach,[13] with a subsequent quasi-Newton optimization to refine the TS’ structures and energies. All the local minima and TSs were verified by vibrational frequency calculations. For Pdₙ clusters (n=2, 3, 4, 7, 13, 55, 147), the geometry structures with the highest symmetry were chosen,[14, 15] as shown in Figure 1. To avoid image interaction, the shortest distances between the image clusters were set to be more than 10 Å. In these cases, the Gamma point only calculations were performed. For the Pd(111) and Pd(100) surfaces, (3×4) supercells with five atomic layers were used. The vacuum regions between the slabs were set to 15 Å, and the k-points sampling was generated following the Monkhorst-Pack procedure with a 3×3×1 mesh. For the Pd surface models, the bottom two layers were fixed at a bulk truncated position, while the top three layers and the adsorbates were allowed to be fully relaxed.

For the practical use, the Pd clusters would be loaded on the oxide surfaces, such as anatase TiO₂(010). Computationally, to model the anatase TiO₂(010) surface, a five-layer p(1×4) slab was used and the utmost surface was fully hydroxylated (Figure S1). Since GGA was not able to correctly describe the electronic structure of Ti⁴⁺, we adopted the GGA+U approximation with the Dudarev ‘‘+U’’ term with a U-J value of 4.2 eV for the d electrons of Ti atoms.[16] The binding energies of the Pdₙ and PdₙCO cluster on TiO₂(010) surface were calculated via \( \Delta E_{\text{bind}} = E_{\text{cluster/TiO₂(010)}} - E_{\text{cluster}} - E_{\text{TiO₂(010)}} \), where \( E_{\text{cluster/TiO₂(010)}} \) denoted the energies of supported clusters, \( E_{\text{cluster}} \) represented the energies of free clusters and \( E_{\text{TiO₂(010)}} \) stood for the energy of TiO₂(010) surface. DFT calculations showed that not only the Pdₙ clusters but also PdₙCO clusters (n=2-7) could strongly interact with the surface oxygen atoms over TiO₂(010) with the \( \Delta E_{\text{bind}} \) of -1.64 eV~ -2.95 eV.

The adsorption energy (\( \Delta E_{2\text{H}} \)) were defined as \( \Delta E_{2\text{H}} = E_{2\text{H/surf}} - E_{\text{H₂}} - E_{\text{surf}} \). Here \( E_{2\text{H/surf}} \), \( E_{\text{H₂}} \), and \( E_{\text{surf}} \) represented the energies of the surfaces with two adsorbed H atoms, molecular H₂ and the clean surface, respectively. The reaction energy (\( \Delta E \)) for styrene hydrogenation was defined as \( \Delta E = E_{\text{ads/surf}} - E_{\text{PhCHCH₂}} - E_{2\text{H/surf}} \), where the sum of the energies of H preadsorbed surface (\( E_{2\text{H/surf}} \)) and molecular styrene (\( E_{\text{PhCHCH₂}} \)) was used as energy reference. The activation barrier for each elementary step was defined as \( \Delta E_a = E_{\text{TS}} - E_R \), where \( E_R \) and \( E_{\text{TS}} \) were the energies of the reaction intermediate and the corresponding transition state, respectively.
Figure S1. Top view (left) and side view (right) of the optimized structure of anatase TiO$_2$(010) surface. The light gray, red and white balls represented Ti, O and H atom, respectively.

Figure S2. Top view (top) and side view (bottom) of the optimized structure of (a) Pd$_2$/TiO$_2$, (b) Pd$_2$CO/TiO$_2$, (c) Pd$_3$/TiO$_2$, and (d) Pd$_3$CO/TiO$_2$. The blue, dark gray, red and white balls represented Pd, C, O and H atom, respectively.
**Figure S3.** Top view (top) and side view (bottom) of the optimized structure of (a) Pd₄/TiO₂, (b) Pd₇/TiO₂. The blue, dark gray, red and white balls represented Pd, C, O and H atom, respectively.

**Figure S4.** Top view (top) and side view (bottom) of the TS structures along the reaction path for (a) TS1 on Pd₂/TiO₂, (b)TS1 and (c)TS2 on Pd₂CO/TiO₂, respectively. The blue, dark gray, red and white balls represented Pd, C, O and H atom, respectively.
Figure S5. Reaction pathway for styrene hydrogenation on Pd₃/TiO₂ (black line) and Pd₃CO/TiO₂ (red line) surface. The optimized structures of key intermediates were illustrated in the dash line frame. The blue, red, dark gray and white balls represented Pd, O, C and H atom, respectively.
Figure S6. Top view (top) and side view (bottom) of the TS structures along the reaction path for (a) TS1 and (b) TS2 on Pd$_3$/TiO$_2$, (c) TS1 and (d) TS2 on Pd$_3$CO/TiO$_2$. The blue, dark gray, red and white balls represented Pd, C, O and H atom, respectively.

Figure S7. The optimized structures of (a, c) 2H adsorbed and (b, d) co-adsorption of CO and 2H neighbor to CO over (a, b) Pd(100) surface and (c, d) Pd(111) surface, respectively. The blue, dark gray, red and white balls represented Pd, C, O and H atom, respectively.
Figure S8. The optimized structures of Pd clusters (Pd₂, Pd₃, Pd₄, Pd₇, Pd₁₃, Pd₅₅ and Pd₁₄₇) with co-adsorption of CO and 2H. The blue, red, dark gray and white balls represented Pd, O, C and H atom, respectively.

Figure S9. The optimized structures of (a, c) 2H adsorbed and (b, d) co-adsorption of CO and 2H neighbor to CO adsorbed Pd₄/TiO₂ and Pd₇/TiO₂, respectively. The blue, red, dark gray and white balls represented O, C and H atom, respectively.
Figure S10. Top view (top) and side view (bottom) of the TS structures for H$_2$ dissociation on (a) Pd$_2$CO/TiO$_2$ and (b) Pd$_3$CO/TiO$_2$. The blue, dark gray, red and white balls represented Pd, C, O and H atom.
Figure S11. Top view (top) and side view (bottom) of styrene adsorbed on (a) Pd$_2$CO/TiO$_2$ and (b) Pd$_2$/TiO$_2$, and the corresponding adsorption energy, respectively. The blue, dark gray, red and white balls represented Pd, C, O, and H atom, respectively.
Figure S12. The TEM images of TiO$_2$-EG (a, b), and TiO$_2$ (c & d). (e) The HRTEM of TiO$_2$ showed the exposed (010) facet, which was consistent with the reported work.[2, 3] (f) The top view of anatase (010) facet.

Figure S13. (a) The N$_2$ adsorption/desorption isotherm of the TiO$_2$ at 77K, the sample was degassed at 200 °C for 3 h. (b) The XRD patterns of support before and after Pd$_2$CO cluster deposition. No change was observed after deposition. The XRD pattern revealed the anatase phase of the support.
Figure S14. (a) The zeta-potential of the TiO₂ dispersed in water with different pH values. The isoelectronic point was about 6, therefore, the negatively charged \([\text{Pd}_2(\mu-\text{CO})_2\text{Cl}_4]^{2-}\), would be easily adsorbed. (b) Thermogravimetric analysis (TGA) of TiO₂. The ~2.5% weight loss was ascribed to the dehydration of surface adsorbed H₂O and the surface –OH groups, which could react with \([\text{Pd}_2(\mu-\text{CO})_2\text{Cl}_4]^{2-}\).

Figure S15. The X-band EPR spectrum of the as-obtained TiO₂ and Pd₂CO/TiO₂. No apparent change was observed before and after deposition of Pd₂CO cluster. The small and sharp signal with a g tensor about 2.00 was related to the trapped interior electrons or Ti³⁺.[17, 18] No significant surface vacancies were observed.
**Figure S16.** Low magnification HAADF-STEM image and corresponding EDX elements mapping of Pd₂CO/TiO₂, indicating that palladium was well dispersed on TiO₂.

**Figure S17.** HRTEM images of Pd₂CO/TiO₂. No Pd nanoparticle was figured out on TiO₂.
Figure S18. UV-vis spectrum of the Pd$_2$CO cluster (i.e. H$_2$[Pd$_2$(μ-CO)$_2$Cl$_4$] in THF) and TiO$_2$ powder before and after loading the Pd$_2$CO cluster. The UV-vis spectrum of the Pd$_2$CO cluster with wavelength below 350 nm was related to the metal-ligand electron transfer. Unfortunately, this feature was overlapped with the spectrum of TiO$_2$ at this region (the presence of CO was verified by the DRIFTS in Figure S23). The peaks with wavelength over 400 nm were related to the metal-metal d-d electron transfer.[19, 20] The wavelength of this feature is related to the nuclearity/size of the cluster and the distance between Pd atoms. The predominant peak at ~420 nm indicated that the small Pd clusters Pd$_n$CO with $n$ close to 2-3 were dominated in the as-obtained catalyst.[21, 22]

Figure S19. HAADF-STEM images of Pd$_2$CO/TiO$_2$, the white squire indicates the Pd cluster, and white circle for the single-atom Pd.
Figure S20. (a) The unit cell of (PPh₄)₂[Pd₂(μ-CO)₂Cl₄]. (b) Bond lengths (Å) in [Pd₂(μ-CO)₂Cl₄]²⁻.

Figure S21. The Pd K-edge (a) XAS and (b) XANES of Pd foil, PdO, (PPh₄)₂[Pd₂(μ-CO)₂Cl₄] crystal and Pd₂CO/TiO₂.
Figure S22. EXAFS (a-c) R-space and (d-f) k-space fitting of (a, d) Pd foil, (b, e) (PPh₄)₂[Pd₂(μ-CO)₂Cl₄] and (c, f) Pd₂CO/TiO₂.

Figure S23. The recorded releasing of CO₂ upon adding TiO₂ to the solution of H₂[Pd₂(μ-CO)₂Cl₄]. The control experiment was recorded before TiO₂ adding.
Figure S24. DRIFTS of the as-obtained Pd$_2$CO/TiO$_2$. The predominate bridge-site CO at ~ 1920 cm$^{-1}$ was consistent with that in the precursor.[5]

Figure S25. TPD-MS signal of CO recorded for blank TiO$_2$ and the as-obtained Pd$_2$CO/TiO$_2$. The desorption of CO over 300 °C implied that the adsorption of inherent CO in Pd$_2$CO/TiO$_2$ was very strong.
Figure S26. *In-situ* DRIFTS for Pd\textsubscript{2}CO/TiO\textsubscript{2} in the condition of catalytic ethylene hydrogenation. It showed that the adsorbed CO molecules were preserved during ethylene hydrogenation.

Figure S27. The calculated mass-specific activity and TOF of Pd nanosheets (Pd NSs), Pd nanocubes (Pd NCs), commercial Pd/C, Pd\textsubscript{1}/TiO\textsubscript{2}-EG (Pd\textsubscript{1}), Pd\textsubscript{2}CO/TiO\textsubscript{2} (Pd\textsubscript{2}CO), Pd\textsubscript{1}/TiO\textsubscript{2}-cal (Pd\textsubscript{1}-cal) and Pd\textsubscript{2}/TiO\textsubscript{2}-cal (Pd\textsubscript{2}-cal) for the styrene hydrogenation carried out at 30 °C and 0.1 MPa H\textsubscript{2}. The Pd dispersion was measured by CO titration and calculated with a Pd/CO ratio of 2. The Pd dispersions of Pd NSs, Pd NCs, and Pd/C were 23.7%, 10.8% and 18.1%. The Pd dispersions of Pd\textsubscript{2}CO, Pd\textsubscript{1}-cal and Pd\textsubscript{2}-cal were hard to be measured due to the low mass loading, the dispersions of Pd on these catalysts were estimated to be close to 1. The calculated activity and TOF demonstrated that the supported Pd\textsubscript{2}CO clusters were as active as the surface Pd in large NPs. More importantly, the high Pd dispersion made the supported Pd\textsubscript{2}CO exhibit 4-6 times higher mass-specific activity.
**Figure S28.** Kinetic isotopic experiment for Pd$_2$CO/TiO$_2$. The hydrogenation of styrene was carried out in H$_2$ or D$_2$ atmosphere. The k$_{H}$/k$_{D}$ was calculated to be 2.02, which was much lower than that of the Pd$_1$/TiO$_2$-EG (k$_{H}$/k$_{D}$ = 5.75).[2]

**Figure S29.** EXAFS (a) R-space and (b) k-space fitting of Pd$_2$CO/TiO$_2$ after styrene hydrogenation.
Figure S30. Catalytic performance of Pd₂CO/TiO₂ in five test rounds. Catalysis condition: 0.1 MPa H₂, 30 °C, S/C = 50,000, 10 mL EtOH, and 0.55 mL styrene (5 mmol) was introduced in every test round.

Figure S31. DRIFTS of Pd₂/TiO₂-cal before and after treated with CO.
Figure S32. XAS (a), XANES, (b) EXAFS R-space (c, d) and k-space (e, f) fitting of Pd\textsubscript{2}/TiO\textsubscript{2}-cal after treated with H\textsubscript{2}, and further with CO.

Figure S33. (a) Catalytic styrene hydrogenation performance of Pd\textsubscript{2}/TiO\textsubscript{2}-cal (S/C=50,000) 30 °C, 0.1 MPa H\textsubscript{2}. (b) The Arrhenius plot for Pd\textsubscript{2}/TiO\textsubscript{2}-cal catalyzed styrene hydrogenation at 20, 30, 40 and 50 °C.
Figure S34. (a) Catalytic styrene hydrogenation performance of Pd₁/TiO₂-cal (S/C=2,000) with different amount of CO introduced. (b) Pd Cube (S/C = 10,000) with or without CO pre-treatment. Condition: 30 °C, 0.1 MPa H₂.

Figure S35. (a) The XRD pattern and (b) N₂ adsorption-desorption isotherm profile of γ-Al₂O₃.
Figure S36. TEM images of 0.5 wt% Pd/Al₂O₃. No obvious Pd NP was figured out.

Figure S37. H₂ TPD (blue), CO TPD (yellow), and H₂ TPD with pre-adsorbed CO (red) over 0.5 wt% Pd/Al₂O₃. The H₂ TPD for blank Al₂O₃ (black) was also shown for comparison. The shoulder peak with desorption temperature of 175 °C in H₂ TPD was the desorption of H₂ from Pd, the higher-temperature desorption should be related to the dehydration of the support. For the CO TPD, despite the desorption of CO was hard to discriminate from the background, no desorption feature was observed below 150 °C. Similar to the following result of DRIFTS (almost no change was observed during temperature ramp from 60 °C to 100 °C), the CO TPD indicated the strong binding of CO on Pd cluster. More importantly, the H₂ desorption temperature decreased to about 120 °C when the sample was treated with CO first before H₂-TPD, which unambiguously revealed that the coordination of CO reduced the binding energy of H₂ over small Pd clusters.
Figure S38. The *in-situ* DRIFTS for 0.5 wt% Pd/Al$_2$O$_3$ with pre-adsorbed CO in the catalytic ethylene hydrogenation condition at different temperature. The presence of bridge and hollow site adsorbed CO (1750 - 1950 cm$^{-1}$) suggested the formation of Pd-Pd bond after the pre-treatment.

Figure S39. TEM images of 0.2 wt% Pd$_2$CO/Al$_2$O$_3$. 
Figure S40. EXAFS (a) R-space and (b) k-space fitting of Pd$_2$CO/Al$_2$O$_3$.

Figure S41. Styrene hydrogenation catalyzed by 0.2 wt% Pd$_2$CO/Al$_2$O$_3$. 
Table S1. Adsorption energies of 2H ($\Delta E_{2H}$, eV) for Pd$_n$ (n=2, 3, 4, 7) clusters on TiO$_2$(010) surface in the absence or presence of CO.

| Structure  | $\Delta E_{2H}$ (eV) CO free | $\Delta E_{2H}$ (eV) CO preadsorption |
|------------|-----------------------------|--------------------------------------|
| Pd$_2$/TiO$_2$ | -2.80                      | -0.17                                |
| Pd$_3$/TiO$_2$ | -1.95                      | -0.58                                |
| Pd$_4$/TiO$_2$ | -1.79                      | -1.21                                |
| Pd$_7$/TiO$_2$ | -1.41                      | -1.08                                |
**Table S2.** The Pd-Pd distances (unit: Å) of Pd\(_n\) (n=2, 3, 4, 7) and Pd\(_n\)CO clusters on TiO\(_2\)(010) surface (M/TiO\(_2\)) and the bare ones (M).

| System      | Pd\(_2\) | Pd\(_2\)CO | Pd\(_3\) | Pd\(_3\)CO | Pd\(_4\) | Pd\(_4\)CO | Pd\(_7\) | Pd\(_7\)CO |
|-------------|-----------|-------------|----------|-------------|----------|-------------|----------|------------|
| M           | 2.481     | 2.610       | 2.523    | 2.678       | 2.609    | 2.754       | 2.695    | 2.740      |
|             |           |             | 2.523    | 2.676       | 2.609    | 2.768       | 2.695    | 2.744      |
|             |           |             | 2.523    | 2.677       | 2.609    | 2.669       | 2.695    | 2.756      |
|             |           |             |         |             | 2.602    | 2.665       | 2.695    | 2.757      |
|             |           |             |         |             | 2.600    | 2.758       | 2.650    | 2.759      |
| M/TiO\(_2\)| 2.556     | 2.725       | 2.474    | 2.638       | 2.532    | 2.710       | 2.622    | 2.710      |
|             | 2.501     | 2.782       | 2.518    | 2.648       | 2.512    | 2.737       | 2.780    | 2.737      |
|             | 2.580     | 2.782       | 2.515    | 2.689       |         |             | 2.696    | 2.747      |
|             |           |             |         |             |         |             | 2.673    | 2.756      |
|             |           |             |         |             |         |             | 2.628    | 2.770      |
|             |           |             |         |             |         |             | 2.846    | 2.783      |
|             |           |             |         |             |         |             | 2.679    | 2.799      |
|             |           |             |         |             |         |             | 2.726    | 2.821      |
|             |           |             |         |             |         |             | 2.695    | 2.833      |
Table S3. The total magnetizations (unit: a.u.) of Pd in Pd\textsubscript{n} (n=2, 3, 4, 7) and Pd\textsubscript{n}CO clusters on TiO\textsubscript{2}(010) surface (M/TiO\textsubscript{2}) and the bare ones (M).

| Magnetization | Pd\textsubscript{2} | Pd\textsubscript{2}CO | Pd\textsubscript{3} | Pd\textsubscript{3}CO | Pd\textsubscript{4} | Pd\textsubscript{4}CO | Pd\textsubscript{7} | Pd\textsubscript{7}CO |
|---------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| M             | 2.00                 | 0.12                 | 2.00                 | 0.07                 | 2.00                 | -0.14                | 2.00                 | 0.02                 |
| M/TiO\textsubscript{2} | 1.96                 | 0.07                 | -0.06                | 0.00                 | 0.00                 | 0.22                 | 3.19                 | 0.00                 |

Table S4. The average bader charges (unit: a.u.) of Pd in Pd\textsubscript{n} (n=2, 3, 4, 7) and Pd\textsubscript{n}CO clusters on TiO\textsubscript{2}(010) surface (M/TiO\textsubscript{2}).

| System     | Average Bader charge |
|------------|----------------------|
|            | CO free   | CO preadsorption    |
| Pd\textsubscript{2}/TiO\textsubscript{2} | -0.06     | 0.15                 |
| Pd\textsubscript{3}/TiO\textsubscript{2} | 0.05      | 0.14                 |
| Pd\textsubscript{4}/TiO\textsubscript{2} | 0.04      | 0.11                 |
| Pd\textsubscript{7}/TiO\textsubscript{2} | 0.06      | 0.09                 |
**Table S5.** Crystal data and structure refinement for \((\text{Ph}_4\text{P})_2[\text{Pd}_2(\mu-\text{CO})_2\text{Cl}_4]\).

| Property                                      | Value                            |
|-----------------------------------------------|----------------------------------|
| Empirical formula                             | \(\text{C}_{25}\text{H}_{20}\text{Cl}_2\text{OPd} \) |
| Formula weight                                | 544.68                           |
| Temperature                                   | 100 K                            |
| Wavelength                                    | 1.54184 Å                        |
| Crystal system, space group                   | Triclinic, \(P\)-1              |
| Unit cell dimensions                          | \(a = 9.4475(7) \) Å, \(alpha = 67.334(6)°\) |
|                                              | \(b = 10.2295(8) \) Å, \(beta = 80.486(6)°\) |
|                                              | \(c = 13.1863(8) \) Å, \(gamma = 71.144(7)°\) |
| Volume                                        | 1111.62(15) Å \(^3\)            |
| \(Z\), Calculated density                    | 2, 1.627 g/cm\(^3\)             |
| Absorption coefficient                        | 9.738 mm\(^1\)                  |
| \(F(000)\)                                    | 546                              |
| Crystal size                                  | 0.30x0.10x0.10mm\(^3\)          |
| Theta range for data collection               | 3.636 to 65.563 deg.            |
| Limiting indices                              | -11\(<=h<=11\), -12\(<=k<=11\), -14\(<=l<=15\) |
| Reflections collected / unique                | 3633 / 3729 \([R_{int} = 0.0240]\) |
| Completeness to theta = \(61.08\)             | 99.85 %                          |
| Refinement method                             | Full-matrix least-squares on \(F^2\) |
| Data / restraints / parameters                 | 3729 / 0 / 271                   |
| Goodness-of-fit on \(F^2\)                    | 1.059                            |
| Final R indices \([I>2\sigma(I)]\)            | \(R_1 = 0.0266, wR_2 = 0.0726\) |
| R indices (all data)                          | \(R_1 = 0.0271, wR_2 = 0.0730\) |
| Largest diff. peak and hole                    | 0.615 and -0.791 e. Å\(^{-3}\)  |
Table S6. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for (Ph4P)2[Pd2(μ-CO)2Cl4]: U(eq) was defined as one-third of the trace of the orthogonalized U_{ij} tensor.

|  | x       | y       | z       | U(eq)   |
|---|---------|---------|---------|---------|
| Pd1 | 0.07772(2) | 0.97379(2) | 0.41215(2) | 0.01279(9) |
| Cl1 | 0.03978(7)  | 1.08967(7)  | 0.22060(5)  | 0.02006(15) |
| Cl2 | 0.29993(7)  | 0.79577(7)  | 0.38537(5)  | 0.01989(15) |
| P1  | 0.62454(7)  | 0.59105(7)  | 0.74186(5)  | 0.01223(14) |
| O1  | 0.2264(2)   | 0.8209(2)   | 0.62233(16) | 0.0309(5)   |
| C25 | 0.4328(3)   | 0.5202(3)   | 0.6443(2)   | 0.0156(5)   |
| C14 | 0.7722(3)   | 0.4504(3)   | 0.8261(2)   | 0.0139(5)   |
| C7  | 0.6243(3)   | 0.8237(3)   | 0.7978(2)   | 0.0167(5)   |
| C9  | 0.6031(3)   | 0.7904(3)   | 0.5289(2)   | 0.0168(5)   |
| C20 | 0.4899(3)   | 0.5026(3)   | 0.7410(2)   | 0.0136(5)   |
| C17 | 0.9998(3)   | 0.2248(3)   | 0.9501(2)   | 0.0172(5)   |
| C19 | 0.8288(3)   | 0.3177(3)   | 0.8060(2)   | 0.0166(5)   |
| C15 | 0.8293(3)   | 0.4693(3)   | 0.9083(2)   | 0.0161(5)   |
| C2  | 0.5382(3)   | 0.7345(3)   | 0.7988(2)   | 0.0147(5)   |
| C18 | 0.9441(3)   | 0.2057(3)   | 0.8680(2)   | 0.0171(5)   |
| C10 | 0.6592(3)   | 0.8595(3)   | 0.4251(2)   | 0.0195(6)   |
| C24 | 0.3229(3)   | 0.4539(3)   | 0.6504(2)   | 0.0188(6)   |
| C5  | 0.4190(3)   | 0.9519(3)   | 0.8900(2)   | 0.0200(6)   |
| C22 | 0.3283(3)   | 0.3534(3)   | 0.8477(2)   | 0.0207(6)   |
| C13 | 0.8531(3)   | 0.6321(3)   | 0.5798(2)   | 0.0160(5)   |
| C4  | 0.3336(3)   | 0.8660(3)   | 0.8882(2)   | 0.0196(6)   |
| C11 | 0.8121(3)   | 0.8172(3)   | 0.3988(2)   | 0.0186(6)   |
| C8  | 0.6996(3)   | 0.6757(3)   | 0.6063(2)   | 0.0148(5)   |
| C16 | 0.9425(3)   | 0.3559(3)   | 0.9710(2)   | 0.0183(5)   |
| C6  | 0.5638(3)   | 0.9324(3)   | 0.8437(2)   | 0.0199(6)   |
| C3  | 0.3923(3)   | 0.7562(3)   | 0.8425(2)   | 0.0161(5)   |
| C21 | 0.4389(3)   | 0.4171(3)   | 0.8432(2)   | 0.0179(5)   |
| C23 | 0.2700(3)   | 0.3721(3)   | 0.7515(2)   | 0.0207(6)   |
| C12 | 0.9080(3)   | 0.7038(3)   | 0.4757(2)   | 0.0194(6)   |
| C1  | 0.1256(3)   | 0.8933(3)   | 0.5692(2)   | 0.0207(6)   |
| Sample                      | Shell      | C.N. | R (Å)     | $\sigma^2 \times 10^3 (\text{Å}^2)$ | $E_0$ shift (eV) | R-factor |
|-----------------------------|------------|------|-----------|-------------------------------------|------------------|----------|
| Pd foil                    | Pd-Pd      | 12*  | 2.74±0.02 | 5.4±0.2                             | -5.1±0.3         | 0.003    |
| Pd$_2$CO cluster           | Pd-(CO)   | 2.0±0.8 | 1.96±0.04 | 7.1±6.0                             | -4.8±6.1         | 0.008    |
|                             | Pd-Cl      | 2.0±0.7 | 2.38±0.01 | 6.1±2.5                             | 4.0±1.8          |          |
|                             | Pd-Pd      | 1.1±0.6 | 2.69±0.02 | 3.7±3.3                             | 7.6±4.4          |          |
| Pd$_2$CO/TiO$_2$            | Pd-O       | 2.4±0.6 | 2.03±0.04 | 4.8±3.7                             | 6.5±3.8          | 0.007    |
|                             | Pd-Pd      | 1.2±0.4 | 2.76±0.03 | 5.8±5.5                             | 3.7±5.6          |          |
| Pd$_2$CO/TiO$_2$-aft       | Pd-O       | 1.8±0.5 | 2.02±0.07 | 7.2±5.4                             | 4.6±6.1          | 0.005    |
|                             | Pd-Pd      | 2.8±1.0 | 2.76±0.02 | 7.3±2.6                             | 4.3±2.8          |          |
| Pd$_2$/TiO$_2$-cal+H$_2$    | Pd-O       | 1.2±0.2 | 2.01±0.02 | 2.1±1.1                             | 3.0±2.1          | 0.005    |
|                             | Pd-Pd      | 4.3±0.5 | 2.76±0.01 | 7.1±0.9                             | -4.2±0.8         |          |
| Pd$_2$/TiO$_2$-cal+H$_2$+CO | Pd-O       | 1.1±0.2 | 1.99±0.01 | 1.9±0.8                             | 3.1±2.0          | 0.005    |
|                             | Pd-Pd      | 4.3±0.4 | 2.76±0.01 | 6.5±0.7                             | -4.4±0.7         |          |
| Pd$_2$CO/Al$_2$O$_3$        | Pd-O       | 2.6±0.7 | 2.02±0.03 | 3.7±3.2                             | 5.8±2.8          | 0.005    |
|                             | Pd-Pd      | 1.3±1.0 | 2.77±0.03 | 6.4±5.2                             | 4.9±4.8          |          |
**Table S8.** Production efficiency of the H$_2$O$_2$ following the 2-eAQ hydrogenation route catalyzed by different Pd catalysts reported.

| Cat.             | Pd loading (wt%) | Temp. (℃) | H$_2$ Press. (bar) | Yield (%) | Rate (gH$_2$O$_2$/gPd/h) | Ref. |
|------------------|------------------|------------|--------------------|-----------|--------------------------|------|
| Pd/Al$_2$O$_3$   | 1.0              | 20         | \                 | 93        | 63.24                    | [23] |
| Pd/Al$_2$O$_3$   | 0.50             | 40         | \                 | 96.4      | 32.9                     | [24] |
| Pd/SiO$_2$       | 1.0              | 50         | 6.8                | 50        | 1280                     | [25] |
| Pd/Al$_2$O$_3$   | 0.2              | 60         | 1.0                | 38.2      | 442.7                    | [26] |
| PdIr/Al$_2$O$_3$ | 0.75             | 50         | 3.0                | 92.1      | 2050                     | [27] |
| Pd/Al$_2$O$_3$   | 1.0              | 50         | 3.0                | 61        | 1110                     | [27] |
| Pd/glass         | 2.40             | 50         | 3.0                | 60        | 3800                     | [28] |
| Pd/glass         | 0.32             | 70         | 3.5                | 35.5      | 567.5                    | [29] |
| Pd/Al$_2$O$_3$   | 1.0              | 80         | 3.0                | 95.7      | 3610                     | [30] |
| Pd$_2$CO/Al$_2$O$_3$ | 0.20          | 30         | 2                  | 93        | 1054                     | This work |
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