

Electronic Supplementary Information

Oxidative strong metal-support interactions of supported platinum-group metal catalysts

Hailian Tang,^{†, a, b, c} Yang Su^{†, a} Yalin Guo,^{a, d} Leilei Zhang,^a Tianbo Li,^{a, d} Ketao Zang,^e Fei Liu,^a Lin Li,^a Jun Luo,^e Botao Qiao,^{*, a} and Junhu Wang^{*, a, b}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^b Mössbauer Effect Data Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^c College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

^d University of Chinese Academy of Sciences, Beijing 100049, China

^e Center for Electron Microscopy, Institute for New Energy Materials and Low-Carbon Technologies, School of Materials, Tianjin University of Technology, Tianjin 300384, China

[†] These authors contributed equally to this work.

* E-mail: bqiao@dicp.ac.cn; wangjh@dicp.ac.cn;

Experimental Section:

1. Reagents.

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, 98.5%), ammonia (25 wt%), sodium hydroxide (NaOH, 98%) were purchased from Aladdin Company. Potassium tetrachloroplatinate(II) (K_2PtCl_4 , $\geq 99.9\%$) and tetramminepalladium(II) nitrate solution ($(\text{NH}_3)_4\text{Pd}(\text{NO}_3)_2$, 10 wt% in H_2O , 99.99%) were purchased from Sigma-aldrich Company. TiO_2 (P25) was provided by Evonik Degussa. ZnO nanorod was purchased from XFNANO Inc. Iodobenzene ($\text{C}_6\text{H}_5\text{I}$, $\geq 97\%$) and paraxylene (C_8H_{10} , $\geq 98.5\%$) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Phenylboronic acid ($\text{PhB}(\text{OH})_2$, 99%) was purchased from J & K Chemical Technology Co., Ltd. Potassium carbonate (K_2CO_3 , 99%), ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$, $\geq 99.5\%$) and sodium sulfate anhydrous (Na_2SO_4 , 99%) were purchased from TianDa Chemical Reagent Factory. All reagents were used as received and without further purification.

2. Synthesis of hydroxyapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, HAP).

HAP was synthesized by a chemical precipitation method.^{1, 2} 7.53 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 2.53 g $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in 80 mL distilled water, respectively, and then the pH of both of the two solutions were adjusted to 10.33 by adding 25 wt% ammonia. At room temperature ($\sim 25\text{ }^\circ\text{C}$), the two solutions were dripped into a beaker filled with 15 mL of 25 wt% ammonia with the same rate under vigorous stirring. The resultant milky like suspension was heated to $90\text{ }^\circ\text{C}$ immediately and stirred continuously for 2 h, then cooled to room temperature and aged overnight. The white precipitates were filtered, washed repeatedly with ultrapure water till neutrality, freeze-dried and calcined at $400\text{ }^\circ\text{C}$ for 5 h. Finally, the HAP support was obtained.

3. Preparation of supported catalysts.

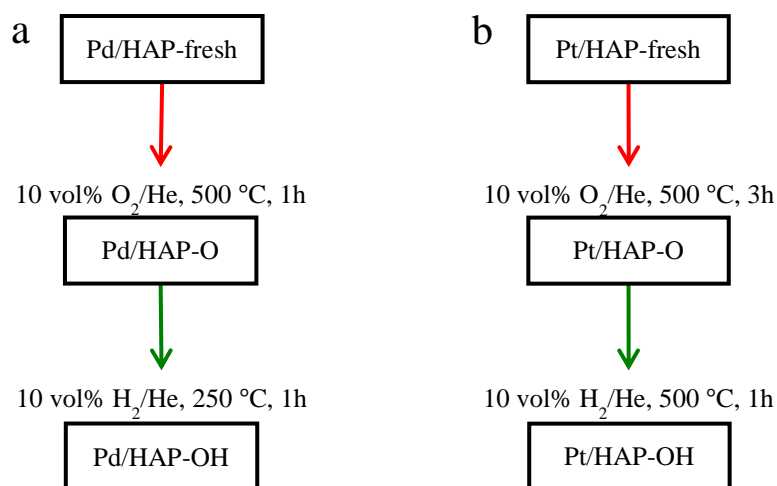
The HAP supported Pt and Pd samples were prepared by a facile adsorption method³: Typically, 2.0 g HAP was added into $(\text{NH}_3)_4\text{Pd}(\text{NO}_3)_2$ (1000 mL) or K_2PtCl_4 (300 mL) aqueous solution with an appropriate concentration at room temperature and stirred overnight. Then the precipitates were filtered

and washed with ultrapure water for several times. Finally, the samples were dried at 60 °C overnight and denoted as Pd/HAP-fresh or Pt/HAP-fresh. The actual metal loading measure by ICP-AES was 0.22 wt% for Pd/HAP and 0.61 wt% for Pt/HAP.

The fresh sample M/HAP-fresh (where M represents Pd and Pt) were further oxidized at 500 °C under 10 vol% O₂/He flow for 1 or 3 h (1 h for Pd/HAP-fresh, 3 h for Pt/HAP-fresh) and denoted as M/HAP-O. For comparison, the M/HAP-O were further reduced at 250 (for Pd/HAP-O) or 500 °C (for Pt/HAP-O) under 10 vol% H₂/He flow for 1 h and denoted as M/HAP-OH. The protocols for thermally treating of the Pd/HAP and the Pt/HAP samples and the nomenclature used here were summarized in the Scheme S1.

The TiO₂ supported Pt sample was prepared by a same method as the Pt/HAP-fresh sample and further reduced at 500 °C under 10 vol% H₂/He flow for 1 h and denoted as Pt/TiO₂-H500.

The ZnO-nanorod supported sample was prepared by a same method as the HAP supported samples and further reduced at 200 °C under 10 vol% H₂/He flow for 0.5 h and denoted as M/ZnO-fresh. Then the M/ZnO-fresh samples were further oxidized at 500 °C under 10 vol% O₂/He flow for 0.5 h and denoted as M/ZnO-O and followed by an reduction at 200 under 10 vol% H₂/He flow for 0.5 h and denoted as M/ZnO-OH.



Scheme S1. Protocol for the thermally treating of the Pd/HAP (a) and the Pt/HAP (b) samples.

4. Characterization methods.

X-ray diffraction (XRD) patterns were collected at a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a copper target (Cu K α , $\lambda = 0.15432$ nm), operating at 40 kV and 40 mA. A continuous mode was used for data collecting in the 2θ range from 10 ° to 80 ° at a scanning speed of 10 ° min⁻¹.

High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM) analyses were performed with a JEOL JEM-2100F microscope operated at 200 kV. For the samples preparation, the samples were ultrasonically dispersed in ethanol and then a drop of the solution was put onto microgrid carbon polymer supported on copper grid. After drying, it was ready for the HRTEM or STEM observation.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were acquired with a BRUKER Vertex 70 spectrometer equipped with an MCT detector and operated at a resolution of 4 cm⁻¹. All spectra were obtained at temperature of 20 °C. Before the experiment, the fresh samples in a powder form were purged for 0.5 h with He at 120 °C. After cooled to 20 °C, the background spectrum was recorded, then a mixture gas of 3 vol% CO/He (33.3 mL min⁻¹) was introduced into the reaction cell until the sample was saturated adsorbed by CO (for the Pd/HAP and Pt/HAP series samples: Pure He was introduced into the DRIFT cell to flash out the gaseous CO before the spectra were collected). (the first round of CO adsorption was obtained). Then an *in situ* oxidation at 500 °C under 10 vol% O₂/He flow for 1 or 3 h (1 h for Pd/HAP-fresh, 3 h Pt/HAP-fresh) was performed followed by He purge, background collection and a new round of CO adsorption at 20 °C. Then an *in situ* reduction at 250 or 500 °C (250 °C for Pd/HAP-O, 500 °C for Pt/HAP-O) under 10 vol% H₂/He flow for 1 h was performed followed by He purge, background collection and the 3rd round of CO adsorption at 20 °C.

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis HSi spectrometer with a monochromated Al K α X-ray source operated at 90 W and magnetic charge neutralizer. Spectral processing was performed using CasaXPS version 2.3.16, with energy referencing to adventitious carbon at 284.6 eV, and surface compositions and peak fitting derived using appropriate instrumental response factors and common line shapes for each element. For the analysis of Pt/HAP-fresh and Pt/HAP-O: the

corresponding sample was loaded into a bespoke Ta crucible held within the analysis chamber, after the system chamber was evacuated to 1×10^{-9} Torr, the analysis was performed. For the analysis of Pt/HAP-OH: the sample of Pt/HAP-O which was analyzed above was subsequently *in situ* reduced under 1×10^{-7} Torr H_2 at 500 °C for 3 h, then the system was evacuated to 1×10^{-9} Torr, and the analysis was performed.

The actual Pd loadings of Pd/HAP series catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

5. Catalytic performance test.

The CO oxidation in simulated auto-emission control test was carried out in a fixed-bed quartz reactor with length of 200 mm and inner diameter of 8 mm. A certain amount of sample (4.22 mg for the Pt/HAP-O; 5.87 mg for the Pt/TiO₂-H500) was loaded in the quartz reactor and purged with He for 30 min. The Pt loading amounts on both samples were reduced to 0.04 wt% to approach the commercial three-way-catalyst (TWC). After the system temperature increased to 400 °C, a feed gas (1.6 vol% CO + 1 vol% O₂ + 0.01 vol% propene + 0.0051 vol% toluene + 10 vol% water and He balance) was allowed to pass through the catalyst bed with a flow rate of 50 mL min⁻¹, resulting in a space velocity (SV) of 640 and 460 L g_{cat}⁻¹ h⁻¹ for Pt/HAP-O and Pt/TiO₂-H500, respectively. The inlet and outlet gas compositions were analyzed by an on-line gas chromatograph (HP 6890) equipped with a TDX-01 column and TCD detector.

The Suzuki cross-coupling reaction was carried out in a flask. Typically, catalyst (50 mg) was added to a solution of water (20 mL), K₂CO₃ (8 mmol) and PhB(OH)₂ (4.8 mmol). Then, iodobenzene (4 mmol) was added and the resulting suspension stirred magnetically for 3 h at 80 °C in a water bath. After the reaction completed, the flask was cooled to room temperature and the reaction solution was extracted by ethyl acetate (2 × 20 mL). Then the organic layers were combined and dried over anhydrous Na₂SO₄. The products in the organics were analyzed by an Agilent 7890B gas chromatography (equipped with a HP-5 column and flame ionization detector) according to the standard curve based on paraxylene. For recycle

test, the recovered catalyst and water (20 mL), K_2CO_3 (8 mmol), $\text{PhB}(\text{OH})_2$ (4.8 mmol) and iodobenzene (4 mmol) were put into the flask and repeated the above procedure up to 5th cycle.

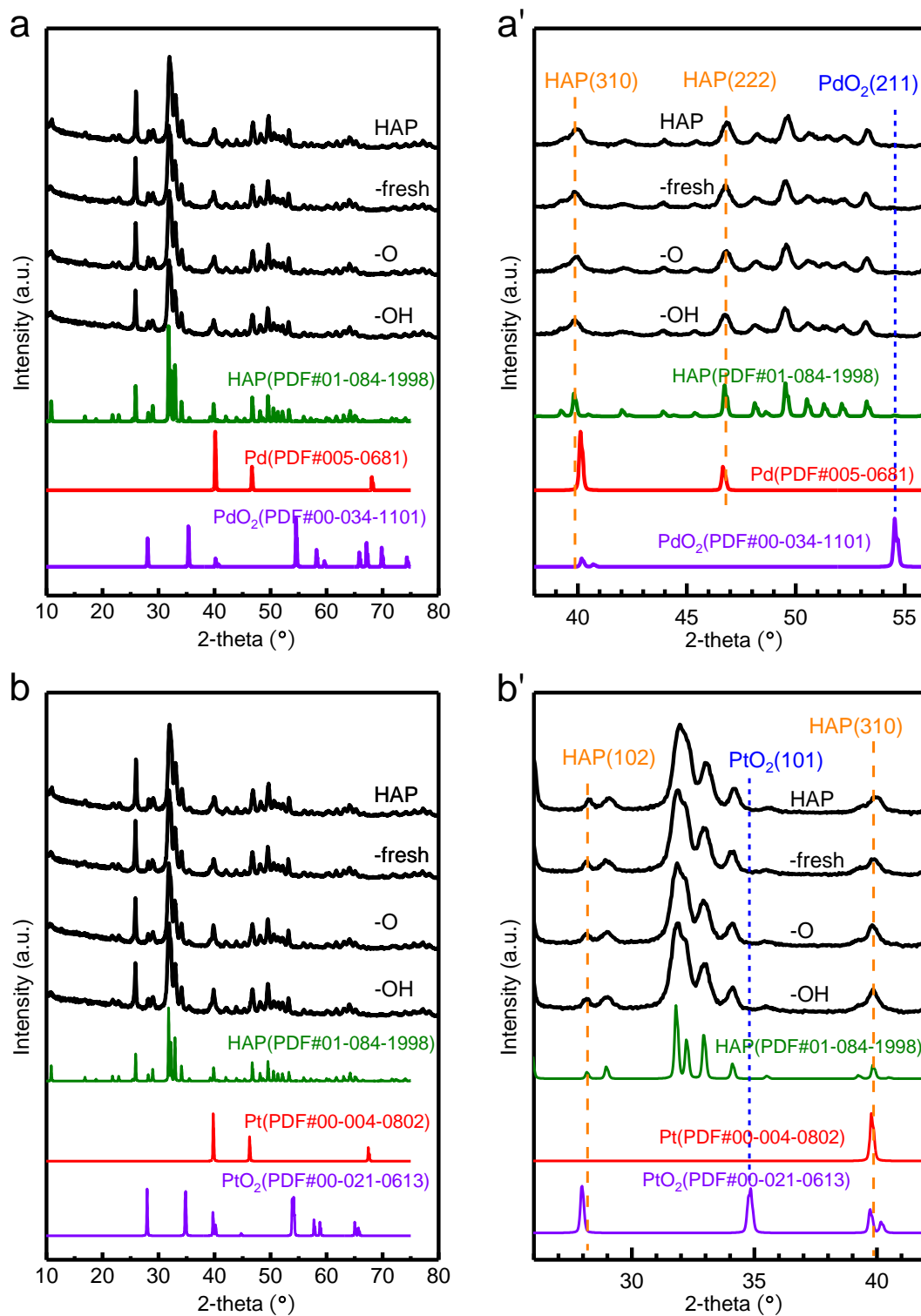


Fig. S1 XRD patterns of Pd/HAP (a-a') and Pt/HAP (b-b') series samples. a' and b' are enlargement of the corresponding area in a and b, respectively.

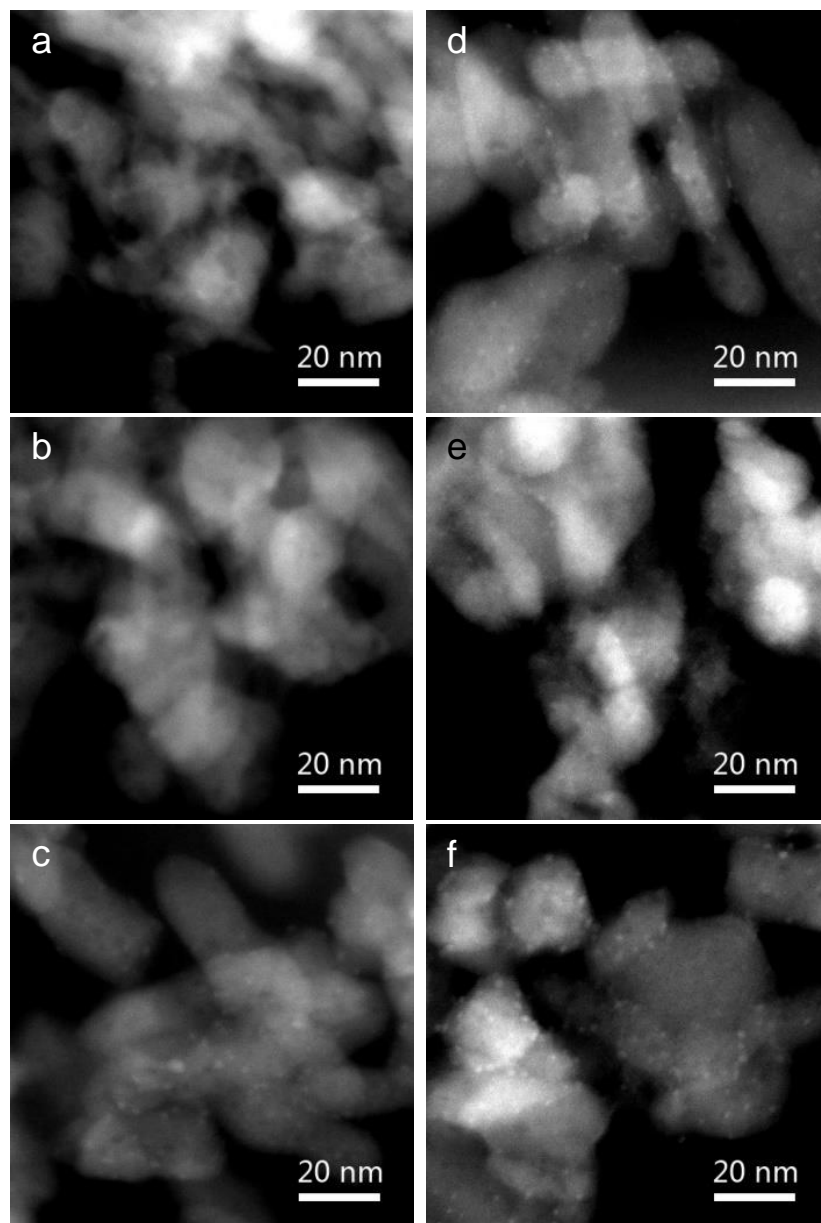


Fig. S2 HAADF-STEM images of various Pd/HAP (a-c) and Pt/HAP (d-f) series samples. (a) Pd/HAP-fresh, (b) Pd/HAP-O, (c) Pd/HAP-OH, (d) Pt/HAP-fresh, (e) Pt/HAP-O and (f) Pt/HAP-OH.

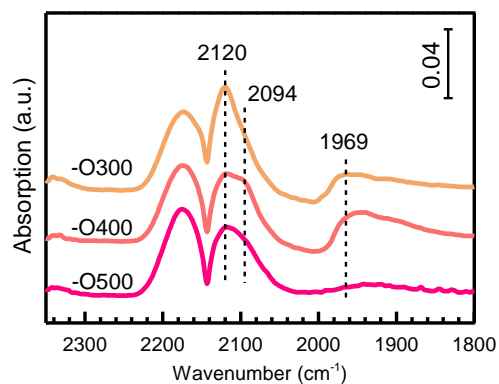


Fig. S3 *In situ* DRIFT spectra of CO adsorption on Pd/HAP-OX (X: the calcination temperature) samples obtained at 20 °C.

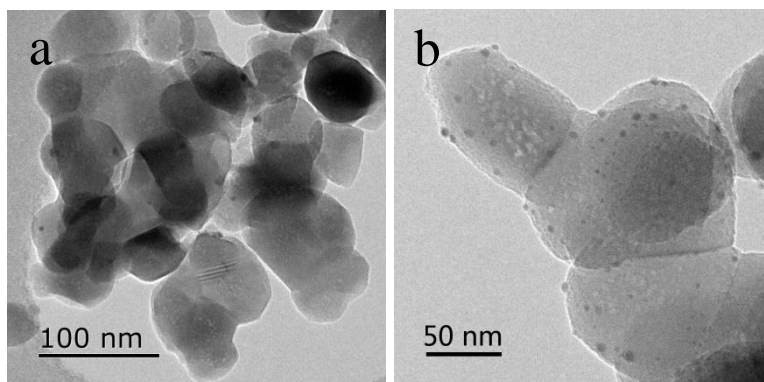


Fig. S4 TEM images of (a) Pd/HAP-RO and (b) Pt/HAP-RO which were treated under 10 vol% H₂/He at 800 °C for 5 h followed by an oxidation under 10 vol% O₂/He at 500 °C for 3 h.

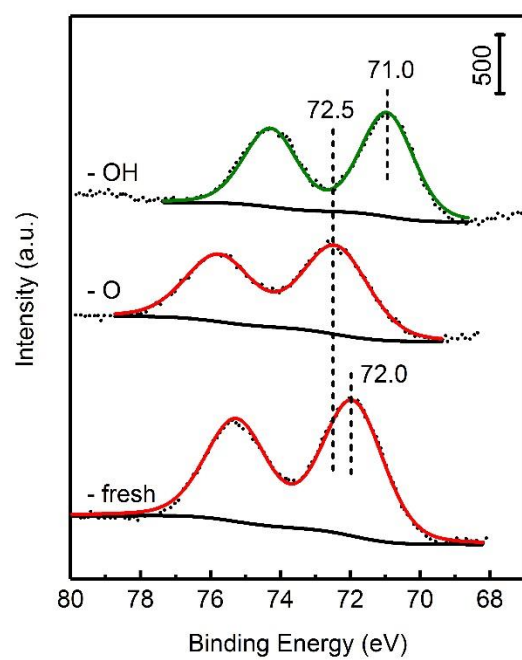


Fig. S5 XPS spectra of Pt/HAP series samples.

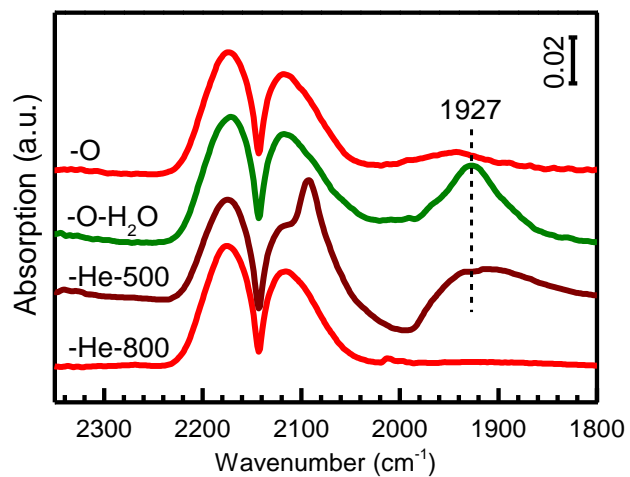


Fig. S6 *In situ* DRIFT spectra of CO adsorption obtained at 20 °C on the sample of Pd/HAP-O, Pd/HAP-O-H₂O, Pd/HAP-He-500 and Pd/HAP-He-800.

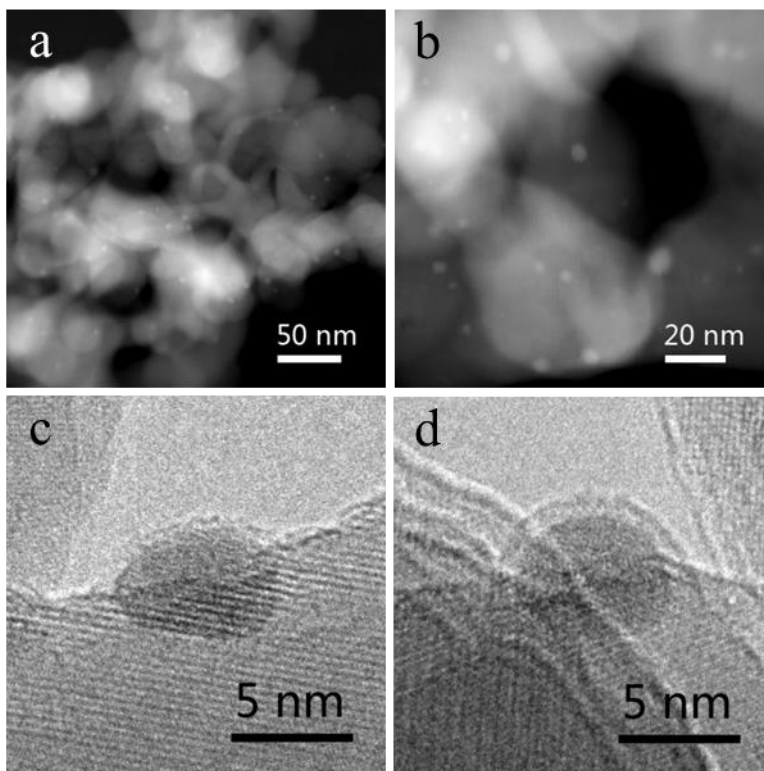


Fig. S7 HRTEM images of the Pd/HAP-He-800 sample.

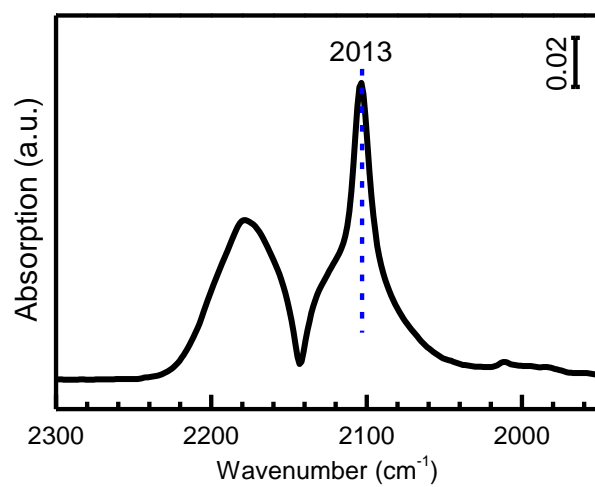


Fig. S8 *In situ* DRIFT spectra of CO adsorption obtained at 20 °C on the sample of Au/HAP-He-800.

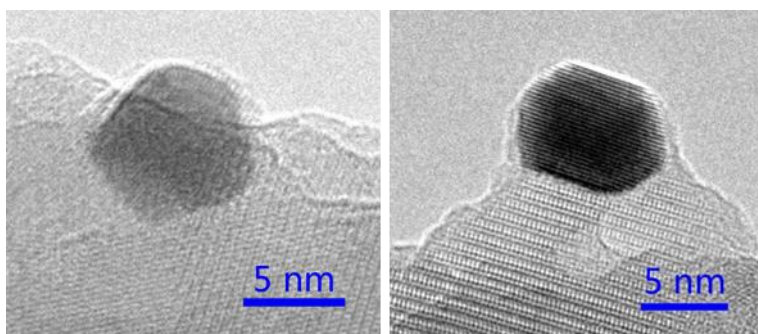


Fig. S9 HRTEM images of the Au/HAP-He-800 sample.

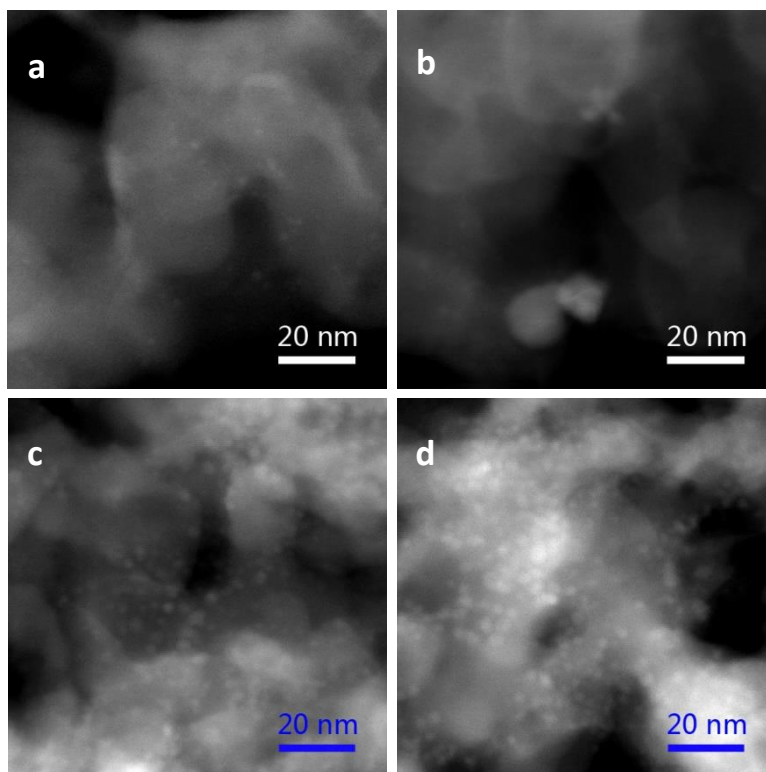


Fig. S10 HAADF-STEM images of the Pd/HAP samples after 5 cycles of Suzuki cross-coupling reaction. (a-b) Pd/HAP-fresh; (c-d) Pd/HAP-O.

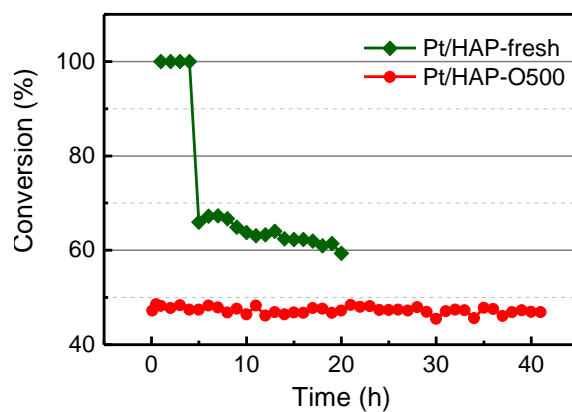


Fig. S11 CO conversion curves as a function of reaction time on the Pt/HAP-fresh and Pt/HAP-O (both of them with a Pt loading of ~0.04 wt%) at 400 °C. SV of both Pt/HAP-fresh and Pt/HAP-O are ~1 690 000 L g_{Pt}⁻¹ h⁻¹.

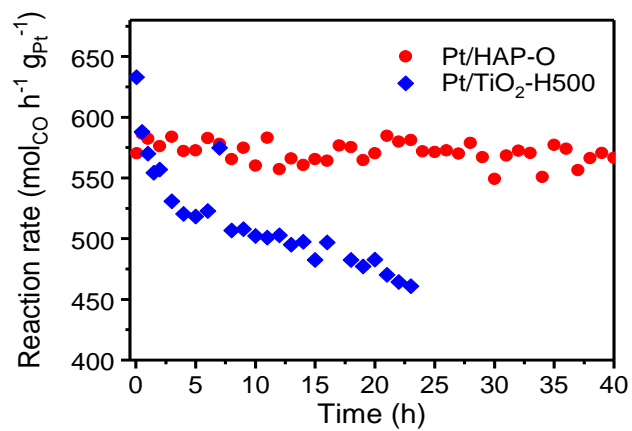


Fig. S12 Reaction rate curves as a function of reaction time on the Pt/HAP-O and Pt/TiO₂-H500 at 400 °C.

Table S1. The content of Pd in Pd/HAP-fresh and Pd/HAP-O before and after 5 cycles of Suzuki cross-coupling reaction measured by ICP-AES

Sample	Pd wt%	
	Before reaction	After 5 cycles reaction
Pd/HAP-fresh	0.36	0.06
Pd/HAP-O	0.36	0.35

Reference

- 1 K. Mori, S. Kanai, T. Hara, T. Mizugaki, K. Ebitani, K. Jitsukawa and K. Kaneda, *Chem. Mater.*, 2007, **19**, 1249-1256.
- 2 K. Zhao, B. Qiao, J. Wang, Y. Zhang and T. Zhang, *Chem. Commun.*, 2011, **47**, 1779-1781.
- 3 B. Qiao, J.-X. Liang, A. Wang, C.-Q. Xu, J. Li, T. Zhang and J. J. Liu, *Nano Res.*, 2015, **8**, 2913-2924.