Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Surfactant-Free Preparation of Supported Cubic Platinum Nanoparticles

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Experimental

Materials

Platinum acetylacetonate (Pt(acac)$_2$, 97%), fumed silica (SiO_2, 99.8%), alumina oxide powders (Al_2O_3, >98%), and acetone (>99.9%) were purchased from Aldrich. Titanium dioxide (TiO_2 P25) was purchased from Degussa. Amorphous carbon black was purchased from Cabot. Hydrogen (H_2, 99.999%), carbon monoxide (CO, 99.99%) and helium (He, 99.999%) gases were purchased from Praxair. All chemicals and reagents were used as received.

Preparation of Cubic Pt/SiO$_2$

The cubic Pt/SiO_2 with a Pt loading of 5 wt.% was prepared by a wetness impregnation method. In a typical procedure, fumed SiO_2 powders were calcined first in air at 700 °C overnight for the removal of adsorbed moisture before use. Pt(acac)$_2$ (0.1 g or 0.25 mmol) dissolved in acetone (8 mL) was added drop wisely onto the SiO_2 (0.95 g) support under continueous stirring. The solid was dried at 60 °C under vacuum and reduced in CO/H_2 (25/5 cm^3/min) by raising the temperature at 5 °C/min to 200 °C and maintaining at 200 °C for 1 h, unless specified otherwise. To examine the effect of a given reaction condition, such as temperature, time, and CO/H_2 feeding ratio, and the support calcining temperature, on the morphology of made Pt particles, we changed only the specific parameter while keeping the others the same.

Preparation of Pt on Other Supports

Several other types of supports, including amorphous C, Al_2O_3, and TiO_2 nanopowders, were used to examine their effect on the final product. C was calcined at 300 °C, and Al_2O_3 and TiO_2 were calcined at 700 °C overnight in air before use. The Pt loading was fixed at 5 wt.% and the reducing procedure was kept the same for all samples.

In Situ FTIR

In-situ Fourier transform infrared spectrometry (FTIR) experiments were carried out using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a liquid nitrogen (LN$_2$) cooled MCT detector. Pt(acac)$_2$/SiO_2 precursors were pressed into a thin pellet (~ 1mm thick, 20 mm in diameter) and placed into a custom-made transmission cell equipped with CaF_2 windows, and a K-type thermocouple and heating belts for temperature control. The pressed pellet was firstly flushed with a He flow (100 cm^3/min) overnight for removal of the adsorbed moisture on the sample. The reducing process was initiated by introduction of a CO/H_2 (25/5 cm^3/min) mixture and raising the temperature at 3 °C/min to 200 °C for 1 h. A trap packed with 3.2 mm pellets of 3A molecular sieve was placed in the CO gas line for the removal of trace iron carbonyls generated in the steel cylinder. Time-lapsed spectra were obtained every two minutes by averaging 32 scans taken with 1 cm^{-1} resolution.

Characterization

Transmission electron microscopy (TEM) images were taken using a FEI Tecnai 12 microscope with an accelerating voltage of 120 KV. High-resolution TEM (HRTEM) characterizations were conducted on the TEAM 0.5 high-resolution microscope, a modified FEI Titan 80-300 microscope equipped with a gun monochromator, operated at 80 KV at the National Center for Electron Microscopy (NCEM). Scanning transmission electron microscopy (STEM) images were taken on a FEI Tecnai F20 microscope operated at 200 KV and incorporated with a guan monochromator. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy measurements were conducted on a Hitachi Schottky Emission microscope (Model S-4300SE/N), operated at 15 KV. FTIR spectra were collected using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a LN_2-cooled MCT detector and a gas flow cell.

Estimation of the Extent of Pt Reduction from Chemisorbed CO

The extent of Pt reduction (X_{Pt}) was estimated by assuming the large Pt nanocubes are grown from their cubic seeds after a burst of nucleation. The assumption is supported by the TEM study of the growing Pt particles. If we assume no new nuclei form after the burst of nucleation process, the number of particles (N_{Pt}) will be a constant. It is known that the amount of chemisorbed CO (normalized, X_{CO}) is proportional to the Pt surface. The correlation between X_{CO} and the edge size of cubic Pt (D_{Pt}) can be described as:

$$X_{CO} = \frac{N_{Pt} \times 6D_{Pt}^2}{N_{Pt} \times 6D_{Pt,f}^2} = \frac{D_{Pt}^2}{D_{Pt,f}^2} \quad \text{(S1)}$$

where $D_{Pt,f}^{2}$ is the edge size of the final product. X_{Pt} can also be depicted using the following equation:

$$X_{Pt} = \frac{N_{Pt} \times D_{Pt}^3}{N_{Pt} \times D_{Pt,f}^3} = \frac{D_{Pt}^3}{D_{Pt,f}^3} \quad \text{(S2)}$$

Thus X_{Pt} can be described using X_{CO}:

$$X_{Pt} = X_{CO}^{3/2} \quad \text{(S3)}$$

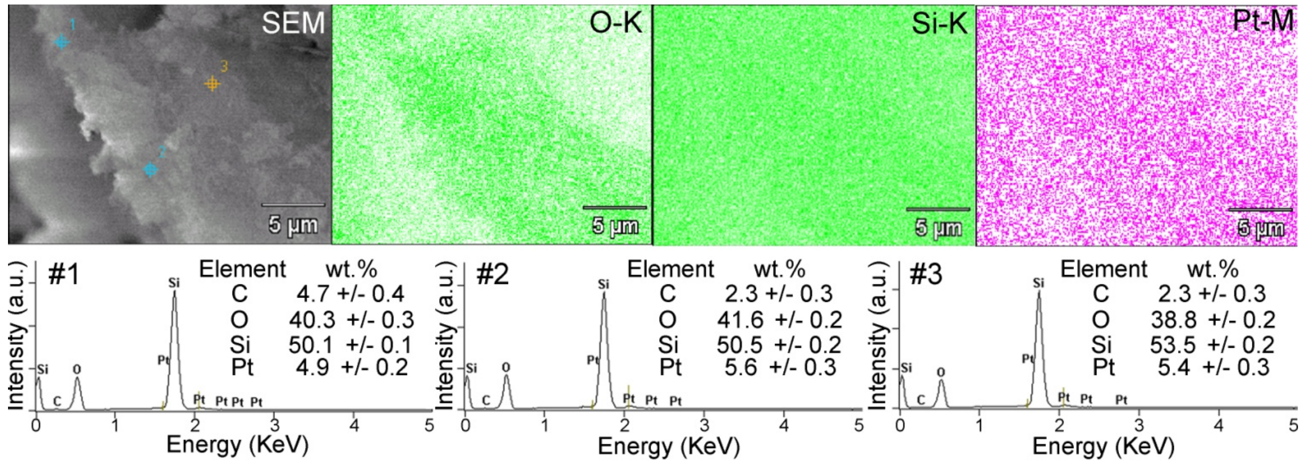

Fig. S1 SEM image, and EDX elemental maps and quantitative analyses of $Pt(acac)_2/SiO_2$ precursors.

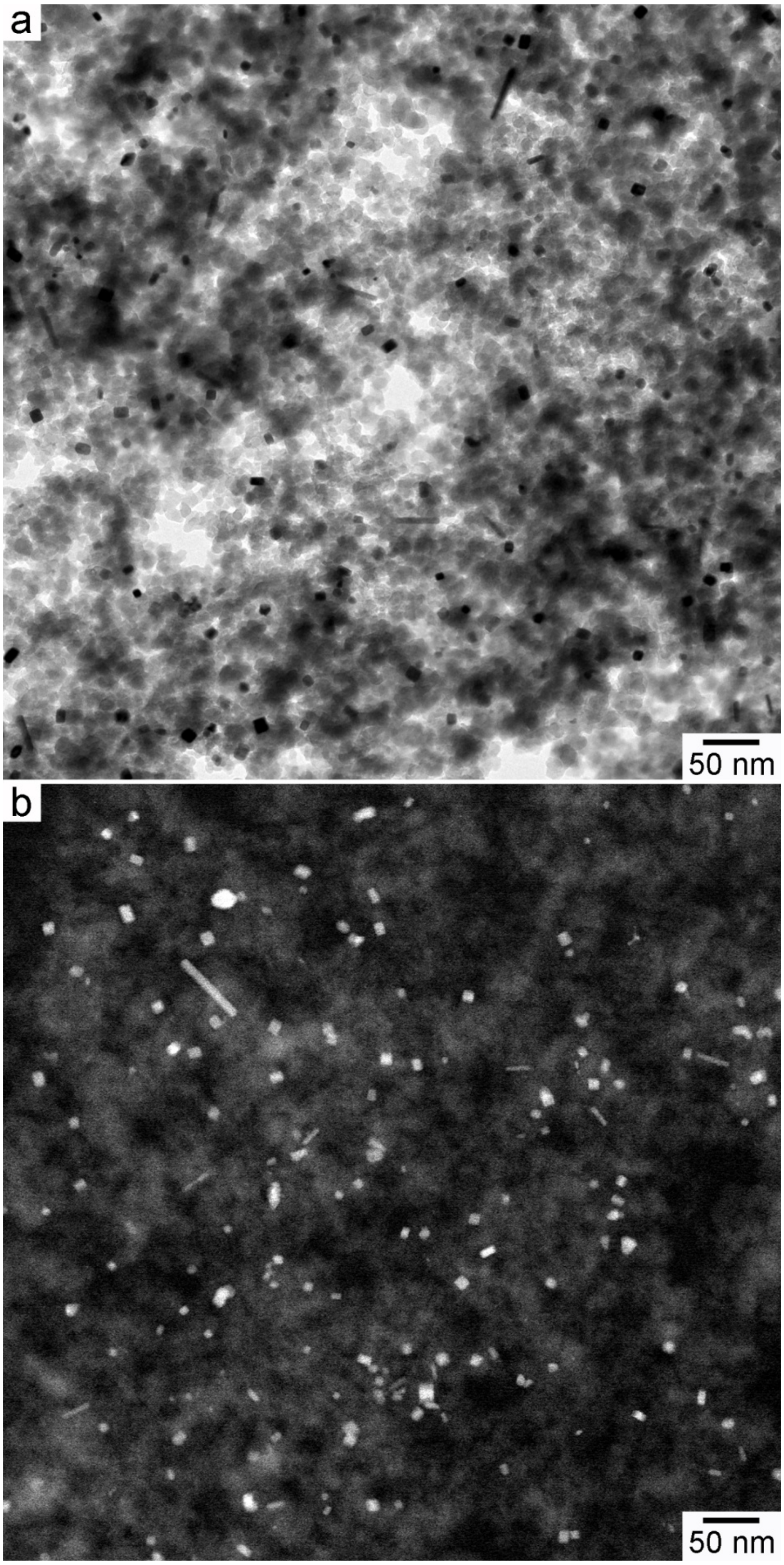

Fig. S2 (a) TEM and (b) STEM of as-prepared cubic Pt/SiO_2 after being reduced for 1 h at 200 °C in 25/5 cm^3/min CO/H_2.

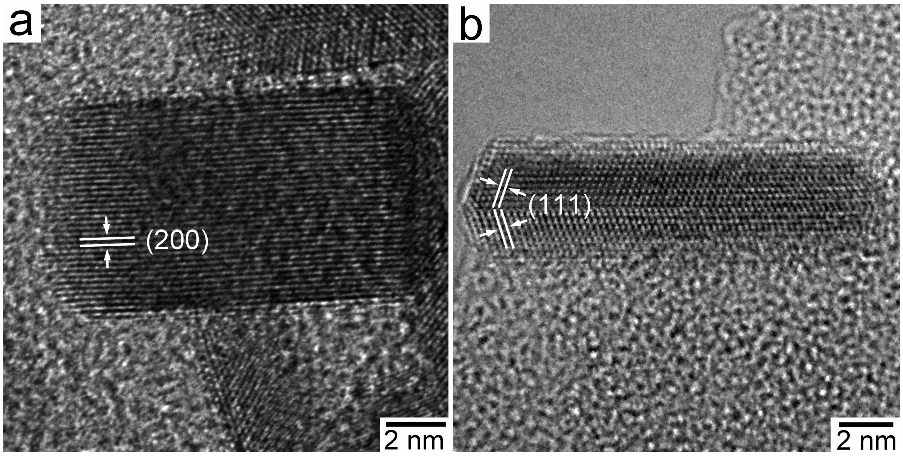

Fig. S3 HRTEM images of the Pt byproduct particles in (a) rectangular and (b) rod-like shapes. Reaction condition: 200 °C/1h in 25/5 cm^3/min CO/H_2.

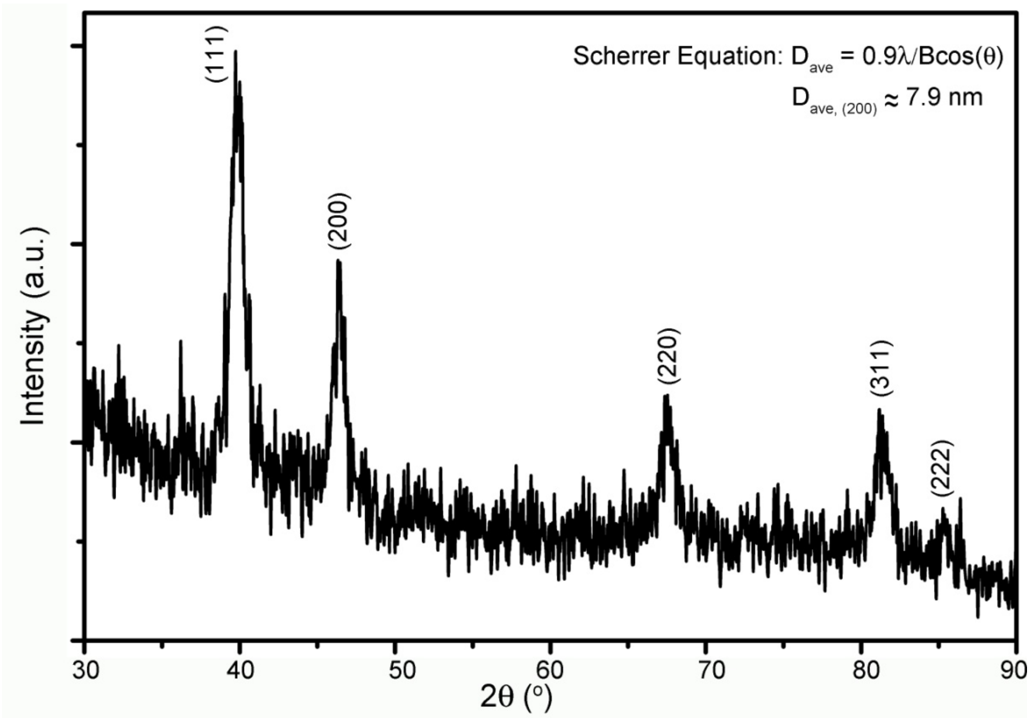

Fig. S4 PXRD pattern of as-prepared cubic Pt/SiO_2 after being reduced for 1 h at 200 °C in 25/5 cm^3/min CO/H_2.

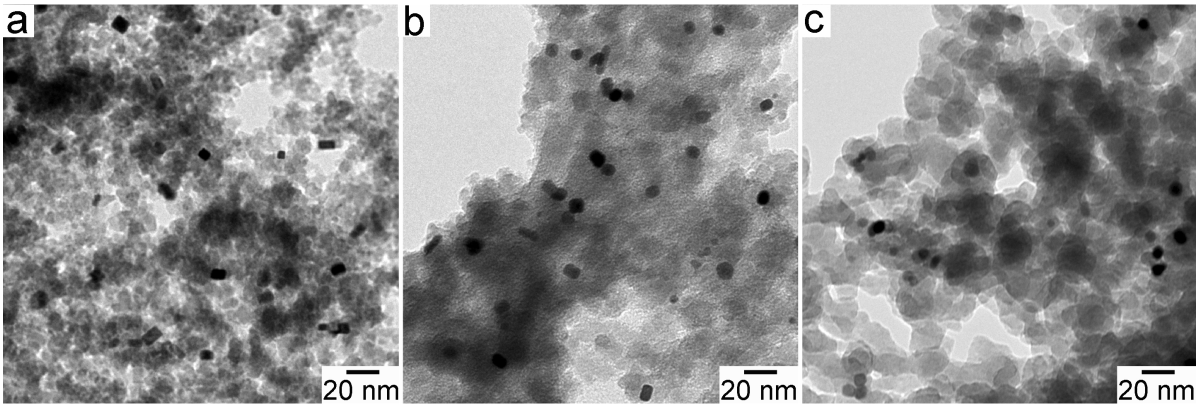

Fig. S5 TEM images of reduced Pt/SiO2 at (a) 150, (b) 250, and (c) 300 °C for 1 h in 25/5 cm^3 CO/H_2.

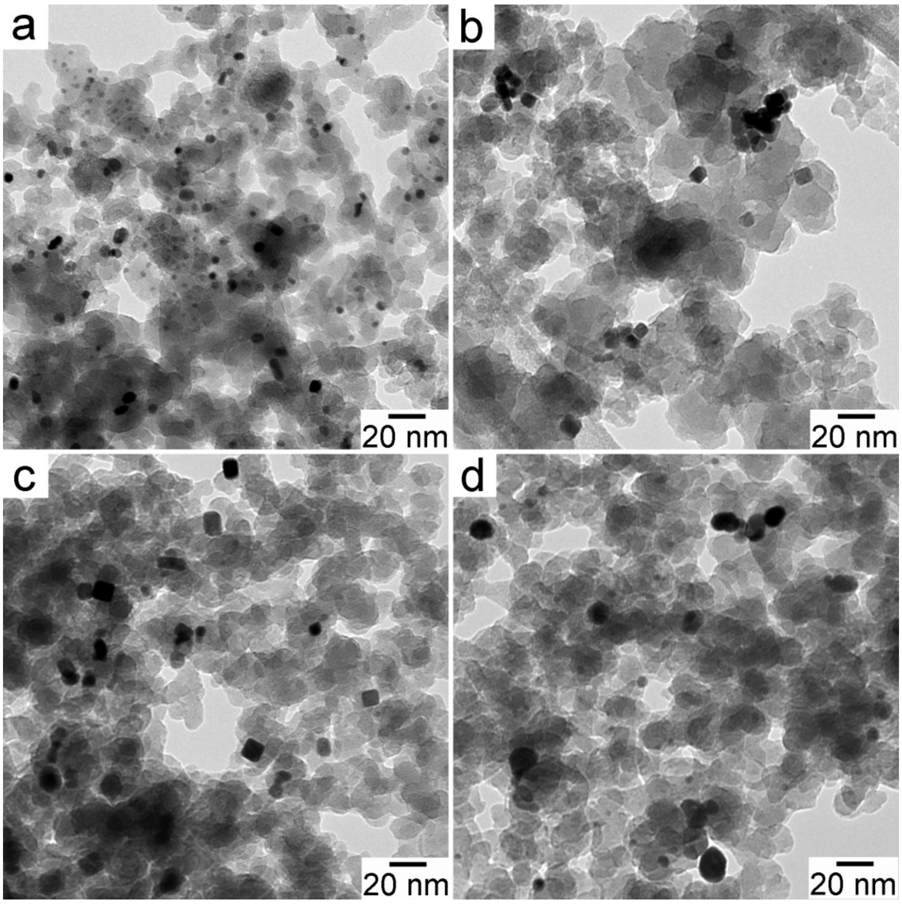

Fig. S6 TEM images of reduced Pt/SiO_2 at 200 °C for 1h in (a) 30/0, (b) 20/10, (c) 10/20, and (d) 0/30 cm^3/min CO/H_2.

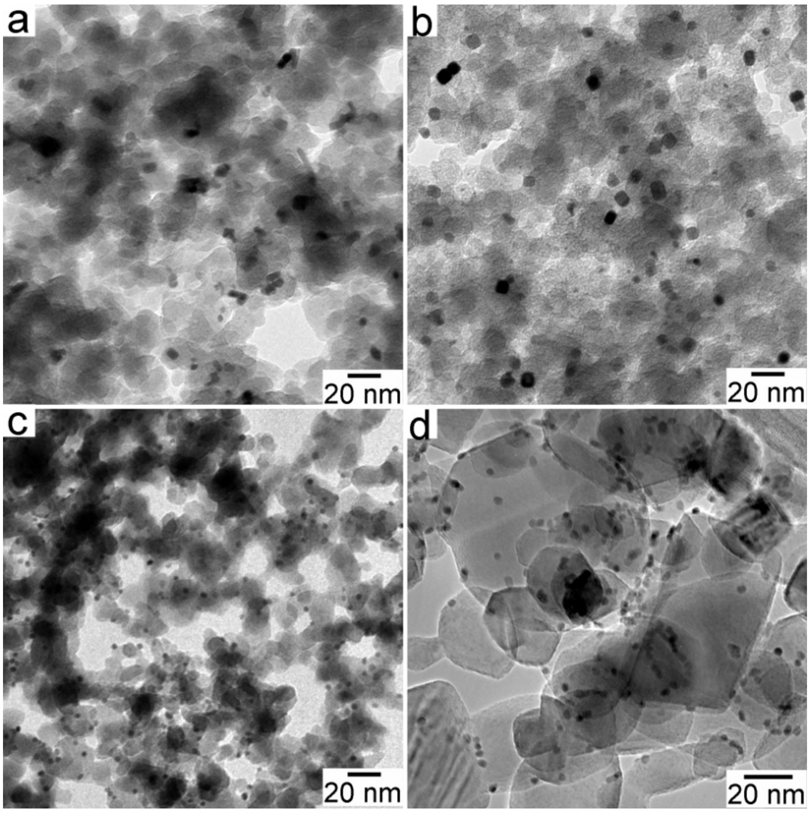

Fig. S7 TEM images of as-made Pt on (a) SiO2 calcined at 300 °C, (b) amorphous C, (c) Al2O3, and (d) TiO2 supports after being reduced at 200 °C for 1h in 25/5 cm^3/min CO/H_2.

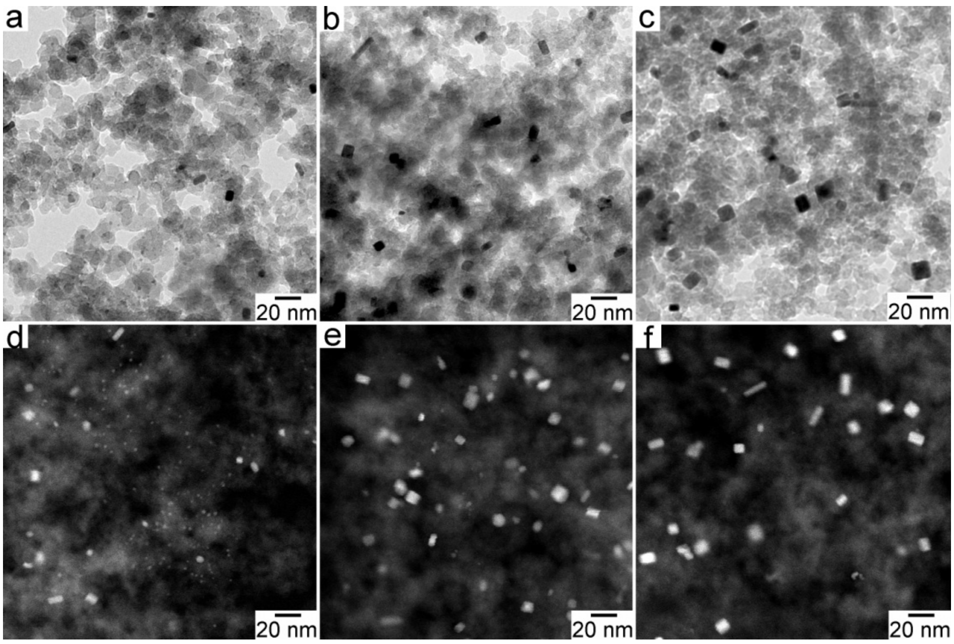

Fig. S8 (a-c) TEM and (d-f) STEM images of Pt/SiO2 after being reduced at (a, d) 180 °C for 1 min, (b, e) 200 °C for 1 min, and (c, f) 200 °C for 10 min in 25/5 cm^3/min CO/H_2.

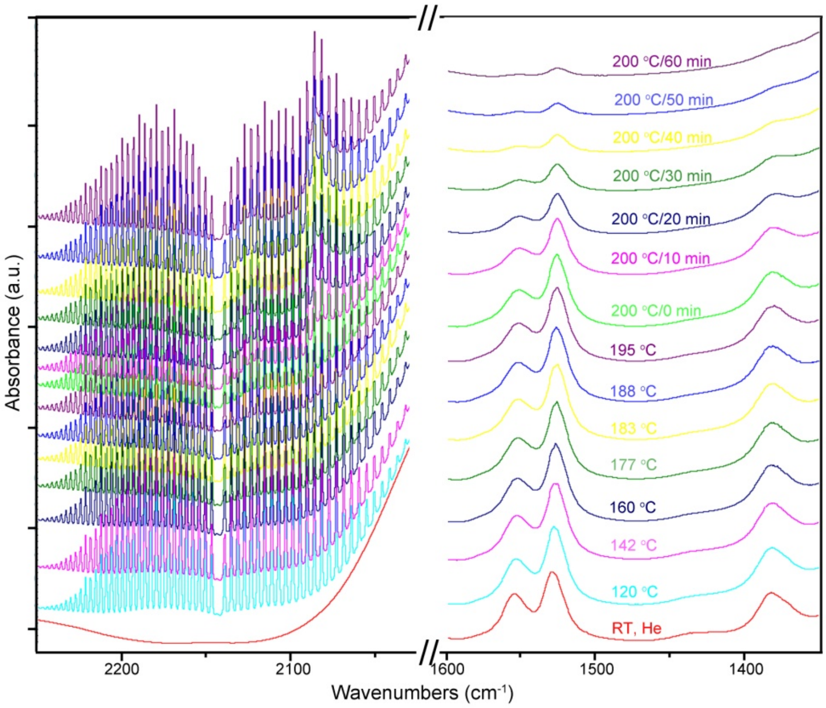

Fig. S9 Original in-situ FTIR spectra of Pt/SiO_2 in its reducing process by being heated at 3 °C/min to 200 °C and kept there for 1 h in 25/5 cm^3/min CO/H_2.

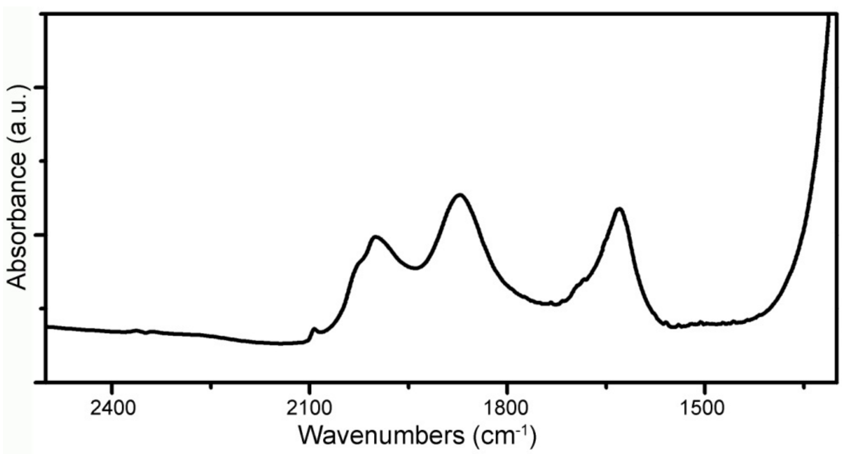

Fig. S10 FTIR spectrum of as-prepared cubic Pt/SiO_2 after being reduced at 200 °C for 1h in 25/5 cm^3/min CO/H_2.