Supporting Information

Single-atom and Nano-clustered Pt Catalysts for Selective CO_2 Reduction

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Characterization techniques

XRD analyses were performed on a PANalytical Empyrean II diffractometer with Cu Kα radiation (λ = 0.15406 nm) at 45 kV and 40 mA to identify the crystal phases and to analyze lattice parameters. Scattering intensity was recorded in the range of $8^o < 2\theta < 90^o$ for all of the samples with a 2θ step of 0.03^o and a count time of 2 s per step. The diffraction patterns were indexed to JCPDS (Joint Committee on Powder Diffraction Standards) files. The actual loading of Pt on the ceria supports was measured by a Perkin Elmer OPTIMA 7300 inductively coupled plasma atomic emission spectroscopy (ICP-AES). Field-emission high-resolution scanning electron microscopy (FE-HRSEM), Field-emission high-resolution transmission electron microscopy (FE-HRTEM) and high-angle annular dark-field -scanning transmission electron microscopy (HAADF-STEM) images were collected on FEI Nova NanoSEM 450 FE-SEM microscope, Philips CM200 apparatus and JEOL JEM-ARM200F STEM, respectively. Textural properties, such as BET surface area, pore volume and pore size of the catalysts were determined from the adsorption and desorption isotherms of nitrogen at −196 ^oC on a Micrometric Tristar 3030 adsorption analyzer. Before measurement, the samples were degassed at 150 ^oC for 3 h. Hydrogen temperature-programmed reduction (H_2-TPR) experiments were carried out on a Micromeritics Autochem II apparatus equipped with a thermal conductivity detector (TCD) detector. The sample (approximately 50 mg) was pre-treated under an Argon flow of 30 mL/min as the temperature was increased at a ramp rate of 10 ^oC/min to 150 ^oC, where it was kept at this temperature for 30 min to remove water. Then, a reducing gas (10% H_2 in Ar) was introduced at a flow rate of 20 mL/min with a ramp of 10 ^oC/min from RT to 700 ^oC. The variation in H_2 concentration of the effluent stream was monitored online by the thermal conductivity detector. X-ray photoelectron spectroscopy (XPS, Thermo Scientific™, UK, model ESCALAB™ 250Xi) was used to probe the Ce 3d, Pt 4f, O 1s and C 1s binding energies [1] of surface species with mono-chromated Al K alpha (energy 1486.68 eV) as the excitation source, operating at 120 W with a spot size of 500 μm. The C1s signal at 284.8 eV

was taken as a reference for BE calculations. electron paramagnetic resonance (EPR) experiments were performed on a Bruker EMS X-Band EPR spectrometer with a quartz sample tube of 3.8 mm. *In-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was undertaken using a Brüker VERTEX 70v FTIR spectrometer, equipped with a liquid N_2 cooled MIR source, KBr optics, and a RockSolid interferometer. For each analysis, approximately 30 mg of catalyst was premixed with the same amount of diamond powder and placed in a commercial *in-situ* DRIFTS cell (HVC-DRM-5, Harrick's Scientific, USA) possessing ZnS windows. The sample was treated in H_2 at 300 ^oC for 1h to remove residual organics on the catalyst surface before being cooled to room temperature (RT) for DRIFTS analysis. Diamond purged by Ar at 200 ^oC for 1h was used as the background. Data was collected by averaging 128 scans at a resolution of 1 cm^{-1}. The spectra were converted to Kubelka-Munk Units (KMU).

Calculation method of reaction rate based on exposed Pt atom ($\boldsymbol{mol_{CO_2} \cdot Atom_{Pt}^{-1} \cdot s^{-1}}$):

Calculation of exposed Pt atom number:

Assuming that the Pt nanoparticle (NP) is spherical with closely packed atoms, the Pt dispersion can be estimated from Pt NP and atomic radius according to the equation [2-3]:

$$Dispersion\ (\%) = \frac{N_S}{N_T} = \frac{R^3 - (R - \sqrt{3}r)^3}{R^3} \qquad Eqn\ (1)$$

Where R is the radius of the Pt NP and r is the radius of a Pt atom.

The calculated dispersion of 2 wt% Pt/CeO_2 is 55.6%. The total atom numbers (N_T) in 0.05g 2wt% Pt/CeO_2 can be calculated using the mass of total Pt/mass of each Pt atom ($9.25\times10^{-4}/3.24\times10^{-22}$), calculated as 2.85×10^{18}. So the number of exposed atoms (N_S) is 1.58×10^{18}.

As no NPs are observed in 0.05wt% Pt/CeO_2, its dispersion can be regarded as 1. Thus N_T is equal to 7.4×10^{16} atoms.

According to He et al. reported in[3], the total number of atoms can be estimated by the equation:

$$N = \frac{4}{3}\pi R^3 d / \frac{AW}{N_A} \qquad Eqn\ (2)$$

Where N is the total number of atoms in the nanoparticle, "R" and "r" are the NP radii and atomic radii respectively, AW is the atomic weight and N_A is the Avogadro constant.

The total number of atoms in a 1.89 ± 1.5 nm (2R) Pt NP is calculated as c.a. 234, and the exposed atom number is 125 atoms.

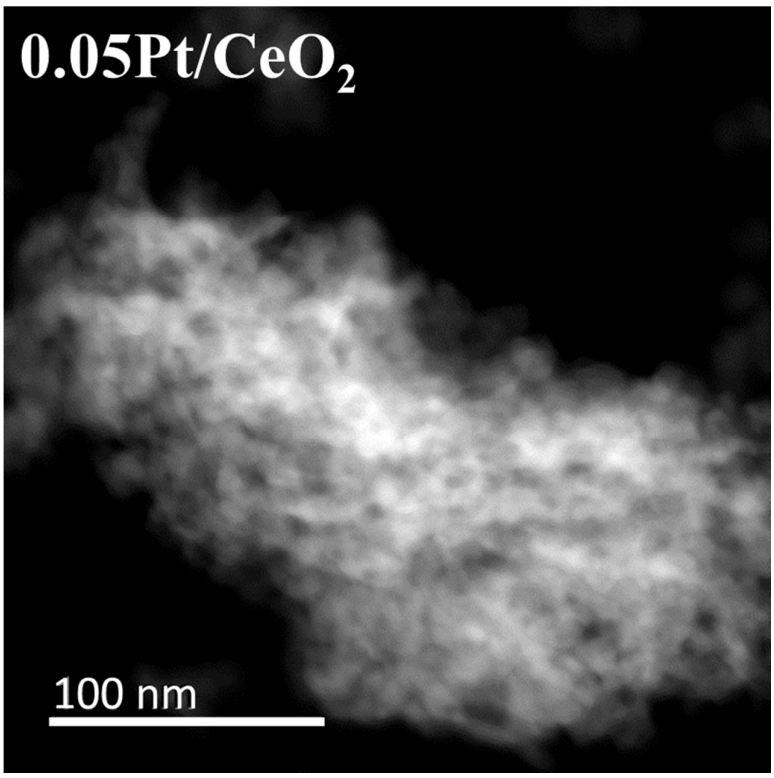

Figure S1: HAADF-STEM image of 0.05Pt/CeO_2 catalyst.

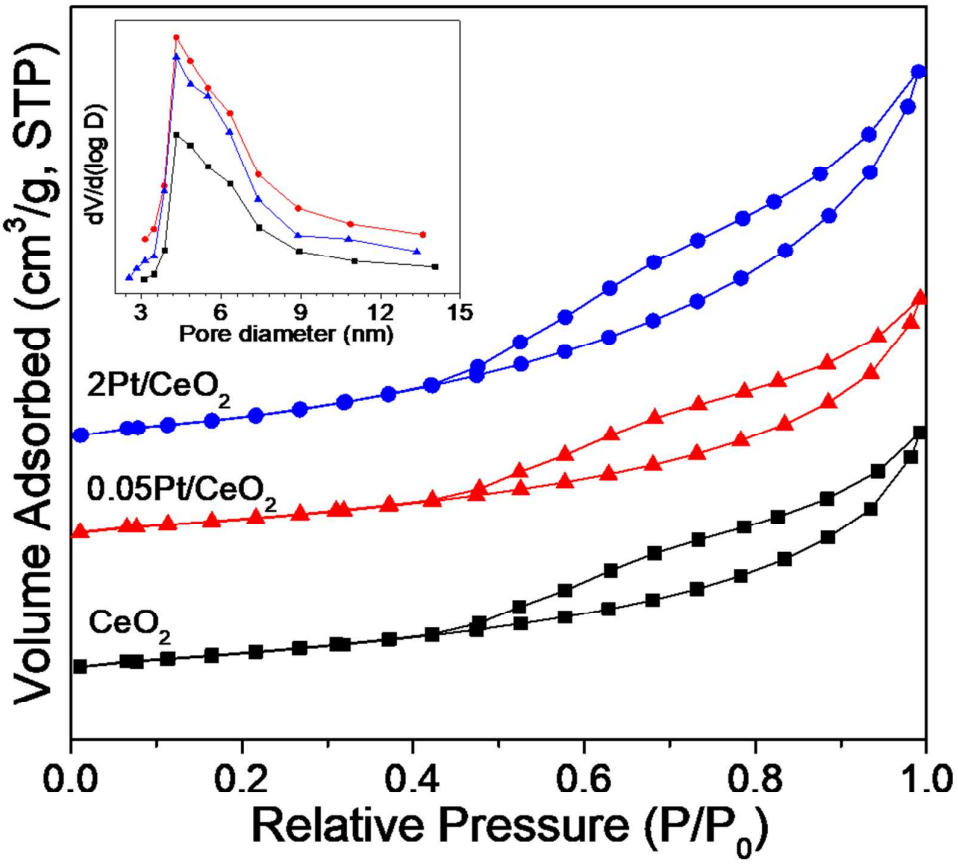

Figure S2: N_2 adsorption-desorption isotherm and pore size distributions (insert) for neat CeO_2 and Pt/CeO_2 catalysts.

The N_2 adsorption-desorption isotherms and pore size distributions of the CeO_2 and Pt/CeO_2 catalysts are shown in Figure S2. All isotherms are type II with a type H3 hysteresis loops over the relative pressure range of 0.4-1, which suggests feature characteristic of a mesoporous solid with pear-shaped pores. The BET surface area of neat CeO_2 is 67.6 m^2/g and decreases to 50.7 m^2/g when introducing Pt on the surface (Table 1).

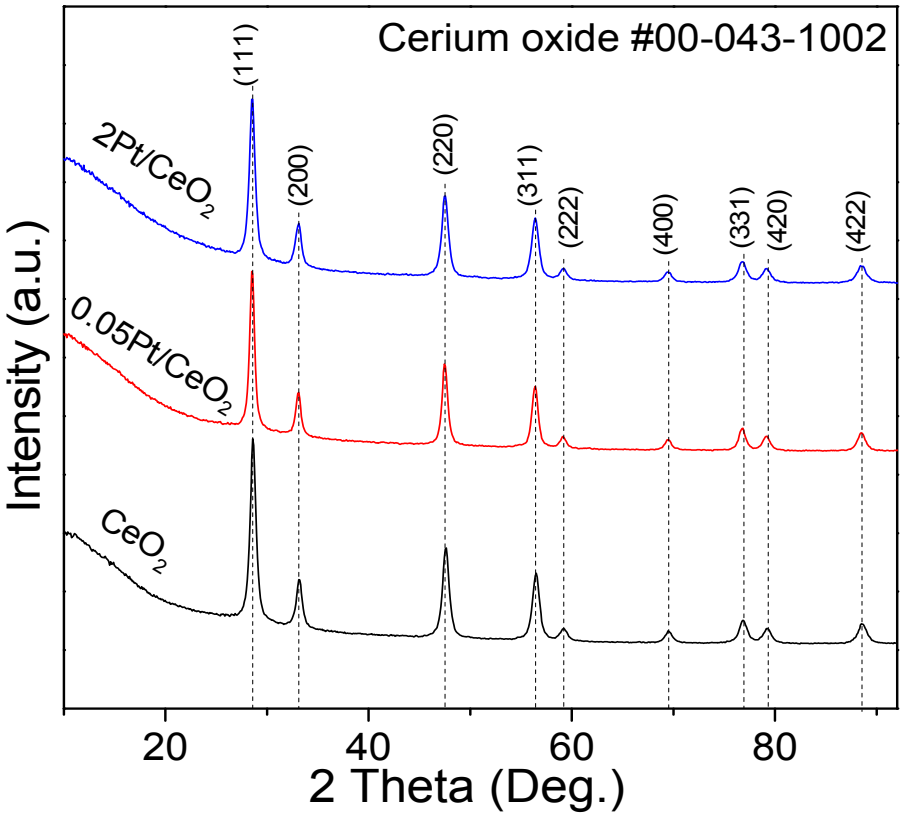

Figure S3: XRD profiles of neat CeO_2 and Pt/CeO_2 catalysts.

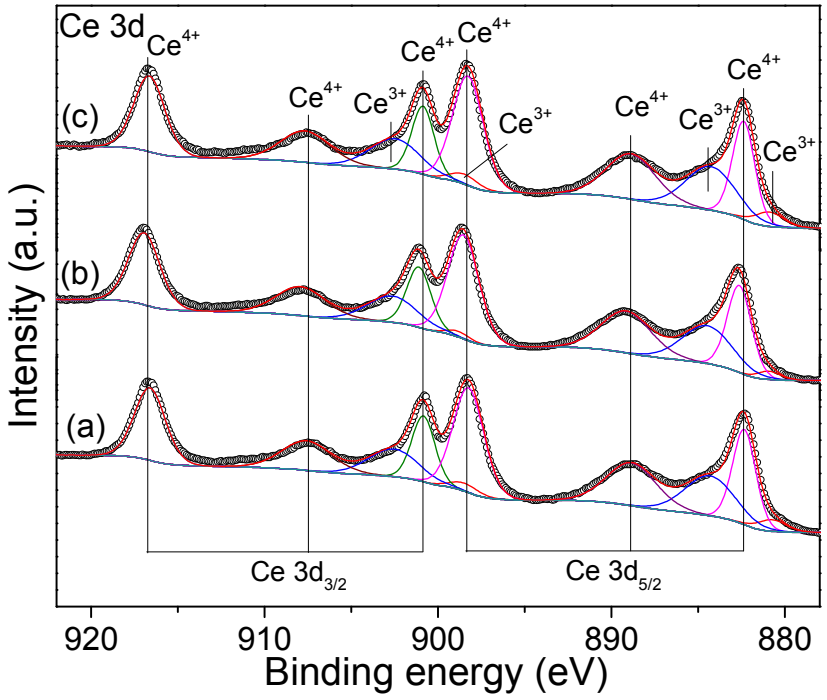

Figure S4: Ce 3d XPS spectra of (a) neat CeO_2, (b) $0.05Pt/CeO_2$ and (c) $2Pt/CeO_2$ catalysts.

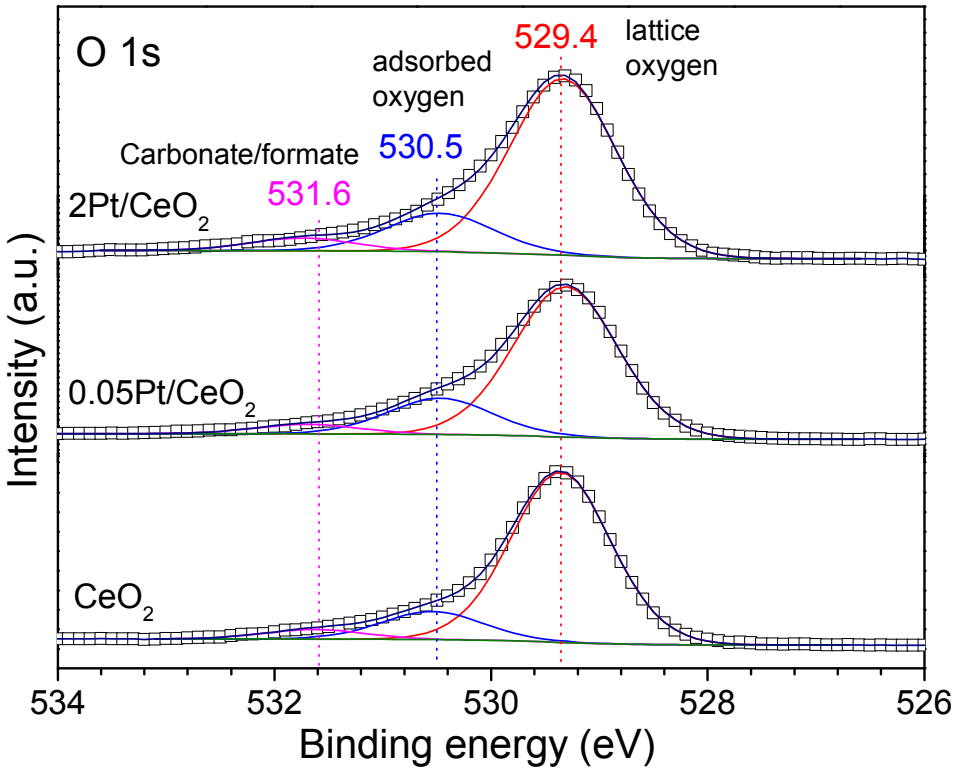

Figure S5: O 1s XPS spectra of neat CeO_2, 0.05Pt/CeO_2 and 2Pt/CeO_2 catalysts.

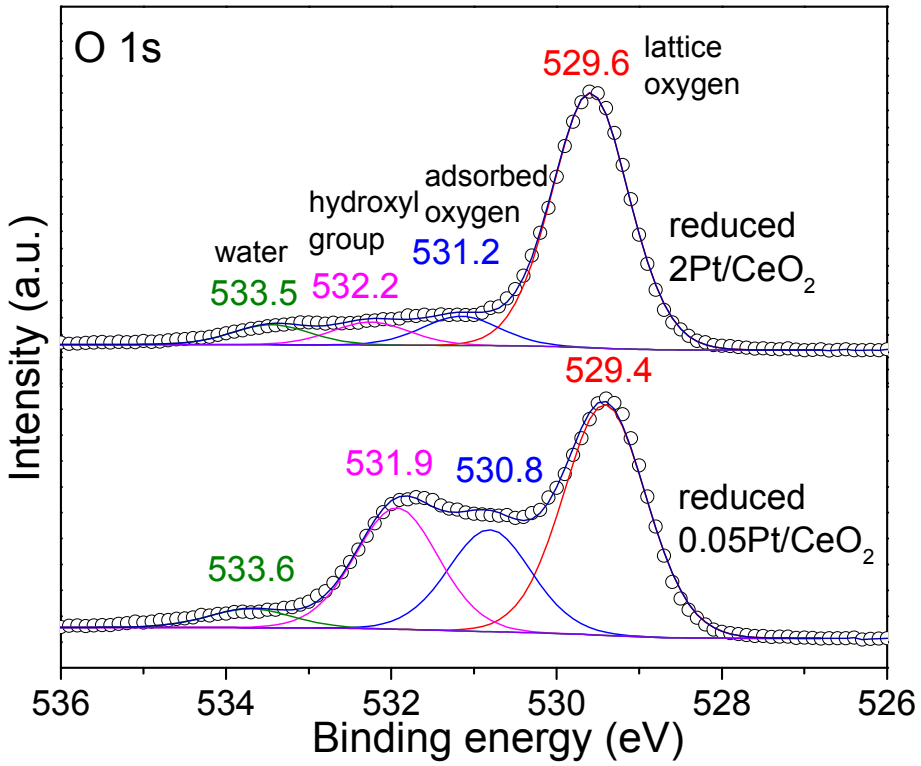

Figure S6: O 1s XPS spectra of reduced 0.05Pt/CeO_2 and 2Pt/CeO_2 catalysts.

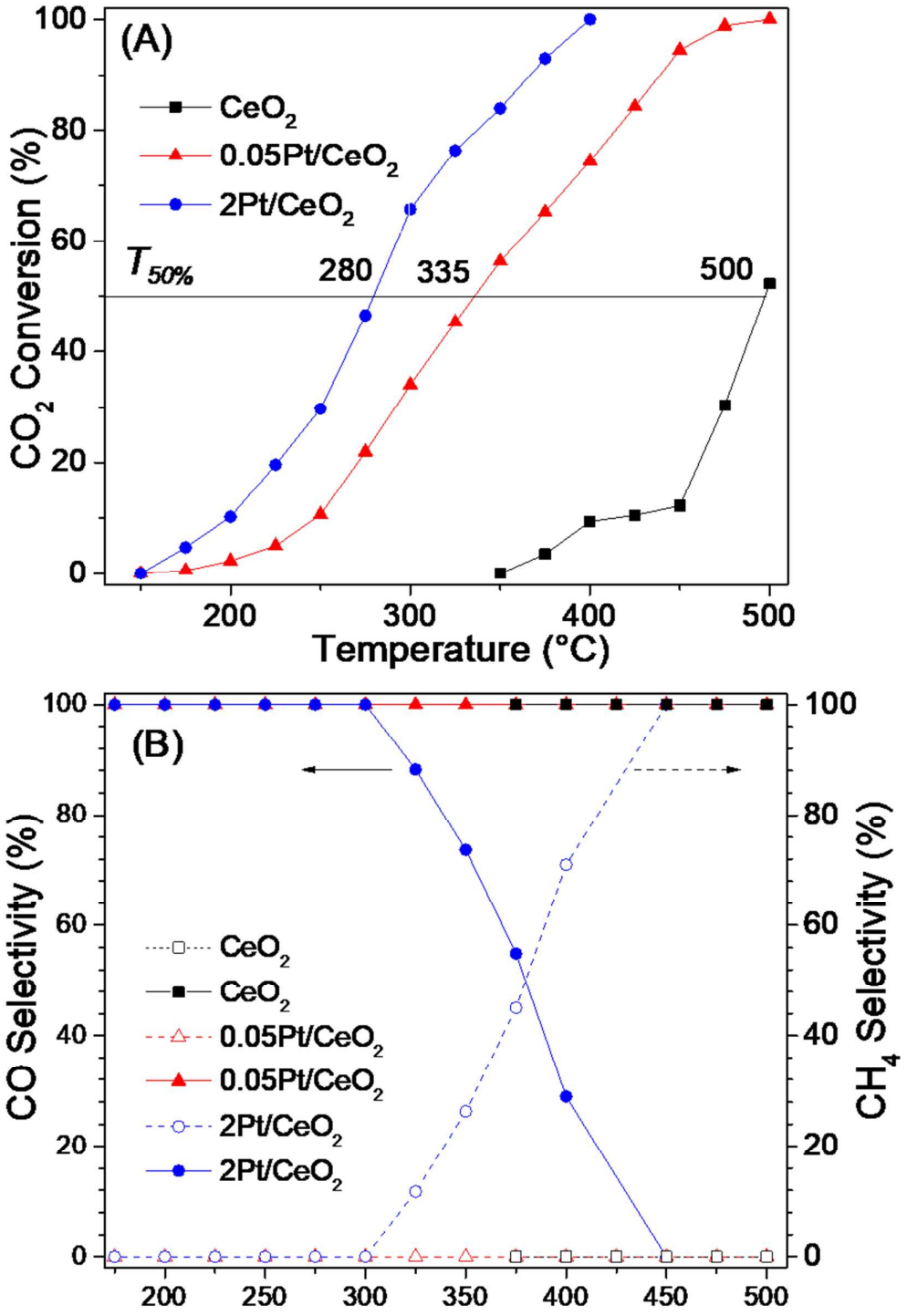

Figure S7. (A) Activity and (B) selectivity for CO_2 reduction over CeO_2 and Pt/CeO_2 catalysts.

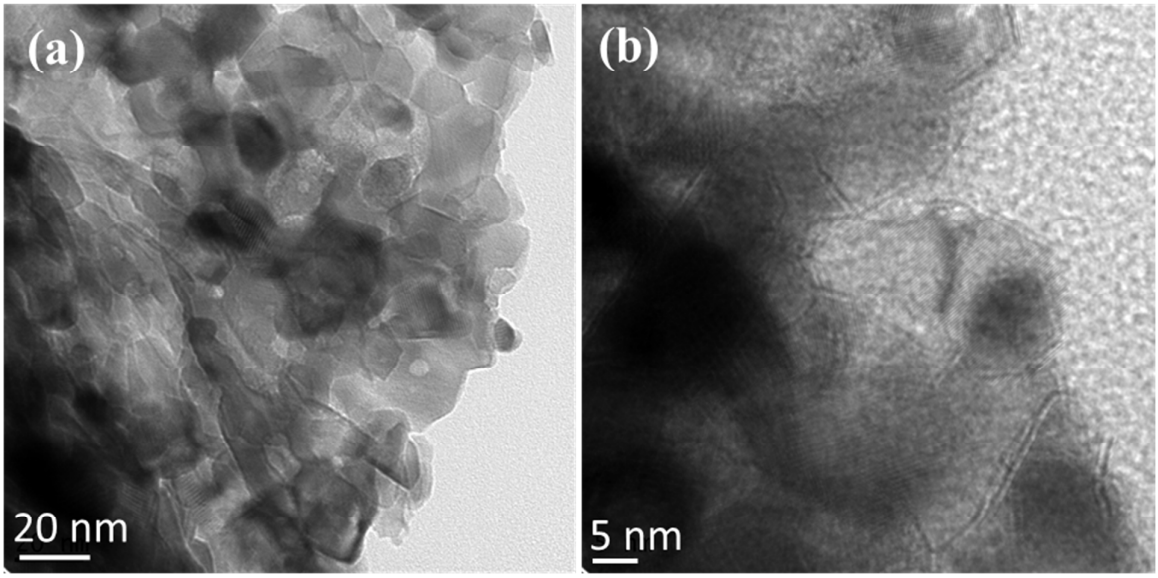

Figure S8. TEM images of aged 0.05Pt/CeO_2 after activity test at 500 °C.

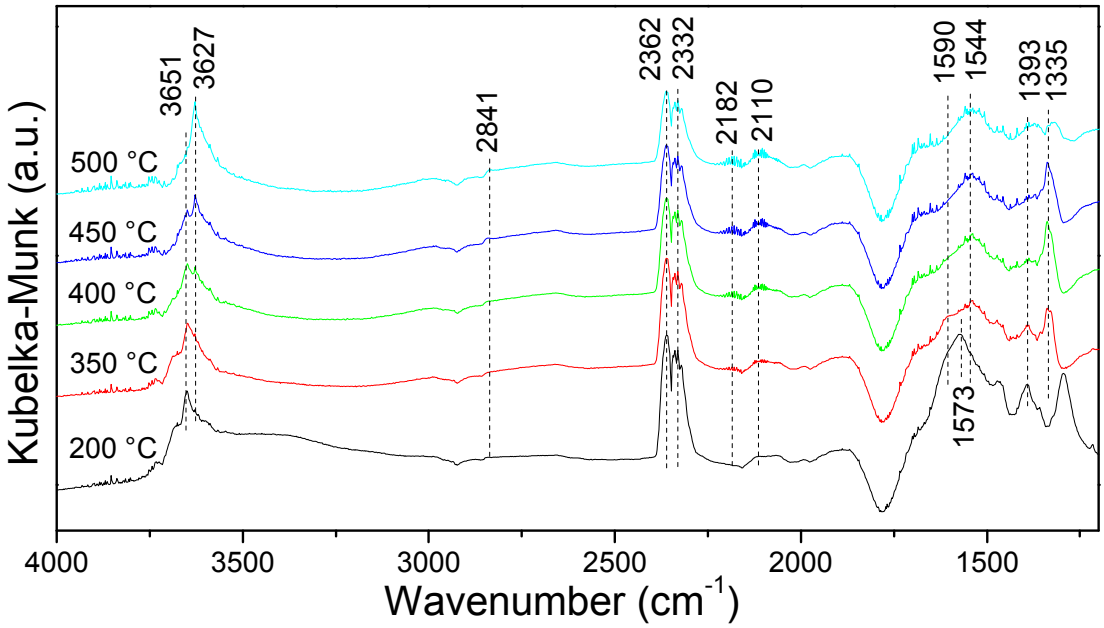

Figure S9. *In-situ* DRIFTS spectra of neat CeO_2 during CO_2 reduction at temperature across the range 200 to 500 °C.

Table S1. O species of reduced Pt/CeO_2 at 300 °C (estimated from XPS).

Catalyst	Reduced sample (%)			
	Lattice oxygen	Adsorbed oxygen	Hydroxyl group	Water
$0.05Pt/CeO_2$	48.8	21.5	25.7	4.00
$2Pt/CeO_2$	77.8	9.00	7.04	6.15

Table S2. CO_2 reduction reaction rates over the temperature range 175 to 250 °C for $0.05Pt/CeO_2$ and $2Pt/CeO_2$ catalysts.

Temperature °C	Reaction rate $\mathrm{mol_{CO_2} \cdot g_{Pt}^{-1} \cdot s^{-1}}$		Reaction rate $\times 10^{-25}\ \mathrm{mol_{CO_2} \cdot Atom_{Pt}^{-1} \cdot s^{-1}}$	
	$0.05Pt/CeO_2$	$2Pt/CeO_2$	$0.05Pt/CeO_2$	$2Pt/CeO_2$
175	0.30	0.07	0.97	0.42
200	1.27	0.15	4.13	0.91
225	2.80	0.29	9.08	1.74
250	5.96	0.44	19.3	2.65

Table S3. BET surface area, pore volume and pore size, as well as the nominated and measured Pt amounts as determined from ICP-AES and ICP-MS.

Catalyst	BET			ICP-MS for Pt amount	
	Surface Area m^2/g	Pore Volume cm^3/g	Pore Size nm	Nominated value wt%	Measured value wt%
CeO_2	67.6	0.26	5.91	-	-
$0.05Pt/CeO_2$	54.2	0.17	5.98	0.05	0.048
$2Pt/CeO_2$	50.7	0.20	6.10	2	1.8

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2. Yu, X.; He, J.; Wang, D.; Hu, Y.; Tian, H.; He, Z., Facile Controlled Synthesis of Pt/MnO_2 Nanostructured Catalysts and Their Catalytic Performance for Oxidative Decomposition of Formaldehyde. *J. Phys. Chem. C* **2012,** *116*, 851-860.
3. He, J.; Ichinose, I.; Kunitake, T.; Nakao, A.; Shiraishi, Y.; Toshima, N., Facile Fabrication of Ag−Pd Bimetallic Nanoparticles in Ultrathin TiO_2-Gel Films: Nanoparticle Morphology and Catalytic Activity. *J. Am. Chem. Soc.* **2003,** *125*, 11034-11040.