Electronic Supporting Information

Epitaxy-Induced PtO_x-TiO_2 Interfaces Boost the Reverse Water-Gas Shift Reaction

Anwen Yu,[a] Xin Wang,[a] Shoujie Zhang,[a] Jiajie Ye,[a,b] Aiyong Wang,[a] Yanglong Guo,[a] Wangcheng Zhan,[a] Li Wang,[a] Xuan Tang,[a] * Yun Guo[a] *

[a.] *State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China.*

[b.] *Sinochem International Science and Technology Innovation Center, Shanghai, 201315, China;*

*E-mail: xuantang@ecust.edu.cn; yunguo@ecust.edu.cn

1. Materials and Methods

1.1 Chemical.

Platinum nitrate ($Pt(NO_3)_2$) was supplied by Sino-Platinum Metals Co., Ltd. Titanium dioxide (TiO_2, Rutile) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Deionized water from Milli-Q integral water purification system (Millipore, 18.2 $M\Omega \cdot cm^{-1}$).

1.2 Catalyst preparation

The catalysts were prepared by a facile incipient wetness impregnation method. Typically, a certain amount of the $Pt(NO_3)_2$ precursors was added to rutile TiO_2, followed by continuous ultrasonic stirring for 30 min. After aging for 6 h, it was transferred to the oven at 110 °C overnight. The PtO_2/TiO_2 was obtained after the calcination process at 400 °C for 2 h. The $Pt/PtO_x/TiO_2$ sample was obtained by the H_2 reduction treatment of PtO_2/TiO_2 at 300 °C for 2 h. The Pt/TiO_2 sample was obtained without calcination treatment, i.e., direct H_2 reduction at 300 °C for 2 h after drying by oven at 110 °C. All Pt/TiO_2 catalysts were prepared following the same protocol to minimize the interference from synthetic conditions. The theoretical Pt loading for each catalyst is 0.5 wt.%.

1.3 Catalytic activity test.

Initially, 100 mg of the catalyst was diluted with quartz sand and loaded into a stainless-steel tube reactor. Prior to the test, the catalyst was in situ reduced under a 10 vol% H_2/N_2 atmosphere at 300 °C for 1 h. Subsequently, the temperature was cooled to below 180 °C, and the reducing gas was switched to a reaction gas mixture of CO_2 and H_2 with a volume ratio of 1:3, at a total flow rate of 20 mL/min. The reactor was connected to an Agilent 7890 A gas chromatograph, and the tubing between the reactor and the GC injection port was maintained at 140 °C to ensure all products remained gaseous. Samples were taken every 0.5 h, with each temperature lasting 1 h. In the Agilent 7890 A GC, a TDX-01 column connected to a TCD was used to monitor CO_2 and CO; a HP-PLOT Q capillary column connected to an FID was used to monitor CH_4, using N_2 as the internal standard. The CO_2 conversion and product selectivity were calculated using the normalization method. The conversion of carbon dioxide (X (CO_2)), product selectivity S (S (CO)), and space time yield (STY (CO)) of CO were calculated using the following equations.

$$X(CO_2) = \left(1 - \frac{N_{2(in)} * CO_{2(out)}}{N_{2(out)} * CO_{2(in)}}\right) * 100\%$$

$$S(CO)=\frac{A_{CO}*f_{CO}*w_{N_2}}{A_{N_2}*f_{N_2}*w_{CO_2}*X_{CO_2}}*100\%$$

$$STY(CO)=\frac{WHSV}{V_m}*w_{CO_2}*X_{CO_2}*S_{co}*M_{CO}*100\%$$

where $N_{2(in)}$ and $N_{2(out)}$ represent the concentration of N2 before and after the reaction, respectively. A represents the GC peak area, f represents the correction factor, w represents the volume concentration, V_m is the molar volume of gas, and M represents the molecular weight.

1.5 Catalyst Characterization.

X-ray powder diffraction (XRD) patterns were obtained from a Bruker D8 focus diffraction spectrometer using Cu Kα radiation (1.54056 Å, 40 kV, and 40 mA), scanning from 10 to 80° at a speed of 4° min^{-1}. Inductively coupled plasma optical emission spectrometer (ICP-OES) was used to quantify the actual loading of Pt in the catalysts on Agilent 725ES. Aberration-corrected scanning transmission electron microscopy (AC-STEM) was operated on a ThermoFisher Themis Z transmission electron microscope equipped with two aberration correctors, operated at 300 kV with a convergence semi-angle of 17.8 mrad. The microscope was aligned using a standard gold sample before observations. High-angle annular dark-field (HAADF)-STEM images were recorded using a camera length of 115 mm on HAADF detectors, and the inner- and outer collection angles of 47 and 200 mrad, respectively. The acquired images were processed by Gaussian blur filter. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi spectrometer. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of CO adsorption on catalysts was measured on a Nicolet Nexus 6700 spectrometer. The DRIFTS were collected with a resolution of 4 cm^{-1} and 64 scans in Kubelka-Munk units. Before CO adsorption, the samples were pretreated by H_2 at 300 °C for 1 h. The CO adsorption on various catalysts was measured at room temperature. CO_2-temperature programmed desorption (CO_2-TPD) was performed on AutoChem II 2920 apparatus. Experiments were carried out in a quartz reactor loaded with 50 mg of the catalyst sample, using the online MS (HIDEN ANALYTICAL HPR-20 QIC) as the detector. Typically, the sample was first pretreated with H_2 at 300 °C for 1 h, and the reactor was cooled to room temperature. Then pure He gas was introduced to remove physisorbed H_2. Finally, He was replaced with 10 vol.% CO_2 flowing at 40 mL min^{-1}. Change to pure He to purge excess CO_2 for 30 min. The reactor temperature was raised to 600 °C with the speed at 10 °C min^{-1} after the stabilization of all the signals. The electron paramagnetic resonance (EPR) experiment was carried out on a Bruker EMX-8/2.7 electron spin resonance spectrometer. Raman spectra were collected on a Horiba HR Evolution Raman spectrometer using a 532 nm excitation laser. In situ DRIFTS experiments were conducted using a Bruker Vertex 70V Fourier Transform Infrared Spectrometer equipped with an MCT detector, with spectra collected in the wavenumber range of 650-4000 cm^{-1}. Prior to in situ reaction DRIFTS testing, all catalysts underwent one hour of in situ pretreatment at 300 °C under 10 vol% H_2. Physical adsorption of H_2 was subsequently removed by Ar purging, and the flow was switched to 10 vol% CO_2 gas at the same temperature for real-time monitoring. To thoroughly analyze the evolution of species on the catalyst surface, a temperature-programmed CO_2 hydrogenation reaction was conducted by introducing a mixed gas of CO_2 and H_2 (CO_2: H_2 = 1:3) at a flow rate of 25 mL min^{-1}. CO chemisorption measurements were carried out using a pulse method on a Micromeritics Autochem II 2920 chemisorption analyzer. Before testing, 50 mg of the samples were placed in a U-shaped quartz reactor and reduced by 10 vol.% H_2/Ar at 200 °C for 30 min. The Pt dispersion was calculated by assuming a CO/Pt average stoichiometry of 1.

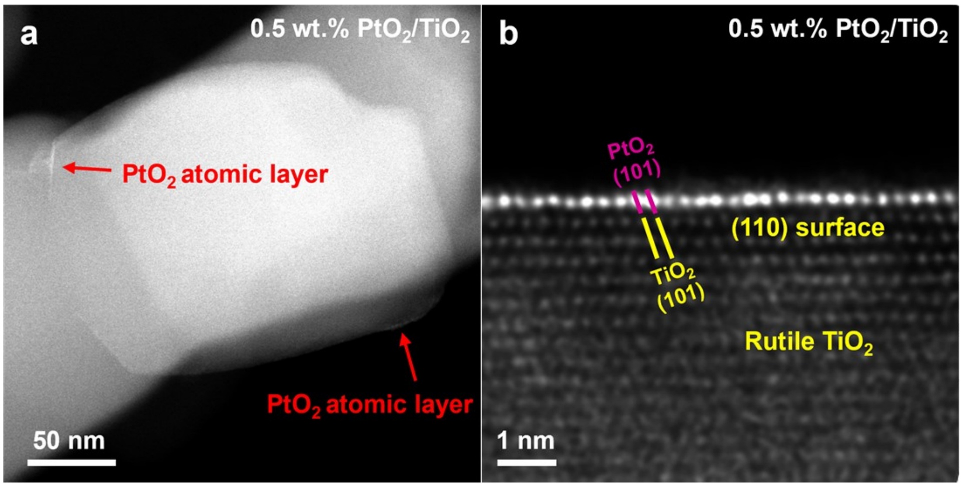

Fig. S1 The representative (a) low-magnification and (b) atomic-scale HAADF-STEM images of 0.5 wt.% PtO_2/TiO_2 sample prepared using $Pt(NO_3)_2$. Reproduced with permission from ref[1].

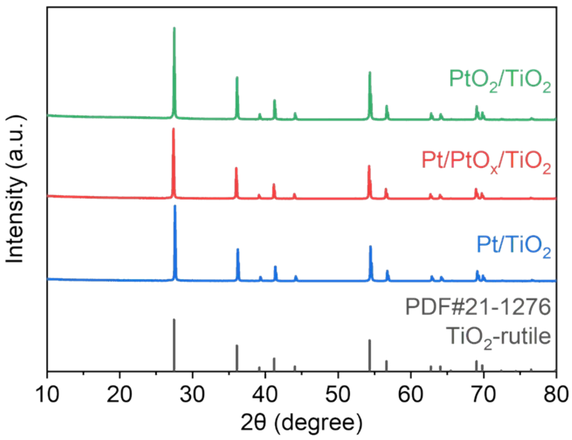

Fig. S2 The XRD patterns of PtO_2/TiO_2, $Pt/PtO_x/TiO_2$ and Pt/TiO_2 catalysts.

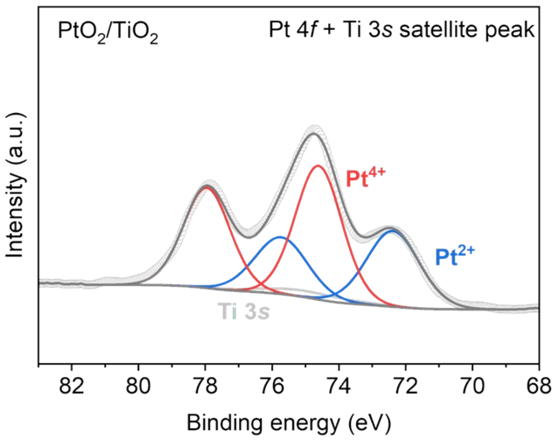

Fig. S3 XPS in Pt 4f region of PtO_2/TiO_2 catalyst.

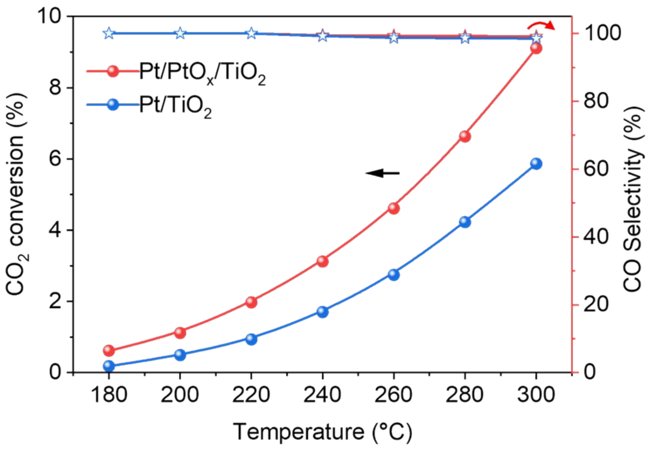

Fig. S4 CO$_2$ conversion and CO selectivity at various temperatures over different catalysts. Reaction condition: F = 20 mL·min^{-1}; CO$_2$/H$_2$ = 1:3; P = 1 bar; T = 180-300 °C.

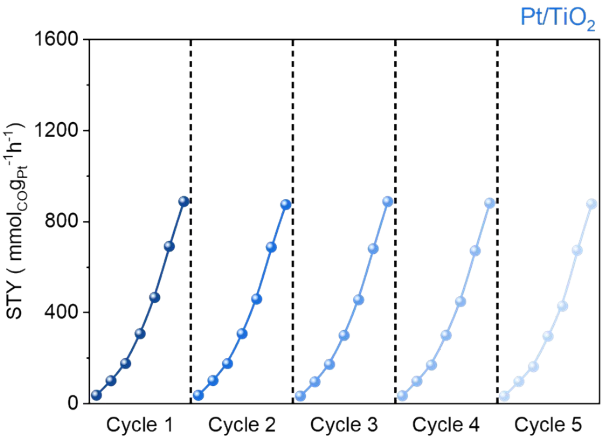

Fig. S5 Cyclic stability tests of the Pt/TiO$_2$ catalyst.

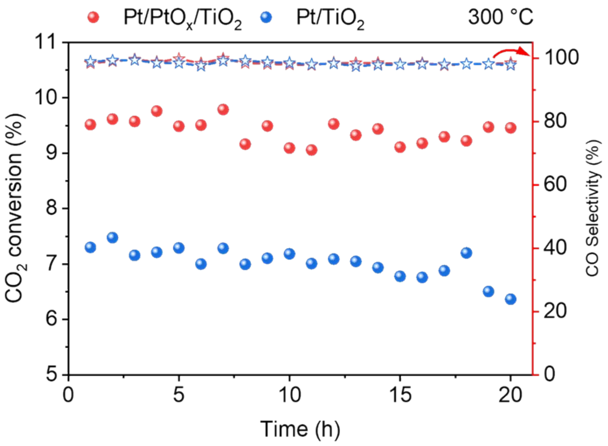

Fig. S6 The long-term stability of Pt/PtO$_x$/TiO$_2$ and Pt/TiO$_2$ catalysts.

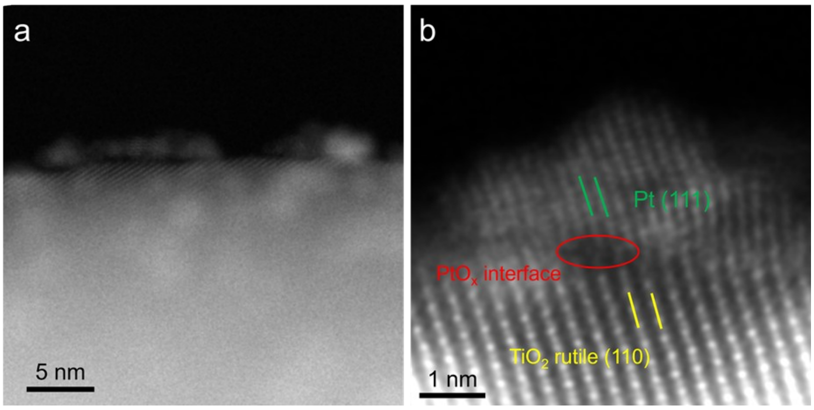

Fig. S7 The HAADF-STEM images of the Pt/PtO$_x$/TiO$_2$ catalysts after reaction.

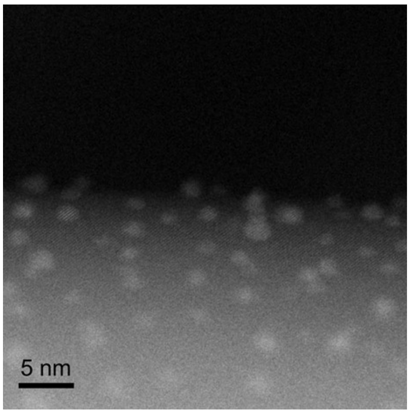

Fig. S8 The HAADF-STEM images of the Pt/TiO_2 catalysts after reaction.

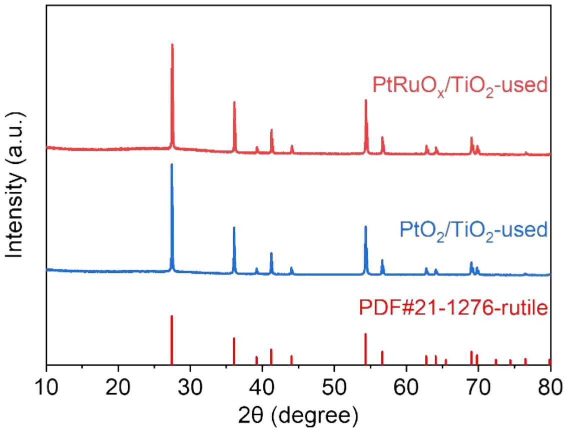

Fig. S9 The XRD patterns of the Pt/PtO$_x$/TiO$_2$ and Pt/TiO$_2$ catalysts after reaction.

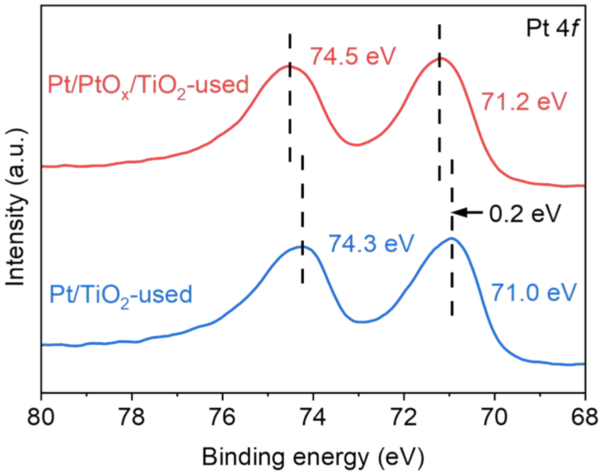

Fig. S10 The Pt 4f XPS of the Pt/PtO$_x$/TiO$_2$ and Pt/TiO$_2$ catalysts after reaction.

Table S1 Chemical compositions of $Pt/PtO_x/TiO_2$ and Pt/TiO_2 catalysts.

Catalyst	**Theoretical Pt content (wt. %)**	**Actual Pt content (wt. %)** [a]
$Pt/PtO_x/TiO_2$	0.5	0.36
Pt/TiO_2	0.5	0.36

a: Determined by ICP-OES

Table S2 The dispersion of Pt for $Pt/PtO_2/TiO_2$ and Pt/TiO_2.

Sample	Pt dispersion (%)[a]
$Pt/PtO_x/TiO_2$	73
Pt/TiO_2	66

a: Determined by CO pulse chemisorption.

references

1. X. Tang, A. Yu, Q. Yang, H. Yuan, Z. Wang, J. Xie, L. Zhou, Y. Guo, D. Ma and S. Dai, *J. Am. Chem. Soc.*, 2024, **146**, 3764-3772.