Supporting information

Coupled system intensifying the photocatalytic reduction of in-situ captured CO_2 to Methane

Shichao Zhang[a,c], Xueyuan Wang[c], Genheng Li[c], Yang Liu[a], Di Huang[a*], Tengfei Yang[a], Junju Mu[c], Yingping Huang[a] Chaofeng Zhang[b,c*] and Feng Wang[c*]

[a] Engineering Research Center of Eco-environment in Three Gorges Reservoir Region of Ministry of Education, China Three Gorges University, Yichang 443002, China

[b] Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, College of Light Industry and Food Engineering, Nanjing Forestry University, Nanjing 210037, China

[c] State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

[*] Corresponding author:

E-mail address: huangdi@ctgu.edu.cn, zhangchaofeng@njfu.edu.cn, wangfeng@dicp.ac.cn

S1. Experimental section

Materials

All reagents and materials are purchased from commercial sources and can be used without further purification. Tetraethylenepentamine (TEPA, 99%) was purchased from Aladdin Co. Ltd (Shanghai China); TiO_2 (Degussa P25) was purchased from Degussa; $PdCl_2$ was purchased from the Non-Ferrous Metal Institute of Shenyang; Mesoporous silica with a diameter of about 1 mm was purchased from Shanghai Huating nanotechnology Co., Ltd (Shanghai China). The deionized water was self-prepared.

Preparation of bifunctional adsorption catalysts

Firstly, the Pd/TiO_2 catalyst was prepared by the traditional impregnation method. Typically, 4.26 mL of $PdCl_2$ aqueous solution (2.348 mg mL^{-1}) was added into a pear-shaped flask filled with 40 mL of deionized water and stirred well. 1.0 g of TiO_2 carrier was gradually added and the flask was transferred to the shaking table for dynamic impregnation at 25 °C and 100 r min^{-1} for 12 hours. Then, the aqueous solution was removed with a rotary evaporator, and the samples were subsequently dried in a vacuum drying oven at 100 °C for 2 hours. The dried samples were calcined at 400 °C for 4 hours. When cooled to room temperature, the samples were further reduced in H_2 flow (30 mL min^{-1}) at 350 °C for 4 hours with a heating rate of 10 °C per minute.

Secondly, based on our previous work, amino-functionalized CO_2 adsorbents were prepared by the impregnation method [1]. Typically, 0.3g of Tetraethylenepentamine (TEPA) was dissolved in 4 mL of anhydrous methanol solution and stirred for 30 min. Then, 0.7g of mesoporous silica was added to the prepared amine solution. Following, the flask was transferred to an incubator shaker and kept at 180 r min^{-1} and 35 ºC for 12 h. Using a rotary evaporator to remove the methanol solution at 50 ºC and 110 r min^{-1} and further dried overnight in a vacuum drying at 85 ºC. Finally, the Pd/TiO_2 catalyst and the solid amine CO_2 adsorbent were mixed according to the mass ratio of 1:2, 1:1, and 1:0.5 to obtain bifunctional adsorption catalysts with different adsorbent contents.

S2. Characterization

X-ray diffraction (XRD) patterns of the samples were acquired on an X-ray diffractometer model Empyrean. The data scanning range of the XRD patterns was 10-80° with a scanning speed of 10° min^{-1}. The changes of specific surface area, pore volume, and pore size distribution of adsorbents before and after amine-functionalization were measured by N_2 physical adsorption on a Micromeritics ASAP 2020 Plus. The adsorbents should be degassed at 110 °C for 8 hours before testing. The total surface area was calculated by the Brunauer-Emmett-Teller (BET) equation, and the pore volume and pore size distribution were calculated according to the BJH method. Transmission electron microscopy (TEM) images of the samples were captured on JEM-F200 with an accelerating voltage of 200 kV and equipped with an energy dispersive spectrometer (EDS).

H_2-TPD was tested by the Autochem II 2920 chemisorption instrument. Generally, 200 mg (40-60 mesh) of Pd/TiO_2 catalyst was loaded into a U-tube and purged with He for 10 min. The temperature was increased to 350 °C at a ramp rate of 10 °C min^{-1}, and the catalyst was pretreated for reduction using H_2 gas (30 mL min^{-1}, held for 60 min). Then the temperature was lowered to 45 °C and kept for 60 min for H_2 adsorption. After the adsorption was completed, the gas was switched to He (30 mL min^{-1}) and purged for 30 min to remove the physically adsorbed H_2. Finally, the catalyst was heated up to 500 °C under He atmosphere at a ramping rate of 10 °C min^{-1} to obtain the programmed ramping desorption curve of H_2.

S3. Density Functional Theory calculation

The density-functional theory (DFT) calculations were conducted utilizing the VASP software package [2, 3]. The affixed plane wave (PAW) method was employed to accurately depict the interaction between the nucleus and valence electrons. Additionally, the Perdew-Burke-Ernzerhof (PBE) generalization within the generalized gradient approximation (GGA) framework was utilized to describe the exchange-associative potential [4, 5]. The Kohn-Sham wave function, based on the plane-wave basis set, was configured with a truncation energy of 450 eV, and calculations that incorporate valence electron spin polarization were performed. The convergence criteria for the total energy and force were set to 10^{-5} eV •Å and 0.02 eV •Å, respectively. Sampling of the Brillouin zone was achieved with gamma points, and a k-point density of 221 was selected. During the calculations, a Hubbard potential parameter of 4.2 eV was applied to the Ti atoms [6], effectively accounting for the contributions of strongly interconnected d-orbital electrons. For the TiO_2 model, the (101) crystal plane of the anatase phase was adopted, featuring a periodic plane surface comprised of six atomic layers, separated by a 1.5 nm vacuum layer. A super-cell of dimensions (3×4) was utilized, with the bottom two layers of atoms being fixed. Pd nanoparticles (Pd_{10}), deposited on the surface of the TiO_2 model, were represented by a face-centered cubic crystalline phase consisting of 10 Pd atoms. The SiO_2 component was modeled in its amorphous phase, and the bottom layer of atoms was fixed during the structural relaxation calculations.

S4. COMSOL simulation

This study modeled CO_2 diffusion and adsorption phenomena using COMSOL Multiphysics in a fully coupled manner. The simulation incorporated two physics interfaces: Transport of Diluted Species for gas-phase diffusion and General Form Boundary PDE for surface adsorption kinetics.[7] A transient model was used for calculations to analyze and simulate the diffusion and adsorption of CO_2. This simulation experiment was conducted inside a test tube with a volume of 5 mL initially. The interior of the test tube contained 500 μL of CO_2, and there was a Pd/TiO_2 catalyst or Pd/TiO_2-TEPA/SiO_2 dual functional adsorption catalyst at the bottom of the tube. Simulations were performed to calculate the concentration changes of CO_2 in both experimental setups.

S5. Photocatalytic CO_2 reduction experimental test

The CO_2 photocatalytic reduction reaction was carried out with a self-constructed photoreactor in our laboratory, during which the light source used was blue LEDs with a single wavelength of 365 nm and an input power of 6.5 W. Generally, 10.0 mg of bifunctional adsorption catalyst was taken into a 5.0 mL quartz photoreactor tube. Then, the atmosphere in the photoreactor tube was replaced with an Ar atmosphere through a glove box. 5.0 mL of H_2 and 500 μL of CO_2 reaction gas were injected into the photoreactor tube. Finally, the photoreactor tube was transferred to a photoreactor, and the reaction was carried out under 365 nm light for 10 h. Be careful to wear UV protective glasses during the placement of the photoreactor tube, and the temperature was maintained at room temperature throughout the reaction. The reaction products were analyzed using a Shimadzu GC-2014, which was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

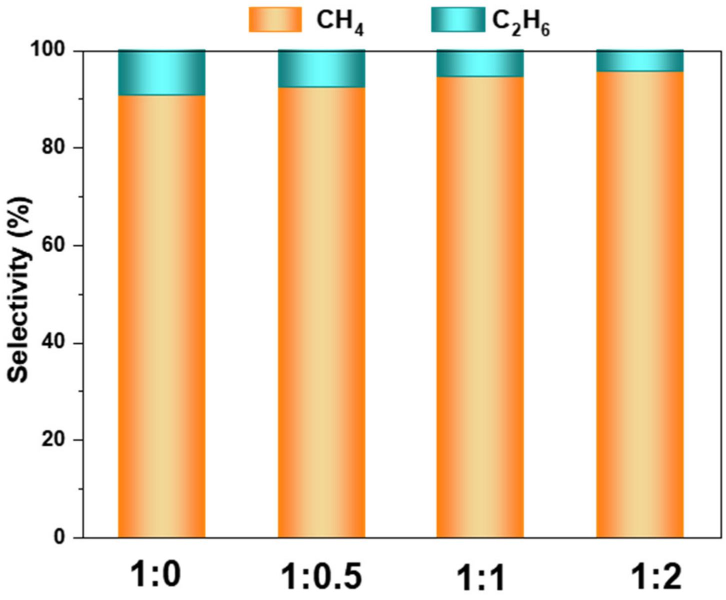

Fig. S1. Product selectivity under different mass ratios of Pd/TiO_2 and $TEPA/SiO_2$

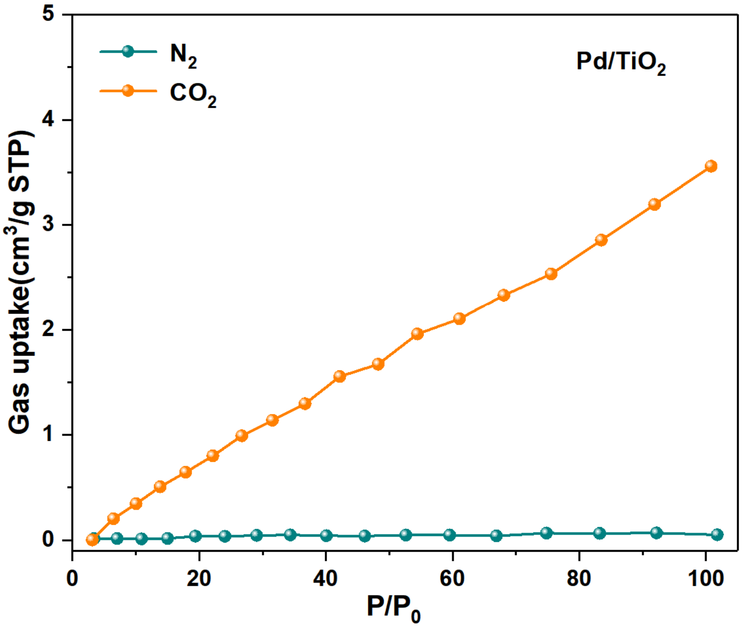

Fig. S2. Adsorption isotherms of CO_2 and N_2 of Pd/TiO_2

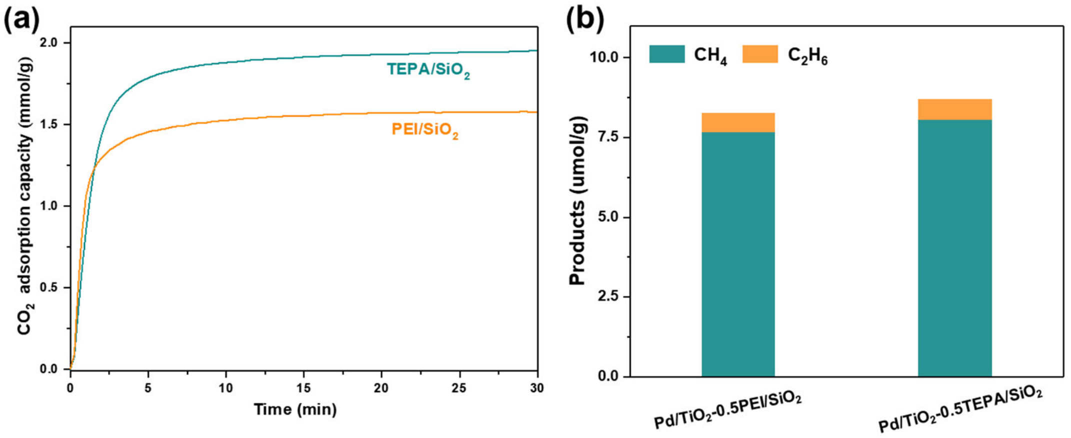

Fig. S3. (a) CO_2 adsorption curve of TEPA/SiO_2 and PEI/SiO_2 with 30 wt% amine-loading; (b) Photocatalytic CO_2 reduction performance under different catalysts.

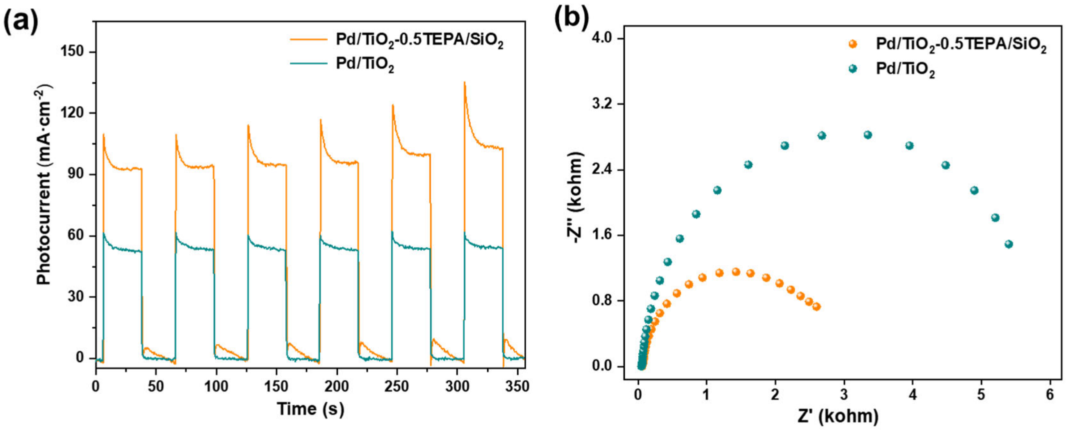

Fig. S4. (a) Transient photocurrent and (b) Electrochemical impedance spectra of Pd/TiO_2 and Pd/TiO_2-0.5TEPA/SiO_2.

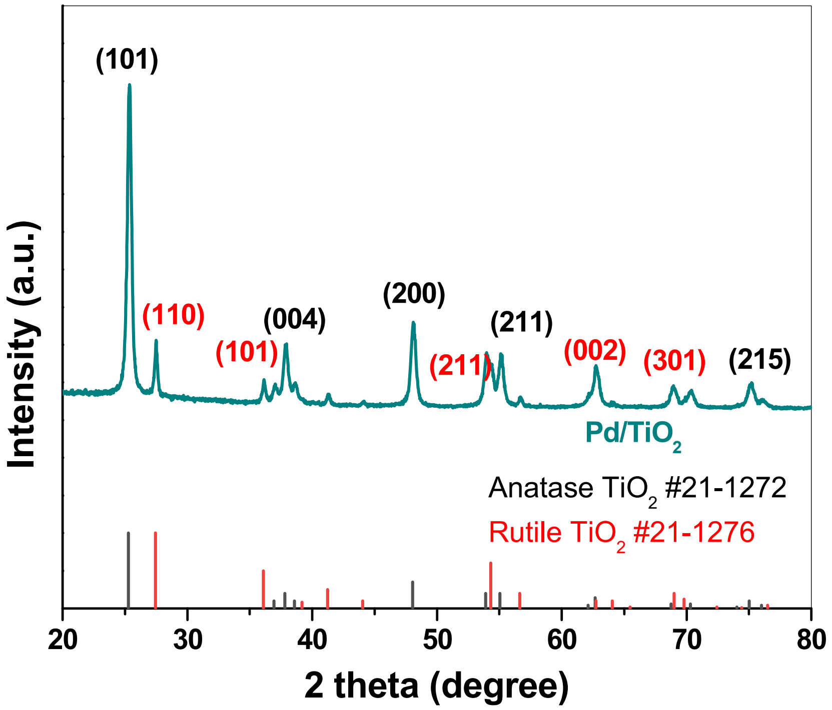

Fig. S5. XRD powder diffraction spectrum of Pd/TiO_2

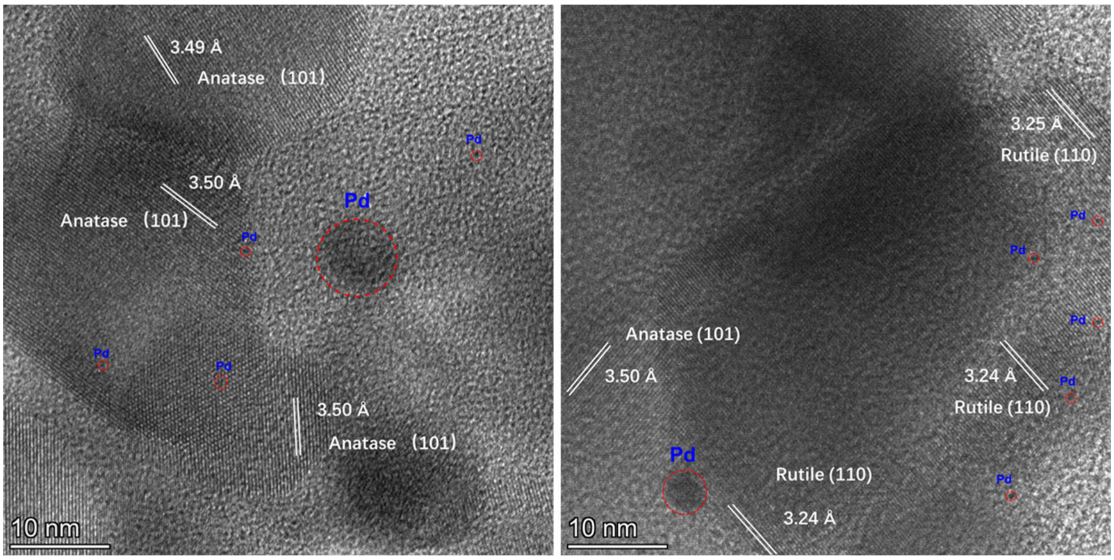

Fig. S6. HRTEM images of Pd/TiO_2

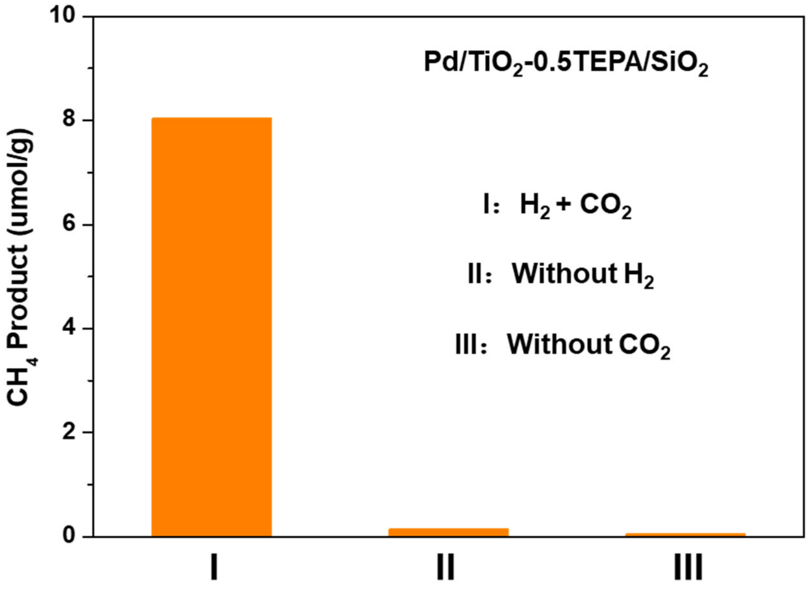

Fig. S7. Control experiments for several conditions

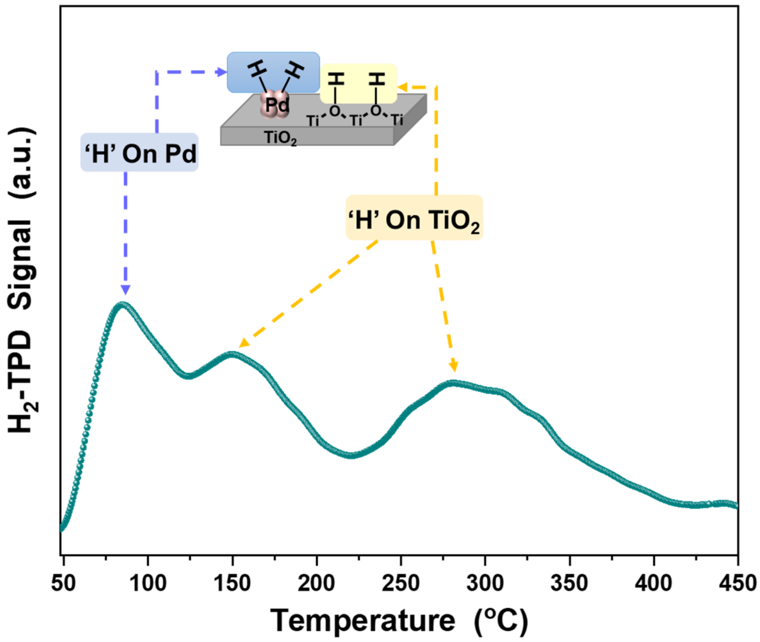

Fig. S8. H_2-TPD curve of Pd/TiO_2 catalyst.

Reference

[1] S. Zhang, H. Dong, A. Lin, C. Zhang, H. Du, J. Mu, J. Han, J. Zhang, F. Wang, ACS Sustain. Chem. Eng. 10 (2022) 13185-13193.

[2] J. Hafner, J. Comput. Chem. 29 (2008) 2044-2078.

[3] G. Kresse, J. Furthmuller, Comput. Mater. Sci 6 (1996) 15-50.

[4] X. Chang, T. Wang, J. Gong, Energ. Environ. Sci. 9 (2016) 2177-2196.

[5] G. Kresse, D. Joubert, Physical Review B 59 (1999) 1758-1775.

[6] D. Wang, Z.-P. Liu, W.-M. Yang, ACS Catal. 8 (2018) 7270-7278.

[7] H. Mohammaddoost, M. Asemani, A. Azari, B. Vaferi, Process Saf. Environ. 180 (2023) 1012-1022.