

Photocatalytic reduction of CO₂ with H₂O: Significant enhancement of the activity of Pt/TiO₂ for CH₄ formation by addition of MgO

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Electronic Supplementary Information

1. Experimental details

(1) Preparation of photocatalysts

TiO₂ (P25), which contained 20% rutile and 80% anatase, was purchased from Degussa. The Pt/TiO₂ was prepared by a photodeposition method. Briefly, a certain amount of TiO₂ was suspended in an aqueous solution of hexachloroplatinic acid (H₂PtCl₆) containing 0.1 M methanol as a hole scavenger. The suspension was irradiated with a 300 W mercury lamp for 2 h. The obtained sample was recovered by filtration, followed by washing repeatedly with deionized water and drying at 373 K for 12 h. Basic metal oxide-modified TiO₂ samples including MgO/TiO₂ were prepared by an impregnation method in aqueous solutions using TiO₂ (P25) and metal nitrate as precursors. After impregnation and drying, the sample was calcined at 773 K for 4 h in air. The Pt–MgO/TiO₂ or other metal oxide-modified Pt/TiO₂ catalyst was prepared by the photodeposition of Pt nanoparticles onto MgO/TiO₂ or other metal oxide-modified TiO₂ using the same procedure as that for Pt/TiO₂.

(2) Characterization of photocatalysts

The photocatalysts were characterized by Powder X-ray diffraction (XRD), N₂ physisorption, transmission electron microscopy (TEM) and CO₂ chemisorption measurements.

XRD patterns were collected on a Panalytical X'pert Pro diffractometer using Cu K_α radiation (40 kV, 30 mA). Only diffraction peaks ascribed to TiO₂ crystallites containing both rutile and anatase phases were observed. No peaks belonging to basic metal oxides (e.g., MgO) or Pt were detected.

N₂ physisorption was carried out with a Micromeritics Tristar 3020 surface area and porosimetry analyzer to measure the surface area of the photocatalyst.

TEM measurements were performed on a JEM-2100 electron microscope operated at an

acceleration voltage of 200 kV.

The amount of CO₂ chemisorption was measured at room temperature with a ASAP2020C Micromeritics apparatus by adopting the procedure reported by Teramura et al.¹

(3) Photocatalytic reaction

Photocatalytic reduction of CO₂ in the presence of H₂O was carried out in a stainless-steel reactor (volume, ~100 mL) with a quartz window on the top of the reactor (Fig. S1). The photocatalyst was placed on a Teflon catalyst holder. The light source was 100 W Xe lamp (Beijing Trusttech Co., Ltd.) at UV-vis ($\lambda = 320\text{-}780$ nm). Typically, 20 mg of catalyst was used. The pressure of CO₂ was typically regulated at 2.0 MPa, and 1.0 mL of water was added in the reactor. The photocatalytic reaction was typically performed at room temperature for 10 h.

The amounts of CO and CH₄ after the reaction were analyzed by gas chromatography. In our work, we adopted an FID detector for quantifying the amounts of products formed from CO₂ to ensure high sensitivities. After the effluents containing CO₂, CO and CH₄ were separated by a carbon molecular sieve (TDX-01) column, CO and CO₂ were further converted to CH₄ by a methanation reactor, and were then analyzed by the FID detector. H₂ was used as the carrier gas. The detection limits of our analytic method for CH₄ and CO were both 2 nmol (0.002 μmol). We performed the same experiment for 3 times for each catalyst, and the relative error was <5%.

Liquid products such as CH₃OH, HCHO and HCOOH possibly formed and dissolved in water were also analyzed by gas chromatography, but no such products were detected under our reaction conditions.

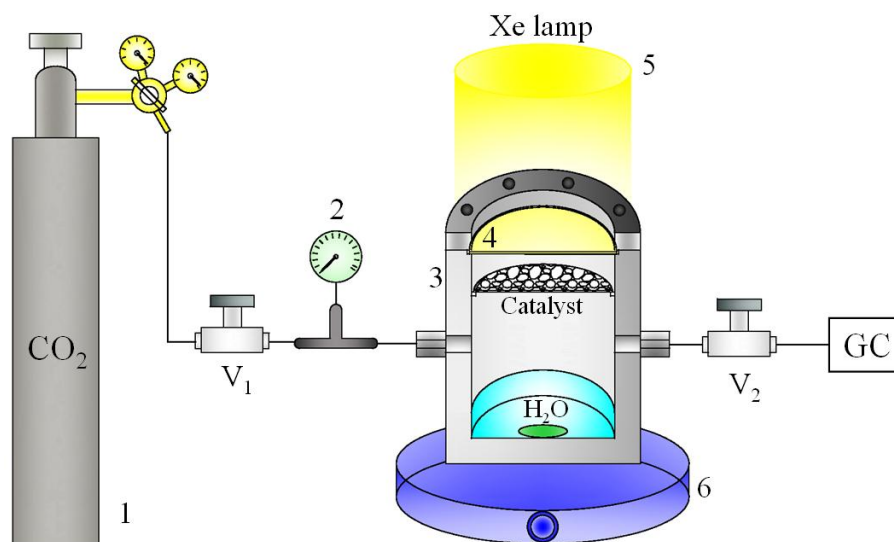


Fig. S1 Reactor used for photocatalytic reduction of CO₂ in the presence of H₂O.

1: CO₂ gas cylinder, 2: pressure digital meter, 3: stainless steel reactor, 4: O-ring quartz window, 5: Xe lamp, 6: magnetic stirrer, V₁ and V₂: valves.

To measure the amount of O₂ formed during the photocatalytic reaction, we also analyzed the products by using an Agilent Micro GC 3000 equipped with a 5A column and a TCD detector. We performed a 30 h photocatalytic reaction for the 0.5% Pt–1% MgO/TiO₂ catalyst under the reaction conditions described above. The amounts of O₂ and CH₄ detected were 13.6 μmol and 5.5 μmol. The molar ratio of O₂/CH₄ was approximately 2.5/1, slightly higher than the stoichiometric ratio (2/1) expected from the photocatalytic conversion of CO₂ with H₂O to CH₄ and O₂. We speculate that the slightly higher ratio of O₂/CH₄ may be due to the formation of other reduction products such as CO.

2. Comparison of CH₄ formations in the photocatalytic reactions in the presence and the absence of CO₂ over 0.5% Pt/TiO₂ and 0.5%–1% MgO/TiO₂ catalysts

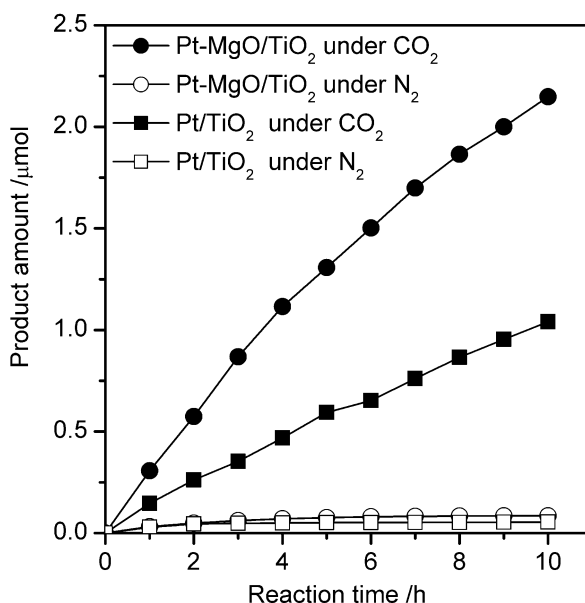


Fig. S2 Amounts of CH₄ formed in photocatalytic reactions in the presence of H₂O under CO₂ or N₂. Reaction conditions: catalyst, 0.020 g; CO₂ or N₂ pressure, 2 MPa; H₂O, 1.0 mL; irradiation time, 10 h.

3. Effect of basic metal oxide modifiers on photocatalytic performances of the 0.5 wt% Pt/TiO₂ catalysts

Table S1 shows the photocatalytic performances of the 0.5 wt% Pt/TiO₂ catalysts modified with various basic metal oxides for the reduction of CO₂ in the presence of H₂O.

Table S1 Effect of basic metal oxide modifiers on photocatalytic performances of the Pt/TiO₂ for the reduction of CO₂ with H₂O.^a

Photocatalyst ^b	S_{BET}^c (m ² g ⁻¹)	Mean size of Pt (nm)	Chemisorbed CO ₂ (μmol g ⁻¹)	Product amount (μmol)	
				CO	CH ₄
0.5% Pt/TiO ₂	55	4.2	5.0	0.22	1.0
0.5% Pt-1% Al ₂ O ₃ /TiO ₂	51	4.0	4.9	0.15	0.90
0.5% Pt-1% CuO/TiO ₂	50	3.9	5.6	0.15	1.2
0.5% Pt-1% ZnO/TiO ₂	44	3.8	5.8	0.12	1.2
0.5% Pt-1% La ₂ O ₃ /TiO ₂	50	4.0	6.6	0.014	1.4
0.5% Pt-1% Lu ₂ O ₃ /TiO ₂	46	3.9	8.8	0.006	1.7
0.5% Pt-1% MgO/TiO ₂	43	4.0	11.5	0.006	2.2
0.5% Pt-1% CaO/TiO ₂	43	4.0	8.7	0.006	1.5
0.5% Pt-1% SrO/TiO ₂	44	4.1	10.6	0.010	1.9
0.5% Pt-1% BaO/TiO ₂	47	4.0	8.3	0.008	1.5

^a Reaction conditions: catalyst, 0.020 g; CO₂ pressure, 2 MPa; H₂O, 1.0 mL; irradiation time, 10 h.

^b The percentage before each component denotes its weight percentage. ^c BET surface area.

References

- 1 K. Teramura, S. Okuoka, H. Tsuneoka, T. Shishido and T. Tanaka, *Appl. Catal. B*, 2010, **96**, 565-568.