



CO₂ photoreduction with H₂O vapor on highly dispersed CeO₂/TiO₂ catalysts: Surface species and their reactivity



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ABSTRACT

Weak interaction between TiO₂ and CO₂ molecules is detrimental to CO₂ photoreduction. To alleviate this drawback, ceria is usually exploited as a basic promoter, but fundamental insights into the correlation of ceria-tuned CO₂ adsorption and the resulting activity of photoreduction are lacking. In this work, highly dispersed CeO₂/TiO₂ and bare TiO₂ catalysts were fabricated and their structural, surface, and optical properties and activity for CO₂ photoreduction were explored. Microcalorimetric measurement and in situ infrared spectroscopy were used to reveal the strengths and states of CO₂ adsorption and the course of photoreduction of CO₂ with H₂O vapor. Monodentate carbonate (m-CO₃²⁻), bidentate carbonate (b-CO₃²⁻), and bidentate bicarbonate (b-HCO₃⁻) are found to be the main surface species for the coadsorption of CO₂ and H₂O on catalyst surfaces. The presence of CeO₂ containing Ce³⁺ strengthens the bonding of CO₂ with catalyst surfaces and increases the production of b-CO₃²⁻ and b-HCO₃⁻ species. Unlike m-CO₃²⁻, b-CO₃²⁻ and b-HCO₃⁻ surface species could readily be transformed to surface CO₂ in the presence of H₂O under simulated sunlight irradiation. This might be attributed to the fact that the CO₂ segment in the two species is bound to Ti/Ce atoms that have reductive capabilities under photoirradiation. In addition, the presence of CeO₂ containing Ce³⁺ facilitates photogenerated charge separation. As a result, ceria-tuned CO₂ adsorption and enhanced charge separation are jointly responsible for the increased activity of CeO₂/TiO₂ catalysts.

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1. Introduction

Photocatalytic reduction of CO₂ with H₂O vapor on chemically stable and environmentally benign TiO₂ is gaining increased interest because it is a promising “green chemistry” approach for the direct conversion of CO₂ to value-added fuels (CO, methane, methanol, etc.) driven by sunlight [1–3]. However, TiO₂ photocatalyst suffers from several disadvantages that ultimately lead to low reaction efficiency [4], including (1) low solar energy utilization due to its large band gap (3.2 eV for anatase TiO₂ and 3.0 for rutile TiO₂), (2) fast recombination of photogenerated electron–hole pairs, and (3) weak interaction between CO₂ molecules and TiO₂ surfaces, leading to low coverage of reactive adsorbed species and difficult displacement of the reaction products and/or inactive intermediates by CO₂ molecules [3]. The former two limitations have been extensively addressed in the literature by metal (e.g., Pt, Au) coupling or nonmetal doping, mixed phase TiO₂ [5,6], p–n

heterojunction construction, photosensitizer decoration, and defect production [7,8]. However, limited attention has been focused on the last one, which is also a key factor in CO₂ photoreduction efficiency [3,9–12].

The surface chemistry of CO₂ suggests that two types of surface species for the adsorption of CO₂ exist on the surface of TiO₂, molecularly adsorbed CO₂ and surface carbonates [13,14]. They are easily desorbed from the clean and hydrated TiO₂ surfaces at room temperature due to low adsorption energy [13,15]. Recently, the use of basic additives to improve CO₂ adsorption has attracted some attention due to the fact that CO₂ is an acidic molecule [4]. Indeed, it has been found that alkali and alkaline earth metal additives such as MgO, Na₂CO₃, and NaOH exhibit positive effects on the photoreduction of CO₂ [3,9,10,16]. Meng et al. pointed out the modification of TiO₂ with NaOH can promote CO₂ chemisorption and subsequent activation, thereby resulting in highly effective conversion of CO₂ to CH₄ [9]. Rare earth metal oxides have been widely investigated as basic promoters. Besides promoting the adsorption of CO₂ [4,17], their addition could also provide several other benefits: (1) extending the light absorption of

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TiO₂-based catalysts to the visible region [18,19], (2) promoting photogenerated electron–hole pair separation at ceria–titania interfaces [20–22], (3) increasing the redox capability [23], and (4) tailoring surface states of TiO₂ [24]. Considering these factors, rare earth metal oxides could be promising promoters for CO₂ photoreduction on TiO₂.

Ceria is an important representative of rare earth metal oxides, and a lot of effort has been made to apply CeO₂–TiO₂ composites for photocatalytic oxidation of various organic pollutants such as dyes, toluene [25–27], pesticides, acetaldehyde, or 4-chlorophenol in condensed phase [28,29]. For example, Muñoz-Batista et al. have done systematic studies on photocatalytic degeneration of toluene over ceria–titania composites, revealing degeneration kinetics, the role of CeO₂–TiO₂ interface contact, and g-C₃N₄ modification effect [24–26]. Based on previous studies, it can be concluded that ceria–titania catalysts are advantageous in photocatalytic oxidation of organic pollutants, as compared to bare TiO₂. Unfortunately, little research regarding the photocatalytic reduction of CO₂ over CeO₂–TiO₂ photocatalysts has been reported, except for studies by Wang et al. [18], Matějová et al. [28], and Jiao et al. [30]. Wang et al. [18] and Jiao et al. [30] mainly focused on the preparation of ordered macro- and meso-porous CeO₂–TiO₂ materials and attributed enhanced CO₂ photoreduction performance to their special composition and structure. The work by Matějová et al. [28] indicated that the introduction of ceria to TiO₂ adjusted the energies of electrons and holes of the catalysts, thereby enhancing the CO₂ photoreduction activity. These three studies focused on the relationship between the structural/electronic properties of the CeO₂–TiO₂ catalyst and its CO₂ photoreduction activity. To the best of our knowledge, however, the fundamental role of ceria-tuned CO₂ adsorption in its photoreduction has not yet been investigated.

Interface plays an important role in catalytic reactions [22,24,31]; e.g., the presence of interfaces obviously facilitates photogenerated charge separation in photocatalysis. Reducing particle size can effectively increase the interfacial areas, thus achieving desirable catalytic activity [24]. In view of this, highly dispersed CeO₂ on TiO₂ catalysts were prepared by a one-pot hydrothermal method in this work. Their structural, surface, and optical properties and activity for CO₂ photoreduction were systematically studied. Microcalorimetric measurement and in situ infrared spectroscopy (IR) were used to reveal the strengths and states of CO₂ adsorption and the course of photoreduction of CO₂ with H₂O vapor. The presence of CeO₂ tuned adsorptive states of CO₂ on catalyst surfaces in the presence of H₂O, resulting in increased production of bidentate carbonate (b-CO₃²⁻) and bidentate bicarbonate (b-HCO₃⁻) relative to monodentate carbonate (m-CO₃²⁻) (shown in Scheme 1). The two surface species could be readily transformed to surface CO₂⁻ under simulated sunlight irradiation, which is a key intermediate for CO₂ photoreduction. The present work deepens the understanding of the role of ceria in CO₂ photoreduction at TiO₂ catalysts and the course of catalysis of CO₂ photoreduction in the presence of H₂O vapor.

2. Experimental

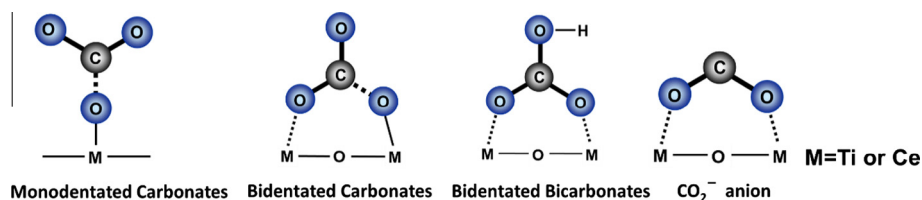
2.1. Synthesis of photocatalysts

Highly dispersed CeO₂ on TiO₂ photocatalysts was prepared through a one-pot hydrothermal method using titanium (IV) bis (ammonium lactate) dihydroxides (TALH; AR, Alfa Aesar) as Ti source and Ce(NO₃)₃·6H₂O (AR; Aladdin) as Ce source, respectively. In detail, a desired amount of TALH and Ce(NO₃)₃·6H₂O was dissolved into 120 mL of distilled water in the presence of 0.1 g polyethylene glycol (PEG, M_w = 6000; AR, Aladdin). The solution was transferred to a 175 mL Teflon-lined stainless steel autoclave, which was sealed and placed in an electric oven under stirring at 250 °C for 2 h with a heating rate of 2 °C/min. The as-formed slurry was filtered and washed with distilled water. The filter cake was dried at 80 °C for 4 h and then annealed in air at 450 °C for 2 h. The as-prepared CeO₂/TiO₂ photocatalysts with CeO₂ 10, 20, and 40 wt.% were denoted as 0.1 CeO₂/TiO₂, 0.2 CeO₂/TiO₂, and 0.4 CeO₂/TiO₂, respectively. For reference, the bare TiO₂ and CeO₂ were synthesized using the same method.

2.2. Photocatalyst characterization

The chemical compositions of prepared photocatalysts were analyzed by an ARL-9800 X-ray fluorescence spectrometer (XRF). The surface area and pore size were determined using an Autosorb-IQ-MP autosorption analyzer. Experiments were carried out at 77.3 K using N₂ as an adsorbate. The samples were degassed at 473 K for 2 h before the measurements. The pore size distributions were estimated by the BJH method using the desorption branch of the isotherms. X-ray diffraction (XRD) patterns of samples were collected in ambient atmosphere by a Bruker D8 powder diffractometer with Cu Kα radiation (λ = 1.5408 Å) generated at 40 kV and 30 mA. Diffraction intensities were recorded from 20° to 80° at a rate of 6°/min. Transmission electron microscopy (TEM) characterization was performed on a JEOL-JEM 2100 electron microscope. X-ray photoelectron spectroscopy (XPS) was performed using a VG Microtech MT500 with an Mg Kα X-ray source. The binding energy scale was corrected for surface charging using the C1s peak of contaminant carbon as a reference at 285.6 eV.

The UV–vis diffuse reflectance spectra (DRS) of photocatalysts over the range 200–800 nm were obtained on a UV–vis spectrophotometer (ShimadzuSolidSpec-3700DUV) with an integration sphere diffuse reflectance attachment. The photocurrent experiments were performed in three-electrode quartz cells with 0.1 M Na₂SO₄ electrolyte solution. A platinum electrode was used as the counter electrode, and saturated calomel electrodes (SCE) were used as the reference electrodes. Working electrodes were prepared as follows: ITO glasses were washed sequentially with distilled water and ethanol in an ultrasonic cleaner for 30 min. A quantity of 10 mg of catalysts was fixed on the pretreated ITO glasses to form photocatalyst-modified ITO electrodes. A 300 W xenon lamp was used as light source, which was 15 cm away from the working electrode.



Scheme 1. Schematic diagram of surface species for the coadsorption of CO₂ and H₂O on TiO₂ and/or CeO₂ surfaces [52,57].

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