1 Photocatalytic conversion of carbon dioxide to methane on
2 TiO₂/CdS in aqueous isopropanol solution

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Abstract

The photocatalytic conversion of CO₂ to CH₄ on hybrid TiO₂/CdS catalysts in water in the presence of isopropanol (IPA) was explored. As compared to TiO₂, TiO₂/CdS increased the production of CH₄ by a factor of ~10, whereas the production of H₂ and CO remained comparable. The amount of CdS loaded on the TiO₂ was not observed to significantly affect the yields and distributions of the products. An electron impact time-of-flight mass spectrometry (TOF-MS) study revealed ¹³CH₄ to be a dominant product in the early stages of the photocatalysis under ¹³CO₂ atmosphere, whereas only ~25% of the total observed methane accounted for ¹³CH₄ resulting from ¹³CO₂ in the prolonged photocatalytic reaction over 6 h. Although the remainder of the methane originated from unlabeled carbons (e.g., from ¹²C-IPA and ¹²C-organic contaminants), the use of deuterated IPA in the TOF-MS study did not provide evidence for the contribution of the methyl groups of IPA. Furthermore, the diffuse reflectance infrared Fourier transform analysis showed the adsorption of aquated CO₂ species (e.g., (bi)carbonate via mono- and bi-dentate modes at pH ~4.5) to be enhanced by the coupling of CdS to TiO₂, which was found to significantly weaken after the reactions. On the other hand, the IPA-associated IR bands were influenced to a lesser extent by the photoreaction.

Keywords: Artificial photosynthesis, Electron donor, Isotope, Diffuse reflectance infrared Fourier transform, Carbon dioxide radical anion

Introduction

There is renewed interest in the photocatalytic conversion of CO₂ into value-added chemicals using various heterogeneous semiconductor particles [1-3]. Common CO₂ reduction products are C1 chemicals (CO [4,5], HCOOH [6-9], CH₃OH [10], and CH₄ [11]) in aqueous photocatalysis, and the production of C2-C3 hydrocarbons (e.g., C₂H₆ and C₃H₈) has also been reported [12,13]. However, the low conversion efficiency and product selectivity remain major challenges to overcome.

From the viewpoint of the reaction process and mechanism, there are several issues that need to be addressed. For example, the one-electron reduction of CO₂ ($E^\circ(\text{CO}_2/\text{CO}_2^{\bullet-}) = -1.9 \text{ V}$) [14] is thermodynamically unfavorable on most semiconductor photocatalysts because of the low level of their conduction band (CB) (e.g., R3 in Scheme 1). This reaction has often been proposed to occur in CO₂-dissolved water without convincing evidence [6,15], whereas in another study, the ESR signal of CO₂^{•−} was detected on irradiated TiO₂ in supercritical fluid CO₂ [16]. A two-electron, one-proton reaction was also proposed as an initial step in the reduction of CO₂ on the TiO₂ surface [11]. Nevertheless, semiconductors with high CB levels (e.g., CdS) were computed to be capable of driving the one-electron reduction of CO₂ adsorbed via a bi-dentate mode [13,17]. Meanwhile, the proton is a competitor for the CB electrons, leading to the formation of a hydrogen atom (H[•]) (R4) followed by numerous intermediates and products, including H₂, CO, HCO₂[•], and HCO₂[−], in the early stage of the photocatalytic process (e.g., see R1 and R6). This pathway does not require the CO₂^{•−} intermediate (R5).

In addition, there has been some concern that the hydrocarbon products arise from organic contaminants included in the semiconductor particles and chemical reagents,

rather than from the dissolved CO₂ [4,18]. Sacrificial electron donors are often introduced to suppress the re-oxidation of intermediates and have proven capable of achieving measurable product yields. However, this results in a large uncertainty in the CO₂ reduction pathway and actual CO₂-derived products yields. Even though experiments are often performed with ¹³C-labeled isotopes to confirm the ¹³CO₂-derived products, ¹²CO₂ is found in the samples, even in a high-purity ¹³CO₂ cylinder, due to various sources of ¹²C. For example, it was reported that CO and CH₄ could arise from the oxidation of organic electron donors (e.g., triethanolamine, methanol, and isopropanol) by valence band (or trapped) holes in CdS, ZnS, and TiO₂ (R2) in addition to the pathways involving CO₂ [19,20]. On the other hand, ¹³CO₂ experiments showed that ¹³C-carbons are found in CO and formate in aqueous suspensions of CdS with triethanolamine [21] and in C1-C3 hydrocarbons in CdS-coupled titanate suspensions without any electron donor [13].

With this in mind, this study was performed to examine the photocatalytic conversion of CO₂ to CH₄ in CdS-coupled TiO₂ (TiO₂/CdS) suspensions with isopropanol (IPA). TiO₂/CdS is the most representative hybrid semiconductor in that the valence band and conduction band of CdS are suitably placed with respect to those of TiO₂ for charge separation while CdS can absorb a substantial fraction of visible light ($\lambda_{\text{onset}} \sim 500$ nm) [22]. In addition, IPA has been widely employed as a sacrificial electron donor (i.e., hole scavenger). Even though the use of IPA was found to significantly enhance the yields of C1-C3 hydrocarbon products, however, no evidence for the source of the products (dissolved CO₂ vs. IPA) was provided [13]. In this study, we synthesized and characterized TiO₂/CdS composites via X-ray diffraction (XRD) and UV-vis spectroscopy, and examined the photocatalytic production of headspace H₂, CO, and CH₄ in Ar and

CO₂-purged aqueous suspensions of IPA. Diffuse reflectance Fourier transform (DRIFT) and isotopic labeling experiments using high-purity ¹³CO₂ were also carried out to examine possible reaction mechanisms and identify the specific origin of the observed products.

2. Experimental methods

2.1. Preparation of catalysts

CdS-loaded TiO₂ composites were prepared using a conventional hydrothermal technique [13]. In a typical procedure, commercially available Degussa P25 TiO₂ (0.7 g) was suspended in an aqueous cadmium acetate (Cd(CH₃COO)₂·2H₂O, Sigma-Aldrich) solution (0.02 M, 40 mL) in a 50 mL Teflon container and stirred for 20 h. Then, sodium sulfide (Na₂S, Sigma-Aldrich) at 0.02 M was added to the slurry, which was subsequently placed in a stainless steel autoclave and maintained at 180 °C for 24 h in a conventional laboratory oven to obtain hexagonal CdS particles (see Fig. 1b). After cooling to room temperature, the resulting slurry was centrifuged to obtain TiO₂/CdS composites, which were then aged at 100 °C before use. Catalysts were thermally stored for extended periods to minimize the presence of residual volatile organics on the TiO₂/CdS surface. The same procedures were carried out using variable cadmium(II) and sulfide(II) concentrations to achieve a variation in the CdS loading levels on TiO₂. Loading levels of CdS at three and five times the base preparation described above are indexed as TiO₂/CdS-3 and TiO₂/CdS-5, respectively. The weight fractions of loaded CdS with respect to TiO₂ were approximately 11.4, 23.6, and 33.7% for TiO₂/CdS-1, 3, and 5, respectively. The Brunauer-Emmett-Teller (BET) surface areas of TiO₂, CdS, and TiO₂/CdS-3 were

estimated to be 52.2, 1.43, and 42.1 m²·g⁻¹, respectively. The TiO₂/CdS-3 samples were selected for further modification with elemental Pt deposits at 0.5 wt%. For this, TiO₂/CdS-3 (0.5 g) was suspended in an aqueous hexachloroplatinic acid (H₂PtCl₆, Aldrich) solution. After mixing for 3 h, the slurry was centrifuged at 8000 rpm for 1 min. The resulting powder was dried for 20 h in a freeze-vacuum dryer and subsequently annealed at 300 °C in a N₂ and H₂ mixed atmosphere (8:2 by volume) for 2 h.

2.2. Surface characterization of catalysts

Catalyst samples were characterized by XRD using a Philips X'pert Pro with Cu-Kα radiation. UV-vis diffuse reflectance spectra were obtained using a spectrophotometer (Shimadzu UV-2101PC) with an integrating sphere attachment (ISR-2200). For this, sample powders were thoroughly mixed with BaSO₄ powder and their reflectance (R) was measured with respect to pure BaSO₄. The obtained reflectance was converted into absorbance using the Kubelka-Munk function ((1 - R)²/2R). The absorption onsets (λ_{on}) were also determined by linear extrapolation from the inflection point of the curve to the baseline and the intersection point was considered as the effective optical absorption of TiO₂/CdS [23]. Then the λ_{on} values were converted to optical bandgap energies (E_g/eV = 1239.6/λ_{on}/nm). The surface morphologies and elemental compositions of TiO₂ and TiO₂/CdS-3 were examined by ultra-high-resolution field emission scanning electron microscopy (UHR-FE-SEM; Hitachi S-5500) operating at 30 kV. DRIFT spectra of the catalysts (freshly made and treated with aqueous CO₂/IPA) were acquired with an FTIR spectrometer (Bio-Rad FTS-45), which was coupled with a liquid N₂-cooled mercury cadmium telluride (MCT) detector at a 4 cm⁻¹ resolution using a Spectra-Tech Controller

diffuse reflectance accessory. For the DRIFT analysis, catalyst suspensions were centrifuged at 8000 rpm for 1 min, after which the centrifuged powder was isolated after freeze drying for 20 h ($-45\text{ }^{\circ}\text{C}$; 80 ~ 100 millitorr).

2.3. Photocatalysis and product analysis

The photocatalytic reduction of CO_2 was carried out in an airtight glass reactor (ca. 120 mL) equipped with a quartz disc for light penetration. Sample catalysts (0.1 g) were suspended in aqueous IPA solutions (1.0 M, 100 mL), which were purged with either high-purity Ar or CO_2 (both 99.99%) for 1 h. The reactor was then sealed with a rubber stopper and irradiated with a 450-W Xe arc lamp in combination with 320 nm or 420 nm-cutoff filters. The reaction temperature was controlled in the range of $20 - 25\text{ }^{\circ}\text{C}$. Each experiment was performed independently, at least twice.

During irradiation, the gas in the reactor headspace was intermittently sampled and quantified for H_2 , CO, and CH_4 using a gas chromatograph (GC, HP 5890 series II) equipped with thermal conductive detection (TCD) with a $5\text{ }\text{\AA}$ molecular sieve column. N_2 was used as the carrier gas for H_2 , whereas He was used for the CO and CH_4 analyses. For quantification, each standard gas (Fluka) was allowed to flow through the GC-TCD, and standard curve fits between each gas concentration and the corresponding spectral area were obtained. Liquid samples were also analyzed with ion chromatography (IC) and GC-MS. Formate (HCOO^-), formaldehyde (HCOH), and methanol (CH_3OH) were not always detected, and even when they were detected, they were only present in trace amounts.

In the ^{13}C -labeled isotope experiments, the catalyst suspensions were purged with

isotopic $^{13}\text{CO}_2$ (99.3%, Cambridge Isotope Laboratories). Contaminant ^{13}C -hydrocarbons were removed from the $^{13}\text{CO}_2$ cylinder by adding two hydrocarbon gas trappers (HC 2-2446 and SUPELPURE) in series to the $^{13}\text{CO}_2$ gas cylinder outflow before introducing $^{13}\text{CO}_2$ into the suspensions. After the photoreaction, the composition of the headspace gas was analyzed using a GC / electron impact time-of-flight mass spectrometer (GC/EI/TOF/MS, Waters, GCT, Premier). This instrument was equipped with a standard 6890N Agilent GC for the injection of samples. Data were acquired and analyzed using MassLynx software version 4.1. The abundance of diagnostic ions was determined from the peak areas of integrated selected ion chromatograms. A suspension of the catalyst in deuterated IPA ($(\text{CD}_3)_2\text{CDOD}$), 99.5 atomic % D, Sigma-Aldrich) was purged with CO_2 and the methane concentration in the headspace was analyzed by GC/EI/TOF/MS after the photoreaction.

3. Results and discussion

3.1. Characterization of photocatalysts and photocatalytic CO_2 conversion

Fig. 1a shows the UV-vis diffuse reflectance absorption spectra of bare TiO_2 and TiO_2/CdS particles. The absorption edges of TiO_2 and TiO_2/CdS -1 were ~ 400 and ~ 480 nm, respectively, whereas large loadings of CdS relative to TiO_2 shifted the edge to the long wavelength region. Accordingly, the optical bandgaps (E_g) of TiO_2/CdS were estimated to be 2.57, 2.40, and 2.34 eV as CdS was loaded once, twice, and thrice, respectively. The shifts of these optical bandgaps simply indicate that the optical influence of CdS becomes stronger as the mass loading of CdS increases. The as-synthesized CdS particles (i.e., without TiO_2) displayed a hexagonal structure (100,

002, 101, 110, and 112, with phases at $2\theta = 25.6, 26.7, 27.8, 44.1$, and 52.3° , respectively; JCPDS 77-2306), whereas the XRD pattern of TiO_2/CdS -3 showed mixed phases of anatase (101, 103, 004, 112, 200, 105; #JCPDS 84-1286), rutile (110, 101, 111, 211, 002, 301; JCPDS 88-1175), and hexagonal CdS (Fig. 1b). None of the other composites displayed changes in their XRD patterns. The SEM images of TiO_2 and TiO_2/CdS -3 shows that the apparent particle size was ~ 50 nm (Fig. 1c; see also Fig. S1 in *Supplementary Data*). The elemental mapping of TiO_2/CdS -3 further indicates that CdS particles were uniformly distributed on TiO_2 particles (Fig. 1d and 1e).

Fig. 2a shows the H_2 evolution in aqueous TiO_2 and TiO_2/CdS suspensions containing IPA purged with either Ar or CO_2 gas under irradiation ($\lambda > 320$ nm). H_2 evolved rather linearly at a rate of $\sim 8 \mu\text{mol}\cdot\text{h}^{-1}$ in the Ar-purged TiO_2 suspension, whereas the H_2 production rate decreased to $\sim 2.5 \mu\text{mol}\cdot\text{h}^{-1}$ in the case of CO_2 -purged TiO_2 . This indicates that CO_2 is a competitive electron acceptor against H^+ (R1 vs. R3). As compared to bare TiO_2 , TiO_2/CdS displayed enhanced H_2 production in an Ar atmosphere due to increased light absorption and enhanced charge separation, although the H_2 production decreased in the CO_2 atmosphere as a result of the competition for electrons. It is of note that the H_2 production in the CO_2 -purged TiO_2/CdS was even lower than that in CO_2 -purged TiO_2 , but that the rate of H_2 production was very similar among the three TiO_2/CdS composites (Fig. S2 in *Supplementary Data*). It appears that the reaction mechanism is altered only when CdS is coupled to TiO_2 and that the CdS load plays an insignificant role in CO_2 conversion under the present reaction conditions.

Fig. 2b compares the CO production in the same experimental sets that were described above. CO was produced at $\sim 0.8 \mu\text{mol}$ for 10 h in a TiO_2 suspension purged

with CO₂, the amount of which increased by a factor of ~3 with Ar-purging. In addition, CO was the sole carbon-containing product from the Ar-purged TiO₂ suspension and the irradiation of IPA (without TiO₂) also produced CO at ~0.6 μmol in 6 h. This suggests that the photolytic and photocatalytic incomplete oxidation of IPA (due to the limited amount of oxygen in solution) contributes to the observed CO products (R2). The decrease in CO production with CO₂ purging was attributed presumably to the competition between CO₂ and IPA to adsorb on the TiO₂ surface (e.g., >Ti-OH₂⁺ and >Ti-OH) [18,24], thereby inhibiting the hole oxidation of IPA (R2). In contrast to this tendency, TiO₂/CdS produced an approximately three-fold larger amount of CO with CO₂ purging compared to Ar purging, presumably due to the favored adsorption of CO₂ on CdS [25] as well as enhanced charge separation and transfer [13,22,26-29]. A quadrupole mass spectrometry study showed TiO₂/CdS to have a higher relative uptake of gaseous CO₂ by a factor of 2.4 compared to TiO₂ (Fig. S3 in Supplementary Data), confirming the former speculation.

We have also observed the production of methane (~18 μmol in 10 h) in CO₂-purged TiO₂/CdS (Fig. 2c), the amount of which is significantly larger than that of CO. Ar purging significantly reduced the production of methane (~2 μmol in 10 h). In a CO₂ atmosphere, trace amounts of the other C₂ hydrocarbons (C₂H₄ and C₂H₆) were also detected. The irradiation of TiO₂/CdS by visible light (λ > 420 nm), i.e., the excitation of CdS alone, produced a similar level of methane, suggesting that CdS plays critical roles, including in the fixing of CO₂ and in catalyzing multi-electron transfer to CO₂ (R3 – R7). When Pt was coupled to TiO₂/CdS, CO and CH₄ were not observed, whereas only H₂ was produced at an increased rate of 12-fold that of Pt-free TiO₂/CdS, a result attributed to the

superior catalytic properties of Pt for the hydrogen evolution reaction (data not shown). In comparison to TiO₂/CdS, the amount of methane produced with TiO₂ alone was as low as ~1 μmol in 10 h, which is approximately four times larger than that in an Ar atmosphere.

3.2. ¹³CO₂ conversion

Although the use of IPA enhances the photocatalytic reduction of CO₂, considerable uncertainty remains as to the CO₂ reduction pathway and actual CO₂-derived product yields (particularly CH₄), as caused by the presence of IPA and unidentified residual organic contaminants. To examine this possibility and gain insight into the reaction pathway, the TiO₂/CdS suspension in IPA was purged with ¹³CO₂ (99.3%), following which the gaseous products were analyzed with TOF-MS. It is of note that a cylinder of ¹³CO₂ was found to contain trace amounts of ¹³CH₄ as a hydrocarbon contaminant. Accordingly, m/z signals of 17, 16, and 15 were found in the initial sample (before the reaction) and attributed to ¹³CH₄, ¹³CH₃, and ¹³CH₂, respectively (Fig. 3a). The ratio of signal 16 to signal 17 in the initial sample was 0.526, which is characteristic of ¹³CH₄ based on our mass spectral conditions. After the photoreaction, signal 16 can be considered a combination of ¹³CH₃ and ¹²CH₄, which originate from the ¹³CH₄ fragments produced from the reduction of ¹³CO₂ and from those of the oxidation of IPA or residual organic contaminants, respectively. Therefore, the authentic amount of ¹³CH₄ produced from ¹³CO₂ can be calculated based on the analysis of the signal at m/z = 16. Taking the 1 h-sample as an example (Fig. 3b), ¹³CH₃ accounted for 70.70% (= (98.53 × 0.526)/73.31) of the total CH₄ amount (¹²CH₄ and ¹³CH₄ combined) and the exact amount of ¹³CH₄

produced from $^{13}\text{CO}_2$ could be obtained after subtracting the initial amount of $^{13}\text{CH}_4$.

Based on this, the relative signal intensities of $^{13}\text{CH}_4$ to $^{12}\text{CH}_4$ as a function of reaction time were obtained and are depicted in Fig. 4. The intensity of both the $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ signals increased with time; the formation rate of $^{12}\text{CH}_4$ was ~2.5 times higher than that of $^{13}\text{CH}_4$. Furthermore, the relative amount of $^{13}\text{CH}_4$ decreased compared to $^{12}\text{CH}_4$ in the later stages of the reaction. After 6 h, only ~25% of the total observed methane accounted for $^{13}\text{CH}_4$ resulting from $^{13}\text{CO}_2$, whereas the remainder was formed from the ^{12}C -IPA and ^{12}C -organic contaminants. Visible light irradiation ($\lambda > 420$ nm) also led to the similar conclusion that $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ are equal contributors to total CH_4 formation. The methyl radical generated from IPA during photocatalysis could lead to CH_4 formation as follows.

This possibility was examined by using deuterium-labeled IPA ($(\text{CD}_3)_2\text{CDOD}$). However no deuterated CH_4 was observed (Fig. S4 in Supplementary Data), suggesting the absence of a direct contribution by the photooxidation of IPA.

3.3. DRIFT study and reaction mechanism

The DRIFT spectra of three of the TiO_2/CdS samples (as-prepared, before, and after photocatalysis) were obtained to gain insight into the reaction mechanism occurring on the catalyst surfaces (Fig. 5). Compared to the as-prepared material, the sample treated with CO_2 -saturated IPA aqueous solution (i.e., before photocatalysis) exhibited several strong vibrational bands, the intensities of which decreased after photocatalysis. For

example, the band ($\sim 3400\text{ cm}^{-1}$) associated with the hydroxyl groups on TiO_2 (e.g., $>\text{Ti-OH}$) [30] and/or CdS (e.g., $>\text{Cd-OH}$) [31] intensified with aqueous CO_2/IPA treatment, most likely due to the adsorption of water (Fig. 5a). The CO_2/IPA treatment additionally led to the formation of a new band at $\sim 3000\text{ cm}^{-1}$ and induced a band at $\sim 1630\text{ cm}^{-1}$, which may be attributed to molecular IPA physisorbed through H bonding and molecular water formed via the dissociative adsorption of IPA, respectively [32].

A notable difference is found in the region of $1000 - 1600\text{ cm}^{-1}$, from which several bands disappeared after the reaction (Fig. 5b and 5c). Some of these bands were associated with adsorbed (bi)carbonate species, including bidentate carbonate (1320 , 1367 , 1537 , and 1560 cm^{-1}) [4,33,34], monodentate carbonate (1409 cm^{-1}) [4], and bicarbonate (1498 cm^{-1}) [4], whereas the remaining bands could most likely be attributed to IPA (1350 cm^{-1} , $\delta_s\text{ CH}_3$; 1439 and 1471 cm^{-1} , $\delta_{\text{as}}\text{ CH}_3$) [32] (Fig. 5b). It is of note that the typical pH of a CO_2 -purged IPA solution was ~ 4.5 , which suggests that aquated CO_2 (i.e., $\text{CO}_2\cdot\text{H}_2\text{O}$, HCO_3^-) could be adsorbed as a form of surface-bound carbonate species. The bands in the region of $1100 - 1200\text{ cm}^{-1}$ are characteristic of the ρCH_3 , $\nu\text{C-O}$, and $\nu\text{C-C}$ vibrations [32], whereas the vibrational bands of the monodentate and bidentate modes of free and adsorbed carbonate species occur at $1000 - 1100\text{ cm}^{-1}$ [35]. In this regard, the bands at 1113 , 1137 , and 1169 cm^{-1} were speculated to be associated with IPA (ρCH_3 , $\nu\text{C-O}$, and $\nu\text{C-C}$, respectively) (Fig. 5c) [32]. Identifying the binding mode of the carbonate species in the region of $1000 - 1100\text{ cm}^{-1}$ was less straightforward. Considering the general rule, which determines that an increase in molecular bond strength leads to an increase in the wavenumber, the bands observed at $1000 - 1050\text{ cm}^{-1}$ and $1050 - 1100\text{ cm}^{-1}$ were presumed to be associated with bidentate and monodentate carbonate (and/or

carbonate), respectively [35].

These differences in the DRIFT spectra were not observed for the TiO₂ sample (Fig. S5 in Supplementary Data). This suggests that the aforementioned changes in the vibrational bands should be attributed to the favored adsorption of dissolved CO₂ species on the CdS surface (>Cd-OH₂⁺ and >Cd-SH₂⁺ surface sites below the point of zero charge pH ~7.5). These CdS species can lead to inner-sphere surface complexation of the carbonate species as follows:

It is noteworthy that, although the bands associated with both of the CO₂ and IPA weakened after photocatalysis (Fig. 5b), the former bands either completely disappeared or significantly decreased compared to the latter (Fig. 5c). This opens up the possibility of the photocatalytic formation of CO₂^{•-}, because formation of surface-bound (bi)carbonate species may reduce the relative energy barriers for the reduction of CO₂ [13,17,36]. It was reported that photogenerated electron transfer requires the presence of suitable unoccupied molecular orbitals (LUMO) on CO₂ and that the LUMO energy decreases with decreasing O-C-O bond angle [37]. Accordingly, the formation of surface-bound carbonate species effectively reduces the C-O bond angle, which should lead to favorable conditions for electron transfer to CO₂ [37]. This suggests that the photocatalytic reduction of CO₂ on CdS-modified TiO₂ is initiated with a bent carbonate-like species bound to CdS. In contrast, the conversion of CO₂ to CH₄ is less likely if the target carbonate species are not adsorbed on the catalyst surface. It appears

that some IPA continues to remain adsorbed onto TiO₂/CdS even after photocatalysis (Fig. 5c). The adsorbed IPA would be expected to trap photogenerated holes more efficiently, thereby leading to multi-electron transfer to CO₂ and a higher CH₄ yield. Furthermore, the resulting isopropyl carbon-centered radical may also enhance CO₂ reduction because of its strong reduction potential and its injection of an electron into the conduction band of CdS (i.e., a current-doubling effect) [38].

4. Conclusions

The photocatalytic conversion of CO₂ to CH₄ on TiO₂-based catalysts in the presence of IPA is feasible in spite of apparent unfavorable thermodynamic conditions. However, relatively low conversion efficiencies are obtained, because multiple near-surface electron transfers are required. In this study, the deposition of CdS on TiO₂ enhanced the rate of CH₄ formation and improved overall CH₄ yields. This could be attributed to a) facilitated electron transfer from the CdS to surface-bound CO₂, leading to the formation of CO₂^{•-} that bounds to the positively charged CdS surface and b) the geometry of surface-bound bicarbonate that enhances CH₄ formation due to lower energy barriers compared to the linear O=C=O molecule. Despite the fact that CH₄ formation on CdS-modified TiO₂ is confirmed to be more efficient than on unmodified TiO₂, the contribution of CH₄ originating from IPA is significant. In other words, the introduced CO₂ as well as the *in situ* generated CO₂ (via oxidation of IPA) both contribute to the observed CH₄ yields. In addition, hydrocarbon contaminants present during catalyst preparation may account for a fraction of the observed yields. Finally, this study found that H₂ is produced via the reduction of water by photogenerated electrons, whereas CO

is produced via the reduction of CO₂ as well as the oxidation of IPA.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org...>

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Figure Captions

Fig. 1. (a) UV-vis diffuse reflectance absorption spectra of TiO_2 and TiO_2/CdS samples. Numbers at TiO_2/CdS ($\text{TiO}_2/\text{CdS}\text{-}\#$) refer to the loading cycles of CdS. (b) XRD patterns of commercial CdS and $\text{TiO}_2/\text{CdS}\text{-}3$ samples. A and R refer to anatase and rutile TiO_2 , respectively, while S refers to CdS. Note that only the primary peaks were assigned. (c) SEM image and (d – e) elemental mapping of $\text{TiO}_2/\text{CdS}\text{-}3$.

Fig. 2. Time-profiled productions of (a) H_2 , (b) CO, and (c) CH_4 in aqueous TiO_2 and TiO_2/CdS suspensions with isopropanol (1 M) purged with Ar or CO_2 (for 1 hour prior to irradiation) under irradiation ($\lambda > 320$ nm). If necessary, visible light ($\lambda > 420$ nm) was used for irradiation. Unless otherwise indicated, $\text{TiO}_2/\text{CdS}\text{-}3$ samples were used.

Fig. 3. Mass spectra of methane produced with an aqueous TiO_2/CdS suspension with isopropanol (1 M) purged with $^{13}\text{CO}_2$ (for 1 hour prior to irradiation) under irradiation ($\lambda > 320$ nm). (a) before irradiation, (b) after irradiation for 1 h. Despite the use of high-purity $^{13}\text{CO}_2$ ($>99.3\%$), trace levels of hydrocarbon contaminants ($^{13}\text{CH}_4$, $^{13}\text{C}_2\text{H}_4$, and $^{13}\text{C}_4\text{H}_{10}$) were found. However, the amounts of $^{13}\text{C}_2\text{H}_4$ and $^{13}\text{C}_4\text{H}_{10}$ remained relatively constant throughout reaction, while the total amount of CH_4 ($^{12}\text{CH}_4$ and $^{13}\text{CH}_4$) increased continuously during the reaction.

Fig. 4. Time-dependent changes in the fractions and yields of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$. See Fig. 3 and text for detailed information.

Fig. 5. (a) DRIFT absorption spectra of TiO₂/CdS samples: freshly prepared (black) and treated with a CO₂-purged IPA solution (red: before photocatalysis, green: after photocatalysis). (b and c) Deconvoluted DRIFT absorption spectra. “rxn” refers to “reaction”.

Scheme Caption

Scheme 1. Proposed reaction pathways of photocatalytic CO₂ conversion on TiO₂/CdS in the presence of IPA under UV irradiation. Blue-colored chemicals were identified as primary products, whereas radical species (CO₂⁻ and H[•]) were speculated to be produced transiently. The approximate band energy levels of TiO₂ and CdS were shown. The production of H₂ via water (or proton) reduction (R1) competes with CO₂ reduction (e.g., R3) for photogenerated electrons. The oxidation of IPA by holes can result in the production of acetone as an intermediate, which was not shown for simplicity. If IPA undergoes one-electron oxidation, then only ~0.1% of initial IPA is decomposed. Note that upon visible light irradiation, the oxidation of IPA on TiO₂ is very limited due to the absence of TiO₂ holes.

Figure 1. Park et al.

Figure 2. Park et al.

Figure 3. Park et al.

Figure 4. Park et al.

Figure 5. Park et al.

Scheme 1. Park et al.

Graphical Abstract