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Artificial Photosynthesis over Crystalline TiO_2-Based Catalysts: Fact or Fiction?

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Abstract: The mechanism of photocatalytic conversion of CO_2 and H_2O over copper oxide promoted titania, Cu(I)/TiO_2, was investigated by means of in situ DRIFT spectroscopy in combination with isotopically labeled $^{13}CO_2$. In addition to small amounts of ^{13}CO, ^{12}CO was demonstrated to be the primary product of the reaction by the 2115 cm^{-1} Cu(I)−CO signature, indicating that carbon residues on the catalyst surface are involved in reactions with predominantly photocatalytically activated surface adsorbed water. This was confirmed by prolonged exposure of the catalyst to light and water vapor, which significantly reduced the amount of CO formed in a subsequent experiment in the DRIFT cell. In addition, formation of carboxylates and (bi)carbonates was observed by exposure of the Cu(I)/TiO_2 surface to CO_2 in the dark. These carboxylates and (bi)carbonates decompose upon light irradiation, yielding predominantly CO_2. At the same time a novel carbonate species is produced (having a main absorption at $\sim$1395 cm^{-1}) by adsorption of photocatalytically produced CO on the Cu(I)/TiO_2 surface, most likely through a reverse Boudouard reaction of photocatalytically activated CO_2 with carbon residues. The finding that carbon residues are involved in photocatalytic water activation and CO_2 reduction might have important implications for the rates of artificial photosynthesis reported in many studies in the literature, in particular those using photoactive materials synthesized with carbon containing precursors.

Introduction

In photosynthesis, solar energy is converted to chemical energy by reaction of CO_2 and H_2O to e.g. glucose and O_2. It has been reported that titania-based catalysts induce artificial photosynthesis, yielding single-carbon molecules in photocatalytic CO_2 reduction, such as CO, CH_4, CH_3OH, formaldehyde, and formic acid. Titania catalysts were first used in aqueous suspension for photoelectrocatalytic CO_2 reduction.[1] Hirano et al. used copper−metal supported TiO_2 suspended in aqueous solution for photocatalytic CO_2 reduction.[2,3] CH_3OH and HCHO were detected to be the main products. During illumination, trace amounts of formic acid were also detected in the liquid phase, while CO and CH_4 appeared in the gas phase. Tseng et al. confirmed these data and reported that illumination of titania-supported copper catalysts (Cu/TiO_2) in the presence of CO_2 in the liquid phase resulted in the formation of methanol.[4,5] For 2 wt % Cu/TiO_2, the methanol yield reached 12.5 μmol/g-catalyst/h after 20 h of irradiation, which was $\sim$25 times higher than that obtained for TiO_2 (sol−gel method) and 3 times higher than that for Degussa P25 TiO_2 tested in the same system. Recently, Wu et al. also tested Cu(I)/TiO_2 materials in an optical-fiber reactor for gas phase photocatalytic CO_2 reduction. The maximum methanol yield for 1.2 wt % Cu(I)/TiO_2 was 0.46 μmol/g-catalyst/h under 365 nm UV irradiation.[6] Besides these studies on crystalline TiO_2 based catalysts, Ti-containing siliceous materials, such as TS-1, Ti-MCM-41, Ti-MCM-48,[7−9] Ti-ZSM-5,[10] Ti-zeolite Y,[11−13] and Ti-SBA-15,[14] were found

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to yield high methane production rates in gas phase photocatalytic CO_2 reduction. The production yield of highly dispersed titanium oxide catalysts (in μmol/g-Ti/h) was increased 10−300 times as compared to crystalline TiO_2. Pt was found to further enhance the performance of Ti-MCM-48, resulting in an 8-fold increase of CH_4 over CH_3OH selectivity. Despite these numerous studies on photoreduction of CO_2 over TiO_2 based catalysts, relatively little is known about the surface chemistry and the mechanism of the reaction. Anpo et al. proposed a mechanism for isolated excited $(Ti^{+III}-O^{-I})^*$ sites, based on EPR data,[15] over which simultaneous reduction of CO_2 and decomposition of H_2O are proposed to lead to CO and C radicals, and H and OH radicals, respectively. Subsequently, these photoinduced C, H, and OH radicals recombine to final products, such as CH_4 and CH_3OH.

IR studies focused on photoinduced CO_2 activation are rare. Rasko et al.[16,17] observed bent CO_2^- species on prereduced TiO_2 upon illumination at 190 K, and proposed a mechanism for photon induced decomposition of these species into CO over a Rh/TiO_2 catalyst. The most comprehensive IR study to date focused on a Ti silicalite molecular sieve (TS-1).[18] CO was observed as the initial redox product of gaseous CO_2 photoreduction. Through labeled CO_2 and CH_3OH experiments, the origin of CO was proposed to be the secondary photolysis of HCO_2H, which was the 2-electron reduction product of CO_2 over photoexcited Ti centers generated by a LMCT transition $(Ti^{+IV}-O^{-II} \rightarrow Ti^{+III}-O^{-I})$.

In the present study the surface chemistry of crystalline $Cu(I)/TiO_2$ was further investigated employing a combination of DRIFT spectroscopy and isotopically labeled $^{13}CO_2$. The strong adsorption of CO on Cu(I) sites was used to identify the origin of this product, indicating that carbon residues are very important in determining the initial reactivity of photocatalysts active in CO_2 reduction. Moreover, a rich surface carbonate chemistry was observed for $Cu(I)/TiO_2$, with an interconversion of CO_2 induced carbonate formed in the dark to CO induced carbonate formed upon illumination. The implications of this study for studies in the literature using photoactive materials synthesized with carbon containing precursors will be discussed.

Experimental Section

Material Preparation. $Cu(I)/TiO_2$ was synthesized by a modified sol−gel method. The precursors titanium(IV) butoxide (TBOT, $Ti(OC_4H_9)_4$) and copper nitrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) were used as received. 17 mL of TBOT, 0.15 g of ($Cu(NO_3)_2 \cdot 2.5H_2O$), 2 g of polyethylene glycol (PEG), and 102 mL of 0.1 M nitric acid (HNO_3) were added to induce hydrolysis, and polycondensation was achieved by thermal treatment at 353 K for 28 h. The final sol was filtered, dried at 423 K for 3 h, and then calcined at 773 K for 5 h with a heating rate of 1 K/min. Based on elemental analysis, 1% (weight basis) copper was deposited. The as-synthesized $Cu(I)/TiO_2$ catalyst had a grass-green color. A reference $Cu(I)/TiO_2$ catalyst was prepared according to the same procedure, in the absence of polyethylene glycol (PEG). Finally, TiO_2 was also prepared following the same procedure, only without adding copper nitrate.

In Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy. Photocatalytic CO_2 reduction experiments were carried out using a Nicolet Magna 860 spectrometer, equipped with a liquid N_2 cooled MCT detector, and a three window DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) cell. Two ZnSe windows allowed IR transmission, and a third (Quartz) window allowed the introduction of UV/vis light into the cell. Prior to the illumination experiments, 25 mg of the as-synthesized catalyst were heated up to 393 K in He (30 mL/min) for 0.5 h, to remove the majority of adsorbed water without changing the oxidation state of copper oxide. Before recording a background spectrum of the still grass-green catalyst, CO_2 (50 vol % in He, 20 mL/min) was purged for 20 min. For experiments involving water vapor, CO_2 was bubbled through a saturator at room temperature (300 K), which added approximately 4 vol % water vapor to the CO_2 feed. During illumination, reactants were held stationary in the cell at room temperature (303 K). In situ IR signals were thus recorded every 10 min under UV/vis light irradiation (100 W Hg lamp, λ: 250−600 nm).

CO_2 (Linde Gas, 99.995%), $^{13}CO_2$ (ISOTEC, 99.9%^{13}C), CO (Linde Gas, 5% in He), and ^{13}CO (ISOTEC, 99%^{13}C) were used as received. CO (or ^{13}CO) adsorption experiments were performed by introducing CO (2500 ppm in He, 20 mL/min) over $Cu(I)/TiO_2$ for 20 min. To estimate the CO adsorption capacity, He (30 mL/min) was used to flush the catalyst and remove weakly adsorbed CO molecules.

To further illustrate the role of carbonates in photocatalytic conversion of CO_2, an illumination experiment was conducted in the absence of CO_2, after pre-exposure of the surface of the catalyst to CO_2. Specifically a flush−dose cycle of exposure of the catalyst to $^{13}CO_2$ for 20 min, followed by flush in He, was repeated four times, to increase the surface concentration of ^{13}C-labeled carbonates.

Coking Experiments. The catalyst under investigation was also pretreated to achieve different degrees of coking. Coked catalysts were prepared by introducing a batch of fresh $Cu(I)/TiO_2$ catalyst (70 mg) into an isobutane flow at 873 K (30 mL/min consisting of 1% C_4H_{10} and 50% CO_2). By varying the exposure time, variable amounts of coke were successfully deposited on $Cu(I)/TiO_2$.

Results

Illumination of $Cu(I)/TiO_2$ in Different Conditions. Figure 1 shows DRIFT spectra of the $Cu(I)/TiO_2$ catalyst after 80 min of illumination in different atmospheres, against background spectra of the catalyst obtained after flushing with the different respective gas compositions for 20 min. The spectra are dominated by an absorption band at 2115 cm^{-1}, which can be assigned to the stretching mode of CO, consistent with literature.[19−21] CH_4, often detected by gas chromatography in photocatalytic CO_2 reduction studies, is not observed, with quantities being too small to be detected in the gas phase in our DRIFT cell (with limited IR path length). Adsorption on the catalyst surface of methane is not expected. CH_3OH, should be visible in an adsorbed state if formed in sufficient quantity, but is not detected. In an inert (He) and oxidizing atmosphere (10% O_2/He), a small quantity of CO evolved after 80 min of illumination. In the case of water vapor (spectrum 1c), a significantly higher intensity of the CO band at 2115 cm^{-1} can be observed. By introducing CO_2 and water vapor (1d), the CO band broadens and blue-shifts to 2117 cm^{-1}. The broadening of the CO band suggests that CO_2 coadsorption slightly alters the nature of the Cu(I) site. Without H_2O cofeed (spectrum 1e), CO_2 leads to a CO band of an even higher intensity, which might imply that in the presence of water subsequent hydrogenation of adsorbed CO takes place. $^{13}CO_2$ was used to identify the

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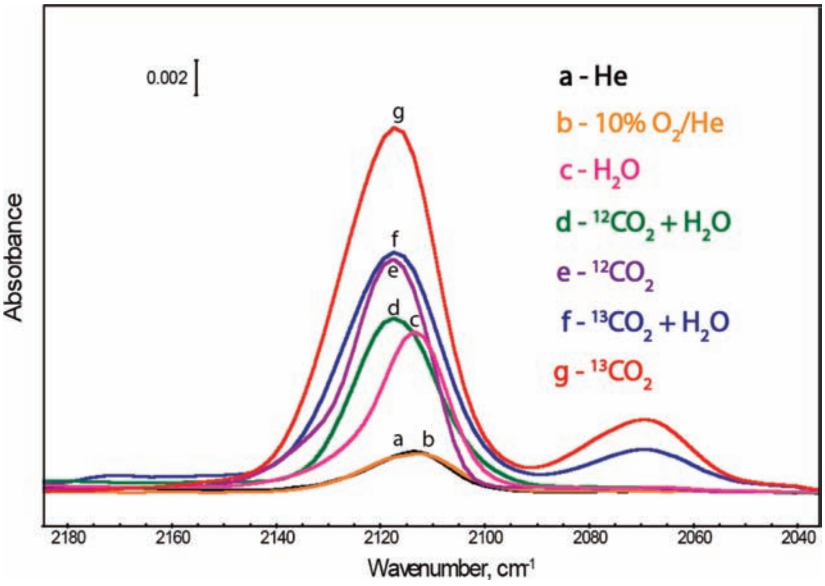

Figure 1. FT-IR spectra of Cu(I)/TiO_2 obtained after 80 min of irradiation in the presence of (a) He, (b) 10%O_2/He, (c) water vapor, (d) $^{12}CO_2$ and water vapor, (e) $^{12}CO_2$, (f) $^{13}CO_2$ and water vapor, and (g) $^{13}CO_2$.

origin of the CO product. Spectrum 1f shows two CO bands, at 2069 and 2117 cm^{-1}. The former one is assigned to adsorbed ^{13}CO, in agreement with a calculation based on the harmonic equation[22] and spectra after dosing ^{13}CO over Cu(I)/TiO_2, which will be described later. Unexpectedly, there is still a majority of ^{12}CO formed during illumination, despite the absence of $^{12}CO_2$, demonstrating that carbon residues on the catalyst surface are involved in the reaction. Thermal gravimetric analysis (TGA) was performed for the as-synthesized catalyst, which showed no distinguishable weight loss, indicating that these residues are present in small quantities and cannot be easily removed by calcination.

In the absence of water vapor, the intensity of the band of adsorbed CO was enhanced (compare spectra 1f and 1g), in agreement with the experiment conducted with $^{12}CO_2$. As expected, in reference experiments over pure TiO_2, CO absorption bands in the 2115 cm^{-1} region were absent, indicating that Cu(I) sites serve as a probe to visualize CO formation in IR spectroscopy.

Figure 2 shows the spectral development in the region of carbonate absorptions (1200−1800 cm^{-1}) during an experiment where Cu(I)/TiO_2 is illuminated in an atmosphere of $^{13}CO_2$ (compare Figure 1g). In the presence of $^{13}CO_2$, irradiation enhances carbonate intensities. There are also decreasing bands observable (at approximately 1650 and 1210 cm^{-1}), indicating that specific surface species are involved in the formation of CO.

To further evaluate the dynamics in the intensities of the carbonate vibrations, presaturation of the TiO_2 surface by treatment with $^{13}CO_2$ was conducted. The ^{13}C-labeled carbonate containing surface was subsequently illuminated in a He atmosphere. The spectral changes are displayed in Figure 3. Clearly ^{12}CO (2115 cm^{-1}) is formed upon illumination, together with a minor amount of ^{13}CO, in agreement with the data shown in Figure 1. Rather than positive carbonate features, as observed in the presence of gas phase $^{13}CO_2$, negative features are observed in the spectral region of 1800 to 1200 cm^{-1}, including these at 1650 and 1210 cm^{-1}, indicating that carbonates are decomposing upon illumination. This mainly produces gas phase $^{13}CO_2$, as is evident from IR absorption features at 2280 cm^{-1}. In addition, the complex spectral signature in the carbonate region contains positive contributions at ∼1560, 1420, and ∼1350 cm^{-1}, which can be assigned to the formation of carbonate species formed by (re)adsorption of CO, as will be discussed in the following paragraph. Finally Figure 3 shows significant depletion in the hydroxyl region (3000 to 4000 cm^{-1}), suggesting that hydroxyl groups and surface adsorbed water are participating in the surface reactions.

Reference Spectra. To allow a better comprehension of the changes in the carbonate region (see Figures 2 and 3), Figure 4 shows the deconvolution of the region of the carbonate bands, formed by exposure of the Cu(I)/TiO_2 catalyst to CO_2 or $^{13}CO_2$, respectively. The corresponding band assignments are summarized in Table 1. In agreement with literature data,[23,24] we assign the bands to bidentate carbonates (1363, 1554 cm^{-1} for CO_2 and 1319, 1508 cm^{-1} for $^{13}CO_2$), monodentate carbonates (1409 cm^{-1} for CO_2 and 1374 cm^{-1} for $^{13}CO_2$), bicarbonates (1481, 1663 cm^{-1} for CO_2 and 1461, 1649 cm^{-1} for $^{13}CO_2$) and carboxylates (1663 cm^{-1} for CO_2 and 1649 cm^{-1} for $^{13}CO_2$). The assignment at 1663 and 1649 cm^{-1} is ambiguous, due to the difficulty of distinguishing the contributions of bicarbonates or carboxylates. The preadsorbed carbonates were in a separate experiment exposed to D_2O, to evaluate if specific carbonate bands would shift, providing further evidence for spectral assignment. Unfortunately, D_2O has strong absorptions in the

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(22) Harmonic equation was useful for calculating the theoretical peak shift for isotopic molecules. The vibration frequency is inverse-proportional to the square root of reduced mass.

$$\nu = \frac{1}{2\pi}, \sqrt{\frac{\kappa}{\mu}}, \mu = \frac{m_1 \times m_2}{m_1 + m_2}, \nu \propto \sqrt{\frac{1}{\mu}}$$

$$\nu_{^{13}\mathrm{CO}} = 2117 \times \sqrt{\frac{(12 \times 16)/(12 + 16)}{(13 \times 16)/(13 + 16)}} = 2069\ \mathrm{cm}^{-1}$$

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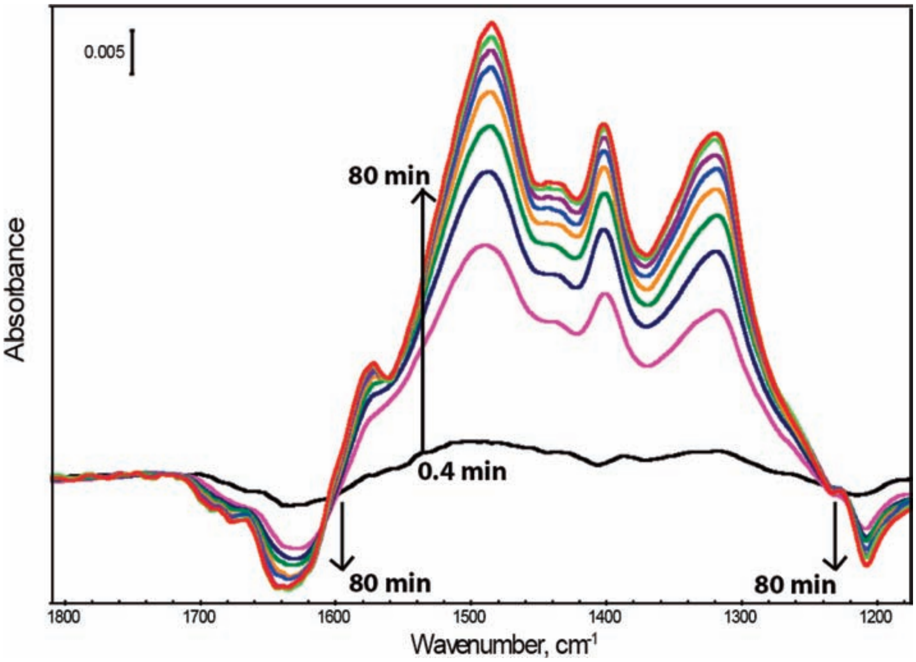

Figure 2. Trend in carbonate formation over Cu(I)/TiO_2 in the presence of $^{13}CO_2$ during 80 min of illumination. Time-profiled DRIFT spectra between 0.4 and 80 min of illumination.

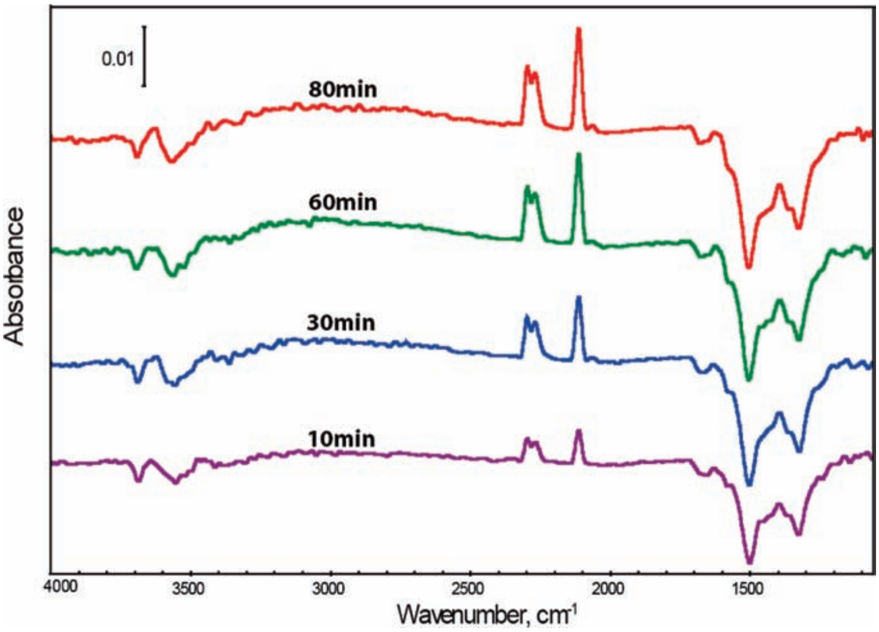

Figure 3. Time-profiled FT-IR spectra of Cu(I)/TiO_2, preloaded with $^{13}CO_2$. Spectra were recorded after illumination times of 10, 30, 60, and 80 min, respectively.

1200 cm^{-1} region, disguising any shifts in position of the 1210 cm^{-1} band. In addition, bands at 1650 and 1210 cm^{-1} have been assigned to a bent CO_2^- conformation, formed by CO_2 adsorption on Ti^{3+}-sites in the vicinity of Rh.[16,17] Following this assignment, the 1650 and 1210 cm^{-1} bands observed in the present study might be associated with CO_2 adsorption in the vicinity of the Cu(I) centers. Among the surface species, bidentate carbonates dominate the spectra and are thermally the most stable species. It must be noted that the control experiments (CO_2 and $^{13}CO_2$) over pure TiO_2 synthesized by the same sol−gel method showed similar surface species, which confirms that most carbonates, bicarbonates, and carboxylates are adsorbed on titania, not on copper sites.

Figure 5 contains reference spectra obtained by adsorption of CO and ^{13}CO on the catalyst surface, in the absence or presence of CO_2. Cu(I)/TiO_2 was first exposed to CO, followed by a He flush. A strong adsorption of CO is observed, with a band composed of two contributions at 2107 and 2115 cm^{-1}. By introducing $^{13}CO_2$ the band at 2107 cm^{-1} rapidly disappears, and the band at 2115 cm^{-1} blue shifts to 2120 cm^{-1}, in agreement with observations reported in the literature. This blue shift was explained by a dynamic interaction between adsorbed CO and CO_2 molecules from the gas phase.[25,26] After removing CO_2 by purging with He, the band of adsorbed CO gradually red shifts back to 2115 cm^{-1}. The stability of adsorbed CO under illumination is shown in Figure 5b. Clearly desorption is

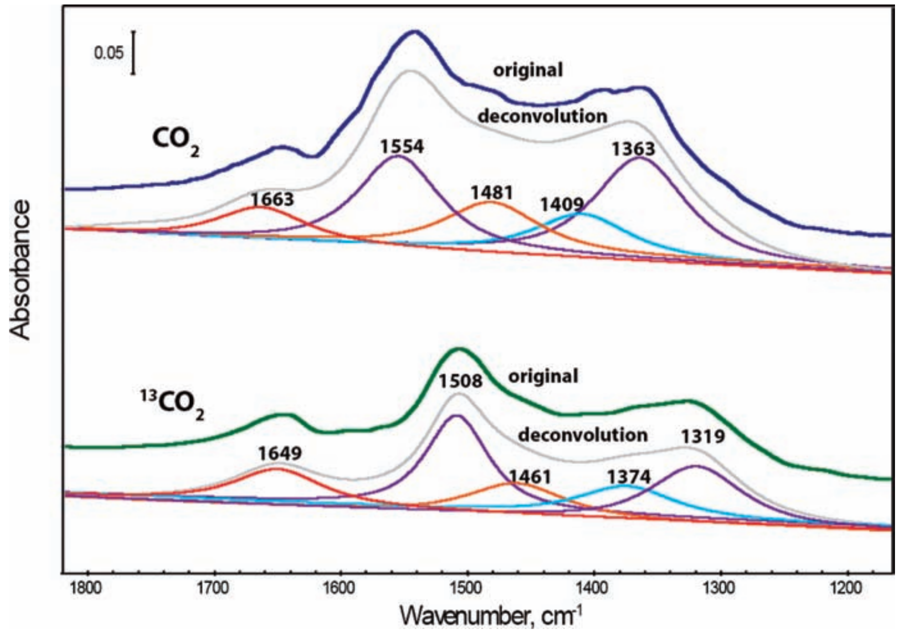

Figure 4. Deconvolution of IR spectra obtained by adsorption of CO_2 and $^{13}CO_2$ on the surface of Cu(I)/TiO_2.

Table 1. IR Spectral Assignment of Surface Species Formation after Inducing CO_2, $^{13}CO_2$, CO, or ^{13}CO over Cu(I)/TiO_2

adsorbed molecule	IR peak position (cm^{-1})	species	vibration mode
CO_2	1363	bidentate carbonate	ν_{as}COO
	1409	monodentate carbonate	ν_{as}COO
	1481	bicarbonate	ν_sCOO
	1554	bidentate carbonate	νC=O
	1663	bicarbonate/CO_2^- carboxylate	ν_sCOO
$^{13}CO_2$	1319	bidentate carbonate	ν_{as}COO
	1374	monodentate carbonate	ν_{as}COO
	1461	bicarbonate	ν_sCOO
	1508	bidentate carbonate	νC=O
	1649	bicarbonate/CO_2^- carboxylate	ν_sCOO
CO	1349	bidentate carbonate	ν_{as}COO
	1419	monodentate carbonate	ν_{as}COO
	1492	bicarbonate	ν_sCOO
	1563	bidentate carbonate	νC=O
	1665	bicarbonate/CO_2^- carboxylate	ν_sCOO
^{13}CO	1315	bidentate carbonate	ν_{as}COO
	1378	monodentate carbonate	ν_{as}COO
	1468	bicarbonate	ν_sCOO
	1569	bidentate carbonate	νC=O
	1645	bicarbonate/CO_2^- carboxylate	ν_sCOO

stimulated by illumination, in view of the significant reduction in intensity of the band at 2070 cm^{-1}. A slight positive growth is observed at ~2115 cm^{-1}, again indicative of conversion of a carbon residue by surface adsorbed water.

Figure 6 shows the (deconvoluted) carbonate intensities formed upon exposure of the Cu(I)/TiO_2 catalyst to CO and ^{13}CO, respectively. While the features are similar to those obtained by adsorption of CO_2 (compare Figure 4), intensity differences can be noted. In particular, bands at 1563, 1419, and 1349 cm^{-1} are indicative of CO adsorbed on surface Ti(O) sites as bidentate and monodentate carbonates, at 1492 cm^{-1} as bicarbonates, and at 1665 cm^{-1} as the contribution of bicarbonates and carboxylates. A corresponding peak assignment can be made for ^{13}CO adsorbed on surface Ti(O) sites at 1569, 1378, and 1315 cm^{-1} as bidentate and monodentate carbonates, at 1468 cm^{-1} as bicarbonates, and at 1645 cm^{-1} as the contribution of bicarbonates and carboxylates.

Illumination of Pretreated Cu(I)/TiO_2. To eliminate the contribution of surface carbon species, the catalyst was pretreated for a prolonged period of time in moist air under UV illumination. The subsequent experiment with preloaded $^{13}CO_2$ is shown in Figure 7. As compared to the fresh catalyst, much less CO is produced upon illumination. Figure 7 also shows the amount of CO evolved for a catalyst that was prepared without PEG in the synthesis mixture. An even smaller CO formation rate is observed.

To further evaluate the influence of carbon residues on CO_2 reduction rates over Cu(I)/TiO_2, coked catalysts were prepared with variable carbon content. By thermal gravimetric analysis (TGA) it was determined that coke amounts of 0.009, 0.144,

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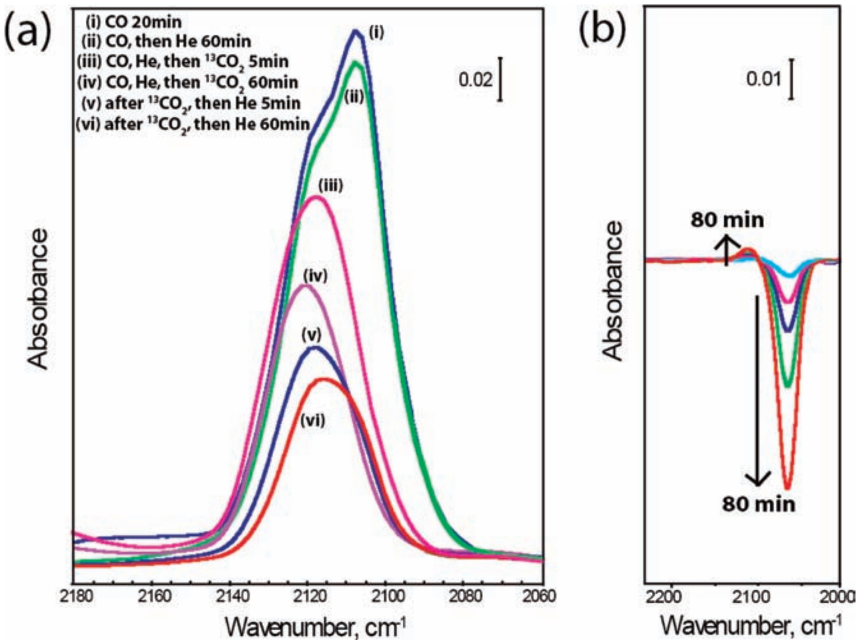

Figure 5. (a) $CO_{(ads)}-{}^{13}CO_{2(g)}$ interaction. FT-IR spectra of Cu(I)/TiO_2 after (i) 2500 ppm CO/He adsorption 20 min, (ii) flush with He 60 min, (iii) 2500 ppm $^{13}CO_2$/He 5 min. (iv) 2500 ppm $^{13}CO_2$/He 60 min, (v) flush again with He 5 min, and (vi) He 60 min. (b) Time-profiled IR spectra of Cu(I)/TiO_2 preloaded with ^{13}CO during 80-min light irradiation.

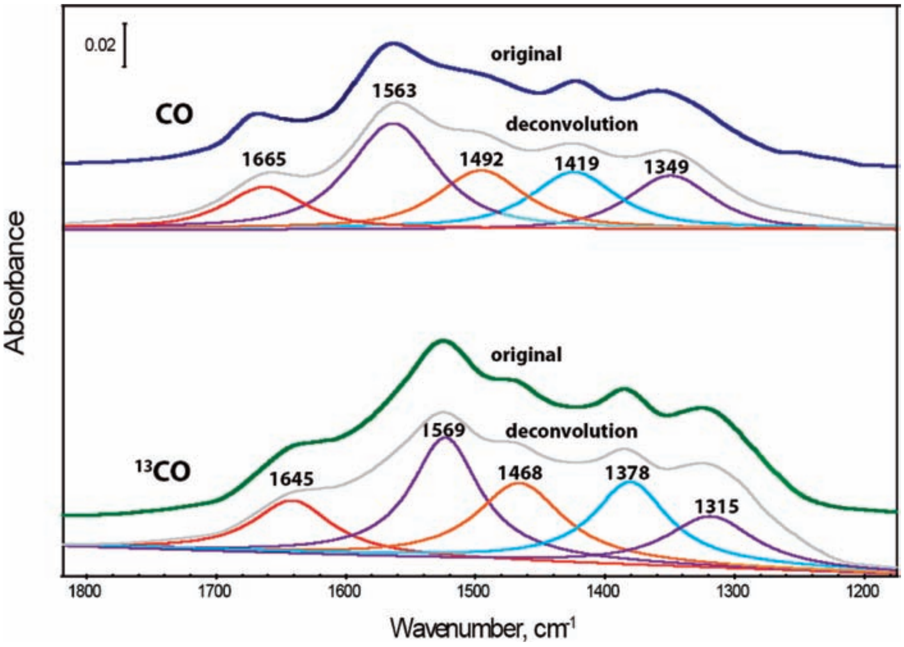

Figure 6. Deconvolution of IR spectra obtained by adsorption of CO and ^{13}CO on the surface of Cu(I)/TiO_2.

and 0.297 wt % were obtained after reaction times in the applied iso-butene/CO_2 mixture of 10, 30, and 60 min, respectively. Figure 8a shows the DRIFT spectra of coked catalysts recorded after 80 min of illumination in the presence of $^{13}CO_2$. Only the ^{12}CO band at 2117 cm^{-1} was observed for all the coked catalysts. Furthermore, compared to as-synthesized Cu(I)/TiO_2, coked catalysts show a smaller CO production after 80 min of illumination. The more coke is present on the surface of the Cu(I)/TiO_2 catalyst, the less CO is formed upon light irradiation. In the spectral region of carbonates (1200−1600 cm^{-1}), the same tendency is exhibited: less carbonates accumulate on the surface the higher the coke level of the applied catalyst.

To further characterize the coked Cu(I)/TiO_2 catalysts, DRIFT analyses of adsorbed CO were performed (Figure 8b), in the presence of gas phase CO (2500 ppm), and after a subsequent He flush. A significant amount of adsorbed CO can be observed in the presence of gas phase CO, which decreases as a function of increasing coke level. Furthermore, the stability of the adsorbed CO is smaller than observed for the as-synthesized Cu(I)/TiO_2 catalyst (see Figure 5), in view of the significant reduction in intensity after a He flush. It should be noted that the intensities of adsorbed CO are significantly higher than those obtained after 80 min of illumination in the presence of CO_2, which demonstrates that there are still enough Cu(I) sites to

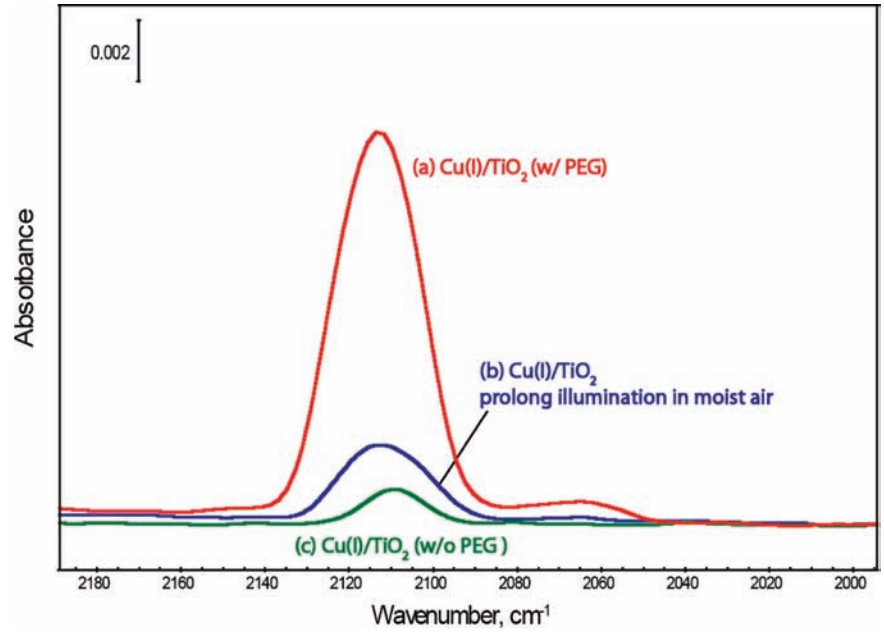

Figure 7. FT-IR spectra of Cu(I)/TiO_2 preloaded with $^{13}CO_2$ after 80-min illumination. Comparison of (a) fresh Cu(I)/TiO_2 (synthesized with PEG), (b) Cu(I)/TiO_2 cleaned by illumination in humid air for 14 h, and (c) reference Cu(I)/TiO_2 (synthesized without PEG).

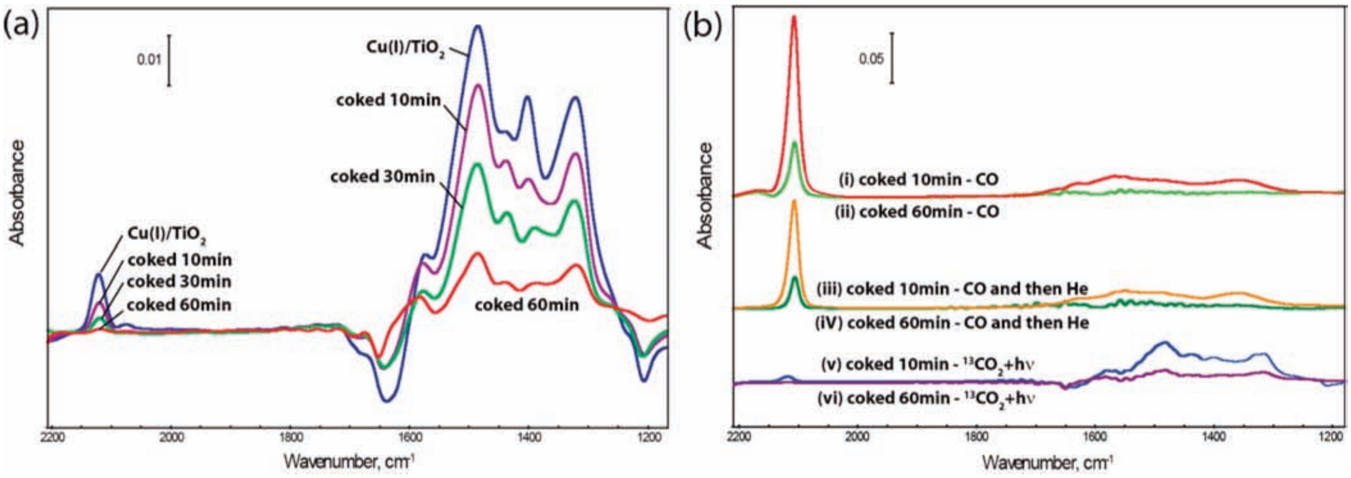

Figure 8. (a) FT-IR spectra after 80-min light irradiation in the presence of $^{13}CO_2$ for Cu(I)/TiO_2, and the coked analogue for 10, 30, and 60 min; (b) CO adsorption capacity. Spectra of (i) coked 10 min catalyst in the presence of CO, (ii) coked 60 min catalyst in the presence of CO, (iii) coked 10 min catalyst loaded with CO and then flushed by He for 30 min, (iv) coked 60 min catalyst loaded with CO and then flushed by He for 30 min, (v) coked 10 min catalyst after 80-min light irradiation loaded with $^{13}CO_2$, and (vi) coked 60 min catalyst after 80-min light irradiation loaded with $^{13}CO_2$.

allow CO adsorption. This shows that for coked catalysts the decreasing CO band (Figure 5a) is related to a smaller CO formation rate upon light irradiation. Finally, the intensity differences and changes in the carbonate region suggest that the Cu(I)/TiO_2 surface is indeed largely covered by coke, leading to lower intensities and the lower stability of the CO induced carbonate species.

Discussion

Formation of CO by Carbon Assisted Photocatalytic CO_2 Reduction. The experimental data presented herein demonstrate that CO is formed in significant quantities over Cu(I)/TiO_2 catalyst during illumination in the presence of CO_2, in particular if PEG is applied in the synthesis procedure. Using isotopically labeled $^{13}CO_2$, it is shown that carbon residues and surface adsorbed water significantly contribute to the formation of CO. The ratio of ^{12}CO over ^{13}CO is approximately 6. Two reactions can be proposed to explain the formation of ^{12}CO, i.e. the reverse Boudouard reaction, eq 1, and H_2O induced photocatalytic surface carbon gasification, eq 2:

$$^{13}CO_2 + {}'^{12}C' \rightarrow {}^{13}CO + {}^{12}CO \tag{1}$$

$$H_2O + {}'^{12}C' \rightarrow {}^{12}CO + H_2 \tag{2}$$

In view of the high ^{12}CO over ^{13}CO ratio, eq 2 must have a predominant contribution to the products formed. The source of H_2O is probably surface adsorbed water, which is activated upon illumination. In addition it is well-known that surface OH groups are involved in oxidation reactions over TiO_2 surfaces, which might also contribute to CO formation.

As stated in the introduction, usually additional products are obtained upon illumination of a Cu(I)/TiO_2 catalyst in the presence of CO_2, including methanol or methane. In view of the small quantities produced, we have not observed any spectral features that can be related to these species. However, it is to be expected that by consecutive reaction with H_2, CO formed by eqs 1 and 2 can be converted to e.g. CH_4.

Besides the isotopically labeled experiments, it was also demonstrated by prolonged exposure to UV-irradiation in the presence of water vapor that eq 2 plays a major role in the formation of CO over Cu(I)/TiO_2. In a way it is surprising that adding additional coke did not lead to extensive formation of CO. Apparently the surface coverage achieved was that considerable that the surface had become highly hydrophobic. This limits the reactive adsorption of CO_2 and, more importantly, significantly decreases the extent of surface hydration, as witnessed by the smaller intensity of the negative water bands in the 1620−1680 cm^{-1} region (Figure 8a). Clearly this is detrimental to the production of CO. Furthermore, the coke layer might simply prevent efficient light activation of the catalyst by absorption of light by the carbon layer, as was observed e.g. by Xia et al.[27] The surface chemistry of Cu(I)/TiO_2 in the photocatalytic CO_2 reduction is discussed in more detail in the following.

Surface Carbonate Chemistry. The Cu(I)/TiO_2 catalyst is very reactive toward CO_2 and CO at room temperature, leading to various carboxylate, bicarbonate, and carbonate species. Generally IR intensities are higher upon exposure to CO_2. When CO_2 approaches Cu(I)/TiO_2, carbonate species likely form on titania sites which are not fully coordinated, i.e. in the vicinity of the Cu(I) centers. This is in agreement with a study of Rasko et al., who investigated CO_2 adsorption and photocatalytic decomposition over prereduced Rh/TiO_2.[16,17] It was demonstrated in their study that, on prereduced Rh/TiO_2, oxygen vacancies in the vicinity of Rh offered sites for carboxylate formation, specifically with a C atom of CO_2 linked to Rh and one O atom of CO_2 bonded to the oxygen vacancy of titania. It is generally accepted that, by illumination with light of sufficient energy, electron−hole pairs are generated in titania. Rasko et al. propose that electrons are transferred to CO_2, yielding CO, while holes are involved in neutralizing the Ti^{3+} sites to Ti^{4+}. It is thus proposed by Rasko et al. that bent adsorbed CO_2 species are the precursor of CO, with the oxygen atom being incorporated in the TiO_2, changing the oxidation state from Ti^{3+} to Ti^{4+}. Also in our study we observe a depletion of the 1650 and 1220 cm^{-1} bands upon illumination, suggesting that these might be involved in the formation of CO by CO_2 dissociation. However, rather than being incorporated in the Cu(I)/TiO_2 lattice, we believe the remaining oxygen is predominantly transferred to residual carbon, yielding an additional CO molecule, according to eq 1.

The experiment conducted on a $^{13}CO_2$ pretreated catalyst (Figure 3) demonstrates that, in addition to carboxylates/bicarbonates, CO_2 induced surface carbonates are also unstable upon illumination, yielding $^{13}CO_2$. As previously discussed, the large selectivity for ^{12}CO in the experiment is related to water induced reactions of carbon residues, according to eq 2. This is followed by ^{12}CO adsorption on Cu(I) sites (2115 cm^{-1}) and surface TiO_2 sites, yielding ^{12}CO induced carbonates, explaining the growth of the demonstrated features (at 1560, 1420, and 1350 cm^{-1}) in Figure 3.

It should be noted that the (bi)carbonate and carboxylate species formed are most likely a strong function of the extent of surface hydration of the applied TiO_2 catalysts. Morterra[28] has evaluated the interaction of CO with TiO_2 surfaces. He demonstrated that removal of water molecules and decomposition of surface hydroxyl groups (OH) lead to the formation of surface Lewis acid sites that reversibly chemisorb CO at ambient temperature. While Morterra removed water and hydroxyl groups by evacuation in a vacuum IR cell, it is obvious (Figure 3) that the degree of hydration is also largely affected by the illumination procedure.

Artificial Photosynthesis, Fact or Fiction? Many (recent) studies discuss the performance of modified TiO_2 catalysts in the photocatalytic reduction of CO_2.[29] Generally methane and/or methanol are the products reported to be formed. In view of our study, the data reported in various related studies should be interpreted with caution. Frei and co-workers already observed for mesoporous materials that carbon residues can be involved in the production of primary products in the photocatalytic reduction of CO_2.[30−32] In view of our data, also for crystalline TiO_2 materials, water induced gasification of these carbon residues might be affecting the product quantities and distribution (reaction 2). This is particularly true if alkoxides (propoxide, butoxide) were used as the precursor[33] or if carbon supported TiO_2 was used.[27] Also in the synthesis procedure of N-doped TiO_2, organic solvents were used, the residue of which might have contributed to the observed activity.[34] Clearly, contribution of these reactions leads to an overestimation of the rate of the real artificial photosynthesis reactions, such as $2CO_2 + 4H_2O \rightarrow 2CH_3OH + 3O_2$. It is highly recommended in future studies on photocatalytic CO_2 reactions to add a test of activity in the absence of CO_2 but in the presence of H_2O to exclude the participation of catalyst associated carbon residues in the formation of products.

While there is no doubt that carbon residues contribute to catalytic performance, based on our study we cannot entirely exclude artificial photosynthesis. ^{13}CO was formed in various experiments, and it is necessary to isolate the reversed Boudouard reaction from true artificial photosynthesis. This would require careful evaluation of the production of O_2. To close the oxygen balance is however extremely difficult, and usually irreproducible data are obtained due to fluctuations in background oxygen pressures. The most conclusive evidence that CO is formed in the absence of carbon residues is again provided by Frei and co-workers[18] in a high vacuum IR cell, in the case of isolated Ti sites in mesoporous materials. Ozonation was a very efficient way of removing residual carbon in their study. The onward CO_2 reduction performed under $^{13}CO_2$ and H_2O showed merely ^{13}CO production, which is significant evidence for true artificial photosynthesis. However, mechanistic studies on highly pure crystalline metal oxide systems are needed to definitively prove that artificial photosynthesis over these materials is fact as well as to further reveal the chemical pathway

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of CO_2 reduction, including the complexity in the dynamics of surface carbonates.

Conclusions

Carbon residues largely participate in the formation of CO over Cu-promoted crystalline TiO_2 catalysts, as demonstrated by the combined use of DRIFT spectroscopy and ^{13}C labeled CO_2. These residues are formed during the catalyst synthesis procedures, often involving the use of Ti-alkoxides and organic solvents, such as polyethylene glycol (PEG). Removal of these residues by thermal activation in air is incomplete, while prolonged exposure to water vapor and UV-irradiation is more efficient. Coking of Cu(I)/TiO_2 showed that extensive carbon coverage of Cu(I)/TiO_2 diminishes CO formation during illumination in the presence of CO_2.

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Supporting Information Available: Additional data figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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