

Solar fuel production from CO₂ photoreduction on CuO_x/TiO₂ nanoparticles: the role of surface oxygen vacancy and copper species

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Introduction

The activation of CO₂ on TiO₂ is the most important step in CO₂ photoreduction reaction, which likely involves an electron transfer to CO₂ and hence the transformation of linear structure to a bent form in which the C–O bond is much more reactive.^[1,2] However, this one-electron reduction of CO₂ is thermodynamically unfavorable, based on a very negative redox potential for this process in an aqueous homogeneous system, $E^{\circ}(\text{CO}_{2\text{aq}}/\text{CO}_{2\text{aq}}^{-\bullet}) = -1.9\text{V}$ vs NHE.^[3] It is hence very essential to improve the electron transfer to CO₂. The addition of copper into TiO₂ matrix could change interfacial charge transfer and the dynamics of electron-hole recombination, thus improving the efficiency and selectivity of CO₂ reduction.^[4,5] Moreover, surface oxygen vacancy (V_O) is reported to act as active sites for CO₂ photoreduction,^[6,7] which can be introduced into TiO₂ by post-deposition treatment (annealing, reduction in reductive or inert gas) and doping anions or transition metals.

However, there are two important questions that are not addressed in the literatures at the molecular-level: (1) what are the specific surface sites and specific configuration of adsorbed CO₂ on oxidized and reduced CuO_x/TiO₂? (2) How and which copper species (Cu²⁺, Cu⁺, Cu⁰) significantly contribute in enhancing the photocatalytic activity? Accordingly, our work employed in situ FTIR to gain insight into the CO₂ reduction mechanism on the oxidized and reduced CuO_x/TiO₂ catalysts. The results demonstrate that CO₂ is spontaneously activated and dissociated into CO on the reduced CuO_x/TiO₂ through dissociative electron attachment process, which is facilitated by UV-vis illumination. Most importantly, surface V_O and Cu⁺ species are the essential factors to enable the spontaneous dissociation of CO₂. These studies will advance the fully fundamental understanding of CO₂ photoreduction mechanism and surface redox chemistry of TiO₂-based nanostructures.

Experimental

In brief, 1g TiO₂-P25 (Degussa) was mixed with 100 ml 0.25M NaOH solution, and a required amount of CuCl₂ solution was added dropwise. After stirred 6h, the samples was filtered, washed and dried at 80 °C for 15h, and finally calcined at 400 °C for 3h in air. The powder was further in situ reduced by helium (He) or hydrogen (H₂) at 400 °C. The resulting samples were denoted as A-Cu/Ti, He-Cu/Ti and H₂-Cu/Ti, respectively.

In situ Fourier transforms Infrared (FTIR) spectra were obtained by Nicolet 6700 spectrometer (Thermo Electron) and displayed in Absorbance units. The resolution of the spectra was 4 cm⁻¹, and the scan number was 32. The chamber capable of high temperature operation was irradiated by a 450W XENON lamp through liquid light guide. The samples were irradiated in the presence of 10% CO₂/He (Praxair, 4.0 ml/min). All the spectra in this paper are collected by subtracting the background (the spectra of the catalyst without CO₂). The in situ FTIR for CO₂ photoreduction is illustrated in Figure 1.

Results and Discussion

Characterization of copper valence

In situ FTIR of CO adsorption was used to probe the copper valence state (data not shown). The results demonstrate that Cu²⁺ ions dominate the surface of A-Cu/Ti, and Cu⁺ is present as minority surface species. For He-Cu/Ti, Cu⁺ ions are the primary components dispersed on the surface. For H₂-Cu/Ti, Cu⁺ and Cu⁰ ions co-present the surface, but Cu⁰ should be the majority since the color of H₂-Cu/Ti turns into dark blue that is different from the light green A-Cu/Ti and light gray He-Cu/Ti.

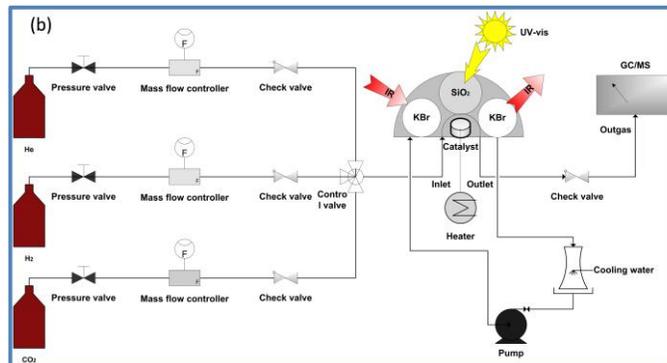


Figure 1. The diagram for in situ FTIR of CO₂ interaction with CuO_x/TiO₂ under UV-vis illumination at 25 °C

CO₂ interaction with CuO_x/TiO₂

A dramatic change occurred when the CuO_x/TiO₂ was illuminated in the presence of CO₂. In Figure 1a, negative CO₂⁻ species were acquired at 1247 cm⁻¹ through electron transfer proceeding from Ti³⁺ centers to adsorbed CO₂,^[1,2] the intensity of which was much stronger on the reduced He-Cu/Ti and H₂-Cu/Ti than that on the oxidized A-Cu/Ti. This CO₂⁻ increased in intensity at the initial 8min, and then decreased gradually. In the meantime, well-observable CO band appeared after the short 1min illumination (Figure 1b), indicating the splitting of CO₂ into CO upon dissociative electron attachment process.^[7] Moreover, the relative intensity of CO on A-Cu/Ti was negligible, while on He-Cu/Ti was stronger. On H₂-Cu/Ti surface, there is additional weak peak for Cu⁰-CO at 2095 cm⁻¹.^[8] In fact, ¹²CO₂ and labeled ¹³CO₂ adsorption results also demonstrate that CO₂ is spontaneously dissociated into CO on He-Cu/Ti and H₂-Cu/Ti at 25 °C even in the dark, but not on A-Cu/Ti (data not shown). Generally, the removal of surface oxygen in the insert or reductive atmosphere leaves two unpaired electrons (UPEs) that are engaged in the two Ti–O bonds as surface V_O is formed.^[6] These UPEs can readily migrate to adsorbed CO₂, yielding CO₂⁻ anions, which are metastable and subsequently dissociated into fragments or desorb as neutral species. The V_O is healed by the oxygen atom released during the dissociation process. The overall reaction is described as follows:

$$\text{Ti}^{3+}\text{-V}_\text{O} + \text{Cu}^+ + \text{CO}_2 \rightarrow \text{Ti}^{4+}\text{-O}_\text{v} + \text{Cu}^+\text{-CO} \quad (1)$$

However, this V_O can be regenerated upon He pretreatment. On the oxidized A-Cu/Ti, no V_O is available, and Cu²⁺ ions are not very effective to help the activation and dissociation of CO₂ on TiO₂.

The change of FTIR spectrum areas of CO₂⁻ and CO with the time were plotted to further illustrate the role of these Cu⁺ and Cu⁰ species and the influence of illumination. As shown in Figure 2a, without UV-vis illumination CO₂⁻ species decreased at a relatively higher rate on He-Cu/Ti after 5min, while under UV-vis illumination it exhibited a slow decreasing rate. Similar changing trend can be observed on H₂-Cu/Ti surface. Accordingly, illumination of the surface results in an enhancement of charge transfer from Ti³⁺ to adsorbed CO₂.

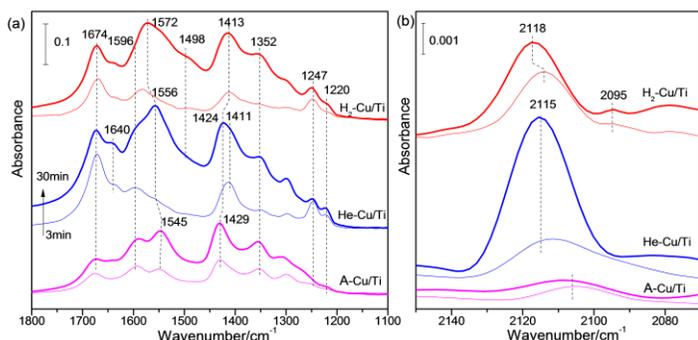


Figure 2. In situ FTIR spectra of CO_2 interaction with (a) and the formation of CO (b) on A-Cu/Ti, He-Cu/Ti and H_2 -Cu/Ti under UV-vis illumination at 25 °C

Most importantly, illumination induced more CO produced than without illumination on He-Cu/Ti. CO sharply decreased after 10min in the dark and nearly vanished completely after 35min, whereas gradually decreased after 20min upon irradiation. Therefore, another importance of illumination is greatly to promote the dissociation of CO_2 into CO. On the other hand, the disappearance of CO_2^- on He-Cu/Ti was faster than that on H_2 -Cu/Ti either with or without illumination. Simultaneously, the formation of CO on H_2 -Cu/Ti was at a low rate, and relative concentration is also lower than that on He-Cu/Ti. This result suggests that Cu^+ ions should be more favorable than Cu^0 to assist the dissociation of CO_2 on TiO_2 . This is probably due to the formation of stable Cu^+ -CO species, which is considered as additional driving force for the dissociation of CO_2 .

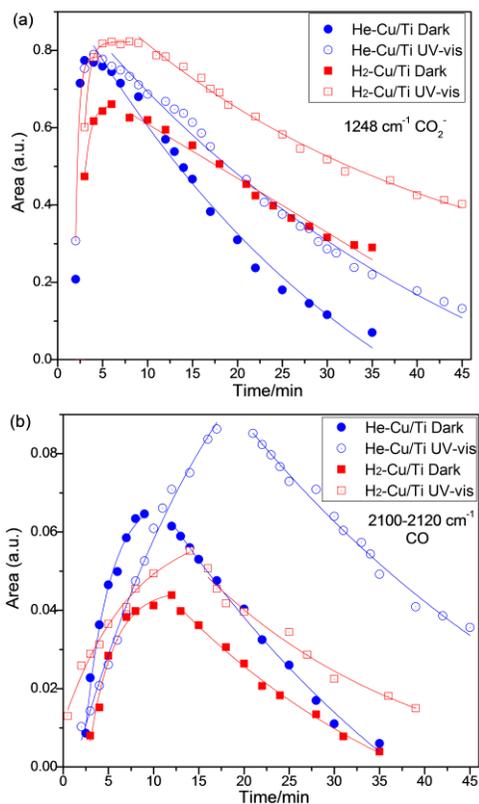


Figure 3. The change of FTIR spectrum area of CO_2^- and CO species on He-Cu/Ti and H_2 -Cu/Ti

Photocatalytic experiments on CO_2 reduction by $\text{CuO}_x/\text{TiO}_2$

Experiments on photocatalytic activity of CO_2 reduction have been conducted in a photoreactor described in our previous study.^[3] The experimental results correlate with the in situ FTIR analysis that Cu^+ is the most active states to enhance CO_2 photoreduction and that oxygen vacancies on reduced TiO_2 samples facilitate electron transfer and thus result in a higher yield of CO_2 reduction.

Conclusions

CO_2 is spontaneously dissociated into CO on the reduced $\text{CuO}_x/\text{TiO}_2$, but not on oxidized $\text{CuO}_x/\text{TiO}_2$. Such surface redox chemistry on the reduced titania is to a large extent associated with surface oxygen vacancy, since these defective sites provide electron transfer. This CO_2 activation and dissociation process is facilitated by UV-vis illumination. In addition, Cu^+ ions are more active than Cu^{2+} and Cu^0 to accelerate the transformation of negative CO_2^- species and the formation of CO on the surface of TiO_2 .

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