On the general mechanism of photocatalytic reduction of CO$_2$

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ABSTRACT

This paper is going to make a global view of the reaction mechanism of photocatalytic reduction of CO$_2$. During the past decades, extensive studies have been conducted to identify the photocatalytic products of CO$_2$ conversion and their reaction mechanisms. There is a need to propose a general mechanism pattern covering the results of these original researches. Among many factors affecting the redox reaction pathway, this paper focuses on the effect of reductant type as an important issue on the product diversity and selectivity of CO$_2$ photocatalysis. We first tried to show the reaction mechanism of CO$_2$ photocatalysis in the solitary presence of the most common reductants, H$_2$, H$_2$O (both gaseous and aqueous phases), CH$_4$, and CH$_3$OH. Then, a general mechanism has been suggested for CO$_2$ conversion in the mixture of the reductants, based on the fact that in the photoreduction process of CO$_2$, all of the reductants can be derived from one of them.

1. Introduction

The global warming caused by the accelerative accumulation of atmospheric carbon dioxide (CO$_2$) from both natural and anthropogenic resources is the most crucial issue for human being. CO$_2$ is a noncondensing and stable molecule which is not thermodynamically easy to be transformed into other chemicals at mild reaction conditions. In the past decades, photocatalysis of CO$_2$ has been regarded as a promising sustainable pathway for CO$_2$ mitigation. Indeed, by means of photocatalysis, CO$_2$ can be served as a building block for the synthesis of other useful chemicals and chemical intermediates [1,2].

Some semiconductor materials like TiO$_2$ [3], ZnO [4], WO$_3$ [5], and ZnS [6] in the bare or improved forms of them have been used for this purpose. The reduction of CO$_2$ into hydrogenated compounds needs to reducing substances like H$_2$O, H$_2$, CH$_4$, and alcohols (like methanol and ethanol), which act as both the hydrogen sources and holes scavenges [7]. The photocatalytic process of CO$_2$ follows a relative unknown and complex mechanism leading to different products at the same time. Thus, understanding the mechanism of CO$_2$ conversion could be effective in the control of product selectivity. Photocatalytic-based conversion of CO$_2$ mostly produces the organic compounds such as CO, CH$_4$, HCOOH, HCHO, CH$_3$OH and other light hydrocarbons [2,8,9]. The effect of reductant on the yield and distribution of these products has been studied in many literatures. Although most studies on the mechanism of photocatalytic reduction of CO$_2$ have focused on TiO$_2$, the results could be applicable for other photocatalysts.

This paper first highlights the role of reductants (H$_2$O, H$_2$, CH$_4$, and alcohols) in the diversity and distribution of products of CO$_2$ photocatalysis regardless of the potential levels of the excited charge carriers. In other words, it was assumed that the reactions can proceed as much as possible without any limitation relating to the position of conduction and valence band edges. Then, a general mechanism for CO$_2$ reduction in the presence of all the reductants has been offered.

2. Basic principles of photocatalysis

Photocatalysis is a process in which the absorption of light photons having energy equal to/greater than the band gap energy (E_{bg}) of a semiconductor catalyst (SC) excites electron (e^-) and hole (h^+) to the empty conduction and valence bands (CB and VB), respectively. These energetic charge carriers initiate various redox reactions to produce final products [2,10]. Eqs. (1) and (2) show the semiconductor activating reactions.

$$SC + h\nu \ (\geq E_{bg}) \rightarrow h^+ e^- \tag{1}$$

$$h^+ e^- \rightarrow h^+{}_{VB} + e^-{}_{CB} \tag{2}$$

These photoinduced charge carriers may follow different routes. The photogenerated electron and holes could migrate

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and trap at the shallow and deep trapping sites. In the case of TiO_2, $Ti^{III}OH$ and $Ti^{IV}OH^{\bullet}$ (in the hydrated surface) are the shallow trapping sites of electron and hole, respectively. The electrons could also be trapped at bulk trapping sites in the form of Ti^{III}. If the electrons fail to find any trapped sites, or the energy band gap of the semiconductor is very small, they recombine and generate thermal energy at the surface or bulk of photocatalyst. Indeed, charge trapping is needed to avoid charge recombination, and increase photoactivity. Finally, the generated electron-hole could be transferred to the adsorbed species on the photocatalyst surface. The final route is the most desirable event for efficient application of photocatalysis [11–13].

The capability of a photocatalyst to succeed a typical redox reaction depends on the positions of the energy levels of the photocatalyst and adsorbed substrate. For driving a reduction reaction, the potential of conduction band should be more negative than the potential required for the reduction reaction. Similarly, an oxidation reaction may happen if the potential of the valence band be more positive than that of the oxidation reaction [2,14].
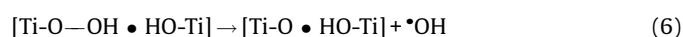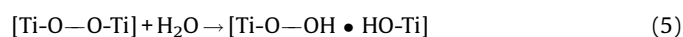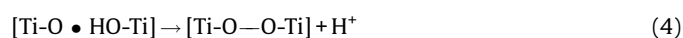
3. Photocatalytic oxidation of reductants

When CO_2 is reduced by photogenerated electrons, an equal number of holes has to be served to decrease the probability of charge recombination and increase the lifetime of electrons. By utilization of electron donor reductants, the holes not only could be scavenged, but they also supply the hydrogen needed for synthesis of hydrogenated products. In fact, the hydrogenated products of CO_2 conversion are not formed, unless the hydride reductants simultaneously be oxidized by oxidizing agents. Thus, we first need to know about the oxidizing agents and oxidation mechanism of reductants. In this section, the oxidation mechanism of aliphatic has been discussed to find the reactive radicals, products and by-products of photocatalytic oxidation of methane and methanol as reductants.
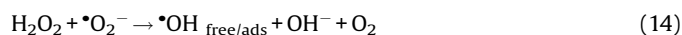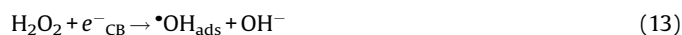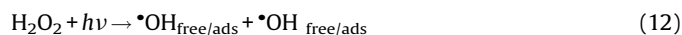
3.1. Oxidizing species

In order to understand the reaction mechanism of CO_2 photocatalysis, it is essential to clarify the oxidizing species generated at the excited photocatalyst surface or bulk phase. Apart from the holes as primary oxidizing species that drive a direct oxidation process, the other main oxidizing species include hydroxyl radicals (free radical: $^{\bullet}OH_{free}$ and adsorbed radical: $^{\bullet}OH_{ads}$) [15], superoxide ($^{\bullet}O_2^{-}$) [16], and singlet oxygen ($^1O_2$) [17]. Additionally, in some photocatalytic oxidation processes, participation of hydrogen peroxide (H_2O_2) and molecular oxygen has been reported [13,16].
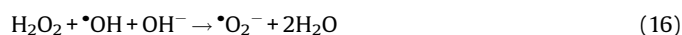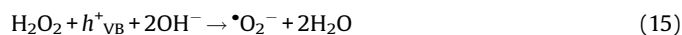
$^{\bullet}OH$ radicals are mainly created by oxidation of surface hydroxyl or adsorbed water. The oxidation process initiated by $^{\bullet}OH$ is considered as indirect oxidation. In the case of TiO_2, $^{\bullet}OH$ formation was suggested by the reaction pathway including a nucleophilic attack of water on a surface trapped hole (Eqs. (3)–(6)). The final reaction (Eq. (6)) is based on breaking the O—O bond in TiO—OH [13].

$$[Ti\text{-}O\text{-}Ti] + h^+{}_{VB} + H_2O \rightarrow [Ti\text{-}O \bullet HO\text{-}Ti] + H^+ \tag{3}$$

$$[Ti\text{-}O \bullet HO\text{-}Ti] \rightarrow [Ti\text{-}O\text{—}O\text{-}Ti] + H^+ \tag{4}$$

$$[Ti\text{-}O\text{—}O\text{-}Ti] + H_2O \rightarrow [Ti\text{-}O\text{—}OH \bullet HO\text{-}Ti] \tag{5}$$

$$[Ti\text{-}O\text{—}OH \bullet HO\text{-}Ti] \rightarrow [Ti\text{-}O \bullet HO\text{-}Ti] + {}^{\bullet}OH \tag{6}$$

In general, $^{\bullet}OH$ radicals could be produced via direct oxidation of OH^- (Eq. (7)), or through the intervention of H_2O_2 (Eqs. (8)–(14)). Some of these reactions can only produce the adsorbed $^{\bullet}OH$ radicals and others, both the adsorbed and free $^{\bullet}OH$ radicals [16,18].

$$OH^- + h^+{}_{VB} \rightarrow {}^{\bullet}OH_{ads} \tag{7}$$

$$O_2 + e^-{}_{CB} \rightarrow {}^{\bullet}O_2^{-} \tag{8}$$

$$O_2 + 2e^-{}_{CB} + 2H^+ \rightarrow H_2O_2 \tag{9}$$

$${}^{\bullet}O_2^{-} + {}^{\bullet}O_2^{-} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{10}$$

$$2{}^{\bullet}OH_{ads} \rightarrow H_2O_2 \tag{11}$$

$$H_2O_2 + h\nu \rightarrow {}^{\bullet}OH_{free/ads} + {}^{\bullet}OH_{free/ads} \tag{12}$$

$$H_2O_2 + e^-{}_{CB} \rightarrow {}^{\bullet}OH_{ads} + OH^- \tag{13}$$

$$H_2O_2 + {}^{\bullet}O_2^{-} \rightarrow {}^{\bullet}OH_{free/ads} + OH^- + O_2 \tag{14}$$

Superoxide radical as a weak oxidizing species is less important in starting oxidation reaction. $^{\bullet}O_2^{-}$ is the product of either one-electron reduction of molecular oxygen by a conduction band electron (Eq. (8)), or oxidation of H_2O_2 by valence band hole (Eq. (15)) or by $^{\bullet}OH$ (Eqs. (16) and (15) is the major reaction to give superoxide radical anion from H_2O_2 [16].

$$H_2O_2 + h^+{}_{VB} + 2OH^- \rightarrow {}^{\bullet}O_2^{-} + 2H_2O \tag{15}$$

$$H_2O_2 + {}^{\bullet}OH + OH^- \rightarrow {}^{\bullet}O_2^{-} + 2H_2O \tag{16}$$

Singlet oxygen, a strong oxidant, is known as the product of reaction between $^{\bullet}O_2^{-}$ and a trapped hole. In spite of the high reactivity of $^1O_2$, its short lifetime (2 μs) on TiO_2 surface than that of $^{\bullet}OH$ (ca. 10 μs) makes it less important compared with hydroxyl radical [13,17].

3.2. Photocatalytic oxidation of aliphatic (alkanes and alcohols)

Since alkanes (mainly methane) and primary alcohols (mainly methanol) are usually utilized as common reductants for photocatalytic reduction of CO_2, it needs to be investigated their photocatalytic oxidation mechanisms. For the oxidation of alkanes, the subsequent reactions are thought to be initiated by direct (Eq. (17)) or indirect (Eq. (18)) oxidation processes. Based on the underlying mechanism, alcohols are the first by-product of photocatalytic oxidation of alkanes, so this mechanism also involves the oxidation of primary alcohols.

$$RCH_3 + h^+{}_{VB} \rightarrow {}^{\bullet}RCH_2 + H^+ \tag{17}$$

$$RCH_3 + {}^{\bullet}OH \rightarrow {}^{\bullet}RCH_2 + H_2O \tag{18}$$

In the next step, alcohols can be yielded from the produced alkyl radicals via two different pathways, Eq. (19) or according to consecutive Eqs. (20)–(23):