Heterogeneous Photocatalytic Conversion of Carbon Dioxide

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Abstract Carbon dioxide is a greenhouse gas, which may contribute to the global warming. The conversion of carbon dioxide to more useful chemicals is not an easy task because of a high thermodynamic barrier, which requires much energy consumption. However, we should not use energy from fossil resources to convert the carbon dioxide because the use of them produces carbon dioxide; therefore, it is desirable to use natural energy for this purpose. Photocatalysis, which can utilize solar energy and break the thermodynamic limitation, is a possible green technology available for the carbon dioxide conversion and many studies have been carried out. In this chapter, after a description of the importance of the photocatalytic system, the physical and chemical basis for carbon dioxide conversion, and the basis for photocatalysis and photocatalysts, we will review a brief history about heterogeneous photocatalytic conversion of carbon dioxide to other compounds, such as methane, methanol and carbon monoxide, by using reducing reagents such as water, hydrogen and methane. The perspectives related to the field of nanotechnology will also be described.

1 Introduction

Since the global warming issue has become worldwide concern, the methodology for the mitigation of carbon dioxide as a greenhouse gas has been investigated. There are several strategies to reduce carbon dioxide emissions, such as energy-

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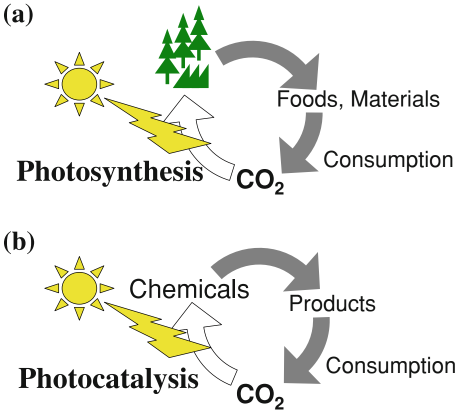


Fig. 1 Carbon neutral cycles through (**a**) agriculture and forestry with photosynthesis, and (**b**) artificial route with photocatalysis

conservation, carbon dioxide capture and storage, enhanced oil recovery and so on [1]. One such method, artificial conversion of carbon dioxide to other useful chemicals, has attracted much attention.

In the ecological system in nature, photosynthesis (Eq. 1) takes place in plants to convert carbon dioxide and water to sugars and oxygen by using solar energy [2].

$$6\ CO_2 + 6\ H_2O\ +\ \text{photoenergy} \rightarrow C_6H_{12}O_6 + 6\ O_2 \tag{1}$$

Plant photosynthesis demonstrates the viability of converting carbon dioxide to chemicals and also converting sunlight into chemical potential. Since carbon dioxide is one of the most stable molecules, as mentioned later, the conversion of carbon dioxide to other chemicals must involve energy injection. This means that plants can store the energy from the incident solar irradiation in the form of chemical bonds. The carbon neutral cycle is driven by solar energy (Fig. 1a).

However, the efficiencies of energy-conversion in natural photosynthesis are not enough to satisfy our demands. We need an artificial photosynthetic method. Photocatalysis with solar light is one potential approach as an artificial photosynthesis (Fig. 1b).

Clearly, utilization of the diluted carbon dioxide in atmosphere is difficult because of its large entropy and therefore requires much cost for collection, separation and purification [3]. Diluted carbon dioxide is released from stationary sources, such as electric power stations and blast furnaces in industry, as well as from the mobile sources such as cars, aircrafts, trains and ships [3, 4]. On the other hand, concentrated carbon dioxide is more preferred as a carbon dioxide source. There are many stationary sources emitting the concentrated carbon dioxide, including several kinds of industries for processing of natural gas, production of ethanol by fermentation, and production of bulk chemicals such as ammonia and ethylene oxide, as well as inorganic industries for production of cement, limestone and soda ash [3, 4]. Thus, we should just diminish the diluted emission from both the stationary and mobile sources, and should effectively utilize the concentrated carbon dioxide before diffusion.

Currently, carbon dioxide is used in various ways: for beverage carbonation, or fire extinguishers, also as a refrigerant for food preservation (as dry ice), a supercritical solvent, a pressurizing agent and a neutralizing agent. In addition, carbon dioxide is regarded as an important green chemical reagent as a mild oxidant or as a weak acid for many synthetic reactions [3, 4]. Catalytic reactions involving carbon dioxide and producing valuable products have been well reviewed, e.g., by Xiaoding and Moulijn [4], Song [3], Sakakura et al. [5] and Aresta and Dibenedetto [6]. Although establishing a chemical industry based on a renewable feedstock like carbon dioxide is still challenging, some reactions have already been industrialized or are one step away from commercialization [5]. The fixation of carbon dioxide as compounds is valuable for reducing the carbon dioxide in the atmosphere until the products will finally be disposed and transformed to carbon dioxide again. However, we must also consider that the amount of fixed carbon dioxide converted to chemical compounds will be much smaller than that of carbon dioxide emission through combustion of fossil fuels on the global scale. Moreover, fixation reactions require activation energy, which is usually produced in conjunction with more carbon dioxide emissions. Thus, these reactions using carbon dioxide as a raw material may not necessarily contribute to reduce the greenhouse effect as much as desired. Currently, less than 1% of carbon dioxide emissions are used in chemical reactions [4]. Of course, even if it is only 1%, it is still very important. However, we must also provide and develop other methods that are more environmentally benign. The photocatalytic conversion of carbon dioxide described in this chapter has a potential to become a useful method [1, 7] because these methods require no chemical reagents except for water, hydrogen and methane.

2 Properties of Carbon Dioxide in Chemical and Thermodynamical View

2.1 Acidic Properties of Carbon Dioxide

Carbon dioxide is one of the most stable molecules among carbon compounds, and is, therefore, the final product in the oxidation/combustion of organic and carbonaceous compounds. The molecule consists of a linear connection of a carbon and two oxygen atoms (O=C=O) and it does not have a dipole moment. However, as a chemical reagent, it is not an inert molecule.

This molecule is often recognized as an acidic gas. Since it can be adsorbed by the surface base sites of heterogeneous catalysts, it can be used as a probe molecule for these sites in measurements of FT-IR spectra and temperature programmed desorption (TPD) profiles [8]. In this adsorption, the carbon atom of carbon dioxide molecule accepts the electron lone pair of the surface oxygen ion at the metal oxide surface, and the oxygen atom having a lone pair in the carbon

Fig. 2 Adsorbed forms of carbon dioxide

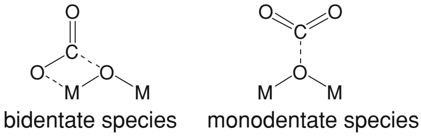


Table 1 Gibbs free energy (ΔG_f^0/kJ mol^{-1}) for each compound

Gas phase		Liquid phase		Solid phase	
C_6H_6	+130	C_6H_6	+124		
C_2H_4	+68			C (graphite)	0
H_2, O_2	0			Ni, Mg	0
NH_3	−16	C_6H_{14}	−4		
CH_4	−51	HCHO	−102		
CO	−137	CH_3OH	−166		
H_2O	−237	H_2O	−228	NiO	−212
CO_2	−394	HCOOH	−361		
		CO_2	−368		
		CO_3^{2-}	−528	MgO	−569
		HCO_3^{-}	−586	CaO	−603
		$C_2O_4^{2-}$	−671	$NiCO_3$	−613
				$MgCO_3$	−1012
				$CaCO_3$	−1130

The values are from [3]

dioxide molecule can donate these electrons to the surface acidic sites, to form various kinds of adsorbed species, such as carbonate-like species (Fig. 2).

The acidic property of carbon dioxide promotes the formation of carbonate with alkaline and alkaline earth cations to become more stable. In the Table 1 the values of Gibbs free energy for the representative compounds are given [3]. We can recognize the thermodynamically stable properties of carbon dioxide, carbonate anion and metal carbonates. Thus, carbon dioxide is the last product in combustion of compounds containing carbon, and metal carbonates are found as stable natural resources.

2.2 Chemical Reactions of Carbon Dioxide

On the other hand, carbon dioxide can function as a mild oxidant since carbon dioxide cannot be oxidized any further. For example, it is well-known that the reaction between methane and carbon dioxide can produce syngas (carbon monoxide and hydrogen), which is called a dry reforming of methane (DRM) or CO_2 reforming of methane (Table 2, entry 7) [9]. In this reaction, carbon dioxide oxidizes methane to yield carbon monoxide, while carbon dioxide itself is reduced by methane to become carbon monoxide. The DRM is a thermodynamically unfavorable reaction and can only proceed at high temperature, typically more than 1,000 K, even by using catalysts [10]. There are many other reactions using

Table 2 Change of Gibbs free energy at 298 K for various reactions related to the photocatalytic reduction of carbon dioxide

Entry	Reductant	Product	Chemical equation			ΔG^0/kJ mol^{-1}
1	H_2	Carbon monoxide	$CO_2 + H_2$	→	$CO + H_2O$	29
2		Formic acid	$CO_2 + H_2$	→	$HCOOH$	43
3		Formaldehyde	$CO_2 + 2\ H_2$	→	$HCHO + H_2O$	63
4		Methanol	$CO_2 + 3\ H_2$	→	$CH_3OH + H_2O$	4
5		Methane	$CO_2 + 4\ H_2$	→	$CH_4 + 2\ H_2O$	−114
6		Carbon	$CO_2 + 2\ H_2$	→	$C + 2\ H_2O$	−63
7	CH_4	Carbon monoxide	$CO_2 + CH_4$	→	$2\ CO + 2\ H_2$	171
8		Acetone	$CO_2 + 2\ CH_4$	→	$CH_3COCH_3 + H_2O$	115
9		Acetic acid	$CO_2 + CH_4$	→	CH_3COOH	71
10		Formaldehyde	$CO_2 + CH_4$	→	$2\ HCHO$	240
11		Carbon	$CO_2 + CH_4$	→	$2\ C + 2\ H_2O$	−12
12	H_2O	Formic acid	$CO_2 + H_2O$	→	$HCOOH + 1/2\ O_2$	272
13		Carbon monoxide	$CO_2 + H_2O$	→	$CO + H_2 + O_2$	486
14		Formaldehyde	$CO_2 + H_2O$	→	$HCHO + O_2$	521
15		Methanol	$CO_2 + 2\ H_2O$	→	$CH_3OH + 3/2\ O_2$	690
16		Methane	$CO_2 + 2\ H_2O$	→	$CH_4 + 2\ O_2$	801
17		Carbon monoxide	CO_2	→	$CO + 1/2\ O_2$	257
18			$H_2O(g)$	→	$H_2 + 1/2\ O_2$	229
19			$H_2O(l)$	→	$H_2 + 1/2\ O_2$	237

Calculated from the data of gaseous states in most cases [12, 13]

carbon dioxide as an oxidant, where carbon dioxide is reduced instead, as reviewed in the literature [4–6].

Table 2 shows the representative reactions of carbon dioxide with simple small molecules, i.e., hydrogen, methane and water, with the values of the change of Gibbs free energy at 298 K for each reaction. In these reactions, these molecules reduce the carbon dioxide as reductant to yield products such as carbon monoxide, formic acid, acetic acid, formaldehyde, acetaldehyde, methanol, methane and carbon. A reaction can proceed preferably when the change of Gibbs free energy is negative. However, most of reactions listed here show positive values, meaning that they are thermodynamically unfavorable reactions.

When we reduce the carbon dioxide with hydrogen, the products will be the reduced C1 compounds or carbon (Table 2, entries 1–6). In the case of the reactions to form carbon monoxide, formic acid and formaldehyde, the changes of Gibbs free energy are positive values in range from 29 to 63 kJ mol^{-1} (Table 2, entries 1–3). This means that these reaction systems require the energy and store it as chemical potential in the products. This type of the reaction is called an "uphill reaction" (Fig. 3a) [11]. On the other hand, in the reactions with hydrogen producing methane and carbon, the changes of Gibbs free energy are negative values such as −114 and

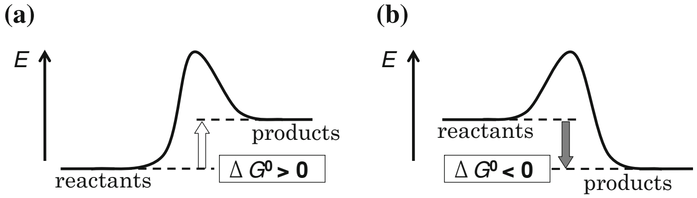


Fig. 3 Energy diagrams for (**a**) up-hill reaction and (**b**) downhill reaction

−63 kJ mol^{-1} (Table 2, entries 5 and 6). This type of the reaction is called a "downhill reaction" (Fig. 3b). The reduction of carbon dioxide by hydrogen to produce methane (Table 2, entry 5) is not an attractive reaction since the system must lose the chemical potential by consuming hydrogen of high chemical potential, and in the economical sense, hydrogen is more expensive than methane [4]. However, if the hydrogen could be obtained easily through utilizing solar energy, e.g., through the photocatalytic water splitting, rather than through consumption of fossil fuels, this reaction may become appealing.

When we reduce carbon dioxide with methane, the products vary more than the case of the reduction by hydrogen. In Table 2, entries 7–11, the representative products are listed. Among them, most of the reactions are uphill. Thus, when we try the photocatalytic reduction of carbon dioxide by methane, the yields of these products will be valuable.

The reduction of carbon dioxide with water seems extremely thermodynamically-unfavorable reaction, since the changes of Gibbs free energy are largely positive values greater than 272 kJ mol^{-1}. These values are larger than the value for the water splitting (Table 2, entries 18 and 19), especially the value is as high as 801 kJ mol^{-1} for the methane formation (Table 2, entry 16); this value is too high to proceed through usual catalysis. These reactions are the reverse reactions for the complete oxidation of carbon compounds. However, there are many studies reporting the photocatalytic reduction of carbon dioxide by water as a reductant with a heterogeneous photocatalyst to yield carbon monoxide, methanol, methane and so on, as mentioned later.

There are many reports on the utilization of carbon dioxide through the organic synthetic reactions [4–6]. In these cases, carbon dioxide is regarded as a chemical feedstock that is required for the specific reaction. However, it is not clear whether these reactions can contribute to the mitigation of carbon dioxide. In these reactions, we use the chemically active reagents having high chemical potentials such as epoxide, acetylene, diyne, diene, allene and amine, to yield oxygen-containing stable molecules such as carbonate, carbamate carboxylic acid, ester and lactone [5], where the changes of Gibbs free energy are usually negative and thus the reaction can proceed more favorable, but always with energy consumption. When we discuss the conversion of carbon dioxide in the viewpoint of environmental issue, it is very important that we avoid using the fossil energy. If we use the energy obtained from fossil fuels or the active chemicals derived from the fossil sources for the carbon dioxide conversion, it may be almost meaningless. Most desirable is a direct utilization of the solar energy, that is, photoenergy.

Table 3 Some electrochemical reactions with their corresponding reduction potential (E^0_{redox} vs. NHE at pH 7)

Entry	Product	Reaction			E^0_{redox}/V vs. NHE
1	Carbonate anion radical	$CO_2 + e^-$	→	$\bullet CO_2^-$	−1.90
2	Formic acid	$CO_2 + H^+ + 2\ e^-$	→	HCO_2^-	−0.49
3	Carbon monoxide	$CO_2 + 2\ H^+ + 2\ e^-$	→	$CO + H_2O$	−0.53
4	Formaldehyde	$CO_2 + 4\ H^+ + 4\ e^-$	→	$HCHO + H_2O$	−0.48
5	Hydrogen	$2\ H^+ + 2\ e^-$	→	H_2	−0.41
6	Methanol	$CO_2 + 6\ H^+ + 6\ e^-$	→	$CH_3OH + H_2O$	−0.38
7	Methane	$CO_2 + 8\ H^+ + 8\ e^-$	→	$CH_4 + 2\ H_2O$	−0.24
8	Oxygen	H_2O	→	$1/2\ O_2 + 2\ H^+ + 2\ e^-$	0.82

The values are from [1]

Direct decomposition to produce carbon monoxide and oxygen is thermodynamically difficult with a large positive change of the Gibbs free energy (Table 2, entry 17). Photoexcitation by a part of solar light can dissociate carbon dioxide into excited states of carbon monoxide and oxygen atom. However, the required light for the photoabsorption and photodissociation of carbon dioxide are VUV light. The threshold wavelength is around 90 nm (corresponding to 1,330 kJ mol^{-1}) [14]; neither UV nor visible light can excite carbon dioxide. Thus, the solar energy reaching the surface of the earth is not enough for photochemical dissociation. Therefore, in order to utilize available sunlight, we must apply suitable photocatalysis to activate the carbon dioxide.

2.3 *Redox of Carbon Dioxide*

When carbon dioxide is activated in a redox system, such as electrochemical, photochemical and photocatalytical systems, it can be reduced by receiving one or several electrons to become the corresponding reduced forms (Table 3) [1]. For example, a carbon dioxide molecule that receives one electron becomes a carbonate anion radical ($CO_2^{\bullet -}$) (Table 3, entry 1). It is notable that this reaction is highly endergonic because of the negative adiabatic electron affinity of CO_2 [1, 15]. This step may be the first step for the photoreduction of carbon dioxide. This suggests difficulty in the photoreduction of carbon dioxide, which is even more difficult than the hydrogen production from water (Table 3, entry 5). However, the experimental data revealed that adsorbed carbon dioxide was photocatalytically reduced to form the carbonate anion radical (CO_2^-), as mentioned later. Thus, it is suggested that the special interaction between the photocatalyst surface and carbon dioxide is very important. This suggests that the development of the structure and surface state of the semiconductor photocatalyst on the nanoscale will enable enhancement of their photocatalytic activity.

When the anion radical is further reduced by receiving multiple electrons with protons (or hydrogen radicals), a formate anion (HCO_2^-), carbon monoxide (CO), formaldehyde (HCHO), methanol (CH_3OH) and methane (CH_4) are obtained. We usually consider that carbon dioxide is reduced gradually in this order, since the production of each product requires two, four, six or eight electrons and protons. Thus, we often assume that formic acid, carbon monoxide and formaldehyde are the early products, while methanol and methane are subsequently obtained by deep reduction of these intermediates. However, in the sense of potential energy, the reactions producing methanol and methane can more easily proceed than the formation of other compounds and hydrogen. It has not yet been determined which proceeds more easily: consecutive photoreduction or complete reduction to methane.

To reduce carbon dioxide, we can use the electrochemical method by using electricity produced by solar cells. However, the use of the photoenergy for the chemical conversion by using photocatalysis is a more direct and effective way. Thus, in the following chapter, we focus on the photocatalytic conversion.

3 Photocatalytic Reactions and Photocatalysts

Here, introduced are the basis of photocatalysis in view of thermodynamics and two types of heterogeneous photocatalysts.

3.1 Photocatalytic Reactions

Photocatalytic reactions can promote thermodynamically unfavorable and difficult reactions at low temperature (e.g., room temperature). This brings some advantages, such as reduced energy consumption, less catalyst deactivation and more safety and stability of the reactor. Usually, the photoenergy that can be used for photocatalytic reactions, typically UV light, is larger than the activation energy for many kinds of chemical reactions. We can determine the energy of one photon in a certain wavelength light using Planck's constant. For example, photons with 300 nm wavelengths (UV light) have energies of 399 kJ mol^{-1}. Even though this energy is too low to directly break the C=O bond in carbon dioxide (estimated to be 799 kJ mol^{-1}) [16], it is expected that the use of a suitable photocatalyst would enable activation of even stable molecules. As mentioned above, the molecules adsorbed by the surface of a heterogeneous catalyst are in a certain stable state as shown in Fig. 2, which may provide an easier route for the reaction.

For example, the changes of Gibbs free energy for the reduction of carbon dioxide with water to produce methane is a largely positive value (801 kJ mol^{-1}), as mentioned above (Table 2, entry 16) and this value corresponds to the energy of the VUV light of about 150 nm in wavelength. Normally, in order to promote a reaction, activation energy (ΔE_a) is required and it must be larger than the change

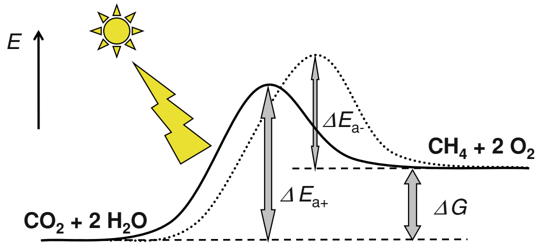


Fig. 4 Energetic scheme of photocatalytic reduction of carbon dioxide, where the photoenergy is partly converted to a higher chemical potential of products. ΔG is the change of Gibbs free energy, ΔE_{a+} is the activation energy for the forward reaction and ΔE_{a-} is that for the backward reaction

in Gibbs free energy (ΔG), as shown in Fig. 4. Thus, one may think that the direct promotion of this reaction should be impossible. However, in actuality, this reaction is reported to photocatalytically proceed on a suitable photocatalysts upon irradiation by UV light or even visible light, as discussed later. Thus, we believe that photocatalysts with the multiple photons of high energy can enable the thermodynamically unfavorable reactions ($\Delta G > 0$) to proceed photocatalytically under mild conditions (Table 3, entry 7).

In principle, a photocatalyst uses the photoenergy for the activation energy and the increment of the Gibbs free energy (ΔG^0). When the ΔG^0 is positive (uphill reaction), the photoenergy is converted to the higher chemical potential of products as shown in Fig. 3. Solar energy cannot be stored as it is. Thus, it is very valuable that we can store the photoenergy in chemicals, such as hydrogen, which can be stored and transferred easily. It opens the possibility to utilize the abundant solar energy conveniently and efficiently.

In the case of the thermal catalytic reaction, the reaction is finally controlled by thermodynamic equilibrium, where the forward and backward reactions can equally proceed. The thermodynamic values of the molecules and the reaction temperature determine the equilibrium composition. Since a usual catalyst promotes both the forward and backward reactions, the system will reach the equilibrium composition at the temperature. On the other hand, some photocatalytic reaction systems can break the thermodynamic equilibrium [9], although there are some exceptions. In many cases, the forward and backward reactions could be considered two different reactions in photocatalysis. The excited molecules and the excitation light wavelength are usually different from each other: e.g., the excited molecules are carbon dioxide or water in the forward reaction and methane or oxygen in the backward reaction. In addition, the reaction mechanism and the excitation state are also different (Fig. 4). Thus, it is possible to avoid the progression of the undesired backward reaction in some cases, meaning it is possible for the photocatalytic reaction to break the thermodynamic equilibrium.

All of these matters mentioned above are the benefits of the photocatalytic reactions. However, unfortunately, the yield obtained from the photocatalytic

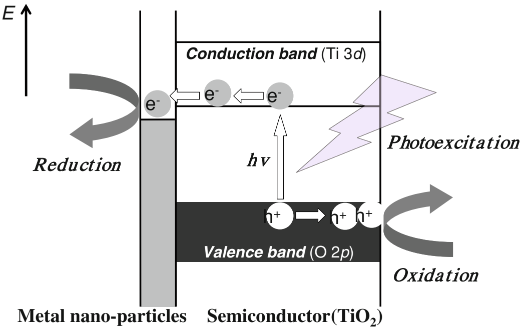


Fig. 5 Photoexcitation and successive photocatalytic reactions on a titanium dioxide semiconductor photocatalyst with a co-catalyst of metal nano-particles

reactions is still very low in many cases. Therefore, development of photocatalytic system is required at present.

3.2 *Types of Heterogeneous Photocatalysts*

The heterogeneous photocatalysts introduced in this chapter can be roughly divided into two groups: semiconductor photocatalysts and highly-dispersed photocatalysts.

Examples of the semiconductor photocatalysts include metal oxide, sulfide, nitride and oxynitride [11]; the most famous is TiO_2. Metal additives, such as Pt nanoparticles, are often employed to enhance the photocatalytic activity. When the TiO_2 photocatalyst absorbs incident light of larger energy than its band gap, photoexcitation occurs as electrons transfer from the valence band (O2p) to the conduction band (Ti 3d), as shown in Fig. 5, and the holes and electrons in the valence and conduction bands, respectively, migrate to the surface. When the metal nanoparticles are deposited on the surface, the excited electrons migrate to them. Holes and electrons promote oxidative and reductive reactions, respectively. This type of photocatalyst has a large and intense band in the UV spectrum. For example, the spectrum of TiO_2 is shown in Fig. 6a [17].

On the other hand, the highly-dispersed photocatalyst has unique structures and excitation states [18]. An example is monomers of titanium oxide supported by insulating materials, such as silica, where one titanium cation is coordinated by oxygen anions on the surface of the support. The photoexcitation takes place at the isolated titanium sites, which is often expressed as follows:

$$\mathrm{Ti}^{4+} - \mathrm{O}^{2-} + \text{ photon} \rightarrow \mathrm{Ti}^{3+} - \mathrm{O}^{-} \qquad (2)$$

Since the species exist on insulating materials, the excitation state is localized on the moiety. Compared to the semiconductor photocatalysts, this type photocatalyst shows a narrow and less intense absorption band in UV spectra. Figure 6b shows an example, the spectrum of silica-supported titanium oxide photocatalyst containing 0.3 mol% of Ti, Ti(0.3)/SiO_2 [17]. In the following chapter, another

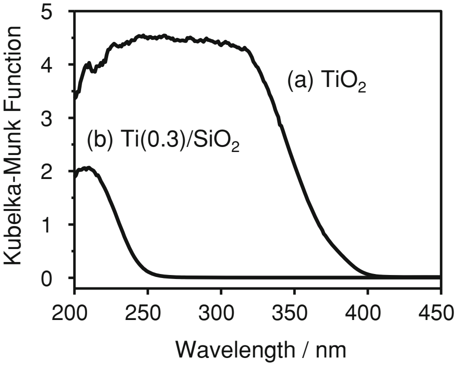


Fig. 6 Diffuse reflectance UV-visible spectra of (**a**) TiO_2 as a semiconductor photocatalyst and (**b**) $Ti(0.3)/SiO_2$ as a highly-dispersed photocatalyst

type of photoactive site, the surface carbonaceous species derived from adsorbed carbon dioxide, will be also described.

4 Photocatalytic Conversion of Carbon Dioxide

Photocatalytic conversion of carbon dioxide will be a most desirable method because this can mitigate the carbon dioxide as a greenhouse gas, utilize the carbon dioxide as a carbon source, and convert the solar energy to storable chemical energy. In addition, the processes consume no fossil energy in principal and are free from carbon dioxide emission. The photoenergy is high enough to activate even a stable molecule such as carbon dioxide on the surface, and the reactions have a potential to proceed with breaking the thermodynamics barrier. Thus, the photocatalytic conversion of carbon dioxide can proceed if the condition of the system including the photocatalyst is satisfied. So far, many researchers have examined many photocatalytic reaction systems in both homogeneous and heterogeneous systems. In this chapter, we will survey only the heterogeneous ones, and describe the brief history and the current situation of the photocatalytic conversion of carbon dioxide.

In this chapter, the photocatalytic reductions of carbon dioxide are classified into three groups by means of the reductant; i.e., water, hydrogen and methane as shown in Table 2.

4.1 Photocatalytic Reduction of Carbon Dioxide by Water

4.1.1 Semiconductor Photocatalysts

Since the discovery of the electrochemical photocatalysis on TiO_2 for water splitting by Fujishima and Honda in 1972 [19], this system has received much attention. This led to the revelation that the photocatalytic system can convert solar energy to hydrogen. Several years later, in 1978, although the reduction of carbon dioxide is a more difficult reaction as mentioned above, Hemminger et al. reported that methane was formed from gaseous water and carbon dioxide (ca. 4 kPa) through a photocatalytic reaction on $SrTiO_3$ single crystal in contact with Pt foil [20]. The reaction took place on a clean and reduced surface of $SrTiO_3$ (111) without any externally applied potential between the foil and the substrate, and in the absence of liquid electrolyte, upon the photoirradiation with light of greater energy than the band gap (from a 500 W high-pressure mercury lamp through an infrared filter consisting of $NiSO_4$ solution). The initial rate of methane formation corresponded to one molecule of methane for each 10^4 incident photons. Although the reaction stopped after 10 min due to poisoning, the total amount of the methane was 5–10 times larger than the number of the surface sites on the $SrTiO_3$ crystal, indicating the photocatalytic reaction proceeded. Other products were not observed. In the same year, Halmann reported that carbon dioxide in water was reduced to formic acid, formaldehyde and methanol on a p-type, Zn-doped GaP photocathode in an electrochemical photocell using a high-pressure mercury lamp [21]. The maximal solar energy conversion efficiencies for formaldehyde and methanol in this system were estimated to be 0.97 and 0.61%, respectively.

In 1979, Inoue et al. showed that carbon dioxide was photocatalytically converted to organic compounds, such as formic acid, formaldehyde, methanol and methane, in the presence of various semiconductor powders, like TiO_2, ZnO, CdS, GaP and SiC, suspended in water as photocatalysts [22]. Reduced compounds, such as formaldehyde and methanol, were mostly obtained on SiC, which has a conduction band with a highly negative potential. A correlation between the conduction band energy and the yield of methanol was found: the yields of methanol increased as the conduction band became more negative with respect to the redox potential of H_2CO_3/CH_3OH (Table 3, entry 6), while methanol was not produced on WO_3 (with a more positive conduction band than the redox potential of H_2CO_3/CH_3OH). The estimated quantum yields of production for photocatalytic reduction of carbon dioxide were ca. 5.0×10^{-4} for formaldehyde and 1.9×10^{-4} for methanol with a TiO_2 photocatalyst, and 4.5×10^{-3} for methanol on SiC, measured against the absorbable incident photons. These photocatalytic systems employing semiconductor photocatalysts have also been tested under sunlight irradiation for utilization of solar energy, and the formation of formic acid, formaldehyde, methanol, methane, acetaldehyde and ethanol were confirmed [23–25].

Metal-loaded semiconductors, such as Pt/TiO_2, function as micro-photoelectrochemical cells [26]. For example, Pt-loaded TiO_2 was found to decompose water to hydrogen and oxygen photocatalytically, in 1980 [27]. Then, the Pt/TiO_2 photocatalysts were examined as one of the typical heterogeneous photocatalysts for the reduction of carbon dioxide or carbonate. In 1983, Chandrasekaran and Thomas reported that photoirradiation of an aqueous deaerated sodium carbonate solution containing Pt/TiO_2 gave rise to a small yield of oxygen and formaldehyde in the solution [28]. However, extended irradiation led to the loss of formaldehyde. In this work, phthalocyanine-coated TiO_2 was also tested and gave the similar results, where phthalocyanine absorbed light and transferred an electron to the conduction band of TiO_2. In 1984, Halmann et al. found that RuO_2-loaded TiO_2 enhanced the photocatalytic reduction of carbon dioxide to formic acid, formaldehyde and methanol, where formic acid was the major product [29]. Tennakone examined several kinds of metals (Pt, Au, Ag, Co, Pb, Hg) as the additive on TiO_2 [30] and found that Hg/TiO_2 provided the highest yield of formaldehyde from the water containing CO_2 upon photoirradiation from a 200 W medium-pressure Hg lamp. Raphael and Malati reported that Pt/TiO_2 in aqueous sodium carbonate gave methanol, carbon, formaldehyde and formic acid [31]. Hirano et al. [32] reported that the coexistence of suspended TiO_2 and Cu metal powders promoted the photocatalytic reduction of carbon dioxide to yield methanol, formaldehyde and a trace amount of formic acid and carbon monoxide. Since Cu(II) ions were also observed in this system, the copper metal particles do not only offer the reaction sites for photoreduction of carbon dioxide with the excited electrons but also act as a sacrificial reagent to react with positive holes in the valence band. In this work, they mentioned that the presence of $KHCO_3$ in the solution enhanced the photocatalytic yield of methanol. In 1993, Ishitani et al. investigated the activity of various metal-deposited TiO_2 photocatalysts [33]. Metal particles of 2 wt%, such as Pd, Rh, Pt, Au, Cu and Ru, were loaded on TiO_2 by the photochemical deposition method and examined for the photocatalytic reduction of carbon dioxide in water. Although only a small quantity of methane was produced by using non-deposited TiO_2, the deposition of Pd, Rh, Pt or Au on TiO_2 greatly enhanced the methane formation. Among them, Pd/TiO_2 exhibited the highest activity. The second one was Rh/TiO_2. They also confirmed that when $^{13}CO_2$ was employed instead of $^{12}CO_2$, $^{13}CH_4$ was obtained, while $^{13}CH_4$ was not detected under $^{12}CO_2$, which clearly evidenced the photocatalytic reduction of carbon dioxide to methane. Solymosi and Tombácz reported that Rh-loading TiO_2 and Rh-loading W-doped TiO_2 photocatalysts provided formic acid, formaldehyde and methanol [34]. Reductive pretreatment for the latter photocatalyst offered high conversion and high selectivity to methanol.

Cu/TiO_2 has been investigated by several groups. In 1994, Yamashita et al. showed that anatase TiO_2, which has a large band gap and numerous hydroxyl groups, showed high efficiency for photocatalytic formation of methane while Cu-loaded TiO_2 showed additional formation of methanol [35]. Further, they observed photogenerated Ti^{3+}, H and CH_3 radicals as reactive intermediates by ESR at 77 K. Tseng et al. also reported that methanol was obtained on Cu/TiO_2, where TiO_2 was prepared by a sol-gel method [36, 37]. They found that the addition of NaOH increased the methanol yield, suggesting that the basic solution dissolved a larger amount of carbon dioxide than pure water and the hydroxy anions in the solution react with holes to accelerate the photocatalytic reaction. Wu et al. showed that the most active Cu species on TiO_2 surface were Cu_2O clusters and they played an important role for the formation of methanol in a study using an optical fiber photoreactor [38]. Nguyen and Wu reported that Fe and Cu co-loaded TiO_2 produced ethylene and methane and trace amount of ethane and methanol [39]. This catalyst exhibited higher activity for ethylene production than the catalysts loaded with either Cu or Fe, indicating a synergistic effect for photoreduction of carbon dioxide with water to ethylene. In this condition, Cu/TiO_2 produced methane more favorably than ethylene.

In many of the reports mentioned above, the formation of molecular oxygen was scarcely mentioned in the photocatalytic reduction of carbon dioxide with water, although oxygen should be formed, as indicated in Table 2, entries 12–16. In some papers, the formation of molecular oxygen was confirmed. For example, an oxygen sensor detected the molecular oxygen dissolved in the solution, which was produced over the Cu/TiO_2 photocatalyst, though the amount was less than expected from the stoichiometric ratio [36]. In the case of water splitting, non-stoichiometric evolution of oxygen has also been frequently observed and ascribed to the photoadsorption of O_2 or O_2^- onto semiconductor particles [40–42] or the formation of surface ${O_2}^{2-}$ peroxide species [40, 41]. Photoadsorption of O_2 on highly hydrated TiO_2 surface was also directly observed [43, 44]. A H_2/O_2 ratio greater than stoichiometric is observed only when the photocatalytic reaction is slow, and this is attributed to the adsorption of O_2 on TiO_2; if the reaction is fast, the reaction stoichiometry is not influenced by the photoadsorption [42]. In the system of the photocatalytic reduction of carbon dioxide with water, the photoadsorption of oxygen was mentioned as a possible reason for the difficulty in detecting oxygen [35], implying that the reaction rate was low in these reaction systems. The decreasing rate for products evolution might be due to this photoadsorption.

In 1993, Sayama and Arakawa discovered that the photocatalytic decomposition of pure water proceeded over non-loaded ZrO_2 powder, without any loaded metals upon photoirradiation in a closed gas-circulating system with an inner irradiation quarts reactor equipped with a 400 W high-pressure Hg lamp, at an almost constant rate for long period ($\sim$20 h) [45]. Moreover, in the presence of $NaHCO_3$ in water, H_2, O_2 and CO were constantly produced at rates of 309, 167 and 3 μmol/h, respectively, over the ZrO_2 photocatalyst, and 19, 11 and 2.5 μmol/h, respectively, over Cu-loaded ZrO_2. These results suggest that photocatalytic water decomposition (Table 2, entry 19, $2H_2O(l) \rightarrow 2H_2 + O_2, \Delta G^0 = 474\,\text{kJ mol}^{-1}$) and photocatalytic reduction of carbon dioxide (in water HCO_3^-) to form CO, H_2 and O_2 (Table 2, entry 13, $CO_2 + H_2O(l) \rightarrow CO + H_2 + O_2, \Delta G^0 = 494\,\text{kJ mol}^{-1}$) can proceed, although photocatalytically produced hydrogen might reduce the carbon dioxide, yielding CO (Table 2, entry 1, $CO_2 + H_2 \rightarrow CO + H_2O(l)$, $\Delta G^0 = 20\,\text{kJ mol}^{-1}$). Since the ZrO_2 semiconductor has a highly negative flat-band potential and a wide band gap, it can promote both photocatalytic water decomposition and the photoreduction of carbon dioxide without loaded metals. In this study, some kinds of loaded metal and metal oxides, such as Pt, RuO_2, Au, and Cu, were examined, and it was found that the loaded co-catalyst change the reaction selectivity.

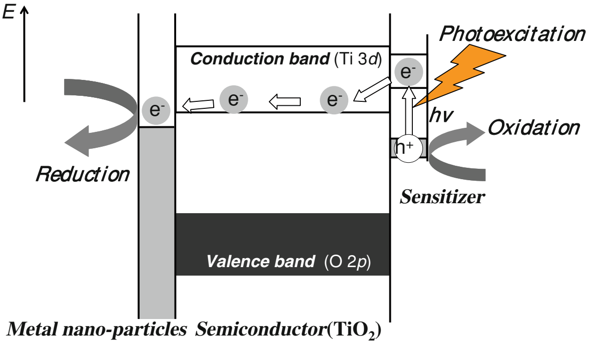
To reveal the fundamental aspects, several studies have been carried out on TiO_2 photocatalysts with and without loaded metals. High-pressure CO_2 (1 MPa) was effective for the production of methanol as a major product on a TiO_2

photocatalyst in pure water, and higher pressure (2.5 MPa) was effective for gaseous minor products, such as methane, ethane and ethene on Cu-loaded TiO_2 and pure TiO_2. While in the NaOH solution, the higher pressure gave high yields of acetaldehyde, ethanol and methanol [46, 47]. Under a high-pressure of carbon dioxide liquid (13.8 MPa), bare TiO_2 homogeneously dispersed on Nafion® films produced formic acid and methanol as major products and acetic acid as a minor product [48], while Ag-loaded TiO_2 onto Nafion® films produced methanol as a major product and formic acid as a minor one [49]. The effect of the reaction temperature was varied between 298 and 473 K on TiO_2 and the reaction rate increased with increasing temperature [50], where the activation energy (E_a) for the formation of methane was calculated to be ca. $2\,\mathrm{kJ\ mol^{-1}}$ around room temperature and almost zero at 473 K. The product desorption was suggested to be the rate limitation step. In supercritical carbon dioxide (8 MPa, 308–323 K) with a small amount of water, TiO_2, and a mixture of TiO_2 and metal Cu photocatalytically converted carbon dioxide to formic acid and methanol [51]. During photoirradiation of TiO_2 in liquid-phase carbon dioxide without any proton source was found to produce carbonate anion radicals, and after pressure reduction the addition of water resulted in the formation of formic acid, suggesting that the photoreduction of carbon dioxide with water to produce formic acid proceed in two steps, the photoreduction of carbon dioxide to form the radical intermediates and the successive protonation [52]. Yahaya et al. reported the effect of the photoirradiation time by using high-intensity light of 355 nm wavelength from a Nd:YAG laser [53]. The amount of methanol produced from carbon dioxide increased with the irradiation time on TiO_2 and ZnO and then decreased, while hydrogen was continuously produced. From these results, they discussed reaction schemes including consecutive oxidation of methanol to formaldehyde and carbon monoxide with formation of hydrogen.

The effect of the particle size also has been studied. Kočí et al. investigated the effect of the particle size of anatase TiO_2 in the range from 4.5 to 29 nm crystallites, determined by X-ray diffraction [54]. Hydrogen, methane, methanol and CO were obtained, and the optimum particle size for the production of both methane and methanol was 14 nm, which would result from some competing effects such as specific surface area, photoexcited carrier dynamics and light absorption efficiency. Yang et al. studied that the size effect by using the TiO_2 nanocrystallites supported on SAB-15 mesoporous silica [55], where the size was changed from 1.4 to 8.3 nm by changing the loading amount. The optimum amount of TiO_2 loading for methanol production was 45 wt%, corresponding to the 5.5 nm crystallites of TiO_2. Quantum size effects of the metal sulfide photocatalysts in the photocatalytic reduction of carbon dioxide using sacrificial electron donors were reviewed by Yoneyama [56].

The structure of the TiO_2 is also important. A study on the single crystals of $TiO_2(100)$ and $TiO_2(110)$ showed that the former was more active for the formation of methane and methanol than the latter [57]. The photocatalytic activity of TiO_2 nanotubes (20 nm in diameter × 300 nm in length × 5 nm in thickness) was compared to that of TiO_2 nanoparticles (P-25, Degussa, 20–50 nm in size

Fig. 7 The mechanism of photosensitization with dye or quantum dot upon visible light irradiation



determined by HRTEM), both of which were loaded with Pt. For the reaction between gaseous carbon dioxide and water vapor [58], the Pt-loaded TiO_2 nanotubes exhibited a higher activity in forming methane than the nanoparticles, especially under a high H_2O/CO_2 ratio.

In recent years, many researchers have developed photocatalysts that can function upon irradiation of visible light, since it is the main component of solar light. One strategy is the application of the dye-sensitized semiconductor photocatalysts, which is conceptually depicted in Fig. 7. For example, the addition of tris(2,2'-bipyridyl) Ru(II) chloride, perylene diimide derivatives [59] and Ru(II) (2,2'-bipyridyl-4,4'-dicarboxylate)$_2$-$(NCS)_2$ (N3 dye) [60] as visible light sensitizers on metal loaded TiO_2, such as Pt/TiO_2 and Cu-Fe/TiO_2, offered the activity to yield methane in visible light. In these systems, the photoexcited electron generated on the sensitizer is transferred to the conduction band of the semiconductor and then to the metal co-catalyst. The electron leads the reduction of carbon dioxide on the metal. In these examples, carbon dioxide was reduced to form methane. However, at the same time, the hole remains on the sensitizer. When the holes cannot be consumed, the photocatalytic reaction stops and the dye sensitizer is oxidized. This means that some sacrificial reagent is required to consume the holes. Like dyes, semiconductors can also serve this function. Recently, Wang et al. applied CdSe quantum dots of 2.5 nm in size as a photosensitizer to Pt/TiO_2 photocatalyst [61]. Although the conduction band of bulk CdSe is only slightly above that of TiO_2, quantum confinement shifts the conduction band of CdSe quantum dots to higher energies, which enables charge injection into the TiO_2. Then, the electron on the Pt/TiO_2 reduces carbon dioxide. On this CdSe/Pt/TiO_2 heterostructured photocatalyst, carbon dioxide was reduced to give methane as a major product and methanol, hydrogen and CO as minor products. However, the consumption of hole generated on the quantum dots was still a problem, which led to the oxidation of the quantum dots, decreasing the photocatalytic activity during the photoreaction.

As another strategy to design visible light photocatalysts, many materials have been examined and many viable semiconductor photocatalysts have been found, especially in the field of photocatalytic water splitting [11]. Also in the field of

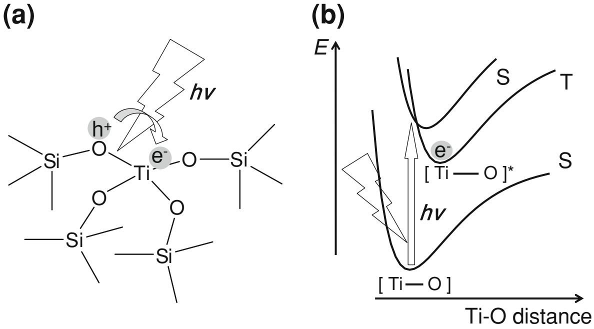


Fig. 8 Photoexcitation of highly-dispersed titanium species in silica matrix: **a** a model of the photoactive tetrahedral sites on silica, and **b** a schematic model for localized photoexcitation at Ti-O moiety

photocatalytic reduction of carbon dioxide, many photocatalysts have been found. $CaFe_2O_4$, a p-type semiconductor with a small band gap (1.9 eV) was found to produce formaldehyde and methanol under UV light, but the activity was not enough to perform the photoreduction under visible light irradiation without a sacrificial reducing agent [62]. In 2007, Pan and Chen reported that $NiO/InTaO_4$ photocatalysts produce methanol upon visible light irradiation [63]. Jia et al. reported that C and Fe co-doped $LaCoO_3$ exhibited photocatalytic activity to yield formaldehyde and formic acid [64]. Kudo and co-workers developed photocatalysts, such as $Ag/NaTaO_3$:Ba and $Ag/BaLa_4Ti_4O_{15}$, which produced H_2, O_2 and CO from an aqueous medium with a carbon dioxide flow system [65, 66]. These photocatalysts exhibited a high production rate for CO (38 and 25 μmol/h, respectively). These semiconductors were previously reported as active photocatalysts for water splitting [67, 68] and the Ag co-catalyst was found to be suitable co-catalyst for these photocatalysts to reduce carbon dioxide. Liu et al. found that a $BiVO_4$ photocatalyst reduced carbon dioxide with water to yield ethanol and O_2 under visible light irradiation from a 300 W xenon lamp [69]. When the irradiated light was extended to the UV region, the rate of ethanol production increased on the monoclinic $BiVO_4$ photocatalyst. The intensity of the light plays an important role in ethanol formation; both methanol and ethanol were formed when a 36 W fluorescent lamp was used.

4.1.2 Highly-Dispersed Photocatalysts

For the photocatalytic reduction of carbon dioxide with water, highly-dispersed photocatalysts (Fig. 8) have been also developed. In 1992, Anpo and Chiba prepared highly-dispersed titanium oxide anchored onto porous Vycor® glass through a facile reaction between the surface hydroxy groups and $TiCl_4$ [70]. This anchored catalyst showed photocatalytic activity for the reduction of carbon dioxide with water to yield methane, methanol and carbon monoxide. A small amount of O_2 was also detected. An ESR study revealed the formation of C radicals and H atoms, as well as Ti^{3+} ions. Thus, the highly-dispersed titanium oxide species was photoexcited to a charge-transfer excited state, a trapped hole center (O^-) paired with an electron center (Ti^{3+}), i.e., $[Ti^{3+}–O^-]^*$, which activated the carbon dioxide to produce radicals. When the reaction system involved CO_2 and D_2O in place of H_2O, the major composition of photoformed methane was CD_4, indicating that the water functioned as the reductant.

When titanium oxide species are well-dispersed on silica materials, such as amorphous silica, mesoporous silica and zeolites, the highly-dispersed species become tetrahedral [18]. Mesoporous silica materials containing Ti, Ti-MCM-41 and Ti-MCM-48 were hydrothermally synthesized and applied to the photocatalytic reduction of carbon dioxide with water [71]. Although it is difficult to compare the photocatalytic performance of the highly-dispersed titanium oxide catalysts with bulk powdered TiO_2, the product selectivity was clearly different, i.e., while the bulk material produced predominantly methane, the highly dispersed one produced methanol in addition to methane. The Ti-MCM-41 showed similar activity to TS-1, which is a famous MFI-type zeolite containing Ti, while the Ti-MCM-48 showed much higher activity than either TS-1 or Ti-MCM-41, and similar selectivity to them. TiO_2-loaded zeolites and Ti ion-exchanged zeolites were prepared by the impregnation and ion-exchange methods, respectively, and examined for the photoreduction of carbon dioxide with water [72]. The sample containing 10 wt% TiO_2 showed high selectivity to methane, similar to bulk anatase, while the sample of 1 wt% TiO_2 gave methanol as minor product in addition to methane. The Ti ion-exchanged MFI-zeolite produced methanol and methane with comparable rates. These results suggest that the highly-dispersed titanium oxide species are more suitable for methanol formation than bulk TiO_2. Furthermore, the addition of Pt to the Ti ion-exchanged zeolite resulted in a high methane yield with high selectivity. Although the structure and size of the platinum species and the junction between Pt species and Ti species were still unclear, the Pt species would promote the charge separation, increasing the methane yield.

Ikeue et al. prepared two types of Ti-β zeolites by a hydrothermal synthesis method under different conditions using OH^- and F^- as anions of the structure-directing agents, referred to as Ti-β(OH) and Ti-β(F), respectively [73]. The titanium species in both samples were in a highly-dispersed, tetrahedral coordination state in the zeolite frameworks. The Ti-β(OH) was hydrophilic, while the Ti-β(F) was hydrophobic. It was confirmed by XANES that the highly-dispersed Ti species in Ti-β(OH) interacted with water molecules. Both samples exhibited photocatalytic activity in the photocatalytic reduction of carbon dioxide with water to yield methane, methanol, and trace amounts of CO, C_2H_4 and O_2. The Ti-β(OH) exhibited a much higher activity and higher selectivity to methane than TS-1, and Ti-β(F) exhibited a lower activity and higher selectivity to methanol than TS-1. This means that hydrophilic behavior is important to enhancing photocatalytic activity in the reduction of carbon dioxide with water to methane, while hydrophobic behavior is suitable for methanol production. This is consistent with another report: among other type of Ti-containing porous silica films prepared by solvent evaporation, the more hydrophobic sample with small amount of surface hydroxy groups exhibited higher methanol selectivity [74].

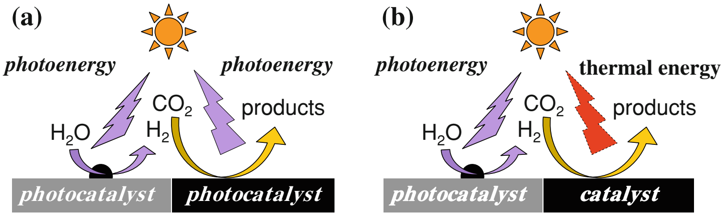


Fig. 9 The reduction of carbon dioxide with water by hybrid photocatalysts in which a photocatalyst for water splitting is combined with (**a**) a photocatalyst or (**b**) a catalyst for the reduction of carbon dioxide with hydrogen

On the other hand, Frei et al. found the formation of CO and O_2 in the photocatalytic reduction of carbon dioxide with water over Ti-MCM-41 upon photoirradiation by 266 nm light from a Nd:YAG laser by using in situ FT-IR spectroscopy and mass spectrometric analysis [75]. They concluded that a single UV photon induced the splitting of CO_2 with H_2O to CO and a surface OH radical, i.e., $CO_2 + H_2O \rightarrow CO + 2\ OH \rightarrow CO + 1/2\ O_2 + H_2O$. They also observed that this type of photoreduction of CO_2 could be promoted by a metal to metal charge transfer (MMCT) at Zr–O-Cu(I) moiety formed on MCM-41, Zr(IV)-O-Cu(I) →[Zr(III)-O-Cu(II)]* [76], although a MMCT on Ti–O-Cu(I) moiety could not induce the reaction.

4.2 Photocatalytic Reduction of Carbon Dioxide by Hydrogen

The reduction of carbon dioxide using hydrogen seems unattractive because of economics, i.e., hydrogen is relatively expensive. However, if we can use hydrogen as a reductant, the carbon dioxide can be converted to other products more easily, since the reduction with hydrogen is less unfavorable thermodynamically than the reduction with water, as shown in Table 2. Since many types of highly active photocatalysts have been developed for water splitting to produce solar hydrogen [11], we can use the solar hydrogen as the reductant for the reduction of carbon dioxide (Fig. 9a). Thus, we should also consider studying the photocatalytic reduction of carbon dioxide with hydrogen.

In 1982, Thampi et al. [77] found that methanation of carbon dioxide, the reduction of carbon dioxide by hydrogen to produce methane and water (Table 2, entry 5), was promoted by highly-dispersed Ru/RuOx loaded on TiO_2 at room temperature even in the dark, and furthermore the reaction rate was greatly enhanced by photoirradiation. The reaction proceeded photocatalytically and the selectivity was very high (>99%). They proposed that (i) the carbon dioxide was first reduced by 4 electrons on the Ru species to form Ru–C and active oxygen species, such as O^{2-}, (ii) hydrogen was oxidized by holes to form protons and react with the active oxygen species to form water, and (iii) the Ru–C species also

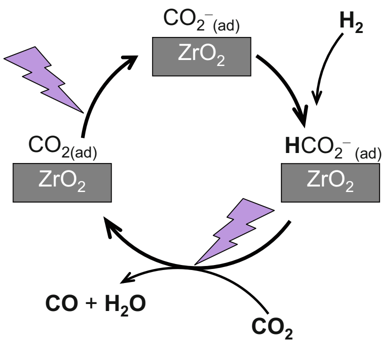


Fig. 10 Proposed mechanism for photocatalytic reduction of carbon dioxide by hydrogen over ZrO_2

reacts with hydrogen to yield methane and regenerate the Ru. Since this reaction is not an uphill reaction (Table 2, entry 5), the suitable catalyst can promote the reaction catalytically, even at room temperature in the dark. However, combined with water splitting, considering utilization of the solar hydrogen (Table 2, entry 18), the whole reaction becomes thermodynamically unfavorable (Table 2, entry 16). In 1999, Kohno et al. reported that the reduction of CO_2 with hydrogen to form CO or CH_4 proceeded on Rh-loaded TiO_2 in the dark, but was enhanced upon photoirradiation [78]. In this system, the metallic Rh species showed low activity but high selectivity to CH_4, while the mixture of Rh in metallic and oxidized states showed high activity and high selectivity to CO. Furthermore, it was found that the photocatalytic activity decreased with a decrease of the particle size of the Rh species during the photoreaction [79].

As mentioned above, the ZrO_2 photocatalyst without any co-catalyst promoted the photoreduction of carbon dioxide with water, where the carbon dioxide was actually aqueous carbonate [45]. The products were hydrogen, oxygen and carbon monoxide. Since the product distribution was not consistent with the equation shown in Table 2, entry 13, it was clear that water splitting also occurred. Thus, in this system, there is a possibility that the carbon oxide is reduced photocatalytically by hydrogen or hydrogen radical species in water produced through photocatalytic water splitting. In 1997, Kohno et al. [80] reported that gaseous carbon dioxide was reduced to carbon monoxide by hydrogen on a ZrO_2 photocatalyst without loading a co-catalyst in a closed static system with light of sub-300 nm wavelength from a 500 W ultrahigh-pressure Hg lamp. Among several samples, including TiO_2, ZrO_2, V_2O_5, Nb_2O_5, Ta_2O_5, WO_3 and ZnO, only ZrO_2 was active for this reaction. FT-IR spectroscopy clarified that the surface formate species existed as surface intermediates [81]. On ZrO_2, it was revealed that the photocatalytic reaction consisted of the following three steps, as shown in Fig. 10; (i) adsorbed carbon dioxide or carbonate was photoexcited and received an electron from ZrO_2 to become an adsorbed $\bullet CO_2^-$ anion radical [82], (ii) the anion radical reacted with hydrogen to form an adsorbed formate, even in the dark, and (iii) upon photoirradiation the formate species reduced the carbon dioxide molecule to yield carbon monoxide and water, where the surface formate species functioned as

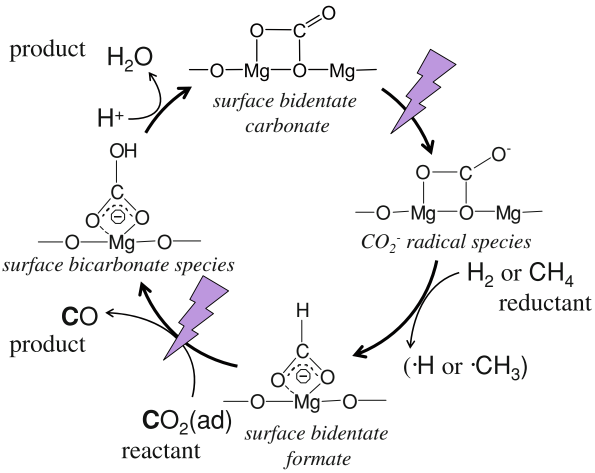


Fig. 11 A main mechanism of photocatalytic reduction of carbon dioxide on MgO by hydrogen or methane as a reductant

a reductant to become adsorbed carbon dioxide. For the photocatalytic reduction of carbon dioxide, at least two photons were required at the first and the third steps. ZrO_2 is a semiconductor with a wide band gap (5.0 eV) and can be excited by the light with wavelength shorter than 250 nm. However, the reaction proceeded even under light with wavelengths longer than 290 nm and the surface formate was formed even under the light with wavelengths longer than 330 nm. The photoluminescence spectroscopy revealed that adsorbed carbon dioxide species (or carbonate) can absorb the light above 300 nm in wavelength [81]. Therefore, the photoactive species is not the bulk ZrO_2, but the surface photoactive species. This means that a new type of photocatalytic reduction system was found: the adsorbed carbon dioxide species act as the photocatalytic active species [83].

Since it is known that the CO_2^- anion radical can form on MgO [84], the photocatalytic reduction of carbon dioxide by hydrogen was examined and discovered on MgO [85]. Teramura et al. revealed that the reaction proceeded by a similar mechanism to that on ZrO_2 (Fig. 11) [86]. On the surface of MgO, the carbon dioxide was adsorbed in the form of the surface bidentate carbonate and can be photoactivated to form a surface CO_2^- anion radical. This can be reduced by hydrogen to form the surface bidentate formate species, which can reduce another carbon dioxide to carbon monoxide as an actual reductant upon photoirradiation. These surface species can act as photocatalytically active species. These studies confirmed the new type of photocatalytic reduction of carbon dioxide that occurred in the manner of the surface photochemistry on the metal oxide of an insulator, rather than a semiconductor. Hydrogen is used as a reductant of the surface species in the photocatalytic cycle. As mentioned later, methane can similarly act as a reductant of the surface species on both MgO [86] and ZrO_2 [83, 87, 88].

Lo et al. [89] confirmed that the photoreduction of carbon dioxide over TiO_2 was enhanced using a gaseous mixture of hydrogen and water vapor to yield methane as a major product, compared with the using solely hydrogen or water.

On the other hand, the photoreduction of carbon dioxide over ZrO_2 with hydrogen gave a higher yield of carbon monoxide compared with using water or the mixture of hydrogen and water vapor, supporting the results presented above.

Teramura et al. [90] reported that Ga_2O_3 promoted the photoreduction of carbon dioxide by hydrogen to yield carbon monoxide selectively around room temperature. The conversion of carbon dioxide was approximately 3% using β-Ga_2O_3 calcined at 1,073 K for 3 h. Both carbon dioxide and hydrogen can be chemisorbed on Ga_2O_3 [91, 92] and the highest yield was obtained when the amount of adsorbed hydrogen reached saturation. Since the effect of the introduced amount of hydrogen was not observed on MgO, the photoreduction mechanism on Ga_2O_3 is expected to be different from that over basic metal oxide such as MgO and ZrO_2. The photoreaction on Ga_2O_3 was proposed to proceed between the adsorbed substrates according to the Langmuir–Hinshelwood mechanism.

Guan et al. [93] successfully demonstrated that the hydrogen produced through photocatalytic water splitting could be used for the reduction of carbon dioxide by a hybrid catalyst, in which a Pt-loaded $K_2Ti_6O_{13}$ photocatalyst ($Pt/K_2Ti_6O_{13}$) was combined with an Fe-based catalyst supported on a dealuminated Y-type zeolite (Fe-Cu-K/DAY) under concentrated sunlight in water. Upon photoirradiation from an Hg lamp around room temperature, the $Pt/K_2Ti_6O_{13}$ photocatalyst promoted the water splitting to produce hydrogen and somewhat reduced carbon dioxide to organic compounds though the Fe-Cu-K/DAY catalyst did not work. On the other hand, in concentrated sunlight, since the temperature of the system reached about 600 K, the hybrid catalyst produced hydrogen, formic acid, methanol, ethanol and methane, where the $Pt/K_2Ti_6O_{13}$ photocatalyst promoted the water splitting and the Fe-Cu-K/DAY catalyzed the reduction of carbon dioxide with produced hydrogen. The sunlight provided both the excitation light for the photocatalyst to produce hydrogen and the thermal energy to enhance the catalysis for the reduction of carbon dioxide (Fig. 9b). This study shows a new strategy to utilize the sunlight as both photoenergy and thermal energy.

4.3 Photocatalytic Reduction of Carbon Dioxide by Methane

Methane might be a good candidate as a reductant for the conversion of carbon dioxide [9]. Methane is known as an abundant underground resource (a fossil fuel), and also a renewable resource that can be naturally generated from ecosystems and artificially produced from biomass. Moreover, since methane can act as a greenhouse gas with an even higher global warming potential (GWP) than carbon dioxide [94], it is desirable to reduce its release into the environment and to utilize and convert it to more useful compounds. The reaction between methane and carbon dioxide can be catalyzed at high temperature to form syngas (carbon monoxide and hydrogen). This reaction is called a “dry reforming of methane” (DRM) or “CO_2 reforming of methane”, as shown in Table 2, entry 7. A short history of the DRM can be found in literature [95]. The DRM is a thermodynamically unfavorable reaction and only can proceed at a high temperature, typically over 1,000 K, even when using catalysts. However, the photocatalytic reaction between methane and carbon dioxide can proceed at room temperature or mild temperatures.

Photocatalytic reduction of carbon dioxide with methane was found to proceed over ZrO_2 [83, 87, 88] and MgO [86] at room temperature. After the photoreaction, carbon monoxide and hydrogen were detected, although the amount of hydrogen was very low compared to the amount of carbon monoxide. It was confirmed that carbon monoxide was produced from carbon dioxide, not from methane. Methane acted as a reductant of the surface carbonate anion radical species to form the surface bidentate formate, as shown in Fig. 11. In these systems, the photoexcitation of adsorbed carbon dioxide forms a surface carbonate anion radical, followed by the reduction with methane to form the surface bidentate formate, and another carbon dioxide is photocatalytically reduced by the surface bidentate formate to yield carbon monoxide.

A Cu/CdS-TiO_2/SiO_2 photocatalyst was reported to yield acetone as the major product (Table 2, entry 8) with a high selectivity in the photocatalytic conversion of carbon dioxide with methane under UV irradiation at 393 K [96], where the selectivity for acetone was 92% at a 0.74% conversion of carbon dioxide. Other products, such as ethane and CO were also detected with selectivities of 3.1% and 4.6%, respectively. At a lower temperature (353 K) only ethane and CO were produced with selectivities of 47% and 53%, respectively. However, the conversion of methane and carbon dioxide ceased after about 2 h due to the photocorrosion of CdS by the TiO_2.

Recently, we found the photocatalytic reduction of carbon dioxide by methane to produce CO and hydrogen, i.e., photocatalytic DRM (Table 2, entry 7) by using Ga_2O_3 under photoirradiation at 473 K in a closed reactor [97]. As a side reaction, photocatalytic non-oxidative coupling of methane [98] to yield hydrocarbons (mainly ethane) was also observed. Since only a trace amount of carbon monoxide was obtained at room temperature, it was clear that thermal energy is required to yield the desired products. The production of carbon monoxide increased with increasing reaction temperature. The thermal activation energy (E_a) for carbon monoxide formation was ca. 10 kJ mol^{-1} at 473–673 K and ca. 60 kJ mol^{-1} at 673–873 K, which were much lower than that obtained from the catalytic thermal DRM on this Ga_2O_3 sample without UV irradiation ($E_a = 110$ kJ mol^{-1} at 773–973 K). This mild thermal activation energy at 473–673 K can be used for a mild activation step in the photocatalytic reaction mechanism, such as product desorption or electron migration from the bulk to the surface of Ga_2O_3. As mentioned above, sunlight can provide both the photoenergy and thermal energy and, therefore, the thermally assisted photocatalytic reaction at a moderate or high temperature is also possible. The methane conversion at 473 K was 0.27% after 3 h, which was superior to the equilibrium conversion (0.21%). This means that the photocatalysis can promote the difficult reaction under mild condition beyond the thermodynamic equilibrium conversion.

In this system, both carbon dioxide and hydrogen existed as reactant and product, respectively, and a Ga_2O_3 photocatalyst was reported to promote the photocatalytic reduction of carbon dioxide by hydrogen to yield carbon monoxide [90]. Quite recently, we prepared a series of Ga_2O_3 photocatalysts by homogeneous precipitation and examined the photocatalytic reduction of carbon dioxide with methane at 523 K [99]. We obtained Ga_2O_3 samples consisting of homogeneous granules with a short, rod-like morphology with similar size (300–500 nm in diameter and 1–2 μm in length), and calcination at various temperatures provided two polymorphs with various specific surface areas and crystallites sizes. We found that the Ga_2O_3 photocatalysts of low specific surface area selectively promoted reduction of carbon dioxide by methane at moderate temperature to yield carbon monoxide and hydrogen, while those of high specific surface area additionally promoted consecutive photocatalytic reduction of carbon dioxide by produced hydrogen to provide carbon monoxide selectively. The surface sites of Ga_2O_3, such as low coordination sites or surface hydroxy groups, would preferably catalyze the photoreduction of carbon dioxide by hydrogen. This demonstrates that the structure of the semiconductor photocatalysts, including crystallites size (or the specific surface area) and the surface sites, is very important for controlling the photocatalytic reactions. Further improvement is expected with the aid of recent developments in the nanotechnology.

5 Conclusion and Perspective

In this chapter, we reviewed the bases and history of the photocatalytic reduction of carbon dioxide by heterogeneous photocatalysts with three kinds of reductants: water, hydrogen and methane. The most preferable way to reduce carbon dioxide uses only water and sunlight. The investigations of using of hydrogen or methane accelerate the development of photocatalytic systems for carbon dioxide conversion. The idea of using the hydrogen generated by photocatalytic water splitting for the reduction of carbon dioxide is one of the realistic ways. The utilization of biomethane or other biomass is also meaningful.

Now, we note that, among the investigations introduced in this chapter, many photocatalysts have been prepared by conventional methods. On the other hand, we are now developing nanomaterial syntheses that can produce finely designed materials. As shown, the structure of the photocatalysts is very important, e.g., the crystallites size, specific surface area, surface structure and electronic band structure of the semiconductors. The structure and physicochemical properties of the co-catalysts and the local structure of the dispersed photoactive sites are also important. It is expected that the nanotechnology will enable us to design the structure and function of these photocatalysts with precise control, which will provide effective photocatalysts. The conversion of carbon dioxide using solar energy is fundamentally important for our sustainable future. We hope that the development of the photocatalysis with nanomanufacturing realizes the reduction of carbon dioxide with solar energy in the near future.

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