

A new type of photocatalysis initiated by photoexcitation of adsorbed carbon dioxide on ZrO_2

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ZrO_2 has been found to be an effective photocatalyst for reduction of CO_2 by hydrogen or methane at room temperature. The effective photon energy is less than the band gap energy of ZrO_2 (5.0 eV), indicating that photoexcitation of bulk ZrO_2 is not involved. The reaction is initiated by photoexcitation of surface carbonates derived from adsorption of CO_2 to convert it to a CO_2^- radical, which in turn reacts with hydrogen or methane to form surface formate. The formate is stable at temperatures below 573 K, but works as a reductant of CO_2 under photoirradiation. A new type of reaction mechanism is proposed.

KEY WORDS: photoreduction of CO_2 ; ZrO_2 ; CO_2 anion radical; surface formate

1. Introduction

There is an urgent necessity to decrease emission of carbon dioxide to protect the environment from greenhouse effect. Thus, the development of effective methods to convert carbon dioxide to more valuable compounds inexpensively is desirable. From this standpoint, catalytic reduction of carbon dioxide with a reductant such as hydrogen [1–3] or methane [4,5] has been studied. Carbon dioxide is a very stable and inert compound, and CO_2 reduction hardly occurs at room temperature under ambient pressure. On the other hand, irradiation to the photoactive catalyst often enables us to reduce CO_2 at a significant reaction rate under mild conditions of room temperature and low pressure because the energy of light assists the reaction. In fact, many studies have reported the possibilities of CO_2 photoreduction over various heterogeneous photocatalysts [6–17].

Among these reports, titanium oxide or metal-loaded titanium oxide systems have mainly been used as photocatalysts [6–10]. Zirconium belongs also to the 4A group on the Periodical table and is listed at the period just below titanium. However, only a few papers have been reported on the effective photocatalysis by zirconium oxide. Sayama *et al.* reported that zirconium oxide showed an excellent photocatalytic activity under irradiation of light of $\lambda < 250$ nm for photodecomposition of water and photoreduction of aqueous carbonate [18,19]. The interesting point of their report is that metal loading inactivated zirconium oxide, in contrast to the case of TiO_2 . This fact suggests a different mechanism from that over typical photocatalysts, although the reported energy of effective light corresponds to the band-gap of zirconium oxide (5.0 eV), and a novel route to development of a new type of photocatalysis for CO_2 reduction may be opened. Thus, we started the investigation of photoreduction of CO_2 by zirconium oxide [20–22].

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2. Catalysts and reaction procedures

Zirconium oxide used in the series of studies was prepared by hydrolyzing zirconium oxychloride by aqueous NH_3 , followed by drying at 373 K overnight and calcination at 773 K for 5 h in a dry air stream. The BET surface area was found as $68 \text{ m}^2 \text{ g}^{-1}$ by nitrogen physisorption. The XRD pattern indicated that the resulting powder was a mixture of zirconium oxide in monoclinic and tetragonal phases.

The photoreaction was carried out in a closed static system connected to a vacuum line. A 500 W ultrahigh-pressure mercury lamp (Ushio Denki USH-500D) was used as a UV light source. 0.3 g of zirconium oxide was placed on the flat bottom of a quartz reactor and subjected to irradiation from the bottom. The area subjected to irradiation was 12 cm^2 . For conditioning, the sample was heated at 673 K for 30 min in air and evacuated for 30 min at the same temperature, followed by treatment with 8 kPa O_2 for 75 min and evacuation for 30 min at 673 K. A mixture of CO_2 (150 μmol) and hydrogen or CH_4 (50 μmol) was admitted to the reactor and the total pressure in the reactor was *ca.* 25 kPa. After a given time of photoreaction, the gaseous products were analyzed, and after 2 min evacuation at room temperature, the sample was heated at 673 K for 20 min and the desorbed gases were also analyzed. This will be referred to as heat treatment hereafter.

3. Photoreduction by hydrogen

3.1. General features of the reaction

The activity for photoreduction of CO_2 by hydrogen was investigated for TiO_2 , ZrO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , WO_3 , and ZnO . Among them, only ZrO_2 was found to be active. With ZrO_2 , 1.0 μmol of CO was detected after 6 h photoirradiation, and no other reduced product was detected. ZrO_2 is stable under photoirradiation and no appreciable difference

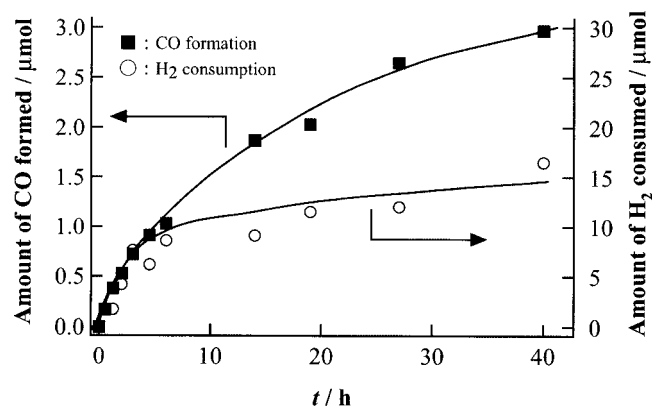


Figure 1. Time dependence of the amount of CO formation and H₂ consumption over ZrO₂ under irradiation. Initial amounts of CO₂ and H₂ were 150 and 50 μmol , respectively.

was found in Zr L_{III} edge XANES spectra of ZrO₂ before and after photoreaction.

When the reaction was carried out in the dark at room temperature, no CO was detected, although ZrO₂ is known as a solid base and may activate CO₂ by adsorption of CO₂ on the surface [23]. This indicates that photoirradiation is essential for this reaction. Figure 1 shows the time dependence of the amount of CO formation and H₂ consumption. The rate of CO formation mildly decreased from 8 to 40 h irradiation. On the other hand, the consumption rate of H₂ was very fast at the beginning and then slowed. The amount of consumed H₂ was quite larger than that of evolved CO at all times. These suggest that some compounds containing hydrogen, carbon, and oxygen were accumulated on the surface during the photoreaction.

We then tried to decompose adsorbed species by heating the catalyst sample after the photoirradiation. More CO evolution was observed, while the amount of desorbed H₂ was very small. Thus, after 6 h photoirradiation, 1.0 μmol of CO was detected, as mentioned above, and when the catalyst sample was heated at 673 K for 20 min after 2 min evacuation (heat treatment), 3.3 μmol of CO was evolved. When the photoirradiation time was extended to 40.5 h, 3.2 μmol of CO was formed, and by the heat treatment, 5.8 μmol of CO was evolved. This observation shows that photoirradiation to the catalyst surface produces some material which is decomposed into CO by heat.

3.2. Effects of the wavelength of irradiation light and temperature

ZrO₂ is a semiconductor with a wide band gap (5.0 eV), and does not absorb light of $\lambda > 250$ nm as confirmed by the measurement of the UV-VIS spectrum of ZrO₂ used in this study. Therefore, if photoexcitation of ZrO₂ to form electrons and holes is essential for this reaction, the reaction would not proceed by irradiation of light of $\lambda > 250$ nm. However, if a different mechanism works on the reaction, the reaction may proceed under irradiation of light with longer wavelengths.

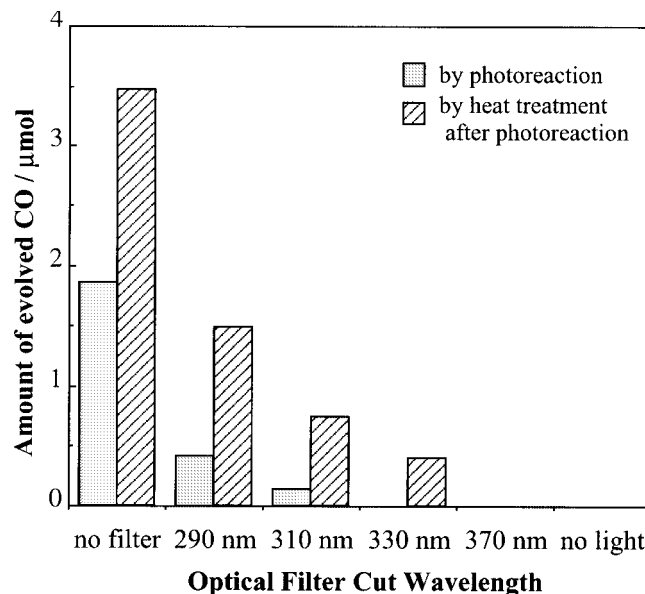


Figure 2. Relationship between the wavelength region of irradiation light and the amount of evolved CO. The dark and light bars illustrate the amount of CO evolved during photoreaction and that of CO formed by heat treatment after photoreaction, respectively.

Table 1
Effect of reaction temperature on the photoreaction of CO₂ + H₂ over ZrO₂.^a

Temperature (K)	Under photoirradiation (μmol)		In the dark (μmol)	
	CO(g) ^b	CO(s) ^c	CO(g) ^b	CO(s) ^c
335	1.3	1.5	n.d.	n.d.
373	2.2	4.3	n.d.	n.d.
423	4.1	7.4	–	–
473	6.1	9.0	0.1	9.1
523	7.6	9.5	–	–

^a Reaction time was 6 h; initial amount of CO₂ and H₂ (D₂) was 150 and 50 μmol , respectively.

^b The amount of CO produced during reaction.

^c The amount of CO yielded by heat treatment at 673 K after reaction (reflecting the amount of surface formate, see text).

The dependence of CO evolution upon the wavelength of irradiation light was investigated. Photoreactions were carried out under irradiation of light with various wavelengths using glass filters. The results are shown in figure 2. The results are obviously not in accord with the optical properties of ZrO₂. Indeed, while the amount of CO evolution decreased apparently as the cut wavelength became longer, light with wavelengths $\lambda > 290$ nm could promote the reaction. This result suggests that excitation of bulk ZrO₂ is not required for this reaction: that is, the photoactive species is not a simple ZrO₂, and some other photoactive species are expected to exist.

Next, we investigated the effect of reaction temperature on the reaction. If the reaction were purely a photoprocess, the reaction temperature would affect the rate a little. The results are shown in table 1. Evidently, we can find that the activity of ZrO₂ for CO₂ photoreduction increases with an increase in the reaction temperature. Without irradiation,

tion, the reaction hardly took place at 373 K. However, at 473 K, a very small amount of CO was detected and it is noteworthy that a significant amount of CO was evolved by the heat treatment of the sample at 673 K after the dark reaction for 6 h. This means that the formation of surface species is brought about without irradiation at a moderate temperature, which is consistent with the studies reported by Kondo *et al.* [24] and He and Ekerdt [25]. This species is stable at 473 K and only a small part of the species decomposed to CO. On the other hand, CO formation under irradiation was much easier than in the dark. Thus, the reduction of CO₂ at an elevated temperature includes photoprocesses, although a thermal process has strong influence on the reaction rate.

Now, characteristics of reduction of CO₂ over ZrO₂ under irradiation were emerged. This is a photoassisted reaction, but photoexcitation of bulk ZrO₂ forming electrons and holes is not essential, as light with energy smaller than the band gap is also effective to the reaction. The elevated temperature is favorable to the reaction, but it is still a photoreaction and thermal energy seems to enhance formation of some surface species, which is stable at moderate temperatures and decomposes to CO at 673 K. These findings suggest that the reaction proceeds by a mechanism different from the general one over TiO₂ catalysts [26].

3.3. Intermediates

The surface species mentioned above might be an intermediate and identification of this species is important to clarify the mechanism of this reaction. We investigated the nature of the species by several techniques. Figure 3 shows the infrared spectra of ZrO₂ (a) before and (b) after introduction of CO₂ and H₂ in the dark, and (c) after photoirradiation for 21 h in CO₂ and H₂. The inset of figure 3 is the subtraction of (b) and (a), indicating the spectrum of adsorbate. Introduction of CO₂ causes the appearance of six bands in the range between 1800 and 1000 cm⁻¹, as shown in the inset of figure 3. All of these bands were assigned to bidentate surface carbonate or bicarbonate (hydrogen carbonate) species

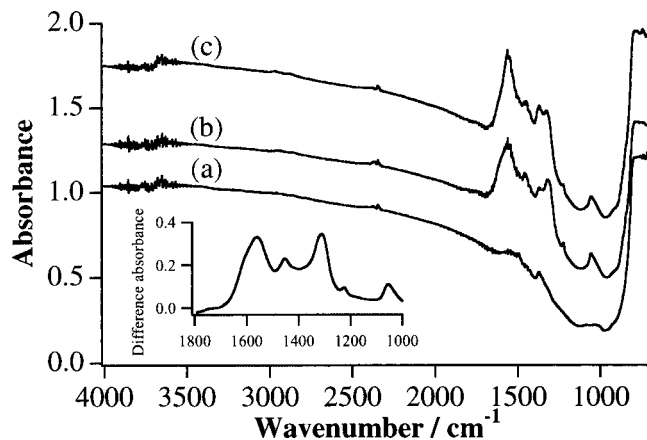


Figure 3. Infrared spectra of ZrO₂ (a) after pretreatment, (b) after introduction of CO₂ and H₂ to (a), and (c) after photoirradiation to (b). The inset is the difference spectrum between (a) and (b), indicating the spectrum of adsorbate.

according to the previous studies [24,25,27]. Both of these two species were formed by introduction of carbon dioxide even in the dark, and they were not removed from the surface by evacuation at room temperature since the absorption bands did not disappear upon evacuation.

The contact of hydrogen with the zirconium oxide pre-adsorbing CO₂ led to almost no spectral change. Dissociative adsorption of hydrogen on ZrO₂ has been reported to form Zr-H at room temperature. This was evidenced by appearance of a band at around 1560 cm⁻¹, when hydrogen is contacted with ZrO₂ at room temperature [28–30]. However, on our ZrO₂ the band assigned to the dissociative hydrogen was not observed. Therefore, we conclude that hydrogen is not activated on ZrO₂ at room temperature at least in the dark. The discrepancy between the present results and the previous works would result from the difference in the pretreatment temperature; in the previous studies, ZrO₂ was pretreated at above 973 K, while ZrO₂ used in this study was pretreated at 673 K.

The spectral change caused by photoirradiation was so small that it was hardly observed in figure 3. However, by plotting difference spectra between before and after photoirradiation, new bands emerged clearly at 2970 and 2886 cm⁻¹. The bands became intense as the irradiation time was extended. In the wavenumber region between 1800 and 1000 cm⁻¹, changes by photoirradiation were also observed but not so clear since the strong absorption bands of surface carbonate and bicarbonate were overlapping to the surface species which is prospected to be an intermediate. By a TPD experiment, we found that almost all of adsorbed carbon dioxide was desorbed by the evacuation at 573 K, whereas the surface species was not decomposed to CO completely until the evacuation temperature reaches to 673 K. Accordingly, if the sample is evacuated at 573 K, only the surface species will remain on ZrO₂ and the difference spectrum between the two samples evacuated at 573 and at 673 K will give the absorption bands of the surface species. Figure 4 illustrates such a difference spectrum. Three peaks positioned at 1566, 1390 and 1372 cm⁻¹ were clearly observed. These bands disappeared by continuous evacuation at 673 K. This is consistent with the result of the TPD experiment. From these results, we concluded that these peaks were derived from the surface species, which

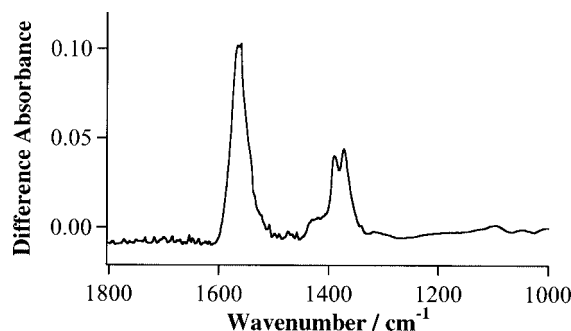


Figure 4. Difference infrared spectrum of the ZrO₂ sample evacuated at 573 and 673 K after photoirradiation in CO₂ and H₂.

was formed during photoirradiation of ZrO₂ by the reaction between hydrogen and adsorbed carbon dioxide.

The surface species is assigned to surface formate ion, because characteristic bands were observed at 2968, 2882, 1568, 1382, and 1368 cm⁻¹ when formic acid was adsorbed on ZrO₂, and these bands were assigned to surface formate ion [25,31]. Consequently, it is concluded that surface formate is formed by photoreaction of CO₂ and H₂ over ZrO₂ at room temperature, and the formate is decomposed to CO by heat treatment at 673 K.

3.4. Reactions with formic acid

At this stage, a question arises. What is the role of the surface formate? Is this on the reaction path or just a spectator? The fact that the formate was not decomposed completely at 573 K might suggest the spectator. To clarify the role of formate in the reaction, we carried out some reactions under several conditions using formic acid as a substrate. If the surface formate is a “true” intermediate, the evolution of carbon monoxide will be observed in the reactions using formic acid as one of the reactants under a proper reaction condition.

The results of such reactions are summarized in table 2. Only in the case that carbon dioxide was introduced with formic acid and photoirradiation was performed on ZrO₂, the reaction proceeded and a significant amount of carbon monoxide (0.7 μmol) was evolved. When ¹³CO₂ was used for the reaction, the evolution of ¹³CO was observed. From these results, we conclude that the formate is a “true” reaction intermediate and converts CO₂ to CO, and that this reaction is also a photoreaction, as the formation of surface formate is. The surface formate should be a reductant of carbon dioxide to carbon monoxide.

It is not clear to what the surface formate is converted upon photoreaction with carbon dioxide. The surface formate must be oxidized by carbon dioxide during the photoreaction, since it is a reductant of carbon dioxide. Therefore, we guess that the surface formate is oxidized to surface carbonates (carbonate or bicarbonate) or gaseous carbon dioxide. The carbonates may be again reduced to formate when hydrogen coexists in the reactor.

Table 2
The results of reactions using formic acid as one of substrates.^a

Substrate(s) ^b	Reaction condition	Amount of evolved CO (μmol)
HCOOH	Under photoirradiation	0.0
HCOOH + H ₂	Under photoirradiation	0.0
HCOOH + CO ₂	Under photoirradiation	0.7
HCOOH + CO ₂	In the dark at 313 K	0.0

^a Reaction time 6 h, reaction temperature – room temperature unless otherwise noted, ZrO₂ sample 0.3 g.

^b Introduced amount of substrate(s): HCOOH 10 μmol, HCOOH 5 μmol + H₂ 50 μmol, HCOOH 5 μmol + CO₂ 150 μmol, HCOOH 5 μmol + CO₂ 150 μmol.

3.5. Formation of CO₂⁻ radical

In the previous sections, we conclude that that reaction of CO₂ and hydrogen brings about formation of the surface formate as a reaction intermediate over irradiated ZrO₂ surface. The effective wavelength of the light does not necessarily correspond to the band gap of ZrO₂. Carbon dioxide is adsorbed as carbonates on the surface, but photoirradiation is essential for the formation of the formate. These suggest that some photoexcitation processes are included in the activation of CO₂. The activated species may be a radical, as photoexcitation of molecules very often causes radical formation.

To verify the radical formation, we recorded EPR spectra of zirconium oxide with preadsorbed CO₂. Figure 5 shows spectra recorded after irradiation of ZrO₂ pre-adsorbing CO₂. As shown in the figure, sharp and intense signals at *g* = 2.002 and 1.996 were observed with small background signals due to coordinatively unsaturated Zr³⁺ centers [32] and color centers [33]. Once produced by irradiation, these sharp signals were stable after the irradiation light was turned off. Even after 60 min in the dark following to irradiation, the signal intensity was almost the same as that under irradiation (compare figure 5 (A) and (B)). These results show that a new paramagnetic species arises on ZrO₂ by irradiation, and that the paramagnetic species is stable even in the dark.

The *g* values suggest a CO₂⁻ radical, referring to the earlier EPR studies on CO₂ or CO adsorption on MgO [34] or SiO₂ [35]. This is confirmed by recording the EPR spectrum of ¹³C-labeled CO₂. The spectrum is represented in figure 6(A). In the figure, signals around *g* = 2 are background due to color center, and it is clear that the main signal in figure 5 split into doublet signals at the both sides showing that the new paramagnetic species contains one carbon atom (nuclear spin of ¹³C: *I* = 1/2). The signals at around *g* = 2 were almost the same as observed after irradiation of bare ZrO₂. From this result, we judged that the color center

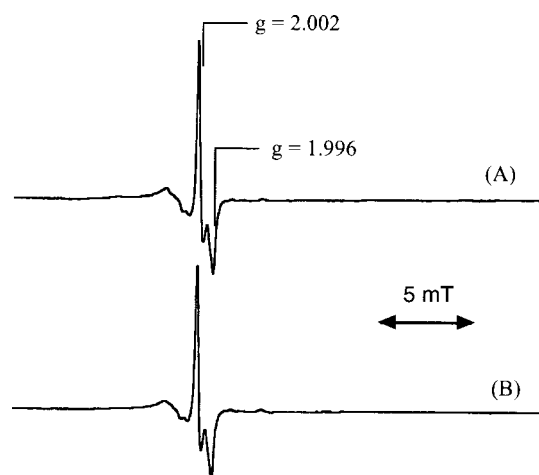


Figure 5. EPR spectra of ZrO₂ with adsorbed CO₂ (A) under irradiation for 60 min, and (B) in the dark for 60 min following to (A).

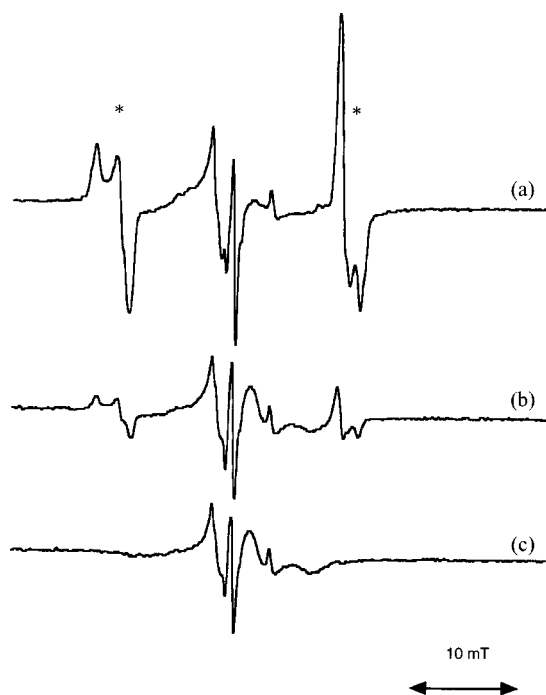


Figure 6. EPR spectra of ZrO₂ with adsorbed ¹³CO₂ (a) under irradiation for 60 min, (b) 5 min after introduction of H₂ (7 kPa) to (a), and (c) 30 min after H₂ introduction to (a). The signals corresponding to ¹³CO₂ are marked *.

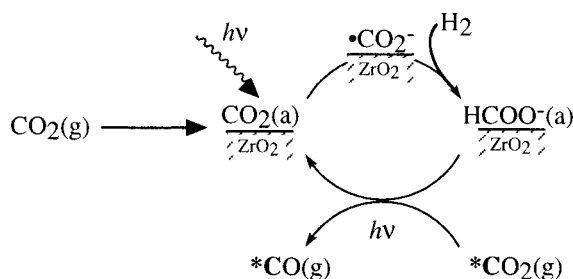
is affected neither by adsorption of CO₂ nor by irradiation of ZrO₂ with adsorbed CO₂.

We made hydrogen be in contact with ZrO₂ pre-irradiated for 60 min with adsorbed ¹³CO₂ in the dark. As shown in figure 6(B), we observed an obvious decrease in the intensity of the signals assigned to the ¹³CO₂⁻ radical after the introduction of 7 kPa of hydrogen. After 30 min, the signals disappeared completely (figure 6(C)). As the CO₂⁻ radical is stable in the dark at least for 60 min under vacuum (see figure 5), the result shows that the CO₂⁻ radical reacts with hydrogen without irradiation. From the results of IR study mentioned previously, it is natural to conclude that the reaction between CO₂⁻ radical and H₂ yields the surface formate.

It is plausible to postulate that the precursor of the CO₂⁻ radical is carbonate on the surface. Unfortunately, we did not succeed in obtaining evidence to support this postulate. A TPD study revealed at least two kinds of adsorbed CO₂; one is desorbed at around 350 K and the other at a temperature higher than 400 K. The latter would interact with base sites on the ZrO₂. Although the activation by the base sites will not be so strong as that by MgO, some modification of bonds in CO₂ is expected. This may be the species which absorbs the light of $\lambda > 290$ nm and is converted to CO₂⁻. The nature of the electron transition caused by irradiation is now under investigation by means of molecular orbital calculations.

3.6. Reaction mechanism

On the basis of results mentioned above, we can deduce a possible reaction mechanism as shown in the scheme 1.



Scheme 1.

The most striking feature of this scheme is that the active species is a CO₂⁻ radical which is formed by photoactivation of adsorbed CO₂. In other words, photoexcitation of bulk ZrO₂ is not involved in the photoactivation of CO₂ directly. The role of ZrO₂ is thermal activation of CO₂ by adsorption on the base site. A carbonate or bicarbonate species is formed on the site, and the species absorb light with $\lambda < 300$ nm and form CO₂⁻ radical under irradiation. The CO₂⁻ radical reacts with hydrogen (presumably) molecules to form surface formate which works as the reductant of CO₂. The formate itself is stable at the temperature below 600 K in the dark, but reacts with CO₂ under irradiation.

4. Photoreduction by methane

4.1. Characteristics of the reaction

Photoreduction of CO₂ over ZrO₂ was also conducted with methane [36]. Figure 7 shows the time dependence of CO formation under photoirradiation (thick line). The amount of CO formation increases with the irradiation time, although the rate of CO formation is slightly slowed down. Without photoirradiation, even a trace of CO was not detected, although CO₂ adsorption on zirconium oxide does not need photoexcitation. When the short wavelength region ($\lambda < 290$ nm) in the irradiation light was cut off by a glass filter, merely a small amount of CO (0.1 μ mol) was evolved. In the case that CO₂ or CH₄ alone was admitted to the reactor, no CO was detected even after UV irradiation. From these results, we concluded that this reaction was a photoreaction, not a thermal redox reaction between ZrO₂ and CO₂, or between CH₄ and ZrO₂. In other words, the C–H bond of methane is activated in the presence of carbon dioxide on ZrO₂ under irradiation.

When the sample was heated under vacuum after photoreduction of a given time, the evolution of CO, H₂, and CH₄ was observed. For example, after 5 h of irradiation, 0.7 μ mol of CO was detected and when the sample was heated at 673 K for 20 min after 2 min evacuation, 1.5 μ mol of CO, 0.2 μ mol of H₂, and 0.2 μ mol of CH₄ were evolved. No other products were detected. As shown by the thin line in figure 7, the amount of CO formation by the heat treatment was also increased with the irradiation time. This indicates that some material decomposed to yield CO by heat arises on the surface of zirconium oxide by irradiation. One significant difference from the hydrogen reduction mentioned previously

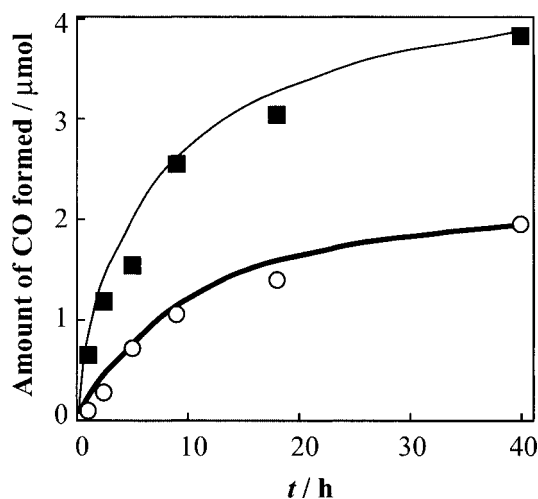


Figure 7. Time dependence of CO formation over ZrO₂ by photoirradiation (thick line) and by heat treatment after a given time of photoreaction (thin line); initial amount of CO₂ and CH₄ were 150 and 50 μmol, respectively.

is that some carbonaceous residue remained on the surface even after evacuation at 773 K. This species can be burnt out by oxygen at 673 K.

To investigate the effect of the reaction temperature, the reaction was carried out at 673 K and compared to the results obtained at room temperature. Without irradiation, the reaction between CO₂ and CH₄ hardly proceeded over ZrO₂ and any products were not detected at all. This agrees with the report that ZrO₂ itself has no activity for the (thermal) CO₂ reforming of methane, although it shows an excellent performance as the support of catalysts for the reaction [37]. On the other hand, large amounts of CO and H₂ were produced by the reaction under irradiation. While the photoreaction at room temperature for 5 h yielded 0.7 μmol of CO, the amount of CO produced at 673 K was *ca.* 30 times larger than that at room temperature.

4.2. Carbon source of CO

The origin of the carbon atom contained in the products and surface species was investigated by carrying out photoreactions between CO₂ and CH₄ over ZrO₂, where the carbon atom of either CO₂ or CH₄ was labeled with ¹³C. The results are shown in table 3. The carbon monoxide evolved into the gas phase during irradiation was found to stem from the reduction of CO₂. The CO produced by heat treatment after the photoreaction contained the carbon atom only from CO₂ in accord with TPD experiments where ¹³CO was selectively desorbed from the ZrO₂ sample after the photoreaction between ¹³CO₂ and ¹²CH₄ [36]. From these, it can be concluded that CH₄ is hardly oxidized to CO, while CO₂ is reduced to CO by CH₄. On the other hand, the CO₂ evolved by O₂ treatment after evacuation at 773 K was found to originate mainly from CH₄. The species not removed from the surface by evacuation at 773 K is the carbonaceous residues mentioned previously. Therefore, this result indicates that CH₄ participating in the photoreduction of CO₂ is not released into the gas phase as a product, but remains on the

Table 3
The origin of the carbon atom contained in the products.^a

Product	Origin of carbon atom
CO produced by photoreaction	From CO ₂ ^b
CO produced by heat treatment after photoreaction	Only from CO ₂ ^c
CO ₂ produced by O ₂ treatment after evacuation at increased temperature	From CO ₂ < from CH ₄ ^d

^a The origin of carbon atom was traced using ¹³C isotope after photoreaction of either between ¹³CO₂ and ¹²CH₄ or between ¹²CO₂ and ¹³CH₄ for 6 h at room temperature. Substrates: CO₂ 150 μmol, CH₄ 50 μmol.

^b Possibility of CO from CH₄ cannot be excluded, but no definite evidence of CO originating from CH₄ was obtained.

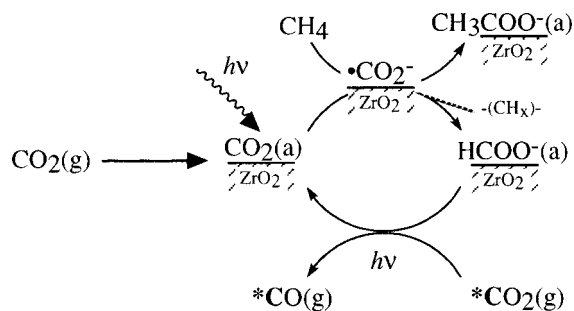
^c This is confirmed by TPD experiments for ZrO₂ submitted to ¹²CO₂ photoreduction with ¹³CH₄.

^d CO₂(from CO₂)/CO₂(from CH₄) ≈ 0.3.

surface as carbonaceous residues. However, the carbonaceous residues are not due to CH₄ only. The results shown in table 3 indicate that part of the carbon (1/4) involved in the carbonaceous residues was originated from CO₂. It suggests that some part of the carbonaceous residues is a compound made of both CO₂ and CH₄.

4.3. Intermediates

Experimental results described in the previous sections revealed that at least two kinds of surface species arose during photoreaction; one is decomposed to CO by heat treatment at 673 K and the carbon atom in the species originates from CO₂, while the other is less reactive and not decomposed by heat treatment even at 773 K. To identify these species, IR spectroscopy was applied. In the dark, CO₂ was adsorbed as carbonates as described previously, and CH₄ did not affect the spectrum in the dark, indicating that no reaction proceeded in the dark between CO₂ and CH₄. Some spectral change was detected after irradiation of ZrO₂ with CO₂ and CH₄. In the difference spectrum of ZrO₂ before and after irradiation for 36 h, two peaks were clearly observed at 2970 and 2878 cm⁻¹. On the other hand, in the range from 1800 to 1000 cm⁻¹, the strong absorption bands by the surface carbonates made the change by the irradiation unclear. To obtain a spectrum free from the interference with the surface carbonates, the same technique adopted in the case of photoreduction by hydrogen was also applied; removing the carbonates by evacuation of the sample at 573 K and setting up a difference spectrum between spectra evacuated at 573 and 673 K. The obtained difference spectrum resembled that shown in figure 4, indicating formation of the surface formate. However, there was some indication of the existence of other species, as the spectrum was a little complex compared to the spectrum of adsorbed formate. In fact, the evacuation at 673 K did not bring about cleanup of the surface but some species still remained. In the spectrum recorded after evacuation at 673 K showed two peaks at 1538 and 1454 cm⁻¹, while no peak was detected between 3000 and 2800 cm⁻¹. These bands can be assigned to acetate by comparison with the spectrum of acetic acid adsorbed on



Scheme 2.

ZrO₂, although both spectra were not identical. Therefore, we concluded that the surface species remaining after evacuation at 673 K is mainly the surface acetate. Some part of the acetate would be desorbed during evacuation at 673 K making the difference spectrum between spectra evacuated at 573 and 673 K a little complex.

The IR spectroscopic study has revealed acetate as a carbonaceous residue. However, the results shown in table 3 suggest some polymeric species as another residue. The acetate is naturally expected to be formed from one molecule of CO₂ and one molecule of CH₄. Then, CO₂ formed by burning the acetate should be comprised of equimolecular ratio of carbon atoms originating from CO₂ and CH₄. On the other hand, the experimental results show three fourths of CO₂ was originated from CH₄. This indicates that part of carbonaceous residues was formed from CH₄ only. High stability at 773 K of this species, as well as the fact that the surface of ZrO₂ colored pale brown after the reaction, suggests a polymeric compound such as $-(CH_x)_n-$ species. Since the bands due to the C–H stretching mode were not observed in the IR spectra, the polymeric compound may be a highly carbonaceous one. The band at around 1585 cm^{−1} given by the graphitic carbonaceous residues [38] was in this case hindered by the strong absorption band at 1538 cm^{−1} due to the surface acetate. The surface acetate seems not to be a reaction intermediate, because a reaction using the acetic acid as a reductant of CO₂ scarcely proceeded.

The formation of formate and acetate should result from the reaction of CO₂^{•−} radical and CH₄, because EPR experiments revealed that CO₂^{•−} radical disappeared within 30 min upon contact with CH₄.

4.4. Reaction mechanism

Based on the results mentioned in previous sections, we propose the reaction in scheme 2 for the photoreduction of CO₂ by CH₄ over irradiated ZrO₂.

The carbon dioxide adsorbed on the surface of ZrO₂ is photoexcited under irradiation of ZrO₂ to form CO₂^{•−} anion radical. The CO₂^{•−} radical reacts with CH₄ to yield both surface acetate and surface formate. The former does not react further but stays stabilized on the surface. On the other hand, the latter works as a reductant of another CO₂ to CO

under irradiation. During the reduction of CO₂ by the surface formate, the formate itself is perhaps oxidized to become the adsorbed CO₂ species again. The production of CO proceeds via the above two-step reaction (*i.e.*, formation of surface formate and reduction of CO₂ to CO by the surface formate) as in the case of reduction by hydrogen.

We observed the strong enhancement of the activity in the photoreaction of CO₂ and CH₄ at 673 K. Considering the reaction mechanism as well as the fact that the surface formate is decomposed at around 623 K to yield CO [20,36], one can conclude that the enhancement is caused by the decomposition of the surface formate by heat. At 673 K, the surface intermediate need not work as a reductant of another CO₂ molecule. Instead, the surface formate itself is decomposed at 673 K to yield CO directly.

5. Conclusion

ZrO₂ is found to be active for photoreduction of CO₂ by hydrogen and methane. The photon energy less than the band gap energy is effective to the reaction, indicating that photoexciting bulk ZrO₂ to form electrons and holes is not essential for this reaction. Thus, a new type of photocatalysis proceeds on ZrO₂. The role of photoirradiation is to convert adsorbed carbonates to CO₂^{•−} radicals and also assist the reaction of CO₂ and formate which is derived from CO₂^{•−} and hydrogen or methane. The formate works as a reductant and is not decomposed at a temperature below 573 K, but decomposed to CO at the higher temperature to 673 K. In the case of photoreduction by methane, two kinds of inert compounds are formed; one is acetate and the other is possibly a polymeric species. These are resistant to evacuation at 773 K.

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