

Photo-enhanced reduction of carbon dioxide with hydrogen over Rh/TiO₂

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Abstract

Photoreduction of gaseous carbon dioxide to carbon monoxide with hydrogen over Rh-loading TiO₂ was investigated. As the reaction proceeded even in the dark but was enhanced under irradiation, the reaction should be considered as “photo-enhanced reaction”. When Rh in Rh/TiO₂ was strongly reduced to be in a fully metallic state, the activity was lowered and the main product changed from CO to CH₄. A similar effect was obtained by changing the loading amount of Rh: when the loading amount of Rh was raised, the activity was lowered and the main product shifted from CO to CH₄. The results of an X-ray absorption spectroscopic analysis showed that the ratio of Rh in a metallic state to that in an oxidized state increased along with the increase of the amount of Rh loading on Rh/TiO₂. The photocatalytic activity was higher as Rh was richer in the component of metallic and oxidized state. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The increase in the concentration of CO₂ in the air is thought to be a severe problem in recent years as it causes the increase in the temperature of the atmosphere. Therefore, investigators make special efforts to find the effective methods to reduce the CO₂ concentration. Among them, a catalytic conversion of CO₂ into more useful compounds is one of the most promising methods. However, since CO₂ is a rather inert and stable compound, the reduction of CO₂ is difficult in general. To convert it by force, a severe condition of high pressure/high temperature is often required. On the other hand, there is some hope in the conversion of CO₂ under a mild condition using photocatalysts. In the photocatalytic reaction, CO₂ may be reduced under the condition of room temperature and low pressure because the energy of light helps to activate CO₂ to a more reactive state.

TiO₂ is the most common semiconductor material as a photocatalyst because it shows an excellent photocatalytic activity as well as it is cheap, harmless and stable against photoirradiation [1]. The photoactivity of TiO₂ is based on the semiconductivity of TiO₂: a pair of an excited electron and a positive hole is generated under band-gap irradiation

of TiO₂. When some metal is loaded on TiO₂ (M/TiO₂), the photocatalytic activity of the system is enormously reinforced. The loaded metal is thought to assist the separation of a pair of an excited electron and a positive hole generated by irradiation. The M/TiO₂ is effective for many photoreactions; for example, the decomposition of water [2,3], the degradation of organic pollutants [4,5] and the reduction of nitrite and nitrate ions to ammonia [6]. The photoreduction of CO₂ has also been tested using TiO₂ with various loaded metals [7] such as Hg [8], Pd [9] and Pt [10], or TiO₂ suspension mixed with Cu powder [11].

In 1987 Thampi et al. [12,13] reported that Ru-loading TiO₂ showed a high activity towards CO₂ photoreduction by hydrogen. In the study they obtained methane selectively as a product, and asserted that the Ru/TiO₂ was the most effective for CO₂ reduction when Ru was in a partially oxidized state (Ru–RuO_x). As the conversion of CO₂ into CH₄ proceeded even in the dark although the reaction rate was lower than under irradiation, they claimed that the reduction of CO₂ over Ru–RuO_x/TiO₂ was a ‘photo-enhanced reaction’.

On the other hand, Solymosi and Klivényi [14] reported the photo-induced formation of CO₂^{•−} anion radical on K-doped Rh(1 1 1) surface. It was further reported that Rh/TiO₂ had an ability to activate CO₂ under photoirradiation and the cleavage of a C–O bond in CO₂ was observed [15]. It indicates the probability of CO₂ photoreduction over Rh/

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TiO₂. In fact, Solymosi and Tombácz [16] examined the reduction of CO₂ with H₂O over Rh/TiO₂, and detected the production of formic acid, formaldehyde or methanol. In this study it was also suggested that the pretreatment temperature and atmosphere of Rh/TiO₂ (in air at 773 K, or in H₂ at 473 K) influenced the activity and selectivity of the reaction.

In the present study, we tried the CO₂ photoreduction by H₂ in a gas phase over Rh/TiO₂, and confirmed that Rh/TiO₂ exhibited an excellent photoactivity towards the CO₂ reduction to yield CO mainly. As CO is a substrate of many industrial processes such as the Fischer–Tropsch synthesis or methanol synthesis, CO is a more preferable product than methane, which is obtained as a major product in the photoreduction of CO₂ on Ru/TiO₂ in the previous work reported by Thampi et al. [12,13]. The factor controlling the activity and selectivity of this reaction was also discussed. In the gas phase reaction, the reaction mechanism is expected to be more simple and therefore the factor influencing the activity and selectivity will be less complex than in the liquid phase. The photoreaction was performed on samples with Rh in various states, and the relationship between the reactivity and the state of Rh on TiO₂ were investigated using an X-ray absorption spectroscopy.

2. Experimental

2.1. Sample preparation

The Rh/TiO₂ samples used in this study were prepared by a simple impregnation method. First, TiO₂ supplied from Japan Catalysis Society (JRC-TIO-4) was impregnated with an aqueous solution of RhCl₃·3H₂O (Wako Chemical). It was then evaporated to dryness in a water bath at 353 K. After the obtained solid was dried at 373 K overnight, it was calcined at 773 K for 5 h. The loading amount of Rh was varied from 0.3 to 4 wt% as metal. Hereafter, Rh(X)/TiO₂ denotes the sample containing X wt% of Rh. The XRD pattern showed no peak assignable to Rh crystals in every Rh/TiO₂ sample. The BET specific surface areas of the samples were almost the same (50.1 m²/g for Rh(1)/TiO₂, and 50.3 m²/g for Rh(4)/TiO₂), indicating that the Rh loading had no influence on the surface area of the sample.

2.2. Photoreaction

The photoreaction was carried out in a closed static system connected to a vacuum line in a similar manner described elsewhere [17]. A Rh/TiO₂ sample weighed 0.3 g was spread on the flat bottom of a quartz reactor. Before photoreaction, the sample was heated at 673 K for 30 min in the air and evacuated for 30 min at the same temperature, followed by treatment with 8 kPa O₂ for 60 min and evacuation for 30 min at 673 K. After that, the temperature was lowered to 523 K, and the sample was treated with 8 kPa H₂

for 120 min followed by evacuation for 30 min at 523 K. After the above pretreatment, the sample was cooled to room temperature, and a mixture of CO₂ (150 μmol) and H₂ (50 μmol) was admitted to the reactor unless otherwise noted. The total pressure in the reactor was ca. 25 kPa. A 500 W ultrahigh-pressure mercury lamp was used as the light source, and the reactor was illuminated from the bottom. The area subjected to illumination was 12 cm². When the short wavelength part of irradiation light required to be cut-off, a series of glass filters (Toshiba UV-29, UV-37 and Y-45, which permitted 50% transmission of lights at the wavelength 290, 370 and 450 nm, respectively) was placed between the mercury lamp and the reactor. After photoreaction for 6 h, the gaseous products were analyzed. In some cases, after 2 min evacuation at room temperature following to the photoreaction, the sample was heated at 573 K for 20 min, and the desorbed gases were also analyzed. To avoid the reaction between desorbed gases, they were trapped by the adsorption to a high surface area SiO₂ kept at 77 K. The analysis of products was performed with an on-line TCD gas chromatograph (Shimadzu GC-8A) equipped with Molecular Sieve 5A packed column using argon as a carrier gas, which could detect H₂, CH₄, and CO.

2.3. X-ray absorption spectroscopy

X-ray absorption (XAS) experiments were carried out on the beam line BL-10B at Photon Factory in the High Energy Accelerator Research Organization, Tsukuba, Japan (proposal no. 93G170). All spectra were recorded using an in situ cell in a transmission mode at room temperature with an Si(3 1 1) two-crystal channel-cut monochromator.

Data analysis was performed using a FACOM M1800 computer of Kyoto University Data Processing Center. Normalization of XANES spectra and data reduction of EXAFS were carried out as described elsewhere [18].

3. Results

3.1. Photoreduction of CO₂ with H₂ over Rh/TiO₂

We tried to reduce CO₂ by H₂ on Rh(1)/TiO₂ under photoirradiation. After 6 h irradiation, 9.2 μmol of CO and a small amount (0.1 μmol) of CH₄ were produced. Any other products such as hydrocarbons or oxygenates were not detected. The activity was very high compared to those reported by us previously using the same reaction system with ZrO₂ samples [19,20]. When only CO₂ was introduced and no H₂ was admitted to the reactor, no product was detected even after photoirradiation. On the contrary, when only H₂ (i.e., no CO₂) was introduced, the evolution of CH₄ was observed. This indicates that there are some carbon residues on the Rh/TiO₂ sample. However, the amount of CH₄ was too small (0.05 μmol). From these results, we

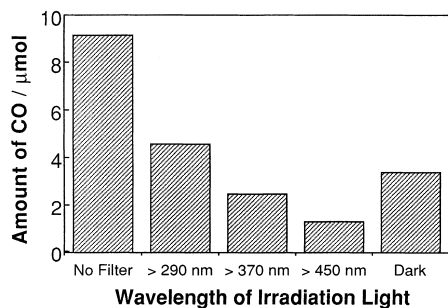


Fig. 1. The dependence of the amount of CO production on the wavelength of the irradiation light over Rh(1)/TiO₂. A shorter part of the wavelength region of the irradiation light was cut-off by a series of optical glass filters. Dark reaction was executed in a water bath at 323 K. Reaction time was 6 h. Initial amounts of CO₂ and H₂ were 150 and 50 μmol , respectively.

concluded that the CO obtained here comes from CO₂, and that this reaction is a reduction of CO₂ by H₂.

The dependence of the reaction on the wavelength of irradiation light was investigated by cutting off a part of the wavelength region of the irradiation light by a series of optical glass filters. Apparently, the activity towards CO production decreased when the irradiation light was filtered on the longer wavelength as shown in Fig. 1. Since the temperature of the reactor was not so different from each other between the case with or without any optical filters, the change in the activity observed here may be due to the change in the wavelength of light rather than in the heat supplied by irradiated light. This result leads us to the conclusion that some photochemical processes are included in this reaction. However, it is not a pure photoreaction because significant amount of CO was produced even when no irradiation was supplied with the reactor slightly temperature-elevated in the water bath (323 K). The amount of CO production in the dark was larger than that with a glass filter cutting $\lambda < 370$ nm or $\lambda < 450$ nm. This is not surprising considering that the temperature of the reactor was lower than 323 K under photoirradiation. From these results, we claim that the CO₂ reduction by H₂ on Rh/TiO₂ is a photo-enhanced reaction similar to the concept suggested with Ru loaded TiO₂ [12,13].

Fig. 2 shows the time course of CO production over Rh(1)/TiO₂ under continuous photoirradiation. In the earlier stage of photoreaction, the amount of CO naturally increased with time; however, the increase stopped about 10 h after the photoirradiation started. On the contrary, the decrease in the amount of CO which ought to be once produced was observed. Along with the decrease of CO, the increase of CH₄ production was indeed observed, but the amount of produced CH₄ was far smaller than that of CO decrease. For this reason we cannot assume that CO is converted to CH₄ by hydrogenation during the long irradiation. As a consequence, it must be hypothesized that the Rh/TiO₂ absorbed the CO. Detailed discussion will be found in the following section.

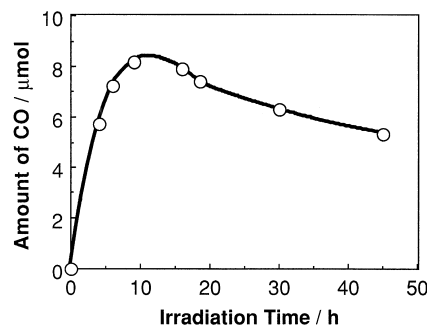


Fig. 2. Time dependence of CO formation (the amount of CO detected in the gas phase in the reactor) over Rh(1)/TiO₂ under irradiation. Initial amounts of CO₂ and H₂ were 150 and 50 μmol , respectively.

3.2. CO₂ photoreduction over various Rh/TiO₂ samples

As described in Section 2, the Rh/TiO₂ sample was reduced by H₂ at 523 K after the oxidation by O₂ at 673 K as a pretreatment before photoreactions. We investigated the effect of H₂ reduction of the Rh/TiO₂ sample in the pretreatment by varying the temperature of H₂ treatment on the Rh(1)/TiO₂. The result is shown in Fig. 3. From this, we can notice that the increase in the reduction temperature above 523 K brings about the drastic decrease in the activity towards CO production. On the other hand, CH₄ production slightly increases when the reduction temperature increases. It suggests that the oxidation state of Rh in Rh(1)/TiO₂ sample controls the selectivity of CO₂+H₂ photoreaction as well as the activity of the reaction. In a word, it seems that when Rh remains oxidized in a proper degree, the activity towards CO production is high. However, when no H₂ treatment was given (i.e., Rh was in a fully oxidized state), the activity was very low either towards CO or CH₄ production: the amount of yielded CO and CH₄ were only 0.2 and 0.1 μmol , respectively. From this, the following ideas are implied: (1) when Rh in Rh/TiO₂ is moderately reduced, the Rh/TiO₂ sample shows the highest activity towards CO production, and (2) as Rh in Rh/TiO₂ is reduced excessively,

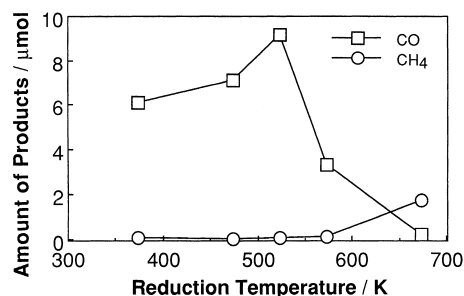


Fig. 3. The amounts of CO and CH₄ yielded after 6 h photoreaction over Rh(1)/TiO₂ samples reduced by H₂ at various temperatures. Initial amounts of CO₂ and H₂ were 150 and 50 μmol , respectively.

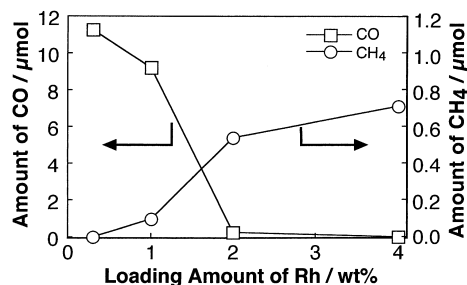


Fig. 4. The amounts of CO and CH₄ yielded after 6 h photoreaction over Rh/TiO₂ samples with various amounts of Rh loading. Initial amounts of CO₂ and H₂ were 150 and 50 μmol, respectively.

the product selectivity shifts from CO to CH₄ along with the decrease in the activity.

We investigated the effect of the loading amount of Rh on the reaction activity and selectivity with the temperature of H₂ reduction treatment fixed to 523 K. Fig. 4 shows the amount of yielded CO and CH₄ over Rh/TiO₂ samples with various amounts of Rh loading after 6 h irradiation. The increase in Rh loading resulted in the decrease in CO evolution. When the amount of Rh increased, thermodynamically preferable CH₄ was yielded rather than CO, although the absolute amount of CH₄ evolution was small. The effect of an increase in the loading amount of Rh seems similar to that of the reductions at higher temperature than 523 K on Rh(1)/TiO₂. From this, it is assumed that the variation of the loading amount causes the change of the state of Rh on TiO₂. When the amount of Rh loading is low, Rh may be in a moderately reduced state on the surface of TiO₂ and assist to produce CO.

3.3. X-ray absorption spectra of Rh/TiO₂ samples

To clarify the assumption mentioned above, we recorded the Rh K-edge X-ray absorption spectra and elucidated the state of Rh on various Rh(X)/TiO₂ (X=0.5–4) samples after pretreatment.

Fig. 5(A) shows the Rh K-edge XANES spectra of Rh/TiO₂ sample with various amounts of Rh loading together with those of Rh foil and Rh₂O₃ as references. Looking at the series of the spectra, we can see that the shape of the spectrum of Rh(4)/TiO₂ is similar to that of Rh foil, and that the shape of the spectra changes gradually to that of rhodium oxide with the increase of loaded Rh.

There have been reports concerning that the XANES spectrum of a sample containing an element in a mixture of different states can be simulated by the linear combination of the spectra of reference compounds corresponding to each oxidation state [21,22]. So we also tried to reproduce the XANES spectra of the Rh/TiO₂ samples by the superposition of the spectra of reference compounds with a suitable ratio. Fig. 6 shows the original XANES spectra of the samples with the simulated ones using Rh₂O₃ and Rh foil as reference compounds. This clearly indicates that the

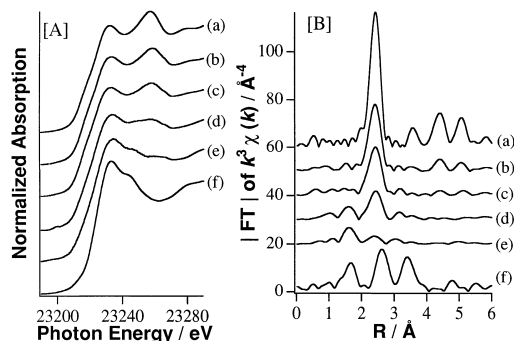


Fig. 5. (A) Rh K-edge XANES spectra and (B) Fourier transforms of k^3 -weighted Rh K-edge EXAFS spectra of several Rh/TiO₂ samples. The samples were (a) Rh foil, (b) Rh(4)/TiO₂, (c) Rh(2)/TiO₂, (d) Rh(1)/TiO₂, (e) Rh(0.5)/TiO₂ and (f) Rh₂O₃.

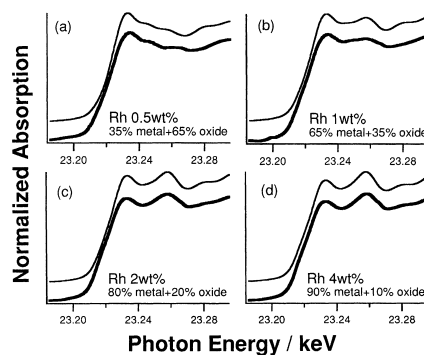


Fig. 6. Experimental (thick curve) and simulated (thin curve) Rh K-edge XANES spectra of Rh/TiO₂ with various amounts of Rh loading after pretreatment: (a) Rh(0.5)/TiO₂, (b) Rh(1)/TiO₂, (c) Rh(2)/TiO₂ and (d) Rh(4)/TiO₂. The simulated spectra were obtained by the linear combination of the XANES spectra of Rh foil and Rh₂O₃.

increase in the Rh loading is responsible for the growth of Rh in a metallic state. It is also shown that even the Rh(0.5)/TiO₂ sample contains 35% of metal.

On the other hand, Fourier-transforms of k^3 -weighted Rh K-edge EXAFS spectra of the Rh/TiO₂ samples and reference compounds mentioned above are shown in Fig. 5(B). While the peak at around 2.4 Å assigned to metallic Rh–Rh bond is very weak in Rh(0.5)/TiO₂, it is enhanced together with the increase in the amount of loaded Rh. The peak at around 1.6 Å is assigned to Rh–O bond, and the intensity of the peak decreases as the amount of Rh increases. The sample richest in Rh, Rh(4)/TiO₂, shows almost no peak at around 1.6 Å.

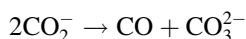
From the above-mentioned results obtained by the XAS experiments, we concluded that the highly active sample for the CO₂+H₂ photoreaction keeps Rh in a state of the mixture of metal and oxide. The state of Rh involves the selectivity of products also: the more the Rh is reduced, the more is CH₄ produced rather than CO. The former notion is again very similar to that proposed by Thampai et al. [12,13] with Ru/TiO₂ sample.

4. Discussion

4.1. Possible reaction mechanism of CO₂ and H₂ reaction on Rh/TiO₂

As described above, the reaction between CO₂ and H₂ over Rh/TiO₂ is enhanced by irradiation. We suppose that the light is absorbed by TiO₂ rather than Rh because no reaction proceeded when Rh/SiO₂ is used instead of Rh/TiO₂. Probably the light generates a pair of an excited electron and a positive hole in TiO₂. The electron moves to Rh to be injected into CO₂ adsorbed on Rh, and the CO₂ is activated to become CO₂⁻. This process has been proposed in the literature [15]. On the other hand, H₂ is adsorbed on Rh dissociatively, and the dissociated hydrogen may migrate onto TiO₂ surface to react with the positive hole. This process results in the formation of H⁺, which may be bound with an oxygen of TiO₂ to form surface hydroxyl group. In such a way the charge will be separated effectively.

As the possibility of the evolution of CO from CO₂⁻, the following reaction has been proposed on K-promoted Rh metal surface [23]:



That is, the disproportionation reaction of two CO₂⁻ anion radicals into CO and carbonate. As the carbonate species will exist in a stable form on TiO₂ surface, the migration of CO₃²⁻ species to TiO₂ surface will further help the above disproportionation reaction.

However, it should be kept in mind that there is a possibility of the CO production via any intermediate such as a formate ion. The CO₂⁻ radical is thought to be more reactive with hydrogen than a neutral CO₂, and the most plausible product in the first step of CO₂ hydrogenation is the formate ion. The formation of the formate ion from CO₂ and H₂ in a thermal reaction on supported Rh has already been reported [24]. The formate is known to decompose rather easily to yield CO. Since the evolution of CO was practically observed on Rh/TiO₂ under irradiation using formic acid together with H₂ as a reactant, we guess that this mechanism is preferable to that explained from the disproportionation of CO₂⁻ radical.

4.2. Changes in activity and selectivity over several samples

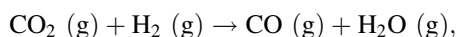
We have found that when Rh is in a partially reduced state, Rh/TiO₂ shows a high activity in the reaction between CO₂ and H₂ to yield CO. On the contrary, when Rh is reduced to a metallic state, the activity is low and the main product is not CO but CH₄. This phenomenon can be expressed from the differences in the ability of H₂ dissociation. When Rh is in a partially reduced state, the H₂ dissociation ability of the Rh is suppressed at a suitable degree. When Rh is fully reduced to a metallic state, the H₂ dissociation ability is too strong, and the dissociated hydrogen not only accepts the positive

hole but also reacts with negatively charged CO₂⁻ to hydrogenate it. If the hydrogenation of CO₂⁻ is completed, the product CH₄ will be released to the gas phase; however, it is suggested that the CO₂⁻ is not easily hydrogenated to CH₄ but remains on the surface as a form of CH_x, because when Rh is fully reduced, the amount of CH₄ is small while the evolution of CO remarkably decreases. This excessive hydrogenation reaction cannot proceed via CO as an intermediate because CO and H₂ did not react on Rh/TiO₂ under irradiation at room temperature.

According to the above view, however, the difference of Ru and Rh in the selectivity in CO₂+H₂ reaction cannot be explained. In addition, one cannot illustrate the reason why the highly reduced Ru/TiO₂ does not exhibit higher activity in CH₄ production than partially reduced one. From this, it should be concluded that the oxide state plays an important role as a promoter in some steps of the reaction. Although it is not clear in which step the oxide state works effectively, it may assist the redox reaction between CO₂ and H₂ by changing its oxidation state.

4.3. CO₂ reduction with H₂ in the dark

Fig. 1 shows the result of CO₂+H₂ reaction under irradiation of several parts of wavelengths, as well as in the dark. It is noteworthy that CO is yielded as a main product of CO₂ reduction even in the dark. CO is an unreasonable product considering the thermodynamic equilibrium of the reverse water-gas shift reaction



$$\Delta G = 28.6 \text{ kJ/mol at } 298.15 \text{ K}$$

at room temperature (or at 323 K). This contradiction indicates the removal of one (or two) product(s) which causes the shift of the equilibrium to the right.

It is thought that the surface of TiO₂ is highly dehydrated after the evacuation at high temperature in the pretreatment. Hence, significant amount of surface hydroxyl group can be produced newly on TiO₂. As H₂ directly forms surface hydroxyl group during the CO₂+H₂ reaction according to the reaction mechanism we proposed in the previous section, it is thought that H₂O need not be released into the gas phase in the dark reaction for a while.

The amount of CO increased from 3.4 to 5.1 μmol when the reaction time was extended from 6 to 24 h in the dark at 323 K. However, the reaction rate is small compared to the case under irradiation. Therefore we have claimed that the reaction is a “photo-enhanced reaction” as Thampi et al. [12,13] previously declared. It should be noted that the dark reactions were performed at 323 K. This temperature is rather higher than the temperature of the reaction system under irradiation. Hence, the amount of CO produced in the dark may be less than 3.4 μmol for 6 h reaction. When the Y-45 optical filter was put to use (i.e., the light with wavelength longer than 450 nm was irradiated), the amount of CO was only 1.4 μmol even under irradiation, although the tempera-

ture of the reactor was not very different from each other under irradiation using any optical filter. Thus the value of $1.4\text{ }\mu\text{mol}$ is to be considered as the contribution of the CO evolution by the dark reaction under photoirradiation, since the light with wavelength longer than 450 nm does not contribute to the excitation of TiO_2 . From this, the amount of CO by pure photoreaction should be $7.8\text{ }\mu\text{mol}$ for 6 h reaction, because the total amount of evolved CO is $9.2\text{ }\mu\text{mol}$ and the amount of CO produced by the dark reaction is $1.4\text{ }\mu\text{mol}$. Therefore, the ratio of the production of CO by the dark reaction to that of the photoreaction under irradiation without any filter is calculated to be only 18%.

4.4. The change of Rh/TiO₂ during photoreaction

As depicted in Fig. 2, we can understand that CO is once yielded at the earlier stage of the reaction, but removed from the gas phase afterwards. It suggests that CO is adsorbed to Rh/TiO₂ or converted to other compounds. Between these two possibilities, the former one (i.e., simple adsorption process) should be excluded. If the adsorption was the main reason, a part of produced CO might have immediately been adsorbed on Rh/TiO₂ after its production, and the other part might have been released to the gas phase since the rate of CO adsorption was thought to be enough fast. Therefore the amount of CO might increase monotonously. In practice, however, the amount of CO in the gas phase decreased after reaching the maximum amount. Hence the simple adsorption should not be the reason of this peculiar behavior. This leads us to the conclusion that CO is converted to other compounds during the long period of reaction.

Many investigators have reported that Rh forms rhodium carbonyl clusters under CO atmosphere [25]. Considering that, we prospected the formation of $\text{Rh}_m(\text{CO})_n$ species during the photoreaction because in later part of the photoreaction the Rh/TiO₂ sample is surrounded with gaseous CO produced in the reaction. The conversion of Rh into $\text{Rh}_m(\text{CO})_n$ species can also be the reason of the decrease in the activity towards CO production. Accordingly, the rapid decrease of gaseous CO after long time irradiation can be successfully explained: the rapid decrease of CO is brought about both by the reaction between Rh and CO, and by the decline of the production of CO.

The formation of $\text{Rh}_m(\text{CO})_n$ is supported by the desorbed gases by heat treatment at 573 K after photoreaction. The main component of the desorbed gases by heat treatment was CO. This indicates that more amount of CO exists on the surface of Rh/TiO₂, although it is not clear in which form they exist on the surface. However, taking it into consideration that the $\text{Rh}_m(\text{CO})_n$ species was decomposed at temperature up to ca. 573 K [26], the carbonyl cluster is one of the candidates of the compounds formed during photoreaction on the surface.

Furthermore, the XANES spectrum of Rh/TiO₂ also suggests the change of the state of Rh before and after photoreaction. The XANES spectra of Rh(1)/TiO₂ and

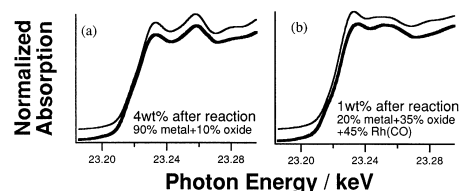


Fig. 7. Experimental (thick curve) and simulated (thin curve) Rh K-edge XANES spectra of (a) Rh(4)/TiO₂ and (b) Rh(1)/TiO₂ after photoreaction. The simulated spectra were obtained by the linear combination of the XANES spectra of (a) Rh foil and Rh₂O₃, and (b) Rh foil, Rh₂O₃ and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$.

Rh(4)/TiO₂ after photoreaction and their simulation spectra using those of reference compounds are shown in Fig. 7. A good fitting result was achieved in the case of Rh(4)/TiO₂ (Fig. 7(a)), while in Rh(1)/TiO₂ the fitting with the spectra of Rh foil and Rh₂O₃ as the reference compounds did not get along well. Taking into account that the spectrum of Rh(1)/TiO₂ before photoreaction could be fit with those of the reference compounds, we concluded that another chemical species than a metal or an oxide formed on Rh(1)/TiO₂ during the photoreaction. It is supposed that the other species is the compound made of Rh and CO. Therefore, we tried to simulate the XANES of Rh(1)/TiO₂ after photoreaction using the spectrum of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ along with Rh foil and Rh₂O₃. The result was a little better than that without $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ as shown in Fig. 7(b). This suggests the formation of rhodium carbonyl compounds in a sense. However, we should not establish the existence of the compounds simply because of the success in the simulation of XANES spectrum by $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. It is only a reinforcement of the hypothesis and the speculation.

The above results are, of course, not enough for the evidences pointing out that rhodium carbonyl compounds form on Rh/TiO₂. However, it is certain that the compound to which CO is converted does not relate to the reaction path of CO₂ photoreduction by H₂: the compound is yielded after the production of CO from CO₂ and H₂. Therefore, if we can remove CO from the reactor by some chemical engineering methods, the photoreaction possibly proceeds continuously because the change in the state of Rh can be avoided.

5. Conclusion

Rh-loading TiO₂ is found to show high activity towards photoreduction of CO₂ by H₂ under mild condition of low pressure and room temperature. When Rh on TiO₂ is in a mixture of metal and oxide, the high activity towards CO₂ photoreduction by H₂ to CO is observed. When Rh is fully reduced, the activity is drastically lowered in addition to the change of the main product from CO to CH₄. This change can be explained by the suppression in the H₂ dissociation ability by Rh in an oxide state as well as the effect of the oxide state as a promoter. The deactivation of the sample and the decrease of once produced CO during a long period of

reaction are both illustrated from the formation of rhodium carbonyl compounds from Rh and CO.

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