

Photoenhanced reduction of CO₂ by H₂ over Rh/TiO₂ Characterization of supported Rh species by means of infrared and X-ray absorption spectroscopy

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Abstract

Rh/TiO₂ samples, which have been found to be effective for photoenhanced reduction of CO₂ by H₂, were characterized by means of infrared spectroscopy and X-ray absorption spectroscopy. Infrared study revealed that adsorbed CO arose even on a strongly reduced samples which showed low activity toward the reaction. Taking the results of X-ray absorption into consideration, it was proposed that the mixture of rhodium in metallic and oxidized states was effective for the release of the adsorbed CO to the gaseous phase. Infrared and X-ray absorption studies further showed that prolonged photoreaction caused the decrease in the particle size of rhodium, and consequently, the ability for the electron transfer from Rh/TiO₂ to adsorbates. This is the reason for the deactivation observed during the photoreaction. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic conversion of carbon dioxide to more valuable compounds is a challenging theme of chemistry. From the viewpoint of both environmental problem and scientific interest, great advantage will be found in the reduction of carbon dioxide. Many ways have been tried for the conversion of carbon dioxide so far [1]. Among them, photo-induced catalytic reduction of carbon dioxide is attractive because the reaction proceeds under mild conditions of low pressure and room temperature with the help of photoenergy.

Solymosi and Klivényi reported that carbon dioxide adsorbed on potassium promoted rhodium metal can be activated by irradiation [2,3]. Rhodium supported on titanium oxide has also been found to have an ability to activate carbon dioxide under irradiation [4,5]. Irradiation of titanium oxide brings about the excited electron, which flows from the titanium oxide to rhodium. The injection of electron to rhodium enhances the donation of electron from rhodium to carbon dioxide, resulting in the formation of a partially negatively charged CO₂^{δ-}. Considering this, one can expect the photocatalytic activity of rhodium loading titanium oxide.

In practice, as a photocatalyst, Rh/TiO₂ coated by NaOH has been found to be active for the photodecomposition of water to H₂ and O₂ [6]. Solymosi and Tombácz also reported photoreduction of aqueous

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carbon dioxide using Rh/TiO₂ and obtained formic acid as a main product [7].

We previously reported that Rh/TiO₂ showed high activity for the reduction of CO₂ to CO using H₂ as a reductant [8]. Since the reaction was enhanced by photoirradiation, it is one of so called “photoenhanced reactions”, like the methanation of CO₂ by H₂ over Ru-loading TiO₂ [9,10].

A drastic decrease in the activity and the shift of the main product from CO to CH₄ were observed along with the increase in the reduction temperature of Rh/TiO₂ by H₂ from 523 to 673 K in the pretreatment. A similar effect was obtained when increasing the loading amount of rhodium from 1 to 4 wt.%. X-ray absorption spectroscopic study revealed that rhodium became more metallic as the loading amount increased. The sample with 1 wt.% of rhodium contained a mixture of both metallic and oxidized states of rhodium. It was concluded that rhodium in a mixture of metal and oxide led to the selectivity toward CO and the high activity of Rh/TiO₂ sample in the photoreduction of CO₂. The change in the activity and selectivity in catalysis caused by the change in the oxidation state of rhodium has been proposed by several groups [9–12]. However, it is still unclear why a mixture of oxide and metal is effective. We made speculation in the previous report [8] that oxide may play an important role as a promoter in some steps of the reaction.

We also observed a deactivation of the highly active Rh/TiO₂ sample during the photoreaction between CO₂ and H₂, together with the decrease in gaseous CO once produced by the reaction of CO₂ and H₂. For the reason of this deactivation, a formation of some rhodium carbonyl clusters during the reaction was proposed, although such species was not detected directly.

In this study, we try to confirm by infrared spectroscopy whether CO is formed or not under CO₂ and H₂ atmosphere on samples in several oxidation states. In the infrared spectroscopy, we observe the changes occurring on rhodium caused by photoirradiation using adsorbed CO as a probe molecule. The change in the state of rhodium is directly detected by X-ray absorption spectroscopy. The difference in the state of rhodium among several Rh/TiO₂ samples as well as the change caused by photoirradiation is discussed using the X-ray absorption spectra and the infrared spectra. These information will help understand the reason why the mixture of metallic and oxidized Rh

brings about high activity, and why the sample is deactivated during the photoreaction.

2. Experimental

Rh/TiO₂ sample was prepared by the impregnation method described elsewhere [8]. Briefly, TiO₂ supplied from Japan Catalysis Society (JRC-TIO-4) was impregnated with an aqueous solution of RhCl₃·3H₂O (Wako Chemical Co.), followed by calcination at 773 K for 5 h. The loading amount of rhodium was 1 or 4 wt.% as metal. Hereafter, Rh(X)/TiO₂ denotes the sample containing X wt.% of rhodium.

Infrared spectra were recorded using a Perkin-Elmer PARAGON 1000 PC Fourier transformed infrared spectrometer in a transmission mode. The Rh/TiO₂ sample (ca. 60 mg) was pressed into a disk (20 mm in diameter) and then set in a holder made of quartz. The holder was suspended with a platinum wire in the quartz cell described elsewhere [13], the inner volume of which was 188 cm³. By moving the holder with the sample to proper positions, a pretreatment, introduction of reactant gases, photoirradiation and recording spectra could be carried out in situ. As a pretreatment prior to recording spectra, the sample was evacuated and treated with 8 kPa O₂ at 673 K for 1 h, followed by reduction with 8 kPa H₂ for 2 h and evacuation at given temperatures. Hereafter, Rh/TiO₂-Y means the sample treated by H₂ at Y K. After cooling down the sample to room temperature, a mixture of CO₂ and H₂ (CO₂/H₂ ≈ 1, total pressure was ca. 5 kPa) were introduced into the cell. Photoirradiation was given at room temperature using a 250 W ultrahigh pressure mercury lamp (USHIO USH-250D) as a light source.

Rh K-edge X-ray absorption spectra were recorded on the beam line BL01B1 at SPring-8 (Hyogo, Japan) with a ring energy of 8 GeV and a beam current of 80–100 mA (proposal no. 2000A0241). All spectra were recorded in a transmission mode at room temperature with a Si (3 1 1) two crystal monochrometer. Before recording the spectra, samples were treated with 8 kPa O₂ at 673 K and 8 kPa H₂ at given temperatures in the same manner as the sample for IR measurement. Some samples were irradiated with a 500 W ultrahigh pressure mercury lamp (USHIO USH-500D) at room temperature. The sample was then transferred into the XAFS cell without exposing to the air. 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 [14].

3. Results and discussion

3.1. Infrared spectroscopy

We first recorded infrared spectra of Rh/TiO₂ samples and tried to detect changes caused by the introduction of reactant, CO₂ and H₂. Spectra (a) and (b) in Fig. 1 indicate infrared spectra of Rh(1)/TiO₂-523 sample in the absence and presence of CO₂ and H₂, respectively. In the spectrum (b), bands appearing at wavenumbers lower than 1700 cm⁻¹ can be assigned to various carbonates adsorbed on TiO₂ surface [15]. Two strong absorption bands were observed at 2350 and 2064 cm⁻¹. The former one disappeared by the evacuation of gaseous CO₂, and should be assigned to the molecularly adsorbed CO₂ [16]. The latter one was attributed to linearly adsorbed CO on metallic rhodium species [17]. The absorption frequency lower than that of gaseous CO (2143 cm⁻¹) indicates an effect of electron transfer from metal to CO. The production of adsorbed CO simply by the introduction of CO₂ and H₂ suggests that the reaction between CO₂ and H₂ proceeds in the dark to produce CO. This agrees well with our previous finding that the reaction proceeds without photoirradiation [8]. In the region at around 3500 cm⁻¹, we can see an increase in the absorption intensity by adsorbed water molecule on TiO₂ after

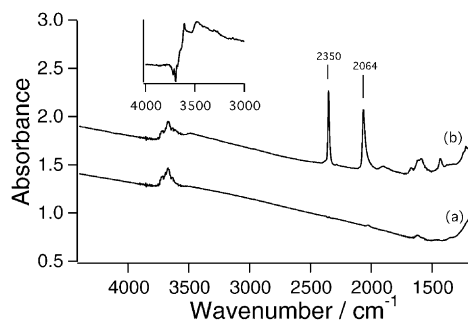


Fig. 1. Infrared spectra of Rh(1)/TiO₂-523 samples (a) in the absence and (b) in the presence of CO₂ and H₂. The inset depicts the difference spectrum between (a) and (b).

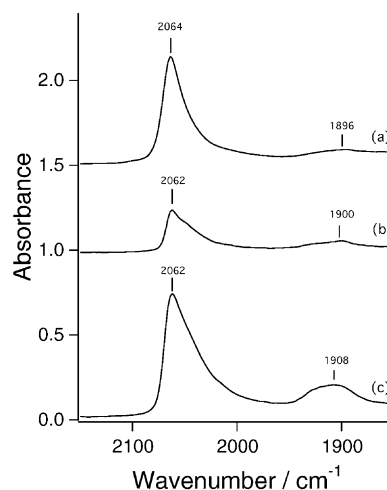


Fig. 2. Infrared spectra of adsorbed CO produced in the CO₂ and H₂ atmosphere on (a) Rh(1)/TiO₂-523, (b) Rh(1)/TiO₂-673 and (c) Rh(4)/TiO₂-523.

the introduction of CO₂ and H₂, as shown in the inset of Fig. 1. The formation of adsorbed water suggests that the reduction of CO₂ by H₂ proceeds to yield H₂O which is immediately adsorbed on the TiO₂ surface.

Fig. 2 illustrates infrared spectra of various Rh/TiO₂ samples in the CO₂ and H₂ atmosphere in the dark. The adsorbed CO was observed on all Rh/TiO₂ samples. In spectrum (a), the peak located at 2064 cm⁻¹ was attributed to linearly adsorbed CO on Rh(1)/TiO₂-523. In addition to this peak, we can see a rather weak one at around 1900 cm⁻¹ which should be assigned to bridging CO, i.e. Rh–CO–Rh [18]. On the other hand, it has been shown from XAFS and IR studies that supported rhodium is dispersed atomically under CO atmosphere and becomes rhodium(I) *gem*-dicarbonyl species, Rh^I(CO)₂ [19,20]. In our case, however, since a pair of absorption peaks at 2100 and 2030 cm⁻¹ characteristic of that species were missing, rhodium was not atomically dispersed as rhodium(I) *gem*-dicarbonyl but existed as a particle. It is reported that the coexistence of hydrogen inhibits the formation of the rhodium(I) *gem*-dicarbonyl species [21].

Spectra (b) and (c) correspond to Rh(1)/TiO₂-673 and Rh(4)/TiO₂-523 in the CO₂ and H₂ atmosphere, respectively. We have already reported that both of these samples show very low activity for the photoreduction of CO₂ to CO by H₂ [8]. However, the

infrared spectra indicate the existence of significant amount of adsorbed CO on both samples in the presence of CO₂ and H₂ at room temperature. Thus, the reason for the low activity of these sample is not the lack of ability to reduce CO₂ to CO. In the thermal hydrogenation reaction of CO₂ on several supported rhodium catalysts including Rh/TiO₂, the reaction rate of CO₂ hydrogenation is higher than that of CO hydrogenation [12,22,23]. Therefore, the reduction of CO₂ to yield adsorbed CO can be considered as a relatively easy step on Rh/TiO₂. From this, we guess that the difference in the activity among Rh/TiO₂ samples is due to the ability to release the adsorbed CO to the gaseous phase.

In order to investigate the influence of photoirradiation on the Rh/TiO₂ sample, we tried to detect the change in the spectra during photoreaction of CO₂ and H₂. The results are shown in Fig. 3. When Rh(1)/TiO₂-523 sample was irradiated in the presence of CO₂ and H₂, the wavenumber of the adsorbed CO shifted to higher value. On the other hand, apparent wavenumber shift of the adsorbed CO was not seen even under irradiation on Rh(1)/TiO₂-673 sample which showed low activity. Generally, the wavenumber of adsorbed CO on rhodium is lower than that of gaseous CO because of an electron transfer from rhodium to CO. Therefore, the higher wavenumber of CO corresponds to a weakness of the electron transfer from rhodium. Although the frequency of the adsorbed CO reflects the surface coverage of CO [17], in this case the absorbance of the adsorbed CO

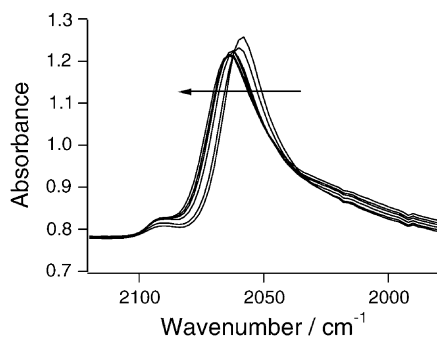


Fig. 3. Change in the infrared spectra of adsorbed CO on Rh(1)/TiO₂-523 caused by photoirradiation for 0, 5, 20, 40, 70, 140 min. Photoirradiation of the sample was carried out in the presence of CO₂ and H₂. The adsorbed CO was produced in the dark under CO₂ and H₂.

was neither enhanced nor reduced by the irradiation. Hence, the amount of adsorbed CO did not change drastically. We can accordingly exclude the possibility that the increase in the amount of adsorbed CO resulted in the weakening of the electron transfer. Therefore, the frequency shift is supposed to be caused by the change in the state of Rh/TiO₂.

As Raskó and Solymosi have suggested in their article [5], we also believe that the electron transfer from Rh/TiO₂ to CO₂ takes place in the first step of the photoreduction of CO₂. Since, the electron transfer from Rh to adsorbed CO was weakened during the photoreaction, a weakening of the electron transfer to CO₂ may also occur during the photoreaction, although such a sign was not detected in the present IR spectra. The weakening of the electron transfer from Rh/TiO₂ means the decrease in the ability to reduce CO₂. Therefore, we concluded that the weakening of the electron transfer caused the deactivation of Rh/TiO₂.

3.2. X-Ray absorption spectroscopy

X-Ray absorption spectra are considered to reflect an electronic state of the sample as well as a local coordination environment. Therefore, we recorded X-ray absorption spectra of several Rh/TiO₂ samples at Rh K-edge to observe directly the electronic and structural state of rhodium.

Fig. 4(A) represents the X-ray absorption near edge structure (XANES) spectra of Rh(1)/TiO₂ samples

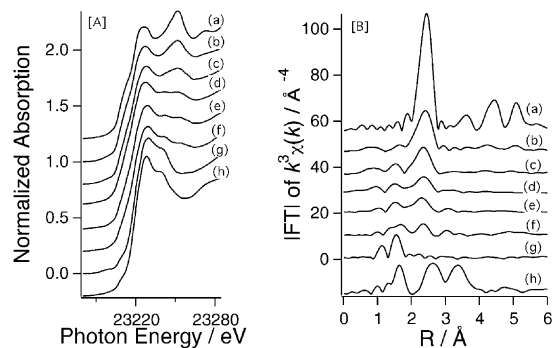


Fig. 4. (A) Rh K-edge XANES spectra and (B) Fourier transforms of k^3 weighted Rh K-edge EXAFS spectra of several Rh/TiO₂ samples. The samples were: (a) Rh foil; (b) Rh(1)/TiO₂-673; (c) Rh(1)/TiO₂-573; (d) Rh(1)/TiO₂-523; (e) Rh(1)/TiO₂-473; (f) Rh(1)/TiO₂-373; (g) Rh(1)/TiO₂ without reduction and (h) Rh₂O₃.

reduced by H_2 at various temperatures from 373 to 673 K, including the sample without reduction. The spectra of rhodium metal and Rh_2O_3 were also illustrated in the figure as references. The spectrum of the sample without reduction by H_2 resembles that of Rh_2O_3 , indicating that most of rhodium atoms are in an oxidized state. As the reduction temperature increased, the shape of the spectra approached that of rhodium metal. From this, it is concluded that rhodium is gradually reduced to a metallic state along with the increase in the reduction temperature.

In the previous study [8], the activity of these samples towards the photoreduction of CO_2 by H_2 has been compared. The most active $Rh(1)/TiO_2-523$ sample contains a mixture of rhodium in metallic and oxidized states. We can guess that the mixed state of metallic and oxidized rhodium on TiO_2 brings the high activity for the CO_2 reduction by H_2 . On the other hand, the results shown in Fig. 2 suggested that desorption process of CO adsorbed on (metallic) rhodium was difficult on highly metallic Rh/TiO_2 samples so that these samples showed poor activity. Taking these into consideration, the rhodium in an oxide state is supposed to work as a promoter to drive out the CO adsorbed on Rh particle to gaseous phase.

Fig. 4(B) illustrates Fourier transforms of extended X-ray absorption fine structure (EXAFS) spectra of the $Rh(1)/TiO_2$ samples reduced at various temperatures. A peak at around 2.4 \AA is assigned to Rh–Rh bonding. Along with the increase in the reduction temperature, the Rh–Rh peak was enhanced. This reflects the increase in the particle size of rhodium in accordance with the increase in the reduction temperature.

We have already observed that the main product of CO_2 photoreduction by H_2 is CO over the $Rh(1)/TiO_2-523$ sample whereas the main product becomes CH_4 over the $Rh(1)/TiO_2-673$ sample [8]. According to Kusama et al. [24], the particle size influences the product selectivity in the CO_2 hydrogenation reaction over Rh/SiO_2 , where the main product shifts from CO to CH_4 by the increase in the rhodium particle size. Applying this idea, we can successfully explain the change in the selectivity caused by the reduction temperature.

Changes in the X-ray absorption spectra during the photoreaction were also investigated. Fig. 5(A) represents the XANES spectra of $Rh(1)/TiO_2-523$ samples before and after photoreaction. Changes

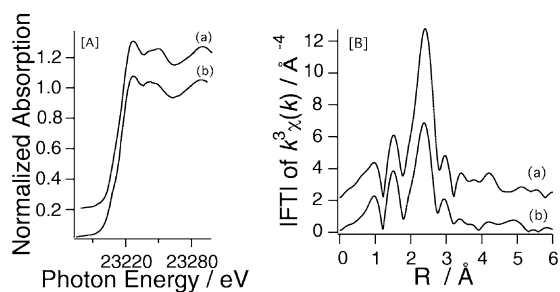


Fig. 5. (A) Rh K-edge XANES spectra and (B) Fourier transforms of k^3 weighted Rh K-edge EXAFS spectra of $Rh(1)/TiO_2-523$ (a) before and (b) after photoreaction of CO_2 and H_2 for 60 min.

caused by the photoreaction were indeed observed but small, suggesting that the difference in the oxidation state of rhodium is small between the samples before and after the photoreaction.

Fig. 5(B) shows the Fourier transforms of EXAFS spectra of $Rh(1)/TiO_2-523$ samples (a) before and (b) after photoirradiation in CO_2 and H_2 . The decrease in the intensity of the Rh–Rh peak at around 2.4 \AA is obviously seen. Taking into consideration that the XANES spectra did not change and that the oxidation state of rhodium was supposed to be identical during the photoreaction, this result indicates the decrease in size of rhodium particle. Therefore, we can conclude that rhodium particle is dispersed along with the reaction between CO_2 and H_2 . Since we scarcely observed the absorption band characteristic of $Rh^I(CO)_2$ species at 2100 and 2030 cm^{-1} in the infrared spectra even after photoirradiation in the CO_2 and H_2 atmosphere, rhodium on TiO_2 was not atomically dispersed. At the same time, the XANES spectra indicated that the oxidation state of rhodium was almost unchanged during the photoreaction. From these, it is concluded that the rhodium was dispersed during the photoreaction maintaining the (metallic) character of the original particle. The driving force of the dispersion of rhodium during the photoreaction is unclear. As CO tends to let supported rhodium be dispersed, it is suggested that CO produced by the photoreaction may cause the dispersion of rhodium particle.

The IR investigation revealed that the ability of rhodium for the electron transfer to adsorbates is diminished in accordance with the procedure of the reaction. This leads to the deactivation observed during the photoreaction of CO_2 over Rh/TiO_2 . From the

result of the X-ray absorption study, the deactivation can be attributed to the dispersion of rhodium during the reaction.

In the previous study, we proposed the formation of rhodium *gem*-dicarbonyl and related it to the deactivation, because we observed a decrease of once produced CO during the long period of the photoreaction [8]. However, we failed to detect a distinct formation of such $\text{Rh}^{\text{I}}(\text{CO})_2$ species by IR. Therefore, the formation of $\text{Rh}^{\text{I}}(\text{CO})_2$ should not be the reason both for the deactivation and for the removal of gaseous CO once produced during the photoreaction. The decrease in the amount of gaseous CO may be caused by the successive reduction of CO to, for example, CH_x species on the surface of Rh/TiO₂. The absence of C–H absorption bands of the CH_x on a rhodium catalyst supported on alumina is also reported [25]. This report is probably in agreement with the fact that we could not detect the CH_x species by IR.

4. Conclusion

A highly active Rh/TiO₂ sample for the photoreduction of CO₂ by H₂ contains a mixture of rhodium in metallic and oxidized states. Fully metallic samples also have an ability to reduce CO₂ to CO. However, on partially oxidized Rh/TiO₂ sample, the desorption of CO from the surface to the gaseous phase proceeds smoothly as well as the formation of the adsorbed CO. The rhodium *gem*-dicarbonyl species, $\text{Rh}^{\text{I}}(\text{CO})_2$, is scarcely formed during the reaction. The deactivation during the photoreaction is brought about by the dispersion of rhodium as a particle.

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