Reactivity of CO₂ and H₂O on TiO₂ catalysts studied by gas phase FT-IR method and deactivation mechanism

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Abstract. The photoreduction of CO₂ to hydrocarbons is a sustainable energy technology that not only reduces emissions but also the need for alternative fuels. Wide band-gap TiO₂ catalysts are considered the most convenient candidates in terms of cost and stability. In this work, anatase TiO₂ powder was deposited on a silica filter paper, and photoreduction experiments were carried out in an FT-IR gas reactor using CO₂ gas with 50% relative humidity as the reactant under the irradiation of a high pressure Hg lamp. CH₄ and CO were detected as the CO₂ reduction products. However, there was a gradual decrease in the amounts of CH₄ and CO that were produced, seemingly because of the deactivation of the anatase TiO₂ surface. We analyzed the surface chemical states using XPS analysis to consider the cause of the TiO₂ deactivation, and found that the amounts of –OH group had increased on the TiO₂ surface after Hg lamp irradiation. Considering the analysis results, we assumed a surface deactivation mechanism.

1. Introduction
Increasing levels of CO₂ in the atmosphere constitutes the main cause of global warming. Recently, many efforts have been made to reduce CO₂ emissions through pre- or post- combustion CO₂ capture followed by compression and geological sequestration [1-7]. These processes are energy intensive and costly. Specifically, there are many uncertainties with regard to the long-term storage of CO₂ geological formations. An alternative and preferable approach is to recycle CO₂ as a fuel feedstock with energy input from cheap and abundant sources, for example solar energy. The photoreduction of CO₂ to hydrocarbons is a sustainable energy technology. This process utilizes ultraviolet (UV) and visible light as the excitation source, and the photo-excited electrons reduce CO₂ with H₂O on the catalyst surface and form energy-bearing products such as carbon monoxide (CO), methane (CH₄), methanol (CH₃OH), formaldehyde (HCHO) and formic acid (HCOOH) [8-14]. A variety of photocatalysts have been studied [15-18], and among them, wide band-gap titanium dioxide (TiO₂) catalysts are considered the most convenient candidates in terms of cost and stability [19-21]. TiO₂ forms three distinct polymorphs: rutile, anatase and brookite [22, 23]. Anatase was one of the most widely studied photocatalysts for environmental applications and there have been many papers dealing with the photoreduction of CO₂ on TiO₂ catalysts of anatase [10-14]. However, although it has many potential applications, the wider practical use of TiO₂ requires a photo-response extended to longer wavelengths and increased photo-efficiency achieved by retarding electron-hole recombination. In addition, focusing on a catalyst’s photoreduction activity, it is reported that the amount of hydrocarbons produced gradually decreases, indicating TiO₂ deactivation [10, 24]. We obtained the
same deactivation results in this work, and so we performed several kinds of bulk analyses (X-ray diffraction (XRD) and diffuse reflectance UV-vis spectra (UV-vis) of samples before and after Hg lamp exposure to consider the cause of the TiO\textsubscript{2} deactivation. However, we could not determine any difference between the two samples. Next, we performed a surface analysis of samples before and after Hg lamp exposure using X-ray photoelectron spectroscopy (XPS) to consider the cause of the TiO\textsubscript{2} deactivation, and obtained different chemical states on an anatase TiO\textsubscript{2} surface before and after Hg lamp exposure. We consider the cause of the TiO\textsubscript{2} deactivation using these results.

2. Experimental

2.1. Sample preparation
Anatase TiO\textsubscript{2} and 2-propanol were obtained from Kanto Chemical Co. Inc., and used without further purification. We used a silica filter paper (QR-100; Advantec Toyo) cut into 20 × 20 mm\textsuperscript{2} squares as a substrate. We prepared a 10 ml 2-propanol suspension containing 0.1 g of anatase TiO\textsubscript{2}. The silica filter papers were immersed in a glass petri dish filled with the suspension, and then 2-propanol was slowly evaporated in a dry nitrogen gas flow for five days. After that we obtained the samples of anatase TiO\textsubscript{2} deposited on the silica filter paper.

2.2. Sample characterization
Surface image of the samples were obtained using a scanning electron microscope (SEM) (SU1510; Hitachi) and a laser microscope (VK-8500; Keyence). XRD patterns of the powders were recorded with a MiniFlexII (Rigaku) instrument using Cu-K\textsubscript{α} radiation. XPS analysis of the samples was performed with a PHI XPS5700 system using AlK\textsubscript{α} radiation (1486.6 eV). The photoelectron spectra were measured for C 1s, O 1s, and Ti 2p core levels. A diffuse reflectance UV-vis spectrometer (U-4100, Hitachi) was used to obtain the UV-vis spectra of the TiO\textsubscript{2} samples before and after Hg lamp irradiation.

2.3. Photocatalytic performance evaluation
We used a commercially available Fourier transform infrared spectroscopy (FT-IR) instrument (Nicolet iS10; Thermo Fisher Scientific) and designed an FT-IR reactor system to realize a photocatalytic reaction based on the FT-IR instrument. The system was not the flow system and was shown in Figure 1. The gas reactor was a glass cylindrical cell with two lengths of glass tube equipped with taps, and it was 32 mm in diameter and 100 mm long. We equipped both sides of the cell with BaF\textsubscript{2} windows, because BaF\textsubscript{2} has a high transmittance of near IR light up to about 1000 cm\textsuperscript{-1}. The light source for the photocatalytic reaction was a high pressure Hg lamp (UM-102, Ushio Inc.) and the output power was 100 W. First, we placed the TiO\textsubscript{2} deposited silica filter paper in the gas reactor. Next, compressed CO\textsubscript{2} (99.995%, Taiyonissann Inc.) controlled by a mass flow controller, was passed through a water bubbler to generate a mixture of CO\textsubscript{2} and water vapor (relative humidity: 50%). The CO\textsubscript{2} gas with 50% relative humidity was then introduced into the cylindrical gas reactor. We replaced the gas in the cylindrical gas reactor three times with generated CO\textsubscript{2} gas that has 50% relative humidity, and after that we closed the two taps of the cylindrical gas reactor. UV light was irradiated through the BaF\textsubscript{2} window using the high pressure Hg lamp. The light intensity of the lamp on the catalyst was 1.1 mW/cm\textsuperscript{2} at 365 nm as measured by a spectroradiometer (USR-45; Ushio Inc.). Hourly FT-IR measurements were carried out, and the concentrations of the generated CO, CH\textsubscript{4}, CH\textsubscript{2}OH, HCHO, and HCOOH gases in the gas reactor were calculated from the absorption differences of 2165.5, 3017.5, 1032.5, 1105 and 2801 cm\textsuperscript{-1}, respectively. The CO and CH\textsubscript{4} calibration curves were obtained respectively using several kinds of diluted standard CO gas or CH\textsubscript{4} gas with compressed CO\textsubscript{2} gas. We obtained the CH\textsubscript{2}OH, HCHO, and HCOOH calibration curves using several kinds of gases with specific concentrations. To obtain the gas with the intended concentrations, we injected the required amounts of each chemical reagent into 50 l Tedlar bags filled with CO\textsubscript{2}.
3. Results and Discussion

3.1. Sample characteristics
The particle size of commercial anatase TiO$_2$ powder was checked using SEM images as shown in Figure 2. Anatase TiO$_2$ powder consisted of particles several ten of µm in diameter, which were aggregates of TiO$_2$ particles several hundred nm in diameter.

![SEM images of commercial anatase TiO$_2$.](image)

**Figure 2.** SEM images of commercial anatase TiO$_2$; (a) $\times350$, (b) $\times15.0K$.

Laser microscope images of the silica filter paper and the TiO$_2$ deposited on it are shown in Figure 3. The TiO$_2$ powder was homogeneously deposited on the silica filter paper.

![Filter paper with TiO$_2$.](image)

**Figure 3.** Laser microscope images of the silica filter paper and the TiO$_2$ deposited on it.

3.2. Photoreduction of CO$_2$
A background test was first performed on the gas reactor containing only the silica filter paper, and no CO$_2$ conversion products (for example CO or CH$_4$) were observed regardless of whether the light was on or off. We also carried out another background test on the gas reactor containing the TiO$_2$ sample deposited on the silica filter paper, and no CO$_2$ conversion products (for example CO or CH$_4$) were
observed when the light was off. The conversion only occurred when TiO$_2$ was present together with Hg lamp irradiation. Figure 4 shows the product concentrations of CH$_4$ and CO in the gas reactor as a function of irradiation time for CO$_2$ photoreduction. The product concentrations of CH$_3$OH, HCHO and HCOOH were below the detection limit (1ppm) for the duration of the experiment. This process was repeated three times to ensure complete replacement. We found that the amounts of CH$_4$ and CO that were produced gradually decreased during the first run. In the second run, the product concentrations of both CH$_4$ and CO were small. CH$_4$ was identified as the major product using anatase TiO$_2$ catalyst. As shown in Figure 4 the measured concentration of CH$_4$ in the gas reactor increased with irradiation time and reached a peak concentration at around 120 min, and then gradually decreased. Similar results were reported by Y. Li et al. [24], namely that the yields of the CO$_2$ photoreduction products decreased once they had reached the maximum values. The reason for this is the deterioration of the photocatalytic activity of the anatase TiO$_2$ surface.

Figure 3. Laser microscope images; (a) silica filter paper, (b) TiO$_2$/Silica filter paper.

3.3. Characteristic of samples before and after UV irradiation

We measured the diffuse reflectance UV-vis spectra of the samples before and after Hg lamp irradiation to investigate the reason for TiO$_2$ deactivation. The reflectance was converted into the ratio ($\alpha$) of absorption coefficient and scattering coefficient using the Kubelka-Munk equation, $\alpha=(1-R_\infty)^2/2R_\infty$, where $R_\infty$ is the diffuse reflectance from a semi-infinite layer. The results are shown in Figure 5, and the band-gap energy of the samples before and after UV irradiation was estimated to be $3.31\pm 0.01$ and $3.29\pm 0.01$ eV, respectively. Considering the error range, two values are almost the same. An XRD measurement was carried out at the same time for the samples before and after Hg lamp irradiation. We used the same samples for both UV-vis and XRD measurements. We obtained the same diffraction pattern (anatase TiO$_2$ only) for both. On the basis of these results, we assumed that the cause of the deactivation would lie in the surface state, and not in the bulk state.

XPS is a valuable method for analyzing surface chemical states, therefore the XPS measurement was carried out for both non-irradiated and irradiated sample surfaces. The elemental concentrations calculated from the XPS intensities using sensitivity coefficients (Ti 2p:32.594, O 1s:13.099, and C 1s:5.214) (PHI Inc.) are summarized in Table 1. The calculated oxygen to titanium ratios were 2.24 and 2.28 for the non-irradiated and irradiated samples, respectively. The kinetic energy of a photoelectron from Ti 2p is about 1030 eV, and the mean free path of a 1030 eV photoelectron is
about 1.4 nm [25]. If the surfaces of the two samples are terminated by oxygen atoms, the titanium atom is about 0.2 nm below the surface, because the bond distance of Ti—O is about 0.2 nm [26]. Considering the position of the Ti atom, the intensity of photoelectron emitted from Ti 2p levels is calculated 1.15 times, and based on this result, the calculated oxygen to titanium ratios are 1.94 and 1.98 for the non-irradiated and irradiated samples, respectively. This indicates that there are no stoichiometric changes on the surfaces of the two samples. In terms of carbon, the elemental concentration calculated from the XPS intensities increased by about 1.6%. The origin of the carbon is the strong adsorption of the contaminant layer onto the surface [27], however the increased components would be related to the deactivation of anatase TiO₂.

![Figure 4. Time dependence of product concentration in gas reactor.](image)

![Figure 5. UV-vis spectra of samples before and after UV irradiation.](image)

The XPS spectra for Ti 2p, O 1s and C 1s are shown in Figures 6, 7 and 8, respectively. The binding energy of the Ti 2p3/2 main peak was calibrated at 458.8 eV to correct the shifts caused by charging. No change was observed in the Ti 2p spectra after the Hg lamp irradiation except for the intensity change that was induced from the change in the amount of carbon on the TiO₂ surface. Shultz et al. reported that there are Ti³⁺ defects on a (110) rutile TiO₂ surface after UV irradiation, and this component has a lower binding energy of 1.7 eV than that of Ti⁴⁺ [28]. In our experiment, we could not detect a component with a lower binding energy of 1.7 eV, and observed a single peak of Ti⁴⁺ indicating that the chemical state of Ti had not changed after UV irradiation.

| Sample                  | Atomic percentage (%) |
|-------------------------|------------------------|
|                         | T₁   | O    | C    |
| Before irradiation      | 27.2 | 61.0 | 11.8 |
| After irradiation       | 26.4 | 60.2 | 13.4 |

For the O 1s and C 1s spectra, the black line describes experimental data of the intensity of the signal in arbitrary units. The O 1s and C 1s spectra were resolved into individual peaks. The binding energies, FWHMs, counts and relative intensities of Ti 2p, O 1s and C 1s are summarized in Table 2. We set the counts of Ti 2p2/3 at 1.0 and calculated the relative intensities of the other components. The O 1s core level spectra had two peaks as shown in Figure 7. The peaks at approximately 530.0 and 531.3 eV are
attributed to anhydrous oxide (Ti—O—Ti) and the hydroxyl group (—OH), respectively [27, 29, 30].

The relative intensity of anhydrous oxide (Ti—O—Ti) decreased by 0.02 and the relative intensity of the hydroxyl group (—OH) increased by 0.04 after Hg lamp irradiation. This indicates that the chemical state of anhydrous oxide (Ti—O—Ti) was converted into the chemical state of the hydroxyl group (—OH) by Hg lamp irradiation. Sasaki et al. and Yu et al. reported that UV irradiation in air increased the amount of the surface hydroxyl groups of TiO₂, and the source of the hydroxyl groups would be water in the air [31, 32]. Although our experiment was carried out in CO₂ gas with 50% relative humidity, the same formation of surface hydroxyl groups would occur between TiO₂ and water on the TiO₂ surface. The calculated percentage of oxygen in the hydroxyl group was 13.5% before irradiation and 16.2% after irradiation.

![Figure 6. Change in Ti2p XPS spectra of TiO₂ before and after UV irradiation.](image6)

![Figure 7. Change in O 1s XPS spectra of TiO₂ before and after UV irradiation.](image7)

![Figure 8. Change in C 1s XPS spectra of TiO₂ before and after UV irradiation.](image8)
Table 2. Binding energies, FWHMs, counts and relative intensities of Ti2p, O1s and C1s.

|                  | Ti 2p | O 1s | C 1s |
|------------------|-------|------|------|
|                  |       |      |      |       |      |      |      |      |
| Binding Energy (eV) | 458.8 | 464.5 | 530.0 | 531.3 | 285.0 | 286.6 | 289.0 |
| FWHM (eV)        | 1.10  | 2.01 | 1.16 | 1.88 | 1.46  | 1.55  | 1.45  |
| Before irradiation | 31504 | 15238 | 38660 | 5228 | 2309 | 851  | 382  |
| Counts           | 1.00  | 0.48 | 1.23 | 0.16 | 0.065 | 0.027 | 0.012 |
| Relative intensity |      |      |      |      |      |      |      |
| After irradiation | 1.15  | 1.98 | 1.21 | 2.16 | 1.48  | 1.49  | 1.55  |
| FWHM (eV)        | 29659 | 14051 | 36012 | 5828 | 2498 | 652  | 410  |
| Counts           | 1.00  | 0.47 | 1.21 | 0.20 | 0.084 | 0.021 | 0.014 |
| Relative intensity |      |      |      |      |      |      |      |
| Chemical species | Ti-O  | Ti-O | Ti-O | Ti-OH | C    | C-OH | C=O  |
| Ti2p 2/3         | Ti2p 1/2 | Ti-O | Ti-OH | C    | C-OH | C=O  |
| FWHM ; full width at half maximum.

The kinetic energy of a photoelectron from O 1s is about 955 eV, and the mean free path of a 955 eV photoelectron is about 1.3 nm [25]. If the sample surface is terminated by oxygen atoms, these atoms are present from the top of the surface to 0.2 nm below the surface, because the Ti—O bond distance is about 0.2 nm [26]. The photoelectron intensity from the O 1s is given as follows.

\[
I_o = \int_0^\infty N_0 \times e^{-x/\lambda} dx
\]  

(1)

In equation (1), \(N_0\) indicates the photoelectron intensity from the surface one layer. The photoelectron intensity of the irradiated TiO\(_2\) was 41,840 (the sum of the O1s counts of 530.0 eV (36,012) and of 531.3 eV (5,828)), and the \(N_0\) was calculated as 32,190 by solving the eq. (1). Then the photoelectron intensity of O 1s from top of the surface to 0.2 nm below from the surface was calculated as 5,980, and the calculated intensity was almost the same of the photoelectron intensity of the hydroxyl group (—OH). For the non-irradiated TiO\(_2\) surface, the photoelectron intensity was 43,890, and \(N_0\) was calculated as 33,760. Then the photoelectron intensity of O 1s from top of the surface to 0.2 nm below the surface was calculated as 6,280, and the experimentally obtained intensity of O 1s in the hydroxyl group (—OH) was about 80% of the calculated intensity. On the basis of these results, 80% of the oxygen in a non-irradiated TiO\(_2\) surface would be in the hydroxyl state (—OH). The other 20% of the oxygen would be in an anhydrous oxide state (Ti—O—Ti), and this oxygen can be changed into the chemical state of the hydroxyl state (—OH) by Hg lamp irradiation, and then almost 100% of the irradiated TiO\(_2\) surface would be terminated by a hydroxyl group (—OH).

The C1s core level spectra had three peaks as shown in Figure 8. The peaks at approximately 285.0, 286.6 and 289.0 eV are attributed to a hydrocarbon, an oxidant carbon such as alcohols and a carboxyl carbon, respectively [27, 29, 30]. The relative intensity of the oxidant carbon decreased by 0.006 and the relative intensity of the hydrocarbon increased by 0.019 after Hg lamp irradiation. Considering these results, we assumed that the carbon that existed near the oxygen in the (Ti—O—Ti) chemical state of the TiO\(_2\) surface, changed into the carbon that existed near the hydrogen in the Ti—OH chemical state of the TiO\(_2\) surface.

On the basis of these results, we proposed a model for the deactivation of the TiO\(_2\) surface by Hg lamp irradiation as shown in Figure 9. 80% of the anatase TiO\(_2\) surface is terminated by a hydroxyl group and this part would not work as a photocatalyst for the CO\(_2\) photo-reduction reaction. The other 20% of the oxygen in the anhydrous oxide state (Ti—O—Ti) can work as a photocatalyst for the CO\(_2\) photo-reduction reaction. However, the oxygen in the (Ti—O—Ti) chemical state is not stable by the Hg lamp irradiation with H\(_2\)O, and the oxygen in the anhydrous oxide state (Ti—O—Ti) gradually...
changes into a hydroxyl group. After almost 100% oxygen of the TiO$_2$ surface had been terminated by a hydroxyl group, the TiO$_2$ changed into the deactivated state for the photo-reduction of CO$_2$.

Although more experiments are needed, the model shown in Figure 9 is reasonable considering the results we obtained in this experiment.

![Figure 9. Surface deactivation models for the TiO$_2$ surface obtained by UV irradiation.](image)

4. Conclusions
We found that anatase TiO$_2$ powder deposited on the silica filter paper was changed into a deactivated state by Hg lamp irradiation, and there was a gradual decrease in the amounts of CH$_4$ and CO that were produced by the CO$_2$ reduction. We analyzed the surface chemical states using XPS analysis to consider the cause of the TiO$_2$ deactivation, and found that the amounts of –OH group on the TiO$_2$ surface had increased after Hg lamp irradiation. On the basis of the analysis results, we assumed there to be a surface deactivation mechanism. However, when the (Ti–O–Ti) chemical state worked as a photocatalyst for the photo-reduction reaction of CO$_2$, the oxygen in the (Ti–O–Ti) chemical state was not stable as a result of the UV irradiation with H$_2$O, and the oxygen in the (Ti–O–Ti) chemical state gradually changed into a hydroxyl group that would not work as a photocatalyst for the photoreduction reaction of CO$_2$.

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