



Title	Development of a Reliable Method to Evaluate Photocatalytic Activity by Colorimetric Analysis without Using Organic Dyes [an abstract of entire text]
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学位論文の要約

博士（環境科学）

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学位論文題名

Development of a Reliable Method to Evaluate Photocatalytic Activity by
Colorimetric Analysis without Using Organic Dyes

（有機色素を用いない比色法による高信頼性光触媒活性試験法の開発）

Photocatalysis is one of the promising methods to overcome environmental problems, e.g., pollutant degradation, because complete degradation of pollutant can be conducted in mild conditions without sludge production. Consequently, development of new photocatalyst has been one of the pivotal topics among researchers and the photocatalytic performance has been evaluated by a photocatalytic-activity test. However, question arises about the reliability of the method used for photocatalytic-activity evaluation whether the method is reliable so that the photocatalyst can be effectively solve the environmental problems, and about how to identify a reliable method for photocatalytic-activity evaluation.

Organic dyes have received much attention among researchers as model pollutants for photocatalytic-activity evaluation, i.e., dye-decoloration system. Even though dye decoloration analysis that is evaluated by a spectrophotometer or a colorimeter is probably the easiest way to evaluate photocatalytic activity, it has been reported by the laboratory where the author belongs that the method is not reliable under visible light irradiation. Under visible light irradiation, dye might sensitize the photocatalyst which then affects the performance of photocatalyst in the evaluation method, i.e., not the actual photocatalytic activity. However, even though the unreliability of photocatalytic evaluation by dye-decoloration system has been reported, the reports about photocatalytic-activity test by dye-decoloration system are still increasing. The reasons are probably because the dye-decoloration system is easy to drive and the only instrument needed is a simple affordable instrument, i.e., a spectrophotometer or a colorimeter, which is a common instrument in the worldwide laboratories. Even though gas-chromatographic (GC) or liquid-chromatographic (LC)

analysis has been well-known as a reliable method for evaluating photocatalytic activity, the instruments are relatively expensive and require a complex set up, e.g., using gas cylinders. Consequently, some researchers with less-equipped laboratories may have to use dye-decoloration analysis for photocatalytic-activity evaluation. Therefore, a study about reliable evaluation methods to evaluate photocatalytic activity by colorimetric analysis is necessary. To obtain reliable data of photocatalytic performance, photocatalyst sensitization should be avoided. Therefore, the purpose of the author's study is to provide a reliable method to evaluate photocatalytic activity by colorimetric analysis without using organic dyes. Chapter I elaborates these background and purpose of this study.

In Chapter II, the reliability of conventional dye decoloration with rhodamine B as a substrate was compared with that of without organic dyes, i.e., using colorless or non-visible-light-absorbing substrate. For the photocatalytic system with organic dye, the photocatalytic decoloration of rhodamine B (RhB) was carried out by mixing photocatalyst in RhB solution. As those without organic dyes, two representatives of photocatalytic activity were used, i.e., (1) methanol dehydrogenation ($\text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2$) and (2) oxidative decomposition of formaldehyde ($\text{HCHO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) with colorless compounds of methanol and formaldehyde (HCHO) as substrates for photocatalytic systems (1) and (2), respectively. Non visible light-absorbing titania, i.e., ST-G1, and visible-light absorbing titania, i.e., Sample A and Sample B (from a private company in Japan), were used. For the light source, a diffraction grating-type illuminator (Jasco CRM-FD) equipped with 300-W xenon lamp (Hamamatsu Photonics C2578-02) had been used as a light source.

In this study, action-spectrum analysis has been used to clarify the source of photoinduced reaction, whether the activity comes from the charge carriers photogeneration of photocatalysts or from the photoabsorption of dye. For RhB decoloration, the action spectra are rather scattered for some samples, but the trend still can be observed. Based on the trend, initially, the photoinduced RhB decoloration resemble to the DR spectra of each photocatalyst, suggesting the RhB decoloration has been caused by the activity of photocatalyst in the UV region. However, at longer wavelengths, i.e., ca. 550 nm photoabsorption peak wavelength of RhB: ca. 555 nm), the activity was increased and more resembled to the photoabsorption spectra of RhB (peak of RhB photoabsorption at $\lambda = \text{ca. } 555 \text{ nm}$) than that of diffuse reflectance (DR) spectra of photocatalysts. This result suggests that the photoabsorption of RhB causes sensitization to the photocatalyst under visible light and induce additional decoloration activity. Therefore, the use of organic dye might cause the unreliability of the evaluation method of photocatalytic activity. On the other hand, this kind of result has not been found the action-spectrum analysis of H_2 evolution and CO_2 evolution suggesting the reliability of the photocatalytic systems that use colorless substrates. Based on these results, it is necessary to use

colorless substrate to obtain reliable method for photocatalytic-activity evaluation under visible light irradiation.

In Chapter III, the study about reliable colorimetric analysis for photocatalytic-activity evaluation is elaborated. As mentioned in Chapter II, it is necessary to use colorless compounds as substrates for photocatalytic-activity evaluation which are usually measured by expensive instruments such as GC or LC. Therefore, it is important to use photocatalytic systems with colorless substrate that the product/substrate can be easily analyzed by a spectrophotometer or colorimeter. Dye is often used in colorimetric analysis because it has a relatively high value of molar photoabsorption coefficient (ϵ) than that of colorless compound so that it is easy to measure. However, it is also possible to increase the value of ϵ of colorless compound to form color compound, e.g., by derivatization. HCHO is one of the best candidates because it is colorless and can be derived into diacetyldihydrolutidine. Therefore, instead of using organic dye, colorless formaldehyde was used as the key compound of analysis. Derivatization was conducted after photoirradiation in the evaluation of photocatalytic activity. Two representatives of photocatalytic systems were evaluated, i.e., methanol dehydrogenation and HCHO oxidative decomposition, and 10 representatives of commercial titania were used in the experiments. A 400-W mercury arc ($\lambda > 290$ nm, Eiko-sha 400) was used as the light source.

For methanol dehydrogenation, a series of titania suspension in 50vol% methanol was prepared in test tubes. The solution was stirred and hexachloroplatinic(IV) hexahydrate was added as a source of platinum (Pt). Bubbling was conducted by argon gas to remove air inside the test tubes and was confirmed by GC. Subsequently, the suspensions were irradiated with vigorous magnetic stirring. The temperature was also maintained at 25 °C using a water bath. After photoirradiation, the productions of hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO) were measured by GC, while formic acid (HCOOH), and HCHO were measured by LC, and spectrophotometer, respectively.

For formaldehyde oxidative decomposition, a freshly prepared solution of HCHO from para-formaldehyde powder was mixed with titania in a 35-mL test tube. The irradiation was conducted for 60 min along with magnetic stirring (1000 rpm). The temperature was maintained by water bath through out the photoirradiation. The consumption of HCHO was measured by a spectrophotometer via derivatization of HCHO. The production of HCOOH, CO_2 and CO were also measured.

The study of chemical balance was conducted for both methanol dehydrogenation and HCHO oxidative decomposition. For methanol dehydrogenation, the consumptions of electrons and positive holes have been compared. On the other hand, in HCHO oxidative decomposition, the consumptions of HCHO have been compared to the total oxidation products. In methanol dehydrogenation, almost

comparable amount of the consumed electrons and positive holes has been obtained. Furthermore, H₂ and HCHO have been found to be the major products for reduction and oxidation reactions, respectively. Therefore, HCHO and H₂ analyses could be the representative analyses for photocatalytic-activity evaluation. A plot of the H₂ production versus HCHO production was prepared to study further about the correlation between both products. The production of HCHO was increased along with the production of H₂. More importantly, high correlation between H₂ and HCHO was obtained at below 300 μmol production of HCHO. Higher production of HCHO leads to the outliers which is probably due to the further oxidation of HCHO to form HCOOH and CO₂. This result suggests that the analysis of H₂ by GC in methanol dehydrogenation system can be substituted by colorimetric HCHO analysis. In HCHO oxidative decomposition, based on the chemical balance study, almost comparable amount of HCHO consumption and total oxidation products has been observed for almost all titania samples. It should be noted that the amount of each oxidation products, i.e., HCOOH, and CO₂, has different ratio to the total oxidation products for all titania samples. Therefore, it seems inappropriate to use only CO₂-production analysis for photocatalytic-activity evaluation. On the other hand, the HCHO-consumption analysis can represent the whole consumption of positive holes better than CO₂-production analysis. Therefore, HCHO-consumption analysis should be used to evaluate photocatalytic activity in the HCHO-oxidative-decomposition system. Based on those results, HCHO analysis by a spectrophotometer can be used to substitute GC analysis in methanol-dehydrogenation and HCHO oxidative-decomposition systems.

In Chapter IV, the reliability of the proposed HCHO analyses under UV- or visible-light irradiation was studied by using GC analyses as reference. Colorimetric analyses of HCHO production and HCHO consumption were compared to the GC analyses of H₂ evolution (methanol dehydrogenation) and CO₂ evolution (HCHO oxidative decomposition), respectively. The colorimetric analysis of RhB decoloration was also evaluated. ST-G1, Sample A and Sample B were used as photocatalysts in this experiment. During photocatalytic activity test, UV LED or green LED were used as light sources.

Similar trends of GC analyses and colorimetric analyses were observed for both photocatalytic systems under UV- or visible-light irradiation. These results suggest that colorimetric analyses of HCHO has similar reliability with that of GC analyses. Therefore, colorimetric analysis of HCHO can reliably substitute GC analysis in the evaluation of photocatalytic activity. On the other hand, ST-G1 (non-visible-light-absorbing titania) has shown RhB decoloration activity even under visible-light irradiation. This activity confirms the unreliability of the RhB-decoloration system which has been suggested due to photocatalyst sensitization under visible light irradiation.

Chapter V summarize all the results and discussions. Colorless substrate should be used in the photocatalytic system to obtain a reliable result of photocatalytic activity. In two representatives of photocatalytic systems that use colorless substrates, i.e., methanol dehydrogenation and HCHO oxidative decomposition, colorimetric analysis of HCHO has similar or even higher reliability than that of the reliable GC analyses of H₂ or CO₂ production. Therefore, simple colorimetric analysis of HCHO could be used for a reliable evaluation of photocatalytic activity. In conclusion, the present study about development of a reliable photocatalytic-activity evaluation by only using a spectrophotometer has been developed.