



Title	Development of a Reliable Method to Evaluate Photocatalytic Activity by Colorimetric Analysis without Using Organic Dyes [an abstract of dissertation and a summary of dissertation review]
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学位論文内容の要旨

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)

Despite the increasing number of published papers reporting the development of new photocatalyst materials, some questions remain. Is the used photocatalytic-evaluation method reliable so that the photocatalysts could be effectively used for further applications? What is a 'reliable' method to evaluate photocatalytic activity? Organic dyes are often used as model pollutants to evaluate the photocatalytic performance of synthesized photocatalysts. While dye-decoloration analysis by a spectrophotometer or even a colorimeter is probably the easiest way to evaluate the performance of a photocatalyst, it has been reported from the laboratory in which the candidate belongs that, at least 15 years ago, dye-decoloration analysis is not reliable especially under visible-light irradiation due to dye sensitization to the photocatalyst, i.e., not the actual photocatalytic activity. However, even after the unreliability of the dye-decoloration method has been revealed, published reports about photocatalytic evaluation using dye-decoloration analysis still keep increasing. The possible reasons are because dye-decoloration reaction is easy to drive and only requires simple affordable instrument, i.e., a spectrophotometer or colorimeter, which is easily available in chemical laboratories. Thereby, dye-decoloration analysis is so popular among researchers and some researchers may not have any choice but to use dye-decoloration analysis to evaluate photocatalytic activity. Therefore, study about reliable evaluation method that can show the true or actual photocatalytic activity is important. To obtain reliable data of photocatalytic performance, it is necessary to eliminate the effect of sensitization by dyes. Therefore, the purpose of the candidate's study is to provide reliable colorimetric method to evaluate photocatalytic activity without using organic dyes. Chapter I summarizes these background and purpose.

In Chapter II, the conventional photocatalytic system with organic dye, i.e., rhodamine B (RhB) decoloration, was compared with that of without organic dyes, i.e., using colorless/non-visible-absorbing substrate, such as (a) methanol dehydrogenation ($\text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2$) under deaerated conditions with ex-situ platinum (Pt)-photodeposition on photocatalyst and (b) formaldehyde (HCHO) oxidative decomposition ($\text{HCHO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) under aerobic conditions. Action-spectrum analysis, i.e., wavelength dependence of apparent quantum efficiency (AQE), was utilized to confirm the origin of photocatalytic activity. For all photocatalytic systems, the action spectra almost resembled the diffuse reflectance (DR) spectra of the respective photocatalyst suggesting the photoinduced reactions were solely due to the transfer of photoexcited electron and positive hole generated by photoabsorption of photocatalysts, i.e., true photocatalytic activity, except for RhB-decoloration system. Under visible-light irradiation, RhB decoloration was enhanced at ca. 550 nm (photoabsorption peak wavelength of RhB:

ca. 555 nm) which is probably due to RhB-sensitization to the photocatalysts, i.e., not the actual photocatalytic activity. Therefore, the results suggest that colorless substrates could provide a reliable photocatalytic-evaluation test. However, colorless substrates usually require more expensive and more complex instruments for the substrate or product analysis such as a gas chromatograph (GC) or liquid chromatograph (LC) which is not readily available in some laboratories. Therefore, it is important to use colorless substrate that a spectrophotometer or colorimeter could still measure. HCHO is one of the best candidates because it is colorless and could be analyzed by a spectrophotometer via derivatization.

The study about the possibility of using colorimetric HCHO analysis to evaluate photocatalytic activity is shown in Chapter III. To enable the detection of HCHO by a spectrophotometer or colorimeter, derivatization of HCHO into yellow diacetyldihydrolutidine (DDL, molar photoabsorption coefficient (ϵ) = ca. $8 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ at the peak wavelength of 412 nm, in aqueous solution) was conducted by utilizing the well-known Hantzsch reaction. Two photocatalytic systems were evaluated, i.e., methanol dehydrogenation with in-situ platinum photodeposition from deaerated aqueous methanol (50vol%) and HCHO oxidative decomposition, with 10 kinds of commercial titanium(IV) oxide. The colorimetric analysis of HCHO liberation or HCHO consumption is proposed to substitute the conventional gas-chromatographic analysis of H_2 and CO_2 for the former and latter photocatalytic systems, respectively. The chemical balance study, i.e., comparison of electron and positive-hole consumption; or comparison of substrate consumption and product liberation, suggested that, in methanol dehydrogenation, colorimetric HCHO-liberation analysis could substitute the H_2 GC analysis by adjusting the product HCHO amount to be below ca. 300 μmol or ca. 0.5% of methanol conversion. On the other hand, for HCHO oxidative decomposition, the colorimetric HCHO-consumption analysis is more reliable than CO_2 -evolution GC analysis because the colorimetric HCHO analysis could represent the whole positive-hole consumption.

The reliability of the colorimetric HCHO analysis as well as RhB analysis to evaluate photocatalytic activity under UV- or visible-light irradiation was studied in Chapter IV. Colorimetric HCHO-analyses were compared to the gas-chromatographic analyses of H_2 or CO_2 , as reference, in methanol dehydrogenation and HCHO oxidative decomposition, respectively. Three kinds of photocatalysts were used, i.e., non-visible-absorbing titania (ST-G1) and visible-absorbing titania (Sample A and Sample B from a private company in Japan). The result showed that colorimetric analysis of HCHO for the system under UV or visible-light irradiation shows similar trend with that of gas-chromatographic analyses, suggesting that colorimetric HCHO analysis could reliably replace the gas-chromatographic analysis in both photocatalytic systems. For HCHO oxidative decomposition, the colorimetric analysis of HCHO consumption is even more reliable than that gas-chromatographic analysis of CO_2 . In contrast, RhB decoloration proceeded under visible-light irradiation even with non-visible absorbing titania, which was probably due to RhB sensitization, suggesting the unreliability of RhB-decoloration analysis under visible-light irradiation.

Those results and discussion are summarized in Chapter V. Based on those results, colorimetric analysis of HCHO has similar or even higher reliability than that of gas-chromatographic analysis. Therefore, colorimetric HCHO analysis could be used as a reliable method to evaluate photocatalytic activity. In conclusion, the present study on successful development of reliable photocatalytic-activity evaluation is believed to be one of the milestones of photocatalysis studies to guide them scientifically correct and fair.