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Research paper

Effects of the structure of the Rh^{3+} modifier on photocatalytic performances of an Rh^{3+}/TiO_2 photocatalyst under irradiation of visible light

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ABSTRACT

For a rhodium ion-modified TiO_2 (Rh^{3+}/TiO_2) photocatalyst responding to visible light, control of the structure of the Rh^{3+} modifier and effects of the structures of the Rh^{3+} modifier on photocatalytic activities were examined. A TiO_2 support was pre-calcined to maintain crystallinity and specific surface area during post-calcination, and the structure of the Rh^{3+} modifier for Rh^{3+}/TiO_2 was changed by post-calcination without causing changes in the crystallinity and specific surface area of the TiO_2 support. In mineralization of acetone under irradiation of visible light, the photocatalytic activities of the post-calcined Rh^{3+}/TiO_2 showed a volcano-like tendency as a function of post-calcination temperature. The results of this study showed that an atomically isolated structure of the Rh^{3+} modifier was preferable for high activities and that aggregation of the Rh species led to a decrease in the activities.

1. Introduction

Various materials for utilization of renewable light energy that is almost unlimitedly supplied as sunlight have been developed to achieve a long-term sustainable society [1–4]. A photocatalyst is a semiconductor material that works by absorption of photons having larger energy than that corresponding to its band gap [5]. Photocatalysts have been widely applied to many reactions including hydrogen production via water splitting [3,6], mineralization of pollutants [7–9], organic synthesis [10–14] and other reactions [15,16]. Titanium (IV) dioxide (TiO_2) is a representative photocatalyst exhibiting high activities, however, it works only under irradiation of UV light due to its wide band gap (3.2 eV) [5]. Thus, many research groups have developed photocatalysts working under irradiation of visible light which was contained abundantly in solar light [17–20]. Various types of photocatalysts responding to visible light have been developed in the past few decades, and some researchers have developed TiO_2-based photocatalysts modified with transition metal compounds. In the modified TiO_2 photocatalysts, transition metal modifiers such as oxides [21–24], hydroxides [25–27] and halogenides [28–31] are not doped in lattices but are just fixed on the surface of TiO_2 nanoparticles, and charge transfers occur between the metal modifiers and TiO_2. The photocatalysts exhibited high photocatalytic activities under irradiation of visible light.

On the other hand, we have synthesized novel photocatalysts responding to visible light: metal ion-modified TiO_2 photocatalysts (M^{n+}/TiO_2) [32–36]. The M^{n+}/TiO_2 photocatalysts were simply prepared by the equilibrium adsorption method, and visible light absorption of M^{n+}/TiO_2 corresponds to charge transfer between the metal ions and TiO_2. We have examined various kinds of M^{n+}/TiO_2 photocatalysts and we have reported that rhodium ion-modified TiO_2 (Rh^{3+}/TiO_2) exhibited high activities for mineralization of volatile organic compounds (VOC) in gas phase [32–34] and that Rh^{3+}, ruthenium and palladium ion-modified TiO_2 (Ru^{3+}/TiO_2, Pd^{2+}/TiO_2) showed good performance for selective oxidation of

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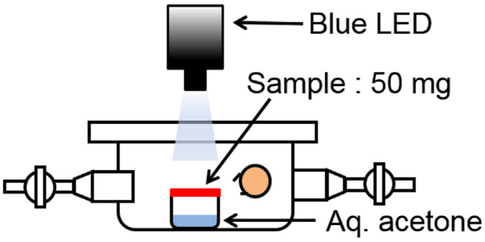

Fig. 1. Reactor used for photocatalytic mineralization of acetone with a constant vapor pressure under irradiation of visible light.

aromatic alcohols in liquid phase [36]. We have also shown that physical properties of TiO_2 greatly affected the photocatalytic performance of M^{n+}/TiO_2 and that utilization of TiO_2 having appropriate physical properties enabled control of the photocatalytic performance of the M^{n+}/TiO_2. Therefore, desirable photocatalytic performances can be achieved in M^{n+}/TiO_2 photocatalysts because many candidates of metal ions and TiO_2 powders having various physical properties are available.

We have carried out detailed investigation of the effects of physical properties of TiO_2 supports on the photocatalytic activities of M^{n+}/TiO_2, however, we have not examined the effects of structures of the metal ion modifiers. In modified TiO_2 photocatalysts, the structure of metal modifiers is also an important factor since the photocatalytic performance also depended on the structure of metal modifiers, e.g., TiO_2 photocatalysts having metal modifiers composed of an identical metal element having different structures exhibited different photocatalytic performances [22,23,25,27,29,34,37]. Thus, we expected that examination for control of the structure of metal ion modifiers and investigation of effects of the structure of metal ion modifiers on photocatalytic performance would contribute to further variation of the photocatalytic performance of M^{n+}/TiO_2.

From another aspect, removal of the effects of change in the physical properties of TiO_2 supports during change in the structure of metal modifiers is necessary since change in the physical properties greatly affects change in the photocatalytic activities. If the physical properties of TiO_2 supports change simultaneously with change in metal modifiers, the results of the photocatalytic reaction are complex and understanding of the results is difficult. Therefore, examinations should be conducted under the same conditions of physical properties of TiO_2 in order to determine the effects of modifier structures on photocatalytic activities. However, there have been few studies in which the effects of change in the modifier structure on the photocatalytic activities were investigated without changes in physical properties of the TiO_2 support

In this study, we examined control of the structure of the metal ion modifier and investigated the effects of the structure of a metal ion modifier on photocatalytic activities under the same conditions of physical properties of the TiO_2 support. We used Rh^{3+} as an ion modifier since Rh^{3+}/TiO_2 was reported to show high activities for various photocatalytic reactions and because the characteristics of Rh^{3+}/TiO_2 have been clarified [32–34,38]. A TiO_2 support was pre-calcined for maintenance of its physical properties during post-calcination and then modified with Rh^{3+} by using the equilibrium adsorption method. The structure of the Rh^{3+} modifier was changed by post-calcination at various temperatures without causing changes in physical properties of the TiO_2 support. The structure of the Rh^{3+} modifier after post-calcination was investigated by various characterizations. The photocatalytic activities of the post-calcined Rh^{3+}/TiO_2 samples for mineralization of acetone in gas phase under irradiation of visible light depended on the post-calcination temperature. We found that an atomically isolated structure of the Rh^{3+} modifier was preferable for high activities and that aggregation of Rh species led to a decrease in the activities.

2. Experimental

2.1. Sample preparation

All of the chemicals were used as received without further purification. HyCOM (Hydrothermal Crystallization in Organic Media) method reported previously [39] was applied to synthesize a TiO_2 support for modification with Rh^{3+}. Titanium(IV) butoxide (25 g) in toluene (70 cm^3) was heated at 300 °C for 2 h in an autoclave in the presence of water (25 cm^3) fed in a space separated from the alkoxide solution. The resulting powders were washed repeatedly with acetone and dried in air at ambient temperature. Pre-calcination at 550 °C for the as-prepared HyCOM-TiO_2 was performed in a box furnace under air for 1 h. The pre-calcined TiO_2 sample was modified with Rh^{3+} by using the equilibrium adsorption method [32–34]. The pre-calcined TiO_2 powder was added to an aqueous solution of rhodium (III) chloride ($RhCl_3$), the amount of which corresponded to 1 wt% modification of metal, and then stirred and heated in a water bath at *ca.* 90 °C. The suspension was filtered, and the filter cake was washed repeatedly by distilled water for removal of chloride ions and dried in vacuo for 1 h and then Rh^{3+}/TiO_2 was obtained. We confirmed that all of Rh^{3+} in the aqueous solution of $RhCl_3$ was fixed on TiO_2 by analysis of Rh^{3+} in the filtrate using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500). Post-calcination at various temperatures (150, 350, 450, 550 °C) for Rh^{3+}/TiO_2 was performed in a box furnace under air for 1 h to change the structure of the Rh^{3+} modifier on the surface of TiO_2.

2.2. Characterization

A synchrotron powder XRD measurement was performed at the RIKEN Materials Science beamline BL44B2 of SPring-8 (Hyogo, Japan) [40]. Data were acquired using a Debye-Scherrer camera equipped with an imaging plate as an X-ray detector. The incident wavelengths were 0.5003 Å, which were obtained by calibration using CeO_2 as a standard powder sample. The X-ray beam was collimated by a double slit of 0.5 mm by 3.0 mm. Powder samples were sealed in borosilicate glass capillaries *in vacuo*. Specific surface area of the samples was obtained using the Brunauer-Emmett-Teller (BET) single-point method on the basis of nitrogen (N_2) uptake measured at −196 °C using a Shimadzu Flowsorb 2300. Diffuse reflectance spectra were measured using a Shimadzu UV-2400 UV–vis spectrometer equipped with a diffuse reflectance measurement unit (ISR-2000) and recorded after Kubelka–Munk analysis. Rh K-edge XAFS spectra of the prepared samples and reference samples (Rh foil and Rh_2O_3) were recorded at the BL01B1 beamline at the SPring-8 in transmission mode for the Rh foil and Rh_2O_3 and in fluorescence mode for the prepared samples at ambient temperature. An Si (311) two-crystal monochromator was used to obtain a monochromatic X-ray beam. The photon energy was calibrated at the inflection point of the absorption edge of an X-ray absorption near edge structure (XANES) spectrum of the Rh foil. Data reduction was carried out with Athena and Artemis included in the Ifeffit package [41].

2.3. Photocatalytic decomposition of acetone at a constant concentration under irradiation of visible light

A sample (50 mg) was suspended in a small amount of distilled water and then the powder was spread on a glass filter (GF-75, 26 mm in diameter, Advantec) with a Buchner funnel under suction.