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Photocatalytic degradation of 2-propanol over metal-ion-loaded titanium(IV) oxide under visible light irradiation: Effect of physical properties of nano-crystalline titanium(IV) oxide

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ABSTRACT

Using the adsorption method, small amounts of rhodium ion (Rh^{3+}) or copper ion (Cu^{2+}) were loaded on nanocrystalline titanium(IV) oxide (TiO_2) with various physical properties prepared by the HyCOM (hydrothermal crystallization in organic media) method and subsequent calcination at various temperatures. In photocatalytic degradation of 2-propanol under visible light irradiation, Rh^{3+}-modified HyCOM-TiO_2 samples exhibited higher levels of activity than did Cu^{2+}-modified HyCOM-TiO_2 samples and the nitrogen-doped TiO_2 sample. The Rh^{3+}-modified HyCOM-TiO_2 samples showed a volcano-like tendency with calcination temperature, suggesting that the balance of surface area and crystallinity of TiO_2 is important in an Rh^{3+}/TiO_2 photocatalyst. Rutile-type TiO_2 modified with Cu^{2+} exhibited the highest level of activity among the $Cu^{2+}/$HyCOM-TiO_2 samples.

1. Introduction

Titanium(IV) oxide (TiO_2) photocatalyst has been used for removal of harmful compounds in air and water and is also expected to solve the problem of air pollution in houses with volatile organic compounds (VOC), such as formaldehyde, causing sick house syndrome [1]. When TiO_2 is irradiated with UV light, the energy of which is larger than that of the band gap, electrons in the valence band are excited to the conduction band, generating holes in the valence band. However, since the amount of UV light in our living spaces is limited, photocatalytic performance of TiO_2 is insufficiently utilized. Therefore, many efforts have been devoted to synthesis of photocatalysts that respond to visible light. To the best of our knowledge, these photocatalysts can be roughly classified into four types. The first type is TiO_2 doped with various elements such as nitrogen [2,3], sulfur [4] and transition metals [5]. In the two former cases, the energy levels of nitrogen and sulfur were inserted in the forbidden band of TiO_2, resulting in response to visible light. However, since the elements used for TiO_2 doping often work as recombination sites, the photocatalytic activity under UV light is generally decreased. The second type is a photocatalyst having narrow band-gap loaded with a co-catalyst. Recently, Abe et al. [6] reported that platinum-loaded tungsten(VI) oxide (WO_3) exhibited a high level of photocatalytic activity for decomposition of organic compounds under irradiation of visible light. At almost the same time, Sayama and co-workers [7] reported a high level of photocatalytic performance of palladium-loaded WO_3 in decomposition of VOC under visible light irradiation. However, since WO_3 is dissolved in alkaline solutions such as ammonia solution, TiO_2-based photocatalysts are preferable for practical use in a kitchen, bathroom and toilet, in which cleaners containing alkaline compounds are often used. The third and fourth types are semiconductors modified with copper ions (Cu^{2+}) utilizing interface charge transfer (IFCT) [8] and TiO_2 samples modified with an inorganic sensitizer such as platinum(IV) and rhodium(III) chlorides [9–11]. The third and fourth types of photocatalysts have various good properties such as high activity, excellent light absorption and high stability because of the varieties of semiconductors, metal ions and sensitizers. In addition, the third and fourth types of photocatalysts can be easily prepared by the impregnation method using TiO_2 powders and metal sources followed by thermal treatment. On the other hand, several complicated processes and precise control of conditions are required for preparation of the first type of photocatalyst, i.e., the doped photocatalyst. In this sense, it can be concluded that the third and fourth types of photocatalysts are environmental friendly catalysts. However, as far as we know, there have been few reports on these two types of photocatalysts [12]. In addition, there have been few reports on the effects of physical properties

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of semiconductors on total photocatalytic activities of the third and fourth types of photocatalysts, although control of the physical properties of semiconductors in a wide range is important for developing a highly active photocatalyst. We have investigated correlations between physical properties and photocatalytic activities of TiO_2 in many reaction systems under irradiation of UV light [13]. Photocatalytic reaction involves various processes such as photoabsorption, adsorption of a substrate(s), formation of electron–hole pairs, charge separation, capture of electrons and holes, and further chemical reaction. Photocatalytic activity is the result of a combination of these processes. Since these processes are affected by physical properties of semiconductors, photocatalytic activity will be enhanced by controlling the physical properties. In addition, preparation of photocatalysts responding to visible light using a simpler method is preferable from the viewpoint of practical use.

Recently, we briefly reported a new TiO_2-based photocatalyst responding to visible light [14]. The photocatalyst, a rhodium ion (Rh^{3+})-modified TiO_2 sample [14], was prepared very simply using the equilibrium adsorption method followed only by filtration and drying (not by thermal activation). Metal-doped TiO_2 samples have generally been prepared by impregnation of the metal source and subsequent thermal treatment at a high temperature. Rhodium chloride fixed on a TiO_2 sample has been prepared by impregnation of rhodium chloride followed by calcination for fixation [10,11,15]. Therefore, the rhodium ion-modified TiO_2 samples were previously reported is different from rhodium-doped TiO_2 and rhodium chloride fixed on TiO_2 [10,11,15]. In this study, rhodium ion-modified TiO_2 samples were used for decomposition of VOC under irradiation of visible light, and effects of the physical properties of TiO_2 on the photocatalytic activity were examined. In addition, the investigation was expanded to Cu^{2+}-modified TiO_2 samples. Here, TiO_2 was prepared by HyCOM (hydrothermal crystallization in organic media) [16], which is one of the solvothermal methods. Since the HyCOM-TiO_2 was highly crystallized and possessed high thermal stability, the physical properties can be gradually changed with elevation of calcination temperature [13].

2. Experimental

2.1. Sample preparation

All of the chemicals were used as received without further purification. HyCOM-TiO_2 powder was synthesized by a procedure reported previously. 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 (10 cm^3) fed in a space separated from alkoxide solution. The resulting powders were washed repeatedly with acetone and dried in air at ambient temperature [13]. The HyCOM-TiO_2 powder was calcined at various temperatures in a box furnace for 1 h.

The HyCOM-TiO_2 samples calcined at various temperatures were modified with metal ions by using the equilibrium adsorption method. Each sample was added to an aqueous solution of rhodium(III) (or copper(II)) chloride, the amount of which corresponded to 0.2 wt.% modification of metal, and stirred and heated in a water bath at *ca.* 85 °C. Then the suspension was filtered and the filter cake was dried at 110 °C overnight. The amount of metal ions fixed on TiO_2 was determined by analysis of metal ions in the filtrate using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500). Hereafter, calcined HyCOM-TiO_2 is designated Hy(*T*), where *T* means calcination temperature in degree Celsius; for example, the HyCOM-TiO_2 sample calcined at 450 °C is shown as Hy(450). Modified TiO_2 is shown as Rh^{3+}/Hy(450), which means Hy(450) modified with Rh^{3+}.

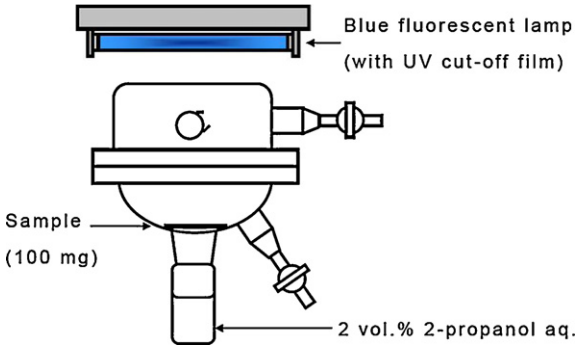

Fig. 1. Reactor used for decomposition of 2-propanol with a constant vapor pressure.

2.2. Characterization

Specific surface area (S_{BET}) of the samples was determined 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. Before the N_2 adsorption, each sample was dried at 120 °C for 20 min in a 30% N_2–helium flow. Diffuse reflectance spectra were obtained using a Shimadzu UV-2400 UV-vis spectrometer equipped with a diffuse reflectance measurement unit (ISR-2000) and recorded after Kubelka–Munk analysis. The crystal structure of TiO_2 samples was measured with powder X-ray diffraction (XRD) of Cu Kα radiation using a Rigaku MultiFlex equipped with a carbon monochromator. The crystallite size of samples was calculated from the half-height width of the 1 0 1 diffraction peak of anatase and the 1 1 1 diffraction peak of rutile using the Scherrer equation; the value of the shape factor, *K*, was arbitrarily taken to be 0.9.

2.3. Photocatalytic decomposition of 2-propanol at a constant concentration under irradiation of visible light

A sample (100 mg) was suspended in a small amount of distilled water and then the powder was spread on a glass filter (GF-75, 55 mm in diameter, Advantec) with a Buchner funnel under suction. The glass filter together with the sample was dried at 50 °C overnight. A glass vessel containing an aqueous solution of 2-propanol (2 vol.%) was connected to the bottom of a separable flask (reactor), and a glass filter together with the sample was placed in the reactor as shown in Fig. 1. Gas phase in the system was replaced with artificial air (oxygen (O_2) (20%)–N_2 gas mixture), and 2-propanol gradually evaporated and then the vapor was saturated in the reactor overnight. Irradiation of the photocatalyst with visible light was started after adsorption of 2-propanol had reached equilibrium. The light source was a blue fluorescent lamp (10 W, S-3410, Sudo, maximum energy at 450 nm, designated as BFL hereafter) doubly covered with a UV-cut filter. The brightness on the surface of the glass filter was 6000 lx, and the spectrum of light coming from filtered BFL is shown in Fig. 2. The amounts of organic compounds (2-propanol and acetone) and CO_2 were determined by using a Shimadzu GC-14B gas chromatograph with a Polyethylene glycol 20M column and a Shimadzu GC-8A gas chromatograph with a Porapack Q column.

3. Results and discussion

3.1. Sample characterization

In Fig. 3, XRD patterns of HyCOM-TiO_2 samples uncalcined and calcined at various temperatures are shown. In the XRD pattern of the uncalcined HyCOM-TiO_2 samples, peaks assignable to anatase-