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# Photocatalytic Degradation of 2-Propanol under Irradiation of Visible Light by Nanocrystalline Titanium(IV) Oxide Modified with Rhodium Ion Using Adsorption Method

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Using adsorption method, a small amount of rhodium ion ($Rh^{3+}$) was loaded on nanocrystalline titanium(IV) oxide ($TiO_2$) with various physical properties prepared by HyCOM and subsequent calcinations 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 nitrogen-doped $TiO_2$ sample and 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.

Titanium(IV) oxide ($TiO_2$) photocatalysts have been used for removal of harmful compounds in air and water and are also expected to remediate air pollution in houses with volatile organic compounds (VOCs), such as formaldehyde, causing sick house syndrome.[1] However, since the amount of UV light in 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: 1) various $TiO_2$ samples doped with nitrogen,[2,3] sulfur,[4] and transition metals,[5] 2) narrow band gap semiconductors with cocatalysts such as tungsten(VI) oxide ($WO_3$) with metal[6,7] or metal ions,[8] 3) semiconductors modified with copper ions utilizing interface charge transfer (IFCT),[8] and 4) $TiO_2$ samples modified with inorganic sensitizers such as platinum(IV) and rhodium(III) chlorides.[9–11] The third and fourth types of photocatalyst have various possibilities 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 photocatalyst can be easily prepared by 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 photocatalyst are environmentally friendly catalysts. However, as far as we know, there have been few reports on these two types of photocatalyst.[12] In addition, there have been few reports on the effects of physical properties of semiconductors on total photocatalytic activities of the third and fourth types of photocatalyst although control of the physical properties of semiconductors in a wide range is very important to develop 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 simpler method is preferable from the viewpoints of practical use.

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

Titanium(IV) butoxide (25 g) in toluene (70 mL) was heated at 300 °C for 2 h in an autoclave in the presence of water (10 mL) fed in a space separated from alkoxide solution. The resulting powders were washed repeatedly with acetone and dried in air at ambient temperature. The HyCOM-$TiO_2$ powder was calcined at various temperatures in a box furnace for 1 h. HyCOM-$TiO_2$ samples calcined at various temperatures were modified with $Rh^{3+}$ by using the very simple method, i.e., equilibrium adsorption method only followed by filtration and drying at 110 °C: Each sample was added to an aqueous solution of rhodium chloride, the amount of which corresponded to 0.2 wt % modification of metal, and the suspension was 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 $Rh^{3+}$ loaded on $TiO_2$ was determined by analysis of metal ions in the filtrate using inductively coupled plasma atomic emission spectroscopy. A glass vessel containing an aqueous solution of 2-propanol (2 vol %) was connected to the bottom of a separable flask as the reactor, and a glass filter together with the sample (100 mg) was placed in the reactor (Figure 1). After the gas phase in the system had been replaced with artificial air (oxygen ($O_2$) (20%)–$N_2$ gas mixture), the 2-propanol vapor was saturated in the reactor overnight. After adsorption of 2-propanol had

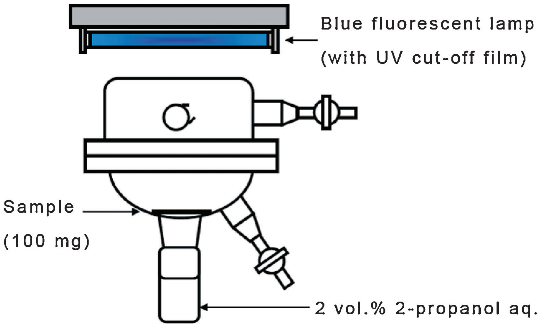

**Figure 1.** Reactor used for degradation of 2-propanol with a constant vapor pressure.

**Table 1.** Physical properties of uncalcined and calcined HyCOM-$TiO_2$ samples and the amount of $Rh^{3+}$ loading

| $T_{cal}$/°C | Phase | $d^a$/nm | $S_{BET}$ /$m^2 g^{-1}$ | $Rh^{3+}$ loading /wt % |
|---|---|---|---|---|
| Uncalcined | A | 11 | 96 | |
| 450 | A | 11 | 93 | 0.20 |
| 550 | A | 14 | 81 | 0.20 |
| 700 | A | 29 | 35 | 0.20 |
| 800 | A, R | 48 | 12 | 0.20 |
| 900 | R, A | 130 | 5.0 | 0.17 |

[a]Crystallite size of sample.

reached equilibrium, the sample was photoirradiated by visible light of a blue fluorescent lamp (10 W, maximum energy at 450 nm) doubly covered with a UV cut filter (Figure S1). The brightness on the surface of the glass filter was 6000 lx. The amounts of organic compounds and carbon dioxide ($CO_2$) were determined by gas chromatography. Details of experimental procedure (characterization and photocatalytic reaction) are provided in Supporting Information.[16]

The $TiO_2$ phase, crystallite size, and BET surface area of the as-synthesized HyCOM-$TiO_2$ sample were anatase, 11 nm, and 96 $m^2 g^{-1}$, respectively, as shown in Table 1. With increase in calcination temperature, the crystallite size of HyCOM-$TiO_2$ samples increased, whereas the specific surface area gradually decreased as also shown in Table 1. Rutile phase was clearly observed after calcination at 900 °C. These calcined samples exhibited diffuse reflection spectra typical of anatase and rutile phases as shown in Figure 2a. Figure 2b shows diffuse reflection spectra of 0.2 wt % $Rh^{3+}$-modified HyCOM-$TiO_2$ samples previously calcined at various temperatures. Absorption in the visible light region was observed in all of the $Rh^{3+}$-modified samples. It should be noted that modification of $TiO_2$ with only a small amount (0.2 wt %) of $Rh^{3+}$ using the simple adsorption method followed by filtration and drying caused the absorption in the visible light region. Light absorption intensity was almost independent of the physical properties of HyCOM-$TiO_2$ samples. A surface $Rh^{3+}$ complex(s) formed on $TiO_2$ might act as a sensitizer, although direct electron transfer from large amount (ca. 5 wt %) of rhodium chloride fixed on the $TiO_2$ surface to the conduction band of $TiO_2$ has been proposed.[14]

In this system, 2-propanol molecules were adsorbed onto photocatalysts and then photocatalytically decomposed under photoirradiation. Since 2-propanol in the gas phase was continuously supplied from the aqueous solution in this photocatalytic reaction system, the concentration of 2-propanol in the gas phase was almost constant. Therefore, photocatalytic activity of each sample can be evaluated under the condition in which adsorption equilibrium was continuously attained. In actual living spaces such as cooking and living areas, VOCs are always released to the gas phase and adsorbed on walls in the room. Figure 3 shows time courses of the amounts of products over bare HyCOM-$TiO_2$ calcined at 550 °C (Hy(550)) and 0.2 wt % $Rh^{3+}$-modified Hy(550) ($Rh^{3+}$/Hy(550)) under irradiation of visible light. For comparison, results for a nitrogen-doped $TiO_2$ sample are also shown. Formation of oxidized products was negligible when bare Hy(550) was used, indicating that band gap excitation of $TiO_2$ did not occur under the present irradiation conditions. On the other hand, acetone and $CO_2$ were continuously formed by modification of Hy(550) with only a small amount (0.2 wt %) of $Rh^{3+}$ using the adsorption method. It was also shown that $Rh^{3+}$/Hy(550) had a much higher level of activity than that of the nitrogen-doped $TiO_2$ sample. The rate of acetone formation gradually decreased, and the amount of acetone became almost constant at 42 µmol. The rate of $CO_2$ generation decreased slightly in the early stage and became almost constant. Details of kinetic study of this reaction system will be reported separately.

As the amount of acetone in the gas phase became constant after 30-h irradiation of visible light, the photocatalytic activity of the samples was evaluated by the amount of acetone and $CO_2$ produced over a period of 30 h. As shown in Figure 4, the 0.2 wt % $Rh^{3+}$-modified HyCOM-$TiO_2$ samples showed a

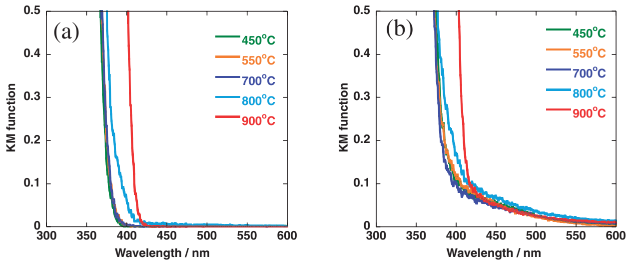

**Figure 2.** UV–vis diffuse reflection spectra of (a) bare HyCOM-$TiO_2$ samples and (b) 0.2 wt % $Rh^{3+}$-modified HyCOM-$TiO_2$ samples calcined at various temperatures.

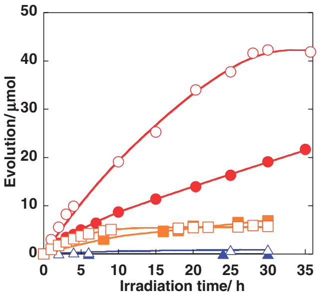

**Figure 3.** Time courses of formed acetone (open) and $CO_2$ (closed) over bare Hy(550) (triangles), $Rh^{3+}$/Hy(550) (circles) and nitrogen-doped $TiO_2$ (squares) in photocatalytic reaction of 2-propanol under irradiation of visible light.

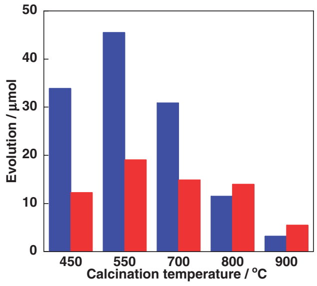

**Figure 4.** Amounts of acetone (left) and $CO_2$ (right) formed in photocatalytic reaction of 2-propanol after irradiation of visible light for 30 h over 0.2 wt % $Rh^{3+}$-modified HyCOM-$TiO_2$ calcined at various temperatures.

volcano-like tendency with calcination temperature, i.e., the $Rh^{3+}$/Hy(550) sample exhibited the highest level of activity in photocatalytic generation of acetone and $CO_2$, suggesting that calcination both positively and negatively affected the photocatalytic activity. As mentioned above, calcination of HyCOM-$TiO_2$ gradually changed the physical properties. The specific surface area of a photocatalyst is an important factor for improving the activity in heterogeneous photocatalytic decomposition of a pollutant in gas phase. A photocatalyst with a large specific surface area generally possesses a high ability for adsorption of the target molecule, which results in high photocatalytic activity. If the photocatalytic activity was dependent only on the specific surface area, the sample calcined at 450 °C with the largest specific surface area should have exhibited the highest level of activity. However, this was not the case. Crystallinity was also an important factor for controlling the photocatalytic activity and became higher with increase in calcination temperature. It is generally accepted that crystallinity is related to the amount of defects and that it affects various properties such as electron conductivity, hole mobility, and electron–hole recombination probability. These two properties, i.e., specific surface area and crystallinity, changed inversely when samples were calcined. In the case of HyCOM-$TiO_2$ samples modified with a small amount (0.2 wt %) of $Rh^{3+}$ simply prepared using the adsorption method, these results suggest that both specific surface area and crystallinity of $TiO_2$ affected the photocatalytic activity of $Rh^{3+}$-modified $TiO_2$ and that the balance of them is important for a higher level of photocatalytic activity.

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16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.