Fabrication of the photocatalyst thin films of nano-structured potassium titanate by molten salt treatment and its photocatalytic activity

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Abstract

The thin films of potassium titanate photocatalyst were fabricated by molten salt treatment and oxidation in air, using TiO2 thin films formed on Al2O3 balls as the substrate. The thin films were characterized by SEM, EDS, and XRD. The photocatalytic activity was evaluated by measuring the degradation rate of a methylene blue (MB) solution. The formation of nano-structured potassium titanate in the molten salt mixture and the influence on photocatalytic activity are discussed. The results show that the molten salt treatment was simple and useful to fabricate the thin films of nano-structured potassium titanate. The nano-lamellar potassium titanate with amorphous was formed, which is closely related to the carbonate ion in the molten salt mixture. 6-potassium titanate with nano-needle crystals was formed by crystallizing the potassium titanate during oxidation in air. The potassium titanate with the nano-lamellar had high adsorptivity, whereas 6-potassium titanate with nano-needle crystals had high photocatalytic activity.

1. Introduction

Titanium dioxide (TiO2) has been studied as a potential photocatalyst for many years [1]. TiO2 photocatalyst can be applied to the degradation of organic/inorganic pollutants, purification of air and water, and so on [2–7]. Recently, TiO2 derivatives, particularly layered titanate, have been shown to exhibit high photocatalytic activity [8,9]. These materials can be prepared by traditional processes, including hydrothermal, solid-phase, or sol–gel synthesis. Crystalline layered titanate compounds, including K2Ti6O13, and K2Ti3O7, are characterized by high adsorptivity relative to the parent TiO2 powder. However, the main disadvantage of layered titanate as a photocatalyst is that its activity in the visible spectral range is lower than that of TiO2 [9,10]. Tret’yachenko et al. studied the synthesis, adsorption, and photocatalytic activity of semiconductor materials based on amorphous potassium titanate powder modified with transition metal oxides/hydroxides. The powder was found to exhibit high photocatalytic activity under simulated solar radiation [10].

In addition, nano-structured titanates prepared by the hydrothermal treatment of TiO2 with strong alkaline solutions have attracted much interest due to their unique combination of physico-chemical and structural properties [11]. Titanates, particularly potassium titanate, exhibit attractive physical–chemical properties owing to their distinct crystal structures, which show great potential for photocatalysis [12]. Numerous potassium titanates with unique crystal structures (i.e., layered and tunnel structures) have been synthesized [13–16]. Potassium titanates can be fabricated in the form of whiskers or fibers, and have been used as photocatalysts for water cleavage [17,18]. Masaki et al. adopted a hydrothermal oxidation of titanium metal powder in concentrated potassium hydroxide solutions above 150 °C to obtain potassium titanates (K2TiO4, K4Ti3O8, and K2TiO7(OH)) as a single phase, as well as fibrous amorphous compounds that were transformed into K2Ti3O7, K2Ti6O13, or K2Ti2O5 by calcination [19]. Hydrothermal reaction of TiO2 nano-particles in KOH solution resulted in titanate (K2TiO12) nanowires with diameters under 10 nm and lengths ranging from 500 nm to 2 μm [20,21].

On the other hand, some drawbacks hinder the practical application of TiO2 photocatalysts. First, most TiO2 photocatalysts are prepared in the form of TiO2 nano-particles. Therefore, it leads that the handling for the applications, particularly for the treatment of flow pollutants in water and air; furthermore, the cost of recycling will be high. Many studies of TiO2 photocatalyst are oriented toward photocatalyst immobilization in the form of thin films [22–24]. In our early work, TiOx/Ti composite photocatalyst thin films were fabricated by a mechanical coating technique (MCT) and subsequent oxidation [25]. In addition, we fabricated nano-structured photocatalyst thin films by the treatment of Ti coatings in molten salt of KNO3 under different temperatures [26]. In the current study, the nano-structured potassium titanate with amorphous was formed on the surface of TiOx thin films in the molten salt mixture of KNO3 and K2CO3 after oxidizing the Ti coatings formed

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on \(\text{Al}_2\text{O}_3\) balls by MCT. In addition, nano-potassium titanate was synthesized by oxidizing the nano-structured potassium titanate. The potassium titanate thin films and Ti coatings were characterized by SEM, ESD, and XRD. The photocatalytic activity was evaluated by measuring the degradation rate of MB solution.

2. Experimental

2.1. Fabrication of the potassium titanate thin films

Ti powder (purity of 99.1%, average diameter of 30 \(\mu\)m) and \(\text{Al}_2\text{O}_3\) balls (purity of 93.0%, average diameter of 1 mm) were used as coating materials and substrates, respectively. A planetary ball mill (Type: P6, Fritsch) was employed to perform the mechanical coating operation, and the details could be found in our previous work [25]. First, \(\text{Al}_2\text{O}_3\) balls and Ti powder were charged into an \(\text{Al}_2\text{O}_3\) pot, and a planetary ball mill was used to fabricate Ti coatings. The MCT time was 10 h and the rotation speed was 480 rpm. After MCT, the Ti coatings were oxidized at 973 K for 2 h in air. The TiO\(_2\) thin film samples were then put into the molten salt mixture of KNO\(_3\) with 5 wt.% K\(_2\)CO\(_3\) at 773 K. The holding time was 5, 10, 15, and 20 min (labeled K-5, K-10, K-15, and K-20). The treated samples were washed with distilled water after the molten salt treatment. To obtain a higher amount of potassium titanate on the TiO\(_2\) thin films, the samples were treated in the molten salt mixture of KNO\(_3\) and K\(_2\)CO\(_3\) with an extended holding time of 20 h (labeled K-20), and then oxidized at 973 K for 20 h in air (labeled KH-20).

2.2. Characterization

The morphology and elemental composition analyses were carried out by using scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS, JEOL JSM-5300LV), X-ray diffraction (XRD) patterns were recorded through Cu K\(_\alpha\) radiation (JEOL JDX-3530). The patterns were measured within the scattering angle of \(2\theta\) of 10°–60°. The XRD patterns were analyzed using the standard JCPDS files.

2.3. Photocatalytic activity

Evaluation of photocatalytic activity was performed according to the Japanese industrial standard (JIS R 1703-2). First, the ball-shaped samples were dispersed as one layer on the bottom of the cylinder-shaped cell with dimensions of \(\Phi 40\) mm \(\times\) 30 mm. Then, 35 ml MB solution (0.2 \(\mu\)mol) for absorption was poured into the cell and maintained in dark for 18 h. For the evaluation test, the MB solution was drained and a fresh MB solution for the evaluation test (0.1 \(\mu\)mol) was poured into the cell. Finally, the specimens were irradiated with UV-light from 320 to 410 nm with a maximum around 365 nm (FL20S BLB, Toshiba) with 10 W/m\(^2\), and the MB concentration was measured at intervals of 20 min to 3 h using a digital colorimeter (mini-photo 10, SANSHIN). At the same time, the test in the dark was conducted for K-20 to compare with the results of the light irradiation test because the thin films fabricated by the molten salt treatment have high adsorptivity.

3. Results and discussions

3.1. The thin films fabricated by MCT and molten salt treatment

Fig. 1 shows SEM images of the surfaces of Ti coatings, TiO\(_2\) thin films, and the samples treated in the molten salt mixture (K-5, K-10, K-15, and K-20). Some compounds seem rutile TiO\(_2\) were formed on the surface of TiO\(_2\) thin films. Nano-lamellar compounds were formed on the surface after the molten salt treatment. The lamellar thickness is under 100 nm, and these compounds appear to spread and grow as the holding time increases. After the molten salt treatment, most compounds grow from the surface of the samples. Table 1 shows the composition analysis by EDS of TiO\(_2\) thin films, and the samples treated in the molten salt mixture (K-5, K-10, K-15, and K-20). The potassium content of the samples increases with expanding the holding time. This result hints that the nano-lamellar compounds are potassium titanate, and are formed by the reaction of TiO\(_2\) and potassium in the molten salt mixture.

Table 1: Elemental composition of TiO\(_2\) thin films, and the samples treated in the molten salt mixture of KNO\(_3\) and K\(_2\)CO\(_3\) (K-5, K-10, K-15, and K-20).

<table>
<thead>
<tr>
<th>Element (at.%)</th>
<th>Ti</th>
<th>O</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>39.9</td>
<td>60.1</td>
<td>–</td>
</tr>
<tr>
<td>K-5</td>
<td>30.6</td>
<td>69.2</td>
<td>0.12</td>
</tr>
<tr>
<td>K-10</td>
<td>29.9</td>
<td>69.6</td>
<td>0.5</td>
</tr>
<tr>
<td>K-15</td>
<td>33.4</td>
<td>65.9</td>
<td>0.7</td>
</tr>
<tr>
<td>K-20</td>
<td>31.3</td>
<td>67.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Fig. 1. SEM images of surfaces for (a) Ti films, (b) TiO\(_2\) films, and the samples treated in molten salt mixture of KNO\(_3\) and K\(_2\)CO\(_3\) for (c) K-5, (d) K-10, (e) K-15 and (f) K-20.
films after oxidation. Although the nano-lamellar compounds on the samples are formed as shown in Fig. 1, an obvious change in the diffraction patterns does not appear after the molten salt treatment. These results suggest that the nano-lamellar compounds are probably amorphous [27].

To study the formation of the nano-lamellar compounds, some samples were fabricated by changing the molten salt mixture or the experimental conditions. As shown in Fig. 1, the nano-lamellar compounds formed on the surface of TiO2 thin films after the molten salt treatment, are not present in the non-oxidized Ti coating samples treated in the molten salt mixture under the same conditions. In addition, the nano-lamellar compounds do not form during the molten salt treatment using only KNO3 for TiO2 thin films obtained by oxidizing Ti coatings. Considering these results, it could conclude that the nano-lamellar compounds are formed by the reaction of TiO2 and K2CO3 in the molten salt mixture. On the other hand, the nano-lamellar compounds do not form on the surface of TiO2 thin films treated in solid K2CO3 at 773 K (solid-state reaction). Furthermore, TiO2 thin films dissolve in molten K2CO3 at 1173 K (liquid-state reaction). These results hint that TiO2 thin films react with ionized potassium carbonate in molten salt mixture of KNO3 and K2CO3, and the titanate ion (TiO3)2− forms on the surface as reported by reference [28]. This also shows that the nano-lamellar compounds are potassium titanate.

### 3.2. The potassium titanate thin films by oxidation process

Fig. 3 shows the SEM images of the surfaces of the samples treated in the molten salt mixture for 20 h ((a) K-20h) and then oxidized at 973 K for 20 h in air ((b) KH-20h). Fig. 3(b) shows that nano-needle compounds are formed from the nano-lamellar potassium titanate of KH-20h. The diameter is about 70 nm, and the nano-needle compounds grow alongside the nano-lamellar potassium titanate, which could increase the surface area and photocatalytic activity.

Table 2 shows the results of the EDS composition analysis of the K-20h and KH-20h samples. The potassium content of KH-20h is higher than that of K-20h, which probably related to crystallization of the amorphous lamellar compounds during the oxidation after the molten salt treatment. On the other hand, although there is no obvious difference in the SEM images of K-20 (Fig. 1(f)) and K-20h (Fig. 3(a)), K-20h contains more potassium (3.4 wt%, Table 2) than K-20 (1.2 at.%, Table 1), which means that the potassium content in the thin films increases with longer holding times.

Fig. 4 shows the X-ray diffraction patterns of the K-20h and KH-20h samples. Some peaks of 6-potassium titanate appear in the KH-20h sample. This indicates that the nano-lamellar potassium titanate with amorphous crystallizes during oxidation and forms 6-potassium titanate [29]. This result also reveals that the nano-lamellar compounds formed in the molten salt treatment are amorphous. Gorokhovsky et al. have also reported that the formation of 6-potassium titanate during the molten salt treatment of potassium salts and subsequent oxidation of TiO2 [28].

Moreover, although the X-ray diffraction peaks of 6-potassium titanate do not appear in the sample of K-20 after oxidation, the peaks appear in the sample of KH-20h. This shows that the sample of K-20 does not contain enough potassium to form 6-potassium titanate.

### 3.3. Photocatalytic activity and absorption of the potassium titanate thin films

Fig. 5 shows the relationship between MB solution concentration and irradiation time in the evaluation of photocatalytic activity and absorption of TiO2 thin films, K-20h, and KH-20h. After irradiation for 3 h, the MB solution concentration decreases by about 5% for TiO2 thin films, and about 15% for KH-20h. Moreover, with irradiation for 3 h, the MB solution concentration decreases by about 5% for TiO2 thin films.
solution concentration shows a large decrement, reaching about 25% for KH-20h. However, the MB solution concentration also decreases by about 20% in the dark (dashed line), due to the high adsorption of K-20h. A comparison of these results suggests that the decrement of 5% of the MB solution concentration was in fact due to degradation by photocatalytic activity. The degradation of MB solution by photocatalytic activity of KH-20h was about three times higher than those of K-20h.

4. Conclusions

The proposed process of molten salt treatment is simple and useful for the fabrication of thin films of nano-structured 6-potassium titanate. The nano-lamellar potassium titanate shows high adsorptivity, whereas nano-lamellar 6-potassium titanate shows high photocatalytic activity.

References


Fig. 4. X-ray diffraction patterns of the samples treated in the molten salt mixture of KNO3 and K2CO3 for 20 h (KH-20h), and subsequent oxidation (KH-20h).

Fig. 5. Photocatalytic degradation of MB under UV irradiation and absorption in dark place by TiO2 thin films and the samples treated in molten salt mixture of KNO3 and K2CO3 for 20 h (K-20h), and subsequent oxidation (KH-20h).