A novel preparation of titanium dioxide from titanium slag

Yongjie Zhang, Tao Qi, Yi Zhang

Abstract

A novel method of caustic hydrothermal decomposition of titanium slag followed by acidification of the sodium titanate product was adopted to prepare titanium dioxide. The effects of temperature, sodium hydroxide concentration, alkali-to-titanium slag mass ratio and reaction time on the titanium extraction were studied. Almost complete extraction of titanium was achieved when finely ground titanium slag (~61+51 μm) was reacted with a NaOH solution with a concentration of 10 mol kg⁻¹ H₂O and the alkali-to-titanium slag (based on TiO₂) mass ratio of 4:1 at 220 °C for about 4 h. The XRD pattern shows that the hydrothermal product obtained under optimal conditions was Na₄Ti₃O₈. Titanium dioxide with a rutile structure was obtained by acidification and cation exchange of Na₄Ti₃O₈. The effects of pH value, temperature, mass ratio of liquid-to-solid, and different acid medium on the product of cation exchange were studied together with the variation of titanium and iron concentration in solution. Under optimal conditions, the purity of titanium dioxide was >99.0%.

1. Introduction

Titanium dioxide is an important inorganic chemical material, especially the best-quality white pigment. Titanium dioxide also has a high potential application in environmental purification, gas sensors, and in photovoltaic cells due to its unique characteristics (Adachi et al., 2000). The commercial technologies for the manufacture of pigment grade titanium dioxide are the Sulfate Process and Chloride Process (Langmesser et al., 1973; Mackey, 1974; Chernet, 1999; Sasikumar et al., 2004; Jabłoński et al., 2001; Krchma and Schaumann, 1951; Sohn and Zhou, 1999; Morris et al., 1998). In the Sulfate Process, ilmenite is digested with strong sulfuric acid, yielding a titanium sulfate solution which is then hydrolyzed and precipitated to form a TiO₂ pigment and a solution waste consisting mostly of acidic ferrous sulfate. In the Chloride Process, rutile first reacts with chlorine gas to form titanium tetrachloride, which is then converted directly to the TiO₂ pigment with the liberation of elemental chlorine by heating the vapor in admixture with oxygen or air at high temperature. Both processes face the problems of producing large amount of wastes or toxic by-products and needing serious action to avoid pollution to the environment (Wang et al., 1999; Liu et al., 1998; Wang and Ma, 2004).

In the present work, a new process is proposed for the production of titanium dioxide from titanium slag. Based on the principles of cleaner production, the new technology can serve as a moderate process with the recycling of alkaline and acid solution. In this process, high titanium slag was decomposed with concentrated NaOH solution by a hydrothermal method to form the intermediate, Na₄Ti₃O₈, which was then converted to titanium dioxide through acidification and cation exchange. The present work mainly focuses on the decomposition behavior of titanium slag and the acidification/cation exchange process.

2. Experimental

2.1. Materials

All the chemical regents employed were analytical grade and deionized water was used throughout. Water for analysis was super-purified by a water super-purification machine (Milli-Q, Millipore). The titanium slag sample used was supplied by Guo’ai Ferroalloy Company (Hebei, PR of China) and was ground, dried and screened (based on TiO₂) mass fraction of 4:1. The detailed chemical composition of the titanium slag shown in Table 1 was examined by ICP-OES (Optimal 5300DV, Perkin-Elmer, USA).

2.2. Apparatus

The hydrothermal decomposition experiments were carried out in a 500 mL stainless steel autoclave equipped with a mechanical
agitator and pure nickel liner at the autogenous pressure. A stirring speed of 700 rpm was applied to keep the slurry suspended during the decomposition experiment. The temperature of the reactor was thermostatically controlled with a precision of ±1 °C. The acidification/cation exchange experiments were performed in a flask reactor with a reflux condenser which was heated by an oil bath, thermostatically controlled to within ±0.5 °C.

2.3. Procedure

All the experiments were conducted in batches. To assure the reproducibility of the results, every experiment was carried out at least three times. For each decomposition run, 80 g NaOH dissolved in the required amount of deionized water was first charged into the autoclave followed by the amount of titanium slag. Then the autoclave was sealed and the mixture of the reactants was stirred at 700 rpm while heated. After the reaction at temperature and cooling, the product was filtered and the solid phase was washed by deionized water and dried at 80 °C. The alkali solution could be recycled by adding fresh sodium hydroxide to decompose fresh titanium slag.

The hydrothermal reaction of titanium slag with NaOH solution formed sodium titanate. The titanium extraction was calculated by dissolving a sample of the product in HCl solution while the un-reacted titanium slag was not dissolved. After filtration, the chloride solution was analyzed for its titanium content by ICP-OES.

For each acidification/cation exchange experiment, a required amount of dried sodium titanate was mixed with deionized water under magnetic stirring and then either HCl, H$_2$SO$_4$ or HNO$_3$ was dropped in to adjust the pH of the mixture to pH=0.6. The mixture was refluxed at 100 °C for 5 h to perform hydrolysis and the TiO$_2$ product was filtered, washed with deionized water and finally dried at 80 °C for 4 h.

The structure and morphology of the sodium titanate and TiO$_2$ product were characterized by XRD and Scanning Electron Microscope (SEM) (JSM-6700, JEOL, Japan). The chemical composition of sodium titanate was analyzed by ICP-OES and the purity of the TiO$_2$ product, was analyzed by metal aluminum reduction method (Standardization Administration of the People’s Republic of China, 1993) after calcination at 950 °C for 2 h.

3. Results and discussion

3.1. Hydrothermal decomposition

3.1.1. Effects of decomposition temperature and concentration of NaOH solution

The effects of temperature and concentration of NaOH solution on the extraction of titanium were examined in NaOH solution of 8, 8.75, and 10 mol kg$^{-1}$ H$_2$O, respectively, with the alkali-to-titanium slag (based on the TiO$_2$) mass ratio of 5:1, reaction time of 8 h and temperature in the range of 200–260 °C. From the results in Fig. 2, it can be seen that the titanium extraction increases rapidly with increasing decomposition temperature. In NaOH solution with 8 mol kg$^{-1}$ H$_2$O, the titanium extraction increases from 64.5% to 89.8% with the increase of the decomposition temperature from 200 °C to 260 °C. While in NaOH solution with 10 mol kg$^{-1}$ H$_2$O, the titanium extraction increases from 58.2% to 100% with the increase of temperature from 200 °C to 220 °C and 240 °C.

3.1.2. Effect of alkali-to-titanium slag mass ratio

The effect of alkali-to-titanium slag mass ratio on the extraction of titanium was investigated at various temperatures and NaOH solution concentration. The results are shown in Fig. 3. It can be seen that the titanium extraction increases with increasing alkali-to-titanium slag mass ratio. At 200 °C, 220 °C and 240 °C, the titanium extraction increases from 58.2% to 100% with the increase of alkali-to-titanium slag mass ratio from 5:1 to 8:1.

Table 1

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Ti</th>
<th>Cr</th>
<th>Mg</th>
<th>Mn</th>
<th>Al</th>
<th>Ca</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;61/+51</td>
<td>55.47</td>
<td>1.05</td>
<td>0.23</td>
<td>0.23</td>
<td>1.64</td>
<td>1.31</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern of titanium slag.

Fig. 2. Effect of temperature and NaOH concentration on titanium extraction. Other conditions: alkali-to-titanium slag mass ratio 5:1 and decomposition time 8 h.

Fig. 3. Effect of alkali-to-titanium slag mass ratio on titanium extraction in NaOH solution with concentration of 8.75 mol kg$^{-1}$ H$_2$O at 200 °C, 220 °C and 240 °C. Other conditions: decomposition time 8 h.
concentrations with reaction time of 8 h as shown in Fig. 3. The results show that the titanium extraction increases rapidly from 88.7% to 100% when the alkali-to-titanium slag mass ratio increases from 2:1 to 4:1 in NaOH solution of 8.75 mol kg\(^{-1}\) H\(_2\)O at 260 °C. However, at 200 °C the titanium extraction was only around 50–60% in NaOH solution of 10 mol kg\(^{-1}\) H\(_2\)O over the range of mass ratios examined. But in the same solution at 220 °C and 240 °C the titanium extraction was almost 100% at 4:1 mass ratio.

3.1.3. Effect of decomposition time

The effect of reaction time on the extraction of titanium in NaOH solution of 10 mol kg\(^{-1}\) H\(_2\)O at 220 °C with the alkali-to-titanium slag mass ratio of 4:1, shown in Fig. 4, indicates that the titanium extraction increases sharply with the increase of reaction time and reaches 100% at about 4 h. This appears to be the optimal reaction conditions from the overall investigation.

3.1.4. Decomposition product

The XRD pattern of product obtained at the optimal reaction conditions (Fig. 5) indicates that the product is Na\(_4\)Ti\(_3\)O\(_8\). This is confirmed by the ICP analysis which shows the mole ratio of Na/Ti=1.32. Therefore the reaction may be described as follows: 3TiO\(_2\) + 4NaOH → Na\(_4\)Ti\(_3\)O\(_8\) + 2H\(_2\)O. The SEM micrograph of Na\(_4\)Ti\(_3\)O\(_8\) (Fig. 6) shows that it is fibrous.

3.2. Acidification/cation exchange of Na\(_4\)Ti\(_3\)O\(_8\)

In the traditional Sulfate Process, the TiO\(_2\) is obtained by hydrolysis of an acidic titanium(IV) solution. In the present study, a method of acidification and cation exchange under more moderate conditions is proposed and the acid solution can be recycled and reused.

3.2.1. Effect of pH value and solid:liquid ratio

The pH value influences the structure of the product directly. The XRD patterns of products obtained by acidification and cation exchange at different pH values in H\(_2\)SO\(_4\) medium at 100 °C, with the solid-to-liquid mass ratio of 1:100, show that when pH≤1.20, the product was TiO\(_2\) with a rutile structure. When 1.20<pH≤1.50, Na\(_4\)Ti\(_3\)O\(_8\) was not completely acidified and cation exchanged, i.e., not all the Na atoms in the structure of Na\(_4\)Ti\(_3\)O\(_8\) were exchanged for protons. When the pH was ≥1.90, no reaction with acid happened.

At pH=0.20 there was no significant effect of solid-to-liquid mass ratio ranging from 1:150 to 4:25 and all the products were TiO\(_2\) with a rutile structure.

3.2.2. Effect of temperature

Effect of temperature on the acid reaction was investigated from room temperature to 110 °C in H\(_2\)SO\(_4\) medium with the solid-to-liquid mass ratio of 1:100 and pH=0.20. The XRD patterns of the product obtained at room temperature was not TiO\(_2\), and if the temperature was lower than 60 °C, the Na\(_4\)Ti\(_3\)O\(_8\) simply dissolved and no precipitate was obtained. But when the temperature was >60 °C, total reaction happened and the product was TiO\(_2\) with a rutile structure.

3.2.3. Effect of acid type

In the aqueous hydrolysis of titanium(IV) solution, it was reported that when mono-protic strong acids, such as HCl, HNO\(_3\), and HF etc., were used to dissolve the titanium material, the corresponding hydrolysis product was anatase TiO\(_2\), while strong acids with multi-charged anions, such as H\(_2\)SO\(_4\) and H\(_3\)PO\(_4\), gave rutile TiO\(_2\) product (Tang, 2001). In this work, HCl, HNO\(_3\) and H\(_2\)SO\(_4\) were used to adjust the pH value at 100 °C with pH=0.20, but the XRD patterns showed that the products were all rutile TiO\(_2\). They did however show different morphologies in the SEM micrographs (Fig. 7). In HCl medium, the TiO\(_2\) was fibrous with a high aspect ratio, while in HNO\(_3\) and H\(_2\)SO\(_4\) medium, the TiO\(_2\) was fibrous with a low aspect ratio.

3.2.4. Effect of time on Ti(IV) and Fe(III) in solution

In order to investigate the behavior of the main ions, Ti(IV) and Fe(III) during the reaction, the variation of their concentrations in HCl medium at pH=0.20 with time was studied at 100 °C using a solid-to-
liquid mass ratio of 1:150. The samples, analyzed by ICP (Fig. 8), show that the concentration of Ti(IV) in solution has a maximum value at about 20 min and then goes down sharply until 120 min before keeping at about 29 mg L\(^{-1}\). The concentration of Fe(III) in solution increases from the start to about 120 min and keeps around 58 mg L\(^{-1}\) with further time. It indicates that at the beginning of the reaction, some of the titanium in the solid phase dissolves as Ti(IV) which is then hydrolyzed to form TiO\(_2\) leading to the decrease of Ti(IV) concentration in solution to reach its natural solubility in acid medium at the corresponding temperature. As far as Fe(III) is concerned, more and more iron in the solid phase may be dissolved in the acid medium with time until it is all dissolved, leading to the increase of iron concentration in solution.

According to the results, the main reaction in the acidification/cation exchange process may be described as follows: (1) \(\text{Na}_4\text{Ti}_3\text{O}_8 + 4\text{H}^+ \rightarrow \text{H}_4\text{Ti}_3\text{O}_8 + 4\text{Na}^+\) and (2) \(\text{H}_4\text{Ti}_3\text{O}_8 \rightarrow 3\text{TiO}_2 + 2\text{H}_2\text{O}\).

3.2.5. Purity of ion-exchange product

The purity of the TiO\(_2\) obtained was analyzed by the metal aluminum reduction method. It is observed that the purity of the TiO\(_2\) obtained by reaction in HCl medium was higher than that in H\(_2\)SO\(_4\) or HNO\(_3\) medium with other conditions similar. The purity of the TiO\(_2\), obtained in HCl medium at pH=0.20 with a solid-to-liquid mass ratio of 1:150 was 99.4%, 98.4% and 98.4% at 80 °C, 100 °C and 110 °C respectively.

4. Conclusions

A hydrothermal decomposition of titanium slag in concentrated caustic solution, combined with acidification/cation exchange method of production of titanium dioxide was proposed. The effects of several reaction conditions on the titanium extraction were studied. When finely ground titanium slag (−61/+51 μm) was reacted with NaOH solution with a concentration of 10 mol kg\(^{-1}\) H\(_2\)O in the alkali-to-titanium slag (based on TiO\(_2\)) mass ratio of 4:1 at 220 °C for about 4 h, almost complete extraction of titanium was achieved. At these optimal conditions, the hydrothermal product was Na\(_4\)Ti\(_3\)O\(_8\) which could be separated as a pure intermediate solid. Titanium dioxide was obtained by acidification/cation exchange of Na\(_4\)Ti\(_3\)O\(_8\) in HCl, H\(_2\)SO\(_4\) or HNO\(_3\) medium. The obtained TiO\(_2\) had a rutile structure without calcination. In HCl medium under optimal conditions, the purity of the TiO\(_2\) was >99.0%. The spent alkali and acid solutions could be recycled after separation although any iron impurity in Na\(_4\)Ti\(_3\)O\(_8\) builds up in the acid solution. Further work is required to investigate the build up and removal of other impurities such as silica.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (No. 50574084) and China Postdoctoral Science Foundation (No. 2005038393).

References


