Structure transition of nano-titania during calcination

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Abstract: In order to study the structure transition during calcination, nano-titania powders prepared by hydrolyzing precipitation approach and calcined at 300, 400, 500, 600 and 700 °C were characterized by XRD, TEM and electron diffraction(ED), respectively. The results show that titania powders calcined below 500 °C are almost composed of anatase, rutile appears below 500 °C and its ratio increases gradually with increase of calcin temperature; nano-titania particles are smaller than 40 nm mostly and the dispersion is related to calcining temperature; the inter-planar distances of nano-anatase single crystalline change gradually when calcing temperature increases to 500 °C; so do that of nano-rutile single crystalline when calcining temperature charges from 600 to 700 °C. The conclusions can be drawn that the temperature of transformation from anatase to rutile is below 500 °C and the process carries on gradually. Both inter-planar distances and the structure of nano-titania transform gradually with increasing calcing temperature.

Key words: nano-titania; phase transformation; structure transition; inter-planar distances

CLC number: TB137

1 INTRODUCTION

Titania has three crystallines: brookite, anatase and rutile. Their basic structural unit is the same [TiO6] octahedron, but their lattice structures are different. For example, brookite belongs to rhombic crystallo-series, while rutile and anatase belong to square crystallo-series. Though rutile and anatase are the same crystallo-series, their symmetrical elements and unit-cell parameters are different [4].

In recent years, much attention has been paid to phase transformation of titania particle, especially to the temperature of phase transformation from anatase into rutile [5-8]. Little attention was focused on lattice structure transition of nano-titania particle. Bokhimi et al. [9] regarded that when rutile was annealed at different temperatures, its lattice parameters were almost the same, and the bond length of rutile prepared by using TiCl4 as precursor did not depend on crystal size, which is between 9.77 and 145 nm. The above conclusion is based on titania polymorph, not single nano-crystalline. So, a study on lattice structure transition of nano-titania particle is necessary and valuable in fabrication and usage of nano-titania powder.

2 EXPERIMENTAL

Titanium tetrachloride was added into the diluted hydrochloric acid dropwise, while stirring to keep the temperature below 40 °C during mixing. After being cooled to room temperature, the mixture was turned into a flask, heated to 90 °C and refluxed for a while until precipitate was produced. Then the precipitate was filtrated and washed with deionized water and absolute ethanol. The product was dried at 60 °C and calcined at different temperatures. Finally, the samples were characterized by XRD, TEM and electron diffraction(ED).

3 RESULTS

3.1 XRD

The XRD patterns of titania nano-powder calcined at different temperatures are shown in Fig. 1. In Fig. 1, it can be seen that the nano-powders prepared and calcined below 500 °C are composed of anatase almost. When the calcination temperature is up to 500 °C, rutile diffraction peak appears. Below 700 °C, the diffraction intensity of anatase peaks becomes stronger and stronger with increasing calcining
temperature. After rutile is developed at 500 °C, its diffraction intensity becomes stronger and stronger with increasing the experimental temperature. At 800 °C, the diffraction intensity of rutile is stronger than that of anatase for the first time.

3.2 TEM

TEM results are shown in Fig. 2. In Fig. 2, it is seen that the morphology of nano-titania is sphere-like and their size is smaller than 40 nm mostly. The dispersion of nano-titania powders calcined at different temperatures is different. The dispersion of the powder calcined at 600 °C is the best and at 700 °C is the second with a few congregating particles, as shown in Fig. 2 (b) and 2(a), respectively. The powder calcined at 400 °C congregates severely, as shown in Fig. 2(c).

3.3 Electron diffraction

The electron diffraction patterns of titania nano-particle prepared and calcined at different temperatures are shown in Fig. 3.

In Fig. 3, patterns (a), (c), (d) and (g) show multi-crystalline forms, the others are single crystal forms. The lattice structure and their planar distances of crystal forms are estimated according to the index direct demarcation way:

\[d = \frac{\lambda L}{R}\]

where, \(d\) is the inter-planar distance, nm; \(\lambda\) is the constant of camera, nm · mm\(^{-1}\); \(R\) is the distance between central spot and diffraction spot, which is measured from the original plat, mm.

The lattice parameters of nano-titania single crystalline are shown in Table 1.

![Table 1 Estimated results of lattice parameter](image)

<table>
<thead>
<tr>
<th>Pattern</th>
<th>t/°C</th>
<th>(d_1/\text{nm})</th>
<th>(d_2/\text{nm})</th>
<th>(d_3/\text{nm})</th>
<th>(G_2/G_1)</th>
<th>(G_3/G_1)</th>
<th>2θ/(°)</th>
<th>Belt</th>
<th>Series</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b)</td>
<td>uncalcined</td>
<td>0.155</td>
<td>0.155</td>
<td>0.100</td>
<td>1.000</td>
<td>1.550</td>
<td>120</td>
<td>([123])</td>
<td>bcc</td>
<td>anatase</td>
</tr>
<tr>
<td>(e)</td>
<td>500</td>
<td>0.155</td>
<td>0.145</td>
<td>0.137</td>
<td>1.069</td>
<td>1.131</td>
<td>120</td>
<td>([123])</td>
<td>bcc</td>
<td>anatase</td>
</tr>
<tr>
<td>(f)</td>
<td>600</td>
<td>0.103</td>
<td>0.103</td>
<td>0.084</td>
<td>1.000</td>
<td>1.226</td>
<td>105</td>
<td>([123])</td>
<td>fcc</td>
<td>rutile</td>
</tr>
<tr>
<td>(h)</td>
<td>700</td>
<td>0.155</td>
<td>0.145</td>
<td>0.137</td>
<td>1.069</td>
<td>1.131</td>
<td>120</td>
<td>([123])</td>
<td>bcc</td>
<td>anatase</td>
</tr>
<tr>
<td>(i)</td>
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<td>0.084</td>
<td>0.084</td>
<td>2.381</td>
<td>2.381</td>
<td>120</td>
<td>([123])</td>
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