Preparation and Characterization of Anatine TiO$_2$/Expanded Graphite with High Expansion Volume

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Abstract. Element of Ti was introduced to expandable graphite surface by Sol-gel method; TiO$_2$/expanded graphite was prepared after expansion of high temperatures. Detection by scanning electron microscope(SEM), X-ray diffraction(XRD), energy disperse spectroscopy(EDS) and differential scanning calorimetry(DSC) to semples, the results were founded: The better process conditions with high expansion volume are as follows: graphite that particle size is more than 180μm, expansion temperature is about 650 °C-750°C. The contents of Ti in compounds of anatine TiO$_2$/expanded graphite can be reached 3.16%; the volume of compounds can be reached 234ml/g. The results showed that the lower temperature and smaller particle size of graphite is benefit for anatine type of TiO$_2$, but higher temperature is good to high expansion volume. The preparation condition should be balanced with crystal type, heat loss and expansion volume.

1. Introduction

TiO$_2$ photocatalyst is drug-free, stable, high catalytic activity, anti-chemical corrosion and corrosion-ray [1-2]. In many papers, carrier is discussed as a major problem, such as activated cabon [3-7], carbon fiber [8-9], et.al. Mounting of TiO$_2$ onto activated carbons and carbon fibers were reported to result in certain reduction of specific surface area of carbons. This was reasonably supposed to be due to the preferential deposition of TiO$_2$ particles at the entrance of the pores on the surface of substrate carbon. So, the expanded graphite was chosen not only because expanded graphite is flexible, compressible, and elastic, as well as being lubricious and resistant to heat and corrosion, it has been applied in large quantities in stuffing, gaskets, heat insulators, etc. [10], but also because of its oil absorption, 1g of a lump of expanded graphite sorbing more than 80g of heavy oil [11].

In the present work, therefore, TiO$_2$ particles were precipitated on the surface of the graphite intercalated compounds (GIC) to obtain gelation-GIC (gel-GIC), and then being followed by expansion at high temperature in order to obtain rutile TiO$_2$/expanded graphite with high expansion volume. And the structures of TiO$_2$/ expanded graphite were characterized.

2. Formatting the title, authors and affiliations

2.1. Preparation

Nature graphite in this study is divided into three groups according to its particle sizes: (a)>450μm, (b) 250-180μm, and (c) 106–85μm. Other reagents include sulfuric acid (AR), nitrate acid (AR), and potassium permanganate (AR).

A quantity of nature flake graphite with different particle size are dried at 80°C in a vacuum oven for 24h, concentrated different condition of acid and potassium permanganate are stirred in the flask.
After 60 min, the mixture is carefully washed and filtrated with deionized water until the pH level of the solution reaches 6. After being dried at 60°C in a vacuum oven for 24h, the graphite intercalated compound (GIC) is prepared. TiO₂ particles were adhesived onto the surface of GIC through the tetrabutyl orthotitanate (TBOT), triethanolamine (TEA) and ethanol, m (tetrabutyl titanate):m (triethanolamine) =1:0.4. GIC of 10 g was suspended in the solution in order to get gel-GIC. And the gel-GIC was prepared after the sol was dried at 373 K for 24 h and grounded to powder. Then the substrate GIC was expanded at high temperature for 10-15 s in a muffle furnace to form expanded graphite.

2.2. Characterization
Scanning electron microscope (SEM) and energy disperse spectroscopy (EDS) studies were carried out on a VEGA’s electron microscope (VEGA II XMH). X-ray Diffraction patterns were obtained by a Broker’s diffractometer (D8 ADVANCE). Differential scanning calorimetry (DSC) was made by a TA’s Analyzer (TA-Q20-DSC). The expansion ratio of GIC is denoted using expansion volume (ml/g).

3. Experimental results and analysis
3.1. Preparation condition
The data in Table 1 shows the expansion volume for different particle size of graphite. It is found that the expansion volume of composites is higher when large particle size is used. Although the expansion volume of gel-GIC is smaller than GIC with the same particle size, the particle size of more than 180 μm of gel-GIC can be reach 200 mL/g.

Table 1. Expansion volume for different size of the gel-GICs

| Size(μm) | 450-850 | 250-180 | 106-85 |
|---------|---------|---------|--------|
| 1.143   | 0.285   | 0.286   | 0.593  |
| 1.43    | 0.285   | 0.067   | 0.796  |
| 0.571   | 0.109   | 0.600   | 0.439  |

3.2. Structure and microstructure analysis of gel-GIC

The figure 1 shows the difference of DSC that gel-GIC have with different particle size. The bigger the graphite particle size is, the more heat that gel-GIC absorbed, and the higher temperature gel-GIC needs.

The SEM of the GIC (figure 2) shows the different surface state between the big gel-GIC and the small one. TiO₂ particles are all adhesived on the surface of gel-GIC. And the shapes are often spherical or spherical approximation. But the particle size of gel-graphite of (a) is about 1-2 μm, bigger
than the particle size of gel-graphite of (C). And also, the micro-lays of big gel-GIC are larger than small gel-GIC as pure GIC have [12]. It shows the solution-gelatin method did not affect GIC. The XRD patterns of gel-GIC are showed in figure 3. The peaks at about 28°, 55° and 87° become weak with the particle size decrease. And the diffraction intensity of sample is also weak from (a), (b) and (c), indicating that the bigger the gel-GIC is, the higher crystalline gel-GIC is.

3.3. Structure and microstructure analysis of TiO2/expanded graphite

XRD patterns of prepared samples at 950°C are presented in figure 4. With the larger of the particle size, the greater the degree of rutile type. So the particle size is important for anatase phase. It also shows the temperature is the key for TiO2. Carbon formed need to suppress the phase transformation from anatase to rutile, which usually occurred on pure TiO2 formed by the present method above 550°C, Carbonization temperature being the higher, the amount of rutile formed was larger. The lower temperature is necessary if anatase phase wants to be obtained. But the effect of temperature was listed in figure 5. The expansion volume is down if the temperature lower. The best condition is as follows: The particle size is more than 180μm, the temperature is between 650°C-750°C. Under this condition, the higher expansion volume (>200ml/g) and anatase phase compounds can be obtained.
The influence of temperature lies not only on the expansion volume of graphite and crystal type of titanium dioxide, but also heat loss of compounds. The heat loss measurements at the different temperatures are presented in figure 6. As the temperature rises, there is a little downward trend with the range from 550°C to 700°C, and the heat loss is of a lower rate of not more than 5% at this stage. At the higher temperature, the heat loss of expanded graphite has a basic upward trend. Electron spectroscopy of TiO\textsubscript{2}/expanded graphite was shown in table 2. The contents of Ti are as follows: (a) is 1.01%, (b) is 3.60%, (c) is 1.51%. So (b) has the most element of Ti. The higher expansion volume (>200ml/g), the temperature of 550°C-650°C and high contents of anatase phase compounds can be obtained with the (b).

Table 2. EDS of TiO\textsubscript{2}/expanded graphite with different particle size

| Atomic ratio | Separation energies |
|--------------|---------------------|
| C            | 87.74 a 90.16 b 83.47 c |
| O            | 11.24 a 6.09 b 15.01 c |
| Ti           | 1.01 a 3.60 b 1.51 c |

4. Conclusion
The better process conditions with high expansion volume are as follows: graphite that particle size is more than 180μm, expansion temperature is about 650°C-750°C. The contents of Ti in compounds of anatine TiO\textsubscript{2}/expanded graphite can be reached 3.16%; the volume of compounds can be reached 234ml/g. The results showed that the lower temperature and smaller particle size of graphite is benefit for anatine type of TiO\textsubscript{2}, but higher temperature is good to high expansion volume. The preparation condition should be balanced with crystal type, heat loss and expansion volume.

5. References
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