Preparation and properties of TiO\textsubscript{2}/fumed silica composite photocatalytic materials

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Abstract

The fumed silica used to produce the photocatalytic materials. TiO\textsubscript{2} gel was obtained using tetrabutyl titanate as a precursor via an acid catalyzed sol-gel process. A novel TiO\textsubscript{2}/fumed silica porous ceramic material was produced using a 4\% phosphoric acid binder. The influence of heating temperature on the crystalline phases of TiO\textsubscript{2}, and the properties and photocatalytic activity of TiO\textsubscript{2} was investigated. The experimental results showed that the transformation of TiO\textsubscript{2} from anatase to rutile began at 725 °C. The photocatalytic porous ceramic materials which were heated at 700–800 °C exhibited high tensile strength (7.67–8.18 MPa), high specific surface areas (25.01–25.07 m\textsuperscript{2} g\textsuperscript{-1}), high anatase content (>90\%) and good photocatalytic activity, as confirmed by the complete degradation of a 10 mg·L\textsuperscript{-1} methyl orange solution using 15W·m\textsuperscript{-2} with ultraviolet light irradiation over 24 h. This technique successfully overcomes the difficulties in separation and recovery commonly associated with most commercial TiO\textsubscript{2} in a superfine powder state.

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Keywords: Shaping; TiO\textsubscript{2}; SiO\textsubscript{2}; Phase transformation; Catalytic properties

1. Introduction

The photocatalytic properties of titanium oxide (TiO\textsubscript{2}) may result in a promising reactive technique for the removal of pollutants from air or water as self-cleaning surfaces and anti-algal coatings can be produced because of the biological and chemical stability, high photoactivity, non-toxicity and low cost of TiO\textsubscript{2}\textsuperscript{[1-2]}. Although the preparation of nano-TiO\textsubscript{2} is well established, one problem still generally exists

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during production: commercial TiO$_2$ usually consists of small particles while it is difficult and expensive to separate and recover these ultrafine particles from the suspension after purification [3], especially when it coexists with multi-charged ions. And also it is well known that anatase-type TiO$_2$ exhibits the best photoactivity among the three polymorphs of TiO$_2$ (anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic)), the anatase phase has poor thermal stability and transforms to the more stable rutile form between 400 and 500 °C. A drastic decrease in photoactivity accompanies this transformation, which limits applications within this temperature range [4]. Therefore, stabilization of the anatase phase at high temperature is another key problem for the application of TiO$_2$[5-7].

Currently, the supporting technologies include preparing dense porous TiO$_2$ films or coatings by different processes such as the sol-gel process [5], hydrothermal methods [6-8], reactive methods [9], sputtering [10], chemical vapor deposition [11] pulsed laser deposition [12] or fibers as a carrier medium. However, controlling the synthesis and deposition is difficult, making it difficult to produce a thick crack-free and homogeneous coating. In addition, the derived TiO$_2$ films or coatings often have low reactive surface areas, low photocatalytic efficiency and high cost. A number of researchers have found ways to stabilize the anatase phase at high temperature and to optimize the photoactivity of titania by doping with different additives. The mixed oxides Al$_2$O$_3$/TiO$_2$, ZrO$_2$/TiO$_2$, SnO$_2$/TiO$_2$ and SiO$_2$/TiO$_2$ with different dosage rates and various preparation methods have been investigated and reported [13-17]. The most common way to produce SiO$_2$/TiO$_2$ materials is through a sol-gel process where the preparation of titania sol and silica sol is carried out separately and then they are mixed at various ratios to achieve the desired outcome [18-21] or they are prepared by direct formation. A second method is to introduce TiO$_2$ into a pre-synthesized or commercial silica-containing material such as honeycomb ceramics [22], pillared clays [23], Y-zeolite [24], c-zeolite [25], MCM-41 [26], SiC [27], polymers [28] or ordered SiO$_2$ materials in a post modification method. The SiO$_2$ loading amount can be varied from 3 to 80 wt%. The shape of the final combined materials depends on the supporting silica-containing materials. Titania can be situated at different places in the porous network. For example, the particles can be inside or outside the porous channels and the generated titania powder can dissociate from the substrates because of weak bonding forces. In summary, all the concerns about stabilizing the anatase phase of TiO$_2$ are related to its powder state and/or the difficulty in its separation and recovery [29-33]. It is important to resolve the above issues at the same time.

This paper introduces a novel ceramic processing technology for the preparation of photocatalytic materials. The process introduced here involves the use of a fumed silica and titania gel blend as a starting material followed by mixing, shaping and heating to obtain a porous product. As a result of the flexibility of the ceramic shaping method, photocatalytic materials with a desired strength and in a variety of shapes can easily be produced. This can be achieved by simply changing the mould and adjusting the binder type and dosage, and as such has enormous potential for a variety of applications. In addition, this paper describes how fumed silica, recycled from a ferroalloys factory [34], may be used as a carrier for TiO$_2$/SiO$_2$ photocatalytic materials. The high thermal stability, the effect of heating temperature on phase transformation and the photocatalytic properties are discussed.

2. Experimental

2.1. Fumed silica

The fumed silica used in this study was obtained from XIBEI Iron Alloy Company, Xian, China. The chemical composition of the fumed silica was examined by XRF and the results are given in Table 1. The particle size distribution is shown in Table 2.
Table 1 Chemical compositions of the fumed silica by wt%.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>LOI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fumed silica</td>
<td>91.94</td>
<td>2.06</td>
<td>1.65</td>
<td>-</td>
<td>-</td>
<td>0.90</td>
<td>0.30</td>
<td>-</td>
<td>3.15</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 2 Particle size distribution of the fumed silica.

<table>
<thead>
<tr>
<th>Size Interval (nm)</th>
<th>f(D)(%/nm)</th>
<th>Mass Fraction %</th>
<th>Cumulative %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1~5</td>
<td>0.15</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>5~10</td>
<td>0.34</td>
<td>1.7</td>
<td>2.3</td>
</tr>
<tr>
<td>10~18</td>
<td>0.27</td>
<td>2.2</td>
<td>4.5</td>
</tr>
<tr>
<td>18~36</td>
<td>0.68</td>
<td>12.2</td>
<td>16.7</td>
</tr>
<tr>
<td>36~60</td>
<td>0.92</td>
<td>22</td>
<td>38.7</td>
</tr>
<tr>
<td>60~96</td>
<td>0.87</td>
<td>31.3</td>
<td>70</td>
</tr>
<tr>
<td>96~140</td>
<td>0.43</td>
<td>18.7</td>
<td>88.7</td>
</tr>
<tr>
<td>140~200</td>
<td>0.15</td>
<td>8.8</td>
<td>97.5</td>
</tr>
<tr>
<td>200~300</td>
<td>0.03</td>
<td>2.5</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Mean size D=82.0(nm)  Median Size d=70.2 (nm)  Distribution Spread B=49 (nm)

2.2. Preparation of fumed silica immobilized on titania powder

The tetrabutyl titanate, absolute alcohol and nitric acid used in this study were all pure analytical reagents obtained from commercial sources. Firstly, 10 mL of butyl titanate was dissolved in 30 mL absolute ethanol and stirred for 60 min. The pH of the solution was then adjusted to 1–2 with concentrated HNO₃ using a Delta320 pH monitor. Addition of 10.04 g fumed silica to the acidified solution was followed by the slow addition of 10 mL of distilled water (volume ratio of butyl titanate: absolute ethanol: water = 1:3:1) into the system using a pipette. The resulting solution was stirred until it gelatinized. The product was dried at 80 °C for 2 h and then calcined at 700 °C to produce the fumed silica immobilized nano-TiO₂ photocatalyst powder sample.

2.3. Preparation of shaped materials

Approximately 4% of the phosphoric acid was added as binder to the fumed silica immobilized nano-TiO₂ photocatalyst powder. A paste was formed using donut shaped metal moulds, as shown in Fig. 1 (with a dry sample weight of 2.0 g). Batches of dry donut samples were heat treated at various temperatures (400, 500, 600, 700, 800, 900, 1000 and 1100 °C) for 1 h at a heating speed of 150 °C·h⁻¹.
2.4. Properties test and characterization

A MTS-880 tensile strength testing machine was used to test the tensile strength of each sample. The specific surface area of each sample was determined by the BET nitrogen gas adsorption/desorption method using an accelerated surface area and a porosimeter (ASAP2000) from Micromeritics Instrument Co., Norcross, GA. A Philips Xpert-MPD X-ray diffractometer (Cu Kα1 target with an electric current of 40 mA, voltage of 40 kV and a scanning speed of 4° min⁻¹) from Almelo, Netherlands was used to analyze the crystalline phases. The comparative content of each crystalline phase was calculated using Rietveld Quantification software. A Philips XL 30ESEM scanning electron microscopy was used to observe the microtopography of each sample and their chemical compositions were determined by energy dispersive X-ray spectroscopy (EDS). The catalytic activity was determined by the degradation (colorimetric) rate of a methyl orange solution upon irradiation with a 15 W ultraviolet lamp. The absorbance of methyl orange at 464 nm was measured with a 722 grating spectrophotometer and the degradation rate was calculated using the absorbance.

3. Results and discussion

3.1. Tensile strength and specific surface area

The tensile strength and specific surface area for each sample heated at different temperatures is listed in Table 3. These results show that the strength is strongly dependent on the increase in temperature. The sample heated at 400 °C has low strength and is easily crushed at 3.56 MPa and, therefore, does not meet the requirements for the intended applications. The samples heated at higher than 600 °C have strengths that can resist pressures greater than 6 MPa and are suitable for use in many applications. The specific surface area only increased from 24.18 to 25.07 m² g⁻¹ from 400 to 800 °C (Table 3). This result is due to volatilization during the heating process and the micropores remain at the original sites, which increases the porosity and surface area. However, when the heating temperature is increased from 800 to 1100 °C, the specific surface area decreases dramatically indicating that a phase transformation has occurred and a liquid phase has emerged. The liquid phase causes permeation into the pores and this decreases the surface area while enhancing the strength considerably. This interpretation is supported by tensile strength data, which is 16.52 MPa at 1100 °C (Table 3).

Tensile strength is very important in the production of photocatalytic porous materials for a range of practical applications. For example, if used in water treatment applications, it must withstand potential...
erosion by water and other external forces such as stress, stirring and friction. Inorganic materials may be strengthened by liquid-state and solid-state reactions during heating, which does occur in this instance. Specific surface area has a positive correlation with adsorption capability and photocatalytic abilities, which is another key property of these samples.

Table 3 Tensile strength, porosity and specific surface area of the samples.

<table>
<thead>
<tr>
<th>Heating temperature/ °C</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength / MPa</td>
<td>3.56</td>
<td>4.25</td>
<td>6.12</td>
<td>7.67</td>
<td>8.18</td>
<td>10.43</td>
<td>12.11</td>
<td>16.52</td>
</tr>
<tr>
<td>Specific surface area/ m²/g</td>
<td>24.18</td>
<td>24.24</td>
<td>24.96</td>
<td>25.01</td>
<td>25.07</td>
<td>21.25</td>
<td>17.58</td>
<td>12.90</td>
</tr>
</tbody>
</table>

3.2. Photocatalytic activity

In this study, the photocatalytic activity was defined as the degradation rate of a methyl orange solution. The degradation rates for the samples heated at 500 to 1000 °C are shown in Fig. 2 (there is no corresponding data for the sample heated at 400 °C because of its very low tensile strength and its decomposition in the methyl orange solution). The samples heated at 500 and 600 °C show the strongest photocatalytic activity with degradation rates reaching 86% in 4 h and 99.8% in 12 h, as shown in Fig. 2. Compared to the samples heated at 500 and 600 °C, the 2 samples heated at 700 and 800 °C show a relatively low degradation efficiency over the first 8 h because of their relatively low anatase content but then their degradation efficiency increases rapidly with time. However, after 24 h, these samples show similar degradation to those heated at 500 and 600 °C. However, the photocatalytic activity of the samples heated at 900, 1000 and 1100 °C are comparatively weaker. After 24 h, these samples were still light yellow and had a degradation rate of lower than 55%. Therefore, the materials heated at 600 to 800 °C have a combined ideal tensile strength and photocatalytic abilities.

3.3. XRD analysis

XRD patterns for the samples heated at 400 to 1100 °C are shown in Fig. 3 and the properties of these phases are listed in Table 4. At 400 °C, both TiO₂ and fumed silica are still amorphous because no diffraction peaks assignable to them are present (Fig. 3). An anatase phase was apparent at 500 °C and a complete transformation to an anatase phase occurred between 500 and 700 °C. Transformation into the rutile form of TiO₂ increased steadily with temperature. From 700 to 900 °C, both the anatase phase and the rutile phase are present. The anatase type TiO₂ is the main phase at 700 and 800 °C as its content is greater than 90%. At 900 °C, the anatase phase is reduced to 7.4% (Tables 4 and 5). At 1000 °C, diffraction peaks due to the silica phase appear and all the peaks of the anatase phase disappear. This transformation indicates that the amorphous silica in the fumed silica begins to crystallize into a cristobalite phase at 1000 °C. At this temperature, the sample is composed of 38.3% rutile type TiO₂ and 61.7% cristobalite type. However, at 1100 °C, the amorphous silica has completely crystallized and the ratio of rutile to cristobalite is 29.3 to 70.7. The crystalline phase changes determined by XRD analysis are consistent with the results derived from strength, specific surface area and photocatalytic activity.
Fig. 2. The degradation rate of methyl orange for each sample.  Fig. 3. XRD patterns of the samples heated at different temperatures.

Table 4 Crystalline phase content (%) of the samples calcined at 500–1000 °C.

<table>
<thead>
<tr>
<th>Heating temperature/ °C</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase type TiO₂ / %</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>90.7</td>
<td>7.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rutile type TiO₂ / %</td>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>92.6</td>
<td>38.3</td>
<td>29.3</td>
</tr>
<tr>
<td>Cristobalite low (SiO₂) /%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>61.7</td>
<td>70.7</td>
</tr>
</tbody>
</table>

Table 5 Crystalline phase content (%) of the samples calcined at 700–850 °C.

<table>
<thead>
<tr>
<th>Heating temperature/ °C</th>
<th>700</th>
<th>725</th>
<th>750</th>
<th>775</th>
<th>800</th>
<th>850</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase type TiO₂ / %</td>
<td>100</td>
<td>98.4</td>
<td>97.3</td>
<td>95.6</td>
<td>90.7</td>
<td>16.2</td>
</tr>
<tr>
<td>Rutile type TiO₂ / %</td>
<td>-</td>
<td>1.6</td>
<td>2.7</td>
<td>4.4</td>
<td>9.3</td>
<td>83.8</td>
</tr>
</tbody>
</table>

The samples heated at 500 and 600 °C have superior photocatalytic abilities compared to the other stages of heating because a pure anatase phase is produced, however, their strength is relatively low so their durability and type of application they can be used for is restricted. However, the samples heated at 700 and 800 °C have high strength as well as good photocatalytic abilities and can be considered ideal candidates for various applications. XRD analysis can be used to describe the phase composition in this temperature range and to identify the phase over small temperature increments (Fig. 4 and Table 5). In Fig. 4, very weak rutile phase diffraction peaks were present for the 725 °C sample, which indicates that the anatase phase begins to transform at this temperature. The amount of rutile phase initially increases slowly and then more rapidly as the temperature increases. From 800 to 850 °C, the anatase phase of TiO₂ decreases from 90.7 to 16.2% and this corresponds to the considerable decrease in photocatalytic activity.
3.4. SEM observations

Fumed silica contains superfine particles with an average size of around 80 nm making it an excellent absorbent. Figures (a)—(g) show SEM images of the samples heated from 500 to 1100 °C. The sample heated at 500 °C has uniform spherical and narrowly-dispersed particles (Fig. 5(a)). As the temperature increases, the particles gradually aggregate (Figs. 5(b), 5(c) and 5(d)) but remain porous. Compared with samples heated from 500 to 800 °C, the surface area of the samples heated at 900 and 1000 °C (Figs. 5(e) and 5(f)) decreased dramatically. The sample heated at 1100 °C (Fig. 5(g)) showed sintering characteristics and the surface was covered with a glass phase layer. These phenomena observed in the SEM micrographs are consistent with those of the previous XRD analyses. In all the samples, fumed silica particles are mixed with nano-TiO2 particles and are difficult to distinguish. A SEM/EDS analysis (Fig. 6) showed that the main elements are O (30.1%), Si (29.9%) and Ti (40.0%), which indicates that nano-TiO2 particles are well distributed in the fumed silica.
4. Conclusions

The most functional photocatalytic materials produced during this study have tensile strengths of 7.67 to 8.18 MPa and specific surface areas from 25.01 to 25.07 m²/g when heated from 700 to 800 °C. For these materials, the main phase (content greater than 90%) is an anatase type TiO₂. The good photocatalytic activity observed for this material was confirmed by the complete degradation of a 10 mg·L⁻¹ methyl orange solution within 24 h using 15 W of ultraviolet light irradiation.

The heating temperature has a significant influence on the crystalline phase, strength and photocatalytic activity of the fumed silica/TiO₂ materials. The pure anatase phase is stable between 500 and 725 °C and the corresponding samples show superior photocatalytic abilities. The anatase phase begins to transform to a rutile phase at 725 °C and the anatase and rutile phases coexist between 725 and 900 °C. At 1000 °C, amorphous SiO₂ starts to crystallize into cristobalite and the photocatalytic ability of the sample decreases dramatically.

Acknowledgments

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References


