A comparative study of different porous amorphous silica minerals supported TiO$_2$ catalysts

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Abstract.

Three porous amorphous silica minerals, including diatomite, opal and porous precipitated SiO$_2$ were adopted to prepare supported TiO$_2$ catalysts by hydrolysis–deposition method. The prepared compound materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Through morphology and physical chemistry properties of the resulting TiO$_2$/amorphous SiO$_2$ catalysts, it was proposed that the nature of silica supports could affect the particle size and the crystal form of TiO$_2$ and then further influence the photocatalytic property of TiO$_2$/amorphous SiO$_2$ catalysts. The catalytic properties of these porous amorphous silica supported photocatalysts (TiO$_2$/SiO$_2$) were investigated by UV-assisted degradation of Rhodamine B (RhB). Compared with the other two TiO$_2$/amorphous SiO$_2$ catalysts, TiO$_2$/DE photocatalyst exhibits better catalytic performance at different calcined temperature, the decoloration rate of which can be up to over 85% even at a relative low calcined temperature. The TiO$_2$/DE photocatalyst possesses mixed-phase TiO$_2$ with relatively smaller particles size, which might be responsible for higher photocatalytic activity. Moreover, the stable and much inerter porous microstructure of diatomite could be another key factor in improving its activity.

Keywords: TiO$_2$; Diatomite; Opal; Porous precipitated SiO$_2$; Photocatalytic activity

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1. Introduction

In recent years, semiconductor TiO$_2$ has been extensively used to mineralize toxic and non-biodegradable environmental pollutants due to its high effectiveness, long-term photostability and nontoxicity [1-4]. However, there are some obvious drawbacks in using fine TiO$_2$ powders, such as low quantum efficiency, small specific surface area and low adsorption ability, which significantly limit the efficiency of photocatalysis. On the other hand, both costly and difficult separation from the reaction media and inadequacy for continuous processing limit the industry application of pure TiO$_2$ powders. As a result, a number of investigations have focused on the immobilization of nano-TiO$_2$ onto porous minerals, such as diatomite [5], bentonite [6], kaolinite [7, 8], zeolite [2, 9], palygorskite [10], perlite [11] and activated carbon [12, 13], which can not only promote catalytic reactions by offering more active sites but also permits the recycling and reuse of the catalysts [14, 15].

Recently, amorphous SiO$_2$ has shown some advantages in preparing highly active supported catalysts, due to its special physicochemical properties such as high adsorption capacity. For the supported TiO$_2$ catalysts, the nature of supports is one of the most important influence factors affecting photocatalytic performance [16, 17]. There are many hydroxyl groups and acid sites on the surface of amorphous SiO$_2$ materials, which can be considered as adsorption sites for pollutant [18-20]. Based on this consideration, TiO$_2$ coated on these sites can provided the new generated composite for photocatalytic activity. Moreover, the immobilization of TiO$_2$ on a suitable and inert matrix can exhibit a higher photodecomposition of organic and inorganic pollutant than that of pure TiO$_2$ [21, 22]. It is well known that TiO$_2$ crystallographic forms, TiO$_2$ particle size, TiO$_2$ crystallinity and porous structure of matrix have great influence on the photocatalytic performance of composite materials.

This study chose non-metallic typical porous silica minerals including diatomite (DE), opal (OP) and porous precipitated SiO$_2$ (PPS) as substrates for supporting TiO$_2$. The photocatalytic performance of three supported materials with same loading amount of TiO$_2$ was evaluated by the degradation of Rhodamine B (RhB) in aqueous solutions. TiO$_2$ crystallographic forms, TiO$_2$ particle size, TiO$_2$ crystallinity and porous structure of matrix were systematically characterized in order to understand the role of three supports during photocatalytic process and the nature of active sites, respectively.

2. Experimental

2.1. Preparation of TiO$_2$/amorphous SiO$_2$ composites
The preparation of TiO\textsubscript{2}/ amorphous SiO\textsubscript{2} composites was undertaken by hydrolysis–deposition method: Firstly, the diatomite (Jilin province, China), opal (Liaoning province, China) and porous precipitated SiO\textsubscript{2} (Guangdong province, China) powders were respectively dispersed in deionized water under stirring at room temperature and amorphous SiO\textsubscript{2} suspension (liquid-solid ratio is 30:1) was obtained. Secondly, TiCl\textsubscript{4} solution (0.43 mol/L) and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} solution (1.5mol/L) were parallelly added to the prepared amorphous SiO\textsubscript{2} suspension according to the 2:1 (molar ratio) of \([\text{Ti}^{4+}] / [\text{SO}_4^{2-}]\) at a particular dropping rate. The theoretical loading amount of TiO\textsubscript{2} is determined as 20 wt.%, which is controlled by the adding amount of TiCl\textsubscript{4} solution. The final pH value of the dispersion was adjusted to about 5 through addition of ammonia solution, followed by successively stirring for 1.5 h and aged for 12 h. Then, the dispersion was filtrated by a vacuum filter and washed free of chloride anions as determined by the use of the AgNO\textsubscript{3}, dried at room temperature, and dried further in an oven at 105 °C for 12 h. Finally, the obtained precipitate was calcined under static air atmosphere at 300°C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C for 2h.

2.2. Characterization of photocatalysts

The specific surface areas and pore size distribution of the samples were determined on a constant volume adsorption apparatus (JW-BK, JWGB Sci. &Tech) by the N\textsubscript{2} BET method at the liquid nitrogen temperature. X-ray diffraction patterns were obtained by a PANalytical X’Pert PRO X-ray diffractometer. The AST powders and prepared composite samples were pressed in stainless samples holders. Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 40 kV and 40 mA, with Cu K\textalpha radiation of 1.541 Å. The incident beam passed through a 0.04 rad soller slit, a 1/2 ° divergence slit, a 15 mm fixed mask, and a 1 ° fixed antiscatter slit. The surface morphology of samples was examined by scanning electron microscopy (S-3500N, FEI Company). The transmission electron microscopy (TEM) was carried out on a Tecnai G220ST Spectrograph (FEI Company). Dried samples were analyzed by XPS (ESCALAB 250Xi, MgKa X-ray source at 15 kV and 20mA emission current). A survey spectrum (0–1100 eV) was recorded. Fourier-transform infrared spectroscopy was applied in this work, and the spectra were obtained using a Thermofisher Nicolet 6700 spectrometer. The samples were prepared in potassium bromide (KBr) pellets. The infrared spectra of prepared samples between 400 and 4000 cm\textsuperscript{-1} were recorded.
2.3. Photocatalytic activity

Photocatalytic activity of the as-prepared catalysts was evaluated by degradation of Rhodamine B (RhB) in aqueous solutions under UV irradiation using a 300 W high-pressure mercury UV lamp ($\lambda = 365$ nm). For the degradation of RhB, 0.1g of as-prepared composites was added into 100 mL of 10 ppm RhB dye. Prior to UV illumination, the suspension was stirred in dark for 10 min to disperse the catalyst. The remaining dye in the solution was measured at 548 nm ($\lambda_{\text{max}}$) using a UV–vis spectrophotometer. The percentage of RhB degradation ($D_R$) was calculated by the following equation:

$$D_R (%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100,$$

where $C_0$ and $C_t$ are concentrations of RhB before and after degradation, respectively.

3. Results and discussion

Fig. 1. Photocatalytic activities of three TiO$_2$/ amorphous SiO$_2$ catalysts after heat treatment at different temperature for 2 hours.

The photocatalytic propeties of three TiO$_2$/ amorphous SiO$_2$ composite photocatalysts with same TiO$_2$ loading are shown in Fig.1. All the photocatalysts are active for decoloration of Rh B under the tested conditions. TiO$_2$/OP photocatalyst has the optimum removal effect after heat treatment at 600 °C, the decoloration rate of which is up to 88.6%. TiO$_2$/PPS photocatalyst exhibits relatively high photocatalytic activity, and the optimum calcination temperature for 96.5% Rh B decoloration is 700 °C. A better photocatalytic activity is obtained from TiO$_2$/DE photocatalyst, the decoloration rate of which achieves 96.8% after heat treatment at 700 °C for 2h, which shows higher catalytic activity than the other two TiO$_2$/ amorphous SiO$_2$ composites. Moreover, it is found that TiO$_2$/DE photocatalyst shows good catalytic performance at different calcined temperature, even at a relative low calcined temperature, the decoloration rate of which can be up to over 85%. The above results indicate that the
types of amorphous SiO₂ supports could considerably affect the photocatalytic property of TiO₂/
amorphous SiO₂ composite for Rh B removal.

Table 1. Main physical parameters of the three amorphous SiO₂ and TiO₂/ amorphous SiO₂
catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE</td>
<td>11.05</td>
<td>0.058</td>
<td>15.403</td>
</tr>
<tr>
<td>OP</td>
<td>52.64</td>
<td>0.139</td>
<td>14.550</td>
</tr>
<tr>
<td>PPS</td>
<td>136.96</td>
<td>0.235</td>
<td>7.537</td>
</tr>
<tr>
<td>TiO₂/DE</td>
<td>10.47</td>
<td>0.055</td>
<td>15.082</td>
</tr>
<tr>
<td>TiO₂/OP</td>
<td>49.92</td>
<td>0.135</td>
<td>16.256</td>
</tr>
<tr>
<td>TiO₂/PPS</td>
<td>113.48</td>
<td>0.290</td>
<td>17.188</td>
</tr>
</tbody>
</table>

The specific surface area and pore structure parameters of the original supports and the three TiO₂/
amorphous SiO₂ catalysts after calcination are summarized in Table 1. Among three supports, PPS
exhibits the highest specific surface area, followed by OP and then DE. Compared with the three
original supports, the specific surface areas of three obtained composite photocatalysts just decrease a
little after coating TiO₂. Generally speaking, photocatalysts with larger specific surface areas would be
favorable to higher catalytic activity [23]. It is clear that there are some different trends from the
precious studies between the specific surface area of amorphous SiO₂ support and the catalytic
activities of composite catalysts. For example, the diatomite with the smallest specific surface area
exhibits a better photocatalytic performance than the other two supports with higher specific surface
area. The above results may suggest that the nature of amorphous SiO₂ supports has no direct
relationship with the catalytic activity.
Fig. 2. XRD patterns of three TiO$_2$/ amorphous SiO$_2$ catalysts after heat treatment at different temperature for 2 hours, A: TiO$_2$/ diatomite; B: TiO$_2$/ opal; C: TiO$_2$/porous precipitated SiO$_2$.

XRD patterns of the three TiO$_2$/ amorphous SiO$_2$ catalysts after heat treatment at different temperature for 2h are shown in Fig. 2. The XRD pattern of all three TiO$_2$/ amorphous SiO$_2$ catalysts calcined at a relative low temperature expressed as amorphous phase of SiO$_2$. When the calcination temperature is over 400 °C, a broad diffraction peak appears at $2\theta= 25.2^\circ$ and $37.8^\circ$, which are assigned to amorphous anatase TiO$_2$ (101) and anatase TiO$_2$ (004) phases, respectively [24]. With the increase of
the calcination temperature, the crystallinity degree of anatase TiO$_2$ is improved significantly. Moreover, when the calcination temperature reaches over 800 °C, typical diffraction peaks corresponding to rutile TiO$_2$ appear in the XRD patterns of TiO$_2$/DE and TiO$_2$/PPS composites. On the other hand, TiO$_2$/OP composite shows no obvious presence of rutile TiO$_2$ particles under high calcination temperatures. It has been proved from the literature that the increase in the crystallinity of TiO$_2$ and the mixed phase can usually lead to an improvement in the photocatalytic effect [7, 25-27]. The mixed phase TiO$_2$ should be one key factor for the relative higher catalytic activity of TiO$_2$/DE and TiO$_2$/PPS catalyst. Compared with the XRD patterns of TiO$_2$/DE and TiO$_2$/PPS composites, the intensity of the diffraction peaks is much weaker for TiO$_2$/OP composite, which might be due to the characteristic structure of opal restricting the formation and growth of TiO$_2$ crystal phase during hydrolysis–deposition process. According to the Scherrer equation, the crystalline sizes of anatase TiO$_2$ in samples are estimated and depicted in Fig. 3.

![Crystalline sizes of anatase TiO$_2$ existed in three TiO$_2$/amorphous SiO$_2$ catalysts after heat treatment at different temperature for 2h.](image)

The calculated results indicate that the crystalline sizes of anatase TiO$_2$ in samples increase gradually with the calcination temperature increasing from 300 °C to 900 °C. From the above results, the calcinations temperature strongly affects the crystalline sizes of TiO$_2$ particles coated on amorphous SiO$_2$. Among three TiO$_2$/amorphous SiO$_2$ catalysts, TiO$_2$/DE catalyst shows the smallest crystalline sizes of anatase TiO$_2$, followed by TiO$_2$/PPS and then TiO$_2$/OP. In general, catalyst with smaller particle size would be favorable to higher catalytic activity [17]. As a result, the relative small TiO$_2$ particle size
should be another important factor for the higher catalytic activity of TiO$_2$/DE catalyst.

Fig. 4. SEM micrographs for diatomite (A), TiO$_2$/ diatomite(B), opal (C), TiO$_2$/ opal (D), porous precipitated SiO$_2$ (E) and TiO$_2$/porous precipitated SiO$_2$ (F).

Fig. 4 shows the SEM images of three supports and prepared TiO$_2$/ amorphous SiO$_2$ catalysts calcined at the optimum temperature for 2h. From the SEM micrographs obtained from DE and TiO$_2$/DE with same magnification, it is found that the diatom as the carrier shows a disc structure with a radius of about 30–40 μm. The diatom of the obtained TiO$_2$/DE is out of shape to some extent because of calcination. However, the internal pore structures on the surface of diatomite are still very distinct, which benefits for adsorption capacity as the photocatalyst supporter [28]. Compared with the clean surface of initial diatomite, the TiO$_2$/DE sample is apparently rougher than the uncoated
diatomite, which is due to that the TiO$_2$ particles are deposited on the surface of diatom. The SEM images of the opal and TiO$_2$/OP are shown in Fig.4 (C) and Fig.4 (D). It is observed that the opal is composed of a large quantity of small agglomerated particles. Moreover, the material shows highly porous like structure which facilitates the diffusion of substrate into the holes and creates the ultimate contact with the coated photocatalyst [25]. The similar morphology is revealed by the SEM images of the PPS and TiO$_2$/PPS. The TiO$_2$ particles are deposited on the edges of PPS, which can be in direct contact with pollutant.
Fig. 5. TEM micrographs of prepared TiO$_2$/ amorphous SiO$_2$ catalysts. TiO$_2$/ diatomite (a and b); TiO$_2$/ opal (c and d); and TiO$_2$/porous precipitated SiO$_2$ (e and f).

TEM images of the prepared TiO$_2$/ amorphous SiO$_2$ composite photocatalysts calcined at the optimum conditions are pictured in Fig. 5. Fig. 5 (a) shows the direct observation of TiO$_2$/ diatomite, which clearly presents large pores on the edge of disc like diatom. Fig. 5 (b) displays the morphology of the pores with higher magnification and the high-resolution images of the edge of pores. The sample was reduced by copper embedding technology in advance. TiO$_2$ nanoparticles with the size of 5~15 nm are observed on the wall of diatom, which is in line with the XRD results. Moreover, the nanoparticles are uniformly distributed without obvious aggregation. The surface morphology of TiO$_2$/ opal is presented in Fig. 5(c). It is found that the TiO$_2$ nanoparticles observed as bright spots are homogeneously disperse on the supports surface. Moreover, from the cross section micrograph of sample (Fig. 5(d)), the TiO$_2$ nanoparticles with the size of 5~20 nm are deposited on the edge of pores. The thickness of the coating layer is about 100~150nm. The similar surface and cross section morphology of TiO$_2$/PPS is observed from Fig. 5(e) and Fig. 5(f), respectively. The average particle size of TiO$_2$ in TiO$_2$/PPS is determined to be around 5~20 nm, which is similar as that of TiO$_2$/OP catalyst.
Fig. 6 shows the FT-IR spectra of three supports and prepared TiO$_2$/amorphous SiO$_2$ catalysts calcined at the optimum temperature for 2h. For all the samples, both the broad bands with maximum at 3400–3450 cm$^{-1}$ and bands at 1630–1645 cm$^{-1}$ are attributed to the stretching vibration and the bending vibration of O-H bond in physisorbed water indicating the hydrophilic character of amorphous SiO$_2$, respectively. It appears that the O–H stretching vibration is shifted to relatively lower wavenumber after coating, which could be attributed to TiO$_2$ particles adsorbed on the surface of SiO$_2$, which replaces the water molecules [29]. Peaks at the wave number of 1094–1110 cm$^{-1}$ and 792–816 cm$^{-1}$ are caused by Si-O-Si asymmetry stretching vibration and the Si-O-Si symmetric stretching vibration peak, respectively. The peaks at 469–485 cm$^{-1}$ are the Si-O-Si bending vibration peak. In the spectra of prepared catalysis samples, bands connected with Ti-O bond vibrations occur at about 620 cm$^{-1}$ [8], the intensity of which is relative low. According to the related literatures [23, 30], it was known that reaction of TiO$_2$ with surface Si–OH groups of silica supports to form Si-O-Ti bonds could occur during the calcinations steps. However, the band at 950 cm$^{-1}$ attributed to Si-O-Ti antisymmetric
stretching vibration was not observed at the spectra of three prepared TiO$_2$/amorphous SiO$_2$ catalysts, which probably due to a small number of these bonds in prepared samples.

Fig. 7. XPS spectra of (a) O 1s and (b) Ti 2p for prepared TiO$_2$/diatomite, TiO$_2$/opal and TiO$_2$/porous precipitated SiO$_2$.

XPS technique was carried out to study the chemical state of the Ti and O elements on three different supports. The O 1s spectra of three TiO$_2$/amorphous SiO$_2$ catalysts are shown in Fig. 7a. There is one main peak in the O 1s spectra with a shoulder peak at a relatively lower intensity. The high intensity peaks of about 533 eV correspond to oxygen bonded to silicon atoms (Si–O–Si bond) [31]. On the other hand, the lower energy signals appearing close to 530 eV are assigned to oxygen bonded to Ti atoms (Si–O–Ti bond) [32, 33]. It is found that the intensity of Si–O–Ti bond for TiO$_2$/PPS is relatively lower than that of TiO$_2$/OP and TiO$_2$/DE catalysts, which might be due to the fact that more physical adsorption occurred when TiO$_2$ particles are coated on the porous precipitated SiO$_2$. Fig. 7(b) shows the XPS spectra of three TiO$_2$/amorphous SiO$_2$ catalysts where the binding energies of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ are present. The peak position of Ti 2p$_{3/2}$ corresponds to that of the Ti$^{4+}$ oxidation state [34]. The shape of the Ti 2p excludes the presence of other oxidation state, which are separated by about 3–4 eV from the Ti$^{4+}$ peak [34, 35]. It appears that the TiO$_2$ phase coated on different supports has no much difference, since the binding energies of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ for three TiO$_2$/amorphous SiO$_2$ catalysts
are similar. Combining with the above XRD, SEM, TEM, FTIR and XPS analysis, it seems that the porous structure, high specific surface area and a large amount of Si–OH groups of three kinds of amorphous SiO₂ attribute to the formation of TiO₂ nanoparticles and good photocatalytic performance of the obtained samples. The relative higher photocatalytic performance of TiO₂/DE catalysts should be mainly governed by the nature of active sites, such as mixed-phase TiO₂ and small particles size. Concerning with the role of three different supports, the diatomite is quite stable and much inerter than the other two supports at a high temperature which attributes to the maintenance of porosity. As a result, the prepared composite catalyst could retain high adsorption capacity after deposition, which is the premise for high photocatalytic performance.

4. Conclusion

All three TiO₂/ amorphous SiO₂ catalysts which are prepared by a simple hydrolysis–deposition method exhibit high degradation of Rhodamine B. The nature of silica supports could affect the particle size and TiO₂ crystal form and then further influence the photocatalytic property of the obtained catalysts. The mixed-phase TiO₂ and small particles size are critical factors for better photocatalytic activity over TiO₂/DE catalyst. On the other hand, the special pore structure and good adsorption capacity of diatomite make significant contribution to the excellent activity of TiO₂/DE catalyst. The TiO₂/ amorphous SiO₂ catalysts show good potential for application in water purification for their good adsorption and photocatalytic properties.

Reference


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