



Article In Situ Etching Synthesis of TiO₂-SBA-15 Nanocomposite Enhancing Adsorption and Photocatalytic Degradation

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Abstract: The adsorption-enhancing TiO_2 -SBA-15 photocatalyst has been synthesized by an in situ etching displacement method, which possesses unique regular hexagonal pores and large specific surface area. The as-prepared TiO_2 -SBA-15 can effectively adsorb and increase the concentration of pollutants in the photocatalyst and collision likelihood with the photogenerated radicals, thus improving the efficiency of photocatalytic organic degradation. The structure and morphology have been characterized by N₂ adsorption isotherms, X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), and scanning electron microscopy (SEM). These characterizations confirm that TiF_4 alcohol solution prefers to react with the internal surface of SBA-15 because of the Siphon effect. Fourier transform infrared (FTIR) spectra demonstrate that a Ti-O-Si bond formed after the reaction of TiF_4 with SBA-15, which reveals a wonderful combination of TiO_2 and SiO_2 even at low temperatures. Through this function, the nanocomposite TiO_2 -SBA-15 could obviously improve the efficiency of photocatalytical removal of toluene in the gas phase.

Keywords: in situ etching synthesis; TiO₂-SBA-15 composites; enhancing adsorption; volatile organic compound (VOC) degradation

1. Introduction

Photocatalysis is driven by light irradiation of the catalyst to produce photogenerated electrons and holes, and later generate hydroxyl radicals [1,2]. It has the wonderful advantage of using rich free solar light, so it shows good application potential in environmental purification, hydrogen production, green organic synthesis, solar cells, etc. [3–10]. However, the photogenerated electrons, holes, and hydroxyl radicals are easily quenched in photocatalysis process, which limits its applications [11,12]. SBA-15 (mesoporous silica molecular sieve, Santa Barbara Amorphous of number 15) is the substrate expected to modify this restriction, due to its large specific surface area, two-dimensional hexagonal arrangement, and uniform channel [13–15]. TiO₂-SBA-15 nanocomposite could be synthesized by several methods such as one-pot hydrothermal, modified implantation, or sol-gel deposition [16–18]. These studies reveal that such mesoporous silica can obviously increase the surface area of the catalyst and improve the activity [19]. However, these composites need complex synthesis processes and calcination under high temperatures. Furthermore, some activity sites of these composites are blocked or diluted by the SiO₂ frame. TiF₄, which has been studied extensively by researchers, should be one of the materials to solve the problem, due to its titanium source and release of HF [20,21]. HF can in situ etch SiO_2 easily, at which point the Ti atom replaces the Si atom space to give out TiO_2 under low temperature. So, TiO_2 could cover the SiO₂ substrate and expose the TiO₂ face. More advanced, it has a high combination of the TiO₂ and SBA-15.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In this paper, TiO₂-SBA-15 is prepared by an in situ etching reaction of TiF₄ and SBA-15. Then, TiO₂ materials grow on the surface of the SBA-15 pores and take the place of the SiO₂ crystal lattice space under low temperature. TiO₂-SBA-15 keeps the morphology of two-dimensional hexagonal arrangement and uniform channel, and has large specific surface area, which increases the local pollutant concentration around the photocatalyst to promote free radicals colliding efficiently the pollutants, and catalytic activity. This in situ etching synthesis method also ensures more exposure of TiO₂ catalytic sites.

2. Results and Discussion

The HR-TEM morphologies reveal that both the SBA-15 and the 20%-TiO₂-SBA-15 samples display a two-dimensional hexagonal arrangement and uniform channel. As shown in Figure 1a,c, the latter is less regular than the former. Compared to the SBA-15 sample in Figure 1b, the HR-TEM morphologies of 20%-TiO₂-SBA-15 in Figure 1d further confirm that the order mesoporous pore has been damaged partially and the SBA-15 wall thickness has become narrower, from 4.9 nm to 4.2 nm. This occurs because the TiF₄ ethanol solution enters the mesoporous pore structure during the evaporation process (the Siphon effect), then the TiF₄ reacts with SBA-15 channel to generate TiO₂ materials. This is further uncovered by the small-angle X-ray scattering (SAXS) results and pore size distribution.



Figure 1. HR-TEM images of the SBA-15 and the 20%-TiO₂-SBA-15 samples: (**a**,**b**) SBA-15 along with (100) and (001) directions, respectively; (**c**,**d**) 20%-TiO₂-SBA-15 along with (100) and (001) directions, respectively.

Figure 2a,b shows the SEM images of SBA-15 and 20%-TiO₂-SBA-15. It shows that the SBA-15 and 20%-TiO₂-SBA-15 materials have a rod shape. After the in situ etching reaction, the morphology of 20%-TiO₂-SBA-15 is not obviously changed, except a little

rough area on the surface. As Figure 2c,d show, both SBA-15 and 20%-TiO₂-SBA-15 contain a large amount of Si and O elements. Comparing to SBA-15, the 20%-TiO₂-SBA-15 also contains Ti and F elements. The atomic percentage of Si, F and Ti is 19.75%, 16.2% and 2.21%, respectively. The large percentage of F element should be due to the enhancing adsorption for SiF₄ on the surface of 20%-TiO₂-SBA-15. After deducting this part of Si and F atoms according to the measurement ratio of SiF₄, titanium dioxide accounts for 15.8% of the total mass ratio. This numeric value is close to the theoretical value of 20%, which reveals that the 20%-TiO₂-SBA-15 was successfully synthesized as intended.



Figure 2. SEM images of the SBA-15 and the 20%-TiO₂-SBA-15 samples (**a**,**b**), (**b**) EDS-mapping of the SBA-15 and the 20%-TiO₂-SBA-15 samples (**c**,**d**).

The wide-angle XRD (Figure 3a) shows peaks at 2 θ values of 24.8, 37.3, 47.6, 53.5, 55.1 and 62.2° reflections of anatase, which match the pattern of JCPDS Card no. 21-1272 [8]. As TiO₂ amounts increase, the intensity of the peak grows first quickly then slowly, which should be due to mesoporous pores that limit its growth. Both TiO₂-SBA-15 samples with wide peaks further confirm the small nanoparticle size, and the average crystallite size is 0.36 nm (calculated by Scherrer's equation in the JADE 5.0 software) [22]. Usually, small-angle X-ray scattering (SAXS) shows the presence of an ordered arrangement of pores with strong intensity of a peak at low angle [23]. Figure 3b reveals an ordered 2D-hexagonal meso-structure because of well resolved (100), (110) and (200) reflections [24]. With increasing TiO₂ content, the gradually decreasing peak intensity suggests a decreasing long-range order. The gradually right deviation peaks also reveal the reducing pore size of the channel, which is further confirmed by the pore size information listed in Table 1.

These materials display similar nitrogen sorption isotherms with narrow pore-size distributions centered at about 3.12–6.62 nm (Figure 4), which is typical for surfactant-templated mesoporous materials [25]. Detailed pore structure information is listed in Table 1. The pore volume and surface area are decreasing with increasing TiO_2 content, which is due to the in situ chemical etching reaction of SiO_2 and TiF_4 to create TiO_2 nanoparticles in their pore channels.



Figure 3. (a) XRD patterns of different TiO₂ loading amounts, (b) SAXS plots of different TiO₂ loading amounts.

Tabl	e 1.	Sampl	le specific	surface a	rea and	pore size	for SBA-	15 and	different	TiO ₂	loading	amounts
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Samples	S _{BET} /m ² /g	D/nm	$V_{pore}/cc \cdot g^{-1}$
SBA-15	773.4	6.62	0.833
5%-TiO ₂ -SBA-15	681.2	5.40	0.801
10%-TiO ₂ -SBA-15	650.5	3.64	0.588
20%-TiO ₂ -SBA-15	628.9	3.52	0.526
30%-TiO ₂ -SBA-15	409.6	3.12	0.046



Figure 4. (a) Pore size curves calculated from the BJH equivalent cylindrical model, (b) N_2 adsorptiondesorption isotherms.

As Figure 5a shows, the binding energy peak at 533.1 eV should belong to O 1 s of SBA-15. Spectrum of 20%-TiO₂-SBA-15 appears to have a broad shoulder peak at 530.3 eV, which should belong to the O 1s of TiO₂ [26,27]. After TiF₄ in situ etching with SBA-15, the Si 2p binding energy slightly shifts 0.3 eV negative, due to the low electro-negativity of Titanium comparing to that of Silicon [28]. This demonstrates that large amounts of Ti atoms are so close enough to Si atoms that Ti could change the binding energy of Si.

The FTIR spectra (Figure 6) shows a broad absorbance peak in the range 3100 to 3450 cm⁻¹ and a strong absorbance peak around 1630 cm⁻¹, which should be attributed to the vibrations of the surface-adsorbed H₂O and Ti-OH or Si-OH bonds. The broad peak at 1080 cm⁻¹ should be attributed to vibration of Si-O-Si flame work [29]. Two new peaks characteristic of Ti-O-Ti and Ti=O bonds are also observed around 754 and 861 cm⁻¹ after the TiF₄ etching reaction [30,31]. Furthermore, a peak of around 960 cm⁻¹ is observed, which belongs to Ti-O-Si according to references [32]. This observation confirms that strong bonding forms between TiO₂ and

SBA-15 without calcination. Referring to the decreasing pore size revealed by SAXS and N₂ adsorption-desorption isotherms, it was revealed that TiF₄ alcohol solution prefers to react with internal surface of SBA-15 due to the Siphon effect. So, the aiming unique structure is synthesized successfully to realize the combined absorption and photocatalysis to improve the efficiency of photogenerated OH•. Based on the above results, it is concluded that the formation of these nanocomposites involves an in situ etching reaction between TiF₄ and SBA-15 (Figure 7).



Figure 5. (a) O 1s XPS spectra of SBA-15 and 20%-TiO₂-SBA-15, (b) Si 2p XPS spectra of SBA-15 and 20%-TiO₂-SBA-15.



Figure 6. (a) FT-IR spectra of SBA-15 and 20%-TiO₂-SBA-15, (b) FT-IR spectra of 20%-TiO₂-SBA-15 (wavenumber from $600-1000 \text{ cm}^{-1}$) from circle marked in (a).

Figure 8 confirms these unique nanocomposites show significantly improved photocatalytic activity. As shown in Figure 8, the conversion of toluene oxidation takes place by the mesoporous nanocomposites with different TiO₂ loadings. When the reactions are conducted under dark conditions, the adsorption balance is observed at 2.0 h. As the TiO₂ amount increased, the adsorption of toluene decreased from 34.9% to 26.3% (from 274.0 to 310.1 ppm), which should be attributed to the smaller surface area and the smaller mesoporous pore size. Under light irradiation, the removal ratio of toluene increases from 34.9% to 59.4%, when the content of TiO₂ is increased from 0 to 20%. A near-twice improvement in toluene decomposition is achieved when 20% of TiO₂ is loaded, unambiguously suggesting a significantly improved photocatalytic activity by the unique structure. However, further increase in TiO₂ content leads to a decreasing catalytic activity, which should be attributed to the presence of a large number of TiO₂ particles in pore channels, slowing down mass transport and reaction rate. In order to prove the wonderful performance of enhancing-adsorption, a 20%-TiO₂-SBA-15 sample has been treated by hydrothermal method to destroy the structure but maintain the component. As Figure 9a shows, the untreated sample performed better than the treated sample in the adsorption and removal ratio of toluene, suggesting that enhancing-adsorption improves the pollutant concentration in the channel of 20%-TiO₂-SBA-15 and the collision likelihood between hydroxyl radicals and toluene, promoting the photocatalytic reaction rate. The similar photocatalytic rate suggests that the hydrothermal method treatment only affects the adsorption structure of SBA-15 but not the performance of TiO₂. P25 is regarded as a highly efficient photocatalyst as a commercial titanium dioxide material. Figure 9b reveals that 20%-TiO₂-SBA-15 and 20%-P25-SBA-15 have similar a photodegradation rate, which demonstrates that the photocatalyst performs very good activity. However, 20%-P25-SBA-15 showed less adsorption ability, which should be due to the blocking of the channel of SBA-15 by P25 particles [33].

According to these characterizations and photocatalytic performance, TiO_2 -SBA-15 enhances adsorption and photocatalytic performance, because the enhanced absorption improves the concentration, as well as the collision likelihood of hydroxyl radicals and pollutants. As Figure 10 shows, TiO_2 -SBA-15 adsorbs toluene and increases the molecule amount in the inner channel. The hydroxyl radicals are produced under UV light irradiation on TiO_2 -SBA-15, which collides efficiently with the toluene inside the pore, then releases the produced CO_2 and H_2O .



Figure 7. Schematic diagram of the in situ etching reaction of TiF₄ and SBA-15.



Figure 8. The photocatalytic performance curve of different TiO₂ loading catalysts degrading toluene, (a) concentration of toluene for removal process, (b) removal ratio of toluene for removal process.



Figure 9. (a) The photocatalytic performance curve of 20%-TiO₂-SBA-15 samples before and after hydrothermal treatment, (b) The photocatalytic performance of 20%-TiO₂-SBA-15 and 20%-P25-SBA-15.



Figure 10. Mechanism of TiO₂-SBA-15 improves the pollutant concentration and the collision likelihood between hydroxyl radicals and Toluene.

3. Materials and Methods

3.1. Materials

Titanium tetrafluoride, surfactant P123 was purchased from Merck Ltd. (Shanghai, China); tetraethyl orthosilicate (TEOS), HCl and alcohol were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China).

3.2. Preparation of TiO₂-SBA-15 Series Catalysts

3.2.1. Preparation of SBA-15

SBA-15 was synthesized by using condensation of TEOS through prehydrolysis of TEOS according to the following procedure: First, a certain amount of TEOS (98%) was introduced into an aqueous solution containing 600 mL of 2.0 M HCl,152 mL of H₂O and 20 g of P123. Then the TEOS was allowed to be prehydrolyzed for 60 min under vigorous stirring at 313 K. After being aged at 383 K for 24 h, the resulting white precipitate was filtrated and dried in a vacuum overnight. Finally, the surfactants and other organic

substances in the samples were extracted and washed away by refluxing in ethanol solution for 24 h. The initial molar ratio in the mother solution was Si:HCl:H₂O = 0.041:0.24:6.67, where Si refers to the total silica source. As-prepared sample was dried in a vacuum overnight at 353 K.

3.2.2. Preparation of TiO₂-SBA-15 Samples

The TiO₂-SBA-15 catalyst was prepared through the in situ etching of SBA-15 support with TiF₄. In a typical synthesis, 1.0 g of the above SBA-15 was added into 15 mL of alcohol solution containing 0.387 g of TiF₄, then the mixture was stirred for 1 h and then dried at room temperature for 12 h. Then it was dried under 373 K for 10 h to obtain 20%-TiO₂-SBA-15. Other TiO₂-SBA-15 series catalyst samples were obtained by adjusting TiF₄ amount (0.0969 g, 0.194 g and 0.581 g), which were labeled as 5%-TiO₂-SBA-15, 10%-TiO₂-SBA-15, and 30%-TiO₂-SBA-15, respectively. Here, the number before TiO₂-SBA-15 is calculated by $m_{TiO2}/(m_{TiO2} + m_{SBA-15})$.

3.3. Catalyst Characterization

The XRD experiments were carried out on a Rigaku D/Max-RB diffractometer with Cu KR radiation. The TiO₂ crystallite size was calculated by Scherrer's equation in the JADE 5.0 software. HR-TEM studies were performed on a JEOL JEM2010 electron microscope, operated at an acceleration voltage of 200 kV. N₂ adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). FTIR spectra were collected with a Nicolet NEXUS 470 spectrometer by using the KBr method.

3.4. Activity Test

The 50 mg TiO₂-SBA-15 photocatalyst was evenly tiled in a glass Petri dish, placed in the reactor (As shown in Figure 11), then sealed, and injected with 4 μ L of toluene through the injection port. Each sample was adsorbed for 2.5 h in the dark, sampling every 30 min. The collector was directly connected with the reactor and gas chromatography for sampling easily. The toluene concentration was determined by gas chromatography. The power supply of xenon lamp (300 W, the distance between the light source and the catalyst) was turned on for photocatalytic performance experiments, and sampled every 60 min to determine the toluene concentration in the reaction tank. Before the degradation toluene experiment, the standard curves of different concentrations of toluene were plotted on the reaction tank to obtain the correspondence between the peak area of gas chromatography and the concentration of toluene. As reference, commercial Degussa P25 was mixed with SBA-15 by the same method of 20%-TiO₂-SBA-15 except the TiF₄. The activity test was also the same as 20%-TiO₂-SBA-15.



Figure 11. Schematic diagram of photocatalytic gas phase degradation of Toluene.

4. Conclusions

Mesoporous TiO₂-SBA-15 nanocomposites have been synthesized by in situ etching method. The as-prepared photocatalyst has a high surface area, well-defined 2D-hexagonal meso-structure and uniform channel. The TiO₂ nanoparticles prefer to appear in the inner channel of SBA-15 due to the Siphon effect. The pore size and surface area decrease with increasing TiO₂ content. TiO₂-SBA-15 enhances adsorption and photocatalytic performance, because the enhancing-absorption improves the concentration of pollutant and the collision likelihood of hydroxyl radicals and pollutant, thus improving photocatalytic activity.

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