超临界 CO₂ 辅助制备 TiO₂ 外负载火山岩复合体及其光催化降解亚甲基蓝性能

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摘要: 以钛酸丁酯为前驱体, 封堵的火山岩为载体, 通过超临界 CO₂ 辅助制备了 TiO₂ 外负载火山岩复合体, 并将其用于光催化降解亚甲基蓝反应, 考察了溶液 pH 值及催化剂浓度对反应性能的影响。结果表明, TiO₂ 外负载火山岩复合体的光催化性能优于纯 TiO₂ 和 TiO₂ 体负载火山岩复合体。这是由于外负载复合体对亚甲基蓝的高吸附性、小晶粒尺寸的 TiO₂ 颗粒以及吸附和光催化降解间的协同效应。亚甲基蓝浓度为 1.5 mg/L, 溶液 pH 为 8, 催化剂浓度为 6.8 mg/L 时, 外负载 TiO₂ 火山岩复合体上亚甲基蓝降解速率最高, 且使用后的催化剂仍具有高的光催化活性。

关键词: 二氧化钛; 多孔火山岩; 溶胶凝胶法; 光催化; 亚甲基蓝; 超临界二氧化碳

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Preparation of Cost-Effective TiO₂-Outerloaded Porous Lava Composites Using Supercritical CO₂ and Their Photocatalytic Activity for Methylene Blue Degradation

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Abstract: Cost-effective TiO₂-outerloaded lava composites (TOLs) were prepared using supercritical CO₂ and sealing lava as well as tetrabutyl titanate as a support and a precursor, respectively. The important factors affecting methylene blue (MB) oxidation efficiency were investigated including the initial concentration of MB, the pH, and catalyst concentration. The results show that TOLs have a higher degradation efficiency than pure TiO₂ and TiO₂-loaded lava composites (TLLs) because of the high adsorption capacity of MB and the small crystalline size of the TiO₂ particles in addition to a synergetic effect for adsorption and photocatalytic degradation. The optimum conditions were a MB concentration of 1.5 mg/L at pH 8 with a TOLs concentration of 6.8 mg/L for the fastest MB degradation. Additionally, the used TOLs retained high activity for MB photocatalytic degradation.

Key words: titania; porous lava; sol-gel process; photocatalysis; methylene blue; supercritical carbon dioxide

Titanium dioxide is an important photocatalyst especially for the detoxification of water and air because of its high activity, chemical stability, robustness against photocorrosion, low toxicity, no-twin pollution, and availability at low cost [1]. However, because fine TiO₂ particles are commonly of nanometer size proportions, the problem of separation and recovery of this photocatalyst from the reaction medium is a major concern. An alternative method involves the immobilization of TiO₂ powder on a suitable porous

support such as silica gel, carbon, boehmite, glass fiber, and zeolite [2–6]. Because of good adsorption properties, TiO₂ photocatalytic activity is enhanced by a synergism between adsorption and photocatalysis. However, most porous materials are expensive and TiO₂ is widely used in wastewater treatment. Porous lava is inexpensive and it possesses high mechanical resistance compared with other porous materials, and reports about the use of porous lava as a support for photocatalysts are rare. Additionally, it is well known that

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coating TiO_2 onto the porous support surface is required for photoactivity. Furthermore, the uptake of TiO_2 into holes reduces the photoactivity of composites because of the reduction in surface area as the micropores become blocked. In this work, we present a new preparation method for TiO_2 -outerloaded lava composites (TOLs). We treated porous lava with supercritical CO_2 (SCC) using isopropanol as a plugging agent and subsequently pretreated the lava so that it acted as a sealing substrate for the nano- TiO_2 particles by a sol-gel process using tetrabutyl titanate as a precursor. Finally, composites of TiO_2 nanoparticles were outerloaded on the lava surface after the removal of isopropanol in the lava by calcination in air. We also studied the effect of photocatalytic conditions on TOL photoactivity and the studied factors include methylene blue (MB) concentration, TOL concentration, and pH.

1 Experimental

1.1 Sample preparation

Porous lava (Grain, diameter of about 2 mm with a surface area of $76.5 \text{ m}^2/\text{g}$, Shandong, China) was used as the substrate to support the TiO_2 nanoparticles. The plugging agent (a desire amount of isopropanol) was dissolved in SCC and then impregnated into porous lava at 120°C and 10 MPa to form sealing substrates over 12 h. Precursor solutions for the TiO_2 sol were prepared as follows. Tetrabutyl orthotitanate (10.5 ml) and diethanolamine (1.5 ml) were dissolved in 80 ml of ethanol. The solution was stirred vigorously for 2 h at 20°C followed by the slow addition of a desire amount of distilled water and ethanol (30 ml). The resulting alkoxide solution was left at 20°C and it hydrolyzed into a TiO_2 sol. The sealing substrates (20 g) were then immersed into the TiO_2 sol of a certain viscosity and subsequently the mixture was stirred in an ultrasonic bath for 1 h. Upon TiO_2 sol coating, the sealing substrates changed into a TiO_2 gel and the TiO_2 gel-coated sealing substrates was vacuum dried. Finally, the grains obtained were calcined at 500°C in air for 2 h to prepare TOLs. In addition, pure TiO_2 was prepared as a reference using the same hydrolysis procedure as for tetrabutyl orthotitanate. Therefore, porous lava replaced the sealing substrate in the TiO_2 -load lava composites (TLLs) prepared by the sol-gel process.

1.2 Characterization of the samples

The samples obtained were characterized by measuring the BET surface area using nitrogen adsorption on a Micromeritics ASAP 2010 instrument at -196°C . The crystalline phase was investigated by X-ray diffraction (XRD,

HZG-4 diffractometer, China). The morphology and particle size of TiO_2 in the prepared samples were determined by scanning electron microscopy (SEM, S-3400N, Japan). The chemical state of titanium, oxygen, and carbon on the surface and near surface of the deposited carbon was studied by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCALAB Mark spectrometer, and $\text{Mg } K_\alpha$ radiation was used (1 253.6 eV). Thermogravimetry and differential thermal analysis (TG-DTA) was performed using a TG-DTA instrument (WCT-2C, Beijing, China).

1.3 Evaluation of the photocatalytic activity

MB was chosen as a model organic compound to evaluate the photoactivity of the prepared samples and to determine the important factors affecting degradation. The photocatalytic experiment was the same as previously described using a UV-lamp (40 W ultraviolet lamp, Institute of Electric Light Source, Beijing) [6]. The MB concentration was calculated from its absorbance at 660 nm using a calibration curve obtained by a UV-Vis spectrometer (JascoV-500, Japan).

2 Results and discussion

2.1 Sample characterization results

Figure 1 shows TG-DTA curves of the TOLs. The TG curve can be roughly divided into three stages. The first stage is from room temperature to 150°C and a mass loss of about 8% is observed, which can be attributed to the evaporation of physically adsorbed water and the combustion of ethanol with an exothermic peak.

Additionally, there is an exothermic peak (around 150°C) that can be attributed to an amorphous to anatase phase transformation. Further weight loss (8%) is evident from the broad exothermic peak between 150 to 900°C and this can be attributed to the thermal decomposition of organic com-

Fig. 1. TG-DTA curves of the TOLs prepared by supercritical pretreatment and the sol-gel method. Scanning rate: $5^\circ\text{C}/\text{min}$.

Fig. 2. XRD patterns of samples annealed at 500 °C. (1) Pure lava; (2) TiO₂/lava; (3) TiO₂/lava surface.

pounds such as diethanolamine, butanol, and isopropanol in the TiO₂ gel. This also indicates that a phase transformation from anatase to rutile occurred.

XRD results of the samples (Fig. 2) indicate that the TOLs and TLLs calcined at 500 °C show some preferential orientation for anatase in the (101) direction. The wider anatase (101) plane diffraction peak ($2\theta = 25.40^\circ$) indicates smaller TOL crystallites compared with the TLLs. The crystallite sizes for the calcined samples were calculated from the FWHM data using Scherrer's formula and is listed in Table 1. The crystalline sizes of the TOLs and TLLs are 30 and 38 nm, respectively. It is obvious that upon supercritical pretreatment, the lava support allows an increase in the bandgap as the crystallite size decreases, which improves the TiO₂ photocatalytic activity. Additionally, upon calcination at 500 °C for 2 h in air, the TLLs and TOLs were mainly composed of elements such as Mg, Ni, Si, P, and Bi, as shown in the XRD patterns (Fig. 2).

XPS analysis provides a valuable insight into the surface structure of the TOLs photocatalyst [7,8]. From the general XPS electron spectrum shown in Fig. 3, the photocatalyst surface contains elements such as Ti, O, C, Cu, Ba, Cd, and Fe. All these elements come from the TiO₂ particles and the lava surface, which confirms the results obtained from the XRD analysis. The TiO₂ particles were possibly doped by

Fig. 3. XPS spectrum of TOLs.

metal elements from the lava.

The chemical structure of the TiO₂ in the produced samples, the BET surface area, and the pore density including the original porous lava and sealing lava are summarized in Table 1. The pore density calculations were based on a method described previously [9–11]. Compared with the original porous lava, the sealing substrate has a very low surface area and pore density because of the impregnation of isopropanol into the lava pores with the assistance of supercritical CO₂. The higher TOLs surface areas and pore densities are attributed to two factors: (1) The TiO₂ sol is only coated on the surface of the sealing substrate, which produces many pores during the calcination process; (2) nano-TiO₂ particles have high surface areas and this increases the surface area of the hybridization catalyst after loading onto the surface of porous lava. The high catalyst surface areas leads to an improvement in the hydroxyl radical content resulting in high photoactivity [12,13].

As shown in Fig. 4, the surface morphology of the porous lava, TOLs, TLLs, and pure TiO₂ was investigated using scanning electronic microscopy. Compared with the original lava (Fig. 4(a)), small-size pores are present on the surface of the lava-supported TiO₂ samples (Fig. 4 (b) and (c)) because of the TiO₂ particle coating. The surface of the TOLs

Table 1 Characteristics and photocatalytic activity of the sample

Sample	Pore number density ^a (10 ² cm ⁻³)	Surface area (m ² /g)	Average pore diameter (nm)	Average size (nm)	K_{app} (10 ² min ⁻¹)
Porous lava	789.3	76.5	69	—	—
Sealing lava	6.7	3.7	13	—	—
TiO ₂	73.6	49.7	—	48	1.08
TLLs	664.2	58.1	47	43	2.19
TOLs	795.2	74.8	58	35	3.93

^aCalculated using the equation described in Refs. [7–9].

Fig. 4. SEM images of the original lava (a), TOLs (b), TLLs (c), and pure TiO₂ (d).

consists of a large amount of pores and spherical microstructures, and it has a dispersing texture composed of spherical particles of 35 nm in size (Fig. 4(b)). However, the TLLs surface contains only a few pore gaps with 43 nm TiO₂ particles (Fig. 4(c)) and it shows a relatively dispersing texture in comparison with pure TiO₂ (Fig. 4(d)). In addition, the smaller TiO₂ particles lead to increased pore density and higher surface areas as listed in Table 1. If the amount of lava on the composite surface is too low, such as for the TLLs, most of the TiO₂ particles are found to be connected to each other and form larger particles, and this is a probably the reason why the TOLs TiO₂ particles are smaller than those of the TLLs.

2.2 Photocatalytic activity of the samples

Under identical experimental conditions, we found that only 2.3% of the MB in solution adsorbed onto pure TiO₂ in the dark after 1 h while the amount of MB removed by the TLLs and TOLs was 6.2% and 8.7%, respectively. This suggests that MB mainly adsorbs onto the lava carrier and the greater adsorption of MB on TOLs compared with TLLs is attributed to the higher surface area of the TOLs. A plot of $\ln(c_0/c)$ against time is shown in Fig. 5. MB photocatalytic degradation is a pseudo first order reaction for pure TiO₂, TLLs as well as TOLs. The apparent rate constant (k_{app}) was obtained directly from a regression analysis of the linear curve in the plot. The results of MB removal by the photocatalysts are also listed in Table 1. Pure TiO₂ showed a low

k_{app} for MB photocatalytic degradation under UV irradiation, however, the k_{app} of the TOLs was two times higher than that of pure TiO₂. The photoactivity of TiO₂ was enhanced by the lava support and by SCC. This is attributed to a synergetic effect for the adsorption and photocatalytic decomposition of MB. To demonstrate the effect of the SCC on the lava substrate during photoactivity, we studied the photodecomposition of MB using the TLLs without SCC. As shown in Table 1, the k_{app} of the TOLs is far higher than that of the TLLs. The decomposition of MB, therefore, mainly occurs on TiO₂ particles and is related to the structure of the composites. Furthermore, the k_{app} of the TOLs is

Fig. 5. Degradation of MB by different catalysts.

far higher than the sum of both the individual values. The higher photoactivity of the TOLs is related to both factors: a large bandgap and a high absorptivity for the organic substrate because of its small crystalline size and high surface area. These factors cooperate and the photocatalytic reaction of the organic molecules improves because the active sites on the TiO₂ surface are more accessible.

2.3 Effect of reaction conditions

The effect of initial MB concentration on the degradation rate was studied by varying the initial concentration from 1.5 to 3.0 mg/L and the results are shown in Fig. 6(a). It is clear that the degradation rate decreases with an increase in the initial MB concentration. A plausible explanation for this behavior can be that as the initial concentration increases, an increasing amount of organic substance is adsorbed onto the surface of TiO₂. However, the intensity of light and illumination time are constant and consequently the $\cdot\text{OH}$ formed on the surface of TiO₂ is constant while the relative number of $\cdot\text{OH}$ radicals attacking MB decreases. Therefore, the photodegradation efficiency decreases too [10]. Additional factors include the type of catalyst, reactor geometry and irradiation source.

The reaction rate as a function of catalyst concentration is important [11,14]. Hence a series of experiments were carried out to determine the optimum catalyst concentration by varying TiO₂ from 2.0 to 7.6 mg/L (Fig. 6(b)). The turbidity of the solution above 6.8 mg/L reduced the light transmission through the solution while below this level adsorption onto the TiO₂ surface and light absorption by TiO₂ were the limiting factors. Ichiura et al. [11] reported that the catalyst concentration has both a positive and negative impact on the photodecomposition rate. An increase in the catalyst concentration increases the quantity of photons absorbed and consequently the degradation rate. A further increase in catalyst concentration beyond 6.8 mg/L may result in the deactivation of activated molecules because of collisions with ground state molecules [14] and an increase in the tur-

bidity of the solution, which reduces light transmission through the solution. At concentrations higher than 6.8 mg/L, TOLs aggregation (particle-particle interactions) may occur and lower the effective surface area of the catalyst, and also the adsorption of the reactant.

Results obtained from experiments where the pH was varied from 2 to 10 are shown in Fig. 6(c). From this plot, the rate constant is obviously lower in the acidic medium compared with the basic medium and the maximum MB degradation occurs at a pH of 8. Strong acid or alkali is, therefore, not available for the decomposition of MB. This is due to the pH affecting the surface properties of the photocatalyst or the chemical form of the substrate. TiO₂ is amphoteric with a point of zero charge at a pH around 6 [10], and the substrate can undergo acid-base equilibria as well. Consequently, the adsorption behavior of the substrate may be affected, which will strongly influence the degradation rate [10,15,16].

To verify the activity of the used TOLs, the decomposition of 1.5 mg/L MB was undertaken. The results are shown in Fig. 7. For TOLs photocatalyst after 3 h of illumination, the values of apparent kinetic constant remained 0.028 1 and 0.020 5 min⁻¹ in the first and second trial, respectively, while in the fourth trial kinetic constant was 0.012 0 min⁻¹.

Fig. 7. Kinetic constant of MB decomposition over TOLs for different utilization times.

Fig. 6. Effect of initial MB concentration (a), TOLs concentration (b), and pH (c) on the kinetic constant.

This value of apparent kinetic constant remained 0.0089 min^{-1} during the 10th trial. This suggests that the used catalyst retained high photocatalytic activity. This was mainly due to the lava supports not being blocked for the TiO_2 decomposition of MB and the lava ensured a high concentration of the organic compound was available because the TiO_2 was distributed well by the absorption process.

3 Conclusions

This study presents an effective method to prepare cost-effective TiO_2 -outerloaded lava composites using supercritical CO_2 . TiO_2 sol coated on the surface of a sealing substrate was calcined to produce many pores and small TiO_2 nanoparticles outerloaded on lava without agglomeration occurring. This results in high surface areas and small crystalline sizes for the TiO_2 particles of the TOLs. TOLs, therefore, show higher relative photocatalytic degradation efficiency toward MB in addition to a synergetic effect for the adsorption and photocatalytic degradation. Additionally, the photocatalytic degradation of MB depends on the initial concentration of MB, catalyst concentration, and solution pH. We found that the MB degradation efficiency was highest when the concentration of MB, the TOLs, and the pH were 1.5, 6.8 mg/L, and 8, respectively. Additionally, the TOLs were successfully used as catalytic materials for the cyclic photocatalytic degradation of MB.

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