Effects of calcination conditions on properties of TiO_2 supported on HZSM-5

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HZSM-5 was used to support TiO_2 photocatalyst through sol-gel method. The XRD patterns reveal anatase TiO_2 and HZSM-5 in the composites. Crystallite sizes increase apparently with increasing calcination temperature, while there is only a slight increase in crystallite size with increasing calcination time. TiO_2 is coated on the surface of zeolite in 50%TiO_2/HZSM-5, while the difference in calcination temperature has very small influence on morphology of the materials. The 50%TiO_2/HZSM-5 calcinated at 450 ^oC for 2 h has the largest surface area of 243.1 m^2/g and the maximum photocatalytic activity on methyl orange degradation.

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1. Introduction

Photocatalytic degradation of organic substances is one of advanced oxidation methods in wastewater treatment [1-2]. Nano-sized TiO_2 has aroused great attention because of its high degradation activity under illumination of UV light [3-4]. Powder TiO_2 photocatalyst is used traditionally in wastewater as suspensions. Although the suspended particles can easily absorb photons and react with pollutants, it is not easy to be applied in large plant due to the obstacle of separation after use. A new approach is to load TiO_2 on the supports in order to solve the problem. Porous materials have large surface area so that TiO_2 can be well dispersed on the external surface. Photocatalytic activity of TiO_2 can be improved due to promoted contact between TiO_2 and pollutants [5-7]. The interactions between the supports and TiO_2 may contribute positive effect on promoting activity of composite materials [8-10].

Natural and synthesized zeolites have large surface area and porous structure, and are applied industrially as adsorbent and catalyst [11]. Some kinds of zeolite were also used to support titanium dioxide for enhanced activity in photocatalytic process [12-15]. In this work, a hydrothermal method was used to modify NaZSM-5 in hydrochloric acid to prepare HZSM-5. HZSM-5 supported TiO_2 was prepared by sol-gel method. The effects of calcination conditions on the physicochemical properties of composite 50%TiO_2/HZSM-5 were studied.

2. Experimental

Material preparation

NaZSM-5 Zeolite (SiO_2/Al_2O_3=50) was provided by Nankai Catalyst Company in China. HZSM-5 was prepared in a hydrothermal reactor through Na^+-H^+ exchanging. 20 g of NaZSM-5 was mixed with 20 mL 0.3 mol/L hydrochloric acid aqueous solution in a 100 mL PTFE container. The hydrothermal treatment was conducted at 150 ^oC for 3 h. After cooling to room temperature, the solid product was filtrated and subsequently washed with distilled water until the pH of the filtrate was between 6 and 7. The HZSM-5 zeolite was dried at 110 ^oC for 12 h, and then was calcinated at 550 ^oC for 4 h for activation.

The composite 50%TiO_2/HZSM-5 was prepared by a sol-gel process. Tetrabutyl titanate was dissolved in anhydrous ethanol. The hydrolysis and condensation reactions were adjusted using acetylacetone and hydrochloric acid. 2 mL tetrabutyl titanate, 0.04 mL acetylacetone, 0.1 mL hydrochloric acid, 6 mL anhydrous ethanol, and HZSM-5 were mixed together under stirring. Another mixture containing 0.6 mL deionized water and 3 mL anhydrous ethanol was slowly added to the former slurry. Tetrabutyl titanate was hydrolyzed on the surface of HZSM-5. A gel might form after 30 min of magnetic stirring. The gel was aged at room temperature for 12 h, and then was dried at 80 ^oC for 7 h. The obtained solid was calcinated at temperatures indicated later. Finally, the composite material was ground into fine powder. The

material was named as 50%TiO_2/HZSM-5, which contained 50% TiO_2 in the composite.

Characterization of the material

The X-ray diffraction measurement was performed using D/max-rB with a Cu Kα source. The surface morphology examination of the materials was conducted on Hitachi S-3400N scanning electron microscope. N_2 adsorption-desorption on the samples was measured by F-Sorb 3400 specific surface area analytical instrument. The specific surface area was calculated from N_2 desorption isotherms, according to Brunauer-Emmett-Teller (BET) equation.

Photocatalytic reaction

Photocatalytic degradation of methyl orange was conducted in a lab-scale photocatalytic reactor. The reactor was composed of a 250 mL glass beaker and a 20 W UV lamp. 50 mL of 10 mg/L methyl orange aqueous solution and 30 mg TiO_2 were used in each experiment. Photocatalytic reaction time was 30 min. The absorbance of methyl orange solution was examined by a 721E spectrophotometer at the maximum absorption wavelength. Methyl orange concentration was calculated according to Lamb-Beer theory.

3. Results and discussion

The XRD patterns of 50%TiO_2/HZSM-5 calcinated at different temperatures are shown in Fig. 1(a). Thermal treatment is essential for the formation of TiO_2 crystalline. Diffraction peaks of TiO_2 and HZSM-5 are found in the XRD patterns of the composites. The characteristic diffraction peaks of TiO_2 demonstrate the formation of anatase TiO_2, which begins to form at 350 ^oC. There is no other form of TiO_2 appearing in the XRD patterns. Phase transformation from anatase to rutile does not occur at the given temperatures as high as 550 ^oC.

HZSM-5 has good thermal stability in the given temperatures. Although the peak intensities of HZSM-5 have no change for the samples calcinated at different temperatures, the peak intensities of anatase TiO_2 increase obviously with increasing calcination temperature. That means high temperature calcination can be beneficial to TiO_2 crystal formation and crystallization.

A preferred orientation for anatase (101) plane is found in the patterns which are in accordance to standard diffraction patterns of anatase TiO_2. The crystalline size of TiO_2 (101) plane is calculated using Scherrer formula, e.g. $L=K\lambda/(\beta\cdot\cos\theta)$. TiO_2 crystalline sizes are 6.5 nm, 11.5 nm, and 22.3 nm for the samples calcinated at 350 ^oC, 450 ^oC and 550 ^oC, respectively. Crystalline sizes apparently increase with increasing calcination temperature, while all the samples are composed of nano-sized crystals. Low temperature calcination is not capable of producing well crystallized TiO_2.

Calcination time can also influence crystallization of anatase TiO_2, as shown in Fig. 1(b). Anatase diffraction peaks appear in the sample calcinated at 450 ^oC for 1 h. The extending of thermal treating leads to better crystallite formation and crystal growing. Crystal sizes are also calculated based on the data of (101) plane. TiO_2 crystalline sizes are 10.5 nm, 11.5 nm, and 11.7 nm for the samples calculated at 450 ^oC for 1, 2, and 3 hrs, showing the improved crystallization during prolonged calcinating.

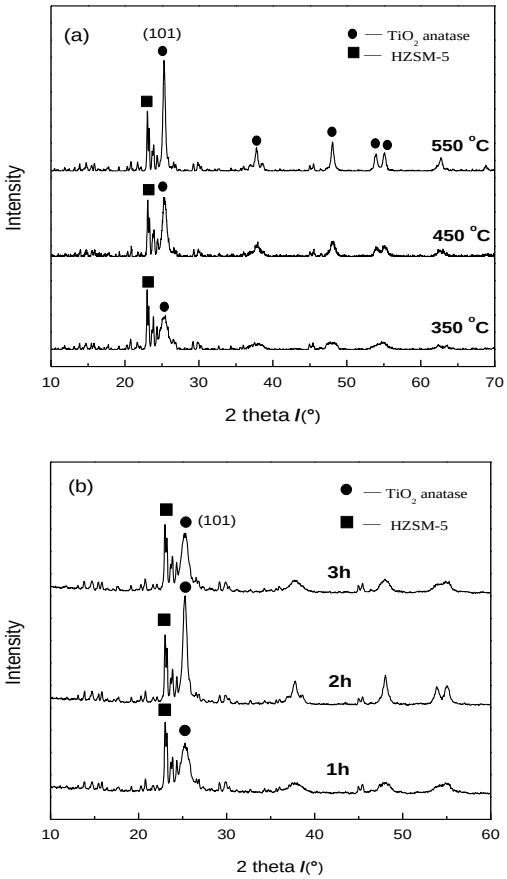

Fig. 1. XRD patterns of 50%TiO_2/HZSM-5. (a) Calcinated at different temperatures for 2 h, (b) Calcinated at 450 ^oC for different time.

The SEM images of 50%TiO_2/HZSM-5 at different calcination temperatures are shown in Fig. 2. The composite 50%TiO_2/HZSM-5 maintains the shape of HZSM-5 particles, although the composite particles aggregate in some extent due to the effects of thermal treatment and conjunction through TiO_2. The 50%TiO_2/HZSM-5 particles are in the size around 2-5 μm. However, the morphology of the composite 50%TiO_2/HZSM-5 is not as smooth and regular as the HZSM-5 particle, indicating the loading of TiO_2 on the surface of HZSM-5. Since HZSM-5 has good thermal

stability in the given temperatures, there is no much difference in the morphologies of 50%TiO_2/HZSM-5 calcinated at different temperatures.

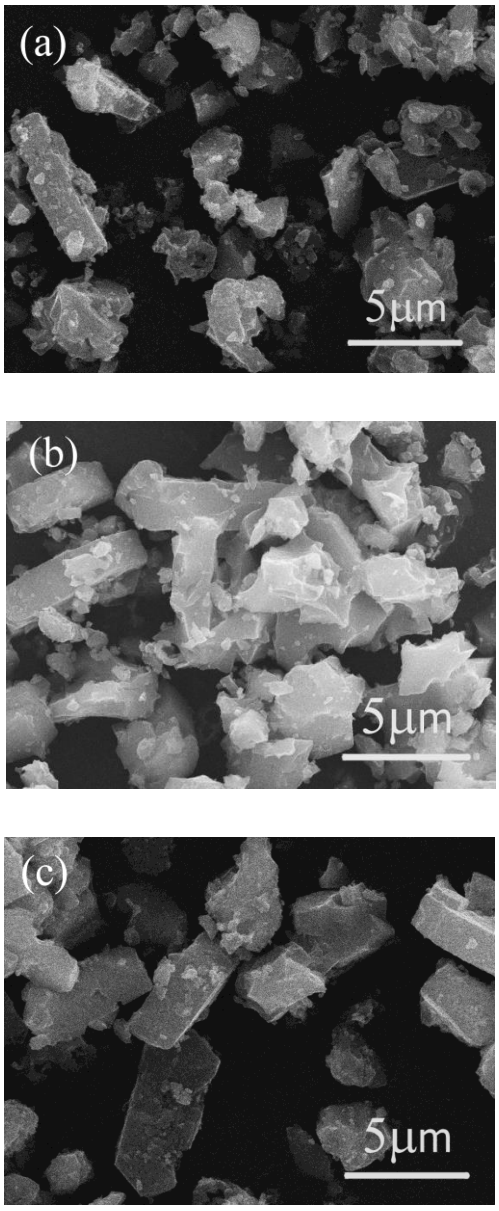

Fig. 2. SEM images of 50%TiO_2/HZSM-5 at different calcination temperature. (a) 350 °C, (b) 450 °C, (c) 550 °C.

The BET surface areas of 50%TiO_2/HZSM-5 calcinated at different temperatures are shown in Table 1. The sample calcinated at 450 °C has the maximum surface area of 243.1 m^2/g. The BET surface area of HZSM-5 is as high as 356.9 m^2/g, while pure TiO_2 has a small surface area of 32.9 m^2/g. The majority of the surface area of the composite comes from the zeolite. The composite 50%TiO_2/HZSM-5 contains equal amount of TiO_2 and HZSM-5. TiO_2 is loaded on HZSM-5 and might block some small pores in the zeolite. Since HZSM-5 is stable under thermal treatment, crystal growing of anatase TiO_2 and particles aggregation may be responsible for the variation in surface area. Some pores of the zeolite are blocked by the large TiO_2 crystals forming at high temperature calcination, leading to shrinking surface area at 550 °C.

TiO_2 crystalline size and surface area are both important for adsorption and photocatalytic activity of the composite. TiO_2 is the photocatalyst and HZSM-5 itself has no photocatalytic activity under the UV light irradiation. Photocatalytic activity is attributed to the loaded TiO_2. The zeolite can help on improving the activity of TiO_2 by adsorbing both TiO_2 and the reactant on the surface.

Table 1. BET surface areas of 50%TiO_2/HZSM-5 calcinated at different temperatures

Calcination temperature / °C	350	450	550
BET surface area /m^2/g	202.1	243.1	154.5

Fig. 3 shows the effect of calcination conditions on photocatalytic degradation activity of the composite 50%TiO_2/HZSM-5. The degradation efficiency increases constantly with increasing calcination temperature from 300 °C to 450 °C. The samples calcinated at 300 °C and 350 °C have low photocatalytic activities because organic substances in the gel are not burnt out thoroughly at low temperature. Meanwhile, the formation of TiO_2 crystals from amorphous phase largely depends upon calcination temperature. The composite 50%TiO_2/HZSM-5 prepared at 450 °C has the maximum degradation activity. 38.7% of methyl orange in the solution is degraded after 30 min of irradiation. As indicated previously, the composite has surface area of 243.1 m^2/g and TiO_2 nano crystals are in the size of 11.5 nm. The continuous growing of TiO_2 crystals in the composite and the aggregation of the composite particles occurring at higher temperature are responsible for the decline of degradation activity.

Fig. 3(b) shows photocatalytic degradation of methyl orange on 50%TiO_2/HZSM-5 as a factor of calcination time at 450 °C. Thermal treating time is another important factor influencing crystallite formation and porous structure of the materials. The sample calcinated for 2 hrs has the maximum photocatalytic activity. As can be seen in Table 2, the material can reach the highest BET surface area after calcinated at 450 °C for 2 hrs.

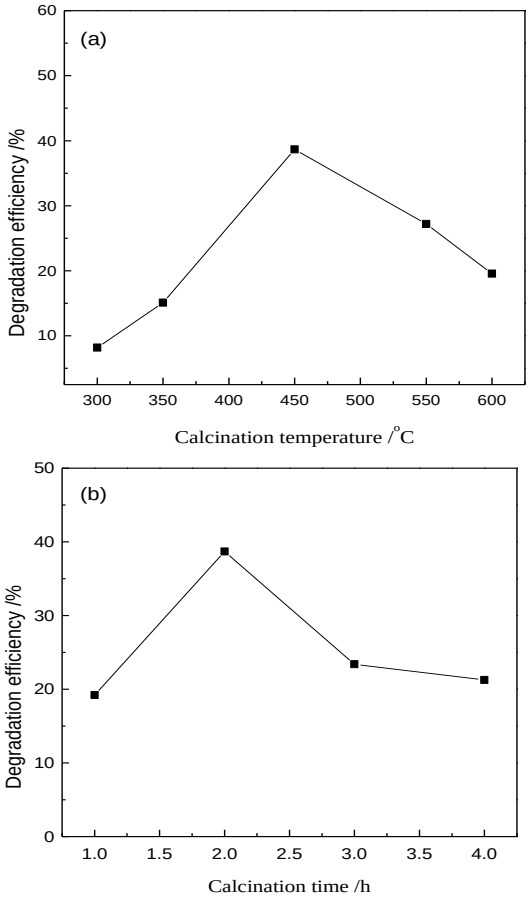

Fig. 3. Photocatalytic degradation of methyl orange on 50%TiO_2/HZSM-5 as the factor of calcination conditions. (a) Calcinated at different temperatures for 2 h, (b) Calcinated at 450 °C for different time.

Table 2. The effect of calcination time on BET surface area of 50%TiO_2/HZSM-5

Calcination time /hr	1	2	3
BET surface area /m^2/g	167.8	243.1	173.5

4. Conclusion

HZSM-5 was used to support TiO_2 photocatalyst by sol-gel method. TiO_2 crystallite size and porous structure of the materials can be influenced by increasing calcination temperature and time. The composite 50%TiO_2/HZSM-5 calcinated at 450 °C for 2 hrs has the largest surface area and the maximum photocatalytic activity on methyl orange degradation.

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