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Preparation of porous TiO_2/silica composites without any surfactants

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ABSTRACT

TiO_2–SiO_2 composites, with high specific surface area (up to 308 m^2/g), large pore volume, and narrow distribution with average pore sizes of 3.2 nm, have been synthesized from wollastonite and titanium sulfate in the absence of any surfactants. Calcium sulfate, a microsolubility salt, plays an important role in the formation of pores in this porous TiO_2/silica composite. The microstructure and chemical composition of composite were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM) equipped with energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectrometer (XPS) and N_2 adsorption and desorption analysis. The as-prepared porous titanium dioxide–silicon dioxide composites with high specific surface area and well-crystallized anatase contents were used as an efficient photocatalyst.

1. Introduction

Titanium dioxide (TiO_2), as an important photocatalyst, has been employed for decomposing organic pollutants in aqueous systems and in air [1–4]. The specific surface areas and polymorphs of the photocatalyst are the key effect factors of photocatalytic activity. Pure ultrafine powders will agglomerate into larger particles, resulting in an adverse effect on catalyst performance [5]. So various strategies have been used to accept large TiO_2 surface areas, such as TiO_2 mesoporous molecular sieves, TiO_2 pillared clays, and titania–silica mixed oxides. For the first strategy, although many cases of the synthesis of porous titania have been reported, there were a few reports on the synthesis of stable porous titania with a crystalline wall that had a high photocatalytic activity [5–8]. TiO_2 pillared clays were used to achieve large specific surface areas. Some of them were only simple mixing of titania and clay mineral dispersions [9] and these TiO_2 pillared clays were amorphous [10]. The layered silicates were also used [5,11] to achieve large specific surface area in the presence of surfactant [5]. All of these methods limited the applications of materials.

Titania–silica materials had been widely used as photocatalysts, acid catalysts, and oxidation catalysts, recently [12–14]. The catalytic function of titania–silica was mainly attributed to TiO_2, and SiO_2 had high thermal stability and excellent mechanical strength. The addition of silica can both enhance the dispersion of titania and improve the activity of TiO_2 [15,16]. To our knowledge, there were few reports on the synthesis of porous titania–silica nanocomposite from raw minerals without any surfactant.

In this work, we succeeded in preparing TiO_2–SiO_2 composite with high specific surface area and narrow pore size distribution from cheap materials by chemical deposition method and a potential photocatalytic application of this composite was also carried out using the photo oxidation of a dye, methyl orange, as probe reaction. No surfactant was used in this reaction system, and the calcium sulfate that formed in the reaction process played an important role in the formation of pores in composite. This new synthesis route is a simple, cost effective for large scale production of titania–silica composite photocatalyst.

2. Experimental

2.1. Preparation of TiO_2–SiO_2 composites

The reagents used were titanium (IV) sulfate (A.R. grade) and commercial wollastonite powder (main substance: $CaSiO_3$, average particle size 50 μm). All compounds were used as received without further purification. Typically, TiO_2–wollastonite composites were prepared in the following way: 1.16 g wollastonite were added into 100 ml, 0.1 mol/L titanium sulfate aqueous solution with constant stirring at ambient temperature, incubation for more than 24 h. Then the suspension was subjected to hydrothermal treatment of 80 °C for 3 h. Then the sediment was centrifugated and washed with plenty of deionized water until it was free of SO_4^{2-} anions according to the test of $BaCl_2$. At last the product was dried at 80 °C for 12 h and calcined at different temperature.

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2.2. Photocatalytic experiment

The evaluation of photocatalytic activity was carried out by the degradation of methyl orange using a beaker made of Pyrex glass equipped with a magnetic stirring bar. For irradiation experiments, 500 ml solution of methyl orange of 50 mg/L concentration was taken into the vessel and required amount of the catalyst (1 g/L) was added into the solution. Before irradiation, the solution was magnetically stirred for 30 min to allow the equilibration of the system so that the loss of compound due to the adsorption can be considered. The degradation rate for the decomposition (decrease in absorption intensity vs. irradiation time) of methyl orange under investigation was monitored by measuring the change in absorbance on a UV-Vis spectrophotometer (Scinco). The absorbance of the methyl orange was followed at 490 nm wavelength. For each experiment, the rate constant was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of the absorbance of the dye as a function of irradiation time.

2.3. Characterization methods

Powder X-ray diffraction (XRD) patterns of the samples were taken on an SHIMADZU-6000 X-ray diffractometer, with Cu$K\alpha$ ($\lambda = 1.54056$ Å) radiation being used at 40 kV and 30 mA. The transmission electron microscopy (TEM) images were obtained by means of HITACHI (H-8100) TEM equipped with energy-dispersive X-ray spectroscopy (EDX), using an accelerating voltage of 100 kV. The N_2 adsorption measurements were performed at 77 K, using a QUANTACEROME AUTOSORB-1C analyzer and utilizing Barrett–Emmett–Teller (BET) calculations for surface area and BJH calculations for pore size distribution for the desorption branch of the isotherm. The XPS analysis of the samples was carried out in an ESCALAB MARK II (VG Scientific) photoelectron spectrometer. The photoelectrons were excited with an X-ray source using Al$K\alpha$ ($h\upsilon = 1486.3$ eV). To correct the measured values of binding energy (BE) for the charging effect, all spectra were calibrated to adjust BE (C1*s*) to 284.4 eV.

3. Results and discussion

The XRD patterns of the starting wollastonite and the obtained TiO_2–SiO_2 composites are shown in Fig. 1. The pattern of pristine wollastonite (Fig. 1a) could be perfectly indexed to 1Tr-type $CaSiO_3$, which is in agreement with JCPDS 271064. When wollastonite were pretreatment for 24 h with titanium sulfate, new peaks occurred. These peaks around 20, 29, and 31 were assigned to $CaSO_4$ (Fig. 1b). After pretreatment, the samples were subjected to hydrothermal treatment, the XRD pattern of washed and unwashed sample were shown in Figs. 1c and d. It can be seen form Fig. 1c that the diffraction peaks of $CaSO_4$ still exist for the unwashed sample, while all the $CaSO_4$ diffraction peaks disappeared after carefully washing. Characteristic diffraction peaks for anatase with *d*-spacings of 3.52, 2.38, 1.89, and 1.69 Å (2θ values: 25.3°, 37.8°, 48.0°, and 54.4°, respectively) can be clearly observed from the XRD pattern of the sample (Fig. 1d enlargement), the reflections can be indexed to pure anatase phase of TiO_2 conforming to a space group of $I4_1/amd$ (141) (JCPDS 841285). It means that the anatase phase has formed during aging process. The hydrothermal-induced crystalline anatase formation manifested itself in the broadening of the XRD peaks at 2θ of about 25.3°. Taking advantage of this broadening, we estimated the diameters of the crystalline anatase in $2\theta = 25.3°$ to be 4.2 nm using the Warren–Averbach method [17].

Transmission electron micrographic image (as shown in Fig. 2) indicated that the TiO_2/SiO_2 composites were in nanometer scale.

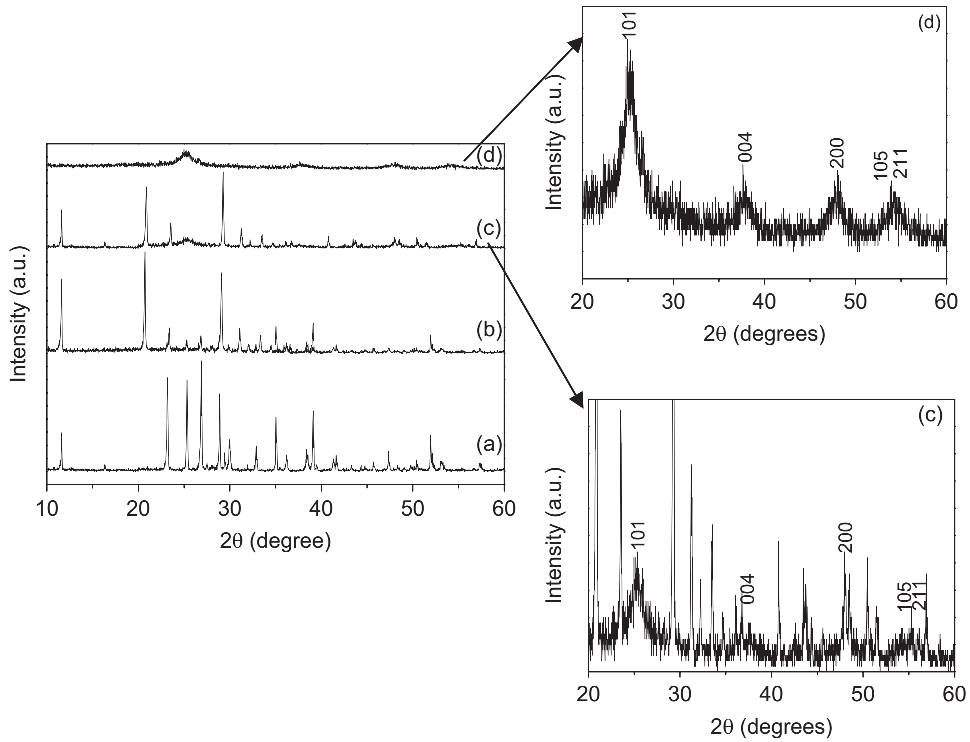

Fig. 1. Powder XRD patterns for samples: (a) wollastonite, (b) the sample after pretreatment, (c) the composite without washing carefully, and (d) the obtained TiO_2–SiO_2 composites. And the enlargements of (c) and (d) are shown right.