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Synthesis, characterization and activity of an immobilized photocatalyst: Natural porous diatomite supported titania nanoparticles

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ABSTRACT

Diatomite, a porous non-metal mineral, was used as support to prepare TiO_2/diatomite composites by a modified sol–gel method. The as-prepared composites were calcined at temperatures ranging from 450 to 950 °C. The characterization tests included X-ray powder diffraction (XRD), scanning electron microscopy (SEM) with an energy-dispersive X-ray spectrometer (EDS), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and nitrogen adsorption/desorption measurements. The XRD analysis indicated that the binary mixtures of anatase and rutile exist in the composites. The morphology analysis confirmed the TiO_2 particles were uniformly immobilized on the surface of diatom with a strong interfacial anchoring strength, which leads to few drain of photocatalytic components during practical applications. In further XPS studies of hybrid catalyst, we found the evidence of the presence of Ti–O–Si bond and increased percentage of surface hydroxyl. In addition, the adsorption capacity and photocatalytic activity of synthesized TiO_2/diatomite composites were evaluated by studying the degradation kinetics of aqueous Rhodamine B under UV-light irradiation. The photocatalytic degradation was found to follow pseudo-first order kinetics according to the Langmuir–Hinshelwood model. The preferable removal efficiency was observed in composites by 750 °C calcination, which is attributed to a relatively appropriate anatase/rutile mixing ratio of 90/10.

1. Introduction

Over the past decades, semiconductor photocatalysis attracted public interest as a promising technology for the removal of dye pollutants from textile and paper wastewater and of volatile organic compounds (VOCs) from indoor air [1,2]. Semiconductor metal oxides, typically such as titanium dioxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), nickel oxide (NiO) and cuprous oxide (Cu_2O), have been used as photocatalysts [3–7]. Among them, TiO_2 is widely investigated because of its high photocatalytic activity, biological and chemical inertness, and non-toxic nature. However, from the standpoint of large-scale practical application and commercial benefits, TiO_2 nanoparticles (NPs) show disadvantages, which may result in a low photocatalytic efficiency and high cost. For example: strong tendency to aggregate, difficult to be recovered from the solution after treatment and low adsorption capacity. To overcome these drawbacks, recently many researchers are focused on immobilizing TiO_2 NPs on supports having large surface area and excellent adsorption capacity. This approach may enhance the TiO_2 NPs distribution in suspension which enables to adsorb and concentrate the target substances. Furthermore, the substances can easily diffuse from the adsorption site to the photocatalytic surface.

It has been demonstrated that heterogeneous photocatalytic reactions occurred on the surface of the catalyst and pre-adsorption of the target substrates around TiO_2 particles is critical for the degradation [1,8]. Ao and Lu et al. [9,10], for example, reported that TiO_2 immobilized onto the activated carbon shown a more effective photocatalytic activity for nitrogen oxide, BTEX (benzene, toluene, ethylbenzene and xylene) and formaldehyde. The strong adsorption of the pollutants over the activated carbon was the main reason pointed by the authors to explain the occurred phenomenon. Recently, porous non-metal minerals have been taken into account as supports of TiO_2-based photocatalysts, such as perlite, zeolite and diatomite due to their low costs [11–14]. The use of porous minerals as support induces a synergistic effect

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by improving the photo-efficiency of the immobilized TiO_2 NPs. This effect can be associated to their high surface areas which avoid the formation of macroscopic aggregations of the photoactive particles.

Diatomite is a light fine-porous mineral consisting of extremely small diatom shells and its main chemical component is amorphous SiO_2. Diatomite has ordered pore-size distribution with specific properties such as high amorphous silica content, high porosity, and low density, which has been widely used in sound and heat insulation, as filters. Moreover, diatomite has outstanding merits as catalyst support for the removal of pollutants [15–18], from point of views of inert characteristics, substantial resources, practical use and environmental requirements [19]. The huge amount of silicon hydroxyl groups, acid sites and hydrogen bonds on the surface of amorphous SiO_2 can be considered as adsorption sites for pollutants [20–22]. Hsien et al. [13] used three kinds of commercial anatase TiO_2 as photoactive particles supported in diatomite to study the photocatalytic efficiency of the bisphenol-A remediation. In our group, Sun et al. [14] evaluated the influence of the different support on the photocatalytic ability of TiO_2/amorphous silica minerals photocatalysts by using $TiCl_4$ as precursor through low-temperature hydrolysis-deposition method. However, [14] only a few investigations have been reported about the effect of calcination temperature on the crystalline structure and photocatalytic performance of the TiO_2/diatomite photocatalysts prepared by sol–gel method. The synthetic method and calcination temperature may strongly affect the TiO_2 crystallinity, phase fraction and porous structure of the matrix, resulting a direct impact on the photocatalytic performance of catalysts [23].

Thus, in this study, a mixed phase TiO_2 immobilized on diatomite (TiO_2/diatomite) was successfully synthesized by a modified sol–gel method using tetrabutyl titanate (TBOT) as precursor. TiO_2 with different phase fraction and crystalline size was found to exist in composites under different calcination temperatures. The photocatalytic performance of TiO_2/diatomite composites were evaluated by the degradation of dye Rhodamine B (RhB) in aqueous solution under UV light. The crystalline properties of TiO_2, porous structure of diatomite and the interface interaction were systematically characterized and studied.

2. Experimental

2.1. Materials

Raw diatomite (Linjiang, Jilin province, China) was used as catalyst support after purification. The process of purification was described in detail elsewhere [24]. The main chemical compositions of the purified diatomite (DE) are listed in Table 1. As summarized in Table 1, it is clear that the main chemical composition of porous diatomite mineral is amorphous SiO_2. Tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, TBOT), ethanol (C_2H_5OH), hydrochloric acid (HCl), acetic acid (CH_3COOH), and Rhodamine B (RhB) were purchased from Beijing Reagent Co. (Beijing, China), which were all analytical reagent grade without any further purification before used. Pure commercial TiO_2 (Degussa P25) particles consists of 75% anatase and 25% rutile purchased from Degussa (Dusseldorf, Germany) was used for comparison purpose. Deionized water was used throughout all experimental procedures.

Table 1
Chemical constituent of purified diatomite (DE).

Constituent	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	L.O.I.[a]
(%)	91.74	2.76	1.14	0.34	0.21	0.12	3.52

[a] Loss on ignition.

2.2. Preparation of TiO_2/diatomite composites

The preparation of TiO_2/diatomite composites was undertaken by a modified sol–gel method as follows. Firstly, 1 g of DE dispersed in 14 mL of ethanol and 1 mL of acetic acid under stirring for 30 min to form diatomite suspension. Secondly, 1.5 mL of TBOT were added dropwise into the diatomite suspension, under continuous stirring, followed by the addition of 12 mL of ethanol: water solution (v:v = 1:1; pH = 2) which led the hydrolysis of the TBOT at moderate rate. After that, this solution was added dropwise into the suspension to arouse hydrolysis of TBOT at a moderate rate. The resulting mixture was stirred for 12 h to become aged and to immobilize as-synthesized TiO_2 colloids on the surface of DE. Finally, the product was dried in an oven at 105 °C for 4 h with subsequent calcination at 450–950 °C for 2 h in air at a heating rate of 2.5°/min. Fig. 1 shows a schematic diagram of the possible pathways of Ti species [such as $Ti(OH)^{3+}$] deposited onto diatom in the synthesis process. In this study, the TiO_2/diatomite composites calcined at X °C were denoted as TD-X series listed in Table 2, respectively.

2.3. Characterization of TiO_2/diatomite composites

The structures and crystal phases of TiO_2/diatomite composites were examined by X-ray powder diffraction (XRD) patterns with a Bruker D8 Advance X-ray diffractometer at 40 kV voltages and 20 mA current, using Cu Kα radiation at a scan rate of 4°/min. Phase content of TiO_2 was estimated from the strongest diffractions of anatase (1 0 1) and rutile (1 1 0), while the crystallite size (D) of TiO_2 was estimated by applying the Debye–Scherrer equation ($D = k\lambda/\beta\cos\theta$), where λ denotes the wavelength of the X-rays irradiation, k is usually taken as 0.89, and β is the corrected full width at half maxima (FWHM). The morphologies of samples were observed by scanning electron microscopy (SEM, EVO 18, Carl Zeiss) with an energy-dispersive X-ray spectrometer (EDS). High-resolution TEM (HRTEM) images and EDS measurement were taken on a Philips Tecnai F20. The Brunauer–Emmett–Teller (BET) specific surface area of samples was determined at liquid-nitrogen temperature (77 K) on a Micromeritcs ASAP 2020 system. The total pore volumes were calculated based on N_2 adsorption at a relative pressure of 0.99. Pore-size distributions were calculated from the adsorption branch of the isotherm, according to the Barrett–Joyner–Halenda (BJH) model [25]. In addition, X-ray photoelectron spectroscopy (XPS) was measured on a Kratos Axis Ultra spectrometer using Al Kα radiation (15 kV, 150 W). The survey spectra were recorded from 0 to 1200 eV at an energy interval of 1 eV/step. The C1s peak at 284.8 eV was used to calibrate the binding energies in XPS spectra. The optical properties of the samples were characterized by UV–vis diffuse reflectance spectroscopy (DRS) using a UV–vis spectrophotometer (Cary 500, Varian Co.), in which $BaSO_4$ was used as the internal reflectance standard.

2.4. Adsorption and photocatalysis of TiO_2/diatomite composites

The adsorption and photocatalytic degradation of RhB were evaluated through a kinetic test. Aliquots were withdrawn from 100 ml of standard RhB aqueous solution (10 mg/L) containing 0.05 g of catalyst (P25 or as-prepared composites). Firstly, the suspensions were stirred in the dark for 1 h to evaluate the adsorption performance. After establishing the equilibrium of adsorption, UV light irradiation was turned on. The photocatalytic reactions were carried out under UV-light irradiation afforded by a 250 W Hg lamp. All the collected samples of RhB solution were analyzed by UV–vis spectrophotometer (UV-9000S, Shanghai Yuanxi). The absorbance was measured at 562 nm. The percentage of RhB degradation (D_R) was calculated by the following equation: