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Enhanced photocatalytic activity of TiO_2/zeolite composite for abatement of pollutants

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ABSTRACT

The TiO_2/zeolite composite was synthesized through a hydrolysis deposition method combined with a calcination crystallization process. The composites were characterized by XRD, N_2 adsorption-desorption, SEM, TEM, XPS and UV-vis DRS. The effect of acid leaching on the physicochemical property, adsorption capacity and photocatalytic performance of the TiO_2/zeolite was analyzed. The characterization results revealed that well-dispersed anatase TiO_2 nanoparticles were loaded on the surface of acid leaching zeolite. The photoactivities of composites were examined by degrading gaseous (formaldehyde) and aqueous (phenol, methyl orange and rhodamine B) organic pollutants. The results indicated that TiO_2/acid leaching zeolite composite had the strong photoactivity than TiO_2/natural zeolite composite. The enhanced photoactivity can be attributed to the higher surface area and more surface hydroxyl groups. The excellent activity reveals that TiO_2/zeolite composite is a promising photocatalyst in pollutants degradation.

1. Introduction

Nowadays, environmental pollution has gained increased research attention. Organic pollutants in water, such as dyes, antibiotics, polycyclic aromatic hydrocarbons and phenols, have complicated compositions and hazardous nature resulting in degradation-resistant [1–4]. Formaldehyde, methylbenzene, benzene and other indoor air pollutants are toxic to human health [5–8]. Feasible ways should be employed to eliminate these pollutants. As an environmental purification method photocatalysis gets increasingly attentions over the past three decades [9–12]. Various photocatalysts such as g-C_3N_4 [13], ZnO [14], WO_3 [15] and Bi-based photocatalysts (BiOCl, BiOBr, Bi_2O_3 et al.) [16] have been reported. Methods including elemental doping [17–20], noble metal deposition [21], coupled semiconductors [22,23] and sensitization [24] have been used to enhance the photocatalytic activity of photocatalyst. Among the photocatalysts titanium dioxide is an attractive semiconductor photocatalyst because of its unique properties such as strong oxidation ability, easy preparation and low cost [25–28]. However, the widespread use of TiO_2 has been restricted because of its some drawbacks including low adsorption capacity, high aggregation tendency and hard reclamation [29,30]. Therefore, many studies have focused on supporting TiO_2 nanoparticles on certain matrix [31,32]. Activated carbon [32,33], molecular sieve [34,35], glass [36], graphene [37,38] and minerals [18,39] have been used as supports of TiO_2. Support serves as adsorbent to enrich the pollutants and then accelerate the photocatalytic rate [40,41]. Furthermore, the dispersion effect of support can inhibit the growth of crystallite sizes of TiO_2 [42]. In some particular cases, support such as graphene can even promote the separating and transferring electron-hole pairs [43,44].

Natural minerals such as montmorillonite [45–47], kaolinite [48,49], diatomite [19,50,51] and zeolite [52,53] had been used for preparing adsorption-photocatalyst composite function materials frequently. The photocatalytic performances of these composites have been investigated intensively. Usually, zeolite has numerous advantages, for instance, high surface area, chemical and thermal stability [54–56]. Therefore, some researches had focused on preparing TiO_2-zeolite composite [57]. Guesh et al. [29] removed the surface Al atoms of zeolite Y using ammonium acetate and ammonium fluoride to endow the zeolite the higher adsorption capacity and lower electron-hole recombination rate, and then enhanced photocatalytic activity. Kuwahara et al. [28] concluded that high hydrophobicity of zeolite can promote the photocatalytic activity of the TiO_2-zeolite photocatalyst. Jansson et al. [58] prepared TiO_2-zeolite composites using five kinds of zeolites. The

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results indicated that the zeolite type and the Si/Al ratio had important influence on the photocatalytic performance of TiO_2-zeolite composites. In a previous study [59], we studied the effect of calcination temperature on the structure, adsorption and photocatalytic property of TiO_2-zeolite composite. The composite calcined at 500 °C exhibited the highest removal efficiency for Cr (VI). However, the natural zeolite has lower surface area and pore volume, which is not beneficial to increase the adsorption and photocatalytic activity substantially. To our knowledge, most of the researches support TiO_2 using the artificial zeolites such as HZSM-11 [60], ZSM-5 [61], zeolite-4A [62] and Y-zeolite [63]. However, fewer papers reported the natural zeolite support TiO_2 nanoparticles. As far as we know, the photodegradation of formaldehyde by the natural zeolite supported TiO_2 composite has not been reported. Meanwhile, the acid leaching natural zeolite supported TiO_2 has not been used in photocatalytic degradation process. Therefore, we prepared TiO_2/zeolite composite with enhanced photocatalytic activity for efficient removal of pollutants such as formaldehyde and rhodamine B.

In the present research, the nano-TiO_2/zeolite composites were prepared using natural zeolite and acid leaching zeolite as supports. The physicochemical properties of the composites were examined by various characterization techniques. The adsorption and photocatalytic performances of TiO_2/acid leaching zeolite were compared with that of TiO_2/zeolite.

2. Experimental

2.1. Photocatalyst preparation

The natural zeolite (Guangxi, China) was used as support for this study. The acid leaching zeolite was pretreated with 50 wt.% sulfuric acid at 95 °C for 2 h according to liquid-solid ratio of 5:1. All chemicals were analytical grade and deionized water was used throughout this study. The main chemical compositions of zeolite and acid leaching zeolite are listed in Table 1. The nano-TiO_2/zeolite composite was prepared as follows. Firstly, 10 g of zeolite powders were mixed with 200 mL of deionized water and 0.5 mL of sulfuric acid under constant stirring. Subsequently, 56.3 mL of titanyl sulfate solution (1 M) were dropwise into the above suspension followed by adjusting the pH to 4.5 using ammonia solution (7.8 wt.%). The white precipitates were filtrated and washed with distilled water, and then dried at 105 °C for 8 h. Finally, the dried powders were calcined at 650 °C for 2 h. The TiO_2 loading amount was 45 wt.% (the mass ratio of TiO_2 to zeolite). The TiO_2/zeolite and TiO_2/acid leaching zeolite were labeled as TiO_2/ZE and TiO_2/AL-ZE, respectively. Pure TiO_2 was prepared through the same method except that zeolite was not added.

2.2. Characterization

The XRD patterns were recorded on a D8 ADVANCE X-ray diffractometer (Bruker) using Cu Kα radiation (40 kV, 40 mA, step size = 0.02°). Specific surface area, pore volume, and average pore diameter were determined by nitrogen adsorption-desorption using nitrogen adsorption apparatus (JW-BK). SEM images were collected by SU8010 field-emission scanning electron microscopy (Hitachi). TEM and HRTEM images were collected by Tecnai G2 F20 transmission electron microscopy (FEI). X-ray photoelectron spectra were recorded on Thermo Escalab 250Xi spectrometer (Thermo) using amonochromatic Al Kα X-ray source. The C 1s (284.8 eV) was used to calibrate the binding energy scale. UV-vis absorption spectroscopy was conducted on a UV9000S UV-vis spectrophotometer (Metash) using an integrating sphere accessory. The zeta potential of the sample was determined by Malvern zetasizer (Nano ZS90).

Table 1
Main chemical compositions of zeolite and acid leaching zeolite (wt.%).

Sample	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	L.O.I.
Zeolite	59.37	11.89	10.11	0.34	0.09	17.14
Acid leaching zeolite	84.61	2.21	0.41	0.17	0.07	10.34

2.3. Photocatalytic activity

The photocatalytic degradation rates for liquid pollutants (RhB, MO and phenol) were evaluated in a photocatalytic reactor (PL-02, Beijing PLSS Ltd. China). Firstly, the suspensions containing 0.1 g of catalysts and 100 mL of pollutants (10 mg/L) were stirred for 60 min under the dark condition. After irradiating with mercury lamp (300 W) for certain period of time the suspensions were collected. The collected solutions were analyzed by measuring the absorbance changes at 554 nm (RhB), 464 nm (MO) or 270 nm (phenol) on an UV-vis spectrophotometer. The degradation efficiency was calculated by the change of absorbance. The photocatalytic degradation for gaseous pollutant (formaldehyde) was conducted on a 250 L photoreactor (PFD-5060, Hunan Huasi Intrument Co. Ltd. China). The UV lamps (365 nm, 40 W) were used as the light source. The glass plate covered by 1.0 g of catalysts was put under UV lamps. The illumination time was 90 min. Formaldehyde solution was injected into the heating unit to make it easy to volatilize. Electric fan was used for circulating the formaldehyde gas. The concentration of HCHO was measured according to the spectrophotometric method (China National Standard GB/T 18204.26–2000) [31].

3. Results and discussion

3.1. Characterization of the photocatalysts

The XRD patterns of the samples are shown Fig. 1. The XRD pattern of ZE exhibits peaks at 9.8°, 19.0°, 21.9°, 29.5°, 32.3°, which are characteristic of stellerite (JCPDS 25–0124) [59], A bit of quartz can be found in the pattern. The AL-ZE treated by acid shows peaks matched to quartz. It means that the structure of stellerite was destroyed during the pretreatment process. No other peaks were observed, confirming the high purity of the AL-ZE. It can also be

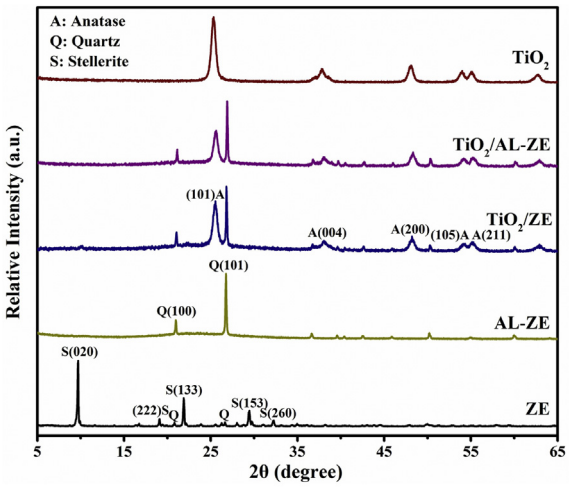

Fig. 1. XRD patterns of the samples.