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Influence of calcination temperature on the structural, adsorption and photocatalytic properties of TiO_2 nanoparticles supported on natural zeolite

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ABSTRACT

TiO_2 nanoparticles supported on natural zeolite (TI-ZE) are prepared via a simple hydrolysis of $TiCl_4$ and then calcined at various temperatures. The as-prepared catalysts were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller analysis (BET), scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDS) and transmission electron microscopy (TEM). The adsorption and photocatalysis ability was evaluated towards Cr (VI) in dark or under UV light. The XRD analysis showed that the increasing temperature destroyed the original framework structure of zeolite (over 500 °C) and the anatase TiO_2 formed at 500 °C. It was found that the calcination temperature influenced the adsorption behavior and photocatalytic activity. The sample calcined at 300 °C presented the optimum adsorption performance because of its highest specific surface area, and the adsorption process followed pseudo-second-order kinetic. The maximum adsorption capacity of different samples has been calculated based on the Langmuir model. The kinetics for the photodegradation of Cr (VI) has been determined in terms of Langmuir–Hinshelwood model. The photocatalysis test indicated that the TI-ZE calcined at 500 °C remained the original zeolite structures and possessed the highest removal ratio because of its relatively larger adsorption capacity and better crystallinity of TiO_2. Furthermore, the removal efficiency of TI-ZE-5 towards Cr (VI) was still more than 75% after five times cycling, which confirms the durability of TiO_2/zeolite catalyst.

1. Introduction

Titanium dioxide has been broadly studied as a promising photocatalytic material for solving environmental problems because of its high efficiency, non-toxicity and chemical stable properties [1–3]. Under UV light, electron–hole pairs with strong redox will be generated on the surface of TiO_2 [4]. Common organic pollutants, such as phenol [5], formaldehyde [6] and dyes [7] can be mineralized into CO_2 and H_2O. Moreover, heavy metal ions, such as Hg [8], Cd [9], Cr [10] and Cu [11], can be degraded into low or none toxic state for environmental purification. To improve the photocatalytic activity, TiO_2 is usually expected to be made into nano-size power. However, pure TiO_2 nanoparticles are easy to agglomerate into secondary particles in practical applications due to their large specific surface area and high surface free energy [12]. On the other hand, the pure TiO_2 nanoparticles are difficult to be recycled during their practical application. Therefore, it has proposed to immobilize TiO_2 nanoparticles on a carrier to overcome shortcomings before mentioned.

Recent years have witnessed a growing interest in using the porous natural mineral to support TiO_2 nanoparticles. Many studies have focused on the research of fixing TiO_2 on diatomite [13], montmorillonite [14], silica [15], zeolite [16], kaolinite [17] and other carriers. It has been convinced that the porous structure, morphology, specific surface area and surface charge of supports could significantly influence the adsorption and catalytic abilities of catalysts [18,19]. Among various supporting materials, zeolite is considered as a promising porous catalyst support due to its unique pores, super adsorption capability and special ion-exchange ability [20,21]. In previous reports, various types of synthetic zeolites such as Y-zeolite [22], 5A zeolite [23] and HZSM-11 [24] have been investigated to be used as TiO_2 supporter. Stellerite is one kind of microporous aluminosilicate minerals among the natural zeolite group, which has high adsorption and ion exchange properties. Compared with synthesized zeolite, natural stellerite has many advantages including abundance, low cost and easily available. In addition, it should be pointed out that the previous studies mainly investigated the effect of calculation temperature on the morphology and microstructure of natural stellerite zeolite and catalysis of TiO_2 separately [25,26]. However, to the best of our knowledge, no attention was paid to the natural stellerite combined with TiO_2.

Cr (VI) is one of common heavy metals in wastewater originated from the effluents of electroplating, mining, metallurgy and tannery industries [27]. It has been listed as a priority pollutant by many countries because of highly toxic causing carcinogenic, mutagenic and

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teratogenic [28,29]. Conventional technologies, such as precipitation, ion exchange, biological treatment and chemical reduction for the removal of Cr (VI), have found limited applications because of their relatively high cost and the production of secondary pollution [30]. TiO_2-based heterogeneous photocatalysis which can reduce Cr (VI) to a less harmful state Cr (III) has considered as a green-chemistry process [31]. Nevertheless, the photocatalytic removal of Cr (VI) pollutants by TiO_2/zeolite composite was rare reported. Hence, the objective of the present work is to determine the effect of calcination temperature on the structural properties of natural stellerite and TiO_2 nanoparticles by evaluating the activity of photocatalytic reduction Cr (VI) in aqueous.

In this study, TiO_2 nanoparticles with anatase phase supported on natural zeolite are synthesized via a simple and cost-effective hydrolysis method of $TiCl_4$. After calcination, the as-prepared samples have high specific surface area, abundant pores and good crystallinity of anatase TiO_2. Then, XRD, BET, SEM-EDS and TEM were employed to characterize the composition and structure of as-prepared catalysts. Finally, the adsorption and photocatalytic reduction behavior of Cr (VI) in aqueous by TiO_2/zeolite composite was investigated.

2. Experimental

2.1. Materials and reagents

Natural zeolite (labeled as ZE) with phase composition of stellerite 93.1% and quartz 6.9% was obtained from Guangxi province, China. The chemical content of the zeolite has been given in Table 1. $TiCl_4$, HCl, $K_2Cr_2O_7$ and other reagents used in this work are analytical grade. All chemicals were used as received.

2.2. Preparation of TiO_2/zeolite

TiO_2 nanoparticles supported on natural stellerite (TI-ZE) are prepared according to previous research from our research group [32,33]. Typically, 2.0 ml HCl and 10.0 g zeolite were added into 300 ml distilled water under stirring. Then, a certain amount of 0.455 mol/L $TiCl_4$ solution (the theoretical TiO_2 loading amount is 30 wt.%) was added dropwise into the suspension, and $NH_3 \cdot H_2O$ was used to adjust pH value to 6 for the hydrolysis precipitation reaction at 40 °C for 1 h. In the following step, the white suspension was separated and washed for several times and dried at in an oven at 105 °C for 10 h. The as-prepared samples were obtained by calcination for 2 h with a ramp rate of 10 °C/min. The TI-ZE calcined at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C were denoted as TI-ZE-3, TI-ZE-4, TI-ZE-5, TI-ZE-6 and TI-ZE-7, respectively.

2.3. Characterization

The crystalline phases of obtained samples were analyzed by XRD using a Bruker D8 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å) in the range of $2\theta = 5$–80°. The specific surface area of the samples was determined by nitrogen adsorption-desorption isotherms on a surface area analyzer (BET, JW-BK, Jingwei). The scanning electron microscopy was recorded on a field emission gun-scanning electron microscope (SEM, S-4800 Hitachi, Japan) with an energy dispersive spectrometer for microanalysis. Transmission electron microscopic (TEM) images were obtained with a JEM-1200EX (JEOL, Japan) electron microscope. The removal effect of Cr (VI) was monitored by a UV–visible spectrophotometer (UV-9000, Shanghai Metash).

Table 1
Chemical composition of natural zeolite.

Composition	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	L.O.I.[a]
wt.%	59.37	11.89	10.11	0.34	0.12	0.09	0.09	17.14

[a] Loss on ignition.

2.4. Dark adsorption, photocatalysis and recycling test

A series of batch experiments on the adsorption of Cr (VI) were carried out with various as-prepared samples in the dark. In a typical run, 100 ml of 25 mg/L Cr (VI) aqueous solution was mixed with 0.2 g samples. The experiments were performed at room temperature (25 °C) and the TI-ZE particles were kept suspended using a magnetic stirrer. At certain time intervals, 3 ml of taken samples were centrifuged and filtered by a 0.45 μm membrane filter in order to separate the particles from the solution. The concentration of filtrate was analyzed for adsorption kinetic studies. To determine the adsorption isotherm of Cr (VI), 0.2 g of various calcined samples and 100 ml of Cr (VI) solution were mixed together. Initial Cr (VI) concentration varying from 2 mg/L to 25 mg/L was used to obtain the equilibrium adsorption capacity of composites at 25 °C. After reaching adsorption equilibrium, the resulting suspension was separated by centrifuge and the supernatant was collected for subsequent analysis.

Photocatalytic experiments were carried out in a BL-GHX-V photochemistry system equipped with a high-pressure Hg lamp (500 W). There were eight of 150 ml cylindrical quartz reactors around the irradiation light. In each experiment, 100 ml of 25 mg/L Cr (VI) solution and 0.2 g catalyst were added into each of cylindrical quartz reactor and stirred by a magnetic stirrer. At a defined time interval, 3 ml solution was collected, centrifuged and filtered by a 0.45 μm membrane filter to remove catalyst powders. Afterward, the filtrates were analyzed. To compare the photocatalytic removal activity, the blank test without catalyst was carried out.

To investigate durability of the TiO_2/zeolite catalyst, the catalyst was filtered, washed and dried at 105 °C. The reused study of catalyst carried out under identical conditions as in the above photocatalytic experiments. For comparison, the reuse steps were repeated five cycles.

The stock solution (1000 mg/L) was prepared by dissolving $K_2Cr_2O_7$ in distilled water, and diluted to the concentration of the working solution (2–25 mg/L). All initial pH of Cr (VI) reaction solution for each experiment was adjusted by HCl and NaOH to maintain the same of 2.0 and monitored by a pH-meter (FE20, Mettler-Toledo Instruments Co., Ltd.). The Cr (VI) concentration was determined at 540 nm by 1, 5-diphenylcarbazide colorimetric method using the spectrophotometer.

The adsorption qualities of Cr (VI) at time t, q_t (mg/g), are calculated according to Eq. (1):

$$q_t = \frac{(C_0 - C_t)V_0}{w} \tag{1}$$

where C_0 and C_t are the initial concentrations and at time t of Cr (VI) solution (mg/L), respectively; V_0 is the volume of aqueous Cr (VI) solution (L); and w is the mass of samples (g).

The removal efficiency (η) of adsorption and photocatalysis was calculated according to Eq. (2):

$$\eta(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{2}$$

where C_0 and C_t are the initial concentrations and at time t of Cr (VI) solution (mg/L), respectively.

3. Result and discussion

3.1. XRD analysis

The XRD patterns of ZE and TI-ZE calcined at different temperatures were investigated and shown in Fig. 1. The diffraction peaks of stellerite and quartz with high crystallinity were observed in raw zeolite and these peaks were found to be in good agreement with the standard XRD patterns of stellerite (JCPDS: 25-0124) and quartz (JCPDS: 78-1252). It can be observed that the peak intensity of stellerite decreased