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Preparation and characterization of V-TiO_2 /fly-ash cenospheres and its photocatalytic properties

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V-TiO_2 /fly-ash cenospheres were successfully synthesized by sol-gel method. The V-TiO_2 /fly-ash catalyst was found to be mainly preserved its anatase phase after calcination at 500°C. The XRD pattern shows the characteristic peaks of TiO_2 anatase phase and the diffraction peaks of SiO_2, Fe_2O_3 and Al_2O_3 disappeared or weakened. Further, there are no obvious peaks of vanadium oxides (V_2O_5 and V_2O_4). From SEM images, there are some 200-300 μm-sized spheric particles covered by V-TiO_2 film. The V-TiO_2 layer is nonuniform and the discontinuous deposits are inhomogeneous with islands being observed on the surface. The XPS analysis indicates that $V^{4+}$and V^{5+} either substitute Ti^{4+} site or embed in the TiO_2 structure. In addition, the UV-Vis spectra reveals the shift of the optical absorption towards the red light zone and this shift depends on the vanadium content in the compound catalyst. The photocatalytic activity was evaluated by the degradation of direct fast scarlet 4BS under UV light irradiation. The degradation rate of V-TiO_2 /fly-ash was higher than that of TiO_2 /fly-ash, which reached up to 98.7% after UV irradiation for 90min. Therefore, the prepared V-TiO_2 /fly-ash possesses better photocatalytic properties.

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1. Introduction

Azo dyes, which cause high concentration of dissolved organic matter and in deep colour, constitute the largest group of colorants used in industry. Traditional treatment methods of wastewater containing dyes including chemical, physical and biological approaches have their respective limitations such as not economically feasibility, non-destruction and not efficiency [1-3]. TiO_2 photocatalytic degradation appears to be one of the most promising and suitable technique due to its superior properties, such as stability, low cost and non-toxicity [4-7]. Recently, modification of TiO_2 has been extensively studied to overcome the shortcomings of pure TiO_2 which has wide energy band gap and low quantum yields, as well as hard recycling [8-10]. Transition metal ions including Ag, Fe, V and Co are deposited onto the surface of titania to lower the band gap [11-14]. Among these elements, V is easy to enter into the lattice of TiO_2 crystal and can contribute to further red-shift in UV-Vis spectroscopy [13-15]. Meanwhile, supports such as activated carbon, silica, clays and stainless steel are used to increase the efficiency and immobility of the catalysts [16-19]. With advantages of unique hollow structure, light mass and high surface area [20-21], fly-ash cenospheres are applied here to support V-TiO_2 in order to enhance photocatalytic activity.

In this work, the V-TiO_2 /fly-ash (V-TiO_2/FA) cenospheres were synthesized by sol-gel method and the direct fast scarlet 4BS was selected as model pollutant for study. The experiments aim at characterizing the structure and morphology of V-TiO_2 /FA catalyst and exploring its photocatalytic properties.

2. Experimental

2.1. Materials

Raw fly ash was obtained from the second thermal power plant, Changchun. The fly ash samples are mainly composed of water stable compounds (SiO_2, Al_2O_3, Fe_2O_3, MgO, TiO_2), highly soluble water compounds (K_2O, Na_2O, etc.), and compounds with limited water solubility (CaO, $MeBO_3$, etc.) Thereinto, the sum of the SiO_2, Al_2O_3 and Fe_2O_3 is above 70%. After water floatation, the received cenospheres were washed in distilled water, by stirring at room temperature for 12 h, to remove the soluble compounds. Then the particles were dried and sieved through 100 meshes for preparation of V-TiO_2/FA cenospheres.

All the major chemicals included tetrabutyl titanate ($Ti(OC_4H_9)_4$), ethanol (C_2H_6O, >99.7%), acetic acid ($C_2H_4O_2$), ammonium metavanadate(NH_4VO_3) and direct fast scarlet 4BS (Direct Red 23, C.I. 29160), while deionized water was used for all the experiments.

2.2. Preparation of V-TiO_2/fly-ash photocatalyst

The V-TiO_2/FA cenospheres were synthesized via sol-gel method. Initially, appropriate amount of $Ti(OC_4H_9)_4$ was mixed with ethanol under constant stirring for 30 min. Next, the acetic acid and ethanol were added with an amount of NH_4VO_3 (1wt%, 2wt% 3wt% of the V-TiO_2, respectively), then the mixture solution was added dropwise to the above solution. Finally, 2g purified fly ash cenosphers were added into the sol as carrier, followed by stirring for 30 min. The formed gel was remained motionlessly for 24h. After dried at 140°C for 5 h, the prepared composites were calcined at 500°C for 2 h. The catalysts prepared by this procedure were assigned V-TiO_2/FA.

2.3. Characterization

The crystalline structure of the catalyst components was evaluated by X-ray diffraction (XRD). Herein, XRD patterns were obtained with a D/max-RA X-ray diffractometer (Aolong, China) equipped with Ni-filtrated Cu Kα radiation (40 kV, 20 mA). The constituents, morphology and size of particles were determined by scanning electron microscopy (SEM)-S4800 (Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS) (Shimadzu, Japan). Diffuse reflectance spectroscopy was carried out with UV-3600(Shimadzu, Japan) spectrometer.

2.4 Measurement of photocatalytic activity

Photocatalytic activities of the as-prepared photocatalysts were evaluated by the degradation of azo dye direct scarlet 4BS aqueous solution under ultraviolet light irradiation (500w) (Yaming, Shanghai). UVmini-1240(Shimadzu, Japan) and UV721 (Shanghai, China) spectrometer were used to inspect the decolorization process of direct scarlet 4BS solution. Colour removal, based on A505 (the absorption at the wavelength of 505 nm) measurement, is calculated using the following equation:

$$\text{Degradation (\%)} = (A_0 - A) / A_0 \times 100 \qquad (1)$$

In which A_0 is the initial absorbance of direct scarlet 4BS and A is the absorbance after the treatments.

3. Results and discussion

3.1 XRD analysis

Fig. 1 shows XRD patterns of the fly-ash cenospheres. The diffraction peaks of SiO_2, Fe_2O_3 and Al_2O_3 are clearly seen because the main components of fly-ash cenospheres are siliceous oxide, ferreous oxide and aluminous oxide [22]. The fly-ash cenospheres, being used as catalyst carrier, are now showing more and more benefits because of their many advantages, such as good thermal and chemical stabilities, ability to fulfill the recovery and utilization of catalyst. From the XRD patterns of V-TiO_2/FA cenospheres, we can see that the characteristic peaks of TiO_2 anatase phase at 2θ of 25.3°, 37.7°, 25.3°, 48°, 53.9° and 55° can be indexed, and the diffraction peaks of SiO_2, Fe_2O_3 and Al_2O_3 disappeared or weakened. It indicates that the fly-ash cenospheres are coated by V-TiO_2 films. No characteristic peaks of vanadium oxides (V_2O_5 and V_2O_4) are found in the XRD patterns implying either vanadium is incorporated in the crystalline of TiO_2, or vanadium oxide is very small and highly dispersed. It is reported that the existing of V^{5+} deposited in TiO_2 formed substitutional doping and induced microstress in the anatase structure which retards the TiO_2 crystallite growth [15].

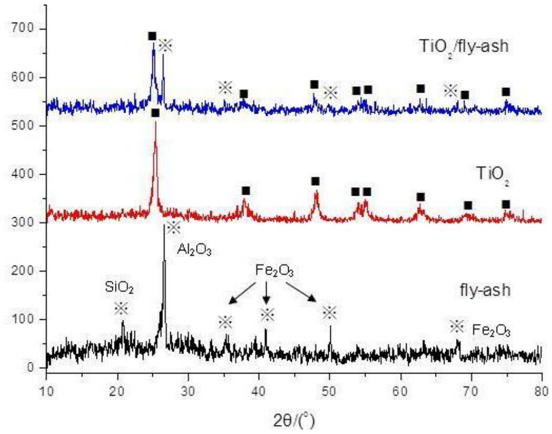

Fig. 1. XRD patterns of the V-TiO_2/ fly-ash cenospheres.

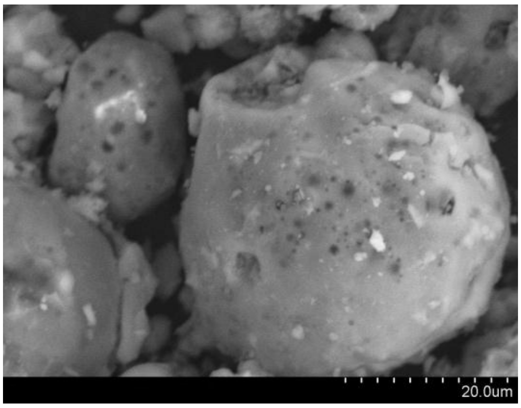

Fig. 2. SEM image of the V-TiO_2/fly-ash cenospheres.

3.2 SEM analysis

Fig. 2 is the SEM image of V-TiO_2/FA cenospheres. It can be seen that there are some 200-300 μm-sized spheric particles. The surface of these particles which seemed crude is covered by V-TiO_2 film. The V-TiO_2 layer is nonuniform and the discontinuous deposits are inhomogeneous with islands being observed on the surface, which reveals that doping of V^{5+} leads to the roughness of surface owing to the shrinkage in the gelling and calcination process. The micropores in the thin film increase the surface area of the catalyst and make it easier to contact with aqueous solution, which generate more surface hydroxyl and radical groups.

3.3 XPS analysis

The XPS analysis illustrates that the sample constituents include Ti, O, V, C and Si, shown in Fig. 3. Thereinto the O 1s peak centeres on 529.6 eV and 532.08 eV respectively which correspond to the Ti-O in the TiO_2 with an anatase phase structure and Ti-OH respectively; meanwhile the peak centered on 103.0 eV corresponds to the Si in SiO_2. The Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks centere on 458.9eV and 464.6 eV respectively which belong to the anatase TiO_2. The peak appears in 516.7 eV is attributed to $V^{5+}2p_{3/2}$ or $V^{4+}2p_{3/2}$. The binding energy of V^{5+} $2p_{3/2}$ is 516.4~517.4 eV which is closed to that of V^{4+}(515.4~515.7 eV), so both signals are easy to overlap [15].

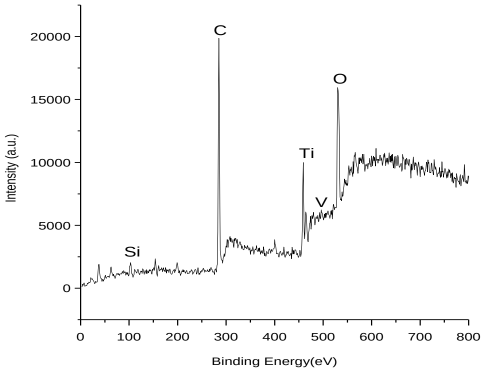

Fig. 3. Spectrum of the V-TiO_2/fly-ash cenospheres.

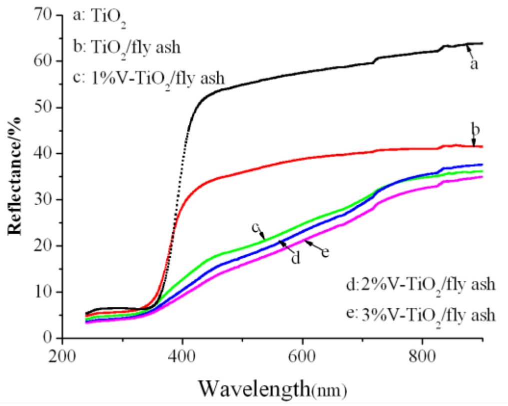

Fig. 4. UV-Vis spectra of TiO_2, TiO_2/FA and V-TiO_2/ fly-ash composites.

3.4 UV-Vis analysis

Fig. 4 shows the UV-visible spectra of different samples. It shows the shift of the optical absorption towards the red light zone and this shift depends on the vanadium content in the compound catalyst. Meanwhile, the 3%V-TiO_2/FA sample expresses the biggest shift. Visible absorption shift in these catalysts is indicative of the excitation of a 3d electron from a V^{4+} center into the TiO_2 conduction band [23]. It is believed that this photoexcited electron enables chemical reactions to occur at the surface of the V-doped catalysts in the presence of visible light because the oxidation of V^{4+} to V^{5+} occurs 2.1 eV below the TiO_2 conduction band [23].

3.5 Photocatalytic activity

The 0.80g catalyst was added to 100ml 50mg/L direct scarlet 4BS solution to investigate the photocatalytic performances of as-prepared TiO_2/FA and V-TiO_2/FA composites under the UV light irradiation. First, the adsorption capacity of the TiO_2/FA and V-TiO_2/FA to direct scarlet 4BS molecules was studied at neutral conditions (pH 6.2) with aeration in the reaction system. From the results shown in Fig. 5, it is found that after the composites were dispersed into the aqueous direct scarlet 4BS solution for 30 min in dark, about 16% decrement of direct scarlet 4BS concentrations occurred. Hereafter, the absorbency was determined at 15 min interval. After UV irradiation for 90min, the photocatalytic degradation rate of V-TiO_2/FA and TiO_2/FA on direct scarlet 4BS reached up to 98.7% and 95.3% respectively. The photocatalyticde gradation effect of V-TiO_2/FA was better than that of TiO_2/FA. Therefore, V-doped TiO_2, as modifier, could enhance the photocatalytic activity.

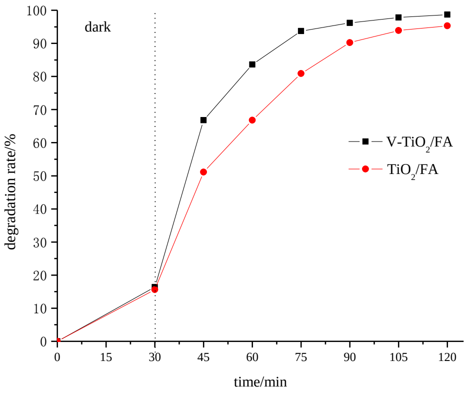

Fig.5. Photocatalytic degradation rate of TiO_2/fly-ash and V-TiO_2/fly-ash cenospheres.

4. Conclusion

The V-TiO_2/FA photocatalyst that is active under UV irradiation has been synthesized using simple sol-gel method. It is concluded that under UV irradiation excited vanadium centers donate an electron to the TiO_2 conduction band, which allows the oxidation of surface adsorbed molecules. The photocatalytic activity of V-TiO_2/FA is increased in comparison with the TiO_2/FA catalyst on direct scarlet 4BS, which reached up to 98.7% after UV irradiation for 90min. Meanwhile, the V-TiO_2/FA catalyst reuse was carried out under the mentioned optimum photocatalytic condition. Its degradation rates of four reuse cycles were 88.5%, 81.8%, 73.9% and 66.5% respectively. These studies reveled that V-TiO_2/FA demonstrated good stability after recovery and that catalyst reuse is effective. Therefore, the prepared catalysts exhibit higher photocatalytic activity and adsorptivity for the decomposition of direct scarlet 4BS and can be easily separated from waste water after reaction.

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