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(Zn, Fe)-Doped Palygorskite Loaded TiO_2 for Visible-Light Active Catalysts†

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Chinese palygorskite doped with zinc and iron loaded TiO_2 was applied as a support for the visible-light active catalyst (ZFPT). The catalyst was prepared by the method of liquid ion exchange and simultaneous precipitation. This new material extends the spectral response from UV to the visible region and exhibit improved photocatalytic activities for methylene blue reduction in aqueous suspension under visible and UV light over the pure palygorskite, P-25 and palygorskite loaded TiO_2.

Key Words: Palygorskite, Visible-light, Catalysts, TiO_2.

INTRODUCTION

Mesoporous materials with tunable pore structure and tailored framework composition are of great interest for broad applications ranging from adsorbent materials, separations, catalysis, energy storage and biological conversions. Palygorskite clay, a species of hydrated magnesium aluminum silicate mineral $[(H_2O)_4(Mg,Al,Fe)_5(OH)_2Si_8O_{20}\cdot 4H_2O]$ with commonly a lath or fibrous morphology, are characterized by a porous crystalline structure containing tetrahedral layers alloyed together along longitudinal sideline chains[1,2]. Nowadays, photocatalytic processes have received special attention because they can make use of abundant solar energy to transform the organic and inorganic polutants' molecules into the redox reaction in water or air. Titanium dioxide is the most widely used semiconductor oxide because of its suitable flat band gap and chemical stability. However, it only absorbs the UV region of the solar spectrum which is about 4 % of the incoming solar energy. Therefore, some attempts have been directed to extend the absorption of TiO_2 the visible part of the spectrum by researchers[3]. They have tried to shift the E_g towards the visible light region by adding transition metal oxides such as CuO, CdO, ZnO, the Al_2O_3 and some metal cations such as Yb^{3+}, Er^{3+}, Ge^{3+}, In^{3+} [4]. In this way, the beneficial effects of the Zn-doping of TiO_2 catalysts has already been reported in water treatment. Herein, we report a novel class of (Zn, Fe)-doped palygorskite loading TiO_2 (ZFPT) nanocomposite catalysts sythesized by a simple impregnation oxygen in absence of any co-reductants exhibits higher photocatalytic activities for the reduction of methylene blue in aqueous suspension than commercial photocatalyst P25 and pure palygorskite loaded TiO_2.

EXPERIMENTAL

The clay used in this work was the palygorskite obtained from Mingguang (Anhui, China), supplied by Mingguang attapulgite Co. Ltd., purified by dispersion-decantation of the < 2 μm fraction. The preparation and characterization of the refined palygorskite clay has also been described by Zhao *et al.*[5]. 5 g palygorskite powder was mixed in distilled water with the weight proportion 1:100, 20 mL 0.1 mol/L $ZnCl_2$ and 20 mL 0.1 mol/L $FeCl_3$ (A.R., Beijing BeiHua Fine Chemical Co. Ltd. China) solution were then dripped down into the palygorkite water slurry quickly with strong stirring at *ca.* 30 ºC, keeping stirring for 4 h, the precipitation was then filtered, washed and passed through 100 mesh sieve to get the product which refered to as (Zn,Fe)-doped palygorskite (ZFP). 1 mL $TiCl_4$ was diluted with 500 mL HCl solution, A certain amount of ZFP powder was put into the $TiCl_4$ solution of just the quantum, then treated with ultrasonic wave, aqueous ammonia solution dripped down slowly into the mixture with strong stirring, keeping stirring not stopping until the pH = 7, the precipitation was filtered and washed until no Cl^- existed by checking with 0.1 mol/L $AgNO_3$ solution. The remainder was heat treated for 2 h at 450 ºC. Then passed through 200 mesh sieve to get the final product, the corresponding product is referred to as ZFPT. To compare, the palygorskite loaded TiO_2 and the palygorskite doped Zn^{2+} loaded TiO_2 catalysts

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were prepared by the same method which refered to as palygorskite loaded TiO_2 (PT) and zinc-doped palygorskite loaded TiO_2 (ZPT) respectively.

The visible-light absorption activity was analyzed by the UV-VIS spectra recorded in a Perkin-Elmer Lambda 20 UV-VIS spectrometer in the spectral window from 800-100 nm. Photocatalytic activity was determined by measuring the decomposition rate of methylene blue (MB) in neutral water solution under the irradiation of an ultra-highpressure mercury lamp (120 w, >360 nm). The lamp was placed above the reaction vessel, 10 cm away from the surface of the test solution in a 100 mL beaker. The initial concentration of MB was 2.0×10^{-5} mol/L and catalyst loading was 1 mg/mL. Vigorous stirring was used to make sure the uniforminity of the solution. After the solution was equilibrated for 0.5 h, 5 mL aliquots were withdrawn at the solution reaction times and centrifuged at 4200 rpm for 20 min. The supernatants were collected for the absorbance messurement by UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Absorption of UV-VIS light: Fig. 1 shows the UV-VIS diffuse reflectance spectra of the pure and variously doped palygorskite samples. Palygorskite loaded TiO_2 displays no significant absorbance in visible light due to its large bandgap of TiO_2 (3.2 eV). Zinc-doped palygorskite loaded TiO_2 shows a spectral response in the visible region (400-700) and the absorbance becomes the explicit stronger with the (Zn, Fe) double doping. The absorption intensity of ZFPT is higher than the other two samples absolutely in the whole wave range from 265-800 nm. The red shift might result from the exsistence of the Zn^{2+}, Fe^{3+} and the highly surface area of the composites.The system could be the active component and the excellent catalytic activity was due to a cooperaration effect between Zn^{2+}, Fe^{3+}, palygorskite and TiO_2.

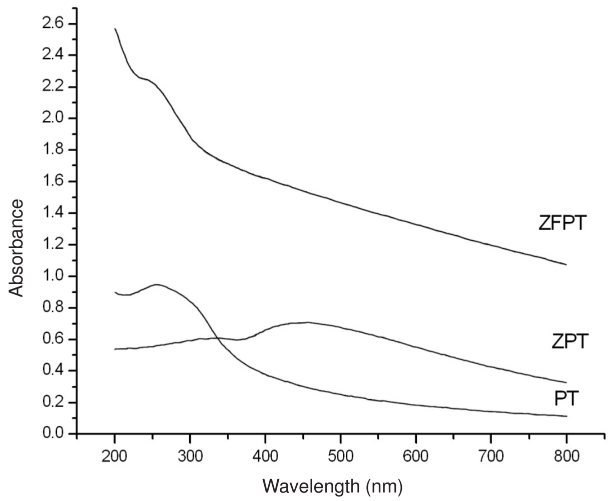

Fig. 1. UV-VIS diffuse reflectance spectra of samples calcined at 400 ºC: (a) palygorskite loaded TiO_2(PT); (b) 1.0 % Zn-doped palygorskite loaded TiO_2(ZPT); (c) 1.0 % Zn and 1.0 % Fe double doped palygorskite loaded TiO_2(ZFPT)

Catalytic activity: The photocatalytic activities of the samples are shown in Fig. 2. Compared to the control experiment, PT and P25 showed a slight photocatalytic activity under the irradiation of the lamp. Zinc-doped palygorskite loaded TiO_2 showed more actice adsorption. The synthesized sample ZFPT showed strong photodegradation activity. More than 84 % methylene blue was decomposed after 3 h reaction.

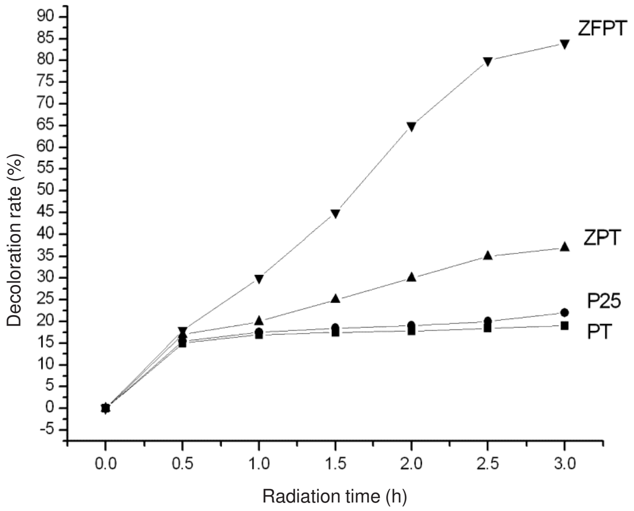

Fig. 2. Decoloration rate curve of the different samples for methylene blue

Conclusion

In summary, titanium oxide photocatalysts were prepared by the method using cation exchange and the method of liquid phase precipitantation. The doped clay absorbed visible light up to 700 nm and rapidly degrading methylene blue by visible light illumination. The results above have indicated that Zn^{2+}, Fe^{3+} and TiO_2 can coexist in palygorskite to extend the photo-absorption and photocatalytic activity of TiO_2 well into the visible regime. The results indicated the ZFPT system could be the active component and the excellent catalytic activity was due to a cooperaration effect between Zn^{2+}, Fe^{3+}, palygorskite and TiO_2.

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