Preparation and characterization of antimony barium composite oxide photocatalysts

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Abstract. In this paper, two kinds of antimony barium composite oxide photocatalysts have been prepared by two methods and characterized by XRD and SEM. The photocatalytic activity was evaluated by a photocatalytic reactor and an ultraviolet spectrophotometer. The results showed that-$BaSb_2O_5 \bullet 4H_2O$, $BaSb_2O_6$ two kinds of antimony barium composite oxide photocatalysts were successfully prepared in this experiment and they showed good photocatalytic properties. In addition, $BaSb_2O_6$ morphology showed more regular, microstructure and better catalytic performance.

1. Introduction

Photocatalytic material has been broadly applied in environmental pollution controlling fields. Developments of new type of photocatalyst are important direction of photocatalystic research. The photocatalytic activity of p zone composite oxides whose d layer fulling of electron is widely attracted interests by the scientists [1], such as indium acid salt (In^{3+}), stannate (Sn^{4+}), antimonate (Sb^{5+}), germanate (Ge^{4+}), gallate (Ga^{3+}). Antimony resources are particularly rich in China. The research, development and utilization of antimony compounds are of great significance.

There are many reports on the study of antimony compounds as photocatalysts. Monteiroa O C etc. [2] prepared antimony complex oxide by self-combustion method and studied its photocatalytic properties; Zuo G L etc. [3] successfully prepared the Sb_2O_3/α-Fe_2O_3 nano heterojunction composite photocatalyst by hydrothermal method and impregnation method; Lamba R etc. [4] synthesized Sb_2O_3-ZnO spindle shape nanocomposites and could degrade methylene blue effectively. Li D Z etc. [5] studied $CaSb_2O_5(OH)_2$ and $Cd_2Sb_2O_{6.8}$, and found their degradation efficiency on benzene contamination were higher than $P_{25}(TiO_2)$; Lin X P etc. [6] prepared MSb_2O_6 (M = Ca, Sr and Ba) by solid-phase method, and observed that photocatalytic effect of $BaSb_2O_6$ was the best through comparation with three antimonites. Chen J etc. [7, 8] synthesized micro-flowers $BaSb_2O_6$ by one-step method and studied their photocatalytic activity.

In this study, antimony barium composite oxides were prepared by hydrothermal method with different antimony sources. The characterization and catalytic properties of the composite were also studied.

2. Experimental section

2.1. Reagents and instruments

All chemicals (Sb_2O_5, $KSb(OH)_6$, $Ba(CH_3COO)_2$, $Ba(NO_3)_2$, NaOH, HCl, methylene blue) were analytical reagent grade and used without further purification; Water used in all experiments was deionized water. Main instruments: KSL-1100X muffle furnace; BL-GHX-V photochemical reaction apparatus; 721 ultraviolet visible spectrophotometer; D8advance X ray diffractometer; Hitachi S-3000N scanning electron microscope (SEM).

2.2. Prepare Sb/Ba oxide composites by using Sb_2O_5 as antimony source

0.005mol of antimony pentoxide was firstly added to some water to form Sb_2O_5 solution, and then potassium hydroxide was added to adjust the pH of above solution to neutral. Then another amount of 0.01mol potassium hydroxide was added, followed by stirring for 10~15min. After that, 0.005mol barium nitrate was added into the system with stirring to make it fully dissolved. Transfer the system into a high pressure reactor at 200 ℃ to carry out the hydrothermal reaction for 4h. Then cooling, and wash the white precipitate from the bottom of the reactor with deionized water for 2-3 times and anhydrous ethanol thoroughly. Finally, the product was dried in an oven at 80℃ for 4h, cooled and collected the outcomes.

2.3. Prepare antimony barium oxide composites with $KSb(OH)_6$ as antimony source

0.32g barium acetate was firstly weighed and dissolved in 10mL deionized water. Then 25 mL, 0.1 mol/L potassium pyroantimonate solution was added dropwise into the system and adjust the pH to 3 by dilute hydrochloric acid. After stirring continuously at room temperature for 12 h, the system was put in a high pressure autoclave and heated in a 200 ° C incubator to hydrothermal react for 4.5 h. Then cooling, and wash the white precipitate from the bottom of the reactor with deionized water for 2-3 times and anhydrous ethanol for 1 time. At last, dry the product in a oven at 60℃ for 4h, then cool, grind and collect the outcomes.

2.4. Photocatalysis experiment

The photocatalytic activity of the samples was evaluated by the methylene blue (MB) decolorization degradation system. Degradation of methylene blue by photocatalyst was carried out in BL-GHX-V photochemical reaction apparatus.

A mixture of methylene blue at a concentration of 14mg/L and 0.05g barium antimonate photocatalyst were added to a quartz tube of the photoreactor. The light source was high pressure UV mercury lamp (500W). Before turning on the light, air was introduced in to start the dark adsorption reaction for 20min, so that the process of the photocatalyst attaching on the methylene blue can reach an adsorption-desorption balance. Then extract a 0min sample as a reference, open the UV lamp, the experiment process should be in a environment with cooling water and air through the whole time, collect samples every 20min, remove the photocatalyst by the microporous membrane, measured the absorbance value of the solution in the 721 UV-visible spectrophotometer with 664nm wavelength.

The activity of the catalyst was characterized by the decolorization rate D% of the MB solution. The calculation method is as follows:

$$D\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

A_0: absorbance value, which indicates that the dye solution in the reaction system absorbed in the dark after 20min;

A_t: absorbance value of the dye solution at reaction time t.

3. Results and analysis

3.1. XRD analysis of antimony/barium oxide composites

The samples prepared by 1.2 and 1.3 were subjected to XRD analysis with CuKα radiation, the current and voltage was 40 mA and 40 kV, respectively. The scanning speed was 10 °/min from 10 to 70 °. The results are shown in figure 1 and 2.

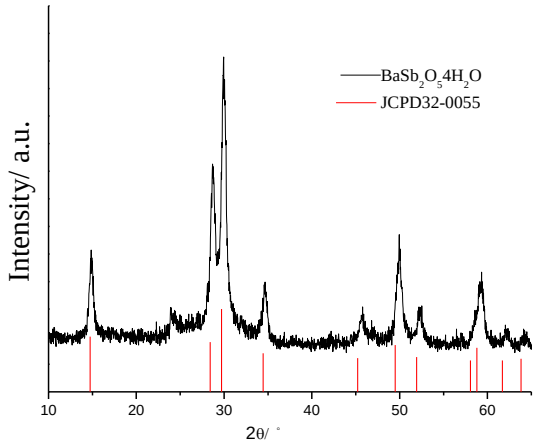

Figure. 1 XRD pattern of $BaSb_2O_5 \bullet 4H_2O$.

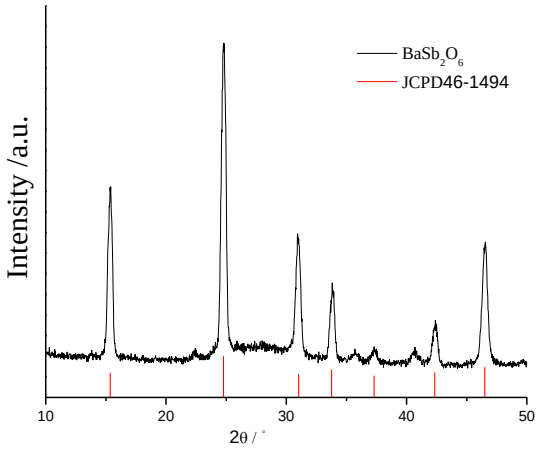

Figure. 2 XRD pattern of $BaSb_2O_6$.

It can be seen from figure 1 that the main diffraction peaks of the samples appear at 14.73°, 28.41°, 29.71°, 49.50° and 58.80°, respectively. All the characteristic peaks are the same of the international XRD diffraction data standard card of JCPDS No. 32-0055, indicating that the prepared sample is $BaSb_2O_5 \bullet 4H_2O$. The product obtained by the preparation method of Sb_2O_5 as antimony source is $BaSb_2O_5 \bullet 4H_2O$, the reaction principle is as follows:

$$2Sb_2O_5 + 2Ba\left(NO_3\right)_2 + 4KOH + 6H_2O = 2BaSb_2O_5 \cdot 4H_2O + 4KNO_3 + O_2 \quad (2)$$

It can be seen from figure 2 that the main diffraction peaks of the samples appear at the 2θ angles of 15.37°, 24.77°, 31.03°, 33.77°, 42.34° and 46.51°, respectively. All the characteristic peaks are the same of the international XRD diffraction data standard card of JCPDS No. 46-1494, indicating that the prepared sample is $BaSb_2O_6$ and the product obtained by the preparation of $KSb(OH)_6$ as antimony source is $BaSb_2O_6$. The reaction principle is as follows:

$$Ba(CH_3COO)_2 + 2KSb(OH)_6 = BaSb_2O_6 + 2CH_3COOK + 6H_2O \quad (3)$$

3.2. SEM analysis of the antimony/barium oxide composites

S-3000N scanning electron microscopy was used to observe the morphology of the prepared samples. Before the test, a small amount of fully dried and polished samples were fixed on the conductive tape, sprayed with gold and observed under vacuum condition. The SEM results of $BaSb_2O_5 \bullet 4H_2O$ and $BaSb_2O_6$ samples are shown in figure 3a.b and 4a.b.c.d, respectively.

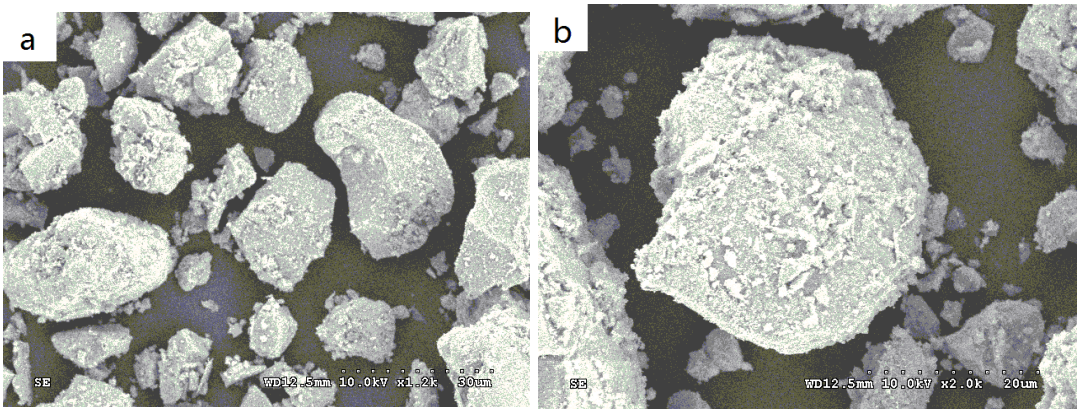

Figure. 3 a.b. SEM images of $BaSb_2O_5 \bullet 4H_2O$.

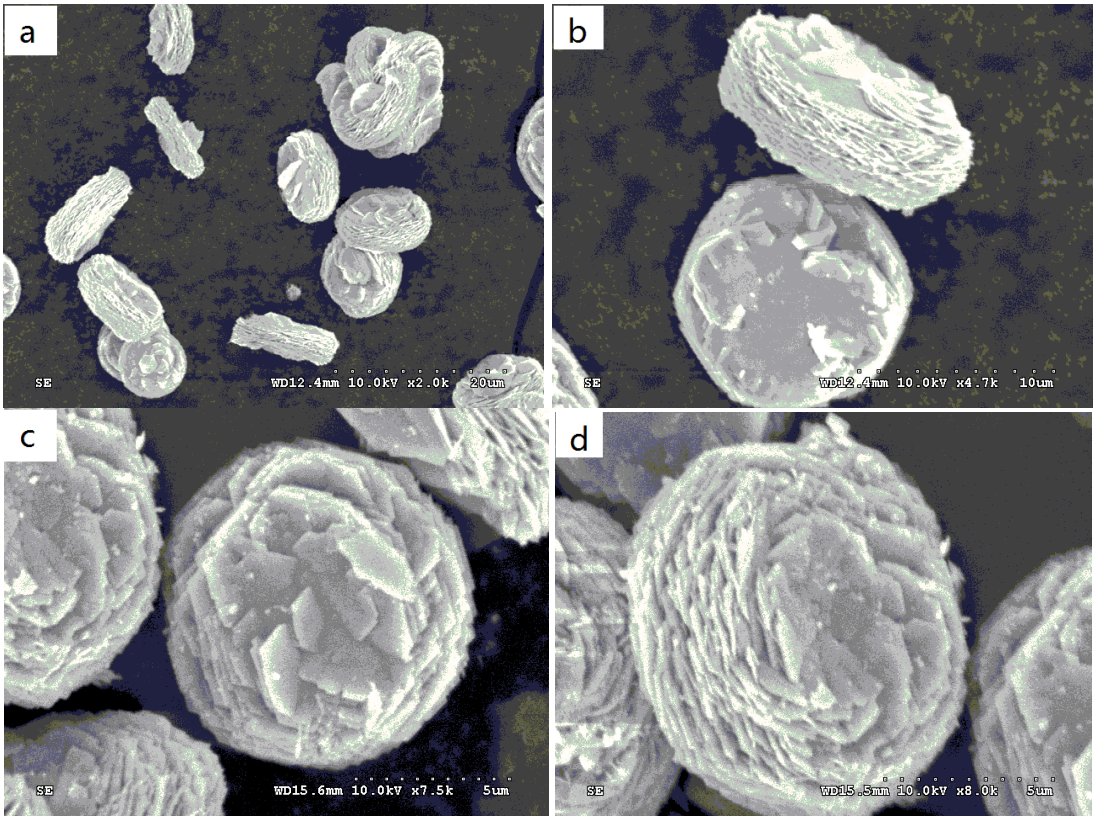

Figure. 4 a.b.c.d. SEM images of $BaSb_2O_6$.

It can be seen from figure 3a.b that the $BaSb_2O_5 \bullet 4H_2O$ is an irregular rocky structure with uneven size. The rough surface and porous structure were readily observed, and there's no obvious agglomeration between particles.

From figure 4a.b.c.d, it can be seen that the prepared $BaSb_2O_6$ particles are lamellar and cake-like structure, round and thick. The center and side of the grains are clear and compact, and look like a "natural open flowers", the size of the grains are almost of the same and they are dispersed uniformly. The diameter of one single particle was about 10μm.

3.3. Photocatalytic property of antimony/barium oxide composites

The prepared $BaSb_2O_5 \cdot 4H_2O$ and $BaSb_2O_6$ were subjected to photocatalytic reaction by the method depicted in section 1.4. The results are shown in figure 5.

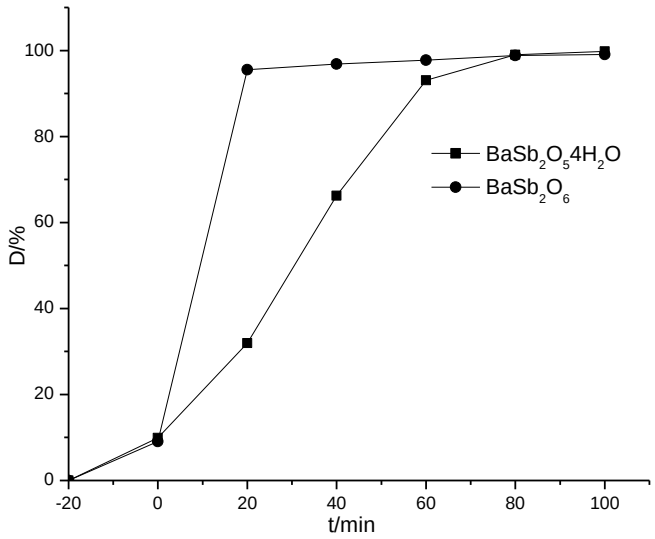

Figure. 5 The degradation curve of MB with $BaSb_2O_5 \bullet 4H_2O$ and $BaSb_2O_6$.

It can be seen from figure 5 that the photocatalytic efficiency of $BaSb_2O_5 \bullet 4H_2O$ and $BaSb_2O_6$ are good. After 100 minutes' lighting, the degradation rate of methylene blue reached higher than 99%. The degradation efficiency of $BaSb_2O_6$ to methylene blue was higher than that of $BaSb_2O_5 \bullet 4H_2O$ at the same lighting time period, which may be attributed to the lamellar microstructure of $BaSb_2O_6$.

4. Conclusions

In this study, the preparation of antimony/barium oxide composite photocatalyst with two kinds of substances as antimony sources was discussed. The results showed that the product obtained by hydrothermal reaction between Sb_2O_5 and $Ba(NO_3)_2$ under alkaline condition is $BaSb_2O_5 \bullet 4H_2O$; the product prepared by hydrothermal reaction between barium pyroantimonate and $Ba(CH_3CH_2COO)_2$ under acidic condition is $BaSb_2O_6$ powder, which has a regular microstructure, look like a "natural open flowers" and the size is uniform, non-agglomerate. Both $BaSb_2O_5 \bullet 4H_2O$ and $BaSb_2O_6$ have good photocatalytic efficiency on methylene blue under ultraviolet light, but $BaSb_2O_6$ was better, which was attributed to its own layered structure.

The results of this study will provide reference for the study of antimony composite oxides as photocatalysts.

Acknowledgements

This work was financially supported by Scientific research project of Hainan higher education institutions(Hnky2015-2), Hainan Natural Science Foundation(20162018), Hainan Natural Science Foundation (217055), Hainan Natural Science Foundation (217018).

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