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Synthesis of ZnS from organic sulfur in petroleum coke and its photocatalysis properties

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Abstract: Organic sulfur in high sulfur petroleum coke was treated as the S source for synthesis of ZnS photocatalyst. Experimental results showed that with ball milling and subsequent heating treatment, ZnS compound could be successfully synthesized and showed considerable photocatalysis activity for decomposing industrial pollutants. The concentration of methyl orange or ethylene blue may be lowered to less than 5% after being decomposed by the synthesized-ZnS photocatalysis. Results of this study suggested a potential technique of turning high sulfur petroleum cokes from industrial wastes into useful products for environment improvement.

Key words: Petroleum coke, photocatalysis, ZnS, ball milling, high-sulfur

1 Introduction

Petroleum coke is a waste product from oil refining processes. It is usually used as fuel due to its high carbon content. For high sulfur petroleum coke a desulfurization process is often necessary before it is used as fuel, otherwise it may result in serious environmental problems. The sulfur element in petroleum coke is mostly of organic, and many methods have been developed for desulfurizing (Li et al, 2006; Wang et al, 2004; Twomey et al, 2004; Lee and Choi, 2000). However, because a strict desulfurization process is usually not economically attractive, it is the obstacle for high-sulfur petroleum coke to be used as fuel on a large scale. High-sulfur petroleum coke is often regarded as a threat to environment rather than a useful resource.

Besides the usage as a fuel, other approaches have also been developed for petroleum coke to be turned into high value-added products, such as activated carbon (Li et al, 2009; Kawano et al, 2008), carbide (Alizadeh et al, 2006; Rao et al, 2009; Narciso-Romero et al, 1999) and composites (Mallick et al, 2009; Blanco et al, 2000). In these new approaches desulfurization is also necessary. In chemical activation process for preparing activated carbon, for example, the specific surface area of the activated carbon does not increase considerably until the sulfur removal rate exceeds 98% (Lee et al, 2000). Anyway, sulfur in petroleum coke is always considered a harmful element and an extra step is necessary to remove it.

In our study, sulfur in petroleum coke is not treated as a harmful element, but a source element for synthesizing photocatalyst ZnS. ZnS is known as a potential photocatalyst for some environmental remediation purposes (Wang et al, 2004; Wada et al, 2002; Torre-Martinez et al, 2001). Therefore, if the sulfur element in petroleum coke can be turned into ZnS compound with photocatalysis ability, it is possible to turn a high-sulfur petroleum coke into commercial products capable of environment treatment, such as photocatalysis activated carbon. As a preliminary attempt, this paper focuses on the synthesis of ZnS from the organic sulfur in petroleum coke and the verification of its photocatalysis activity.

2 Methods and materials

Petroleum coke containing 6.53 wt% sulfur was obtained from Syncrude Canada Ltd. Zn particles (>99.5%) and $ZnCl_2$ (>99.5%) powders were used as Zn source. Petroleum coke and Zn source were mixed according to a S/Zn atomic ratio of 1:1, and put in a stainless steel vial (300 mL in volume) together with hardened steel balls (12 mm in diameter) at room temperature. Then the vial was filled with argon and sealed by an O-ring. The milling process was carried out at room temperature in a QM-ISP Planetary Mill. The ball-to-powder weight ratio was 20:1. The rotational speed was 250 revolutions per minute.

The milled powders were analyzed by X-ray diffraction (XRD) using an Shimadzu XRD-6000 diffractometer. The morphology was examined using a Cambridge S-360 scanning electron microscope (SEM). A Netzsch STA 409PC high temperature differential scanning calorimeter (DSC) was used to measure the chemical reaction heat released during heating with a heating rate of 5 K/min.

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The ball milled and heat treated powders were put into distilled water to prepare a suspension with a ZnS concentration of 0.5 g/L. Methyl orange or ethylene blue as the chemicals to be decomposed was added with a concentration of 0.242 g/L. The pH of the solution was adjusted to 7 with 0.5 mol/L HCl and NaOH. The solution was then put into a 100 mL glass beaker and illuminated at room temperature with a 100 W ultraviolet (UV) light lamp (λ=365 nm), which provided an illumination intensity of approximately 60 mW/cm^2. During the illumination the solution was agitated by an electromagnetic agitator. After the photocatalysis process, the solution was filtered to remove the petroleum coke powders and analyzed using ultraviolet visible spectroscopy.

3 Results and analyses

3.1 Synthesis of ZnS from Zn powder

Fig. 1 shows the backscattered electron image of the Zn-petroleum coke granules mixture before and after ball milling process. The granule size of the petroleum coke decreased remarkably after 40 h of ball milling. Petroleum coke is brittle and low strength, and can be easily fragmented into fine powders by the collision of the milling balls. Usually different metals can be blended into alloy at the atomic level through the ball milling process. However, Fig. 1 shows that the size of Zn powders almost unchanged after 40 h of ball milling, except that some Zn particles agglomerated. The reason might be that the petroleum coke partly serves as the lubricant, and does not affect the Zn powders.

Since the petroleum coke granules were repeatedly fragmented by the collision of the milling balls, fresh surfaces

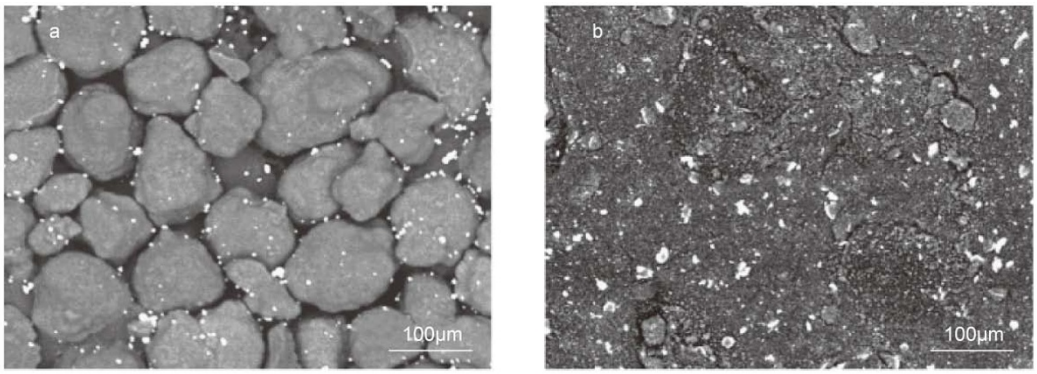

Fig. 1 Backscattered electron image of the Zn-petroleum coke granule mixture before and after ball milling (a) before ball milling, (b) after 40 h of ball milling

of the broken petroleum cokes kept emerging, therefore increased the probability for Zn powders to collide with the sulfur atoms. However, the XRD results in Fig. 2 show that Zn remained as Zn, and no ZnS is observed. In fact, the diffraction peaks of the Zn powders in Fig. 2 did not even broaden after the ball milling process, indicating that the Zn particles did not suffer significant plastic deformation in the ball milling process. Result in Fig. 2 leads to the same conclusion as Fig. 1 that most mechanical energy of the ball collisions was absorbed by the petroleum coke granules, but not the Zn powders. Therefore, even if the Zn particles have chances to contact S anion during the ball milling process, the low collision energy between Zn and petroleum coke makes it impossible to break the C-S bonds and produce ZnS.

However, the ball milling process is not totally useless. Fig. 3 shows the XRD profiles of the ball milled Zn-petroleum coke mixture after heat treatment at 873 K for 1 h in the air. If there was no prior ball milling process, all the Zn powders would be oxidized to ZnO after the heat treatment. If there was a ball milling process prior to the heat treatment process, some weak ZnS peaks were detected. The height of the ZnS peak increased slightly with the increase of the ball milling time.

To further investigate the reaction between element Zn and organic sulfur, the blended powder after different ball

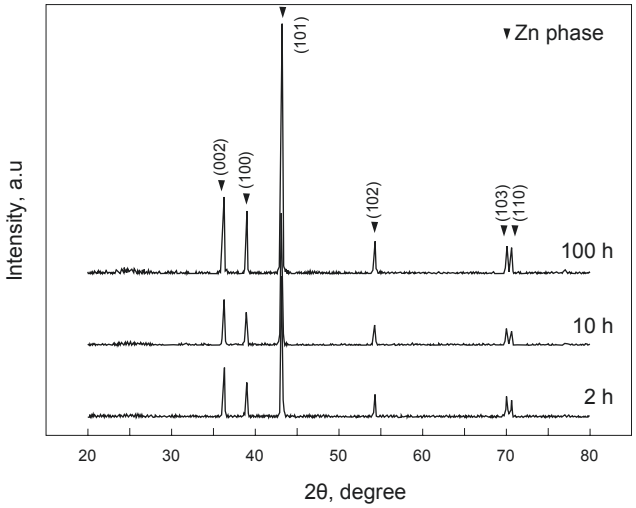

Fig. 2 The XRD profiles of the Zn-petroleum coke granule mixture after different times of ball milling

milling times was subjected to DSC measurement under an argon atmosphere, and the results are shown in Fig. 4. There are two peaks on each DSC curve. Apparently the endothermic peak around 690 K corresponds to the melting of the Zn powder. The exothermic peak on the hot side was

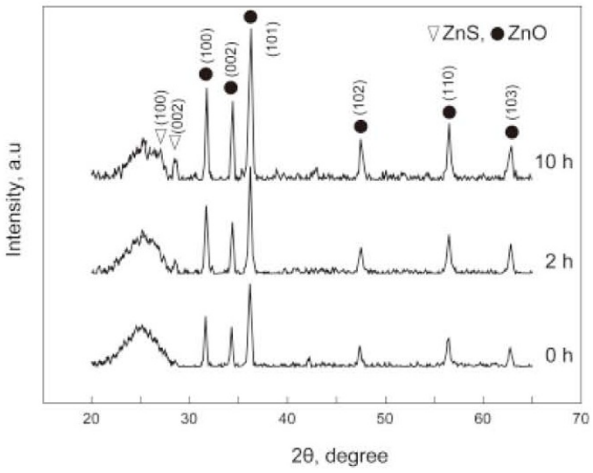

Fig. 3 The XRD profiles of the Zn-petroleum coke mixture after ball milling and subsequent heat treatment at 873 K for 1 h in the air. The ball milling times are labeled in the figure

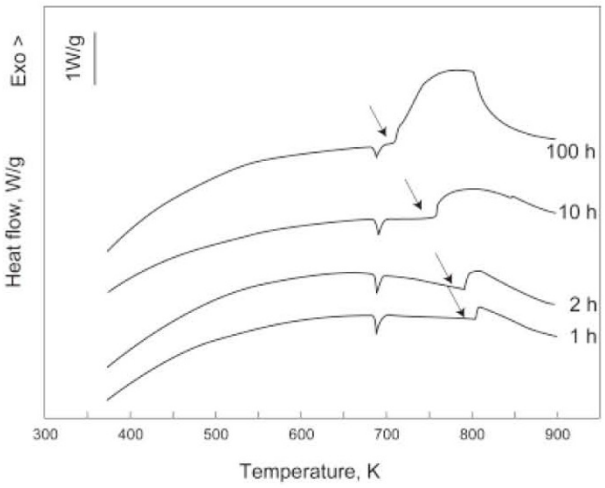

Fig. 4 DSC curves of Zn and petroleum coke mixture after different times of ball milling

considered corresponding to the synthesis of ZnS, because no other chemical reaction should happen under the argon atmosphere. The starting temperature of the exothermic peak decreased, and the peak area increased significantly with the increase of the ball milling time.

The results in Fig. 4 indicate that the ball milling process was favorable to the synthesis of ZnS in two aspects: the first one is to provide more interface energy by generating large quantity of fresh surface through fragmenting the petroleum granules, and thus decrease the synthesis temperature; the second one is to provide a larger probability for Zn and organic sulfur to collide each other, which results in more ZnS products and therefore larger exothermic peak on DSC curves.

3.2 Synthesis of ZnS from $ZnCl_2$ powder

Fig. 5 shows the backscattered electron image of $ZnCl_2$ and petroleum coke granules mixture before and after ball milling process. The granule size of the petroleum coke remained almost the same after 40 h of ball milling. In fact, due to the agglomeration effect of the moist $ZnCl_2$, the coke granules appeared even larger. It seems that the moist $ZnCl_2$ coated the milling balls and the coke granules during the ball milling process, reducing the collision energy. Simultaneously, the $ZnCl_2$ is distributed more uniformly among the coke granules.

Fig. 6 shows the XRD results of the $ZnCl_2$ and petroleum coke mixture after a subsequent heat treatment process at 873

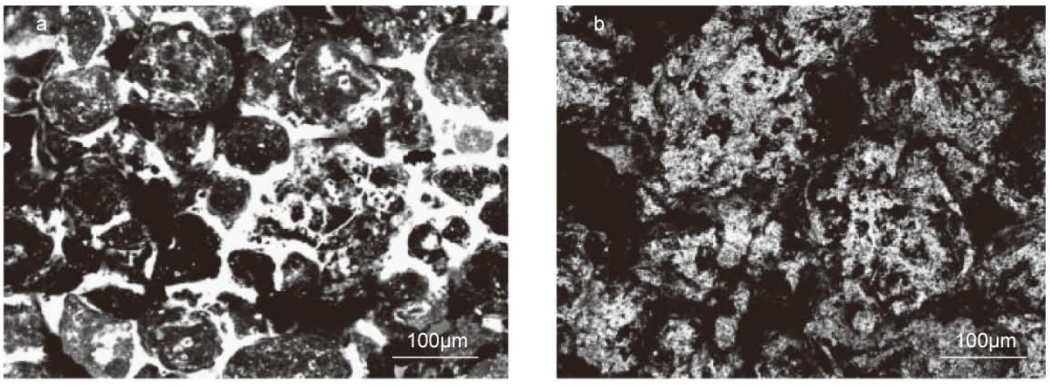

Fig. 5 Backscattered electron image of the $ZnCl_2$ and petroleum coke granule mixture before and after ball milling (a) before ball milling, (b) after 40 h of ball milling

K for 1 h, with and without a prior ball milling process. ZnS was detected even without a ball milling process. Once again, according to Fig. 6 the ball milling process is favorable to the ZnS synthesis. The intensity of the ZnS peaks increased with the increase of the ball milling time, and is overwhelmingly higher than the counterpart in Fig. 3. In comparison with the SEM results, it is reasonable to say that the ball milling process distributes the $ZnCl_2$ more uniformly among coke granules, and therefore increases the probability for Zn cations to contact S anions.

Fig. 7 shows the DSC curves of the blended powders after different times of ball milling under an argon atmosphere. There are also two peaks on each DSC curve, where the endothermic peak around 560 K corresponds to the melting of

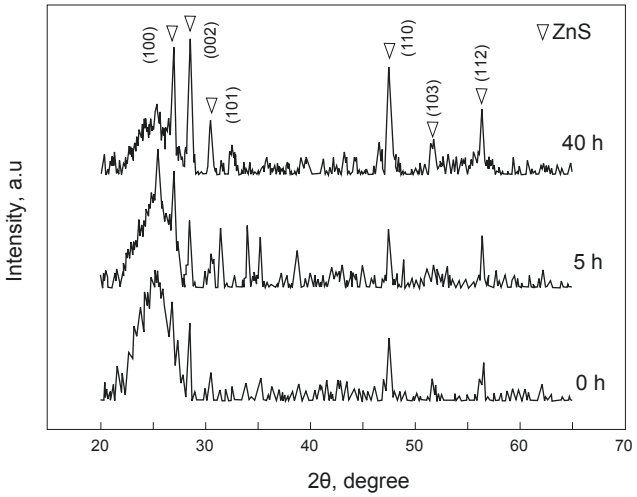

Fig. 6 The XRD profiles of the $ZnCl_2$-petroleum coke powder mixture after ball milling and subsequent heat treatment at 873 K. The ball milling times are labeled in the figure

$ZnCl_2$, and the exothermic peak on the hot side corresponds to the synthesis of ZnS. The starting temperature of the exothermic peak did not change significantly with the increase of the ball milling time. This is accordance with the results in Fig. 5 that the petroleum coke was not fragmented through the ball milling process, and therefore no favorable effect in the synthesis of ZnS. The area of the hot side peaks increased slightly with increase of the ball milling time, but the extent was less than that in Fig. 4. Results in Fig. 7 seems to suggest that the ball milling process is not so important for the synthesis of ZnS when $ZnCl_2$ is selected as the reagent, however in the 3.3 section it will be shown that the ball milling process is in fact important for its photocatalysis activity.

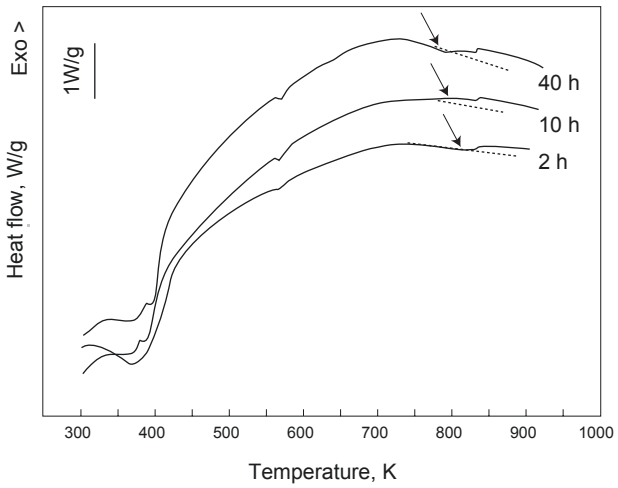

Fig. 7 DSC curves of $ZnCl_2$-petroleum coke mixture after different times of ball milling

3.3 Photocatalytic property of the synthesized ZnS

As a reagent $ZnCl_2$ seems more promising than Zn powder, so the coke+$ZnCl_2$ system was selected for further investigation. Fig. 8 shows the variations of the methyl orange concentration with UV irradiation time. Without $ZnCl_2$ addition, the petroleum coke, after heat treatment at 873 K for 1 h, showed no sign of photocatalysis. By adding $ZnCl_2$, petroleum cokes, after heat treatment process, showed an apparent activity for decomposing methyl orange. The methyl orange concentration decreased with increasing irradiation time and showed an unchangeable trend after 40 min of irradiation. Results in Fig. 8 proved that the synthesized ZnS has considerable photocatalysis activity, and has potential application in dye degradations. Some recent research also showed that ZnS could be successfully applied in the degradation of organic pollutants in water, and exhibited considerable efficiency (Xie et al, 2008; Hu et al, 2005).

It is noted that the photocatalysis activity of the ZnS synthesized from petroleum coke increased significantly after the ball milling process. As shown in Fig. 8, after 20 h of ball milling and subsequent heat treatment, the ZnS-containing

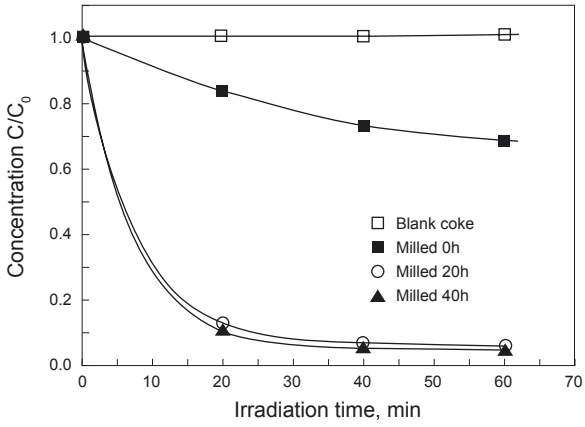

Fig. 8 Variations of the methyl orange concentration with UV irradiation time. The coke+$ZnCl_2$ system was ball milled for different times and heat treated at 873 K for 1 h. For comparison, coke without $ZnCl_2$ (blank coke) is also presented

cokes could almost totally decompose the methyl orange within 20 min of UV irradiation. The photocatalysis activity of ZnS was not improved significantly when the ball milling time was longer than 20 h. Results of decomposing ethylene blue were almost identical to Fig. 8 and thus are omitted here.

Although the results in Fig. 6 and Fig. 7 suggest that the ball milling process did not have significant effect in the synthesis of ZnS, the results in Fig. 8 unambiguously indicated that ball milling process was an important process for promoting the photocatalysis activity of the ZnS synthesized from petroleum cokes. The reason, according to Fig. 5, might be that the ball milling process can distribute the $ZnCl_2$ more uniformly among the coke granules and therefore result in a larger yield of ZnS, which needs further investigation.

It is reasonable to expect a stronger photocatalysis activity if the ZnS synthesis process is combined with the carbon activation process when treating the high sulfur petroleum cokes, since the activated coke has a larger specific surface area and therefore a higher probability of contact between Zn and organic sulfur. If this strategy is successful, activated

carbon with photocatalysis activity ability could be obtained from cheap high sulfur petroleum coke. This will be the next step of this work.

4 Conclusions

In this paper, the organic sulfur in high sulfur petroleum coke is used as the S source for preparation of ZnS. Experimental results showed that ZnS can be successfully synthesized from petroleum coke and Zn (or $ZnCl_2$) mixture through ball milling and subsequent heating treatment. $ZnCl_2$ as the reagent is more promising than Zn for it needs less ball milling time. The synthesized ZnS proved to be able to decompose Methyl orange and ethylene blue under ultraviolet light. The XRD and the photocatalysis results confirmed that the ball milling process is necessary for synthesis of a larger amount of ZnS and especially for improving the photocatalysis activity of ZnS. Results in this paper suggest a potential technique of turning high sulfur petroleum cokes into high value-added activated carbon, which has the novel ability of self-cleaning without the need for the addition of external photocatalysts.

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