



Detailed vacuum-assisted desulfurization of high-sulfur petroleum coke



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ABSTRACT

In this research, the sulfur removal efficiency from high-sulfur petroleum coke in the presence of vacuum was investigated. Different feeding layer depth, heat treatment temperature, holding time, particle sizes, and vacuum degree were studied. The feeding layer has a significant effect on the sulfur removal rate, and the optimal feeding layer was 30 mm. A higher sulfur removal rate was obtained at 1500 °C, with a holding time of 2 h, particle sizes of –150 μm, and 1 Pa vacuum. It was evident that the application of vacuum improved the sulfur removal efficiency. More importantly, elemental sulfur can be obtained instead of SO₂ emission that occurs during traditional desulfurization by high-temperature calcinations. Finally, the mechanism of sulfur removal from petroleum coke was analyzed by XRD.

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1. Introduction

Solar power is energy derived from sun that can be converted into thermal or electrical energy. Because the availability of conventional fossil fuels are drastically decreasing, the effective utilization of solar power as a clean and abundant resource has become vitally important. The solar energy is received by silicon-based commercial solar cells. Currently, more than 80% of commercial solar cells are made of silicon, particularly multi-crystalline silicon [1–3], the same semiconductor material that is used in computers. However, solar silicon cells or semiconductor materials are prepared using metallurgical grade silicon (MG-Si) as the raw material. The rapidly growing worldwide solar cells market requires a large quantity of silicon feedstock [4–6]. MG-Si is conventionally produced in a submerged arc furnace by the carbothermic reduction of silica. Silica and carbonaceous reductants (petroleum coke, coal, woodchips, charcoal, and others) are heated using electric energy in a submerged arc furnace to produce the silicon. The level of impurities of MG-Si is determined by the

impurities of the raw materials (silica, carbonaceous material, and electrodes) [7].

Petroleum coke is considered an attractive fuel because of its low volatility, high calorific value [8], and its low price and availability [9]. However, petroleum coke is the final by-product of a delayed coking process in refinery and its amount has increased rapidly with the development of deep conversion refining technology [10–16]. Therefore, petroleum coke is the best carbonaceous solid reductant for use in the carbothermic reduction of silicon dioxide. However, it is essential to remove the impurities from petroleum coke because the common impurities of petroleum coke affect the quality of the resulting MG-Si. The quality of petroleum coke depends on the concentration of some elements (mainly Ni, V, and S), that cause poisoning of the catalysts used in the refining processes [17,18]. Additionally, due to the quality deterioration of crude oil, there is an increasing amount of petroleum coke with a high sulfur content. When this high-sulfur petroleum coke is used as a carbonaceous solid reductant for silicon production, there can be serious problems during smelting electric arc furnace, such as abrasion and fouling in the furnace linings [19,20]. The sulfur has strong catalytic activities in both the air and CO₂ reactivity of coke in the absence of interference by other impurities [21]. There are reports that petroleum coke can be purified by conventional acid leaching at high temperature (70 °C) though a long treatment

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time is required (6 h) [22]. Recently, a study evaluated the use of ultrasound treatment to remove iron and other impurities from petroleum coke and found it was more effective compared with the conventional stirring method [23]. Ultrasonic energy can enhance the chemical reaction rate because of the cavitation bubbles that are produced [24].

The sulfur in petroleum cokes is mostly organic [25]. To break the C–S bonds in these organic groups, methods including high temperature calcination [26–28], sodium-assisted hydrodesulfurization [29–31], sodium assisted hydrodesulfurization [32–36], and chemical treatment with alkali metal compounds [37–39] have been performed. However, at present, there are no reports on the removal of sulfur from petroleum coke under vacuum. In this work, the desulfurizing efficiency of vacuum of petroleum cokes containing high amounts of sulfur (8% or more) was investigated. Parameters of feeding layer depth, heat treatment temperature, holding time, particle sizes, and vacuum degree were studied. The conventional and vacuum processes were compared.

2. Material and methods

2.1. Materials

The petroleum coke used in this investigation was from Taiwan. The ultimate analysis of the petroleum coke is given in Table 1. The petroleum coke was dried, crushed, and sieved to obtain particle sizes of <125 μm , 125–150 μm , 150–180 μm , 180–300 μm , 300–350 μm , and 350–450 μm .

2.2. Analysis and characterization

The total S in petroleum coke was measured using an intelligent sulfur meter (5E-8S/AII, Changsha, China). The samples (40–60 mg) were put in a crucible and 4–8 min was required to complete the analysis. The S removal efficiency η (%) was calculated using Eq. (1):

$$\eta = \frac{S_0 - S_C}{S_0} \times 100\% \quad (1)$$

where S_0 is the sulfur content of the initial sample (%) and S_C is the sulfur content of the sample after vacuum heat treatment (%).

The crystal structures of the samples were determined using a Rigaku X-ray diffractometer with Cu K α radiation ($\lambda = 0.154056$ nm, 40 kV, 200 mA). The diffractometer was used to scan over an angular two range of 10–80°. Steps of 0.02° were employed at 1 s per step. Similar analytical methods were previously reported [40–54].

3. Results and discussion

3.1. Effect of feeding layer depth

The influence of feeding layer depth on the sulfur removal rate of petroleum coke was investigated for various feeding layer depths using sample particle sizes of 350–450 μm , 10^{−2} Pa vacuum, 1500 °C heat treatment, and a holding time of 1 h. Fig. 1(a)

Table 1
Analysis of the petroleum coke (wt.%).

Ultimate analysis (wt.%)				
C _{daf}	H _{daf}	N _{daf}	S _{daf}	O _{daf}
82.55	5.27	1.25	8.21	0.35

Note: daf – dry and ash free basis.

presents the shape of the charging crucible, which is a circular truncated cone shape (the diameter was 10 mm at the bottom and 20 mm at the surface) made of graphite. The sample sulfur removal rate of three vertical sections of the charging materials were determined as shown in Fig. 1(b). There was a significant effect of feeding layer depth on sulfur removal rate. With the increase of the feeding depth from the surface to bottom, the sulfur removal rate decreased. The sulfur removal rate of the surface feeding layer (30 mm) was 80%, but it was only 20% in the bottom feeding layer (30 mm). The feed permeability declined from the surface to the bottom feeding layer, and the sulfur removal rate of samples decreased. Based on these findings, an optimal feeding layer of the top 30 mm was used for all subsequent experiments.

3.2. Effects of particles size

The influence of particle size on the sulfur removal rate was studied for –125 μm , 125–150 μm , 150–180 μm , 180–300 μm , 300–350 μm , and 350–450 μm size particles at a feeding layer depth of 30 mm, 10^{−2} Pa, 1 Pa, or 100 Pa vacuum, 1 h holding time, and 600 °C or 1000 °C heat treatment temperature [55–65,66–69]. The sulfur removal rates for the different sizes of particles are shown in Fig. 2. For all particle sizes, the removal rate of sulfur at 1 Pa was obviously higher than that at 100 Pa. However, the removal rate of sulfur showed little change between 1 Pa and 10^{−2} Pa compared with the larger change between 1 Pa and 100 Pa. For a given vacuum, a decrease in particle size enhanced sulfur removal rate effectively to a particle size of 125–150 μm . Fig. 3 shows that the surface area (which is directly correlated with particle size) did not increase considerably until the residual sulfur contents were lowered below a certain value, as reported in Ref. [39]. According to Fig. 2, the removal rate of sulfur was steady for particle sizes greater than 125–150 μm . Therefore, an optimal particle size of –150 μm was used for the subsequent experiments.

3.3. Effect of heat treatment temperature

The influence of heat treatment temperature on the sulfur removal of petroleum coke was studied for temperatures of 600, 800, 1000, 1100, 1300 and 1500 °C at a feeding layer depth of 30 mm, 150 μm sample particles sizes, 10^{−2} Pa, 1 Pa, or 100 Pa vacuum, and 1 h holding time. Fig. 4 shows the effect of heat treatment temperature on the sulfur removal of petroleum coke at three different vacuum strengths. At 1000 °C, as the vacuum degree increased from 100 Pa to 1 Pa, there was no change in the desulfurization rate. At 10^{−2} Pa, the sulfur removal rate of petroleum coke increased. Under vacuum, the increase in sulfur removal rate slowed down at temperatures below 1000 °C. At temperatures 1000 °C or higher, the sulfur removal rate of petroleum coke increased with increasing temperature. When the temperature reached 1500 °C, the sulfur removal rate of petroleum coke was 80%. This is likely because the increase in temperature will enhance both the reaction and the diffusion rate of the reactants and reaction products [23]. These results were consistent with the previous findings that at 1623 K calcination temperature (and temperatures above 1873 K) sulfur can be effectively removed from petroleum coke [70–72]. Therefore, we used 1500 °C as an optimal temperature for subsequent experiments.

3.4. Effect of holding time

The influence of holding time on sulfur removal of petroleum coke was conducted at holding times of 0.5, 1, 1.5, 2, 2.5, and 3 h at 30 mm feeding layer depth, the 150 μm size particles, 10^{−2} Pa,

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