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Pore structure modification of diatomite as sulfuric acid catalyst support by high energy electron beam irradiation and hydrothermal treatment

Chong Li [a], Guilong Zhang [b], Min Wang [b], Jianfeng Chen [a], Dongqing Cai [b,*], Zhengyan Wu [b,*]

[a] Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
[b] Key Laboratory of Ion Beam Bioengineering, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

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ABSTRACT

High energy electron beam (HEEB) irradiation and hydrothermal treatment (HT), were applied in order to remove the impurities and enlarge the pore size of diatomite, making diatomite more suitable to be a catalyst support. The results demonstrated that, through thermal, charge, impact and etching effects, HEEB irradiation could make the impurities in the pores of diatomite loose and remove some of them. Then HT could remove rest of them from the pores and contribute significantly to the modification of the pore size distribution of diatomite due to thermal expansion, water swelling and thermolysis effects. Moreover, the pore structure modification improved the properties (BET (Brunauer–Emmett–Teller) specific surface area, bulk density and pore volume) of diatomite and the catalytic efficiency of the catalyst prepared from the treated diatomite.

1. Introduction

Nowadays, the "contact method" is widely used in sulfuric acid production, in which a vanadium catalyst is critical to the reaction efficiency [1,2]. The quality of vanadium catalyst is not only influenced by preparation process, but also related to the quality of catalyst support [1], as catalyst support with high quality can significantly enhance the catalyst performance [3,4]. So far, the prevailing material used as catalyst support is diatomite, a natural clay composed mainly of silica microfossils derived from aquatic unicellular algae, which consists of plenty of diatom units (DU) with various shapes and sizes (10–200 μm) and high porosity (80–90%) [5–7]. Due to the highly porous structure, low density and high specific surface area, diatomite has been widely applied as a filtration medium, adsorbent, and sulfuric acid catalyst support, as the diatomite pores are appropriate to be the reaction fields for the synthesis of SO_3 [8–14]. The porous support provides longitudinal channels or passageways that permit high space velocities of reactants (SO_2 and O_2) with minimal pressure drops. Moreover, the effectiveness factor of the reaction and the effective diffusion coefficient, could be substantially improved by increasing the pore size of the catalyst support. Recently, it has been demonstrated that supports with small internal pores could lead to inefficient use of catalysts because the reactants do not have enough time to reach catalytic metals in pores and tend to be trapped in the pores, participating in undesired secondary reactions [15]. With its excessive mining, it is becoming difficult to obtain diatomites with high quality, and most mined diatomites display improper pore size distribution (PSD), high amounts of impurities, and high bulk density (BD). Therefore, these diatomites are unable to meet the demand of the sulfuric industry and the environment. Hence, improving the properties of diatomite such as PSD and reducing impurity content are essential for the quality of the catalyst support [16].

Until now, several methods have been reported to improve the quality of diatomite [7,8,15,17]. Although they could remove some of the impurities and improve the PSD to a certain degree, the procedures were relatively complex and some of them could produce waste acid solution. Therefore, a facile and environmentally friendly modification approach is necessary to be developed. In this paper, diatomite was modified by high energy electron beam (HEEB) irradiation, coupled with hydrothermal treatment (HT). HT,

* Corresponding authors. Tel.: +86 551 65595012; fax: +86 551 65591413.
E-mail addresses: dqcai@ipp.ac.cn (D. Cai), zywu@ipp.ac.cn, zhengyanwu@gmail.com (Z. Wu).

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as an important technique, has been widely used to fabricate a wide range of solid-state compounds such as oxides, sulfides, halides, molecular zeolites and other microporous phases with specific shapes and sizes. Meanwhile, HT is a facile modification and fabrication method, generating little pollution [18–22]. Therefore, HT was used herein to improve the PSD, remove the impurities and decrease the BD of diatomite through thermal expansion, water swelling and thermolysis effect.

2. Materials and methods

2.1. Materials

Natural diatomite powder, with a particle size range of 5–20 μm, was provided by Aobao Co., Ltd. (Shandong, China). Other chemicals were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Deionized water was used throughout this work.

2.2. HEEB irradiation and hydrothermal treatment

A diatomite sample (50 g) in a plastic bag was irradiated by a high energy electron beam accelerator (10 MeV and 10 kW) with fluences of 10, 20, 30, and 40 kGy at room temperature, and the resulting samples were designated as 10-MD, 20-MD, 30-MD, and 40-MD respectively. 40-MD (50 g) was put into 500 mL deionized water in a 1 L thermal reactor, which was thereafter treated at 180 °C for a certain time. Afterwards, the supernatant was removed and the remains were ground to powders (150–200 mesh) after being dried at 70 °C for 10 h.

2.3. Characterization

The morphology and microstructure of diatomite were observed on a scanning electron microscopy (SEM) (Sirion 200, FEI Co., USA). The PSD and BET specific surface area (S_{BET}) of diatomite were measured using a specific surface area and porosimetry analyzer (Tristar II, 3020 M, Micromeritics, USA). Additionally, the catalytic performance was determined according to the previously reported method [7].

3. Results and discussion

3.1. Effect of HEEB irradiation on diatomite

Diatomite consists of mainly amorphous silica and several types of organic and inorganic impurities such as ferric oxide, alumina, alkali and alkaline-earth metal oxides, etc. [3]. Most of these impurities usually exist in the pores of natural diatomite (ND) making the pores clogged and thus the pore size reduced, which is unfavorable to the catalytic reaction. Consequently, dredging the clogged pores and enlarging the pore size are crucial to improve the quality of diatomite as a catalyst support.

PSD is a dominant factor for quality of diatomite as a catalyst support and the preferred pore size range is 100–1000 nm [7]. The amount of the pore with a certain diameter (APCD) could be represented by dV/dD or dV/dlog(D) pore volume, where D is the pore diameter, V is the total pore volume. As shown in Fig. 1, for ND, the micropores with the highest APCD possessed the size of approximately 12 nm. HEEB irradiation with fluences of 30 and 40 kGy on diatomite could effectively enlarge these micropores from 12 nm to approximately 15 and 20 nm. In addition, HEEB irradiation with fluences of 30 and 40 kGy could also significantly enlarge the mesopores (100–250 nm) of diatomite, and 40-MD possessed the highest APCD of mesopores than ND, 10-MD, 20-MD, and 30-MD. Therefore,

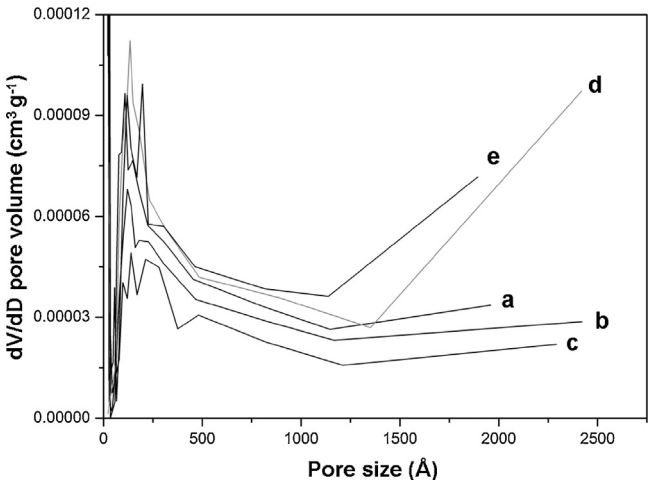

Fig. 1. Pore size distribution of diatomite: (a) ND, (b–e) represent 10-MD, 20-MD, 30-MD, and 40-MD respectively.

40 kGy was selected as the optimal HEEB fluence for the modification of diatomite. Based on the PSD analysis, it was indicated that HEEB irradiation (30 and 40 kGy) could probably make the impurities in the pores of diatomite loose and then remove some of them because of thermal, charge, impact and etching effects [23]. For the thermal and physical impact effects, plenty of electrons with kinetic energy of 10 MeV possessed a much high momentum and could generate much heat during the bombardment process, which could intensify the movement of the impurities atoms and increase the mean distance among the atoms. For the charge effects, the incident electron beam could probably influence the electron clouds of the atoms of these impurities resulting in ionization of these atoms, so that the electrostatic repulsions could separate the atoms away from each other. In a word, these three effects of HEEB irradiation together could effectively increase the dispersion of the impurity atoms, make the impurities loose and then remove some of them by the etching effect.

3.2. Morphology observation

HEEB irradiation could make the impurities in the pores of diatomite loose, which promoted degradation of these organic impurities through the thermolysis effect of HT, and enabled the inorganic impurities to be separated from the inner pore surface and removed from the diatomite pores under the high pressure of the water vapor (thermal expansion and water swelling effect). Therefore, after HT for 8 h, the impurities in the diatomite pores became numerous loose pieces and, meanwhile, the original clogged pores became open and exposed (Fig. 2a and b). When the HT time was prolonged to 12 h, most of the loose impurities pieces were removed from the pores and only a few pieces could be seen on the diatomite surface as shown in Fig. 2c. Hence, the amount of unclogged pores increased. Nevertheless, with the increase of the HT time, the diatomite units (DU) were destroyed and broken into several pieces because of the thermal expansion and water swelling effect (Fig. 2d). Moreover, for 20 h and 24 h treatment, the DU pieces were further damaged and became an abundance of smaller pieces which covered some DU surface areas. In addition, some pieces entered the dredged pores making the pores clogged again, resulting in decreased amount of unclogged pores (Fig. 2e and f). From the morphology investigation above, a conclusion could be obtained that HEEB irradiation and HT showed an effective capability for the modification of the pore morphology through removal of the impurities. Moreover, the optimal hydrothermal time was 12 h, as most pores were dredged clearly and the DU displayed clean appearance.

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