



Microstructural modification of diatomite by acid treatment, high-speed shear, and ultrasound

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ARTICLE INFO

Article history:

Received 26 April 2012

Received in revised form 20 July 2012

Accepted 9 August 2012

Available online 16 August 2012

Keywords:

Diatomite

Pore size distribution

Bulk density

ABSTRACT

Three modification approaches including acid treatment, high-speed shear and ultrasound on the microstructure of diatomite were developed, in order to enlarge the pore size and decrease the bulk density of diatomite and then make diatomite more suitable to be catalyst carrier. The modification effects were investigated and the results indicated that all three approaches had significant cooperative effects on the modification of diatomite. Acid treatment could remove impurities, mainly metallic oxides, of diatomite due to the acid wash effect. High-speed shear and ultrasound were both able to dredge the clogged pores because of the strong centrifugal force in shear process and cavitation effect in ultrasound process resulting in the improvement of the pore size distribution and the remarkable decrease of the bulk density.

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1. Introduction

At present, contact method is widely used to produce sulfuric acid in many countries [1], and vanadium catalyst is a crucial material in this method. Consequently, the quality of vanadium catalyst directly influences the efficiency of sulfuric acid reaction [2]. In practice, the quality of vanadium catalyst is not only affected by production process, but also related to the quality of catalyst carrier [1], for modified catalyst carrier can remarkably enhance the performance of catalyst [3,4]. Currently, the prevailing material used as catalyst carrier is diatomite.

Diatomite is a pale-colored, lightweight sedimentary rock composed mainly of silica microfossils of aquatic unicellular algae. It consists of a wide variety of shape and sized diatom units (DU), typically 10–200 μm , in a structure containing up to 80–90% porosity [5,6]. Diatomite's highly porous structure, low density and high surface area resulted in a number of industrial applications as filtration media for various beverages, inorganic and organic chemicals, adsorbent for water contaminant as well as sulfuric acid catalyst carrier, as the pores of diatomite are suitable to be the reaction field for the synthesis of SO_3 [7–13]. Although diatomite has a unique combination of physical and chemical properties, it still cannot fully meet the demand of the sulfuric industry and the environment yet. Therefore it is necessary to further improve the property of diatomite, especially the pore size distribution,

impurity content and bulk density, which are the dominant factors for the quality of the catalyst carrier [14]. Until now, several approaches have been reported to improve the pore size distribution of diatomite through removal of the existing impurity, however, undesired impurities could sometimes appear [7,15]. In our study, diatomite was modified by high-speed shear, ultrasonic and acid treatment, respectively. Through high-speed shear and ultrasonic treatment, the bulk density of diatomite was significantly lessened and the pore size distribution of diatomite was also improved effectively. Moreover, diatomite could still remain its original chemical components. In addition, the treatment of diatomite with hydrochloric acid could remove mineral impurities significantly.

2. Materials and methods

2.1. Materials

The natural diatomite (N-DT) particles, with average particle size of 10 μm , were supplied by Aobao Co., Ltd. (Shandong, China). Other chemicals were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Company (Shanghai, China).

2.2. Modification methods

2.2.1. Acid treatment

The raw diatomite powder was treated with HCl solution to eliminate impurities including alumina, ferric oxide, alkaline earth and alkali metal oxide [3].

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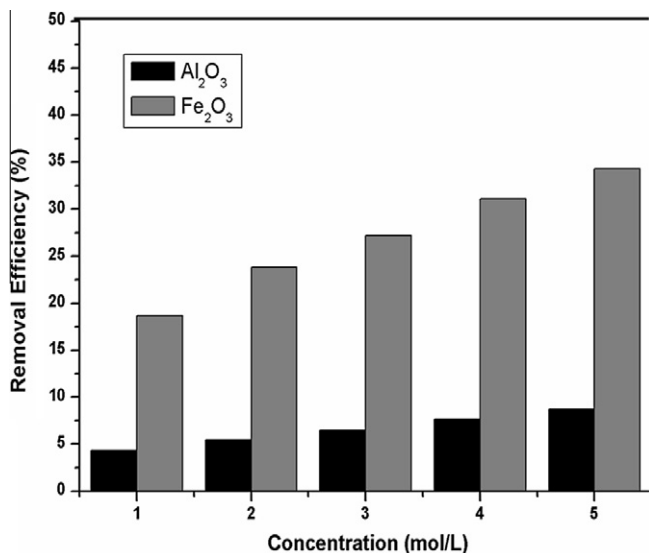


Fig. 1. Effect of hydrochloric acid with different concentrations on the removal efficiency of Fe₂O₃ and Al₂O₃ of diatomite.

Briefly, five diatomite samples (each 2 g) were put into five 250 ml beakers and mixed with five different concentrations of HCl solution (1, 2, 3, 4, 5 M) to make the diatomite suspensions. The suspensions were shaken at 25 °C for 4 h in a shaker (Scientific

Instruments Co., Ltd., Shanghai, China) with a shaking rate of 200 rpm. After being deposited for 2–3 h, each suspension was filtrated by vacuum filter and washed with distilled water 2–3 times and then dried at 70 °C for 10 h. The filtrate was kept for later analysis of metal ions contents.

2.2.2. High-speed shear

Diatomite was modified with high-speed shear by a smash machine (24000 rpm, inner diameter 100 mm, 60–80 mesh, TAISITE Co., Ltd., Tianjin, China). Diatomite (2 g) was put into smash machine for shear with different time and then placed in a 50 ml centrifuge tube. Five milliliter of modified diatomite powder was taken out and its bulk density was calculated.

2.2.3. Ultrasonic treatment

Ultrasonic treatment of diatomite was performed by a 150 w ultrasonic cleaner (KQ3200B, Ultrasonic instruments Co., Ltd., Jiangsu, China). Six diatomite samples with different weights were put into beakers and then placed in ultrasonic cleaner at 25 °C. Five milliliter of modified diatomite powder was taken out and its bulk density was calculated.

2.3. Characterization of modified diatomite

2.3.1. Morphology observation

Scanning electron microscopy (SEM) (Sirion 200, FEI Co., USA) was used to investigate the morphology and microstructure of raw diatomite and modified diatomite.

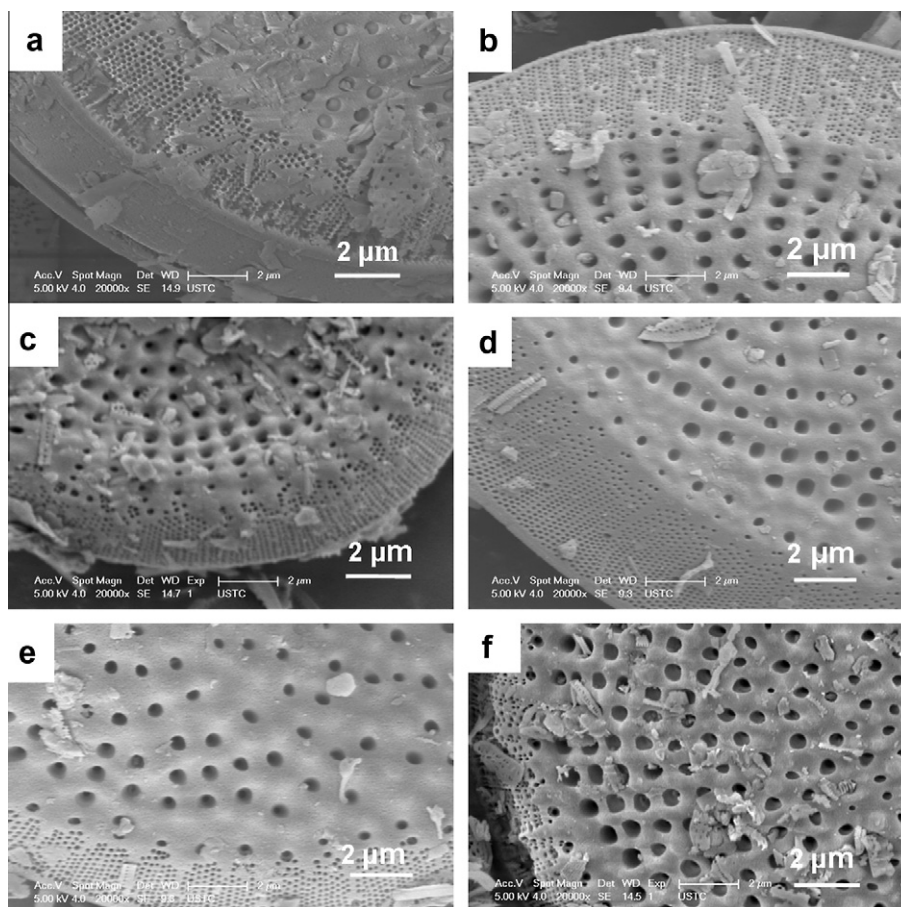


Fig. 2. SEM images of diatomite: (a–f) represent respectively natural diatomite (N-DT); modified by hydrochloric acid with concentrations of 1 M (1DT); 2 M (2DT); 3 M (3DT); 4 M (4DT) and 5 M (5DT).

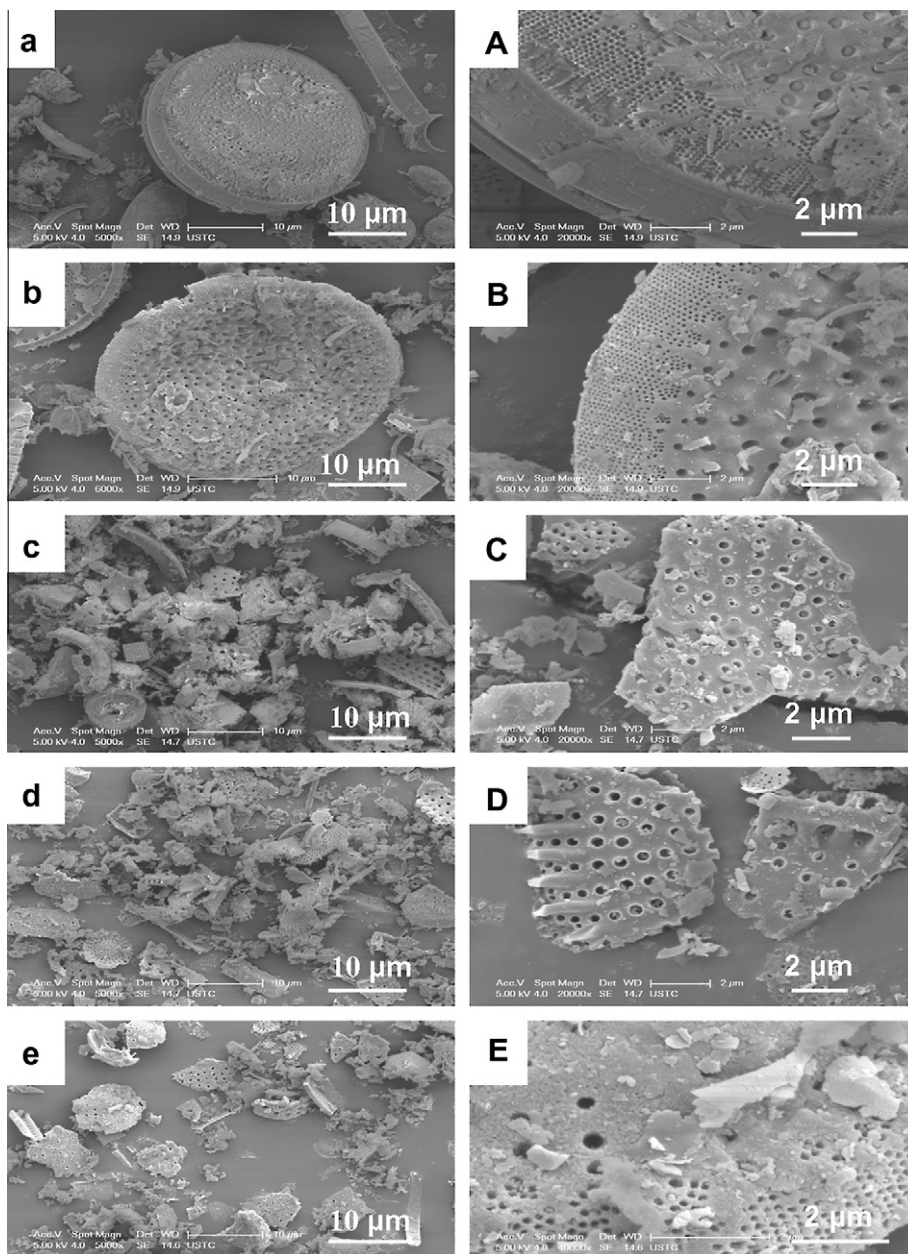


Fig. 3. SEM images of diatomite: (a–e) represent respectively Natural diatomite (N-DT), modified by high-speed shear for 5 s (5s-DT), 1 min (1m-DT), 6 min (6m-DT) and 12 min (12m-DT) in low magnification; (A–E) represent the corresponding images in high magnification.

2.3.2. Specific surface area

The pore size distribution and surface area (S_{BET}) of raw and modified diatomite were measured using specific surface area and porosimetry analyzer (Tristar II, 3020M, Micromeritics, USA).

2.3.3. ICP elementary analysis

Metal ions contents of the filtrate from the HCl solution in which diatomite was soaked were measured by an ICP Elementary Analyzer (ICP 6300, Thermo Fisher Scientific, USA) [16,17].

2.3.4. Catalytic performance

A device to test catalytic performance was developed by our lab (Fig. 9A). Catalysts (cylindrical, diameter of 0.4 cm, length of 0.4 cm) were prepared according to the approach reported [18], and then 20 g of the catalysts were filled in a stainless steel tube (diameter of 1 cm, length of 50 cm) in the device. The catalytic efficiency was determined at 400 °C for 14 min on the device.

3. Results and discussion

3.1. Impurity removal from diatomite by HCl solution

The main component of diatomite is amorphous silica. Some impurities such as ferric oxide, alumina, alkali and alkaline-earth metals oxide [3] were also contained in diatomite. Ferric oxide and alumina are the main impurities for about 1–18% [8]. As shown in Fig. 1, removal efficiency of ferric oxide was significantly enhanced with increasing acid concentration and could reach 35% when hydrochloric acid concentration was up to 5 M. However, removal of alumina by acid could not achieve excellent effect. This may be because of configuration of beta alumina which is the dominant content and could be hardly solved by hydrochloric acid. According to the SEM images of diatomite treated by hydrochloric acid (Fig. 2), we could see that the surface of diatomite, due to the reaction between metallic oxides and hydrochloric acid, was washed.

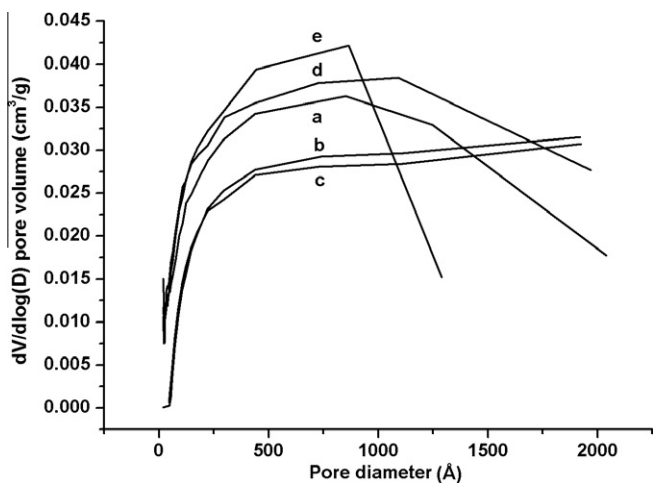


Fig. 4. Pore size distributions of diatomite samples modified by high-speed shear for 0 s (a), 5 s (b), 1 min (c), 6 min (d) and 12 min (e), respectively.

Compared with N-DT in Fig. 2a, the surface of diatomite modified by 1 M hydrochloric acid (1DT) was washed, which resulted in plenty of pores seen clearly in Fig. 2b. With the increasing of acid concentration, the acid wash degree became increasingly severe (Fig. 2c, e and f). Due to the reaction between metallic oxides and hydrochloric acid, the original clogged pores were opened and the pore edges were enlarged gradually seen in Fig. 2a–f. The result indicates that metallic oxide is the main stuff which clogs the pore. It also could be seen in Fig. 2d that ectexine of diatomite was shed by acid wash and most of the pores were dredged.

3.2. Modification effect on the diatomite by high-speed shear

The microstructure of natural and shear-modified diatomite was investigated by SEM (Fig. 3). Compared with natural diatomite, clogged pores were dredged in varying degrees. In addition, overall morphology of diatomite was also displayed. It was found that after high-speed shear treatment the pores could be seen more clearly, which might be because the impurities were removed from the clogged pores. For sulfuric acid catalyst carrier, it is a good phenomenon because more sulfuric acid catalysts could be loaded in the pores. It is worth noting that the modified diatomite still kept integrity after a 5 s shear (Fig. 3b and B). However, the overall

morphology of diatomite was getting destroyed when shear time beyond 5 s (Fig. 3c–e and C–E), which might be not so good for the sulfuric acid catalyst carrier. Therefore, a conclusion could be obtained that high-speed shear is an effective modification approach on diatomite to dredge the pores and the optimum shear time is 5 s.

Pore size distribution (PSD) is an important factor for diatomite to be the catalyst carrier. The preferred pore size range is 100–1000 nm [19,20]. The PSD of N-DT was shown in Fig. 4a. It could be seen that the pore size of N-DT is generally lower than 80 nm, the amounts of the pores with diameter above 80 nm decreased and even decreased fast when diameter above 120 nm. Therefore it is necessary to improve the PSD of diatomite. The PSD of diatomite treated by high-speed shear with different time was investigated as shown in Fig. 4, and the amount of the pore with a certain diameter (APCD) could be represented by $dV/d\log(D)$ pore volume, where D is the pore diameter, V is the total pore volume. The PSD of diatomite treated with 12 min shear (12m-DT) was shown in Fig. 4e, APCD (<100 nm) was greater than that of N-DT and APCD (>100 nm) was lower than that of N-DT. Moreover, the APCD (>82 nm) decreased dramatically. These results imply most of pores in 12m-DT are still the inefficient small size pores. The PSD of diatomite treated with 6 min shear (6m-DT) was shown in Fig. 4d. APCD was completely greater than that of N-DT, but APCD (>115 nm) decreased fast which implies the efficient pores range from 100 nm to 1000 nm are still insufficient. The PSD of diatomite treated with 5 s shear (5s-DT) and 1 min shear (1m-DT) were shown in Fig. 4b and c. Both of them showed, compared with N-DT, less APCD with relatively small diameters and more APCD with relatively large diameters (>140 nm in Fig. 4b and >145 nm in Fig. 4c), which indicates the amounts of inefficient small pores decreased while the efficient larger pores increased. Moreover, the APCD with relatively large diameters remained increasing. Clearly, the PSD was improved. Compared with 5s-DT and 1m-DT, it could be seen that APCD of 5s-DT was completely greater than that of 1m-DT, which means 5 s shear treatment seemed more effective than 1 min shear treatment. As shown in Fig. 3a and A, N-DT remained good integrity but most of the pores still clogged, resulting in the pores with diameter lower than 80 nm is in a majority. After 5 s or 1 min shear, most of the pores were dredged by centrifugal force, leading to much more pores with bigger diameter compared with N-DT. However, 1 min shear could destroy the DU in some degree, therefore the APCD of 1m-DT was lower than that of 5s-DT. When the shear time was prolonged

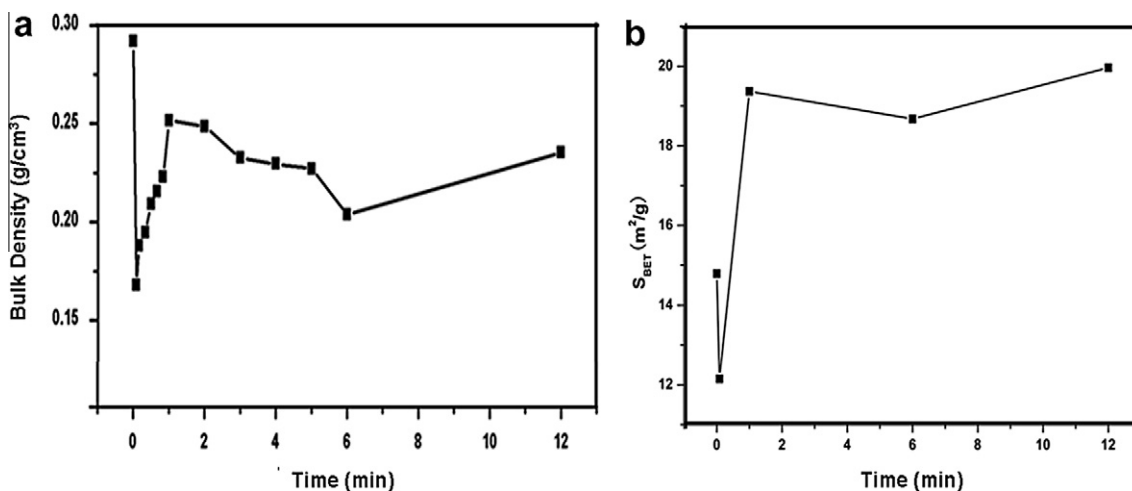


Fig. 5. (a) Effect of high-speed shear time on bulk density of modified diatomite; (b) specific surface area (S_{BET}) of natural diatomite (N-DT), modified diatomite treated with high-speed shear for 5 s (5s-DT), 1 min (1m-DT), 6 min (6m-DT) and 12 min (12m-DT).

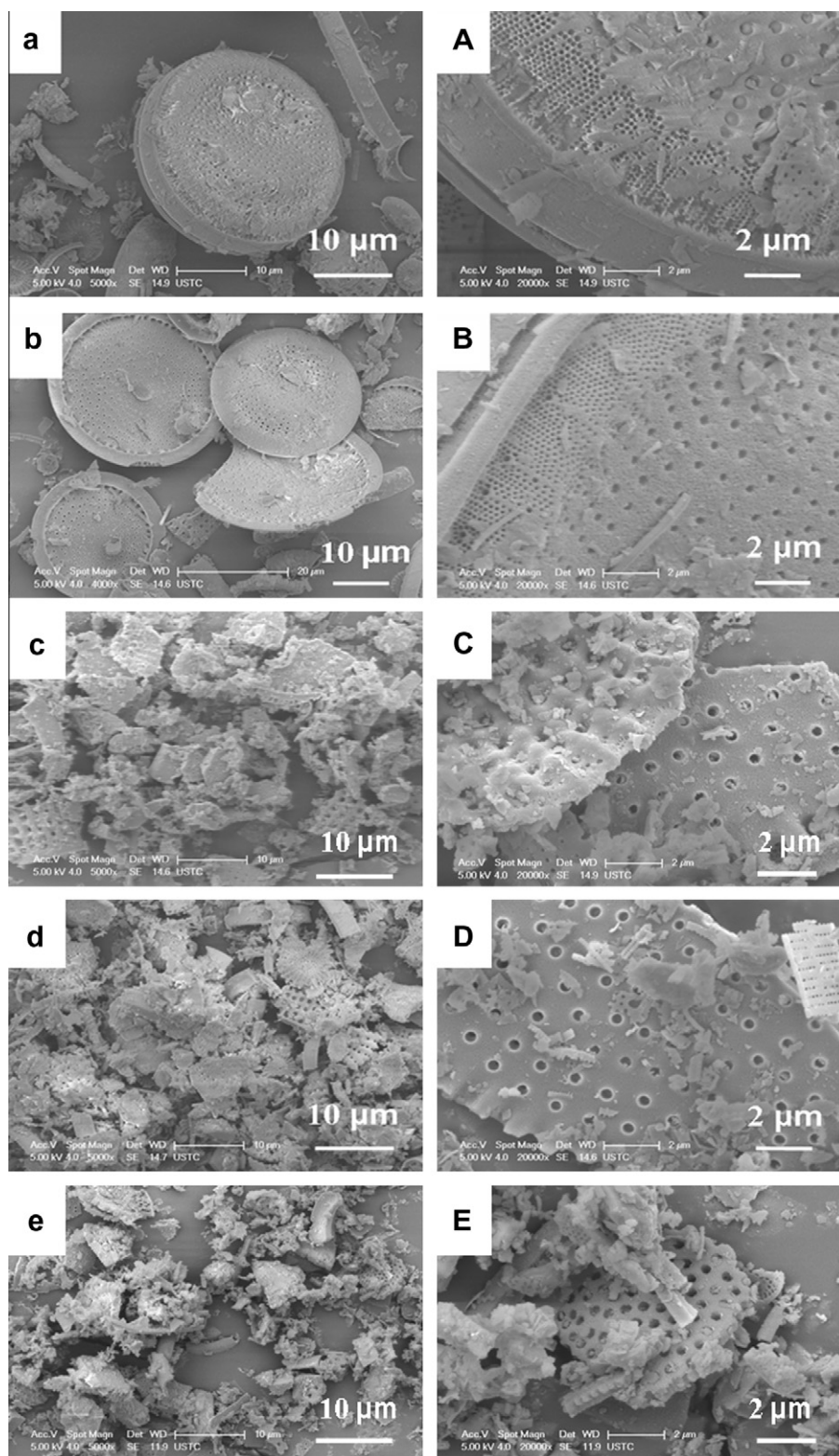


Fig. 6. SEM images of diatomite: (a)–(e) represent respectively natural diatomite (N-DT), modified by ultrasonic for 1 min (1U-DT), 4 min (4U-DT), 8 min (8U-DT), 12 min (12U-DT) in low magnification; (A–E) represent the corresponding images in high magnification.

to 6 min, the DU were damaged more severely (Fig. 3D), so that the APCD (>115 nm) decreased obviously. 12 min shear made the DU destroyed dramatically, resulting in the APCD (>82 nm) decreased much faster. The above results illustrated high-speed shear for 5 s could effectively improve the pore size distribution.

Bulk density is another significant parameter of diatomite to be the catalyst carrier, which can determine the loading amount of the catalyst in carrier [8,19]. Generally, the smaller bulk density of diatomite, the higher loading amount of the catalyst and thus the lower cost. The bulk density–time curve of high-speed shear

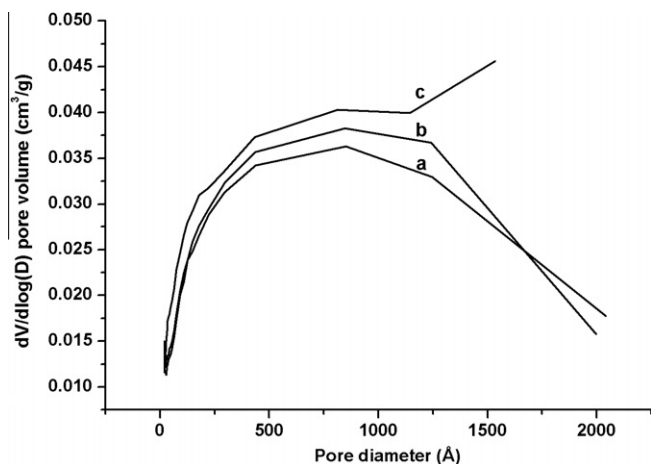


Fig. 7. Pore size distributions of diatomite samples modified by ultrasonic treatment for 0 min (a), 1 min (b), 8 min (c).

treated diatomite was shown in Fig. 5a. It could be seen that the bulk density of diatomite obtained its bottom point at the fifth second. Bulk density of diatomite was closely related to PSD. According to Fig. 4b, compared with other diatomite samples sheared for 0, 1, 6 and 12 min, 5s-DT possessed much more big size pores and thus resulted in the lowest bulk density. From above, a conclusion could be obtained that the optimal shear time of diatomite is 5s.

As seen in Fig. 4b, with shear time the trend of BET specific surface area (S_{BET}) of diatomite decreased at first (<5 s) and thereafter increased obviously. Compared with N-DT, the 5s-DT showed a lower S_{BET} , because 5 s shear treated diatomite possessed much more big size pores and thus increased the volume of diatomite. Five seconds shear made the diatomite appear more loose but still remaining intact morphology of DU and some pores were enlarged. When the shear time was higher than 1 min, most of the DU were broken into pieces, and thus leading to a much higher S_{BET} . This result agreed with that of the structure, pore size distribution and bulk density of diatomite.

Based on the SEM, pore size distribution, bulk density and BET specific surface area analysis above, it could be deduced that high-speed shear might be able to efficiently improve the property of diatomite. The optimal shear time is 5 s to get the best pore size distribution and the lowest bulk density, both of which are critical for a fine catalyst carrier.

3.3. Modification effect on the diatomite by ultrasound

Modification effect on the diatomite structure by ultrasound with different time was also investigated. With the treating time, the diatom units of diatomite were broken more and more heavily (Fig. 6a–e), and meanwhile more and more clogged pores were opened (Fig. 6A–E). At 4th minute there were a few pores still clogged, at 8th minute almost all the pores were opened, and at 12th minute diatom units were broken severely making some opened pores clogged again by some tiny broken DU pieces. Hence, the diatomite treated for 8 min (named as 8U-DT) showed the optimum morphology (best opened without being broken too heavily). In addition, the average pore size of 8U-DT appeared much larger, compared with that of the diatomite treated for 1 min (named as 1U-DT), which is supported by the pore size distribution in Fig. 7. The possible reason is ultrasound wave could radiate forward and generate innumerable vibratory air bubble, which enlarges rapidly in the negative pressure area and shrinks suddenly in the positive pressure area of the longitudinal ultrasonic transmission. Shrunk air bubble could produce thousands of atmospheric pressure to hit surface of diatomite, which can be helpful to dredge the pores of diatomite. Eight minutes ultrasonic treatment leads to a much higher pore number with any diameter (Fig. 7c), lower bulk density (Fig. 8a) and higher S_{BET} (Fig. 8b) than those of 1U-DT.

The pore size distribution of modified diatomite treated by ultrasound was showed in Fig. 7b. We could see that, compared with N-DT, the APCD at 20–170 nm of 1U-DT were much higher, which indicated that a lot of clogged pores were dredged by ultrasonic treatment resulting in a lower bulk density (Fig. 8a) and higher S_{BET} (Fig. 8b). Nevertheless, the APCD (>170 nm) was lower than that of N-DT, which was probably due to the smaller distance between DU under the ultrasound affection.

According to the above results of SEM, pore size distribution, bulk density and S_{BET} , it can be indicated that ultrasound could be used as an efficient modification method of diatomite. With the increase of the treatment time, the pore size distribution become better and the bulk density decreased. The optimal time is 8 min to get the best pore size distribution and the lowest bulk density.

3.4. Catalytic performance analysis

To evaluate the effect of the modification methods on the ability of diatomite as a catalyst support for sulfuric acid production

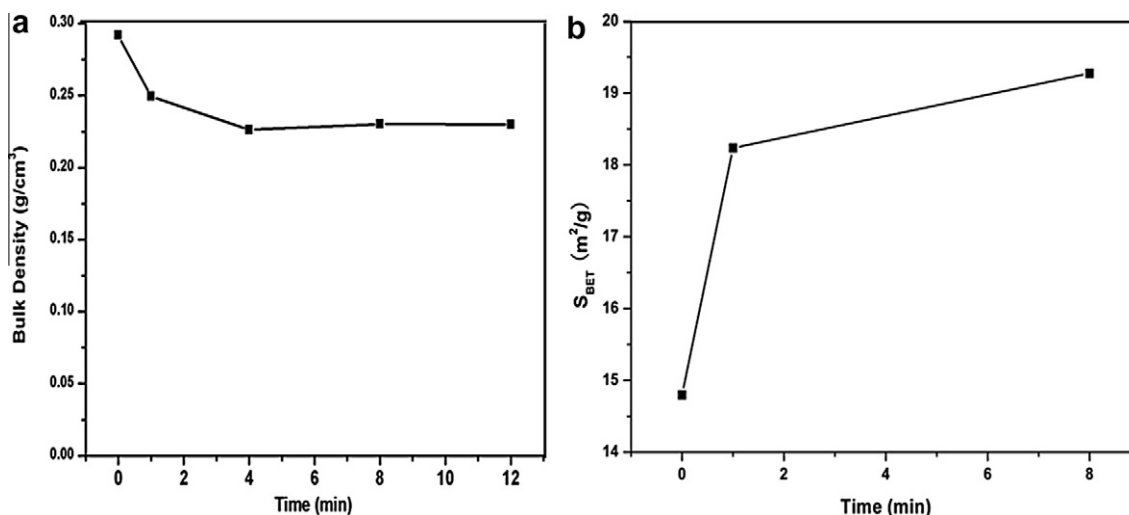


Fig. 8. (a) Effect of ultrasonic time on bulk density of modified diatomite; (b) specific surface area (S_{BET}) of natural diatomite (N-DT), modified diatomite treated with ultrasound for 1 min (1U-DT) and 8 min (8U-DT).

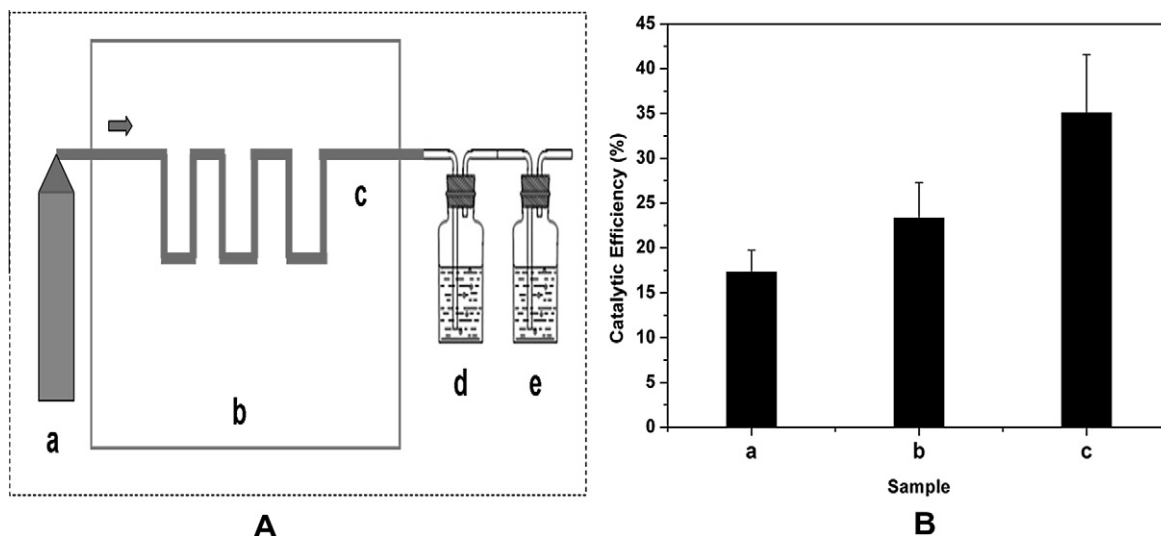


Fig. 9. (A) Catalytic performance testing device: (a) SO_2 source, (b) muffle, (c) reacting tube filled with catalysts, (d) $\text{BaCl}_2\text{-HCl}$ solution, (e) NaOH solution; (B) Catalytic efficiency of the catalysts prepared from (a) natural diatomite (N-DT), (b) diatomite treated with high-speed shear for 5 s (5s-DT) and (c) diatomite treated by ultrasound for 8 min (8U-DT).

process, the catalytic efficiency of the catalysts prepared from N-DT, 5s-DT and 8U-DT was investigated through the device (Fig. 9A). It can be seen from Fig. 9B that the catalytic efficiency of the catalysts prepared from 5s-DT or 8U-DT was higher than that from N-DT. That was to say, high-speed shear and ultrasound were both able to effectively increase the ability of diatomite as a catalyst support for sulfuric acid production process.

4. Conclusions

Modification effects of three methods including high-speed shear, ultrasound, and acid treatment on diatomite used as the sulfuric acid catalyst carrier were studied. Hydrochloric acid could remove most of the impurities containing ferric oxide and alumina from diatomite. The results showed that removal efficiency of impurities could be up to 20% when 5 M HCl was used to treat N-DT. The outstanding low bulk density of 5s-DT was attributed to the higher pore size and intact overall morphology of diatomite. 8 min ultrasonic treatment could dredge and enlarge the pores leading to lower bulk density and higher S_{BET} . It was deduced that the dominant mechanism is that the strong centrifugal force in shear process and cavitation effect in ultrasound which dredged the pores and thus enlarged the pore size quickly and effectively. Modified diatomite showed abundant pores with appropriate size, which could load more catalysts. Therefore the diatomite may be used as sulfuric acid catalyst carrier much more effectively. These methods were proved to be facile and effective. Meanwhile, it is worth noting that all the three methods have their unique modification effects which are complementary and if they are used prop-

erly and cooperatively, the modification effect will probably be much better.

Acknowledgment

The authors acknowledge financial support from The National Natural Science Foundation of China (No. 10975154).

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