Full Length Article

A mullite etching route to tabular α-alumina crystals and application in adsorption desulfurization for dibenzothiophene
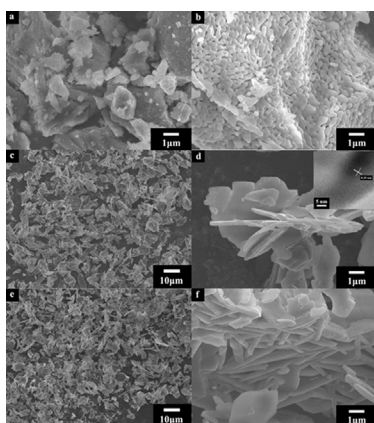
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GRAPHICAL ABSTRACT

SEM images of mullite-corundum composite, sol-gel -Al$_2$O$_3$ and tabular -Al$_2$O$_3$.

ARTICLE INFO

ABSTRACT

Alpha-alumina (α-Al$_2$O$_3$) materials has a wide range of applications because of its excellent properties at high temperature. Tabular α-Al$_2$O$_3$ was unexpectedly synthesized by etching mullite from Si$_x$Al$_y$O$_z$ composites since our original intention was highly porous α-Al$_2$O$_3$. Silica-alumina xerogels with different Al/Si molar ratio as 3, 6, 9 and ∞ (pure alumina) were prepared via sol-gel route, followed by calcination at 1400 °C to obtain Si$_x$Al$_y$O$_z$ composites. XRD results showed that the composite existed as mullite when the Al/Si ratio equaled to 3 and as the combination of mullite and corundum (α-alumina) when the Al/Si ratio equaled to 6 and 9, while pure α-Al$_2$O$_3$ was obtained when Al/Si ratio equaled to ∞ signed as sol-gel α-Al$_2$O$_3$. The mullite phase in Si$_x$Al$_y$O$_z$ composites could be etched completely by hydrofluoric acid under room temperature in terms of the treating time was long enough and left tabular α-Al$_2$O$_3$ for the samples with Al/Si molar ratio as 6 and 9. The interaction between mullite and α-Al$_2$O$_3$ during the thermo process may direct the formation of tabular morphology. Structural and property characterizations show the tabular morphology, low surface area, perfect crystallinity and weak acidity of α-Al$_2$O$_3$. Furthermore, the adsorption of dibenzothiophene, a molecular with planar morphology, on tabular α-Al$_2$O$_3$, sol-gel α-Al$_2$O$_3$ as well as γ-Al$_2$O$_3$ was investigated at room temperature in comparison. Tabular α-Al$_2$O$_3$ exhibited the highest adsorption capacity and best regeneration ability than other two.

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1. Introduction

After burning, the organic sulfur compounds present in the transportation fuels would transform into SO_x, which could further lead to very serious environmental problems. Deep desulfurization of liquid hydrocarbon fuels has attracted more environmental concerns and has been an important research area. Globally, more stringent law has been enacted to limit the sulfur content in the transportation fuels worldwide. So world oil-refinery industry must meet these increasingly stringent regulations on the sulfur contents in the transportation fuels, especially in the diesel fuel due to its higher sulfur content. After the desulfurization requirement turn into deep, even ultra-deep, conventional hydrodesulfurization technology (HDS) is very difficult to remove those refractory sulfur-containing compounds such as 4,6-dimethyl-dibenzothiophene, achieving an ultra-low sulfur level for diesel fuel [1]. Thus, new technologies for deep desulfurization have been explored to meet the urgent needs to produce clean diesel fuel in recent years [1–5]. Deep desulfurization via selective adsorption is regarded as one of the most promising alternative strategy to replace the conventional hydrodesulfurization technology, efficiently removing organic sulfur compounds from diesel fuel [6–10]. It has attracted more and more attentions. The major challenge for deep desulfurization by adsorption is to develop practical adsorbents with high adsorption capacity and high selectivity in adsorbing the sulfur containing compounds that are present in the diesel fuel.

Alpha-alumina (α-Al_2O_3) materials has a wide range of applications which include high strength materials, electronic ceramics, and electrochemical sensors and so on because of its excellent mechanical, thermal, physical and chemical stability at high temperatures. Normally, α-Al_2O_3 crystals are obtained via a sequence of phase transformations such as non-crystalline/amorphous Al_2O_3 to γ to δ to θ to α-Al_2O_3. Different morphologies of α-Al_2O_3 such as 3-dimensional particles, 2-dimentional platelets and 1-dimentional wires or needles can be obtained via different synthesis route [11–14]. It was demonstrated that the morphology of alumina affected the engineering properties. Among various morphologies of α-Al_2O_3, 2-D α-Al_2O_3 that with plate-like or tabular morphology is more useful because of the increasing fracture toughness than the ball-like grains. Previous research has shown that the plate-like α-Al_2O_3 can increase fracture toughness more significantly than ball-like grains because the plate-like α-Al_2O_3 can form crack bridging easily in ceramics matrix [15].

The synthesis of plate-like or tabular α-Al_2O_3 was usually synthesized by adding AlF_3 seeds at the initial synthesis stage. The existence of AlF_3 was considered to direct the crystal growth of plate-like α-Al_2O_3 during the thermal treating process. Furthermore, CaF_2 and MnF_2 were also proved to be used as directing agent for the growth of plate-like α-Al_2O_3 crystal [16]. ZnF_2 is another kind of additive to prepare plate-like α-Al_2O_3. In addition, α-Al_2O_3 platelets were prepared by precipitation method employing material of aluminum nitrate and ammonium salt precipitants with 2 wt% AlF_3 to induce the plate-like morphology [17]. In general, fluoride compounds acting as directing agent is usually necessary during the thermal treating process for the synthesis of plate-like or tabular α-Al_2O_3.

In the present work, we obtained tabular α-Al_2O_3 through a mullite etching route. Silica-alumina xerogels were firstly obtained by sol-gel route from aluminium nitrate ($Al(NO_3)_3·9H_2O$) and tetraethoxysilane (TEOS) with different Al/Si ratios as 3, 6, 9 and ∞. Then the xerogels were heat treated at 1400 °C for 2 h to get $Si_xAl_yO_z$ composites. Followed procedure is to deal the $Si_xAl_yO_z$ composites with hydrofluoric acid at room temperature for fairly long time in order to remove the reactive parts completely and leave the highly pure α-Al_2O_3. To be honest, our original intention of this work was to synthesize α-Al_2O_3 with high surface area to be used as catalyst support for hydrogenation of maleic acid in water. Through this route, solving of silica or mullite from $Si_xAl_yO_z$ composites by hydrofluoric acid (HF) may create more surface or pores so as to improve the surface area of α-Al_2O_3.

Unexpectedly, we got α-Al_2O_3 with tabular morphology other than high surface area. The structural properties of tabular α-Al_2O_3 were characterized by means of XRD, NH_3-TPD, and SEM in detail. At the same time, the adsorption for dibenzothiophene on tabular α-Al_2O_3 was also studied.

2. Experimental

2.1. Synthesis of tabular α-Al_2O_3 crystals

Tetraethoxysilane (TEOS), aluminum nitrate nonahydrate (ANN), ethanol, ammonia solution (25 wt%), hydrofluoric acid (HF, 40 wt%), n-nonane and dibenzothiophene (DBT) was purchased from Aladdin Chemistry Co. Ltd. Deionized water was used throughout the experiments. All the reagents in our study are analytical pure and were used without any further purification.

TEOS and ANN were used as the silica and alumina source respectively. The synthesis procedure was as following: ANN was firstly solved in the mixture of water and ethanol at room temperature to get transparent solution. Different amount of TEOS was then added into the ANN solution under stirring condition with the final molar ratio as ANN:EtOH:H_2O:TEOS = 1:5:4.67:0.33/0.167/0.11, where the Al/Si molar ratio was 3, 6, and 9 respectively. Synthesis was carried out at room temperature and atmosphere. The systems were sealed and continued stirring at room temperature with 800 rpm for 1 h before transferring to 60 °C for aging. All of the three systems formed gel after aging for 3 days. Then the gel was exposed to air at 100 °C to get xerogel followed by thermotreating at 1400 °C for 2 h in argon atmosphere with the temperature increasing rate of 5 °C/min. The obtained samples were named as SA3, SA6 and SA9, respectively. They were then reacted with highly excessive amount of HF solution (10g 40 wt% HF solution for per grammar SA sample) for fairly long time as 30.5 days. In order to remove the reactive components completely, the reaction with HF was repeated for three times under the same condition. For SA3 with Al/Si ratio as 3, the sample is completely dissolved by the HF treatment and nothing can be obtained after stayed with HF solution for the first 30.5 days. The mixtures were filtrated and dried followed by calcination in air at 500 °C to obtain the final materials. The materials obtained from SA6 and SA9 were named as SA6-α-Al_2O_3 and SA9-α-Al_2O_3 respectively. Furthermore, pure alumina was also synthesized by sol-gel route as well as thermotreating at 1400 °C for 2 h in argon atmosphere and the sample was signed as sol-gel α-Al_2O_3.

2.2. Characterization

X-ray diffraction (XRD) detection was carried out on a D8 Advance X-ray powder diffractometer equipped with Cu Kα radiation (λ = 1.54,187 Å). The detection was processed at a scanning rate of 2°/min and with the corresponding work voltage and current as 40 kV and 40 mA respectively. Scanning electron microscopy (SEM) was performed on a scanning electron microscope (JSM-7001F) operated at an acceleration voltage of 10 kV to characterize the morphologies of samples. Brunauer-Emmett-Teller (BET) specific surface areas of samples were determined by nitrogen adsorption-desorption isotherm measurements at -196 °C on Tristar 3020. Prior to the measurement, all samples were degassed at 300 °C for 2 h. Ammonium-temperature programmed desorption (NH_3-TPD) curves were obtained on a TP 5080 automatic multi-purpose adsorption instrument. The sulfur measurement was carried out on a micro coulometer analyzer (Type LC-4, Luoyang-Shuangyang, China).

2.3. Adsorption experiment

The adsorption desulfurization for dibenzothiophene (DBT) on alumina was carried out at room temperature. 14.4 g solution of dibenzothiophene in n-nonane with the sulfur concentration as