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Original Research Paper

The beneficial use of ultrasound in free template synthesis of nanostructured ZSM-5 zeolite from rice husk ash used in catalytic cracking of light naphtha: Effect of irradiation power

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ABSTRACT

A series of ZSM-5 zeolite has been synthesized with ultrasonic energy and their catalytic activity has been investigated in catalytic cracking of light naphtha. ZSM-5 zeolites have been synthesized from rice husk ash without using the organic template. Effect of ultrasound power (100, 200 and 300 W) on physico-chemical properties of synthesized zeolite was investigated. It was found that with varying of the ultrasound irradiation power, the physico-chemical properties of prepared ZSM-5 changed significantly. The XRD analysis showed that the applying ultrasound energy led to decrease the crystal size and crystalinity of ZSM-5. The FESEM analysis showed that the morphology of synthesized ZSM-5 changed from micro-scale hexagonal-shaped to much smaller rough spheres. Furthermore, the external surface area and meso pore volume of ZSM-5 depend on the ultrasound power. Results of catalytic activity test showed that the ultrasound power has great influence on the activity of ZSM-5 and the sample which synthesized with ultrasound power of 200 W showed the highest catalytic activity. TGA-DTG analysis of spent catalyst showed that the amount of coke deposited on the samples is depended on the acidity of catalysts. Furthermore, synthesized catalyst with ultrasound power of 200 W showed the highest structure stability after 12hr catalytic test.

1. Introduction

Light olefins such as ethylene and propylene are important feed-stocks in petrochemical industries. They are produced with thermal cracking, methanol to olefin and catalytic cracking processes [1,2]. In comparison with thermal cracking, catalytic cracking of naphtha produced more propylene at milder operating conditions [3]. Over recent decades, many catalysts including metal oxides, MCM-41, MCM-22, Y-type zeolite and ZSM-5 have been tested in catalytic cracking of hydrocarbons [4–8].

Owning to moderate acidity and high stability, ZSM-5 is an efficient catalyst for the selective production of light olefins in catalytic cracking process [9]. Today's, ZSM-5 are usually synthesized using pure grade materials. The cost of ZSM-5 zeolite can be considerably reduced by using inexpensive starting materials such as kaolin, rice husk and coal fly ash [10–12]. During last decade, some efforts have been made to synthesize ZSM-5 from RHA [13–16]. The rice husk ash includes 90–98% amorphous silica. The impurities of rice husk ash can be eliminated with acid-leaching technique.

The ZSM-5 zeolite is deactivated quickly in catalytic cracking process due to coke deposition. Results from literature show that the diffusion resistances of the reactant and the light olefins within the ZSM-5 micro pores influence on the product distribution [17]. In fact, a shorter diffusion path length through the zeolite micropores leads to prevent sequential reactions leading to decrease of coke formation remarkably. The diffusion path of naphtha and the light olefins can be declined with using smaller size of ZSM-5 [18]. There are many techniques for synthesis of nanocrystalline ZSM-5. Mochizuki et al. Synthesized nanocrystalline ZSM-5 with increasing aging time and aging temperature of gel precursor [19]. However, this method is time consuming approximately. In other methods, surfactant was used in gel precursor in order to separate of the nucleation and growth stages [20,21]. However, high synthesis cost does not permit to use this preparation method in large scale.

Recently, ultrasonic irradiation has been employed to the synthesis wide range of material such as ceramic powders, inorganic materials and catalysts. It is reported that the use of ultrasound

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assisted synthesis methods offers several advantages such as higher surface area and shorter synthesis time in compare of conventional methods. Ultrasonic irradiation has been used in many zeolite synthesis procedures. Synthesized zeolite with this method provided uniform microstructure and interesting physicochemical properties. The acoustic cavitations which resulted from the ultrasonic process can change dissolution, nucleation and crystals growth processes [22]. If the cavitation takes place close to the surface of the particles, high-velocity interparticle collisions occur in a solid–liquid system. Consequently, it leads to increase the chemical reactivity [23]. Results from the literature show that there are some parameters including the dissolved gas, ultrasonic power and frequency can affect cavitation efficiency [24–26].

Sufficient amounts of rice husk can be easily collected at a low cost in north of Iran. Although there are many investigations about using of rice husk ash (RHA) as the silica source for the synthesis of ZSM-5 zeolite, there is relatively little available on the synthesis of high crystalline ZSM-5 zeolite without using an organic template. Furthermore, to our knowledge, there isn't report about the effect of ultrasonic waves on the synthesis of the ZSM-5 zeolite.

In the present work, the ZSM-5 zeolite is synthesized using rice husk ash as a silica source without using the organic structure directing agent. After that, effect of ultrasound power on the physicochemical properties of synthesized catalysts is investigated by using XRD, FE-SEM, NH_3-TPD and N_2 adsorption-desorption isotherm. Then, Catalytic activity of synthesized ZSM-5 is evaluated in catalytic cracking of light naphtha. Finally, the amount of coke deposited on the spent catalyst and structure stability of ZSM-5 during the catalytic test have been investigated with TGA-DTG and XRD, respectively.

2. Materials and methods

2.1. Materials

Analytic grade chemicals of aluminum hydroxide (Riedel-de Haën), sodium hydroxide (Panreac Quimica SAU), hydrochloric acid (Mojalli, 37%) and ammonium nitrate (Merck) were used in synthesis procedure of zeolite. All of them used as received without any further purification. Furthermore, the rice husk was obtained from Iranian rice mill (Langarud). It should be noted that, distilled water was used in the experiments.

2.2. Catalysts preparation and procedures

Catalyst synthesis procedure is schematically illustrated in Fig. 1. As can be seen in this figure, catalyst synthesis can be divided into three stages. Firstly, silica was extracted from rice husk. Rice husk was added to 1 M solution of HCl in a ratio of 10 g:100cc. After 2 h stirring at 90 °C, it was filtered and washed until reach neutral pH. After that, the filtrated cake was dried at 110 °C overnight and calcined at 700 °C for 3 h.

In the second stage, ZSM-5 zeolite was synthesized with the hydrothermal method. At first, silica was added to water and stirred vigorously to prepare a homogeneous slurry. Afterward, a solution of aluminum hydroxide and sodium hydroxide was added to the silica slurry slowly at room temperature. The molar composition of the ZSM-5 gel precursor was 40 SiO_2:1 Al_2O_3:4.5 Na_2O:1500 H_2O. The prepared gel was irradiated with ultrasound at three power levels of 100, 200 and 300 W at 30 °C for 45 min by means of Topsonics (Topsonics Co., Iran) using a titanium probe with a constant frequency of 20 kHz. The gel temperature was controlled with a water bath at temperature of 20 °C. The result mixture was hydrothermal treated at 190 °C in a Teflon-lined stainless steel autoclave for 48 h. The obtained precipitates were washed and dried at 100 °C overnight. For comparison effect of ultrasonic irradiation, a sample was synthesized with same composition under stirring for 45 min without employing ultrasound energy. The synthesized samples are labeled as CZ, ZU100, ZU200 and ZU300 for conventional synthesized ZSM-5, and synthesized ZSM-5 with ultrasound power of 100, 200 and 300 W, respectively.

At the end stage, the synthesized Na-ZSM-5 zeolite was ion exchanged with NH_4NO_3 solution (1 M) at 80 °C for 3 h under reflux condition. After that, zeolite was filtrated and dried overnight. This process was done three times. Ultimately, the ion-exchanged ZSM-5 was calcined at 550 °C for 4 h in air atmosphere. The final powders were shaped as plates which their height and diameter are 5 and 3 mm, respectively.

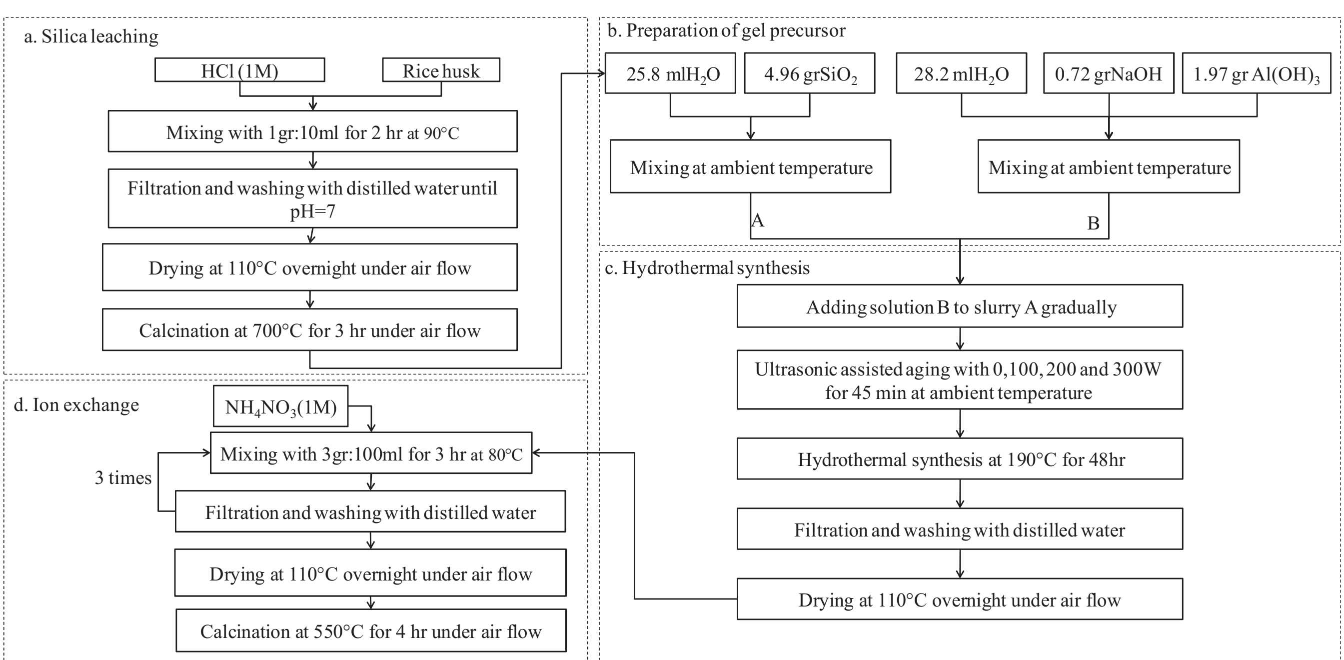

Fig. 1. Schematic flow chart for preparation steps of ZSM-5 zeolite.