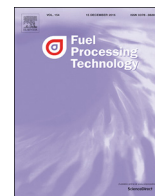




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## Research article

# Preparation of hierarchical structure of Y zeolite with ultrasonic-assisted alkaline treatment method used in catalytic cracking of middle distillate cut: The effect of irradiation time

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## ABSTRACT

Hierarchical structure of NaY zeolite was synthesized with conventional and ultrasonic assisted alkaline treatment methods. Furthermore, their catalytic performance was evaluated in catalytic cracking process. The synthesized catalysts were characterized using XRD, FE-SEM, N<sub>2</sub> adsorption-desorption and NH<sub>3</sub>-TPD analysis. The amount and the type of coke, which formed on the catalysts have also been studied using TGA and FTIR analysis, respectively. The XRD, FE-SEM and BET results revealed that the ultrasonic assisted alkaline-treatment method created more mesopores and lower destruction at zeolite structure, compared to conventional alkaline-treatment method. Furthermore, the results demonstrated that ultrasonic irradiation performed facile creation of hierarchical structure for NaY zeolite. The obtained results from BET analysis showed that by increasing alkaline treatment time, mesoporosity increased gradually. Also, TPD analysis revealed that desilication led to increasing acidity amount. In comparison to the Parent Y catalyst, both the superior catalytic performance and efficient decrease in viscosity, density and molecular weight of liquid product were obtained over the modified Y catalyst which was alkaline-treated, in presence of ultrasound in 60 min. Also the maximum gasoline yield over this catalyst was 47%. Well mesopore structure and moderate acidity also led to decreased coke formation rate and increased catalytic stability and activity.

## 1. Introduction

Currently, crude petroleum is one of the main sources of energy, which used to produce lighter and more efficient fuels, including gasoline and kerosene. Descending world demand of low-quality fuels and unstable oil prices are the serious problems in crude petroleum industries. Moreover, the Earth's primitive petroleum deposits are not renewable and will not last forever. According to some reports, more than half of the crude petroleum reserves are consumed [1,2]. To overcome this problem, the use of other petroleum resources has been considered. Nowadays, to achieve these goals, heavy oil conversion process has been considered in petrochemical and refining industries [1,3].

Conversion of heavy hydrocarbons into light fuels can be separated into various approaches such as thermal cracking [4], catalytic cracking [5], and hydrocatalytic cracking [6]. Among these methods, thermal cracking and hydrocatalytic cracking processes faced with problems such as harsh operating conditions (high temperatures required) and lack of economy, respectively. In order to solve these problems, catalytic cracking has been considered recently.

In many investigations, Y zeolite is demonstrated to be the most effective zeolite in the catalytic cracking of heavy hydrocarbons. High surface area, fairly large pores, strong Brønsted acidity, and high thermal and hydrothermal stability are very important properties to choose an appropriate catalyst for catalytic cracking processes. As Y zeolite has all of these unique properties, it has been extensively applied in many industries, like petrochemical and refinery. The pores in Y zeolite are linked by 12 tetrahedrally, with large diameter about 0.74 nm [7]. However, dimension of heavy hydrocarbon molecules is larger than critical diameter of zeolite micropores. Therefore, the micropores imposes high penetration resistance against the entry of bulky hydrocarbon molecules in catalytic cracking reaction. The penetration resistance leads to poor mass transfer in/out of zeolite micropores. Consequently, the secondary cracking is occurred in the zeolite channels. It leads to formation of undesirable products which cover catalytic active sites of zeolite [8]. It is necessary to facilitate diffusion of macromolecules in/out of zeolite microspores framework.

Transportation of reactant and products in the narrow zeolite channels can be facilitated by creating mesopores in the zeolite framework. Existing mesopores in the zeolite crystals caused to rise of

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inner surface area of the zeolite. Consequently, large number of pore openings are created [9]. The next positive aspect that can be referred to is the increases of catalyst life-time. Rajendra Srivastava et al. [10], found that mesoporous/microporous zeolite exhibited slower deactivation rather than conventional MFI zeolite.

In order to achieve to this purpose, several routs, classified as templating technique [11–13], desilication [14], dealumination [6], have been reported. These strategies were prosperous in acquiring mesoporosity and improved diffusion of molecules. Furthermore, they remarkably enhanced pore accessibility that led to a significant change in product selectivity [15]. However, due to use of expensive templates in the templating techniques, this method introduced serious challenges to large-scale applications [16,17].

Boveri et al. [18] investigated both acid and steam dealumination of mordenite zeolite. These methods directly affected the acidic properties of zeolite due to removal of aluminium from the zeolite framework. However, acidity of catalysts is extremely important in cracking reaction. Therefore, these methods may be associated with dramatically negative impact on catalytic activity. The greatest advantage of desilication method over dealumination method is conservation of initial Brønsted acidity of parent zeolites [19].

Contrary to previous methods, desilication is a low-cost, versatile, simple and highly effective technique with no major Health and Safety Executive (HSE) issues compared to other methods. Because of such advantages, it has become a favorable technique. The selective removal of silicon from zeolite structure caused highly accessible mesoporosity and interconnected mesopores [20]. Most recently, widespread studies were conducted on desilication of various zeolites, such as BEA [21], MFI [22].

Desilication treatment is generally performed with an alkali such as NaOH, KOH,  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{OH}$  [23,24]. There are many factors, in turn, such as concentration of NaOH solution and time of alkaline treatment, which may affect the catalytic activity of zeolites. Juan Rafael García et al. [25] studied the effect of different concentrations of NaOH solution on Y zeolite and evaluated the catalytic performance of modified catalyst in the conversion of 1,3,5-tri-isopropylbenzene. They found that there is a direct relationship between concentration of NaOH solution and congestion of mesopores. According to their results, by increasing concentration of the solution, creation of mesopores (2–10 nm) was enhanced, on the other hand, zeolite crystallinity was reduced. They reported that catalytic performance of modified zeolite was higher than parent-zeolite.

Juan Rafael García et al. [26] introduced mesoporosity to Y zeolite structure by means of alkaline treatment. Pine sawdust bio-oil was upgraded on a fix bed reactor. They reported that catalyst modified by alkaline treatment was more effective than parent zeolite catalyst. Also, coke formation and the selectivity of aromatics respectively on the modified catalyst is lower than the parent catalyst. However, the selectivity of olefins was increased.

Some researchers studied innovative treatments during desilication, such as utilization of microwave irradiation during alkaline treatment [27,28]. Nia Abello et al. [29], used microwave-mediated desilication to introduce mesoporosity into the ZSM-5 zeolite structure. They reported that this method, due to more efficient transfer of thermal heating to zeolite solution, led to enhanced rate of silicon extraction.

Over the last years, many researchers have applied ultrasonic irradiation for the synthesis of zeolites such as zeolite A [30] and MCM-21 [31]. Ultrasound is able to pass through suspension. Transmitted ultrasound irradiation through liquid-solid system led to creation of many unstable micro-bubble in the slurry. Due to collapse of the mentioned micro-bubbles, the micro-mixing phenomenon can occur. Therefore the thickness of diffusion layer was reduced. As a result, it improves mass transfer [32].

In our previous work [33], mesoporous ZSM-5 zeolite was synthesized with ultrasonic assisted alkaline-treatment technique. The research results showed that ultrasound irradiation facilitated the

creation of mesopores in the structure of ZSM-5 zeolite and the catalyst performance interestingly improved; however, it was found that by increasing time of treatment, the structure of zeolite was damaged. Simultaneously, several authors have reported an improved catalytic performance in hydrocarbon conversions over alkaline-treated Y zeolite. However, there is no report about ultrasonic irradiation effects in alkali-treatment on Y zeolite.

The aim of this work was modification of Y zeolite with alkali treatment technique. Therefore, ultrasound irradiation effects on the alkaline treatment were considered and compared with conventional treatment method. The physicochemical properties of prepared samples were characterized by XRD, FESEM, BET and  $\text{NH}_3$ -TPD techniques. The catalytic performance of prepared samples was investigated in the catalytic cracking of middle distillate. Additionally, FTIR and TGA analyses were used to investigate the spent catalysts properties. In order to study the composition of the obtained liquid products from the catalytic cracking reaction, GC/MASS analysis was carried out. In addition, the physical properties of products such as viscosity, density and molecular weight were also analysed.

## 2. Materials and methods

### 2.1. Materials

The raw material which used in this work was sodium hydroxide (Panreac Quimica SAU), and ammonium nitrate (Merck). Furthermore, the NaY zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$ ) was purchased from Naik company (china).

### 2.2. Catalysts preparation and procedures

The preparation procedure of catalysts is summarized in Fig. 1. As it can be seen, the preparation of catalysts can be divided to two stages. At first, the parent NaY zeolite was immersed in 0.5 M aqueous NaOH solution with 1 g zeolite/10 ml ratio. The suspension was kept under stirring at environment temperature (30 °C), for 60 min. The resulted slurry was washed with enough distilled water and filter-suctioned until being neutralized. Finally, the sample was dried at 110 °C overnight. The synthesized sample was referred to as CAY-0.5.

In the ultrasound-assisted alkaline treatment method, the suspension was maintained in exposure of ultrasonic irradiation with 200 W power, using Topsonics (Topsonics Co., Iran). This device has a titanium probe with a constant frequency of 20 kHz. In order to conduct experiments under the same conditions, the alkali-treatment was carried out at 30 °C, in presence of ultrasound irradiation. The slurry was filtrated and washed to reach pH = 7 and dried at 110 °C overnight. In order to investigate the effect of alkali-treatment time on physicochemical properties of zeolite, it was examined at three different point in time (20, 40 and 60 min). These samples were named UAY-20, UAY-40, and UAY-60, respectively.

In the second stage, the parent NaY zeolite and alkaline-treated samples were converted to protonic form. For this purpose, all samples were ion-exchanged three-times with 1 M  $\text{NH}_4\text{NO}_3$  solution at 80 °C for 3 h, under reflux condition. Afterwards, the resultant slurry was washed with hot water and filter-suctioned. The prepared zeolite cakes were dried at 110 °C overnight and calcined under air flow (with flow rate =  $50 \text{ ml}\cdot\text{min}^{-1}$ ), at 550 °C during 4 h.

### 2.3. Catalysts characterizations

Powder X-ray Diffractograms (XRD) patterns were collected, at room temperature, in a PHILIPS-PW1730 diffractometer, using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ), and operated at 40 kV and 30 mA, in scanned angle range ( $2\theta$ ) from 5° to 80°. In order to estimate the Relative Crystallinity (RC) of the samples, total integrated intensities of twelve peaks with miller indices - (111), (220), (311), (331), (511),

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