Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Catalytic cracking of light naphtha over hierarchical ZSM-5 using rice husk ash as silica source in presence of ultrasound energy: Effect of carbon nanotube content

Reza Khoshbin, Shima Oruji, Ramin Karimzadeh *

Chemical Engineering Department, Tarbiat Modares University, P.O. Box 14115-114, Tehran, Iran

A R T I C L E I N F O

Article history:
Received 4 October 2017
Received in revised form 21 April 2018
Accepted 4 June 2018
Available online xxxx

Keywords:
ZSM-5
Ultrasound
Catalytic cracking
Mesopore
Light olefins

A B S T R A C T

Hierarchical structured ZSM-5 was prepared by sonochemical assisted carbon nanotube templated method and their catalytic activity was examined in catalytic cracking of light naphtha. Different amounts of carbon nanotubes (5, 15, 30 wt%) was introduced into the synthesis gel, as a hard template, for mesopore creation. The rice husk ash was used as a silica source. In order to analyse physicochemical properties of synthesized catalysts, multi-techniques such as XRF, XRD, BET, FE-SEM, NH_3-TPD and TGA were used. The obtained results revealed that by adjusting the amount of carbon nanotube, catalyst properties can be favorably tuned. The XRD analysis confirmed successful synthesis of high crystalline ZSM-5 zeolite. According to the FE-SEM analysis, small rough spheres of ZSM-5 were synthesized in all samples. The use of carbon nanotube led to creating new mesopores in the ZSM-5 structure. However, increase in carbon nanotube content led to destruction of micropores of ZSM-5. The acidity of ZSM-5 slightly changed. Results from catalytic activity test showed that high catalyst stability can be achieved in presence of mesopores along with the micropores. The highest olefin yield (54 wt%) and the best catalytic stability were obtained over the synthesized ZSM-5 with 15 wt% carbon nanotube.

1. Introduction

Light olefins are used as raw material for production of polyethylene and polypropylene, vinyl chloride, ethylene oxide, ethyl benzene, and so on. Today, there is growing worldwide demand for light olefins, especially ethylene and propylene. It is predicted that demand for ethylene and propylene will increase by 4.5% and 5.4%, annually [1].

Recently, in order to produce light olefins, various technologies have been used to meet the needs of light olefins market. Nowadays, thermal steam cracking of various kinds of feedstock supply nearly 70% of total propylene production in the world. However, thermal cracking process consumes a lot of energy. Thermal cracking of light naphtha is done at above 800 °C. However, using catalyst in the cracking process reduced operating temperature to 523–700 °C [2]. Consequently, 10–20% of total energy consumption decreased [3]. Furthermore, the amount of greenhouse-gas emissions in catalytic cracking process is lower than thermal cracking process [4]. Ai addition, catalytic cracking led to increasing the amount of propylene to ethylene ratio in the products [3]. Therefore, catalytic cracking of various kinds of feed, including naphtha [5], C_4/C_5 hydrocarbons [6], and heavy oil [7], have been established for the production of light olefins.

Numerous catalysts such as ZSM-5 [8], MCM-68 [9], MCM-22 [4], and Y-type zeolite [10] were used in the catalytic cracking of naphtha reaction. According to the literature, among different zeolites which were examined in the catalytic cracking reaction, ZSM-5 zeolite has been considered as a suitable catalyst in the catalytic cracking reaction due to its strong inherent acidity and good hydrothermal stability [11,12].

The ZSM-5 zeolite is widely synthesized using hydrothermal method. Different silica precursors in various forms of solution, gel, fumed solid, colloidal particles, and organic derivative, were used for zeolite synthesis [13]. The cost of ZSM-5 synthesis highly depends on the type of used raw materials. Hence, the use of low cost silica sources such as rice husk ash and perlite/kaolin has been considered for industrial production of ZSM-5 zeolites [14,15]. The rise husk is an agricultural waste which is obtained as a by-product in rice-milling industries. In north of Iran, rice husk (RH) is easily and adequately accessible. Rice Husk Ash (RHA) is a silica-rich substance which has about 85–98% amorphous silica [16]. There are

---

* Corresponding author.
E-mail address: ramin@modares.ac.ir (R. Karimzadeh).

https://doi.org/10.1016/j.apt.2018.06.001

Please cite this article in press as: R. Khoshbin et al., Catalytic cracking of light naphtha over hierarchical ZSM-5 using rice husk ash as silica source in presence of ultrasound energy: Effect of carbon nanotube content, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.06.001

numerous reports in the literature about the synthesis of different type of zeolites with RHA, as an alternative cheap silica source [17–19]. Using amorphous sources, facilitates dissolution of silica and alumina during hydrogel formation step. The amorphous silica can be extracted from the RH with different thermal and chemical treatments. Kordatos et al. [17], showed that pyrolysis of the RH at temperature above 700 °C led to crystallization of amorphous silica to cristobalite and/or tridymite which was undesirable substances for zeolite synthesis. Krishnarao et al. [20], reported that HCl treatment of the RH led to decreasing the formation of black particles in the RHA.

Due to unique microporous structure of ZSM-5, it has perfect catalytic activity and shape selectivity in the catalytic cracking reaction [21]. However, deactivation of ZSM-5 due to coke deposition is one of the main drawbacks of catalytic cracking of naphtha over ZSM-5. Microporous structure, small channels, and pore size restriction of ZSM-5 zeolite led to diffusion limitation of large hydrocarbon molecules involved in the catalytic cracking reactions. Therefore, cavities of the ZSM-5 was blocked by coke deposition [22,23]. Zhang et al. [24], created secondary porosity in the ZSM-5 structure and used it in the n-heptane catalytic cracking reaction. Their results indicated that the use of hierarchical ZSM-5 led to increasing selectivity of both ethylene and propylene. Different synthesis approaches have been proposed to increase the accessibility of bulky molecules to internal surface of zeolite, such as preparation of nano-size ZSM-5 particles [25], post-treatment to create extra porosity with alkali-treatment method [26] and direct synthesis of mesoporous ZSM-5 [27]. Recently, the creation of mesopores in the zeolite structure has been attracted a considerable attention. The interconnected mesopores act like a channel and facilitates diffusion of reactants and the products [28]. Despite recent successful application of post-synthesis method, this method declined zeolite crystallinity. Moreover, alkaline treatment method impresses acidic sites by altering the Si/Al ratio. It led to decreasing catalyst activity in the catalytic cracking reaction [28]. In contrast, direct synthesis of mesoporous ZSM-5 creates smooth and uniform mesopores in the zeolite crystals [29]. In this method, a secondary template is used for creation of mesopores in to the zeolite structure. In such a case, the mesoporous structure is created during ZSM-5 synthesis with hydrothermal method. The types of templates which were used in this method can be divided into two categories of hard templates such as carbon black [30], carbon nanotube [31], and soft templates including surfactant [32]. Compared to the soft templates, hard templates offer several advantages in facile synthesis and economical point of view [33]. For these reasons, many researchers have studied carbon template synthesis of ZSM-5. By choosing an appropriate carbon substance, the size and volume of mesopores can be controlled [34]. Because micro/meso zeolite is formed by nucleation of zeolite crystals around carbon particles, carbon is trapped inside the zeolite particles [34]. Carbon template was removed by calcination treatment after crystallization. Ultimately, zeolites with intra-crystalline mesopores and controlled pore size distribution was synthesized [35].

It was reported that the kind of template which was used in the synthesis of mesoporous zeolite, has a great impact on the zeolite quality. Carbon black and Carbon Nano Tube (CNT) show some differences in creation of mesopores in zeolite structure. Incorporation of carbon black into the zeolite hydrogel may create cave-like mesopores in the zeolite structure that were not interconnected together. Therefore, the penetration limitation of feed and products did not improve. However, Using carbon nanotube (CNT) led to creation of monotonic and uniform mesopores in the zeolite structure [36]. The Korea Advanced Institute of Science and Technology (KAISTs) produced a carbon mesostructured compound (CMKs). According to the literature, incorporation of this compound in the zeolite gel precursor led to creating more uniform and straight mesopores in the zeolite structure. However, due to its high price, it has rarely been used [37]. Zhou et al. [38], synthesized ZSM-5 zeolite by introducing various templates and evaluated their catalytic activity in the methanol-to-aromatic (MTA) reaction. Their results showed that the highest BTX yields were obtained over the zeolite synthesized with the CNT. Furthermore, they reported that the amount of deposited coke over the synthesized mesoporous zeolite with the CNT template was lower than the other zeolites.

Owning to simplicity and rapid processing, the ultrasound-assisted synthesis method gradually became a preferable technique for synthesis of nanoporous materials. Mu et al. [39], investigated the effect of ultrasound irradiation on the synthesis of the SSZ-13 zeolite. Their results showed that the use of ultrasonic irradiations extremely increased the crystal formation rate. However, they reported that the effect of ultrasound (US) energy on the final structure of zeolite was negligible. The use of ultrasound energy decreased required time for zeolite crystallization. For instance, the presence of the US irradiation reduced time of MCM-41 crystallization from 120 h to 48 h [40]. When the US passes through the solid-liquid, many unstable micro-bubbles are created in the slurry. Due to collapse of mentioned micro-bubbles, the micro-mixing phenomenon occurs. Consequently, the dissolution processes, chemical reactions, nucleation and growth of precipitates are promoted [41].

The effect of the US irradiation power on the ZSM-5 synthesis was investigated in our previous work [42]. Results revealed that the sample which was synthesized with ultrasound power of 200 W had the highest catalytic activity and stability in the catalytic cracking of naphtha reaction. Although carbon nanotube, has been used as a hard template for zeolite synthesis in previous studies, effect of using ultrasound irradiation on the particle size of hierarchical ZSM-5 zeolite has not been reported yet. The aim of this research was to investigate the effect of using different amount of the CNT content on the physicochemical properties and catalytic activity of ultrasonic assisted synthesized hierarchical ZSM-5.

The influence of the CNT content on the physicochemical properties of synthesized ZSM-5 was evaluated by X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Field Emission Scanning Electron Microscopy (FE-SEM), Temperature-Programmed Desorption of ammonia (NH_3-TPD) and Thermal Gravimetric Analysis (TGA). Ultimately, the catalytic activity of synthesized ZSM-5 was investigated in catalytic cracking of naphtha reaction.

2. Materials and methods

2.1. Materials

The starting materials used in synthesis procedure of ZSM-5 zeolite were Analytic grade chemicals of aluminium hydroxide (Riedel-de Haën), sodium hydroxide (Panreac Quimica SAU), hydrochloric acid (Mojalli, 37%), ammonium nitrate (Merck), carbon nanotube (carbon > 90%, 20–40 nm diameter) and distilled water. All of them were used as they were, without making any further purification. Furthermore, rice husk was obtained from Iranian rice mill (Langarud).

2.2. Catalysts preparation and procedures

The preparation steps of synthesis catalysts are schematically shown in Fig. 1. Schematic flow chart for preparation steps of ZSM-5 zeolite. As can be seen in this figure, catalyst synthesis has four steps. In the first, silica was extracted from the RH with

Please cite this article in press as: R. Khoshbin et al., Catalytic cracking of light naphtha over hierarchical ZSM-5 using rice husk ash as silica source in presence of ultrasound energy: Effect of carbon nanotube content, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.06.001