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Review

Recent advances in naphtha catalytic cracking by nano ZSM-5: A review

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ABSTRACT

This review discussed the use of nano ZSM-5 in naphtha catalytic cracking. The impact of nano ZSM-5 on product selectivity, reaction conversion and catalyst lifetime were compared with micro-sized ZSM-5. The application of nano ZSM-5 not only increased the catalyst lifetime, but also gave more stability for light olefins selectivity. The effects of the reaction parameters of temperature and feedstock on the performance of nano ZSM-5 were investigated, and showed that high temperature and linear alkanes as feedstock improved light olefin selectivity and conversion.

1. Introduction

Light olefins, such as ethylene and propylene, are important raw materials and the demands for them are growing. These materials are feedstock used in different industries such as the production of resins, polyethylene, polypropylene, ethylene oxide, fibers and other chemicals [1–4].

The main method for the production of light olefins has been naphtha thermal cracking. Due to high energy consumption, high reaction temperature, high amount of CO_2 emission, difficult control of the selectivity of specific light olefins and also low yield of ethylene and propylene (approx. 25% and 13%, respectively), much attention has been given to developing more efficient processes [5–13]. The catalytic cracking of naphtha is a promising substitute for thermal cracking. Unlike the thermal process, catalytic cracking is more efficient in energy use and gives high yields of propylene and ethylene at relatively low temperatures [14–25].

There are two different pathways for the catalytic cracking of hydrocarbons: the monomolecular and bimolecular mechanisms. The monomolecular pathway involves the protonation of an alkane to form an intermediate pentacoordianted carbonium ion that cracks to yield an alkane and alkene. This is the main mechanism for paraffin cracking. The bimolecular pathway is a sequential process involving the protonation of a double bond to form a tricoordinated carbenium ion followed by isomerization and β-scission to form a free olefin [15,26,27].

Different zeolites such as ZSM-5, zeolite A, zeolite X, zeolite Y, zeolite ZK-5, zeolite ZK-4, synthetic mordenite, dealuminatedmordenite, and naturally occurring zeolites including chabazite, faujasite, mordenite were studied for catalytic naphtha cracking [4,5,20]. The appropriate catalyst for naphtha cracking is an acidic zeolite such as ZSM-5 [14,15,19–34]. ZSM-5 is a synthetic zeolite with a high silica content. The framework

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Table 1
Micropore volume and external surface area of two prepared samples [52].

Sample	V_m (cm³/g)	External surface area (m²/g)
Nano ZSM-5	0.18	35.3
Micro ZSM-5	0.18	5.9

V_m: Micropore volume.

structure of ZSM-5 consists of one straight and one sinusoidal intersecting channels, with a 10-membered ring opening (pentasil zeolite). Due to its high thermal and hydrothermal stability, resistance to deactivation, high acidic and activity, cation-exchange capability, well-ordered pore network and molecular shape selectivity arising from a unique framework structure, ZSM-5 zeolite has received a lot of attention as a catalyst, especially in catalytic cracking [35–43].

However, there are some limitations which hinder ZSM-5 in extensive use for cracking. Generally, in high acidic zeolites, such as ZSM-5, the lifetime of the zeolite decreases due to an increase in coke formation on the catalyst surface [35,42,43]. In fact, coke fouls the catalyst surface and blocks the micropores, resulting in the deactivation of zeolite [18,44]. Moreover, due to large crystal size of the zeolite compare to its micropores, the diffusion and transfer of reactants and product molecules within the pores are limited [45].

One method to overcome these problems is the reduction of the zeolite crystal size to the nano scale. Decreasing of the zeolite crystal size not only provides more surface, and therefore more active sites, but also the resistance to pore diffusion will be reduced [18,35,42,43,45–51]. In fact, it is expected that by application of the nano instead of the micro ZSM-5 as catalyst, the activity and deactivation rate will be improved significantly.

This review discusses different researches on the effect of ZSM-5 crystal size reduction in the naphtha catalytic cracking process. Different factors such as selectivity and lifetime of nano ZSM-5 are compared with those of the micro-sized samples and the results are discussed thoroughly. Moreover, the effect of the reaction parameters of temperature and feedstock were investigated to clarify the most suitable reaction condition for naphtha catalytic cracking using nano ZSM-5.

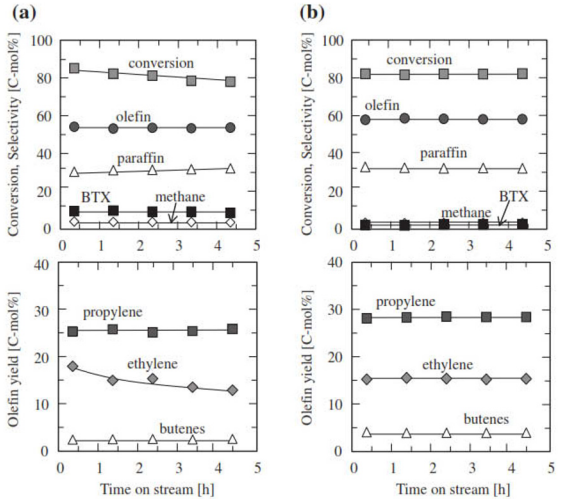

Fig. 1. Conversion, selectivity and olefin yields for *n*-hexane cracking over micro ZSM-5 (a) and nano ZSM-5 (b) [52].

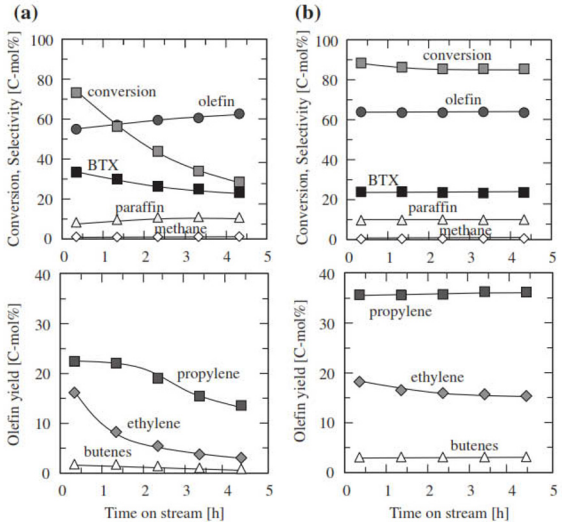

Fig. 2. Conversion, selectivity and olefin yields for cyclohexane cracking over micro ZSM-5 (a) and nano ZSM-5 (b) [52].

2. Nano ZSM-5 application in naphtha catalytic cracking

2.1. Product selectivity and olefin yield

The reduction of the crystal size affects the selectivity and yield of the products by controlling the diffusion rate of reactants and products through the pores of the ZSM-5 catalyst. In fact, smaller catalyst particles result in the reduction of both reactants and products diffusion resistance, so the residence time in the catalyst pores becomes shorter and consequently further reactions which lead to heavier hydrocarbons and coke are inhibited.

In an experiment, Konno et al. [52] synthesized nano ZSM-5 zeolite by the emulsion method [53–58]. For comparison, micro-sized ZSM-5 was also prepared by the conventional method. The size of the nano ZSM-5 was 90 nm and the micro-sized sample was 2300 nm. Table 1 gives the micropore volume and

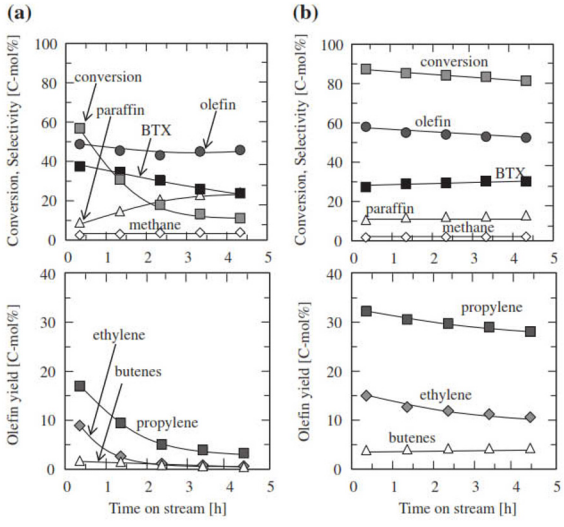

Fig. 3. Conversion, selectivity, and olefin yields for methyl-cyclohexane cracking over micro ZSM-5 (a) and nano ZSM-5 (b) [52].