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Review Paper

Investigation of zeolite modification methods in n-hexane catalytic cracking process

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1. ABSTRACT

One of the main processes of producing light olefins is catalytic cracking. The commercial catalysts used in this process are zeolite catalysts. According to the operating conditions of the reaction, the used catalysts are deactivated after some time. One of the major challenges in this process is finding an optimal catalyst that has proper performance and high selectivity over propylene. Reduction of the diffusion resistance in zeolite micropores and easier access of materials to active sites and create mesopores, numerous modifications were made using pre- and post-synthesis methods (synthesis of zeolite with special morphology, crystal size reduction, dealumination and desilication). These modifications have increased the lifetime and improved catalyst performance. In this research, the recent developments in zeolite catalysts and methods of improving the performance of ZSM-5 zeolite catalysts in the catalytic cracking process of normal hexane have been described.

Keywords: Hierarchical Zeolites; Catalytic Cracking; Post Synthesis; Desilication; Delamination.

2. INTRODUCTION

Propylene is used as a key element for producing polypropylene, propylene oxide, and acrylonitrile in the petrochemical industry. The main process of producing light olefins such as ethylene and propylene is the thermal cracking of naphtha. However, according to the low P/E ratio, low volume of propylene production, greenhouse gases such as CO₂ and high energy consumption at high temperatures (T>800°C) in this process, researchers seek to improve the operational conditions of catalytic cracking naphtha with high efficiency. The use of zeolite catalysts is very common in this process. Due to their catalytic properties, high surface area, special porous structure, abundant acid sites, and thermal stability are widely used in environmental and commercial fields, especially in petroleum and petrochemical industries. According to the conducted research, one of the most appropriate catalysts for the catalytic cracking of naphtha is acidic zeolite that ZSM-5 [1].

Despite having the desired properties in ZSM-5 zeolite such as thermal stability and high acid activity and high selectivity, the catalyst activity is typically associated with the limitation of mass transfer in micropores, long spread pathway and the presence of micropores in this zeolite is not enough. The micropores when reagents or products are massive, resulting in a slow mass transfer of these molecules.

To overcome other challenges, such as the diffusion limitation in zeolites micropores channels, fast deactivation, and the development of a stable catalyst for the catalytic cracking of n-hexane to light olefins, many studies such as reducing the crystal catalyst size to the nano size, preparation of zeolite with special morphology, creation of secondary mesoporous by synthesis of hierarchical zeolites, it has been suggested to reduce the diffusion pathway.

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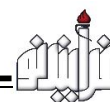


Figure 1. Schematic representation of different strategies of hierarchical zeolite formation [1]

The available methods in the production of hierarchical zeolites are classified into two methods: top-down and bottom-up you can see in Fig.1.

3. RESULTS AND DISCUSSION

3.1. Modifying and improving the performance of HTO process catalysts

3.1.1 Reduction of crystal size

Reducing the crystal size from micrometer to nanometer scale leads to more mass transfer by reducing the length of internal diffusion pathways and more access of reactants to catalytic active sites [2].

Zhou and her colleagues investigated the effect of mesoporous ZSM-5 crystal size (using APTES) on reactant diffusion and the catalytic performance of ZSM-5 in the n-heptane catalytic cracking process. For this purpose, they synthesized of types of zeolites with crystal sizes, one more than 50 nm (HZ-0) and 3 other types with a size of 15 to 50 nm (HZ-1_HZ-3).

$$\text{Thiele modulus } (\varphi) = \frac{\text{The rate of reaction on the surface}}{\text{the rate of diffusion}}$$

$$\text{Effectiveness factor } (\eta) = \frac{\text{The actual rate of the reaction that is taking place}}{\text{Ideal rate of the reaction}}$$

According to the definition of the two quantities above the line; when the Thiele modulus value is lower, the eta value is close to 1, which means that the diffusion rate in that catalyst is reasonable and the reaction rate is not affected by mass transfer limitations.

3.1.2 Synthesis of zeolite with specific morphology

ZSM-5 zeolites with special morphology are designed to reduce the length of the diffusion pathways to improve diffusion efficiency. The specific morphology includes ZSM-5 hollow zeolite, sheet-like MFI zeolite, b-oriented MFI zeolite, composite zeolite, etc.

3.1.3 Hierarchical zeolite synthesis

3.1.3.1 Dealumination

Dealumination is a suitable method to increase the ratio of Si/Al in zeolites without causing a significant collapse in their crystal lattice.

Galal et al [4] investigated the effect of dealumination with different concentrations of 1, 3, and 6 M nitric acid on Mordenite zeolite in the normal hexane catalytic cracking process. In this study, the highest selectivity to propylene with the ratio of propylene to ethylene = 1.26 was related to the modified sample with a concentration of 1 M nitric acid.

3.1.3.2 Desilication

Among the post-synthesis methods, desilication with NaOH solution is used significantly to create mesopores. Wu et al [5] succeeded in creating mesopores during the desilication operation of ZSM-5 using (NaOH + Piperidine) solution. Adding piperidine controls the number of silica atoms removing the structure.

3.1.3.3 Fluorination

Another effective method to modify zeolites is a modification with hydrofluoric acid (HF) solution, which does not significantly change the crystallinity of zeolites modified, and Al species are selectively dissolved, which leads to an increase in the external surface area and mesopore volume and a decrease the acidic sites with higher Si/Al ratio. The catalytic activity increases due to the formation of mesopores after modification with (HF).

3.1.4 Acidic sites on the external surface

A large number of acid sites on the external surface due to the rapid formation of coke on these sites causes the rapid deactivation of the catalyst, which blocks the entrance of the pores.



Using the post-synthesis method (using nitric acid), some of the external acidic sites were selectively removed. The conversion of the modified zeolite catalyst in the catalytic cracking process of n-hexane increased to about 96%.

4. CONCLUSION

The catalytic cracking of the n-hexane process is one of the most important processes for light olefins production. Despite the basic role of zeolite catalysts in this process, the existence of micropores alone influences the negative effect on the mass transfer of reagents (products) to (of) the active sites that result in this, the formation of coke and followed by the deactivation of the catalyst. Many modifications are carried out using pre- and post-synthesis methods (including synthesis of zeolite with specific morphology, a decrease of crystal size, dealumination, and desilication). This modification has led to a rise in longevity (stability), hydrothermal stability, and improved performance of the catalyst. The acidity and support porosity has a great influence on the performance of the catalyst process and alters the performance of the catalyst. The modification of zeolite catalysts and creative mesopores is a significant way to improve mass transfer and access to acid sites and produce high-yield light olefins. Generally, the presence of acid species and zeolite structure has a great influence on the properties of the catalyst; therefore, controlling for both the acidic properties and catalyst architecture, gives a high activity, selectivity, and more stability in the catalytic cracking n-hexane, is a key point for the optimum catalyst design. Despite the numerous methods of zeolite modification and synthesis, the choice of sophisticated methods may be inefficient in terms of economical and industrial aspects. Therefore, the synthesis of the catalysts is expressed by different modification methods, which are cost-effective, as described.

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