Treatment Improvements of Catalysts for Higher Yield of Catalytic Cracking

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Abstract. Catalytic cracking is the major source of light olefins. And it is proved that some aromatics can also be obtained via catalytic cracking. Products are always impacted by many factors, especially catalysts. After a long time of development of industrial and commercial catalysts, a general kind of catalysts used in FCC (Fluid Catalytic Cracking) process is molecular sieves. Zeolites molecular sieves are normally applied to enhance the products of light olefins and BTX(Benzene-Toluene-Xylene). This paper highlights some methods to improve the zeolites from different perspectives based on those conditions that can affect zeolites. Some characteristics are discussed like structure, acid sites, acidity, etc. Besides, the cost of synthesis and regeneration should be considered as well. Some ideas about the modification of zeolites are summarized in this article like ion exchange of zeolites by rare earth metals or acids, which all prove the great success of improvements of zeolites. Olefin and BTX production increase effectively with these modified catalysts. There will be more kinds of catalysts in the future by combinations and modifications.

1 Introduction

Steam cracking used to be the main process to produce light olefins. But there are many disadvantages of steam cracking like hard operating conditions or great emission of wasted gas. With the development of science and technology, other processes are widely applied to replace steam cracking [1].

FCC is a vital processing unit in petroleum refining. It is extensively used to produce light olefins, BTX, fuel oils like gasoline, kerosene and so on. Light olefins and BTX are demanding products of the petroleum industry to manufacture many byproducts, which means that the yield of light olefins and BTX plays an important role in petroleum refining [2]. The relation of different units in the whole refinery process is shown in Figure 1 with a schematic diagram of the whole petroleum refinery process.

The feedstock in the catalytic cracking is often inferior. So, it requires harder operating conditions like high pressure and temperature. But it will bring lots of problems like damage on the equipment and environment due to the continuous operations and emissions. The catalyst is another crucial factor in the process. It is known that catalysts can ease the reactions and lower the activation energy, changing the procedures.

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of reactions. However, there is a variety of catalysts with different components and functions. At the beginning of catalytic cracking in the last century, some natural acidic substances were extracted as initial catalysts. And then, amorphous aluminum silicate was used as catalysts in FCC. Some other metal oxides, especially transition metals, were also applied to FCC. After that, with the molecular sieve’s popularity as an appliance of catalyst materials, the quality and yield of catalytic cracking products improved outstandingly [4]. Molecular sieves developed in the last century and contributed greatly to the development of catalytic cracking. Their unique structure and selectivity promote the production. In many kinds of molecular sieves, zeolite is a type of high activity and selectivity, which follows the shape selectivity mechanism. Main products catalyzed under molecular sieves are those light olefins like C3 and C4. The pathways and acid sites inside molecular sieves are the key point that catalyzes reactions. In the modern petroleum industry, there have been many advanced machines and equipment. But catalyst is exceedingly vulnerable to losing activity because of coke deposits or being poisonous from some alkaline metal compounds. Therefore, it is necessary to adapt reaction conditions to catalysts, as well as seek efficient and economical methods of reactivation. With varieties of molecular sieves, the whole process of catalytic cracking technologies can work longer and have more economic profits.

This article is mainly concerned with some common improvements for molecular sieves in the modern petroleum industry. In recent research, there are some factors that are always considered efficiently to impact the characteristics. For different kinds of molecular sieves, it will take different time and materials to synthesize. The characteristics are affected by conditions like temperature, methods like stirring or the number of materials like Si/Al. Moreover, molecular sieves require some treatments to have catalytic activation by ion exchanging like ammonia, which means that there will be different results using different ion solutions due to the great distinctions of electron structure among elements. Additionally, catalysts usually consist of three parts: activated component, auxiliary and carrier. Some molecular sieves can be combined and function better if mixed properly. New mixed catalysts will have superior functions than single-activated components and overcome some disadvantages when used independently. Since auxiliaries and carriers can provide some concerted enhancement and protection to reactions. The examples of this article will be related to zeolite molecular sieves like ZSM-5, ZSM-10, USY, etc., which can demonstrate the methods mentioned above.

2 Mechanism of catalytic cracking

To produce light olefins, VR (Vacuum Residue), VGO (Vacuum Gas Oil) and naphtha are commonly used as feedstock to produce a series of products. Normally the reactions follow a hierarchy sequence. And it is only one of the purposes to obtain light olefin via catalytic cracking. There are some other products accounting for a great portion of the petroleum refining industry like BTX. The amount of PAH (Polycyclic Aromatic Hydrocarbon) accounts for a great portion of the raw materials. And BTX can be produced via catalytic cracking of PAH. Cracking of PAH requires higher operating conditions. And condensation reactions are more likely to happen due to the existence of PAH. And then much coke may deposit causing damage to equipment and catalyst. So obviously it can be solved with some improved catalysts. Catalytic cracking normally follows the carbocation mechanism. The break of the beta position of carbon cation is the most basic reaction. Alkane loses hydrogen at active medal sites inside molecular sieves and olefins form carbocation. There are single carbocation and double carbocation mechanisms competing with each other. The distribution of products is different if changing the portion of two kinds of reactions [5]. Moreover, PAH accounts for a higher portion of the feedstock. And the aromatics are harmful to the environment. Cracking is a better choice to produce some byproducts. The cracking of PAH is more difficult. Pi bonds within PAH have a conjugation effect, which will make it too stable to crack. Stronger acid is more helpful for the cracking of naphthenic, but condensation reactions of PAH are more likely to happen to produce coke than cracking reactions, which should be inhibited [6]. Solid acid catalysts are common in catalytic cracking technology, especially the widespread appliances of zeolite molecular sieves. The sizes of pathways inside molecular sieves are extremely tiny so the mechanism follows shape selectivity. Reactions carried out with catalysts include seven steps: external and internal diffusion of reactants, adsorption on active or acid sites, surface reactions to products, desorption of products, internal and external diffusion of products. Following the shape selectivity mechanism, pathways of molecular sieves determine the size of molecules of both reactants and products. For example, the size of reactants has to be smaller than the sizes of pathways so that they can diffuse into catalysts. Also, reactants have to break up until the products are able to diffuse out the catalysts. And the structure will restrict the transient state of reactions because of the limitations of inside pathways. This unique selectivity is helpful to acquire specified products, especially some light alkane and alkene of catalytic cracking [4].

3 Enhancement of yields

After knowing the mechanism of catalytic cracking and catalysis, it is necessary to analyse the factors impacting catalytic cracking. From the macroscopic perspective, reaction conditions and design of techniques both have significant impacts on the efficiency of the process. Besides, the quality of feedstock is another factor that cannot be ignored. Feedstocks of catalytic cracking are generally inferior to others. Therefore, reaction conditions are relatively more difficult than other technology, which will have some negative influence on catalysts and waste too much energy. On
the other hand, improvements in catalysts can be another solution to increase yields of catalytic cracking. This section will mainly talk about some improvements to the catalysts from the microscopic perspective, especially zeolites.

3.1 Synthetic conditions of molecular sieves
The methods to synthesize will definitely affect the efficiency and characteristics of molecular sieves. Diameter is one of the main factors because diffusion resistance will decrease in smaller zeolites making it easier to react. For example, in terms of ZSM-11, it is traditionally required to add some seed in hydrothermal conditions. For the methods of synthesis, it always spends too much time like a couple of hours. There is some research on microwave to heat greatly saving the period for the synthesis. It is illustrated by experiments that heating methods have more impact than temperature. Microwave at 110 centigrade can extremely decrease the rate of growth of seed compared with traditional hydrothermal heating at 150 centigrade for several hours to dozens of minutes. However, the size of zeolites is a bit larger. It is explained that microwave makes it heated more actively by the conduction of ions but the growth of zeolites is also impacted by heterogeneity strengthened by microwave. In addition, it is believed that the amount of sodium ions may disturb the reactions and crystallinity. Therefore, the homogeneity and pretreatment will have an important influence on the characteristics of zeolites [7].

Besides the ways to heat, zeolites will be also affected by the ways to mix. Two main characteristics of zeolites that should be evaluated are the size and the crystallinity. For example, Ling Zhang et al. compared three ways to synthesize ZSM-11 zeolites. The first was to add all the materials sequentially while tank stirring. The second was to make three solutions and then mix them by stirring. The third was to make two solutions and mix them by stirring. It is demonstrated by the results that zeolites had smaller sizes but low crystallinity in the first group while high crystallinity but larger size in the second group. The third group had both small size and high crystallinity, which can prove that synthetic conditions have a great impact on the zeolites [8].

These methods mentioned above are all concerned with synthesis. What we are supposed to take into consideration mostly is the difference between reactants and their portions. Silicon, aluminium and base are necessary reactants to synthesize zeolites. But the zeolites are affected by the materials and portions of reactants. It is shown by the results that using silicone gel as reactants can satisfy the requirement of zeolites compared with NaSiO3 or HSiO3 solid. It is illustrated that only in a range of Si/Al can zeolites have high crystallinity. It is the same as the strength of the base: zeolites cannot crystallize at low base strength and too strong a base may decrease the crystallinity [8].

Based on these factors, an appropriate way to synthesize high-quality zeolites still needs a lot of research; Not only the reaction conditions or heating methods but also the portions of reactants should all be considered, even the materials of reactors or some other objective factors that can affect the reactions.

3.2 Modification
It is obvious to conclude according to the mechanism of reactions with catalysts. Proper inhibition or activation of specific reactions may change the yield of desired products. For molecular sieves, the diameters of pathways and structures of molecular sieves are prime factors. Diffusion resistance will be smaller in smaller zeolites. It is concerned with the selectivity. The rate of reactions is controlled and affected by acid sites, especially Bronsted acid and Lewis acid, inside molecular sieves directly, which means that acid quantity and kinds of cation will also determine the activity of catalysis. It is about the extent of the cracking reactions. The skeleton of the molecular sieve is always with a negative charge. Cations are outside the skeleton to balance overall charge and form acid sites to catalyse reactions [4]. There are different solutions to displace cations of molecular sieves to make molecular sieves with different characteristics that can be applied to catalyse different reactions [6]. It will have distinct consequences with too strong or too weak acid strength to solve the problems made by the deficiency.

It is widely used to treat zeolites with some acid, alkali or vapor steam to modify the characteristics of zeolites for the purposes of modifying structures and distributions of inner pathways. It is known that acid sites play a main role to catalyse reactions. So, the most direct impact of acidic treatment is to increase the acidity and sites by ion exchange. Some alkaline ions can be displaced by ion exchange like sodium ions. Another advantage is the erosion of the inner structure by acid. Although too much strong acid may destroy the skeleton, it can help to expand and adapt pores, which will increase the number of acid sites, in other words, the activity of the catalyst. Modified USY zeolites have great quality for catalytic cracking of PAH, as well as the amount of BTX. Shuzhuang Sun et al. modified USY zeolites with different organic acids and hydrothermal treatment. Tartaric acid was the best choice to improve the pore structure and acidic distribution when using single acid. In addition, hydrothermal treatment at 600 centigrade had a remarkable effect to increase acidic quantity without too much damage. Thus, zeolites could be better improved by combining two modifications. In the catalysis of naphthalene, zeolites modified with oxalic acid after hydrothermal treatment could best increase the yield of C8 and C9 products than common USY zeolites [6].

There has been some relevant research about using rare earth ions to exchange in modifications of zeolites. The main effects of rare earth are improving selectivity and stability, especially the resistance to vapor steam and acid. The most common rare earth used in industry is La and Ce, which are more likely to modify. In addition, rare earth can enable zeolites to resist heavy medal like V in catalytic cracking. The amount of heavy metal in Chinese crude is generally higher. It will make it more
difficult to process and obviously catalysts are more easily destroyed in catalytic cracking since these elements may deposit on the surface of catalysts decreasing activity and changing structure [9]. Rare earth was applied initially for X zeolites which were gradually replaced by Y zeolites since Y zeolites are more stable and with higher Si/Al. It is also confirmed dealumination will happen with rare earth [10]. It is known that ZSM-5 zeolites have strong acidic sites and adsorption, which makes reactions happen further resulting in a lower yield of light olefins. Modification by rare earth can weaken the adsorption and hydrogen transfer so that olefins are not likely to be saturated and the yield will increase. To some degree, this modification surely increases the selectivity [1]. Another common modification for ZSM-5 zeolites is by phosphorous. Phosphorous can also improve the selectivity and stability of zeolites. The strong acid sites will be weakened by the displacement of P-OH and the density of acid sites will increase simultaneously, which will not change the overall acid amount and make more pathways for reactions. Moreover, it will prevent dealumination with the modification of phosphorous [1].

3.3 Synergistic effect
The synergistic effect is concerned with two or more catalysts promoting reactions better than a single catalyst. Y molecular sieves are widely used in catalytic cracking as activated components of catalysts including HY, ReY, USY, etc. Due to the unique three-dimensional structure, Y molecular sieves have relatively larger inner space, thus easier for reactants and products to diffuse with less resistance, as well as hydrogen transfer reactions [11]. Macromolecules are able to diffuse into catalysts and contact with acid sites, increasing the frequency of reactions. The changeable range to the synthesis of the ratio of silicon to aluminum is narrow, making Y molecular sieve with a low rate of silicon. Hence, there are more acid sites making hydrogen transfer reactions active. As a result, light olefins are likely to be converted to alkane [4]. Apparently, too larger pathways and too stronger acid sites are not appropriate to produce olefin in catalytic cracking. Due to the zig-zag structure, ZSM-5 zeolite is enabled to have high selectivity to produce isoparaffin with high octane number. Nonetheless, the size of ZSM-5 zeolite is too small to let macromolecules diffuse, which is solved by strengthening pyrolysis to increase the conversion rate. It will simultaneously increase the amount of dry gas and the possibility of deactivation of zeolites. Therefore, ZSM-5 zeolite is better to be an additive component to the catalyst. Appropriate catalysts and a mixing method can have synergistic effects. Zhendong Yang et al. compared the impact of different mixing ways. It is illustrated that completely mixing USY/ZSM-5 as 7:3 was better than the staged bed configuration. The conversion increased by 10.81wt.% and the yield of BTX increased by 2.4wt.%. At the same time, the coke conversion and hydrogen transfer coefficient decreased [11].

4 Conclusion
This paper mainly introduces the relevant information of catalytic cracking including the feedstock and mechanism of the reactions. Since FCC process is always attracting attention from scientists and engineers for its dominant importance in the petroleum refining industry, catalysts are one of the most main factors in FCC process. High-quality zeolites will be significantly helpful to the manufacture of industry. So, the improvements of zeolites will directly determine the profits of the whole process. Zeolites are affected by some factors, especially diameter, structure and acid site. Diameter and structure determine the selectivity of products. Acid sites including the quantity and density affect the rate and degree of reactions. By different methods can zeolites be adapted to diverse manufacturing requirements to increase economic profits.

From a further prospective perspective, FCC process is difficult to be replaced over a long time. And zeolites will have more applications of catalysis not just in the industry even medicine, materials, etc. There have been varieties of zeolites and obviously more in the future. However, the problem that cannot be ignored is the vulnerability of zeolites, especially in an industry in which reactions usually happen at different temperatures and pressure. Also, it is hard to produce zeolites on a large scale because of the unique reactions. In conclusion, more research is needed to solve potential problems and expand the appliance.

References
4. X.F. Xiong, China Univ. Petrol. (East China), (2020).
5. G.N. Fu, China Univ. Petrol. (Beijing), (2020).