

CATALYTIC PERFORMANCE OF ZSM-5 ZEOLITE IN HEAVY HYDROCARBON CATALYTIC CRACKING: A REVIEW

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First Registered on January 21st 2019; Received after Correction on March 5th 2019
Publication Approval on: April 30th 2019

ABSTRACT

Low quality heavy oils and residues, which are subsequently obtained by processing heavy crudes, are considered as alternate suitable source for transportation fuels, energy and petrochemicals. ZSM-5 zeolite with high Si/Al ratio and modified with phosphorous and La has showed not only high selectivity to light olefins but also high hydrothermal stability for the steam catalytic cracking of naphtha. Kaolin is promising natural resource as raw material to synthesis of ZSM-5 zeolite. The utilization of acid catalysts with large pore size or hierarchically structured and high hydrothermal stability to resist the severity of the steam catalytic cracking (or thermal and catalytic cracking) operation conditions to maximize the olefin production.

Keywords: ZSM-5 Zeolite, Kaolin, Light Olefin, Steam Catalytic Cracking.

ABSTRAK

Minyak berat berkualitas rendah dan residu yang diperoleh dari pengolahan fraksi berat minyak bumi, dipertimbangkan sebagai sumber alternatif yang cocok untuk bahan bakar transportasi, energi, dan petrokimia. Zeolit ZSM-5 dengan rasio Si/Al yang tinggi dan dimodifikasi dengan fosfor dan lantanum telah menunjukkan tidak hanya selektivitas tinggi terhadap olefin ringan, tetapi juga stabilitas hidrotermal yang tinggi untuk perengkahan katalitik uap dari nafta. Kaolin adalah sumber daya alam yang potensial sebagai bahan baku untuk sintesis zeolit ZSM-5. Pemanfaatan katalis asam dengan ukuran pori besar atau terstruktur secara hierarkis dan stabilitas hidrotermal tinggi untuk menahan kondisi perengkahan katalitik uap yang hebat (atau perengkahan termal dan katalitik) untuk memaksimalkan produksi olefin.

Kata kunci: Zeolite ZSM-5, Kaolin, Olefin Ringan, Steam Catalytic Cracking.

I. INTRODUCTION

Petroleum oil continues to be major energy source up to 2040. According to OPEC's World Oil Outlook 2017, energy demand increases by 96 mboed (35%, 1.2% p.a.), oil remains dominant (0.6% p.a.), gas contributes most to future energy demand growth (3.6% p.a.), coal demand peaks towards the

end of the period (0.4% p.a.), renewables record the fastest growth rate (6.8%) and fossil fuels still provide over 75% of the world's energy needs by 2040.

Due to the limited amount and depletion of traditional light petroleum resources, low quality heavy oils and or residues, which are subsequently obtained by processing heavy crudes, are considered

as alternate suitable source for transportation fuels, energy and petrochemicals to fulfil the requirements of rapid population and civilization growth. Moreover, many statistical studies have showed that reservoirs of heavy crude are much larger than those of conventional crude, which made the appropriate deep upgrading of heavy crude, for both, refining and petrochemicals, more interesting and is attracting more and more attention from scientists and engineers (Corma et al., 2017).

The large reserves of heavy crude oils and the significant demand of light olefins, particularly propylene, have created new opportunities for developing advanced catalyst and process technologies that efficiently upgrade asphaltene-enriched crudes to high values chemicals. Indeed, many petrochemicals are produced during crude oil refining as side streams, because the primary goal of the crude oil refinery is the production of transportation fuel (Alotaibi et al., 2018).

Such a technology may probably be based on a conversion unit which can handle the heavy fractions of the crude oil, converting it partially to light olefins and reducing the amount of heavy products to minimum. A modified fluid catalytic cracking process would be an ideal candidate. Others units may also be added to complement the conversion unit, such as steam cracking, to crack cleaner and lighter fractions into light olefins (Corma et al., 2017).

Many catalytic and non-catalytic processes were explored to achieve more valuable and cleaner products from the heavy oil (Rana et al., 2007; Ancheyta et al., 2005). The catalytic process is more promising in terms of products selectivity over the non-catalytic (thermal) process because slight adjustment in the catalyst pore size can shift the reaction towards the desired products (Chen, 1996). Moreover, the catalytic method is cheaper compared with the non-catalytic processes which is usually associated with high energy inefficiency (Ren et al., 2006).

Therefore, this attracted the research on zeolite materials to compete with other catalysts since these aluminosilicates are cheaper as compared with common used metals catalysts.

II. ZSM-5 ZEOLITE FOR CATALYTIC CRACKING

Zeolite is aluminosilicate crystal that have pore and 3D framework. Based on their framework, International Zeolite Association (IZA) reported that zeolite have 218 framework. Different type of zeolite framework has different application and properties. They are widely applied in oil refinery and petrochemical industry as catalyst for many reaction such as isomerisation, alkylation, catalytic cracking, hydrolisis, etc (Kovo et al., 2009).

Only as examples of aluminosilicates, beta zeolite and ZSM-5 zeolite are introduced (see structures in Figure 1). Those are probably the two most successful

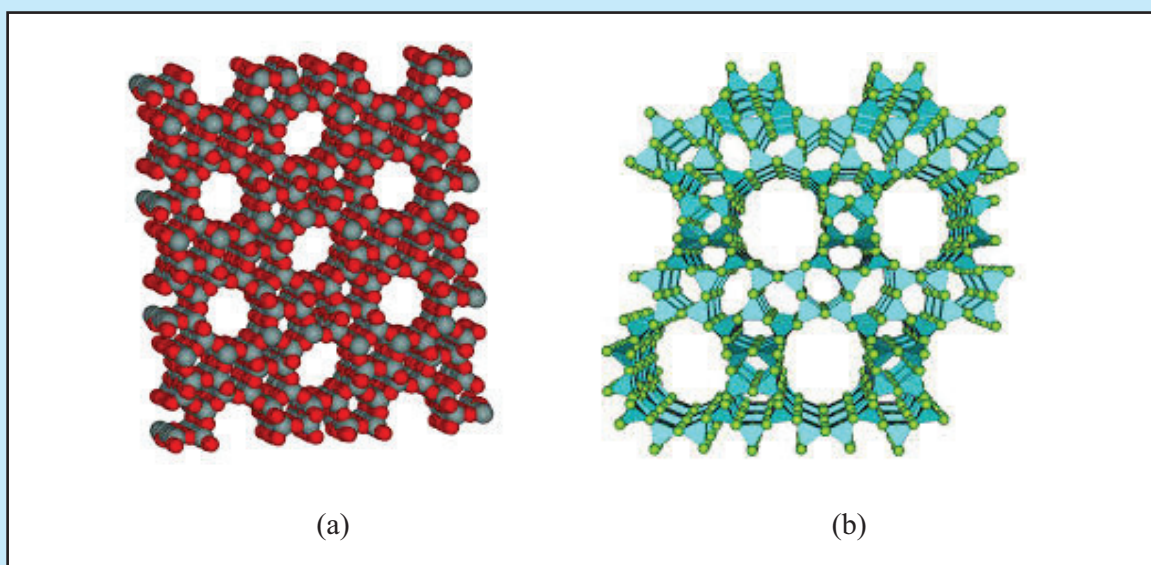


Figure 1
Structures of ZSM-5 Zeolite (a) and β -zeolite (b).

aluminosilicates ever described, where beta is formed by a three-dimensional large pore system (openings of $6.5 - 7 \text{ \AA}$), and ZSM-5 is formed by a three-dimensional medium pore system (openings of $5 - 5.5 \text{ \AA}$).

Catalytic cracking of hydrocarbon is significant for industrial manufacture, due to the advantages of high cracking conversion efficiency, high light alkene selectivity and less carbon deposition compared with thermal cracking (Sadrameli, 2016). Among the catalysts for hydrocarbon catalytic cracking, ZSM-5 zeolite is the most widely used due to its particular advantages of its acidity, special pore structure, and high thermal and hydrothermal stability (Blasco et al., 2006; Xue et al., 2017).

Generally, ZSM-5 synthesized by hydrothermal from silica precursor, alumina, metal cation, and organic template. Conventional synthesis of zeolite using organic template like TPA⁺ (Petushkov et al., 2011), utilization of tetrapropilamonium (TPA⁺) has many problem such as difficult to degradation, high cost, and need of higher temperature to release the template (Dey et al., 2013).

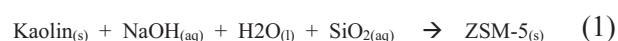
However, there are many different metals can further improved the catalytic properties of zeolite such as Ni, Zr, Nd, Pt and La. Bifunctional catalyst (metal/acid) is the most suitable catalyst for heavy hydrocarbon cracking. The metal site is required for hydrogenation and dehydrogenation while the acid site is required for the cracking and isomerization. The most critical part which determines the stability, activity, and selectivity of the catalyst is the balance between the metal and acid sites as well as the position and the distribution of the metals on the zeolite substrate (Fang et al., 2004; Li et al., 2003).

Nickel incorporated into zeolite showed a promising result in different catalytic applications especially hydrogenation/dehydrogenation and hydrocracking (Fang et al., 2005). There are mainly two practical routes which are commonly being used for metal incorporation with zeolites. Impregnation of the metals to the zeolite surface is the preferred route because it offers a combination of the acid properties of zeolite with the metal catalytic properties. However, this procedure has usually negatively impact on the microporosity by blocking most of these micropores. The next common route is ion exchange; which represents also an efficient way to attach the metals to zeolite. In this route, the metals mainly connected to the zeolite surface and/or inside the pores, which may also affect on the diffusion.

III. SYNTHESIS ZSM 5 ZEOLITE FROM NATURAL SOURCES

ZSM-5 can synthesized from raw material which has high contain of silica and alumina, such as kaolin (Wang et al., 2007; Hartanto et al., 2016), fly ash (Feng et al., 2009), rice husk (Prasetyoko et al., 2012), and serpentin (Dong et al., 2003). Synthesis of ZSM-5 from metakaolin as alumina source and silicate acid as silica source have been studied, activation kaolin at temperature from 600°C to 1100°C to form metakaolin (Pan et al., 2014). But, transformation to metakaolin need high temperature and increase cost of production. The utilize source of silica and alumina from natural resource will decrease cost of synthesis and also temperature calcined.

The high temperature of calcined might able to destroyed zeolite structure and decreasing crystallinity of ZSM-5. So, another promising way to synthesis of ZSM-5 is direct synthesis. Kim et al reported to direct synthesis of ZSM-5 with two step, first is nucleation at 190°C and continuesly by crystallization at $150 - 165^\circ\text{C}$ (Kim et al., 2004). The advantages of direct synthesis is low calcined temperature, no treatment for source of silica and alumina (Kaolin). Synthesis of Zeolite use kaolin as source was reported by many researcher. Direct synthesis also use addition of ZSM-5 seed, after condensation and polymerization reaction, precursor will form zeolite as well as their seed, in the reaction as follow (Xue et al., 2012):



Direct synthesis of ZSM-5 without organic template was influenced by some factor like temperature, Si/Al molar ratio, and also $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio. Generally, the higher temperature increase crystallinity, but every material has their limit. After optimum temperature, crystallinity of ZSM-5 would decrease, its caused higher temperature could broke zeolite structure (Dey et al., 2013; Hartanto et al., 2016). The influenced from $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio have studied to find optimum $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio on ZSM-5 crystal formation from Bangka Belitung kaolin (see Figure 2), the result as showed at Tabel 1.

The highest crystallinity is ZSM-5 with molar ratio 30 with the value 59.44%, its followed by molar ratio 25, 15, 35 respectively. Where Its can use for

Table 1
Crystallinity of ZSM-5 with different H₂O/SiO₂ molar ratio

H ₂ O/SiO ₂	Crystallinity (%)
15	49,88
25	55,49
30	59,44
35	8,52

direct synthesis and its product has different properties based on H₂O/SiO₂ molar ratio. Bangka Belitung kaolin is promising natural resource as raw material to synthesis of ZSM-5 (Hartanto et al., 2017).

IV. STEAM CATALYTIC CRACKING

Thermal cracking or steam cracking is still the main route for the production of light olefins and currently produce 95% of the world's ethylene and 60% of the world's propylene as a by product to ethylene production (Sadrameli, 2016).

The thermal steam cracking of hydrocarbons is a continues process able to produce light olefins with an ethylene to propylene ratio usually below 0.6 at temperatures generally between 750°C and 850°C, steam/oil mass ratio between 0.2 and 1.0 and reaction times usually below one second. The feedstock for the steam cracking process is generally gaseous (e.g., ethane, propane, butane, liquefied petroleum gas) or liquid (e.g. naphtha, gasoil and vacuum gas oils). The selection of the feedstock is a matter of availability and profitability. For instance, gas cracker is convenient when sufficient amounts of the feedstock are available; otherwise, a liquid cracker is more profitable, since gas transportation or gas liquefaction and then transportation are relatively costly (Amghizar et al., 2017).

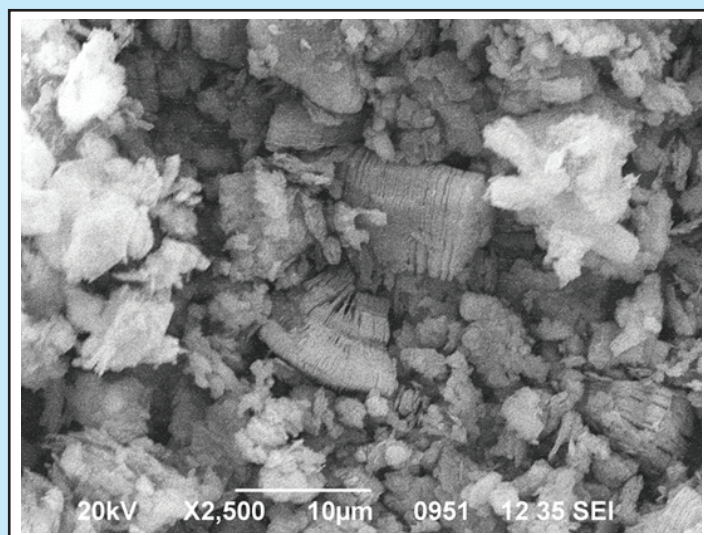


Figure 2
SEM Image of Belitung Kaolin

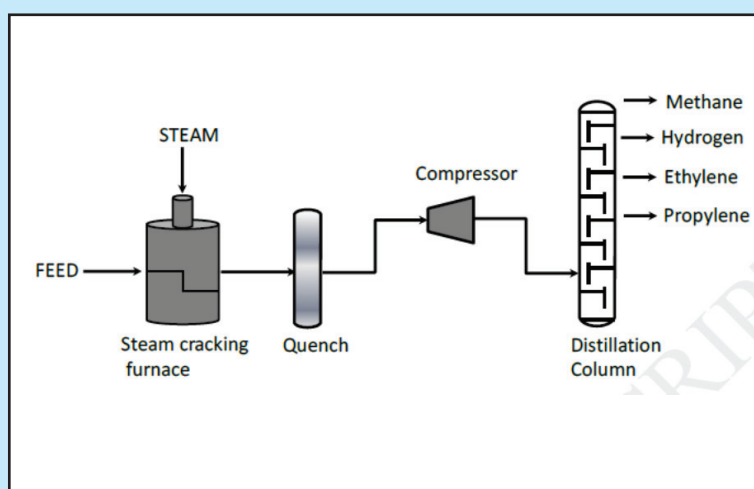


Figure 3
Main sections of a typical steam cracker diagram adapted from (Sadrameli, 2015)

The processing of crude oils in steam crackers is further demanding because of coke fouling issues. Several strategies have been identified: (1) steam cracking of crude oils with controlled vaporization; (2) combining pre-treatment of crude, steam cracking and catalytic cracking of the heavy fraction and (3) steam cracking and bottoms upgrading process combination for petrochemical refinery (Corma et al., 2017).

In order to increase ethene and propene, naphtha steam catalytic cracking has been considered. The cracking of $C_5 - C_{12}$ n-alkanes with ZSM-5 has been studied in absence and in presence of steam and the influence of the operation variables. Irreversible catalyst deactivation by dealumination also occurs in the reactor when the cracking is carried out in the presence of steam. To diminish steam deactivation, the influence of zeolite Si/Al framework and a post synthesis treatment by phosphorous have been studied and optimized. Much more stable catalyst can be achieved that result in an increase in activity without penalty for production of ethene and propene (Corma et al., 2012).

The steam cracker mainly consists of cracking furnace, quench section and fractionators or separation columns, which are displayed in Figure 2.

The hydrocarbon feed and the steam are fed into the cracking furnace that contains a tubular reactor with a length between 45 m and 90 m and a coil outlet temperature between 700°C and 900°C. The steam-oil mixture flows across the furnace with a residence time usually below 1 second and coil outlet pressure between 0.07 and 0.14 MPa. The stream is rapidly quenched at about 350°C in the outlet of the cracking furnace to minimize further cracking and potential polymerization reactions. The quenched stream is sent to a primary column or fractionator to be separated into a gas and liquid product streams. The gaseous mixture is then separated into individual gas by compression and high-pressure separation (Gary et al, 2007). The steam cracker unit is one of the most energy-intensive processes since the steam cracking furnace operates at high temperatures, which can be achieved by combustion of natural gas. Unfortunately, this process produces not only heat but also large amount of greenhouse gas emissions. According to Ren et al., (Ren et al, 2006), the combustion section utilizes 65% of the consumed total energy and 75% of the total exergy is lost in the processing of feedstock.

V. CONCLUSIONS.

ZSM-5 zeolite with high Si/Al ratio and modified with phosphorous and La has showed not only high selectivity to light olefins but also high hydrothermal stability for the steam catalytic cracking of naphtha. This catalyst formulation could be properly tailored to produce olefins from the catalytic cracking of heavy crude oil. It is also generally accepted that olefins production are favoured at low hydrogen-transfer reaction. The steam cracking for upgrading of heavy crude oils to olefins may be an effective technology despite its poor capability to produce high propylene/ethylene ratio and its limitation to use asphaltene enriched crude because of excessive wall coking. These issues could be overcome with the utilization of acid catalysts with large pore size or hierarchically structured and high hydrothermal stability to resist the severity of the steam catalytic cracking (or thermal and catalytic cracking) operation conditions to maximize the olefin production. A suitable (steam) catalytic cracking catalyst for heavy crude oil should contain strong acid sites and hierarchically organized pore structures to crack large molecules into small molecular fragments in large pore size and then diffuse into specific pore micro-cavity with strong acid sites to selectively produce light olefins.

Although, the above mentioned optimizations and modification methods would enhance the conversion of conventional crude oil to light olefins, the unconventional crude oil (e.g., extra heavy oil, residues and natural bitumen) will remain a big challenge.

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