

CHAPTER II

LITERATURE REVIEWS

Between 1949 - 1954, Union Carbide Corp. announced the successfully synthetic Y - type zeolite [1], in which had various useful properties for the industrial processes. Specifically, it found that Y - type zeolite had enormous potential as cracking catalyst. Some of the more prominent studied and the modified zeolites for catalytic cracking reaction were summarized as follows.

Greensfelder et al. [16], proposed that cracking system was assigned to two fundamental classes; each class was described by set of characteristic reactions covering both primary cracking and secondary reaction. Correspondingly, one a free radical (thermal type) mechanism, the other a carbonium ion (acid - activated type) mechanism. Cracking catalysts were available for either type of reaction mechanism; those which accelerate free radical type reaction were non - acidic, and those which accelerate carbonium ion type reaction were acidic such as acid - treated clay, silica - alumina cracking catalyst. Activated pure alumina had weakly acidic properties and produce moderate catalysis of both types of reaction mechanism.

Tiong Sie [17] showed the new mechanism for catalytic cracking reaction which had some features in common with the mechanism of the acid - catalyzed isomerization of paraffin, viz., the intermediate of cyclopropyl structure. This new theory provided an explanation for many of the characteristic features of cracking processes.

Tiong Sie [18] investigated that the protonated cyclopropane mechanism could provide an explanation for many features of cracking product spectra, such as the virtual absence of C_1 and C_2 as primary cracking products,

the high degree of branching in the saturated fraction in contrast to the predominantly linear structures in the light olefin fraction, and relative low formation of C_3 as compare with C_4 .

Abbot et al. [19] revealed that molecular hydrogen has not been formed as an initial product of n-paraffin cracking on HY zeolite at 400 °C. The observation of hydrogen as an initial product by other work might be related to the presence of a hydrogen at a tertiary carbon atom in reactant molecules used in such studies.

Abbot et al. [20] reported that the selectivity of catalytic cracking of a range of paraffin feedstocks could be explained by assuming that cracking occurs only at Bronsted acid sites. They proposed that the cracking reaction was initiated though the formation of pentacoordinate carbonium ion.

Wielers et al. proposed [21] that acid catalytic cracking of paraffin occurred through two different cracking routes, viz ., classical β -scission route and monomolecular protolytic pathway. When increased temperature, decreased aluminium content, decreased pore dimension resulted in the increasing in monomolecular protolytic cracking route as compared to the bimolecular classical route.

Corma et al. [22] studied the cracking of n- heptane on RE-HY zeolite in temperature range 400-470 °C. They revealed that the initial cracking took place on Bronsted acid sites via protolytic cracking or on Lewis acid sites via a classical β -scission mechanism.

Abbot et al. [23] investigated the selectivity phenomena of the alkane cracking on aluminosilicate catalyst. They assumed that the reaction occurred only at Bronsted acid sites. Reaction was initiated by protonation of the feed molecule to give carbonium ion intermediate. Rate of cracking reaction was

inhibited by formation of product alkenes. The Lewis acid sites produced by adsorption of these alkane at Bronsted site to form carbenium ions were much less effective in causing cracking (via hydride transfer process) than the original Bronsted acid site. For branch alkane, the reverse was true. The Lewis sites were generated by adsorption of product alkene at Bronsted sites were more effective in causing cracking than the original sites. In this case, it was propagated via a chain reaction through hydride ion abstraction involving these Lewis acid site.

Guerzoni [24] performed n-octane cracking on H-mordenite at 400 °C. He reported that the formation of aromatic and coke, associated with hydrogen transfer and cyclization processes could be enhanced by the presence of Lewis acid sites on the catalyst surface. Ratio of branched to linear alkane product could not be correlated with the ratio of Lewis to Bronsted site present. Ratio of alkane to alkene could be correlated with change in the ratio of Bronsted to Lewis site present, at a given reaction temperature.

The cracking of n-octane, 2,2,4 trimethylpentane and 1-octene over ZSM-5, β -zeolite, Y, USY and the composites of the two former zeolites as additive to the latter two traditional cracking zeolite at 500 °C and high conversion were investigated by Panagiotis and Ruckenstein [25] and reported that the olefin selectivity at 500 °C and high conversion were lower while the aromatic selectivity were higher over ZSM-5 and β -zeolite than over the faujasites but these behaviors are inverted at low conversion and 400 or 500 °C. This indicated that the final product selectivity had strong dependence on conversion and temperature. Higher aromatic selectivity over ZSM-5 were observed than β -zeolite, because of lower hydrogen transfer capability of the former zeolite which allowed the transformation via oligomerization of the primary olefin in aromatics. In contrast, higher amounts of C₃, C₄ paraffins were detected over the β -zeolite. The C₃, C₄ paraffins selectivities over the USY-base composites higher than those over individual zeolites. This behavior

was attributed to the enhancement of bimolecular condensation-cracking reactions as a result of the involvement the reaction of composite. In the absence of USY, the olefins generated over ZSM-5 or β -zeolite would have been oligomerized to aromatics.

Bonetto et al. [13] studied the performance of mixture of USY and β -zeolite in gasoil cracking. He found that β -zeolite shifted the product distribution toward shorter hydrocarbons and produced more olefin than USY.

Planelles et al. [14] studied the cracking of n-heptane on rare-earth HY zeolite at 400 °C. They concluded that the cracking on large pore zeolite may took place by different parallel routes, involving protolytic and β -cracking of the readily formed branched carbenium ion. The relative important of these three routes depends on the Bronsted to Lewis acid site ratio acid strength distribution and geometrical factors of the cracking catalyst.

Abbot et al. [26] studied n-hexadecane cracking on HY zeolite at 300-400 °C. Consequently, they found that paraffins are the dominant product at 300 °C, whereas olefin are dominant at 400 °C. The saturation products could be accounted for by hydrogen transfer leading to the formation of unsaturated aromatics, coke and saturated paraffins.

Corma et al. [27] revealed that the change in time on stream (TOS) did not have a large effect on the selectivity to different product. This effect was larger where cracking paraffins with less than 10 carbon atoms. The olefin to paraffin ratio product increased with the chain length of the feed and decreased when increasing the level of conversion and TOS.

The deactivation process of the H-type zeolite in n-hexane cracking at 573-773 K by pulse method was performed by Norihisa Mori and coworker [28-29]. They suggested that the deactivation of the H-mordenite was due to

pore blockage by the deposited coke. The HY zeolite was deactivated by the proton coverage, which was considered to be an active site, with the coke. No deactivation of ZSM-5 was observed in the present condition.

Backhaus and coworker [30] investigated about the influence of pretreatment of cracking catalyst. They showed that mild steaming of the catalysts allowed the optimum conversion, gasoline selectivity in catalytic cracking reaction. The calcined catalyst showed a higher starting conversion in the cracking process but the active of steamed and calcined catalyst became equal after few test run.

The effect of the unit cell size of Y zeolite on their performance had been investigated by Takashi Ino [31]. The result was concluded that catalytic activity increased with the increasing of unit cell size and the decreasing through a maximum and correlates directly with the number of 0-NNN aluminium atom (strongest acid sites). The increased coke yield with larger unit cell sizes could be attributed to the increased number of 1,2,3,4 - NNN aluminium atom.

Pine et al. [32] reported that the cracking activity of fluid catalytic cracking (FCC) catalysts increased with increasing of the unit cell size of the zeolite because of the increasing in the total number of acid sites in the zeolite.

Rawlence et al. [33] reported that higher steaming severity resulted in a lower unit cell size and lower acidity. The cracking activity of the zeolite correlated with total number of acid sites in the zeolite, however, the acid strength of active sites was still an important factor affecting the catalytic activity of the zeolite.

Iso Miyanohara and coworker [34] presented the process for preparing Y zeolite had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of at least about 4. The process was comprise of two step, in the first step an aqueous alkali silicate solution and aqueous alkali aluminate solution were mixed together in order to form gel in the mix solution. In the second step, the separated gel is incorporated in an aqueous alkaline silicate-alkaline mixed solution to obtain a slurry and, then, a Y-type zeolite crystal is formed in the slurry.

Klazinga [35] showed process for preparation of modified Y zeolite by treatment with a solution of metal salt and calcination which comprised treating a zeolite having an alkali oxide / aluminium oxide molar ratio about 0.13 with a solution of a multivalence metal salt having a cationic radius 0.6-1.0 °A and converting it by calcination into product having a unit cell size between about 24.21-24.65 °A.

Buchaman et al. [36] studied the effect of high temperature and high ZSM-5 additive level on FCC olefin yield and gasoline composition. The raising temperature from 811-852 K gave a more olefinic gasoline. 25 % ZSM-5 additive increased olefin branching, shifted olefin and paraffin to lower carbon atom, and slightly increasing aromatic.

Anders et al. [37] investigated the cracking of gasoil on HZSM-5 zeolite and on 1:1 mixture of HZSM-5 with Y zeolite. In the present of HZSM-5 the yield of gas increased at the expense of the gasoline yield. In the gasoline fraction a significant enrichment of aromatics took place, both by cracking of olefinic and paraffinic compounds in this boiling range and by formation of aromatics from gases olefins.

The hydrothermal deactivation of Y zeolite and fresh Y zeolite containing 0, 4, 7 and 12 wt% of REO and its effects on catalytic activity, stability, and selectivity were investigated by Maldonado and coworker [38].

For both fresh and deactivated samples, below 4 % wt of REO the total activity, and the hydrogen transfer were increased but beyond this REO concentration the total activity and hydrogen transfer reaction decreased as the REO amount increased. The cell parameter and the total activity were diminished for all sample after deactivation.

Meusinger et al. [39] studied the influence of zeolite composition and structure on hydrogen transfer reaction from hydrocarbons and from hydrogen. It was found that the activity was linearly dependent on the number of Bronsted acid sites for MFI - type zeolite. In the of faujasite zeolite it was observed that the activity per Bronsted site decreased with increasing concentration of acid sites. This was explained by differences in acid strength. The activated hydrogen was found to participate in bimolecular hydrogen transfer reaction during n-heptane cracking. Hydrogen transfer from hydrogen as well as hydrocarbons were influenced in the same way by zeolite structure and acid site density.

Camblor et al. [40] investigated vacuum gasoil cracking on USY zeolite (unit cell size 24.5-24.25). It was showed that smaller crystal sizes produced more gasoline and diesel, and less coke and gas. However, smaller crystal was less hydrothermally stable than bigger crystals. But, if NaY zeolite was made with silicon to aluminium ratio ≥ 3.0 , the smaller crystals were hydrothermally stable and showed a higher activity and better selectivity than bigger crystals, even steaming at 750 °C for 5 hr.

Tang Yi and coworker [41] studied the effect of dealumination defect on the properties of Y zeolite. The unit cell size and IR asymmetric stretch frequency of dealuminated zeolite were defected by the defect structure, because the hydroxyl nest was larger than the SiO_4 tetrahedron but smaller than AlO_4 tetrahedron and the presence of hydroxyl group in the nest weakened the Si-O bounds in the framework. In consequence, the thermal and hydrothermal

stabilities of zeolite were lowered due to the presence of defect structure. The defect structure also influenced the acid distribution. For sample with high defect concentration the strong acidity was reduced and medium acidity was increased significantly because of the composition of zeolite during heat pretreatment.

Elia et al. [42] investigated behavior of ZSM-5 addition to Y zeolite catalyst in FCC unit. At two different severities (500-520 °C) involved a decreased in gasoline yield with a simultaneous increased in the production of olefin (C_3 , C_4). However, the high octane number of gasoline was observed at low severity due to the formation of branched molecule. At high severity, increased octane number was due to the increased aromatic and naphthenes in product spectra.

The catalytic cracking of 1-methylnaphthalene individually and binary combination with n-hexadecane on zeolite catalysts was reported by Guerzoni et al. [43-44]. It was showed that for cracking of the polyaromatic feed over Y zeolite, the major processes were isomerization and disproportionation. In the binary mixture, the product selectivity was unchanged when compare to the cracking individual feed. The relative reactivity of n-alkane in the presence of the alkyldiaromatic was significantly reduced, and might be attributed to blockage zeolite pore or acid sites on the zeolite surface.

The influence of ethene and propene on catalytic cracking of n-heptane at 673 K over HY zeolite was studied by Lemos and coworker [45-46]. The studied revealed that the presence of light alkenes, with an alkene to n-heptane molar ratio in the range of 0.1-1.2, resulted in a decreasing of the initial cracking activity of n-heptane due to competitive adsorption of alkane and alkene, and increased yield of haptene and coke formed.

Basaldella and coworker [47] studied the synthesis of NaY zeolite on fined kaolinite microspheres. At the beginning of the synthesis, a dissolution process took place and a decrease of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the solid was caused by transference of silica and alumina toward the liquid phase. After a few hours treatment, zeolite crystallization was detected not only on the external surface but also on the mesopore.

Corma et al. [48] revealed that the ratio of cracking to hydrogen transfer for n-heptane and gasoil increased with increasing dealumination of USHY zeolite. The adsorption of n-butane and 1-butene on USHY samples known that amount of these adsorbed gases decreased with increasing dealumination. A decrease in the effective concentration of the product on the zeolite would favor monomolecular (cracking) over bimolecular (hydrogen transfer) reaction. The ratio of 1-butene to n-butane adsorbed decreased considerably below 10 Al/uc, indicated a less selectivity adsorption of olefins with respect to paraffins where the hydrophobicity (framework silicon-to-aluminium ratio) of the zeolite increased. These adsorption effect had an important influence on the cracking to hydrogen transfer ratio observed, as hydrogen transfer reaction involved olefins, whereas cracking involved mainly paraffinic.

Coke formation in fluid catalytic cracking was studied by Hollander et al. [49]. They found that the coke yield was hardly influenced by residence time, expect for a minor increased at catalyst to oil ratio = 6.

Raymond Way and coworker [51] investigated the process for produce crystalline zeolite of the faujasite-type zeolite. The zeolite product have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio about 2-3 by mole.

From the above literature reviews, Y-type zeolite catalyst is an important catalyst used in catalytic cracking reaction. However, the effect of preparation conditions on the Y-type zeolite synthesis has not been fully studied. Thus, the preparation conditions of Y-type zeolite synthesis were studied in order to obtain the optimum formula of monophasic Y-type zeolite with high crystallinity. In addition, the synthesized Y-type zeolite was used as catalyst for catalytic cracking reaction.



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