

# CHAPTER I

## INTRODUCTION

### 1.1 Background

Zeolites which are classified as a group of microporous materials are widely used as acid catalysts, especially in the petrochemical industry due to the fact that they possess several desirable properties such as high acidity, unique pore structure with kinetic pore size, high specific surface area adjustable, and hydrophilicity, high thermal stability [1-3]. Many chemical processes rely on the use of Brønsted and Lewis acid such as HF, H<sub>3</sub>PO<sub>4</sub> or AlCl<sub>3</sub> inspite of problems related to corrosion, recovers, regeneration and disposal. Due to environmental concerns, the interest in solid acid catalyst as replacements for liquid acids is growing. Furthermore, the separation of products especially homogenous and catalyst is rather difficult and costly. In order to achieve fully benefit from the unique sorption and shape-selectivity effects in the zeolite micropores without suffering from diffusional limitations, the diffusion path length in the zeolite should be very short. For example, the use of colloidal zeolite nanocatalysts are needed [4]. This work intends to find a new method for effectively synthesizing nanoparticle zeolite beta. Cracking of plastics such as polypropylene and high density polyethylene and also crude oil derived from PP-type plastic is selected for the test reaction for catalytic activities of the zeolite beta samples.

Zeolites are conventionally prepared by the hydrothermal method of gel containing silica, alumina, inorganic or organic cation, and water. Several types of silica are known to produce zeolites. Most of the silica sources used in the synthesis of zeolite are commercially available in the form of solution, a gel, a fumed solid, a colloid and an organic derivative such as tetraethyl orthosilicate. However, it is sometimes observed that the formation of a zeolite phase may be preceded with another phase during the course of zeolite crystallization. This phenomenon, therefore, could be considered as an alternative synthesis strategy for the hydrothermal conversion of one zeolite into another, *i.e.*, zeolite-zeolite transformation [5]. In fact, this method is an attractive research area, since it may provide

information about the crystallization mechanism. Additional to the method is an outstanding route to obtain a new zeolite which cannot be crystallized by a conventional method. However, there are only a few studies concerning this route, in which a particular zeolite is used as a crystalline aluminosilicate source instead of amorphous aluminosilicate gels. The detailed studies on the hydrothermal conversion of a zeolite into hydroxyl-sodalite [6-8] and P-zeolite were carried out by Zones *et al.* and the conversion of various zeolites were investigated, for instance from Y-zeolite (FAU) into SSZ-13 [9] and B-<sup>\*</sup>BEA to B-SSZ-24, B-SSZ-31 and B-SSZ-33 [10] in the presence of a damantane cation and its derivative.

Zeolite beta which has a structure code of BEA established by International Zeolite Association is high silica, large-pore zeolite with a three-dimensional channel system and large 12- membered ring pore openings is the most attractive zeolite nowadays. Zeolite beta is used as a solid acid catalyst for several industrial processes especially cracking [11-13], isomerization [14-17], alkylation [18-20], and oxidation [21-23]. Zeolite beta was first synthesized by Wadlinger in 1967 [24]. Though the synthesis of zeolite beta has not widely developed comparing to ZSM-5 due to the concurrence of its polymorphs, the effective synthesis can be carried out by using a particular pore directing agent, *i.e.* tetraethylammonium hydroxide. After extensive studies in its applications, the development of the synthesis of zeolite beta becomes interesting. Zeolites are known for strong acidity and high specific surface area, but those characteristics are not enough for being excellent cracking catalysts. It was suggested that initial polyolefin cracking occurs mainly at the acid sites on the external surface of a zeolite [25]. Only intermediates small enough are able to enter the zeolite pores or channels and react with the internal acid sites of the zeolite. The external surface area plays more important role than the internal one for cracking of large molecules like polyolefin plastics to valuable small hydrocarbon molecules. Polyolefin plastic wastes become to be the problem of solid waste disposal due to they are highly stable and non-degradable naturally. Polyolefin wastes can be converted into petroleum feedstock, gasoline-range fuel via the cracking method [26]. Thermal cracking of plastic waste without catalyst usually requires a high temperature of 800°C, for instance. Zeolite beta can be synthesized by several methods. The dry-gel method is typically conducted by separation of liquid from the dry gel completely during the course of crystallization. In practice, preparation of the stiff dry gel was

rather inconvenient. The fluoride method was later developed by using the corroding reagent until the large crystal size of zeolite beta was obtained. The latest practical method is the xerogel method which can be regarded as a modified hydrothermal synthesis. The silica sources preferred in the zeolite synthesis are such as fumed silica [27], silica xerogel [11], kanemite [28], FAU [29], MCM-41 [30], and MCM-48 [4]. The synthesis of zeolite beta from mesoporous silica namely SBA-15 has not been reported so far. Thus, this is the first report of the methodology for the synthesis of zeolite beta by using SBA-15 as the silica source. Our nanoparticle zeolite beta exhibits very high activity in polyolefin waste cracking.

## 1.2 Literature Reviews

### 1.2.1 Synthesis of Zeolite Beta

Several studies have been published in terms of synthesis methods of zeolite beta as solid-acid catalysts. Recently, zeolite beta was synthesized under hydrothermal condition using an amorphous solid gel as a starting material [11,13, 31-34,]. In 1998, J. Pérez-Pariente *et al.* [31] studied the efficiency of the synthesis of zeolite beta. The synthesis was synthesized by hydrothermal method, using colloidal silica as a silica source with containing alkali and tetraethylammonium ions. The effect of chemical composition on the synthesis was also studied. It was very difficult to synthesize siliceous zeolite beta effectively. From aluminium rich gels ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$  or  $\text{Si}/\text{Al} = 15$ ), high yield of zeolite beta was easily obtained, whereas from silicon rich gels ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 900$ ), zeolite beta found in a small amount. This synthesis is insufficient due to the inefficiency use of silicon, the mother liquor always being exhausted in aluminium at the end of the crystallization. The incorporation of silicon in zeolite beta could be improved by several means. The presence of ethanol, the absence of aluminum, or the increase in temperature provided reasonable yield of siliceous zeolite beta crystals. M.A. Cambor *et al.* [32] synthesized a zeolite beta hydrothermally at  $140^\circ\text{C}$  in organic a basic medium and in the absence of alkali cations the details of the procedure were decribed in [31]. The crystal size decreased with increasing Al content in the gel. The nanocrystallinity did not affect the thermal stability of the zeolite in terms of crystallinity, but severely reduces the stability of Al in framework during calcination in air. In 2004, R. Nakao *et al.* [13] synthesized zeolite beta by a hydrothermal method. They used colloidal silica as a silica source

and crystallized at 175°C for 3 days and studied the activity of homemade zeolite beta in catalytic cracking of hydrocarbons compared with commercial zeolite beta. The results showed that the homemade zeolite beta had more Brønsted acid site than the commercial one. Also, the homemade zeolite beta exhibited high activity in cracking n-heptane. In addition, homemade zeolite beta gave high n-heptane conversion even after the regeneration treatment. Furthermore, S. Mintova *et al.* [33] synthesized zeolite beta nanocrystals from basic aluminosilicate precursor solutions upon hydrothermal treatment at 100°C. The Si/Al ratio of the initial system was systematically varied from 25 to infinity. The results showed the effect of Si/Al ratio on the precursor species, ultimate crystal size, morphology and yield of zeolite products. It was found that the crystallization kinetics of nanosized zeolite beta were dependent on the amount of Al in the precursor solutions. In the other word, the nucleation and growth processes were faster in Al-rich systems. L. Ding *et al.* [34] studied the effect of the amount of template agent on crystal size of zeolite beta. Zeolite beta was hydrothermally synthesized using the method reported by Cambor *et al.* [32]. The results demonstrated that the amount of template agent played an important role in the determination of the crystal size of zeolite beta. More templates led to more silica species dissolving to the liquid phase so faster inorganic-organic assemblies were formed. The crystal size of synthesized zeolite reduced. Furthermore, the water content in the initial gel did not significantly influence the crystalline size and framework Si/Al ratio of zeolite beta. J. Aguado *et al.* [11] synthesized zeolite beta from amorphous xerogels (Al-Beta, Ti-Beta) and by the fluoride method (Al-Beta/F). It was found that Al-Beta, Ti-Beta exhibited higher aluminium incorporation and higher external surface area as well as much smaller particles. The catalytic degradation of polypropylene and both low density polyethylene and high density polyethylene over zeolite beta has been investigated. The results showed that the incorporation of titanium into the BEA structure has been proved to enhance the catalytic activity as it was noted by the highest conversion per Al.

Another method for the synthesis of nanosized zeolite beta was reported by G. Majano *et al.* [35]. They synthesized nanosized zeolite beta assemblies by using stream-assisted conversion (SAC) method from micro-sized porous amorphous silica grains soaked in a solution containing the alumina source and organic template. The zeolite beta self-assemblies retain the morphological features and size of initial grains.

The degree of crystallinity and phase homogeneity of zeolite beta self-assemblies depended on the temperature and time of SAC treatment as well as the Al loading in the amorphous silica grains. The main advantages of the zeolite beta self-assemblies obtained via SAC method is the fast preparation but difficult to deal with hot-stream. In 2007, M.D. Kadgaonkar *et al.* [36] synthesized NCL-7, polymorph Boron-rich BEA structure using hydrothermal method in a fluoride medium using perchloric acid as promoter. The synthesis of NCL-7 can be achieved in a temperature range of 373-413 K, TEAOH/SiO<sub>2</sub> molar ratio 0.68-0.98, HClO<sub>4</sub>/SiO<sub>2</sub> molar ratio varied from 0.08-1.2 and H<sub>2</sub>O/SiO<sub>2</sub> molar ratio of 9.5. Two other structures namely NCL-5 and NCL-6 with varying degree of polymorph enrichment were also synthesized for studies of physico-chemical properties of these zeolites. In 2009, A. Sakthivel *et al.* [37] synthesized nanosized zeolite beta using the dry gel conversion (DGC) method with tetraethylammonium hydroxide in the surfactants; cetyltrimethylammonium bromide (CTMBr), chloride (CTMCl) and hydroxide (CTMOH). The zeolite beta had uniform particle sizes of 35-60 nm with high BET and external surface areas. The particle size of zeolite beta depended on the concentration and type of counter-anion of the surfactant used. L. Kong *et al.* [38] synthesized zeolite beta in biphasic H<sub>2</sub>O-CTAB-alcohol system using colloidal precursor which contains secondary building units of zeolite beta as silica and aluminum sources. The crystallite aggregates comprising many small particles are obtained. The obtained zeolite beta samples synthesized in the biphasic system displayed higher catalytic activities for *n*-hexane hydrocracking than that synthesized in single aqueous system. Recently, M. Mazaj *et al.* [39] synthesized aluminium-free Ti-beta/SBA-15 composite using a post-synthesis incipient wetness impregnation method. The presence of crystalline nanoparticles in the solution, used for impregnation on SBA-15, was confirmed by HRTEM. The deposition of nanoparticles on the internal SBA-15 pore walls was evidenced also from N<sub>2</sub>-sorption isotherms. The X-ray absorption spectroscopy analysis of local environment of titanium incorporated in the new composite material showed that the product contained five coordination-framework titanium. These titanium sites was the oxidized sites. In 2006, D. Prasetyoko *et al.* [40] synthesized zeolite beta by using a direct hydrothermal route, using crystalline silica of rice husk ash (RHA) as a silica source and tetraethylammonium hydroxide as the structure-directing agent. They demonstrated, therefore, that the natural source of

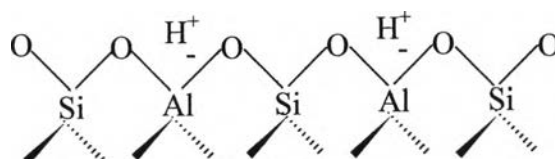
silica containing of the two crystalline polymorphs of silica ( $\alpha$ -cristobalite and tridymite), could be used conveniently for hydrothermal zeolite synthesis. Rice husk ash was completely transformed to pure zeolite beta phase after 2 days of hydrothermal synthesis at 150°C. The transformation of RHA involved dissolution of silica in the highly basic reaction mixture followed by the formation of an aluminosilicate, crystallization of the metastable zeolite Na-P and finally the pure zeolite beta phase. Moreover, T. Selvam *et al.* [28, 41] explored a new method for the synthesis of zeolite beta. They observed the transformation of kanemite into zeolite beta in the presence of TEAOH as the structure directing agent under hydrothermal conditions. The results indicated that the zeolite beta samples obtained were highly crystalline and free from impurities. XRD patterns showed a gradual transition process from kanemite to zeolite Na-P1 and then to zeolite beta. SEM images indicated that the zeolite beta crystallites were of submicron size (0.1  $\mu\text{m}$ ). Zeolite beta samples in high yields (71-97%) were obtained by solid state transformation of TEAOH-intercalated kanemite samples having moderate amounts of TEAOH ( $\text{TEAOH}/\text{SiO}_2 = 0.11\text{-}0.23$ ). In addition, the zeolite beta sample ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 12$ ) obtained was found to be active for the cracking of n-hexane and its performance was comparable to a standard zeolite beta sample ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ ). In 2006, H. Jon *et al.* [29] reported that zeolite beta can be synthesized from crystalline aluminosilicates. The crystallization rate of zeolite beta considerably depended upon the aluminosilicate source employed, namely FAU zeolite, a crystalline source, showed the faster rate than that from  $\text{SiO}_2/\gamma\text{-Al}_2\text{O}_3$ . Moreover, the conversion of FAU zeolite into zeolite beta strongly depended upon the Si/Al ratio of the starting FAU zeolite. The ratio of TEAOH/SiO<sub>2</sub> in the starting synthesis gel could be reduced to 0.1-0.15. Recently, Zeolite beta was synthesized by using a mesoporous material as a silica source. For example, S. Chen *et al.* [42] synthesized zeolite beta by using MCM-41 mesoporous material as a silica source. This specially synthesized zeolite beta not only kept the advantage of microporous zeolite but also inherited some pore structure quality of mesoporous zeolite. Beside good acidity, bigger pore diameter and larger pore volume, this zeolite beta made out of mesoporous matrix gave very small crystal granule close to nanometer size. When applied in hydrocracking catalyst, it made the catalyst suitable for cracking of large molecules of heavy feed oil and the enhanced

activity and improved middle distillate selectivity were observed. T. Takewaki *et al.* [30] explored a new method for synthesizing zeolite beta involving the use of mesoporous materials as reagents. Si-zeolite beta was synthesized by heating TEAOH-impregnated Si-MCM-41 to 150°C for several days. The Si-zeolite beta obtained had a small number of Q<sup>3</sup> sites that were mostly siloxy groups that balance the charge of TEA cations. These phenomena were likely to be caused by the specific relationship between TEA cations and Q<sup>3</sup> sites. Ti-zeolite beta was synthesized from Ti-containing mesoporous silica without adding Al<sup>3+</sup>, alkali metal cations and seeds. The incorporation of Ti into zeolite beta structure was confirmed by UV-visible data. Zeolite beta materials containing Al, B, V, Zr and Zn were also prepared. These results showed that mesoporous materials were promising reagents for synthesizing crystalline molecular sieves. In 2003, P. Prokesova *et al.* [4] synthesized nanosized zeolite beta/MCM-48 composites by simultaneous hydrothermal treatment of mesoporous precursor solution and colloidal solution containing X-ray amorphous zeolite seeds. The composite phases contained nanometer size particles (110-140 nm), which were much smaller than the particles in the pure mesoporous sample and slightly bigger than the colloidal nanosized zeolite beta crystals. These materials were expected to provide a large active surface, improved mass transfer and relatively strong acidity, which would result in high catalytic qualities.

### 1.2.2 Cracking Catalysts

The key reaction in catalytic cracking is the addition of proton (H<sup>+</sup>) to form a positively charged ion. Any acid would do, but in a conventional chemical reaction of hydrocarbons with a strong acid (e.g., H<sub>2</sub>SO<sub>4</sub>), it would be kind of difficult both to separate out what we wanted afterward and avoid corroding cracking reactors. Thus, the catalysts used are solids with acidic surfaces, so they stay where they are put. Acid treated clays were the first catalyst used in catalytic cracking process [43], but have been replaced by synthetic silica-alumina, which is more active and stable. Incorporating zeolites, crystalline alumina silica catalysts improves selectivity towards require products. These catalysts have both Lewis and Brønsted acid sites that promote carbonium ion formation. An important structure of zeolites is the

presence of holes in crystal lattice, which are formed by silica tetrahedral as exhibited in Figure 1.1.



**Figure 1.1** Framework of zeolite consisted of  $\text{SiO}_4$  and  $[\text{AlO}_4]^-$ .

Zeolites as cracking catalysts perform higher activity and better selectivity toward light fraction than amorphous silica-alumina catalysts. This is attributed to a greater acid sites and a higher adsorption power for the reactants on the catalyst surface. The higher selectivity of zeolites is attributed to its smaller pores which allow diffusion of only smaller molecules through their pores, and to the higher rate of hydrogen transfer reactions. Deactivation of zeolites catalyst occurs due to coke formation and to poisoning by heavy metals. In general, there are two types of catalyst deactivation that occur in a catalytic cracking system, reversible and irreversible. Reversible deactivation occurs due to coke deposition. This is reversed by burning coke in the generator. Irreversible deactivation result as a combination of four separate but interrelated mechanisms: zeolite dealumination, zeolite decomposition, matrix surface collapse and contamination *e.g.* by metal such as vanadium and sodium.

### 1.2.3 Catalytic Cracking of Plastic with Heterogeneous Catalyst

In 2001, J.Yanik *et al.* [44] studied the catalytic cracking of plastic waste, *i. e.* PVC, mixture of PVC/PE, or mixture of PVC/PP over red mud, a by product from alumina manufacture process. Red mud showed good effect on adsorbing the emitted HCl from cracking but it had no effect on catalytic cracking of polymers. K. Gobin *et al.* [45] studied the cracking of polyethylene over various microporous materials-zeolites, clays and their pillared analogues. Because of the strong acidity of zeolitic materials, severe over cracking took place resulting into the formation of small molecules that were collected mainly in gaseous fraction,



increasing its yield. Hence the yield to liquid fuel decreased. Y-H. Lin *et al.* [46] investigated the catalytic cracking of polypropylene using various catalysts including mesoporous materials. Because of larger pore size and weaker acidity as compared to zeolites, MCM-41 gave the highest liquid yield and selectivity to gasoline up to 60.56% while zeolitic materials *i.e.* HUSY, HZSM-5, and HMOR were selective to gaseous product which less valuable. The effect of reaction temperature was also studied in their work. As a temperature of reaction was increased, yield of gaseous products increased but liquid yields decreased. It could be concluded that both yield and selectivity could be further influenced by the change in reaction temperature. Recently, J. Aguado *et al.* [47] reported that the catalytic activities of acid solid catalysts *i.e.* ZSM-5, zeolite beta, Al-MAM-41 and Al-SBA-15 were related to their capacity to shift the degradation reaction to lower temperature. Table 1.1 contains a numerical data describing the temperature of maximum reaction rate in catalytic cracking over those catalysts and amorphous silica ( $\text{SiO}_2$ ). The result showed no effect in the cracking temperature when  $\text{SiO}_2$  was used, which confirmed the lack of catalytic activity of non-acid solid catalyst. Despite showing strong acid property, ZSM-5 exhibited a very low catalytic activity on LDPE ceacking. The temperature of maximum degradation rate ( $T_{\text{max}}$ ) for LDPE/ZSM-5 was 443°C, only 33°C below the thermal cracking temperature which was attributed to the diffusion impediments that affected the access of bulky molecule of polymer to its internal active sites.  $T_{\text{max}}$  for LDPE cracking by Al-MCM-41, zeolite beta, and Al-SBA-15 were remarkably reduced to 407 and 417°C, respectively.

The cracking of plastic mixtures, LDPE and ethylene vinyl acetate (EVA) copolymer over nanocrystalline H-ZSM-5, Al-MCM-41 as well as Al-SBA-15 was conducted by Serrano *et al.* [44]. The nanocrystalline ZSM-5 gave the highest conversion about 80% at 400°C and more than 90% at 420°C, the selectivity to the light oil fraction ( $\text{C}_6\text{-C}_{12}$ ) was only about 20% while selectivity of Al-MCM-41 was approximately 45% and Al-SBA-15 gave the highest selectivity up to 55% of light oil fraction. In 2008, Y.J. Lee *et al.* [25] reported the influence of nanocrystalline H-BEA in liquid phase degradation of high density polyethylene at 380°C. Nanocrystalline H-BEA with a crystallite size of about 10 nm and low Si/Al ratio (10.7) was found to be an efficient catalyst in the liquid phase degradation of HDPE, producing a large amount of liquid product (80%) with high selectivities to  $\text{C}_7\text{-C}_{12}$  hydrocarbons at

380°C. Both the crystallite size and the acidity of H-BEA were important factors influencing their catalytic activities and product distribution. The high activity and high liquid yield of nanocrystalline zeolite beta were rationalized by the rapid cracking of HDPE over the strong acid sites on the external surface and fast mass transfer of cracked fragments in the pores of nanocrystalline H-BEA. The decreased intracrystalline residence time of cracked fragment leads to less a high yields of liquid instead of gases. J.M. Arandes *et al.* [48] studied the effect of zeolite commercial catalysts on the cracking of PP pyrolysis wax under FCC condition. The results showed that the catalyst acidity had a significant effect on conversion and compositions of residual lumps. The main effect of increasing catalyst acidity is an increase in coke content on catalyst leading to the decreases of the yields of the gases, and light olefins but increase in the yield of paraffins. In 2009, M.S. Kumar *et al.* [49] studied the influence of pore geometry of microporous (ZSM-5 and Beta) and mesoporous (SBA-15) on dehydrogenation of propane by TEOM (tapered element oscillating microbalance). The catalysts were obtained by incipient wetness impregnation with a Pt solution. Pt-ZSM-5 presented the highest propane conversion followed by Pt-Beta and Pt-SBA-15 indicating that the activity decreases with increasing pore size (ZSM-5<Beta<SBA-15) of the supports. In 2010, N. Katada *et al.* [50] studied the activities for catalytic cracking of octane and hexane on various zeolites (zeolite Y, USY, ZSM-5, mordenite and zeolite beta). Zeolites are divided into Group I and Group II based on the energy parameter measurement. Group I was observed between the heats of adsorption of ammonia and alkane while Group II where not relation between the heats of adsorption of ammonia and alkane was not observed. The heats of alkane adsorption were not be related with the cracking activity adsorption as an index of acid strength was related with the activation energy and TOF. Thus, it was found that the acidity was essential to control the cracking activities of those zeolites.

**Table 1.1** Parameters describing the thermal and catalytic degradation of LDPE and HDPE samples [47]

Polymer	Catalyst	T <sub>initial</sub> (°C)	T <sub>max</sub> (°C)
LDPE	None	419	476
	SiO <sub>2</sub>	419	476
	ZSM-5	374	443
	Beta	370	417
	Al-MCM-41	367	407
	Al-SBA-15	372	417
	HDPE	None	431
SiO <sub>2</sub>		431	479
ZSM-5		385	418
Beta		385	425
Al-MCM-41		355	421
Al-SBA-15		343	426

where, T<sub>max</sub> : Temperature of the maximum reaction rate

### 1.3 Objectives

To study the transformation of mesoporous SBA-15 into zeolite beta under various conditions and study the catalytic activities of synthesized zeolite beta

### 1.4 Scope of Work

1. To prepare SBA-15 from tetraethylorthosilicate using Pluronic 123 as template.
2. To study the transformation of SBA-15 into zeolite beta in the presence of tetraethylammonium hydroxide and aluminum isopropoxide at a constant temperature of 135°C with various other parameters.
3. To study the effect of transformation period SBA-15/AIP ratios and TEAOH/SiO<sub>2</sub> ratios on the transformation of SBA-15 into zeolite beta.
4. To apply the zeolite beta samples to cracking of PP, HDPE and PP-derived crude oil by studying the effect of reaction temperature and catalytic amount.
5. To regenerate the used catalysts and test for their activities.