

## Catalytic Cracking of Polypropylene Waste over Zeolite Beta

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### Abstract

Catalytic cracking of polypropylene (PP) waste has been investigated using zeolite beta (BEA) as a catalyst. BEA was performed by transformation of mesoporous silica SBA-15, a novel synthesis based on the functionalization of Si/Al ratio was studied. The catalyst samples obtained were tested for their catalytic activities in the cracking of PP waste in batch reactor under various conditions. The plastic conversions and the yields of products fractions obviously depend on the the Si/Al ratios and reaction temperatures. The product selectivity is affected by those factors. The thermal cracking of PP waste leads to plastic %conversion lower than catalytic cracking. In contrast, the nanoparticle BEA is found very active up to 95 %conversion. The used catalyst can be regenerated easily by calcination and its activity remains comparable to the fresh catalyst.

**Keywords:** Zeolite beta, Catalytic cracking, Thermal cracking, Polypropylene (PP) waste, %conversion

### 1. Introduction

In recent years, the production and consumption of plastic have increased drastically. The amount of waste plastics generated from domestic and industrial usage of plastic is growing continuously. They are mostly landfilled or incinerated as conventional ways to the disposal of waste plastics. However, these methods are facing a great social resistance due to the air pollution and soil contamination (Lee 2002). In Thailand, plastic waste from household, industrial process and market are 2.7 million ton per year and 0.2 million tons for recycling (TEENT 2012). The recycling plastic waste method has been developed and new recycling approaches are being investigated. The chemical recycling can lead to total depolymerization to the monomers, or partial degradation to other secondary valuable materials. Energy recovery is an effective way to reduce the volume of organic materials by incineration. Among the recycling techniques, the incineration meet with strong societal opposition and mechanical recycling can be carried out only on single-polymer waste streams. However, the most effective method, in accordance with the principles of sustainable development, is chemical recycling also called as feedstock. According to this method, waste polymers can be either converted to original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuel (Scheirs 1998 and Achilias & Karayannidis 2004).

Thermal cracking involves the degradation of the polymeric material with high temperature ( $>700^{\circ}\text{C}$ ) when it is applied under inert atmospheric conditions. In the case of polyolefins like polyethylene, polypropylene, this process has been reported to proceed through a random scission mechanism that generates a heterogenous mixture such as linear paraffins, olefins and aromatic compounds. At low temperature ( $400\text{-}500^{\circ}\text{C}$ ) the three fractions received a high-calorific value gas, condensable hydrocarbon oil and wax (Aguado *et al.* 2008 and Achilias & Megalokonomos 2006). Due to the low thermal conductivity of polymer together with the endotherm of cracking, thermal pyrolysis consumes a large amount of energy. Thus, catalytic technologies have been proposed to promote cracking at low temperature, resulting in reduced energy consumption and higher conversion rates (Manos *et al.* 2002). Catalytic cracking is most important to the shape selectivity exhibited by certain catalysts allows the formation of a narrower distribution of hydrocarbon products, which may be directed towards light and aromatic hydrocarbons with higher market values (Seo *et al.* 2003 and Artetxe *et al.* 2012). Heterogeneous catalysis has been investigated extensively using solids with acid properties. Several studies have been conducted describing the cracking of pure polyolefins over different acid solids like zeolites and mesoporous material (Panda & Singh 2011, Aguado *et al.* 2000, Obali *et al.* 2012 and Aguado *et al.* 2000). 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 adjustable surface area and hydrophilicity, high thermal stability (Renzini *et al.* 2011). Zeolites of the kind employed in the catalytic cracking of hydrocarbon feedstocks such as ZSM-5, zeolite Y and zeolite beta are being the most studied (Manos *et al.* 2002).

Cracking with acid catalysts takes place through the formation of carbocation, which requires the presence of strong acidic regions. Acid strength and textural properties are the main parameters dictating the performance of acid solids in the catalytic conversion polymer. Porosity, surface area and particle size determine to a large extent the accessibility of bulky polymeric molecules to the internal catalytic acid sites of solids.

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 are the most attractive zeolite nowadays. BEA is used as a solid acid catalyst for several industrial processes especially cracking (Renzini *et al.* 2011 and Nakao *et al.* 2004), isomerization (Kumar *et al.* 2007), alkylation (Bregolato *et al.* 2007), and oxidation (Xia & Tatsumi 2005 and Hulea & Dumitriu 2004). Though the synthesis of BEA 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 BEA 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 (Wadlinger *et al.* 1967). Only small enough intermediates 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 wastes can be converted into petroleum feedstock, gasoline-range fuel via the cracking method (Lee *et al.* 2008). BEA can be synthesized by several methods. The dry-gel method is typically conducted by separating liquid from the dry gel completely during the course of crystallization. During the practice, the 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 BEA 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 (Aguado *et al.* 1997), silica xerogel (Aguado *et al.* 2000), kanemite (Ding *et al.* 2006), FAU (Selvam *et al.* 2003) and MCM-41 (Jon *et al.* 2006). In this study we synthesized BEA from mesoporous silica, using it as a silica source which is prepared by using non expensive templating agent (P123). Our BEA have been prepared and compared their activity in the catalytic cracking of PP waste.

## 2. Experimental

### 2.1 Chemicals

Tetraethylorthosilicate (TEOS) and tetraethylammonium hydroxide (TEAOH) were supplied by Fluka and aluminum isopropoxide (AIP) from Merck. Pluronic P123 was purchased from Aldrich and hydrochloric was from BDH Chemicals.

### 2.2 Catalysts

Zeolite beta (BEA) used in this work was synthesized using the transformation of SBA-15 to BEA method. The calcined SBA-15 to be used as a silica source that prepared in acidic media using a triblock copolymer Pluronic P123 as structure directing agent following a method of Zhao *et al.* (1998). The gel with the following molar composition of reaction mixture was:  $\text{SiO}_2 \cdot x\text{Al}_2\text{O}_3 \cdot 0.26\text{TEAOH} \cdot 5.0\text{H}_2\text{O}$  ( $x = 0.0055\text{--}0.049$ ). Thereby, the mixture of AIP and TEAOH solution was drop wise added to calcine SBA-15 with stirring. Then the mixture was aged and stirring. The gel mixture was transferred into a stainless-steel autoclave containing Teflon cup and kept in the oven at 135°C for 48 h. After that white solid sample was separated by centrifugation, washed several times with deionized water and dried in the oven at 110°C overnight.

### 2.3 Characterization

The BEA products were structurally identified using a Rigaku D/MAX-2200 Ultima-plus X-ray powder diffraction (XRD) with a monochromator for Cu  $K_\alpha$  radiation. For the Bragg angle measurement from 5-40 deg, the divergence, scattering, and receiving slits are set at 0.5 deg, 0.5 deg, and 0.3 mm, respectively. Solid state  $^{27}\text{Al}$ -MAS-NMR

spectra were performed using the Bruker Advance DPX 300 MHz NMR spectrometer. The material morphology was characterized using a JEOL JSM-5410 LV scanning electron microscope (SEM). The nitrogen adsorption isotherms were obtained using a BELSORP mini-II with 40 mg of sample. The specific surface area was analyzed using BET plot. The external surface area and micropore volume were determined by the t-plot analysis using the adsorption branch of the isotherm. Acid strength of catalysts was determined using the BEL Japan, BELCAT with the sample weight about 100 mg and highly pure ammonia gas as the probe molecule and helium as the auxiliary gas.

#### 2.4 Catalytic cracking experiments

Degradation of PP waste was performed using BEA catalysts with Si/Al ratio of 30, 60 and 90. Thermal and catalytic cracking reactions were carried out in glass under a continuous nitrogen flow by batch operation. The cracking reaction was performed at 40 min in batch reactor with a continuous nitrogen flow 20 ml/min. The effect of cracking temperature was studied by varying from 350 to 420°C. In each experiment, 5 g of plastic were loaded into the single reactor and mixed with an appropriate amount of calcined catalyst power (plastic/catalyst ratio of 5% w/w). The reactor was heated to the desired reaction temperature within 15 min approximately, and the temperature was hold for 30 min after reading the reaction temperature. Gas products were analyzed using Varian CP 3800 GC equipped with an KCl/Alumina-PLOT column (30 m x 0.35 mm), whereas liquid product obtained from the reaction was separated into two fractions, distillate oil and heavy oil, by vacuum distillation at the heater temperature of 200°C. The distillate oils were analyzed using a Varian a CP 3800 GC with CP-sil 5 column (30 m x 0.25 mm). A flame ionization detector was utilized for all GC analysis. The values of retention time of components in the distillate oil on a gas chromatogram were compared to those of reference compounds in the form of n-paraffins. The values of %conversion and % yield were calculated based on the equations as follows:

$$\% \text{ Conversion} = \frac{(\text{mass of liquid product fraction} + \text{mass of gas fraction}) \times 100}{\text{mass of plastic}}$$

$$\text{mass of gas fraction} = (a - b)$$

Where a = mass of the reactor with plastic and catalyst before reaction

b = mass of the reactor with residue and used catalyst after reaction

$$\% \text{ Yield} = \frac{\text{mass of product fraction} \times 100}{\text{mass of plastic}}$$

### 3. Results and discussion

#### 3.1 Catalysts characterization

##### 3.1.1 Powder X-ray diffraction and Scanning electron microscopy

The XRD patterns of calcined products obtained with different Si/Al ratios are shown in Figure 1. The Si/Al ratios of 30, 60 and 90 exhibited XRD pattern with diffraction peaks coincident with the pure phase BEA structure and high crystallinity can be achieved as shown in Figure 1b and 1c. With further increasing the Si/Al ratio to 90, the intensities of characteristic XRD peaks of BEA (Figure 1d) decreased. For the Si/Al ratio as low as 10, the failure of formation of BEA is depended on the amount of organic template, under the synthesis condition acting as the skeleton for inorganic ions to adhere. Obviously, it was not enough for all ions especially aluminum ionic species to form aluminosilicate building blocks. It seems that higher amount of TEAOH/Si is required for making the BEA with low Si/Al ratio. Thus, the excess amount of aluminum turns to be located at the extra-framework octahedral position instead of the framework tetrahedral site. This fact can be proven by <sup>27</sup>Al-MAS-NMR spectra of products with different Si/Al ratios in Figure 2. The spectra of calcined products show the presence of an intense signal centered at around 55 ppm (tetrahedral framework) and small signal at about 0 ppm (octahedral framework). The product at Si/Al ratios of 90 gives the signal at around 0 ppm with lower intensity than other samples. It indicates that the lower Si/Al ratio, the higher intensity of the peak assigned for the octahedral aluminum site is found. As a

result, the Si/Al ratio of 10 is not suitable to prepare BEA by this method. In other words, the large amount of AIP with the low Si/Al ratio can be considered as the diminishing of the uniform of tetrahedral unit in the structure of BEA. It is obvious that the drastic decrease in crystallinity of high Si/Al ratio is not due to the effect of particle size. It indicates that the Si/Al ratio in reactant media can play an important role on the formation of the BEA structure by this synthesis method

The SEM image of the starting SBA-15 (Figure 3a) is different from all the rest. That is, the particle shape of SBA-15 is the rope-like bundles of rods. In the presence of TEAOH and AIP, the SBA-15 rods disintegrate apart and recrystallize to form BEA at Si/Al ratio ranging from 30 to 90. The sample Si/Al of 10 shows large particles of amorphous phase with some particles of remaining SBA-15 as displayed in Figure 3b. The remaining SBA-15 is in agreement with the small angle XRD results in Figure 1a. Moreover, the SEM images of BEA with various Si/Al ratios are illustrated in Figure 3c to 3e. The BEA particles are fairly spherical shaped and the surface is not smooth. Additionally, the ranges of particle size are not quite different among the three samples of BEA (173-215 nm) with Si/Al ranging from 30 to 90.

### 3.1.2 Nitrogen adsorption

The nitrogen adsorption isotherms of calcined SBA-15 and BEA products with various Si/Al ratios are compared in Figure 4. SBA-15 exhibits a type IV adsorption isotherm which is a characteristic pattern of mesoporous material, and its BET surface area is 797 m<sup>2</sup>/g. The products synthesized using the reactant mixture containing Si/Al ratios of 30 and 60 are the type I isotherms of microporous behavior. It is obvious that the Si/Al ratio of 30 provided with the sample has higher external surface area than the Si/Al ratio of 60 (Table 1). It is evident that the increase in external surface area is affected by the particle nano-size. The BEA product obtained from the reactant mixture with the Si/Al ratio of 90 shows the hysteresis loop in the region of the relative pressure around 0.5-0.8 indicating the mesoporous behavior along with the microporous character at the very low relative pressure. The result is in agreement with the low crystallinity, related to the decreased order of the zeolite structure. The BET surface areas are varied in the range between 455 and 782 m<sup>2</sup>/g. Besides, the samples with high crystallinity show higher BET specific surface areas, and only the BEA sample synthesized with Si/Al of 30 in the starting mixture displays the extremely high external surface area.

### 3.1.3 NH<sub>3</sub>-TPD profiles

Figure 5 exhibits NH<sub>3</sub>-TPD profiles of calcined SBA-15 and transformation products with different Si/Al ratios. The NH<sub>3</sub> desorption peak centered at 170°C is typically assigned to a weaker acid Bronsted, or Lewis site, or even to silanol groups. The component peak at 430°C is assigned to a stronger acid Bronsted and Lewis site. It is found that the peak at 170°C is more pronounced for all samples but in different extent. The acidities of the zeolite samples are concluded in Table 1. It is noted that the total acidity of the zeolite samples is inversely proportional to the Si/Al ratio used in the synthesis course. As usual, the lower the Si/Al ratio, the higher the acidity is the [AlO<sub>2</sub>] tetrahedral units in the zeolite framework are accounted for the acidity of the zeolite samples. It is noticeable that the results are similar to Sakthivel *et al.* (2009). The product with the Si/Al ratio of 30 shows the highest number of acid sites.

## 3.2 Catalytic cracking of polypropylene

### 3.2.1 The effect of Si/Al ratios and reaction temperature

The effect of Si/Al ratios of 30, 60 and 90 was tested in catalytic cracking of PP waste at the low temperature of 350°C. The low temperature was used in order to avoid the competition of thermal cracking of PP waste. The % conversion has been calculated by taking into account only the liquid and gas products that evaporated from the reactor at the reaction temperature. The results are shown in Table 2. The liquid fraction of thermal cracking is not obtained at all and the conversion of plastic is only 2.0% whereas it is in the range from 42.9 to 50.5% for catalytic cracking. The result indicates the difficulty in cracking PP waste without catalyst at low temperature. Therefore, the total weight loss of plastic precursor after reaction is dedicated to gas fraction. In the presence of BEA, the conversion drastically increases from 2.0% to about 42 to 50%. The results indicate that the waxy residue decomposed into relatively lighter liquid hydrocarbons resulting in higher yield of liquid fraction than the case of thermal cracking. The Si/Al ratio of 30 gives the highest %conversion due to the influence of zeolite external surface area and strong acidity, determined by NH<sub>3</sub>-TPD. The high external surface area contains the great numbers of

external acid sites, which may play an important role on the cracking of bulky molecule such as polymer (Isihara *et al.* 1992). This fact favors long-chain polymer scission reactions, and a highly cracked product with shorter hydrocarbon chains is obtained. The synergism of catalyst surface area, external surface area and acidity of BEA Si/Al of 30 contributes to the PP waste conversion in the cracking process. The profiles of gas product distribution of thermal cracking and catalytic cracking are shown in Figure 6. For thermal cracking, propene, *n*-pentane and  $C_5^+$  are the predominant products. In the presence of BEA catalysts, the product distribution in gas fractions is different from that in the absence of catalyst. The main components in gas fractions from catalytic cracking are propene, *n*-butane, *i*-butene and  $C_5^+$ . Figure 7 shows carbon number distribution of distillate oil obtained by catalytic cracking. The major liquid products for all catalyst are distributed in the range of  $C_7$  to  $C_9$ . That is comparable to distribution of distillate oil obtained in this work based on the boiling point range using *n*-paraffin as a reference. In conclusion, the Si/Al ratio of 30 is a powerful catalyst and was selected for the study on the effect of reaction temperature.

BEA with the Si/Al ratio of 30 was used as a catalyst for studying the influence of reaction temperature on its activity and the thermal cracking was tested in comparison. The values of %conversions and product distribution for thermal and catalytic cracking of PP waste at 350, 380, 400 and 420°C are shown in Table 3. The activities of the zeolite in terms of %conversion are very high up to 96% in the temperature range from 380 to 420°C and are temperature independent. Sakata *et al.* (1999) reported that thermal cracking of PP waste at 380°C shows a high amount of liquid and gas product. Below the temperature of 380°C the conversion is affected by the temperature. The distribution of both gas and liquid products are also affected by temperature when the temperature was lowered than 380°C. For the temperature in the range of 380 to 420°C, the products are mainly in liquid fractions at the high yield about 51-53% with minor product in gas fractions at the yield about 42 to 44%. The results are similar to Demirbas (2000). The effect of BEA on PP waste cracking clearly can be observed at the residue of catalytic cracking which dramatically reduces from 78.8 to 4.5% compared with the thermal cracking. Figure 8 shows the distribution of gas fractions provided by catalytic cracking. The major components for catalytic cracking are propene, *n*-butane, *i*-butene and  $C_5^+$ . When the reaction temperature increases, lighter hydrocarbons (methane and ethane) also increase. While the components of thermal cracking are  $C_1$  through  $C_5$ , the major components are propene and *n*-pentane (not shown). The growing yield of volatile components as a function of temperature could be caused by the differences in the thermal stability of polymer chain because the hydrocarbon has reducing thermal stability with increasing temperature. Therefore, the C-C bonds were cracked more easily at 400 and 420°C than at lower temperature, and it resulted in higher yield of volatile products. Considering the gas selectivity of catalytic cracking of PP waste at 420°C, it was found that *n*-butane is lower and *i*-pentane is higher at 400°C due to the effect of thermal cracking with catalytic cracking. Figure 9 shows the carbon number distribution of distillate oil from catalytic cracking with different reaction temperatures. The distillate oil components are mainly in the range of  $C_7$  to  $C_9$  for reaction temperatures at 380 to 420°C while  $C_8$  and  $C_9$  are major products at 350°C. This result indicates that the liquid product distribution depends on the temperature only at low temperature. The conversion and product distribution obtained at the temperatures of 380°C and 400°C are not different. For thermal cracking at 380°C, the liquid fraction is rich of  $C_9$ . For the thermal cracking at 400 and 420°C, the liquid hydrocarbon fractions are distributed in a wide range of equivalent hydrocarbons from  $C_6$  to  $C_9$  (not shown). It is well known that the thermal cracking occurs by random scissoring of the long polymeric chain, and the products of cracking are distributed in a wide range of molecular weights. This result has been observed by Hwang *et al.* (2002), degradation of PP waste are distributed in a narrow range of carbon number compared with thermal degradation.

### 3.2.2 Activities of Regenerated BEA in PP Waste Cracking

The values of %conversion and %yield obtained by the PP waste cracking using fresh and regenerated BEA with Si/Al ratio of 30 catalysts at 380°C are shown in Table 4. The values of %conversion are not different from fresh catalyst. The regenerated catalyst provides relatively lower yield of gas fraction and higher residue comparing to the fresh catalyst. Relatively more amount of residue, especially in form of wax remains in the reactor of the regenerated catalyst rather than that of fresh catalyst. This result suggests that the regenerated catalysts have less specific surface area and acidity than the fresh catalyst. The gas fraction composes the same product distribution. There is no difference in selectivity in gas fraction among the four catalysts. The product distributions of liquid fraction obtained by catalytic cracking of PP waste using the fresh and regenerated BEA provide mainly  $C_7$  and  $C_8$  while  $C_8$  and  $C_9$  are mainly products for the third regenerated, indicating that the acidity of catalyst at the third regenerated is reduced by several calcinations before used.



#### 4. Conclusions

The nanoparticle BEA was successfully prepared by using a novel method. The Si/Al ratios were varied in a range from 10 to 90. It is found that the Si/Al ratio as low as 10, the failure of formation of BEA is owing to amount of organic template under the synthesis condition, acting as the skeleton for inorganic ions to adhere is not enough for all ions especially aluminum ionic species to form aluminosilicate building blocks. It is obvious that the Si/Al ratio of 30 provided with the sample with highest external surface area. BEA is found very active in cracking of PP waste to liquid fuel. The thermal cracking of PP waste leads to plastic %conversion lower than catalytic cracking. The plastic conversions and the yields of products fractions obviously depend on the reaction temperatures and Si/Al ratios. It is interesting to note that the product selectivity is affected by those factors. In the catalytic cracking of PP waste at 380°C over BEA (Si/Al = 30) is powerful catalyst shows greater %conversion than 95% due to the drastic influence of external surface area and acidity of the catalyst. The gas products obtained are mainly propene, *i*-butene and C<sub>5</sub><sup>+</sup>. The liquid products obtained by cracking of plastic are mainly in the boiling point ranging from C<sub>6</sub> to C<sub>9</sub>. The used catalyst can be regenerated easily by calcination and its activity remains comparable to the fresh catalyst

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#### References

- Achilias, D.S., & Megalokonomos, P. (2006). *J. Environ. Prot. Ecol.* **7**, 407-413.
- Achilias, D.S., & Karayannidis, G.P. (2004). *Water Air Soil Pollut. Focus.* **4**, 385-396.
- Aguado, J., Solelo, J. L., Serrano, D. P., Calles, J. A., & Escola, J. M. (1997). *Energy & Fuels.*, **11**, 1225.
- Aguado, J., Serrano, D. P., Escola, J. M., Garagorri, E., & Fernández, J. A. (2000). *Polym. Degrad. Stab.*, **69**, 11.
- Aguado, J., Serrano, D.P., Escola, J. M., & Peral, A. (2008). *J. Anal. Appl. Pyrolysis.* **85**, 352-358.
- Artetxe, M., Lopez, G., Amutio, M., Elordi, G., Bilbao, J., & Olazar, M. (2012). *Chem. Eng. J.* 207-208, 27-34.
- Bregolato, M., Bolis, V., Busco, C., Ugliengo, P., Bordiga, S., Cavani, F., Ballarini, N., Maselli, L., Passeri, S., & Forni, L. (2007). *J. Catal.* **245**, 285.
- Demirbus, A. (2000). *J. Anal and Appl. Pyrolysis.* **72**, 97-102.
- Ding, L., Zheng, Y., Zhang, Z., Ring, Z., & Chen, J. (2006). *Micropor. Mesopor. Mater.* **94**, 1.
- Hulea, V., & Dumitriu, E. (2004). *Appl. Catal. A.* **277**, 99.
- Hwang, E. Y., Kim, J. R., & Choi, J. K. (2002). *J. Anal. Appl. Pyrolysis.* **62**, 351-364.
- Isihara, Y., Nanbu, H., Saido, K., Ikemura, T., & Takesue, T. (1992). *Polymer.* **33**, 3482.
- Jon, H., Nakahata, K., Lu, B., Oumi, Y., & Sano, T. (2006). *Micropor. Mesopor. Mater.* **94**, 72.
- Kumar, N., Masloboischikova, O. V., Kustov, L. M., Hweikkila, T., Salmi, T., & Murzin, D. Y. (2007). *Ultrasound Sonochem.* **14**, 122.
- Lee, K. H., Noh, N. S., & Valenci, S. (2002). *Degradation and Stability.* **78**, 539-544.
- Lee, Y. J., Kim, J. H., Kim, S. H., Hong, S. B., & Seo, G. (2008). *Appl. Catal. B.* **83**, 160.
- Manos, G., Yusof, T., Gangas, N.A., & Papayannakos, N. (2002). *Energy Fuel.* **16**, 485-489.
- Nakao, R., Kubota, Y., Katada, N., Nishiyama, N., Kunitomi, K., & Tomishige, K. (2004). *Appl. Catal. A: General.* **273**, 63.
- Obali, Z., Sezgi, N. A., & Dogu, T. (2012). *Chem. Eng. J.* 207-208, 421-425.
- Panda, A. K., & Singh, R. K. (2011). *J. Fuel Chem. Techno.* **39** (3), 198-202.
- Renzini, M. S., Lerici, L., Sedran, U., & Pierella, L. B. (2011). *J. Anal. Appl. Pyrolysis.* **92**, 450-455.

- Sakata, Y., Uddin, A., & Muto, A. (1999). *J. Anal. Appl. Pyrolysis*. **51**, 135.
- Sakthivel, A., Iida, A., Komura, K., Sugi, Y., & Chary, K.V. R. (2009). *Micropor. Mesopor. Mater.* **119**, 322.
- Scheirs, J. (1998). *Polymer Recycling*. J. Wiley & sons, W. Sussex.
- Selvam, T., Bandarapu, B., Mabande, G. T. P., Toufar, H., & Schwieger, W. (2003). *Micropor. Mesopor. Mater.* **64**, 41.
- Seo, Y. H., lee, K. H., & Shin, D.H. (2003). *J. Anal. Appl. Pryrolysis*. **70**, 383.
- Thailand Energy and Environment Network (TEENT), (2012), *Turning Plastic Waste into Crude Oil*. [online] Available: <http://teenet.tei.or.th/Knowledge/plastictooil.html> (March 12, 2012).
- Wadlinger, R. L., Kerr, G. T. & Rosinski, E. J. (1967). US Pat 3,308,069.
- Xia, Q. H., & Tatsumi, T. (2005). *Mater. Chem. Phys.* **89**, 89.
- Zhao, D., Feng, J., Hua, Q., Malosh, N., Fredrickson, G. H., Chmelka, B. F. & Stucky, G. D. (1998). *Science*. **279**, 548.

Table 1: Transformation of SBA-15 into zeolite beta at various conditions

Silica source	yield %	Si/Al in gel	SEM Particle size (nm)	BET Surface area (m <sup>2</sup> /g)	External surface area (m <sup>2</sup> /g)	Product phase	NH <sub>3</sub> -TPD acidity (mmol/g)		
							weaker (170°C)	stronger (200°C)	total
TEOS	-	-	50 x 110	797	-	SBA-15	n/a	n/a	n/a
SBA-15	n/a	10	n/a	346	n/a	amorphous	n/a	n/a	n/a
SBA-15	79.8	30	173	782	106.9	BEA	1.09	0.12	1.21
SBA-15	71.8	60	215	781	43.4	BEA	0.71	0.23	0.94
SBA-15	6.0	90	211	455	41.1	BEA	0.51	0.28	0.8

Table 2: Values of %conversion and %yield obtained from thermal cracking and catalytic cracking of PP wate over BEA with various Si/Al ratios.

%conversion	Thermal 350°C	Si/Al = 30	Si/Al = 60	Si/Al = 90
		2.0	50.5	42.9
%yield				
1. gas fraction	2.0	33.1	27.5	27.3
2.liquid fraction	-	17.4	15.4	16.9
-% distilled oil	-	85.0	82.5	77.5
-% heavy oil	-	15.0	17.5	22.5
3. residue	98.0	49.5	57.1	55.8

Table 3: Values of %conversion and %yield obtained by thermal cracking and catalytic cracking of PP waste at various temperatures

%conversion	350°C		380°C		400°C		420°C	
	BEA	thermal	BEA	thermal	BEA	thermal	BEA	thermal
	50.5	2.0	95.5	21.2	96.0	60.0	96.1	93.3
%yield								
1. gas fraction	33.1	2.0	42.9	14.3	42.6	25.2	44.5	41.1
2. liquid fraction	17.4	-	52.6	6.9	53.4	34.8	51.5	52.2
- %distillated oil	85.0	-	77.6	55.1	77.9	53.2	75.7	55.3
- %heavy oil	15.0	-	22.4	44.9	22.1	46.8	24.3	44.6
3. residue	49.5	98.0	4.5	78.8	4.0	40.0	3.9	6.7

Table 4: Values of %conversion and %yield obtained by catalytic cracking of PP waste using the fresh and the regenerated catalysts.

	Fresh BEA	1 <sup>st</sup> Regenerated	2 <sup>nd</sup> Regenerated	3 <sup>rd</sup> Regenerated
%conversion	95.8	95.1	93.5	85.6
%yield				
1. gas fraction	42.2	40.5	37.7	36.6
2. liquid fraction	53.6	54.6	55.8	49.0
- %distillate oil	39.0	39.8	42.2	36.8
- %heavy oil	14.6	14.8	13.6	12.2
3. residue	4.2	4.8	6.5	14.4

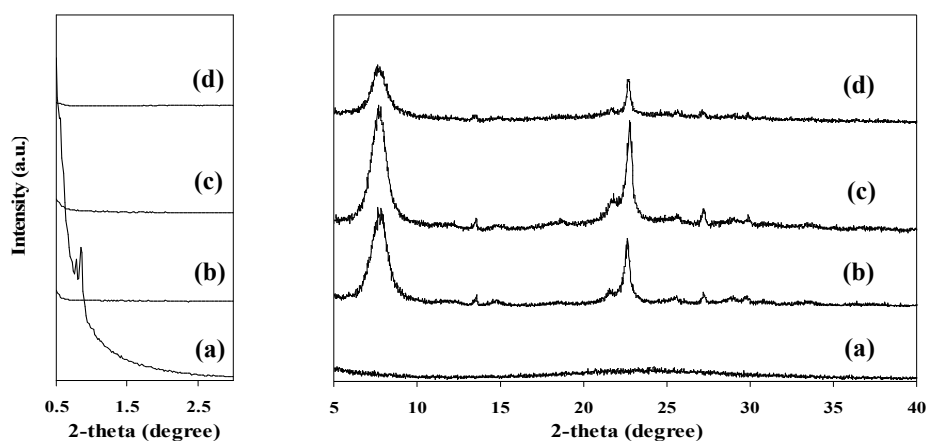


Figure 1: XRD patterns of calcined BEA with various Si/Al molar ratios: (a) 10, (b) 30, (c) 60 and (d) 90.



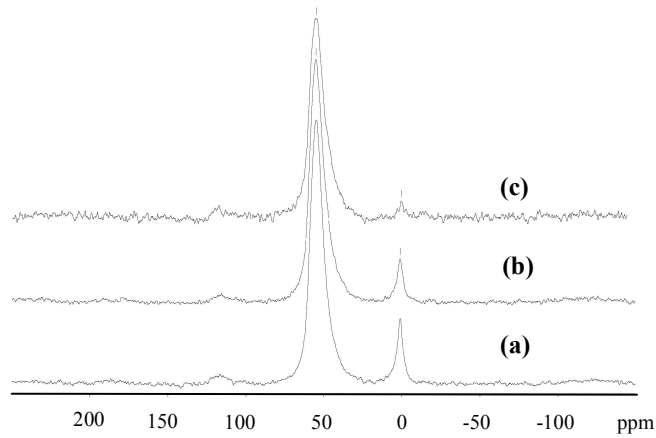


Figure 2:  $^{27}\text{Al}$ -MAS-NMR spectra of calcined BEA catalysts with different Si/Al ratios in catalyst (a) 30, (b) 60 and (c) 90.

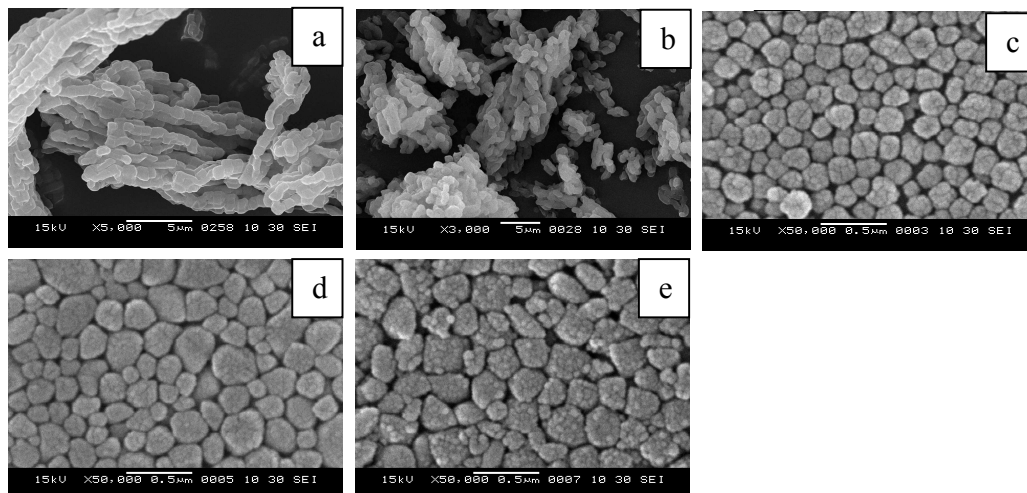


Figure 3: SEM images of calcined BEA with various Si/Al ratios of (a) 10, (b) 30, (c) 60 and (d) 90

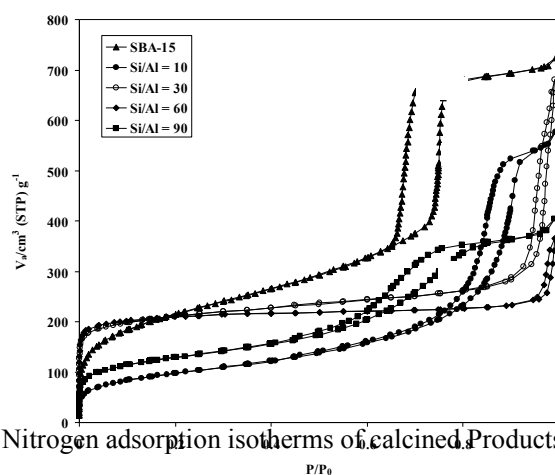


Figure 4: Nitrogen adsorption isotherms of calcined products.

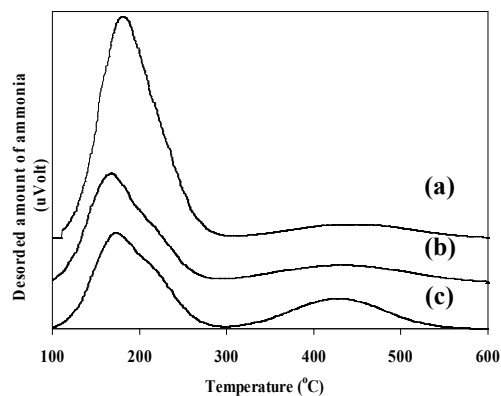


Figure 5: NH<sub>3</sub>-TPD profiles of BEA with various Si/Al ratios in catalyst of (a) 30, (b) 60 and (c) 90.

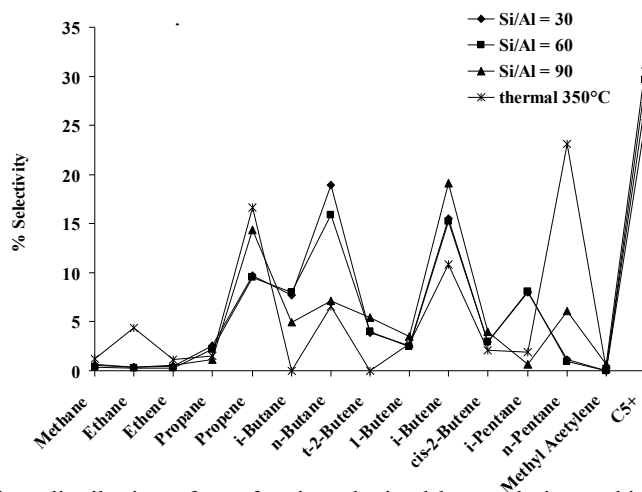


Figure 6: Product distribution of gas fraction obtained by catalytic cracking of PP using BEA with various Si/Al ratios.

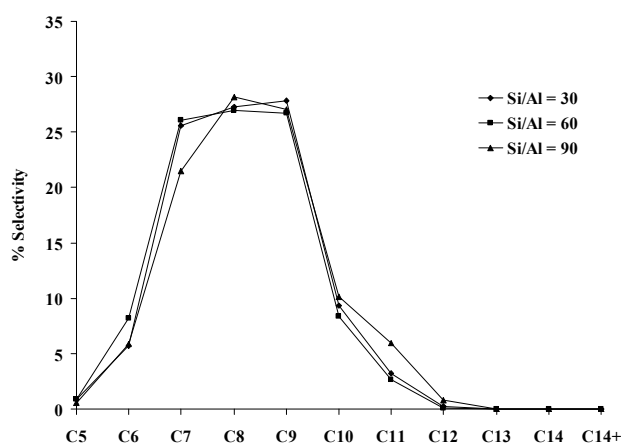


Figure 7: Carbon number distribution of liquid fraction from catalytic cracking over BEA with various Si/Al ratios.

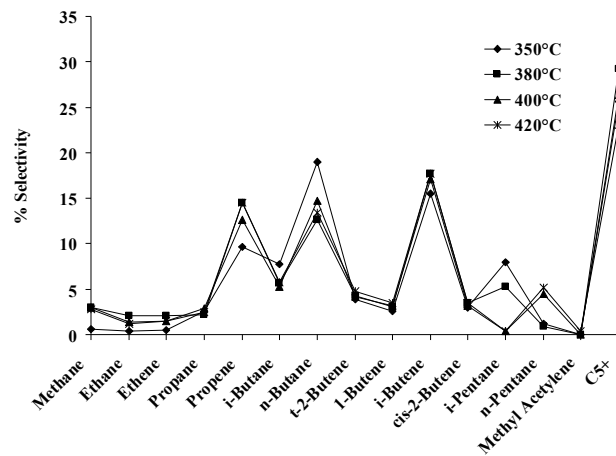


Figure 8: Product distribution of gas fraction obtained by catalytic cracking over BEA (Si/Al = 30) with various reaction temperatures.

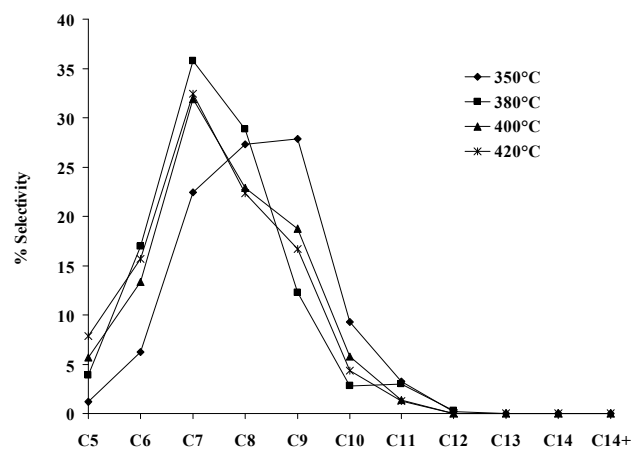


Figure 9: Carbon number distribution of liquid fraction from catalytic cracking over BEA (Si/Al = 30) with various reaction temperatures.

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