

## Characteristics of Metal Supported-Zeolite Catalysts for Hydrocracking of Polyethylene Terephthalat

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**Abstract :** Characterization and modification of natural zeolite (ZA) produced in Sukabumi, West Java, Indonesia, as well as metal supported onto the zeolite for hydrocracking catalysts of polyethylene terephthalat (PET) have been conducted. The natural zeolite was refluxed in HCl 3M for 30 min., drying and heated in a microwave produced the ZAA sample. The transition metal such as Cu, Cr, Ni, or Pd was loaded into the ZAA sample under reflux in methanol using salt precursor of each metal, produced the Cu/ZAA, Cr/ZAA, Ni/ZAA, and Pd/ZAA catalysts. The zeolite based samples were characterized by means of determination of acidity by vapor adsorption of NH<sub>3</sub> and pyridine, catalyst crystallinity by X-ray diffraction (XRD), surface area by surface area analyzer NOVA-1000 and TO<sub>4</sub> (T= Si and Al) site by Infra Red Spectrophotometer (IR). The PET was pyrolyzed in 350 °C produced liquid fraction as a feed for hydrocracking process. The hydrocracking of the PET was carried out in a fixed bed reactor of stainless steel at temperature of 350 °C, H<sub>2</sub> flow rate of 20 mL/min., feed/catalyst ratio of 10. Liquid products of the hydrocracking were analyzed using GC and GC-MS. The characterization results showed that the Indonesian natural zeolite produced in Sukabumi consisted mainly of mordenite crystalline. The HCl treatment towards the natural zeolite caused dealumination, increased its acidity and surface area. Loading of Ni, Cu, Cr, or Pd metal on to the zeolite did not affect the zeolite crystallinity. However, the metal loading decreased surface area of the zeolite. Products of the hydrocracking were liquid, coke, and gas fractions. The liquid products consisted mainly of gasoline fraction (C<sub>5</sub>-C<sub>12</sub>). The highest liquid product conversion was produced by the Pd/ZAA catalyst, i.e. 34.05 wt. %, with selectivity towards gasoline fractions was 97.99 wt. %.

**Keywords:** natural zeolite, characterization, modification, hydrocracking, metal loading, polyethylene terephthalat.

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### I. Introduction

Waste plastics have caused serious environmental problems because it is not degradable. In contrast, waste plastics are regarded as cheap and abundant sources of chemicals and energy. The recycling of waste plastics into useful hydrocarbons, i.e chemicals and fuel fractions is desirable. The usual chemical recycling method used for thermoplastics such as polyethylene was combination method of pyrolysis and catalytic cracking. The pyrolysis of low-density polyethylene (LDPE) [1] as well as PVC waste plastics was carried out under the range temperature of 150-350 °C [2] and that for high-density polyethylene (HDPE) plastic was pyrolyzed in temperature range of 400-450 °C [3]. In the catalytic cracking of waste plastics, the utilization of NiMo/Al<sub>2</sub>O<sub>3</sub> [1] as well as zeolite, i.e mordenite [4-5], or H-ferrierite [6], ZSM-5 [7], and mesostructure [5] catalysts produced high conversion of liquid fractions.

Zeolites play highly important roles as catalyst in catalytic cracking because it has unique properties such as high crystallinity, surface area, acidity, ion-exchanged capacity, and shape-selective character. On the other hand, there are widespread, abundant resources of natural zeolites in Indonesia. Their utilization as catalysts, however, has been little explored, in spite of the fact that their potential effectiveness may contribute to reduce industrial production costs. Synthetic zeolites were used in a wide range as catalysts. However, the synthetic zeolite was expensive and still imported by Indonesia. In spite of the fact that Indonesia have abundant natural zeolites spread out in Java, Celebes, Sumatra and Timor. Indonesian natural zeolites produced in West Java (Bayah and Cipatuja), Center of Java (Wonosari, Yogyakarta) has been known contains large portion of Mordenite. The zeolites showed better performance in crystallinity and acidity after treated with HCl [8-9].

Various methods have been developed to modify their acid properties and to improve their catalytic performance, e.g. supported of transition metals into the  $\text{Al}_2\text{O}_3$  [1] as well as the zeolite framework [10-11].

Based on the above consideration, the authors undertaken characterization of natural zeolite produced in Sukabumi, West Java, Indonesia, and its modifications by treating with an aqueous HCl solution, followed by microwave treatment. In an attempt to increase the zeolite performance as catalyst, transition metals, i.e Ni, Cu, Cr, or Pd was supported into the zeolite framework. Their characters to hydrocrack polyethylene terephthalat (PET) were then evaluated. The results are discussed as followed.

## II. Experimental

### 2. 1. Treatment of Zeolite

Natural zeolite (ZA) produced in Sukabumi, Indonesia was ground and sieved to <100 mesh particles before use. About 5 g of natural zeolite sample in 3N HCl ( $125 \text{ cm}^3$ ) was heated at  $90 \text{ }^\circ\text{C}$  for 30 min. while magnetically stirred. After the HCl treatment, the sample was filtered and washed with deionized water until no chloride ion could be detected by test using  $\text{AgNO}_3$  solution, after which it was dried at  $120 \text{ }^\circ\text{C}$  for 3 h and then heated in a microwave at 450 watt for 30 min. produced the ZAA sample.

### 2. 2. Impregnation of metal onto the zeolite

Twenty five grams of ZAA sample was mixed with  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.25 g) in 200 mL of methanol followed by refluxing. The mixture was laid still for 5 h, after which the solvent was evaporated. After drying at  $120 \text{ }^\circ\text{C}$  for 3 h, the sample was then heated in a microwave at 450 watt for 30 min., followed by reducing under hydrogen gas stream ( $20 \text{ mL/min.}$ ) at  $400 \text{ }^\circ\text{C}$  for 3 h, produced the Ni/ZAA sample. The impregnation of others metal onto the zeolite was carried out under the same procedure using  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1.95 g) produced the Cr/ZAA sample;  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.925 g) produced the Cu/ZAA sample; and  $\text{PdCl}_2$  (0.4 g) produced the Pd/ZAA sample, respectively. The chemicals used were produced by Merck.

### 2. 3. Catalyst Characterization

The effect of modified treatments towards dealumination as well as acid sites in the natural zeolite was analyzed by FT-IR Spectroscopy (Shimadzu). Total acid site amount on zeolite samples was determined gravimetrically using ammonia and pyridine base vapour adsorption. Crystallinity changed of zeolite samples was analyzed by x-ray diffraction (XRD)-Shimadzu, surface area was determined using NOVA-1000, Quantachrome Corporation based on the BET equation, and Si/Al ratio was analyzed by Atomic Absorption Spectrophotometer (AAS) Perkin Elmer 3110, respectively.

### 2. 4. Catalytic Activity Test

Catalytic activity test was carried out in hydrocracking process of the Polyethylene terephthalat (PET). The PET was pyrolyzed in  $350 \text{ }^\circ\text{C}$  to produce liquid fraction as a feed prior for hydrocracking process. The process was conducted in a semi flow reactor system using  $\text{H}_2$  gas at flow rate of  $20 \text{ mL/min.}$ ; for 60 min; reaction temperature  $350 \text{ }^\circ\text{C}$ , feed/catalyst weight ratio = 10 (the feed was a PET). Thermal cracking (without catalyst) of the PET was conducted at  $600 \text{ }^\circ\text{C}$  for 4 h. Thermal cracking (without catalyst) of the PET was conducted at  $600 \text{ }^\circ\text{C}$  for 4 h. The hydrocracking products consisted of gas, liquid, coke, and residue. The liquid product was analyzed by gas chromatography (GC) and chromatography-mass spectroscopy (GCMS) SHIMADZU QP2010S. Oxidation of the used catalyst was conducted at  $500 \text{ }^\circ\text{C}$  for 1 h to determine the amount of coke. The product conversion (wt.%) was quantitatively calculated by means of  $\{(\text{weight of the product})/\text{initial weight of the PET}\}100\%$ . Gas product (wt.%) was quantitatively calculated by means of  $(100 - \text{coke} - \text{liquid} - \text{residue})\%$ . Selectivity of gasoline and diesel fractions was calculated by  $\{\text{GC area of gasoline or diesel}/\text{total area of liquid product}\}100\%$ .

## III. Result And Discussion

Effect of the HCl treatment towards dealumination of zeolite framework was analyzed by Infra Red Spectroscopy (IR) based on the wave number of  $\text{TO}_4$  ( $T = \text{Si or Al}$ ) site at  $1250\text{-}950 \text{ cm}^{-1}$ . The result was shown in Fig. 1.

Fig. 1 showed that the acid treatment caused dealumination of the zeolite sample indicated by the shifted of the wave number from  $1041.56$  to  $1087.85 \text{ cm}^{-1}$ . The successive treatment caused the increase of dealumination. The acid treatment leached Al framework of Indonesian natural zeolites as shown by research undertaken by Trisunaryanti et al. [7-8]. This data was in line with the result of Si/Al ratio (mol/mol) of the ZA and ZAA sample of 4.3 and 6.2. The ratio of Si/Al increased due to the dealumination process.

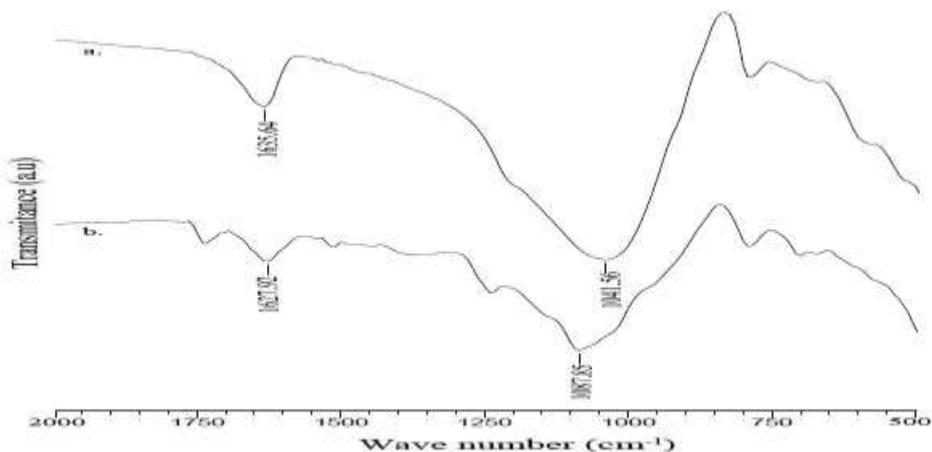


Figure 1 Infra Red Spectra of: a) ZA and b) ZAA

Total acid amount of the zeolite samples determined by ammonia or pyridine base vapour adsorption was shown in Table 1. It was shown that the acid amount determined by ammonia was higher than that of pyridine. This phenomena could be explained by the facts that ammonia was a stronger base than that of pyridine and pyridine has bigger molecular size than ammonia thus pyridine can only adsorbed in the outer surface of the zeolite. Ammonia with smaller molecular size can be adsorbed on outer and inside the zeolite surfaces. It could also be seen that the total acid amount of the zeolite samples increased by the HCl treatment. Impregnation of metals onto the ZAA sample increased the ammonia acidity. On the other hand, pyridine acidity of the ZAA sample increased by loading of Ni or Cu metal, whereas the Cr and Pd did not affect the pyridine acidity of the ZAA. These results indicated that the loading of a small amount of metal onto the ZAA sample performed a new acid site (Lewis acid).

Table 1 Total acid amount of the zeolite samples

Sample	Ammonia (mmol/g)	Pyridine (mmol/g)
ZA	0,44	0,16
ZAA	1,76	0,32
Cr/ZAA	2,57	0,31
Cu/ZAA	2,63	0,68
Ni/ZAA	3,98	0,82
Pd/ZAA	3,58	0,32

The infra Red spectroscopy of the ZAA sample before and after adsorption of pyridine vapour base was shown in Fig. 2. This Figure showed that the Lewis acid (1627.92 and 1735.93  $\text{cm}^{-1}$ ) and Bronsted acid (1543.05  $\text{cm}^{-1}$ ) sites were available in the zeolite sample. This phenomenon described that the zeolite was promising to be used as acid catalyst as well as supported catalyst.

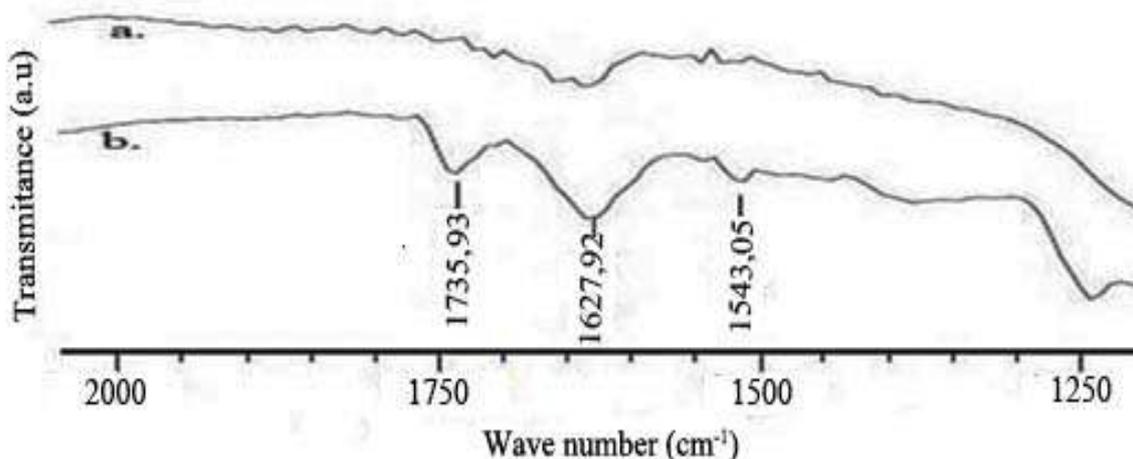


Figure 2 Infra Red Spectra of ZAA sample: a) before and b) after pyridine absorption

Fig. 3 showed the diffractograms of the zeolite samples. It was found that the natural zeolite produced in Sukabumi, West Java, Indonesia consisted mainly of the mordenite type crystalline. Treatment of HCl towards the zeolite as well as impregnation of transition metal on to the zeolite did not alter the zeolite crystallinity.

The BET surface area of the ZA, ZAA, Ni/ZAA, Cr/ZAA, Cu/ZAA and Pd/ZAA was 24.63, 133.75, 46.13, 50.61, 47.47, and 53.89 m<sup>2</sup>/g, respectively. The HCl activation followed by microwave treatment towards the ZA sample extremely increased its surface area. This result indicated that the activation and treatment reduced the impurity that blockage the pore mouth of the zeolite. Impregnation of metal onto the ZAA framework decreased its surface area. This phenomena were taken place may be caused by the non homogeneous distribution of metal in the ZAA surface. Some of the metal atoms may block the pore mouth of the zeolite.

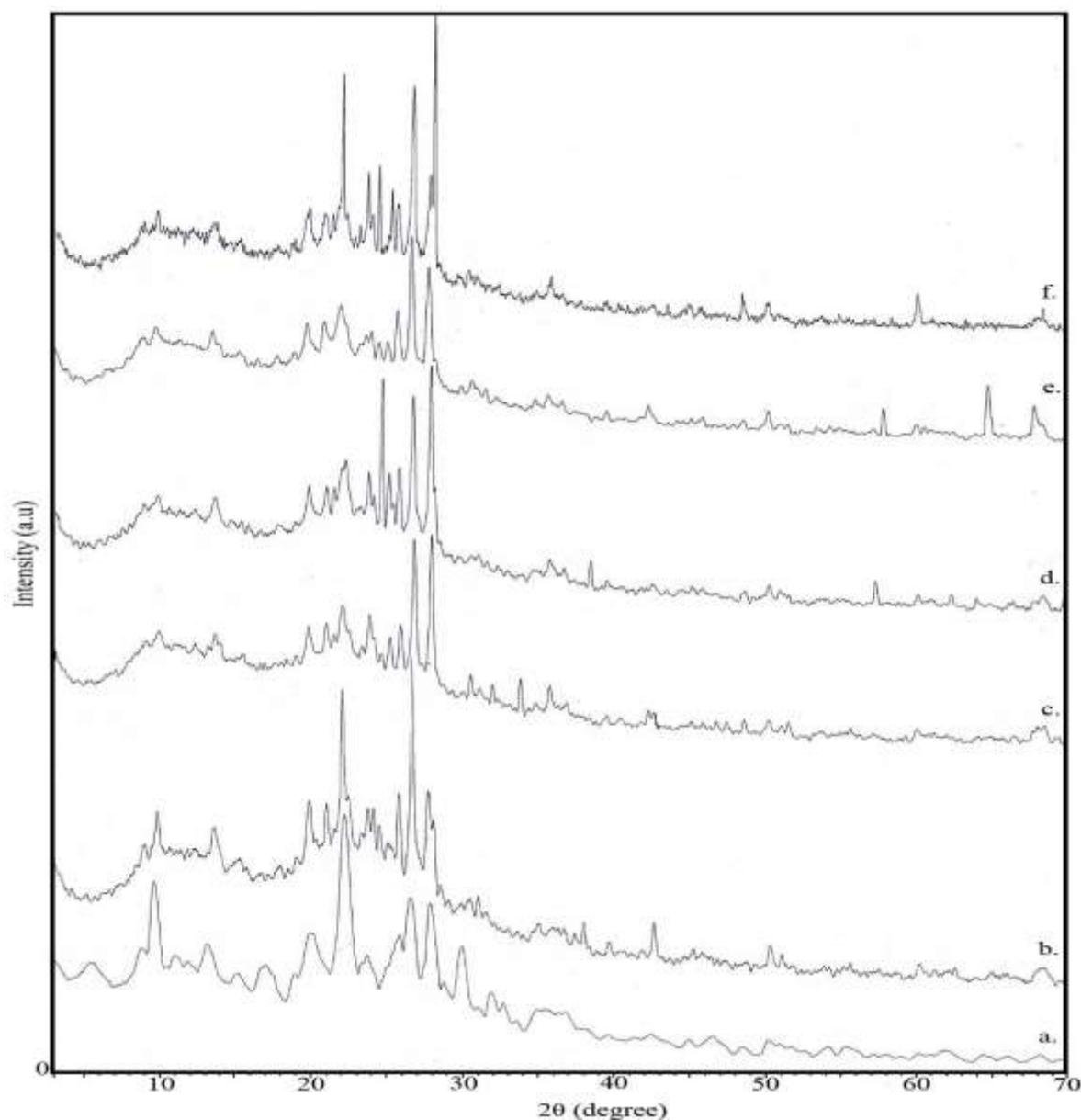


Figure 3 Diffractogram of: a) ZA, b) ZAA, c) Ni/ZAA, d) Cr/ZAA, e) Cu/ZAA and f) Pd/ZAA

Table 2 showed the activity of the zeolite catalysts on hydrocracking of the pyrolyzed PET. It was seen that the thermal process produced the highest number of gas fraction, whereas using zeolites as well as metal supported-zeolite catalysts showed a higher amount of the liquid product. This condition can be described by the fact that the thermal cracking proceed via the radical mechanism. The zeolite based catalyst consisted of acid sites that hydrocracked the PET feed via the carbonium ion intermediate to produce branched alkane and n-alkene in the range of liquid hydrocarbons with carbon number range between C<sub>7</sub>-C<sub>15</sub> [12]. The highest conversion of liquid product was performed using Pd/ZAA catalyst.

Tabel 2 Product distribution of hydrocracking of pyrolyzed PET

Catalyst	Product distribution (wt. %)			
	Liquid	Coke	Residue	Gas
Thermal <sup>a)</sup>	21,90	-	0,09	78,01
ZA <sup>b)</sup>	22,95	2,64	1,77	72,64
ZAA <sup>b)</sup>	24,74	2,65	2,18	70,43
Cr/ZAA <sup>b)</sup>	32,03	2,85	2,39	62,73
Cu/ZAA <sup>b)</sup>	30,85	3,76	3,03	62,36
Ni/ZAA <sup>b)</sup>	29,81	3,35	2,27	64,57
Pd/ZAA <sup>b)</sup>	34,05	1,47	12,28	52,2

Note: a) carried out at 600 °C within 4 h; b) carried out at 350 °C within 60 min.

Table 3 showed the product distribution of the liquid fraction that consisted of gasoline (C<sub>5</sub> – C<sub>12</sub>) fraction in retention time range of 0 - 10 min. and that of diesel (C<sub>13</sub> – C<sub>20</sub>) fraction in the range of retention time of > 10 min. The gasoline fraction was predominant for thermal and catalytic cracking conditions. This result was consistent with the result showed by Aguado, et al [4]. The utilization of metal supported-zeolite catalysts increased the gasoline product. The highest portion of gasoline fraction was shown by Pd/ZAA catalyst (97.99 wt. %) similar to that of Cr/ZAA catalyst (97.45 wt. %). The data was supported by chromatogram of the product showed in Fig. 4.

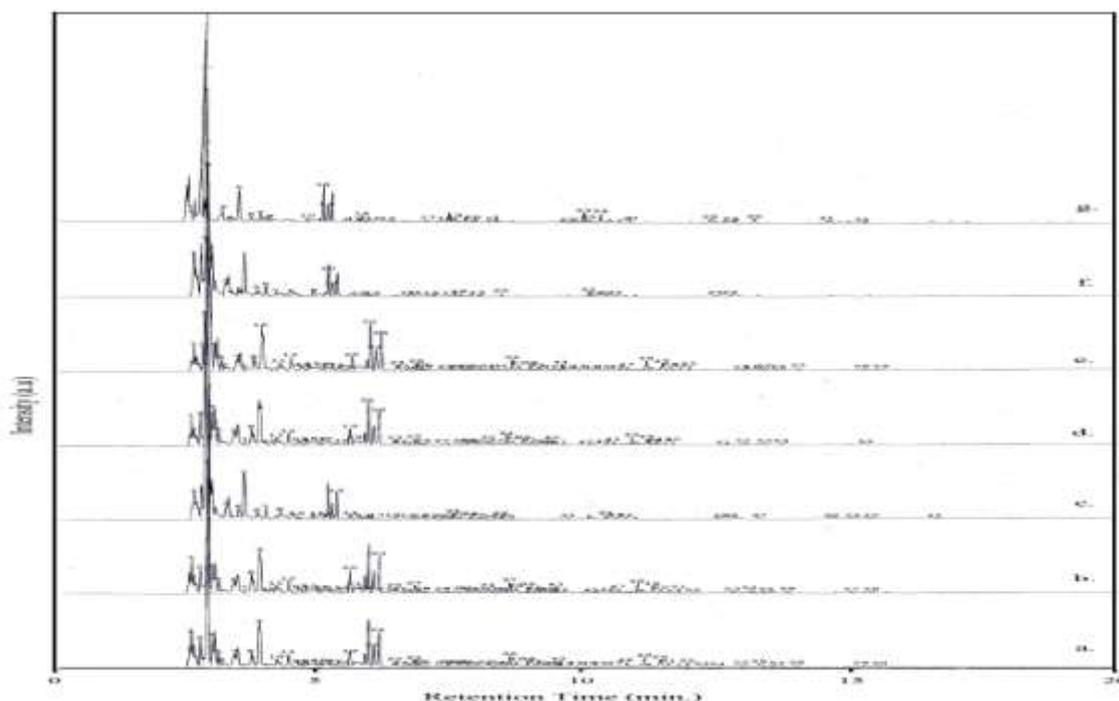


Figure 4 Difractograms of the hydrocracking product of PET using: a) ZA, b) ZAA, c) Ni/ZAA, d) Cr/ZAA, e) Cu/ZAA, f) Pd/ZAA catalyst, and g) thermal

Table 3 Product distribution of liquid fraction

Catalyst	Product distribution (wt. %)	
	Gasoline Fraction	Diesel Fraction
Thermal <sup>a)</sup>	85,49	14,51
ZA <sup>b)</sup>	90,52	9,48
ZAA <sup>b)</sup>	91,05	8,95
Cr/ZAA <sup>b)</sup>	97,45	2,55
Cu/ZAA <sup>b)</sup>	93,93	6,07
Ni/ZAA <sup>b)</sup>	92,30	7,70
Pd/ZAA <sup>b)</sup>	97,99	2,01

Note: a) carried out at 600 °C within 4 h; b) carried out at 350 °C within 60 min.

The thermal cracking was carried out at 600 °C that gave initial liquid product after 2 h run, while that of the catalytic hydrocracking was conducted at 350 °C produced initial liquid product after 30 min. run. These conditions indicated that the catalytic hydrocracking was more effective than that of the thermal cracking in order to produce the lighter liquid fractions from the PET feed.

#### IV. Conclusion

Characterization and modifications of Indonesian natural zeolite produced in Sukabumi, West Java, have been carried out. Loading of a small amount of transition metal onto the activated zeolite was also performed to evaluate their characteristics in hydrocracking of the PET. The results were concluded herein.

The characterization results indicated that the Indonesian natural zeolite produced in Sukabumi consisted mainly of mordenite type crystalline. The HCl treatment towards the natural zeolite caused dealumination, increased its acidity and surface area. Loading of Ni, Cu, Cr, or Pd metal on to the zeolite did not affect the zeolite crystallinity. However, the metal loading decreased surface area of the zeolite. The hydrocracking products of PET were liquid, coke, and gas fractions. The liquid product consisted mainly of gasoline fraction (C<sub>5</sub>-C<sub>12</sub>). The highest liquid product was performed by the Pd/ZAA catalyst, i.e. 34.05 wt. %, with selectivity towards the gasoline fractions was 97.99 wt. %.

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#### References

- [1] P. Shivakumar and K. Anbarasu, Catalytic Pyrolysis of Dairy Industrial Waste LDPE Film Into Fuel, *Intern. J. Chem. Res.* 3 (2012) 52 – 55.
- [2] M.F. Ali and M.N. Siddiqui, Thermal and catalytic decomposition behavior of PVC mixed plastic waste with petroleum residue, *J. Anal. Appl. Pyrolysis* 74 (2005) 282 – 289.
- [3] S. Kumar and R.K. Singh, Recovery of Hydrocarbon Liquid From waste High Density Polyethylene By Thermal Pyrolysis, 28 (2011) 659 – 667.
- [4] J. Aguado, D.P. Serrano, J.M. Escola, and A. Peral, Catalytic Cracking of Polyethylene Over Zeolite Mordenite With Enhanced Textural Properties, *J. Anal. Appl. Pyrolysis* 85 (2009) 352 – 358.
- [5] A. Peral, J. Aguado, D.P. Serrano, J.M. Escola, Catalytic cracking of polyethylene over zeolite mordenite with enhanced textural properties, *J. Anal. Appl. Pyrolysis* 85 (2009) 352–358.
- [6] A. Bonila, D. Baudouin, and J. Perez-Ramirez, Desilication of ferrierite zeolite for porosity generation and improved effectiveness in polyethylene pyrolysis, *Journal of Catalysis* 265 (2009) 170–180.
- [7] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, A. Aranzabal, 2011, Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud, *Applied Catalysis B: Environmental* 104 (2011) 211–219.
- [8] W. Trisunaryanti, R. Shiba, M. Miura, M. Nomura, N. Nishiyama, M. Matsukata, Characterization and Modification of Indonesian Natural Zeolites and Their Properties for Hydrocracking of a Paraffin, *J. Jpn. Petr.Inst.* 1 (1996) 20-25.
- [9] W. Trisunaryanti, A. Syoufyan, S. Purwono, I.Izul Fallah, Padi, P., The effect of hydrochloric acid solution treatment towards characters of Indonesian natural zeolite, *Proceeding of The 2nd International Conference On Chemical Sciences*, Yogyakarta, 2010.
- [10] W. Trisunaryanti, Triyono, Purwono, S., and K. Dewi, Characteristics of Metals Supported-Zeolites Catalysts On Steam Reforming of Bioethanol, *J. Materiala Science and Engineering*, 5 (2011) 239-246.
- [11] J.M. Escola, J. Aguado, D.P. Serrano, A. Garciaa, A. Peral, L. Briones, R. Calvo, E. Fernandez, 2011, Catalytic hydroreforming of the polyethylene thermal cracking oil over Ni supported hierarchical zeolites and mesostructured aluminosilicates, *Applied Catalysis B: Environmental* 106 (2011) 405– 415
- [12] S.T. Sie, Acid-catalyzed cracking of paraffinic hydrocarbons. 3. Evidence for the protonated cyclopropane mechanism from hydrocracking/hydroisomerization experiments, *Ind. Eng. Chem. Res.* 31 (2003) 1881-1889.