The Effect of Metal Loading and Alkaline Treatment on The Zeolites Toward Catalytic Pyrolysis of γ -Valerolactone

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Abstract. γ -Valerolactone (GVL) is a glucose derivatives and its utilization as organic solvent has been developed to extract lignin from biomass. Both GVL and lignin can be used for producing aromatic chemicals (Benzene, Toluene, Xylene – BTX) via catalytic pyrolysis. We present a study focused on the catalyst modification of the zeolites to produce BTX from GVL. The catalysts were modified using wet impregnation method and alkaline treatment using NaOH solution. The addition of metal oxides were examined. Catalyst performance test were carried out in a fixed bed reactor. The feed was flowed at flowrate of 0.2 ml/min in 50 ml/min N_2 . The operating temperature was maintained at 500°C with catalyst-to-GVL ratio of 1:1.5. The results showed that addition of Fe-metal improves zeolites activity compared with parent zeolites. Alkaline treatment had negative impact on HZSM-5 activity because of the change of silica-alumina-ratio (SAR) and average pore diameter.

1 Introduction

Indonesia become the world's largest producer of crude palm oil with recorded a substantial growth over the years, from about 20 million tonnes in 2008 to about 30 million tonnes in 2015 [1]. At conservative estimate, for every tonnes of palm oil another four-thirds tonnes of empty fruit bunches (EFB) are produced. Abundant amount available of EFB provides opportunity and challenge as useful resources [2][3]. Renewable approaches for making aromatics from EFB will reduce the Indonesia dependence on fossil petroleum and mitigate the negative impacts of climate change. One promising approach to utilize EFB is depolymerizing EFB fraction into aromatic compounds such as benzene, toluene, and xylene (BTX) using zeolite as the catalyst.

Benzene, toluene, and xylene (BTX) are considered as important and valuable aromatic chemicals in petroleum industry [4]. These aromatics serve as the most important aromatic platform molecules for the development of high-end products such as plastics, solvents, additives, and other products [5].

There have been a number of studies focusing on modifying the HZSM-5 catalyst to produce aromatic hydrocarbon in higher yield and/or enhance the selectivity to particular target compounds [6-10]. The presence of transition metals on the modified catalyst such as FeHZSM-5 and MgHZSM-5 may impact catalytic behaviour and could improve the aromatics yields [11]. Recently, ZSM-5 with hierarchical structure,

which contains mesopores and micropores, was developed to minimize the diffusion limitation of reactant and to prolong the lifetime of zeolite catalyst in some extent due to the enlarged coke capacity [12] by dealumination and desilication [13].

As part of the study to produce BTX from EFB, we here present our study to convert a biomass derivative solvent from EFB, γ -valerolactone (GVL) to produce BTX. In the present study we have investigated the effect of transition metals (Mg and Fe) over HZSM-5 and HUSY on the aromatics (BTX) yields. Moreover, we evaluate the effect of NaOH concentration in alkaline treatment of zeolite on the BTX yields.

2 Experimental

2.1. Materials

Gamma-Valerolactone (GVL) solvent was purchased from Diaozhen Industrial Park-Jinan City-Shandong-China and was used without further purification. ZSM-5 and USY zeolites were purchased from Pingxiang Naike Chemical Industry Co. Ltd, China.

2.2 Catalyst Preparation

The metal-zeolite catalysts with Fe and Mg content of 2 wt% were prepared by the conventional impregnation method. The stoichiometric quantities of

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ion nitrate $[(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}) \text{ and } (\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})]$ were dissolved in distilled water. Then the zeolites (HZSM-5 and HUSY) was then added at 30°C and stirred to obtain a suspension. After being dried at 120°C for 6h, the powders were calcined in air at 550°C for 3h.

Hierarchical zeolites obtained in the presence of strong inorganic bases, NaOH. The NaOH concentration were varied from 0.3 M to 0.8 M. ZSM-5 was mixed with NaOH solution. The ZSM-5 suspension is then dried overnight. HZSM-5 were obtained by the ion-exchange with ammonium sulphate solution at 85°C for 1 h, prior to calcination.

Pyrolysis of GVL was carried out in a tubular reactor (1.5 cm id) made of quartz glass. As shown in Fig.1, 1.0 g zeolites was loaded in the heating zone with quartz wool before the reaction. GVL was vaporized at 200°C before entering the catalyst bed. During the pyrolysis, GVL was feed into the heating zone by syringe pump (12 ml/h) and purge with nitrogen (50 ml/min). The liquid product is condensed and collected in condenser trap.

Liquid samples were analyzed by GC-FID (Shimadzu GC-2010) equipped with a RTX-5 capillary column. Split injection is performed at a split ratio of 50 using helium (99.999%) as a carrier gas.

Fig. 1. Schematic diagram of the experimental apparatus for the catalytic pyrolysis

3 Results and Discussion

3.1 Catalyst Characterization

The HZSM-5 modification with 0.3 M and 0.5 M NaOH were examined using XRD. The XRD result, presented in Fig. 2, shows that all the investigated samples preserved their surface structure of zeolite (MFI). However, the degree of crystallinity in the mesopore samples was qualitatively influence by the alkaline treatment. The qualitative prediction based on the relative intensities of the reflection at $23^\circ 2\theta$, taking the crystallinity of the parent sample (HZSM-5) to be 100%. The results indicate that the intensity of the diffraction peak of HZSM-5 slightly increases over

NaOH concentration 0.3M and decreases over NaOH concentration 0.5M. It is possibly attributed to the local Si extraction from the zeolite lattice without significant destruction of the framework, thus preserving long range ordering and microporous structure in the material [14].

The observed difference in the pore structure changes among the samples with different silica to alumina ratios is evident from the textural data presented in Table 1. NaOH on alkaline treatment caused the Si atom apart from the tetrahedral framework so that affect the silica to alumina ratio and also make the new pore, so called mesopore. The greater the NaOH concentration makes the silica to alumina ratio decreases (from 36 to 21) and the average pore size larger than the parent HZSM-5 (15.71 Å to 26.50 Å).

Fig. 2. XRD patterns of NaOH desilication-modified HZSM-5 after calcination

Table 1. Textural properties of the catalyst.

NaOH Concentration	Surface area (m^2/g) ^a	Total pore volume (cm^3/g) ^a	Average pore size (Å) ^a	$\text{SiO}_2/\text{Al}_2\text{O}_3$ ^b
parent	315	0.17	15.71	36.13
0.3M	341.04	0.18	16.87	36
0.5M	314.06	0.27	26.50	21.71

^a BET method

^b XRF method

Fig. 3 shows NH_3 -TPD profiles of modified-HZSM-5 using NaOH alkaline treatment. Basically, all samples show two peaks centered around 137°C and 461°C , corresponding to NH_3 eluted from the weak and strong acid sites, respectively. Notably, HZSM-5 modified with 0.3M and 0.5M NaOH shows broader peaks of weak acid sites and narrower peaks of strong acid sites compared to HZSM-5. The acid sites distribution are summarized in Table 2.

The amount of weak acid sites increased with higher NaOH concentration, from 0.032 cc/g to 0.041 cc/g. On the contrary, the amount of strong acid sites decreased with higher NaOH concentration, from 0.0074 cc/g to 0.0023 cc/g.

3.2 Catalyst Performances

The result of catalyst activity test which has been treated with NaOH alkaline treatment is presented in Fig. 4 and Fig. 5. Such treatment leads to a decrease in the yield of BTX product when the NaOH concentration was increased. The BTX yield obtain over HZSM-5 catalyst was 2.88%-C, 0.3M HZSM-5 0.87%-C, 0.5M HZSM-5 1.02%-C, and 0.8M HZSM-5 0.02%-C. Meanwhile, unlike the case with selectivity, increasing NaOH concentration provide improving selectivity of BTX product. The decrease in the yield and the increased in selectivity of BTX is due to the liquid product yield.

Fig. 3. NH₃-TPD profiles of NaOH desilication-modified HZSM-5

Table 2. Acid sites distributions in NaOH desilication method.

NaOH Concentration	Acidity level		Total acid sites (cc/g)
	Low temp. sites (cc/g)	High temp. sites (cc/g)	
parent	0.032	0.0074	0.0394
0.3M	0.038	0.0016	0.047
0.5M	0.041	0.0023	0.026

The greater the NaOH concentration then the liquid product yield decreases, as shown in Table 3. This indicates that the more a product gas is generated due to the forming of Bronsted Acid sites. The Bronsted acid site is very active so that it tends to lead to cracking reactions [15]. Moreover, the greater the NaOH concentration causing the average pore diameter of the catalyst larger, leading the pores are less selective towards the formation of the desired BTX product.

Fig. 5 shows product distribution. The largest product is occupied by toluene, followed by m-xylene, benzene, and o-xylene. In addition, the varying of NaOH concentration did not cause changing of product distribution.

Table 3. The effect of NaOH concentration on liquid product.

Katalis	HZSM-5	0.3M HZSM-5	0.5M HZSM-5	0.8M HZSM-5
Liquid product (g)	0.512	0.335	0.287	0.129

Fig. 4. The effect of NaOH concentration on BTX product yield and selectivity (500°C; 1 bar; catalyst : feed = 1:1.5; feed rate = 12 ml/h; N₂ flow = 50 ml/h)

Fig. 5. The effect of NaOH concentration on BTX product distribution (500°C ; 1 bar ; catalyst : feed = 1:1.5 ; feed rate = 12 ml/h ; N₂ flow = 50 ml/h)

Zeolite HZSM-5 and HUSY has shown to be very active in catalytic biomass pyrolysis and also to enhance the selectivity towards aromatic in the liquid product [16]. Modification of zeolite by metal is considered as one way to improve catalyst activity and help to reduce the coking. The use of iron and magnesium to modify the zeolites would be an attractive option because iron is inexpensive. The product yield and selectivity in the catalytic pyrolysis for the various catalyst of our study are summarized in Fig 6. and Fig. 7, while the product distribution of the pyrolysis liquids is presented in Fig 8.

Fig 6 shows that the deposition of the metal on the zeolite can improve the zeolite activity in producing BTX products. In HZSM-5, iron is the best metal because it can improve the yield of BTX product from

2.88%-C to 4.56%-C otherwise in HUSY, magnesium is the best metal because it can improve the yield of BTX product from 0.21%-C to 0.67%-C.

Fig. 6. The effect of metal on BTX yield (500°C; 1 bar; catalyst : feed = 1:1.5; feed rate = 12 ml/h; N₂ flow = 50 ml/h)

Fig. 7. The effect of metal on BTX selectivity (500°C; 1 bar; catalyst : feed = 1:1.5; feed rate = 12 ml/h; N₂ flow = 50 ml/h)

Iron is known to have ability in facilitating oxygen transfer redox reactions since it has more than one stable state, as such Fe-zeolites (FeHZSM-5 and FeHUSY) catalyst can be used either for selective oxidations or reductions [17]. Iron could find a role in facilitating removal of oxygen in reactions of biomass pyrolysis vapors. Rizkiana *et al* reported that the coke amount formed on Mg loaded zeolite (Mg/USY) is much lower while the hydrocarbon content in the pyrolytic oil is significantly higher [18]. They suggested that the deoxygenation process is mainly occurred by decarboxylation and dehydration reactions over Mg loaded zeolite. One of the possible explanation for the high coke resistance ability of Mg/USY is as follows: Mg species in the form of MgO can easily absorb CO₂ to form carbonate and/or bicarbonate (CO₃²⁻/HCO₃⁻) due to its slight basicity [19] and the formed

carbonate/bicarbonate species might react with hydrogen atom generated from the decomposition of pyrolytic vapor and create formate/carboxylate intermediate on the surface of the zeolite [20].

Fig. 7. The effect of metal on BTX product distribution (500°C; 1 bar ; catalyst : feed = 1:1.5 ; feed rate = 12 ml/h ; N₂ flow = 50 ml/h)

Fig. 7 shows product distribution. The largest product is occupied by toluene, followed by m-xylene, benzene, and o-xylene. In addition, the varying of metal did not cause changing of product distribution.

4 Conclusions

The catalytic performance of alkaline treatment and impregnation on the treated HZSM-5 has been studied.

The result of catalyst activity test in HZSM-5 treated with NaOH alkaline treatment shows that the greater the NaOH concentration in the alkaline treatment, the BTX product decreases. The greater the NaOH concentration causing the average pore diameter of the catalyst larger, leading the pores are less selective towards the formation of the desired BTX product. Modified-zeolite HZSM-5 and HUSY has been shown to be very active in catalytic biomass pyrolysis and also to enhance the selectivity towards aromatic in the liquid product. In HZSM-5, iron is the best metal because while in HUSY, magnesium is the best metal. Iron could find a role in facilitating removal of oxygen in reactions of biomass pyrolysis vapors.

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