Surface modification of ZSM-5 zeolite: effect of cation on selective conversion of biomass-derived oil

W B Widayatno
Research Center for Physics, Indonesian Institute of Sciences, Bld. 440/442, PUSPIPTEK Serpong, Tangerang Selatan 15314, Indonesia

Emails: wathy012@lipi.go.id; wathyubw@gmail.com

Abstract. This paper reports the surface modification of high silica ZSM-5 zeolite, particularly emphasizing the effect of cation type on selective conversion of biomass-derived oil. XRD spectra of the NaOH-treated HZSM-5 showed notable crystallinity decrease at specific crystal plane orientation. The \( \text{N}_2 \)-physisorption tests confirmed mesoporosity evolution as NaOH concentration was increased. \( \text{NH}_3 \)-desorption tests revealed a significant change on surface acidity which involved realumination and cation replacement processes. The utilization of untreated HZSM-5 as well as hierarchical NaZSM-5 for catalytic conversion of bio-oil showed the effect of cation type and mesoporosity on chemicals distribution. The untreated HZSM-5 showed high selectivity to aromatics, which degraded gradually due to deactivation and poisoning of the acid sites. Meanwhile, hierarchical NaZSM-5 showed high selectivity to phenolic compound, which became more stable for 0.4M NaOH-treated zeolite (Na04). The current findings provide an additional insight on the potentials of NaZSM-5 for bio-oil valorization.

1. Introduction
Bio-oil derived from biomass has been targeted as one of top issue in biomass utilization. Different approaches such as catalytic cracking over different zeolites [1], utilization of basic catalysts [2], hydrodeoxygenation [3], and hydrothermal processes [4] have been investigated to get more hydrocarbon from biomass conversion for fuel application. However, since bio-oil contains many chemicals compound, recovering a significant amount of certain chemicals from bio-oil should be more beneficial for many applications, rather than removing them to extract only the hydrocarbons.

Recently, some studies have already used new directions to get more valuable chemicals feedstock [5, 6] such as furfural and acetic acid [5], phenols [7, 8], succinic acid [9], alkanes and polyols [10] for various purposes, instead of only for fuel applications. As a material with high surface area and shape selectivity properties, zeolite has been used as a catalyst or catalyst support to produce certain kinds of chemicals [5, 11]. The microporosity of zeolite serves the separation of molecules based on their molecular size. However, it also induces transport limitation which might hinder complete decomposition of large molecule like sugar [12]. This can be overcome by controlling the crystal size [13], making zeolite composite with other mesoporous material [14], steaming [15], dealumination [15], and desilication [16].

Most zeolite studies for catalytic conversion of bio-oil, always used H-form (protonated) of low silica zeolite to get more hydrocarbons. Some post-treatment studies of zeolite e.g. desilication, also
converted the treated zeolite into protonated or H-form [17-19] to obtain the active form for increasing the hydrocarbons yield. Meanwhile, the initial treated form e.g. alkali form-zeolite is rarely investigated. In addition, most of the existing studies only tested the performance of the fresh treated-zeolite. Other study considered the reusability of zeolite after thermal regeneration [17]. Yet, the catalytic activity of zeolite was degraded due to irreversible deactivation after repeated regeneration [20]. Thus, ensuring a good and stable catalytic activity without excessive regeneration cycle should be beneficial for practical purposes.

This study was aimed to elaborate the effect of surface cation on zeolite’s surface, specifically the cation from post-treatment of zeolite, on the chemical distribution of converted bio-oil, as well as the reusability potential of it without thermal regeneration. In this study, the high silica ZSM-5 type zeolite was desilicated by alkali solution (NaOH) to increase its mesoporosity, and used in its alkali form as catalyst for selective conversion of bio-oil. For comparison, the performances of untreated HZSM and H-form of ZSM-5 after NaOH treatment were also evaluated.

2. Materials and Methods

2.1. Catalyst preparation and characterization

HZSM-5 zeolite (HSZ-890) from TOSOH Corporation with SiO$_2$/Al$_2$O$_3$ of 1500 was used without further treatment as a parent material. The desilication was conducted through chemical washing in 0.1, 0.2, and 0.4 M NaOH solution at stirring temperature of 50 °C for 30 mins to get Na-form zeolite. After that, the zeolite was washed using distilled water until neutral and dried overnight in drying oven at 110 °C. The parent and washed zeolites were then denoted as untreated, Na01, Na02, and Na04 for NaOH concentration of 0, 0.1, 0.2, and 0.4, respectively.

The structure of untreated and NaOH-treated zeolites were compared by X-ray Diffraction (Smartlab, Rigaku, Japan). The pore properties were examined using N$_2$ physisorption measurements (NOVA 4200e, Quantachrome Instruments, USA). The surface area of the samples were determined using Brunauer-Emmet-Teller method (BET), while the micropore surface area and volume were calculated using t-plot method from the isotherm profile. The acid site of the parent and post-treated zeolites were evaluated by comparing the NH$_3$-desorption profile of the samples with the calibration data in the machine (Belcat, Japan). The details of the measurement preparation can be found elsewhere [21].

2.2. Catalytic activity and selectivity

The biomass feedstock used for this experiment was the stem part of Japanese knotweed (Fallopia Japonica). Details of the feedstock properties and preparation step have been described elsewhere [22]. Pyrolysis and catalytic conversion were conducted simultaneously in a down-draft fixed bed reactor using the same arrangements as the previous study [21]. The experiment was carried out from room temperature to 600 °C with a heating rate of 80 °C/min, and held at that temperature for 30 min. In addition to the fresh one, the zeolite beds were also reused three times without regeneration to elaborate their reusability.

The chemical composition of liquid product was evaluated by Gas Chromatography and Mass Spectroscopy method (GC-2010 Plus and GCMS-QP2010 Ultra, Shimadzu Japan). The built-in NIST database was used as a reference to determine the chemicals in the bio-oil. The relative yield of each chemical class was calculated from the GC-MS peak area using the following formula:

\[
\text{Rel. yield} = \frac{\text{specified peak area}}{\text{total peak area}} \times \frac{\text{catalytic oil yield}}{\text{non-catalytic oil yield}}
\] (1)
3. Results and Discussion

3.1 Structural properties of the zeolites

Some reports mentioned that for zeolite with Si/Al > 50, desilication treatment will lead to excessive
dissolution of Si framework and the loss of intrinsic crystallinity [16, 23, 24]. Figure 1 presents the
XRD profile of the untreated and treated zeolite which shows a similar result with the previous works.
The loss of crystallinity was only observed for (101) crystal plane at a diffraction angle of 8° which
became more significant as the NaOH concentration was increased. It was reported that for high silica
zeolite, the extraction of Si was more effective from the crystal surface zone [23]. Thus, the decrease
of peak at (101) crystal plane was correlated with the extraction of Si in the external surface of zeolite.

Table 1 presents the area-volume summary of the untreated and treated zeolite. It can be seen that
the extraction of Si from the surface zone increased the mesopore surface area and gave more access to
the deeper active site after NaOH treatment. As a result, its mesopore volume also increased to some
extent.

It should also be noted that the BET surface decreased when NaOH concentration was increased to
0.2M, yet the mesopore surface area increased due to the extent of Si extraction from the framework
which led to the enlargement of some old micropores. As a result, the neighbor micropores should
collapsed and give extensive decrease of micropore surface area. When NaOH concentration was
increased to 0.4M, the BET and mesopore surface area increased further, while the micropore surface
area decreased slightly. It is highly possible that NaOH treatment only led to the enlargement of the
existing micropores in the surface zone and gave less effect to the inner micropore channels, which
contributes most of zeolite pore volume. The increase of mesopore volume is highly possible due to

![Figure 1. XRD profile of untreated and treated zeolite](image)

Table 1. Area-Volume summary of the untreated and treated zeolite

| Catalyst | $S_{BET}$ (m$^2$/g) | $S_{Micro}$ (m$^2$/g) | $S_{Meso}$ (m$^2$/g) | $V_{Total}$ (cm$^3$/g) | $V_{Micro}$ (cm$^3$/g) | $V_{Meso}$ (cm$^3$/g) |
|----------|----------------------|----------------------|----------------------|------------------------|------------------------|------------------------|
| Untreated | 308          | 279          | 29          | 0.19          | 0.14          | 0.05          |
| Na01     | 335          | 300          | 35          | 0.22          | 0.15          | 0.07          |
| Na02     | 325          | 279          | 46          | 0.23          | 0.14          | 0.09          |
| Na04     | 331          | 271          | 60          | 0.26          | 0.14          | 0.12          |
the increase of external surface roughness [25] or formation of new mesopore structure from the extracted Si and/or Al in the surface zone.

Further investigation by Groen et al. concluded that macropores were formed after NaOH treatment of high silica zeolite [26]. The opposite phenomenon was found in this experiment, as depicted in figure 2. The isotherm profiles from N₂ adsorption test of the NaOH-treated show clear combination of type I isotherm, which is denoted by the high uptake of N₂ at relatively low pressures, and type IV isotherm, which is denoted by the hysteresis of H₄ type due to multi-layer adsorption in the range of 0.5 – 0.99 [27]. Type I isotherm shows the microporosity nature of ZSM-5, while the type IV isotherm confirms the existence of mesoporosity. There is no sign of reversible sorption properties as should be observed for non-porous or macroporous material (type II isotherm), which explain the further increase of mesopore volume while retaining its micropore volume. The different phenomenon compared with the works by Groen et al., can be attributed to the difference of the utilized treatment temperature which led to progressive extraction of Si and Al [23]. A similar explanation has been mentioned in other literatures [28, 29]. The NaOH treatment in this work was conducted at a lower temperature compared with the earlier work. Thus, the rate of Si extraction should be different and the extent of NaOH effect, which led to uncontrolled Si extraction, might be suppressed in the current experiment.

3.2 Acid properties of the zeolites

The NH₃-TPD profile of the zeolites in figure 3 presents the evolution of weak acid site (Low temperature peak, below 400 °C) and the significant decrease of stronger acid site (high temperature peak, above 400 °C). Along with the Si extraction, some of Al in the surface region will be also released from the framework and subsequently reinserted as Al extraframework on the external surface of zeolite [23, 26], which is shown by the significant decrease of high temperature peaks and the increase of low temperature peaks. This Al extraframework can serve as weak Lewis acid site in the surface region. Since the as-treated ZSM-5 was used directly without further activation, the dehydroxylation of Al extraframework into strong Lewis acid site, which favors coke formation, can be avoided.

3.3 Catalytic activity and selectivity of the zeolites

Figure 4 presents the chemical distribution of bio oil after being converted. For the untreated HZSM-5, the highest product selectivity was aromatics compound (≈48%), as shown in figure 4(a), while the unwanted carboxyl compound can be reduced significantly. Since the dominant content of carboxylic
compound in bio oil is acetic acid, the significant decrease of carboxyl compound is highly possible due to the decomposition of acetic acid which can poison the acid sites [30]. The poisoning of acid sites and the fact that HZSM-5 has high coking tendency of hydrocarbons due to its smaller channel resulted to deactivation of acid sites.

After 0.1 M NaOH treatment, some stronger acid sites in the inner structure of ZSM-5 were still remained which enabled strong adsorption of reactant and retain the conversion into aromatics. After several times being reused, those remaining stronger acid sites became inactive gradually due to hydrocarbon deposition and/or acetic acid poisoning. The deactivation of stronger acid sites led to the decrease of phenols dehydroxylation reaction and resulted to decrease of phenols conversion. Figure 4(b) shows the decreasing trend of aromatics when using Na01 catalyst, which implied the existence of remaining strong acid sites and their deactivation after several times reused.

![Figure 4](image-url)

**Figure 4.** Chemical distribution of upgraded bio oil using (a) untreated HZSM-5, (b) Na01, (c) Na02 and (d) Na04.

Unlike Na01, Na02 catalyst showed different phenomenon, which is presented in figure 4(c). Phenols selectivity reached its maximum after the second reuse (r-2) and did not increase furthermore, while aromatics selectivity showed the opposite, due to the extent of NaOH treatment effect. As a result, more OH- concentration dissolved the extra framework in the surface region further, and the weak acid sites decreased.

When Na04 catalyst was used, no carboxyl peaks detected, neither for fresh catalyst nor also for the reused one, as shown in figure 4(d). Furthermore, the chemicals distribution showed the relatively stable selectivity for each chemical class after the first reuse which infers the increase of coking tolerance. It is then suggested that Na04 catalyst has the best performance, in terms of selectivity and stability over several times reuse. Such high selectivity of phenolic compound has also been reported...
by Bu et al. [7, 31] and Choi et al. [8]. However, the reusability of the system in this experiment showed some improvement.

4. Conclusions

Desilication of high silica ZSM-5 zeolite and its effect on the performance of selective phenols production derived from bio-oil have been elaborated in details. NaOH treatment on high silica ZSM-5 decreased the crystallinity at specific crystal plane orientation. The acid sites distribution changed due to realumination and cation replacement processes, resulted to the decrease of strong acid sites and evolution of weak acid sites. Untreated HZSM-5 showed high selectivity to aromatics, yet degraded gradually due to deactivation of acid sites. Meanwhile, NaZSM-5 showed high selectivity and reusability to phenolic compound, especially for Na04 catalyst. This shows that different surface cation on zeolite will produce different chemical distribution. These findings also provide information on the potentials of NaZSM-5 for bio oil valorization to obtain specific chemicals.

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