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Natural Aluminosilicate-based Y Zeolite for Catalytic Cracking of n-Hexadecane

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Abstract

Natural zeolite and kaolin are abundant in Indonesia especially in Java and Belitung islands. These materials generally contain high aluminosilicate minerals that can be used as silica and alumina sources for the formation of NaY zeolite. This research aimed to identify the modification of NaY zeolite structure using Bayat natural zeolite as alumina source and Belitung kaolin as silica source and its catalytic activity for n-hexadecane cracking. Pretreatment of materials were performed in several steps: activation, purification, fragmentation for Bayat natural zeolite, and silica extraction for Belitung kaolin. The synthesis of NaY was performed hydrothermally using seed-assisted method with crystallization times of 24 and 48 h. The surface area analysis showed a typical surface area of microporous zeolite (i.e., a pore diameter of 1.897 nm) and surface area of 309.4 cm²/g. Meanwhile, powder X-ray diffraction characterization showed that the as-synthesized materials have the structure of NaY zeolite. The optimum crystallization time was 24 h with Si/Al ratio of 4.10. Furthermore, both synthetic and natural sourced NaY zeolites were converted into HY zeolites and employed as cracking catalyst of n-hexadecane in a fixed-bed reactor at 500 °C for 75 s. The natural sourced HY resulted in 59.80% conversion and 59.80% yield of gasoline product (C₁₀–C₁₂). These values were lower than the results given by synthetic HY (80%).

Keywords: natural aluminosilicate, NaY zeolites, catalytic cracking, n-hexadecane

Introduction

Zeolites are crystalline microporous aluminosilicates whose structural frameworks contain tetrahedral TO₄ units (T = Si, Al) linked together through oxygen sharing [1]. These materials have been widely used as catalysts in petrochemical industry [1] due to the presence of strong acid sites and the shape selectivity induced by molecular-sized microporosity [2]. Among the zeolites currently used at the industrial scale, zeolite Y is a highly versatile molecular sieve from the faujasite family with a three-dimensional pore structure having a pore diameter of 0.74 nm [3]. Although other porous materials have been synthesized, zeolite Y remains the most popular pyrolysis catalyst because of its inherent surface acidity and good hydrothermal stability [4].

Commercial synthetic zeolites are more often used than natural zeolites due to their higher purity and more uniform particle sizes, thus making them more suitable for most applications and scientific purposes [5]. However, the preparation of synthetic zeolites from chemical sources of silica and alumina relatively consumes considerable amount of chemicals during the synthesis process and is costly. Hence, a low-cost approach must be developed for zeolite synthesis [4]. Examples of zeolite synthesis methods use natural/wastes, such as polish coal fly ash [6], diatomite [7], and rice husk [8]. Our previous work published in Crystals [9] reported our attempt to synthesize NaY using kaolin. Currently, we are attempting to use natural zeolite as source together with kaolin. In this research, NaY zeolite was synthesized using Bayat–Klaten natural zeolite as a source of silica and alumina. This zeolite was synthesized to compare the efficiency of zeolites from the natural mineral Bayat–Klaten zeolite with those from extracted silica from kaolin as reported in a previous study [9].

Here, the synthesis of NaY zeolite using Bayat–Klaten natural zeolite and Belitung kaolin as sources of alumina and silica is reported. Then, the as-synthesized NaY was converted into H-form, followed by its application
as catalyst to the catalytic cracking of \( n \)-hexadecane. For comparison, the catalytic reaction using HY catalyst derived from NaY, which was synthesized from pro analysis precursors, was also carried out.

**Methods**

**General.** Kaolin was provided by PT Aneka Kaoline Utama (Belitung, Indonesia), and natural zeolite was obtained from Bayat, Central Java, Indonesia. The chemicals used were colloidal silica (LUDOX 40\%), sodium aluminate (NaAlO\(_2\)), sodium hydroxide (NaOH) pellet, hydrochloric acid (HCl) p.a., sodium dithionite (Na\(_2\)S\(_2\)O\(_5\)), sodium–citrate–bicarbonate, and sodium acetate (NaOAc) (Sigma Aldrich, Singapore).

**Synthesis of NaY zeolite.** Before being used as materials for synthesis, Bayat–Klaten natural zeolite and Belitung kaolin were subjected to physical activation, purification, followed by fragmentation of Bayat–Klaten natural zeolite using sub-molten salt method [10], and silica extraction [11] for Belitung kaolin. The fragmented natural zeolite and extracted silica were used as the materials for synthesis of NaY zeolite.

The synthesis of NaY zeolite consisted of two steps: synthesis of seed gel and synthesis of feedstock gel by hydrothermal method in 100 mL Teflon lined autoclave, followed by the method described by Wittayakun et al [8]. Seed gel was prepared by adding NaOH to deionized water and stirred using magnetic stirrer at room temperature. LUDOX-40 and NaAlO\(_2\) were added to the mixture at the initial batch composition of 10.67 Na\(_2\)O:1 Al\(_2\)O\(_3\):10 SiO\(_2\):180 H\(_2\)O. The mixture was kept at room temperature for 1 day. For the feedstock, certain amounts of fragmented natural zeolite and extracted silica were dispersed in deionized water followed by NaOH and NaAlO\(_2\) until the molar ratio of the mixture was 4.3 Na\(_2\)O:1 Al\(_2\)O\(_3\):10 SiO\(_2\):180 H\(_2\)O.

The synthesized feedstock was added to the seed gel to form the overall gel and kept at room temperature for another 1 day. The mixture was then transferred to 100 ml polypropylene bottle for crystallization at 100 °C for 24 and 48 h. The resulting product was collected by filtration, washed until pH 8, dried at 60 °C, and labeled as NaY-1 and NaY-2. A similar method was applied to synthesize NaY from pro analysis precursor, i.e., LUDOX and NaAlO\(_2\), and the product was named NaY-S.

**Modification of NaY zeolite.** Modification of NaY zeolite into its H-form was carried out using the NH\(_3\) exchange method. The as-synthesized NaY zeolite was dispersed in 1 M NH\(_4\)Cl (1:100; w/v). The mixture was stirred for 4 h at 100 °C. The process was repeated once using fresh ammonium solution. The resulting NH\(_3\)Y was filtered and dried at 120 °C for 2 h, followed by calcination at 550 °C for 3 h to remove NH\(_3\) and obtained HY zeolite (labeled as HY-1). A similar method was applied to NaY-S, and the product was named HY-S.

**Physicochemical characterizations.** In this study, kaolin, metakaolin, extracted silica, and the as-synthesized material were characterized by extensive solid-state characterization techniques, such as X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FTIR), and scanning electron microscopy (SEM)–energy dispersive X-ray spectroscopy. The identification of functional group of NaY zeolite was attained by Alpha Bruker FTIR spectrometer. For XRD analysis, the samples were observed using PANalytical: X’Pert Pro XRD. Elemental analysis was performed on PANalytical: Epsilon 1 X-Ray Fluorescence Spectrometer (XRF). Complete surface area analysis was conducted using QuantaChrome surface area analyzer. SEM images were obtained using Field Emission SEM FEI Magellan 400 and FIG Quanta FEG 450 at PT Pertamina, Pulogadung. All \(^29\)Si single-pulse magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were performed at NMR National Laboratory at University of Warwick using 7.05 T \(^29\)Si Larmor frequency \( (\nu_r) \) of 59.6 MHz and \(^1\)H Larmor frequency of 300.1 MHz using a Varian/Chemagnetics InfinityPlus spectrometer.

**Catalytic testing.** The catalytic activity of HY zeolites was tested using micro activity test reactor located at PT Pertamina, Pulogadung following a previously reported procedure [12]. Approximately 0.5 g catalyst was placed in the silica reactor and purged with N\(_2\) gas to remove all impurities at temperature of 573 K for 30 min, and 1.35 g \( n \)-hexadecane feed was injected into the reactor for 80 s. After the reaction, the gas and liquid products were collected and characterized with gas chromatography (GC)–refinery gas analysis and GC simulated distillation (Sim Dis), respectively.

**Results and Discussion**

**FTIR.** Figure 1 shows the FTIR spectra of natural-source NaY zeolites with crystallization times of 24 (NaY-1) and 48 (NaY-2) h and pro-analytic as-synthesized NaY (NaY-S). All the key bands of NaY zeolite [13] were observed in both NaY-1 and NaY-2, which slightly differed from that of NaY-S. The peaks at wavenumbers 3700–3200 cm\(^{-1}\) indicate the silanol groups in NaY-1 and NaY-2 [14]. Water molecules (H\(_2\)O) were adsorbed on NaY-1 and NaY-2 surfaces, based on the appearance of peak at 1630 cm\(^{-1}\) which was assigned to the bending vibration of water molecules [15]. Key bands of NaY zeolite at 1250–1000 and 850–550 cm\(^{-1}\) denote the asymmetrical and symmetrical stretching of SiO/AlO, respectively [14]. The peak at 500–600 cm\(^{-1}\) was attributed to the double six-member...
rings of NaY zeolite, which are the characteristic secondary building unit of NaY structure [16].

**XRD.** Characterization with XRD was conducted to confirm the framework of as-synthesized NaY zeolites by comparing the patterns with that of standard NaY [17] (Figure 2). The XRD patterns of Na-S and NaY-1 gave peaks mostly similar to that of the standard NaY, indicating the formation of faujasite structure. On the other hand, NaY-2 showed a pattern that is mostly similar to that of NaP standard [18]. Thus, the synthesis of NaY-1 was more successful with a lesser impurity than that of NaY-2, although the former was less crystalline than NaY-S. The as-synthesized NaY-1 with crystallization time of 1 day was characterized further using XRF, SEM, and Brunauer–Emmett–Teller (BET) method.

**XRF.** XRF characterization was conducted to obtain the composition of the synthesized NaY. Based on the XRF results shown in Table 1, the as-synthesized NaY-1 and NaY-S achieved Si/Al ratios of 4.101 and 3.73, respectively.

**SEM.** The SEM images of NaY-1 and Na-S (Figure 3) showed that part of the as-synthesized NaY-1 contained cubic crystals of NaY zeolite, similar to the morphology of NaY-S crystals. However, spheres, that are the typical shape of NaP, were observed on the surface of the bulk materials in NaY-S [19]. This finding supports the XRD results indicating that the as-synthesized NaY-1 still contained NaP impurities.

**BET.** Figure 4 displays the BET characterization of N₂ adsorption/desorption of NaY-S and NaY-1. The isotherm plot of NaY-S (4a) and NaY-1 (4b) belongs to type I isotherm (defined by IUPAC [20]) which is a characteristic of microporous materials. The pore distribution of NaY-1 (Figure 4(d)) showed that the average pore sizes of NaY-S and NaY-1 were 1.907 and 1.896 nm, respectively. Table 2 summarizes the surface area analysis for both NaY zeolites.

**NMR.** Figure 5 shows the chemical shift in $^{29}$Si and $^{27}$Al MAS NMR spectra of NaY-1. In $^{29}$Al MAS NMR spectra (top), the dominant species in both as-synthesized NaY-S was $Q^1$Si (1Al), followed by equal amounts of $Q^2$Si (2Al) and $Q^3$Si (3Al) species and weaker peak for $Q^4$Si (4Al) at $-80$ ppm to $-90$ ppm. Interestingly, only a shoulder peak was observed at $-100$ ppm to $-110$ ppm, which was assigned to $Q^4$Si (0Al). The shape of 29 Si NMR peaks observed in NaY-1 was broader than that observed in NaY prepared from kaolin only as silica source. Furthermore, the $^{27}$Al MAS NMR spectra indicate that most of Al atoms presented as tetrahedral aluminates ($\text{AlO}_4^{5-}$) as significantly sharp peaks at 60 ppm. However, octahedral aluminates ($\text{AlO}_6^{3-}$) were also created, and the intensity was higher than a similar peak that appeared in NaY reported in Crystals [9]. Overall, the $^{29}$Si and $^{27}$Al NMR data explained that the structure of the as-synthesized NaY already possessed the framework of Faujasite (FAU) [21], although the crystallinity still needs to be improved.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>NaY-1 Mass (%)</th>
<th>NaY-S Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>64.043</td>
<td>75.86</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15.615</td>
<td>20.32</td>
</tr>
<tr>
<td>SiO$_2$/Al$_2$O$_3$</td>
<td>4.101</td>
<td>3.733</td>
</tr>
</tbody>
</table>

**Table 1. Chemical Composition NaY Zeolites**

**Figure 3. SEM Images of NaY-S (Left) and NaY-1 (Right)**

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Modification to HY. Both as-synthesized NaY zeolites were then modified into their H-forms through NH₄ exchange method to increase their acidic and thermal stability, enabling their use as catalyst in n-hexadecane cracking with good catalytic performance [4]. The reactions that occurred during cation exchange are described in Equations (1) and (2).

\[
\text{NaY} (g) + \text{NH}_4^+ (aq) \rightarrow \text{NH}_4Y + \text{Na}^+ (aq) \quad (1)
\]

\[
\text{NH}_4Y (s) \rightarrow \text{HY} (s) + \text{NH}_3 (g) \quad (T = 550 ^\circ C) \quad (2)
\]
FTIR of HY. Figure 6 shows the FTIR spectra of NaY-1, NH_4Y-1, and HY-1. NH_4Y-1 showed –NH bending and stretching vibrations at wavenumbers of 1500–1300 and 3250–3000 cm\(^{-1}\), respectively, indicating that Na\(^+\) was exchanged with NH_4\(^+\) to form NH_4Y. Owing to the calcination process, ammonium was later decomposed to gaseous NH_3, resulting in the formation of HY zeolite [22]. Further analysis also showed that the vibration band at 1250–900 cm\(^{-1}\) became broader in HY-1, indicative of changes in Si–O–Al alkoxy rings due to exchange treatment [13]. XRF characterization confirmed that the ratio of Si/Al of HY-1 was slightly lower than that of the starting NaY (Table 3).

XRD. HY-1 zeolite was characterized using XRD to confirm its final structure. The XRD patterns in Figure 7 show that no significant differences were observed between pattern of NaY-1 and HY-1. Thus, HY-1 maintained its FAU framework.

Catalytic Cracking Test. HY-1 and HY-S were used as catalysts for n-hexadecane cracking as probe molecules because n-hexadecane is the component of crude oil [23]. The resulting gasoline products (C_5–C_{12}) were analyzed using high-temperature GC Sim Dis with the assumption that no cokes occur in the catalytic process. Figures 8(a), 8(b), and 8(c) show the % conversion, % yield, and % selectivity of catalytic cracking, respectively. With % conversion of 60.83%, yield of 59.90%, and % selectivity of 98.47%, the as-synthesized HY-1 from kaolin Belitung and Bayat natural zeolite has shown moderately competitive performance compared with HY-S.

Figure 6. FTIR Spectra of (a) NaY-1, (b) NH_4Y, and (c) HY

Table 3. Chemical Composition Results of NaY-1 and HY-1

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>NaY-1 Mass (%)</th>
<th>HY Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>15.62</td>
<td>16.31</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>64.04</td>
<td>64.49</td>
</tr>
<tr>
<td>SiO(_2)/Al(_2)O(_3)</td>
<td>4.10</td>
<td>3.95</td>
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Figure 7. XRD Data of NaY-1 (Bottom) and HY (Top)

Figure 8. % Conversion, % Yield, and % Selectivity of n-hexadecane Catalytic Cracking
Conclusion

NaY zeolite based on natural minerals was successfully synthesized from Bayat–Klaten natural zeolite and Belitung kaolin as alumina and silica sources, respectively. From this experiment, the optimum crystallization time of micropore NaY synthesis was 24 h, and NaY zeolite resulted when using SiO$_2$/Al$_2$O$_3$ ratio of 4.101. NaY zeolite was then modified into its HY form without changing the framework structure, and the resulting H-Y zeolite with Si/Al ratio of 3.95 was then applied as catalyst to the catalytic cracking of n-hexadecane. Based on the catalytic performance of H-Y zeolite, the resulting % conversion, %yield, and % selectivity of gasoline products were 60.83%, 59.90%, and 98.47%, respectively. From these results, HY-1 zeolite has moderate competitive activity compared with HY-S.

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