Comparative Properties of K/NaX and K/NaY from Ultrasound-Assisted Impregnation and Performance in Transesterification of Palm Oil

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ABSTRACT: This work aims to compare physicochemical properties and catalytic performance of potassium supported on zeolite NaX and NaY (K/NaX and K/NaY, respectively) prepared by ultrasound-assisted impregnation from potassium acetate buffer precursor. Calcination converts the potassium precursor to carbonate, which occupies the zeolite cavities and disperses on the external surface. Both calcined samples show a decrease in zeolite phases, BET surface areas, and pore volumes. With the smaller changes, K/NaX is more stable than K/NaY. Moreover, K/NaX has higher basicity than K/NaY and is more active in the decomposition of 2-methylbut-3-yn-2-ol (MBOH), producing dominant products from basic sites. Both K/NaX and K/NaY are active in the transesterification of palm oil, producing more than 94% of the biodiesel yields in the first run. However, the yields drop in the second run because of the leaching of potassium species into glycerol and biodiesel products. The spent K/NaX has a similar phase to the fresh one, whereas the spent K/NaY shows more structure collapse. With better structural stability, less potassium leaching, and less decline in biodiesel yields in the second run, K/NaX is a better catalyst than K/NaY.

1. INTRODUCTION

Biodiesel is an alternative fuel produced from various renewable feedstocks. The process involves transesterification, a reaction between triglyceride and alcohol (such as methanol) in the presence of a catalyst. One of the most used catalysts is homogeneous alkaline solutions which provide a high product yield. However, a large amount of wastewater is generated from the product purification step. Consequently, there is an increased interest in developing heterogeneous catalysts that are easy to separate from the products and are reusable. Examples of heterogeneous base catalysts for transesterification are carbonates, alkali, metal oxides, and zeolites. Those catalysts require a smaller alcohol volume than acid catalysts. Currently, there are several review articles with various aspects in development on heterogeneous catalysis for biodiesel production including current status and challenges, evaluation on feedstocks, technologies, catalysts, and reactors, advances in reactors, and processing technologies. One of the promising catalysts consists of potassium (K) species on various supports. They have higher basicity and better resistivity to free fatty acids contaminating in triglyceride sources than those with lithium and sodium. They could be reused with fewer activity losses than the other catalysts. Moreover, the dispersion of active species on porous materials could improve the catalyst activity.

Received: September 6, 2021
Accepted: March 2, 2022
Published: March 11, 2022
Among porous materials, zeolites faujasite (FAU) including NaX and NaY are interested in this work. They have well-defined frameworks with a three-dimensional pore system, large surface areas, high ion-exchange abilities, and thermal stability.\(^{14}\) Moreover, they are commercially available in a large scale. Both NaX and NaY zeolite have the same FAU structure but different Si/Al ratios, namely, 1–1.5 in NaX and >1.5 in NaY. The presence of aluminum in the zeolite structure generates a framework negative charge, which requires extraframework cations for charge balancing.\(^{15,16}\)

There are several works on catalysts with potassium supported on NaX and NaY for transesterification of various oils from plants such as palm, soybean, sunflower, and jatropha.\(^{12,13,17−19}\) The catalysts are prepared commonly by impregnation with potassium hydroxide (KOH), potassium nitrate (KNO\(_3\)), and potassium acetate buffer (CH\(_3\)COOK/CH\(_3\)COOH).\(^{12,13,17−22}\) The basicity increases with potassium loading, resulting in better biodiesel yields. Some of those catalysts have problems from the collapse of the zeolite structure or the agglomeration of potassium species. Moreover, there is not much comparison of catalysts on the same condition or the same oil. The understanding of catalyst properties is crucial to pursue the challenges in catalyst design and development.

Early works focused on the preparation of catalysts that produced high biodiesel yields. Noiroj et al. prepared K/NaY with 10 wt % KOH as an effective catalyst for transesterification of palm oil.\(^{18}\) Intarapong et al. found that the increase in KOH loading on NaY increased the basicity but destroyed the zeolite structure.\(^{20}\) Xie et al. reported that K/NaX from 10% KOH was the best catalyst in transesterification of soybean oil.\(^{21}\) Peña et al. demonstrated that K/NaX from KNO\(_3\) gave a high biodiesel yield from transesterification of sunflower oil.\(^{19}\)

There are some works that concern the stability of zeolite supports. Supamathanon et al.\(^{13}\) and Manadee et al.\(^{17}\) prepared K/NaY and K/NaX by impregnating the zeolites with a potassium acetate buffer solution to produce active catalysts for transesterification of Jatropha seed oil. This potassium precursor could minimize the zeolite structure collapse. Both studies showed that the catalysts have smaller surface areas than the parent zeolites after loading with K precursor, probably due to the agglomeration of potassium species. Hence, ultrasound-assisted impregnation was proposed to improve the dispersion.

Ultrasound has been applied to assist material modification and synthesis. The ultrasound causes acoustic cavitation providing the formation, growth, and collapse of hot gas bubbles in a liquid system. The collapsed bubbles then increase the temperature and the pressure, which assists the diffusion of the precursor into support pores and improves surface interaction.\(^{23}\) There are a few reports on ultrasound-assisted impregnation of metal precursors on FAU zeolite.\(^{12,24}\) Rakmae et al. used ultrasound-assisted impregnation to prepare 12 wt % potassium on NaY from potassium acetate buffer.\(^{12}\) The catalyst provided a better biodiesel yield than that from a conventional impregnation. Recently, Ketzer et al. used ultrasound-assisted impregnation to prepare 20% WO\(_3\) on ultrastable zeolite Y (USY) for the production of methyl oleate from oleic acid esterification. The catalyst exhibited a high dispersion of active species with strong interaction over the support and provided a good performance.\(^{24}\)

Although the previous literature shows that the K/NaX and K/NaY are active for the transesterification of various oils, those catalysts were prepared either by different methods or tested on different oils. In addition, there are no reports about the preparation of K/NaX catalysts by ultrasound-assisted impregnation. Consequently, this work aims to compare the physicochemical properties of K/NaX and K/NaY catalysts prepared similarly by ultrasound-assisted impregnation from a potassium acetate buffer solution and their catalytic performance in the transesterification of palm oil under the same condition. Moreover, the properties of the spent catalysts are compared. The in-depth comparison provides an understanding that would be helpful in catalyst design and development.

2. RESULTS AND DISCUSSION

2.1. Characterization of Potassium Catalysts Impregnated on FAU Zeolite. XRD patterns of parent NaX and
NaX and NaY zeolites and as-prepared and calcined K/NaX and K/NaY catalysts are shown in Figure 1. NaX and NaY have similar peak positions (JCPDS No. 38−0237 and 39−1380, respectively) but different intensities because of the different Si/Al ratios. The as-prepared K/NaX and K/NaY show the zeolite characteristic peaks with lower intensities than the bare zeolites. Both samples show additional peaks at 8.88, 14.26, and 27.18°, corresponding to the potassium acetate precursor. The peak at 8.88° of the as-prepared K/NaX sample is stronger than the peak of the zeolite 220 plane. However, the as-prepared K/NaY shows the opposite intensities. The results imply that the potassium acetate precursor covers the external surface of NaX with more extent than that of NaY. After calcination, the peaks of the potassium acetate precursor are not observed from both samples, suggesting complete decomposition. However, the zeolite characteristic peaks from both calcined samples have lower intensities than those of the as-prepared samples. The decreased intensities could be from the partial collapse of the zeolite frameworks by hydrolysis of Si−O−Al bonds. Although K/NaX and K/NaY have the same potassium loading, the calcined K/NaX shows stronger zeolite peaks, suggesting less collapse of the zeolite structure. The XRD results suggest that K/NaX is more stable than K/NaY against the same calcination condition.

The SEM images of calcined K/NaX and K/NaY are compared with the parents NaX and NaY, respectively, in Figure 2. Both NaX and NaY are polycrystals with different morphologies. NaX has round-shaped particles with a diameter of about 1.5 μm. Each particle is a cluster of small crystals with various sizes and thicknesses connecting together. The morphology of K/NaX is similar to the parent zeolite but with the poorer sharpness of crystal edges. Some erosion on the surface is visible in the SEM images. NaY consists of single crystals, either perfect octahedra with a diameter of about 500 nm or imperfect polyhedra with various sizes. There are also clusters of crystals with random patterns. The morphology of the calcined K/NaY is similar to that of the parent NaY. The surface of some crystals also shows signs of erosion.

The N2 sorption isotherms of the calcined K/NaX and K/NaY are compared with the parent zeolites in Figure 3. All samples have type I isotherms, a characteristic of microporous materials. The adsorbed volumes of K/NaX and K/NaY, surface areas, and pore volumes are smaller than the bare zeolites (see Table 1). The decrease could be from the occupation of the impregnated species in the zeolite cavities, blockage of the zeolite pores, and the collapse of the zeolite structure. K/NaX shows a smaller decrease in the adsorbed volume than K/NaY. The results imply that K/NaX has less potassium species in the zeolite cavities or less pore blocking. However, the XRD results indicate that the collapse of zeolite structure in K/NaX is less than that in K/NaY. Because the hydrolysis of the Si−O−Al bond of zeolites under thermal treatment could be assisted by alkali metal species, the smaller amount of potassium species in the cavities of NaX could be the reason for less collapse. Moreover, the hysteresis loops on NaX and K/NaX are type H4 and H2(b) that could be from crystal aggregation and thermal hydrolysis, respectively.

FTIR spectra and assignment of calcined K/NaX and K/NaY are presented in Figure 4a and Table 2. The peaks at 1388 and 1448 cm−1 from K/NaX and 1388 and 1456 cm−1 from K/NaY correspond to asymmetric stretching (v) of carbonate ion (CO32−). More intense peaks of carbonate are observed on K/NaY, consistent with the stronger potassium acetate peaks in the XRD patterns. Both samples also show a small peak at around 880 cm−1, corresponding to out-of-plane bending (δ) of CO32−. The bands of stretching and bending of Si−O−T, where T is the Si or Al atom of the zeolites, decrease because of thermal hydrolysis during the decomposition of the acetate precursor. The formation of K2CO3 on the support surface may relate to the collapse of the zeolite framework. The finding agrees with the FTIR results in the literature.

Raman spectra and peak assignments of both calcined K/NaX and K/NaY are compared with those of the parent zeolites in Figure 4b and Table 2. Both samples show peaks at 1080, 1060, and 700 cm−1 corresponding to the stretching and bending modes of K2CO3. Although both samples were prepared with the same potassium loading, the signal of K2CO3 on K/NaX is stronger than that on K/NaY, implying that larger amount of carbonate species is on the external surface. This could also be from the stronger intrinsic basicity of the NaX zeolite. The vibration of 4- and 6-membered rings of FAU frameworks decreased because of hydrolysis during the thermal treatment of the potassium precursor. The relative peak intensity of the 4-membered ring in the NaX framework is higher than that in the NaY. This result confirms that structure of NaX is more stable, consistent with the XRD results.
Moreover, the forms of potassium species in calcined K/NaX and K/NaY were determined by XPS. The spectra of K/NaX and K/NaY are shown in Figure 4c. The peaks of K 2p1/2 and K 2p3/2 from K/NaX are observed at 295.7 and 293.0 eV, respectively, corresponding to K2CO3.31 Both K 2p peaks from K/NaY shift to lower binding energy, probably due to connection to elements with lower electronegativity.32 The binding energy difference between K/NaX and K/NaY could be attributed to the interfacial interaction between K species and the zeolite surface. The higher binding energy in K/NaX implies a stronger interaction. The peak at 288.5 eV from both samples corresponds to carbonate species on the zeolite surface. The peaks at 284.6 and 285.9 eV are assigned to adventitious carbonaceous compounds.12 These XPS results confirm the presence of K2CO3 on both zeolites, which are not observed by XRD.

The acid–base properties of the catalysts are distinguished by the decomposition of MBOH.33 The conversions of MBOH over the calcined K/NaX and K/NaY and the parent zeolites are compared in Figure 5a and Table 3. The biodiesel yields from first runs were 97.9 and 94.4%, respectively. Table 4 compares the yields from this work with those from the literature. The biodiesel yield of K/NaY from this work is higher than the work from Rakmae et al.12 The difference might be from the methods used for product separation; namely, hot filtration in this work versus room-temperature filtration in Rakmae et al.12 The K/NaX and K/NaY, prepared by the same method, give similar biodiesel yields in the first run despite the more collapse in the zeolite structure in K/NaY. However, the differences are obvious in the second run. From the chromatograms from the second run (Figure 6), the biodiesel yields from K/NaX and K/NaY decreased to 61.3 and 2.7%, respectively. The decrease was mainly due to the leaching of potassium species which is discussed in Section 2.3. This result implies that the amount of K2CO3 as a basic site is the key to catalytic activity. Compared to the literature, the performance of K/NaX is better than that of K/NaY, when prepared either from conventional or ultrasound-assisted impregnation.

Table 1. BET Surface Area and Micropore Volume of K/NaX and K/NaY Compared to Parent Zeolites from N2 Sorption Analysis; and K Content from ICP Analysis

| sample   | BET surface area (m^2 g^-1) | Micropore volume (cm^3 g^-1) | K content (wt %) |
|----------|-----------------------------|-----------------------------|-----------------|
| NaX      | 853                         | 0.254                       | -               |
| NaY      | 899                         | 0.331                       | -               |
| K/NaX    | 352                         | 0.128                       | 11.03 ± 0.07    |
| K/NaY    | 121                         | 0.037                       | 11.40 ± 0.17    |

Figure 3. N2 sorption isotherms of (a) calcined K/NaX and (b) calcined K/NaY compared to their parent zeolites; filled symbols = adsorption and hollow symbols = desorption.
Figure 4. (a) FTIR (KBr method) and (b) Raman spectra of calcined K/NaX and K/NaY catalysts compared with their parent zeolites and (c) XPS spectra of the chemical state of carbon (C 1s) and potassium (K 2p) peaks.

Table 2. Vibration and Peak Assignments of Functional Groups of Samples before and after Calcination

| assignment                                                                 | wavenumber (cm⁻¹) | NaX as-prepared K/NaX | calcined K/NaX | NaY | as-prepared K/NaY | calcined K/NaY | ref |
|----------------------------------------------------------------------------|--------------------|------------------------|---------------|-----|-------------------|----------------|-----|
| Functional Groups Related to Zeolites                                      |                    |                        |               |     |                   |                |     |
| O–T–O bending vibration of S4R (T = Si or Al)                              | 458                | 453                    | 459           | 463 | 449               | 460           |     |
| T–O–T bending vibrations of double rings (D6R)                              | 561                | 563                    | 563           | 573 | 569               | 567           |     |
| symmetric stretching of O–T–O                                             | 673–748            | 671–752                | 679–746       | 698–779 | 690–775           | 685–762      |     |
| asymmetric stretching of Si–O–T                                           | 984–1069           | 962                    | 989           | 1013–1089 | 978               | 999           |     |
| asymmetric stretching of Si–O–Si (shoulder)                               | 1082               | 1067                   | 1089          | 1128 | 1066              | 1090          |     |
| Functional Groups Related to CH₃COOK                                       |                    |                        |               |     |                   |                |     |
| symmetric stretching of COO⁺                                              | 1414               | 1414                   |               |     |                   |                |     |
| asymmetric stretching of COO⁺                                             | 1574               | 1574                   |               |     |                   |                |     |
| C–H stretching of −CH₃                                                   | 2977               | 2980                   |               |     |                   |                |     |
| Functional Groups Related to K₂CO₃                                        |                    |                        |               |     |                   |                |     |
| symmetric stretching of CO₂⁺ (ν₁)                                        | 1060, 1080         | 1060, 1080             |               |     |                   |                |     |
| out-of-plane bending of CO₂⁺ (ν₂)                                        | 883                | 881                    |               |     |                   |                |     |
| asymmetric stretching of CO₂⁺ (ν₃)                                       | 1448               | 1456                   |               |     |                   |                |     |
| in-plane bending of CO₂⁺ (ν₄)                                            | 700                | 700                    |               |     |                   |                |     |
| Hydroxyl Regions Related to Zeolites                                      |                    |                        |               |     |                   |                |     |
| symmetric stretching of T–OH                                              | 3458               | 3393                   | 3454          | 3458 | 3416              | 3462          |     |
| in-plane bending of −OH (H₂O)                                            | 1641               | 1659                   | 1641          | 1653 |                   |                |     |

ACS Omega 2022, 7, 9130–9141

https://doi.org/10.1021/acsomega.1c04912
2.3. Stability of Catalysts. Although K/NaX and K/NaY give high biodiesel yields in the first run, the yields decrease significantly in the second run. The yield from K/NaX is much higher than that from K/NaY. Thus, further investigation on the catalyst stability was conducted. The amount of potassium leaching into glycerol and biodiesel products was determined by ICP-OES. The spent catalysts were characterized by XRD, SEM, FTIR, and Raman spectroscopy.

The total amount of potassium leaching in the glycerol and biodiesel product from K/NaX and K/NaY are 15.6 and 45.2%, respectively. The results indicate that the catalyst deactivation strongly relates to potassium leaching. Namely, the catalyst with more potassium leaching gives the smaller biodiesel yield in the second run. This finding agrees with the reports by Capek et al.\textsuperscript{40} and Mucin\textsuperscript{4} The potassium surface species reacts with glycerol to form a soluble species. The less leaching from K/NaX is consistent with the XPS results in section 2.1. Potassium species in K/NaX has a stronger interaction with the zeolite support.

The XRD patterns of spent K/NaX and K/NaY are compared with the fresh catalysts in Figure 7. The patterns of spent and fresh K/NaX are similar, indicating the zeolite stability against the reaction condition. In contrast, the XRD pattern of spent K/NaY shows characteristic peaks of zeolite NaY on a broad baseline, indicating an amorphous nature. These data confirm the greater collapse of zeolite NaY than that of NaX, consistent with the greater decrease in surface area of K/NaY from the bare zeolite.

The SEM images of the spent K/NaX and K/NaY with 10k and 30k magnification are shown in Figure 8. The images of both spent catalysts are similar to their fresh catalysts. However, the changes in zeolite crystallinity are evident in XRD patterns.

The FTIR-ATR and Raman spectra of spent K/NaX and K/NaY are compared with their fresh catalysts in Figure 9. The IR spectra of both spent catalysts are different from their fresh samples. The carbonate peaks have either lower intensities or different shapes indicating changes after the catalytic test. The changes of the spent catalysts from Raman spectra are more evident than from IR spectra. The decreases in the peaks at 1080 and 1060 cm\textsuperscript{-1} (symmetric stretching) and 700 cm\textsuperscript{-1} (symmetric deformation) agree with the leaching of potassium species. The different shapes of carbonate peaks of spent K/NaX and K/NaY indicate the different interaction.

From this study, both K/NaX and K/NaY deactivate after being tested in transesterification. The causes are the leaching of potassium species, the collapse of the zeolite structure and the changes of carbonate species. However, the contribution of each cause is not clear. Therefore, further investigation is recommended to provide insightful information to improve the catalyst design and development.

Figure 5. (a) MBOH conversion at various times on stream and (b) CO\textsubscript{2}-TPD profiles from calcined K/NaX and K/NaY compared to the bare zeolite supports.

Table 3. Conversion and Selectivity of Products from the Decomposition of MBOH and Basicity by CO\textsubscript{2}-TPD of K/NaX and K/NaY Compared to the Parent Zeolites

| sample  | MBOH conversion\textsuperscript{a} (mol %) | base-catalyzed site | coordinate unsaturated site | basicity by CO\textsubscript{2}-TPD (mmol CO\textsubscript{2} g\textsuperscript{-1} catalyst) |
|---------|----------------------------------|-----------------|-----------------|--------------------------------------------------|
| NaX     | 0.93                             | 45.35 48.65     | 6.00 0.00       | 0.375                                            |
| NaY     | 0.69                             | 14.28 17.70     | 68.00 0.00      | 0.222                                            |
| K/NaX   | 85.90                            | 48.90 51.32     | 0.00 0.00       | 0.867                                            |
| K/NaY   | 41.61                            | 48.67 51.33     | 0.00 0.00       | 0.532                                            |

\textsuperscript{a} Product selectivity from MBOH decomposition was collected at the time on stream at 140 min after reaching the constant conversion.
3. CONCLUSIONS

Potassium catalysts supported on FAU zeolites (K/NaX and K/NaY) were prepared using potassium acetate buffer through ultrasound-assisted impregnation. Calcination converts potassium precursor to potassium carbonate and causes the collapse of zeolite structures. The collapse in K/NaY is more than that in K/NaX. In addition, the basicity of K/NaX is higher than that of K/NaY.

In transesterification of palm oil and methanol, both catalysts provided high biodiesel yields in the first run. The yield decreased 1.6 times for K/NaX in the second run, but K/NaY was almost inactive. Possible causes of the lower performance of the catalysts are the leaching of potassium species, the collapse of the zeolite structure and the changes of the carbonate species. The effects are less pronounced on K/NaX, therefore, it is the better catalyst for this reaction. Further study to understand the interaction of potassium carbonate on the zeolite is recommended to design catalysts with high stability.

Table 4. Comparison of the Catalyst Performance in Transesterification between K/NaX and K/NaY with 12 wt % K Loading from Conventional and Ultrasound-Assisted Impregnation from This Work and Literature

| catalyst             | preparation method       | oil type         | condition | biodiesel yield (mol %) | reference |
|----------------------|--------------------------|------------------|-----------|-------------------------|-----------|
| K/NaX                | impregnation              | jatropha seed oil| 65 °C, 3 h| 83.0                    | 17        |
| K/NaY                | impregnation              | jatropha seed oil| 65 °C, 3 h| 73.4                    | 13        |
| K/NaY                | impregnation              | palm oil         | 60 °C, 3 h| 68.6                    | 12        |
| K/NaY                | ultrasound-assisted impregnation | palm oil         | 60 °C, 3 h| 72.4                    | 12        |
| K/NaY                | ultrasound-assisted impregnation | palm oil         | 60 °C, 3 h| 94.4 ± 0.93            | this work |
| K/NaX                | ultrasound-assisted impregnation | palm oil         | 60 °C, 3 h| 97.9 ± 0.52            | this work |

Figure 6. GC chromatograms of biodiesel products from the conversion of palm oil obtained from (a) K/NaX (1st run), (b) K/NaX (2nd run), (c) K/NaY (1st run), (d) K/NaY (2nd run), and (e) biodiesel yield from first and second run on K/NaX and K/NaY at 60 °C for 3 h.
4. MATERIALS AND METHODS

4.1. Catalyst Preparation. The synthesis methods of NaX (Si/Al = 1.2) and NaY (Si/Al = 2.4) as zeolite supports were modified from the literature. Fumed silica (SiO₂, 99%, Sigma-Aldrich) was used as Si source for both zeolite syntheses. Aluminum trihydrate (Al(OH)₃, Panreac, 90%) and sodium aluminate (NaAlO₂, Al₂O₃ ≈ 55–56%, Riedel-de Haën) were used as Al sources for the synthesis of NaX and NaY, respectively.

The catalysts with potassium loading of 12 wt % were prepared by ultrasound-assisted impregnation. The zeolite supports were dried in a vacuum oven at 100 °C overnight. An acetate buffer was prepared by dissolving 5.70 g of potassium acetate (CH₃COOK, 99.0%, Carlo Erba) in 1.00 M acetic acid (CH₃COOH, 99.7%, RCI Labscan) and adjusted to 25.00 mL. The buffer of 1.20 mL was added to 1.00 g of dried zeolite and sonicated with frequency 37 kHz, power 80 W (Elmasonic E 30H model, Elma) for 10 min. The mixture was dried in a vacuum oven at 100 °C overnight and calcined at 480 °C under a static air atmosphere for 3 h. The obtained catalysts were noted K/NaY and K/NaX.

4.2. Catalyst Characterization. Phase characteristics of the catalysts were studied by X-ray diffraction (XRD) on a Bruker XRD-D8 Advance with Cu Kα radiation (λ = 0.154 nm) operated with a voltage of 40 kV and a current of 40 mA. All patterns were collected by a 2θ scan range from 5 to 50° with a step size of 0.02° at a scan speed of 0.5 s step⁻¹.

Isotherms of all samples were measured by N₂ adsorption—desorption using a BELSORP-mini II. These samples were degassed at 200 °C for 24 h. Surface areas were calculated by Brunauer—Emmett—Teller (BET) method and micropore volumes were estimated by t-plot method from the desorption branch.

Functional groups of samples were confirmed by Fourier transform infrared spectroscopy (FTIR) on a Bruker,
Tensor27-Hyperion, spectrometer equipped with a microscope using the KBr pellet technique. The spectrum was recorded from 4000 to 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and 64 scans.

Raman spectra were collected with FT-Raman spectrometer on a Bruker, Vertex 70v-RAM II equipped with an Nd:YAG laser with an excitation wavelength of 1064 nm operated at a power of 300 mW. A signal was detected by a liquid nitrogen-cooled Ge diode. Each spectrum was recorded from 1500 to 50 cm$^{-1}$ with 500 scans and a resolution of 4 cm$^{-1}$.

The Si/Al ratio of NaX and NaY and potassium content of the catalysts were determined by an inductive coupled plasma optical emission spectrometer (ICP-OES) using an Optima 8000 (PerkinElmer) instrument. Prior to measurement, the catalyst powder was digested using a microwave digestion method (Multiwave 3000 model, Anton Parr).

Both chemical surface species and surface interaction were identified by X-ray photoelectron spectroscopy (XPS) using a ULVAC-PHI PHI5000 VersaProbe II with Al K$_\alpha$ radiation. All binding energy (BE) peaks were calibrated corresponding to the standard C 1s peak at 284.6 eV. A Shirley background subtraction was applied to correct the XPS spectra stemming from inelastic electron scattering. XPS peaks were fitted with a combination of Gaussian (G) and Lorentzian (L) functions with a G to L ratio of 20 to 80. The full width at half-maximum (fwhm) of fitted peaks are in the range of 1.1−1.8 eV and 1.1−1.7 eV for C 1s and K 1s, respectively.

The basicity of the samples compared to the parent zeolites was studied by the decomposition of 2-methylbut-3-yn-2-ol (MBOH) in a fixed-bed reactor described in previous research. A sample of 200 mg was loaded into a tubular stainless reactor and pretreated at 350 °C under a N$_2$ atmosphere. The reactor was then cooled down to 120 °C and flushed with a vaporized mixture of MBOH and toluene (95:5) using N$_2$ carrier gas with a flow rate of 10 mL min$^{-1}$.

The conversion of MBOH and product selectivity were estimated according to equations reported in the literature. The MBOH conversion and selectivity of decomposed products were calculated on the basis of the sum peak areas as follows in eqs 1 and 2, respectively.

\[
\text{MBOH conversion(mol\%)} = \left(1 - \frac{A_{\text{MBOH}}^{\text{REF}_{\text{MBOH}}} / M_{\text{MBOH}}}{\sum_i (A_i r_{\text{REF}} / M_i)}\right) \times 100
\]
product selectivity (mol%) = \frac{A_p \cdot rRF_p / M_p}{\sum (A_i \cdot rRF_i / M_i)} \cdot 100 \quad (2)

where peak area ratio (A), relative response factor (rRF), and molecular weight (M) are mathematical variables for all components i including MBOH and all products. The terms of the desired product and each obtained product are subscripted by p and x, respectively. The calculation method is based on the relative response factor defined by the effective carbon number concept (ECN).

The basicity of the catalysts was investigated by temperature-programmed desorption of carbon dioxide (CO₂-TPD) using a BELCAT-B chemisorption analyzer. A 50 mg sample was packed into a tubular glass reactor and pretreated at 300 °C under helium (He) gas flow with a rate of 50 mL min⁻¹ for 60 min to eliminate physisorbed species. It was then cooled to 70 °C, and a gas mixture of 10% CO₂/He with a flow rate of 50 mL min⁻¹ was introduced into the sample cell for 30 min. After that, it was purged with He for 30 min and heated to 100 °C with a rate of 10 °C min⁻¹ and held for 60 min to remove nonadsorbed CO₂. The TPD process was performed in a temperature range of 100 to 800 °C with a temperature ramp of 10 °C min⁻¹. The basic site density was obtained by integration of the peak area.

4.3. Transesterification of Palm Oil. Transesterification of palm oil was performed according to the previous work. Two-tenths of a gram of catalyst, 2.90 g of methanol (CH₃OH, 99.9%, Carlo Erba), and 5.00 g of refined palm oil (food grade, Morakot Industries PCL, Thailand) were stirred in a round-bottom flask equipped with a condenser at 60 °C for 3 h. The product mixture was separated by hot filtration following the literature. The liquid phase was transferred to a separatory funnel and allowed to separate overnight. The produced biodiesel in the top layer was collected and evaporated to remove methanol using a rotary evaporator.

The quantitative content of methyl esters (xₘethyl esters) was determined according to biodiesel test method EN 14103 by gas chromatography (Agilent 7890 GC) equipped with a flame ionization detector (FID) using a capillary column (Agilent J&W CP-Sil 88, CP7489) with a length of 100 m with a film thickness of 0.20 μm and an internal diameter of 0.25 mm. Helium was used as a carrier gas with a flow rate of 3 mL min⁻¹. The injection was performed in split mode with a split ratio of 50:1. The injector and detector temperatures were 240 and 300 °C, respectively. In the first step, the oven temperature was started at 70 °C for 4 min and heated to 175 °C with a ramp rate of 13 °C min⁻¹ and held for 27 min. In the second step, the oven was heated to 215 °C with a ramp rate of 4 °C min⁻¹ and kept for 15 min. In the final step, the oven temperature was increased to 240 °C with a ramp rate of 4 °C min⁻¹ and kept for 12 min. Methyl nonadecanoate, so-called C₁₉(CH₃(CH₂)₁₅COOCH₃, 98%, Sigma-Aldrich) was used as the internal standard. The content of methyl esters from the received biodiesel was obtained from eq 3, whereas the content of triglycerides (xₜriglycerides) was from the literature. The yield of produced biodiesel was calculated according to eq 4 from the literature.

\[ x_{\text{methyl esters}} = \frac{\left( \Sigma A_{C_{14}} - C_{14} \right) - A_{C_{19}}}{A_{C_{19}}} \times \left( \frac{C_{19}V_{C_{19}}}{m_{\text{sample}}} \right) \times 100 \quad (3) \]

where \( \Sigma A_{C_{14}} - C_{14} \) is the total peak area from methyl ester in C₁₄ to that in C₂₅₋₁ obtained from GC-FID, and \( m_{\text{sample}} \) is the mass of the analyzed biodiesel sample. The GC peak area, concentration, and volume of methyl nonadecanoate solution are represented by \( A_{C_{19}} \) (C₁₉), and \( V_{C_{19}} \) respectively.

The quantitative content of methyl esters (xₘethyl esters) was determined according to the previous work. The spent catalysts were washed with methanol (10 mL) and K₂CO₃ (10 mL). The potassium content was measured by ICP-OES. The K content from the separated liquid products including biodiesel and glycerol was determined. Each liquid product was digested by a microwave digestion method (Multiwave 3000 model, Anton Parr). The percentage of K leaching was calculated according to Čapek et al. 40

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**Notes**

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

S.K. is supported by the Royal Golden Jubilee Ph.D. Program (Grant PHD/0142/2557) from the Thailand Research Fund (TRF) and Thai German S&T Cooperation 3rd Researcher Mobility. The scholarship for C.P. is from the Science Achievement Scholarship of Thailand.

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