Transesterification of palm oil over KOH/NaY zeolite in a packed-bed reactor

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Abstract- The transesterification of palm oil to methyl ester was investigated on a KOH/NaY catalyst using a packed-bed reactor. The KOH/NaY was characterized by using XRD, nitrogen adsorption/desorption, SEM with EDS, CO_2-TPD, and XRF. It was found that the KOH/NaY created strong basic sites, and the agglomeration was greatly increased by increasing the potassium content. The 15 wt % K/NaY exhibited good activity and the yield of FAME reached 92.18 % at 60 °C for 7 h. Additionally, the reusability of the catalyst was tested in order to observe deactivation of the catalyst from potassium leaching.

Keywords- Transesterification; Biodiesel; NaY; Solid catalyst; Leaching.

1. Introduction

Biodiesel is produced by the chemical reaction of vegetable oils with methanol, to yield corresponding fatty acid methyl esters (FAME) and glycerol as a co-product. Commercial transesterification process usually uses a base catalyst such as NaOH or KOH [1]. However, the homogeneous base catalysts often result in many engineering problems, such as equipment corrosion, and some environmental problems such as the depositing of waste catalysts and problems with product purification. Consequently, soap formation reduces the biodiesel yield and causes significant difficulty in the separation of methyl ester and glycerol [2]. Heterogeneous catalyst has some advantages over homogeneous catalyst, since it is easily separated from the reactants and products. Its efficiency is frequently reported, including a potassium series on a solid support [3,4], and NaOH/alumina [5]. It has been proposed that a higher basic strength of a catalyst results in higher activity of a heterogeneous catalyst for transesterification such as K_2CO_3/Al_2O_3 ($9.3 < H\_ < 15.0$), KI/ Al_2O_3 ($15.0 < H\_ < 18.4$) [3,4], Eu_2O_3/ Al_2O_3 [6], and Na/NaOH/γ- Al_2O_3 [7].

However, in most of the experiments using heterogeneous catalysts, the reaction proceeded at a relatively slow rate compared to those conducted with homogeneous base catalysts. Thus, it is desirable to find more efficient catalysts for the transesterification of vegetable oils in commercial production applications. Zeolite, therefore, has been employed. Suppes et al., 2004 [8] studied the activity of ETS-10 and zeolite-X-type catalysts and found that zeolite-X-type enhanced the activity to levels similar to the ETS-10 at temperatures of around 120 °C for 24 h. These approaches are also reported by using NaX zeolite loaded with KOH as a solid base catalyst, and a conversion of 85.6 % was achieved at 120 °C for 8 h [9]. These studies, nevertheless, have involved high reaction temperatures. The reaction at operation temperatures less than 70 °C has been investigated in a limited number of studies. Then, the commercial viability will likely be determined by the costs of the catalysts and useful life of the catalysts.

Although the activity of heterogeneous catalysts had been extensively reported, the reusability and stability of the catalysts were not specially mentioned. Some researchers have proposed a cause for the deactivation of a catalyst after several successive runs in the transesterification [10, 11]. The current debate on the causes of deactivation is as follows: (i) the deactivation of active sites due to their poisoning by some molecules present in the reaction mixture, and (ii) leaching of the active phase to the alcohol phase, where the catalyst would have a smaller number of active sites in successive runs. It was found that the decrease in catalyst activity between catalytic runs was due to leaching of the active species (K/Al ratio remaining in the solid decreased by 40 % and 75 % in the second and the fourth runs, respectively) to the mixture phase [10]. The effect of leaching was reported that if the dissolved metals are inactive, then the catalysis is truly heterogeneous [11]. Besides, the loss of metal over time will present some problems since the dissolved metal is catalytically active as a homogeneous part, and the process advantages of the solid catalyst are lost.

Previously, we also studied the activity of KOH/ Al_2O_3 and KOH/NaY [12], and found that about 51.26 % and 3.18 % of the K, respectively, was leached out. It can be concluded that the type of support strongly affects the activity and leaching of the active species of the catalyst. The influence of K on a NaY support has rarely been referred to, especially the storage ability of the active species and the reusability of the catalyst. Generally, the ability of strong solid bases, especially zeolites, to catalyze chemical reactions is predetermined. The most basic properties of catalysts occur when an alkali base is loaded onto a support. It is generally known that the average oxygen charge or basicity increases with increasing aluminum content of the zeolite and with increasing ionic radius of the alkali cation [13]. The presence of alkali cations enhance the electron density of the framework oxygen, thus acting as basic sites. The strength of these centers depends on the structure of the framework, its chemical composition, and the nature of the interactions.

In the present study, we investigate the performance of a series of KOH/NaY for the transesterification of palm oil. We attempt to provide some insight into the interpretation of the performance of K loaded on NaY zeolite for the transesterification process in a packed-bed reactor. The data clearly demonstrate the involvement of potassium with the activity with basicity and reveal physical properties of the catalysts.

2. Experimental

2.1. Materials

The refined palm oil used in this present research was obtained from the Naval Engineering Command, Thailand, and was used without further purification. These vegetable oils were analyzed based on density at 27 °C, kinematics viscosity (ASTM D-445), free fatty acid content (AOCS Cd 3a-63), moisture content (AOCS Aa 3-38), and fatty acid composition (AOCS Ce 1-62). Zeolite Y (sodium form, NaY) was obtained from TOSOH Corporation (Si/Al = 2–4). Anhydrous methanol (Lab-Scan, 99.95 %), potassium hydroxide (Lab-Scan), sodium sulfate (Fisher Scientific), and heptane (Fisher Scientific, puriss p.a., 99.5 % GC) were used as chemicals in the transesterification. Methyl heptadecanoate (puriss p.a., standard for GC, 99.7 %) supplied by Fluka, was used to measure the methyl ester content.

2.2. Catalyst Preparation

The KOH/NaY was prepared by the method reported by Noiroj et al. The NaY zeolite was dried in an oven at 110 °C for 2 h and was impregnated with an aqueous solution of KOH with various loadings (5, 10, 15, and 20 wt %) for 24 h. Finally, it was dried in air at 110 °C for 24 h.

2.3. Catalyst Characterization

A Bruker X-ray diffractometer system (D8 Advance), equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating CuKα radiation (1.5405 Å), was used as an X-ray source to obtain the XRD patterns at running conditions for the X-ray tube (40 kV and 40 mA). The sample was prepared and held in the X-ray beam. The detector scans the intensity of diffracted radiation and the peak position from the sample as a function of 2θ by starting at the 10 to 90° (2θ) range with a scan speed of 0.02° (2θ)/ 0.5 second. The XRD patterns were compared to the standards to identify the crystalline phases.

The specific surface area and pore size distribution of the catalysts were determined by N_2

adsorption and desorption, or Brunauer-Emmet-Teller (BET) method, using a Sorptomatic model 1990 instrument (Thermo Finnigan). The catalyst was prepared by outgassing for 24 h at 300 °C. Helium gas was used as an adsorbate for the blank analysis, and nitrogen gas was used as the adsorbate for the analysis.

Temperature-Programmed Desorption (Micromeristics, 2900) was used for observing desorbed molecules from the surface when the surface temperature was increased. The basic properties of the samples were determined using the temperature-programmed desorption of CO_2 (CO_2-TPD), which was used as the probe molecule. A fresh 0.1 g sample was degassed by heating in a flow of helium gas at a rate of 10 °C/min from room temperature to 300 °C, and was kept at 300 °C for 2 h. The adsorption of CO_2 gas occurred at 50 °C for 1 h and the physically adsorbed CO2 gas was purged by a He flow at 30 °C for 2 h. CO_2-TPD was performed at a heating rate of 10 °C/ min up to 600 °C. Moreover, the base strength of the samples (H¬_) was determined by using Hammett indicators in a manner similar to that described previously [3,4]. The following Hammett indicators were used: bromthymol Blue (H_ = 7.2), phenolphthalein (H_ = 9.8), 2,4-dinitroaniline (H_ = 15.0), and 4-nitroaniline (H_ = 18.4). The titration method measured the total basicity of the samples [14] and was compared with the CO_2-TPD technique.

Scanning Electron Microscopy (SEM) using a JEOL, JSM-5800LV, was used to capture the morphology of the catalyst, and the Energy Dispersive Spectrometer (EDS) was used to analyze the elements in the examined region of the catalyst by using an X-ray beam. The sample was placed on the stub with a gold coating before placing the sample holder in the SEM machine.

X-ray fluorescence (XRF) spectrometry (Oxford, model ED2000) was used to determine the bulk composition of the catalysts. The potassium content in the fresh and spent catalysts was measured by XRF. Leached potassium refers to the total amount of potassium in the fresh catalyst withdrawn from the amount of potassium in the spent catalyst. The KBr pellet was applied for determining FT-IR spectra of the samples. The spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 400–4000 cm−1 at a resolution of 2 cm^{-1}.

2.4. Transesterification

Fifty grams of palm oil and a desired amount of methanol were weighed and placed in a 500 ml three-necked flask and heated to 60 °C. A magnetic stirrer was used to mix the oil and methanol at 300 rpm. A desired amount of the catalyst was weighed and added into a packed-bed reactor and heated to 60 °C. The reaction mixture was supplied to the bottom of the packed-bed reactor at a constant flow rate (11 ml/min) using a peristaltic pump. The reaction was carried out until reaching the desired reaction time. Then, the methyl esters (biodiesel) were collected for chromatographic analysis.

2.5. Biodiesel Characterization

The FAMEs of the biodiesel were analyzed by an HP 5890 gas chromatograph equipped with a flame ionization detector and a capillary column DB-WAX (30 m x 0.25 mm). The injection and detector temperatures were 200 and 230 °C, respectively. The oven temperature was held at 130 °C for 2 min and increased to 220 °C at a heating rate of 2 °C/min, and then held for 5 min. Methyl heptadecanoate was used as an internal standard to determine the amount of FAMEs.

3. Results and Discussion

3.1. Catalyst Characterization

The XRD patterns of spent catalysts are shown in Fig.1. It was found that the KOH could be highly dispersed on zeolite NaY and had the same XRD pattern as the parent zeolite Y. It should be noted that the KOH/NaY changed to a more amorphous phase after a high amount of KOH was loaded; therefore, using KOH as a modifier has some intense interaction with the surface of the host [15]. The above observations are in agreement with previous results of alkali metal ion-modified ZSM-5 [16]. However, Zhu *et al.*, 1999 reported that the XRD peaks of NaY disappeared after a 16 %KF/NaY sample was evacuated at 700 °C, indicating the collapse of the framework because the interaction between the KF and the AlO_4 and the SiO4 tetrahedral of the zeolite, was accelerated at high temperatures. Therefore, it can be concluded that the collapsing of the framework in the zeolite is strongly affected not only by the loading amount of potassium but also by the temperature.

The mean pore width, pore volumes, and surface areas of the catalyst are shown in Table 1. The mean pore width is in the range of 0.67 to 1.37 nm, which showed that the micropore volumes of the samples decreased with increasing the loading of potassium, and no mesopores (2–50 nm) were observed. The mean pore width is in the range of 0.67 to 1.37 nm, which showed that the micropore volumes of the samples decreased with increasing the loading of potassium, and no mesopores (2–50 nm) were observed. A significant loss of crystallinity was observed for the zeolites; the decrease of surface area and micropore volume with increasing potassium loading could be assigned to a decrease of the available void volume (similar results are reported by elsewhere) [17]. The loss of crystallinity of the Y zeolites was estimated, assuming that decreased micropore volume depends only on the amount of potassium atoms. The crystallinity was evaluated from the ratio of the measured micropore volume (Vμp) to the calculated micropore volume (N_2 sorption % crystallinity = Vμp/Vμpcal x 100), as shown in Table 1. The calculated micropore volume (Vμpcal) was determined from the potassium loaded on the NaY micropore volume corrected by a loss of volume. The crystallinity of zeolite peaks from N_2 sorption decreases with increasing potassium loading, which is in good agreement with the XRD results in Fig.1, where the zeolite pore structure and shape-selectivity necessary for catalysis, are maintained even KOH is added as a modifier.

The morphology of the KOH/NaY is quite similar to that of the NaY sample (Fig.2). The KOH/NaY showed the agglomeration of small particles with the increase of K loading. When the loading amount of K was increased from 5 to 20 wt %, the particle sizes were increased from 9.74 to 21.30 μm. Thus, it can be suggested that a good dispersion of KOH on NaY retained its structure as consistent with the results from BET and XRD. From the crystal size distribution analysis of the samples, it is clear that when the potassium is loaded on the support structure, the derived catalysts have a wide particle size distribution. If the NaY support is the main phase, the potassium covered and deposited on the surface at a low potassium content of 5 to 10 wt % with further increasing of the K content, it is likely that small particles agglomerated into larger sized particles and the standard deviation increased significantly.

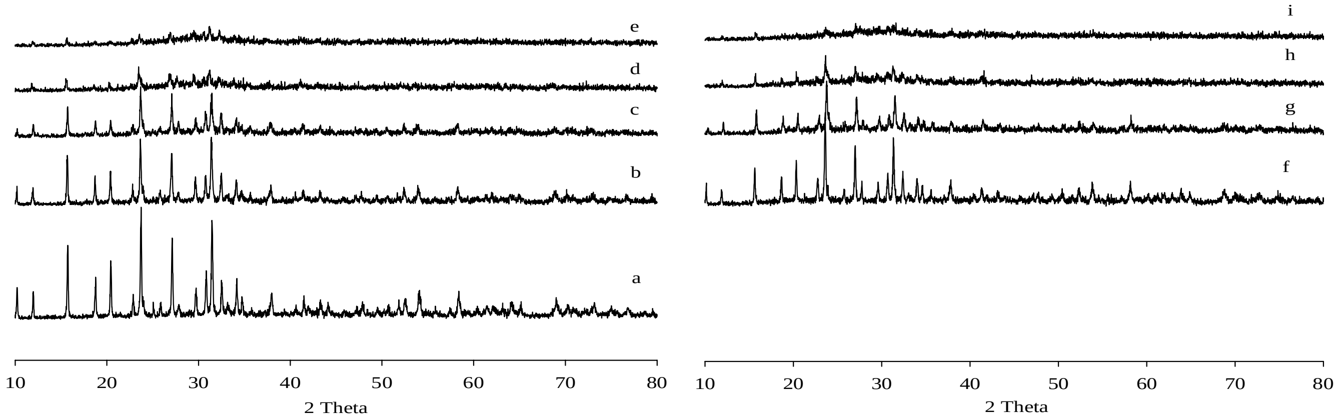


Fig. 1. XRD patterns of the fresh catalysts: (a) NaY, (b) 5% K/NaY, (c) 10% K/NaY, (d)15% K/NaY, and (e) 20% K/NaY; and spent catalysts: (f) 5% K/NaY, (g) 10% K/NaY, (h)15% K/NaY, and (i) 20% K/NaY.

Table 1. Catalytytic activity and characterization of NaY and KOH loaded on NaY catalysts

Sample	FAME[a] (wt%)	Mean pore width (nm)	BET surface area (m^2/g)	% Crystallinity		Basicity (mmol/g)		Average Particle size [d] (μm)
				BET	XRD	(A)	(B)	
NaY	0	0.67	576.89	100	100	[b]1.203	1.52	6.48
5%K/NaY	41.10	0.68	367.40	63.69	86.91	[b]0.905	2.47	9.74
10%K/NaY	88.80	0.74	71.88	12.46	62.40	[b]0.372 [c]0.065	2.61	18.43
15%K/NaY	92.18	0.87	31.81	5.51	32.80	[b]0.051 [c]0.356	2.70	19.67
20%K/NaY	92.24	1.37	10.61	1.84	22.56	[c]0.372	2.52	21.30

a Reaction conditions: methanol/oil molar ratio 15:1, catalyst amount 12 wt %, reaction time 7 h, flow rate 11 ml/min, b CO2-TPD peak at low temperature, c CO2-TPD peak at high temperature, d SEM, e Energy Dispersive Spectrometer, and f X-ray fluorescence; and (A) CO2-TPD and (B) Titration

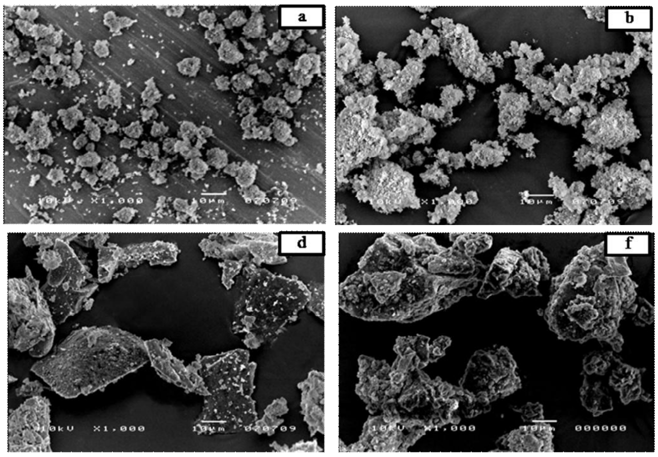
3.2. Transesterification

3.2.1. Effect of Potassium Loading

The overall FAME yield on the KOH/NaY catalysts on the transesterification of palm oil is compared at a methanol-to-oil molar ratio of 15:1, a reaction time of 7 h, and with 12 wt % of the catalyst. As expected, the NaY zeolite did not present any catalytic activity. The incorporation of potassium increased the basic strength of the pure zeolite, resulting in an increase in FAME yield. The results in Table 1 show that the activity increased by increasing the KOH content (the FAME was increased from 41.1 to 92.24 wt %). The catalytic activity is dependent on the basicity, and the high activity of 20 % K/NaY might be due to the presence of a high number of basic sites. However, when the amount of loaded KOH was over 15 wt %, the basic strength and the basic site of the catalyst were not raised, resulting in almost constant biodiesel yield.

The basic strengths of the catalysts were determined by using Hammett indicators. The pure NaY zeolite did not convert the color of bromthymol blue (H¬_ = 7.2), after loading of KOH, the modified NaY zeolites exhibited a higher base strength. They could change the color of phenolphthalein (H_ = 9.8), but failed to convert 2,4-dinitroaniline (H¬_ = 15.0) and 4-nitroaniline (H_ = 18.4). The basic strengths could be assigned to activity for transesterification and the result agrees well with CO_2-TPD analysis.

Figure 3 shows the CO2-TPD profiles of the samples. Typically, four regions are observed at 100–300, 300–400, 400–500, and >500 °C in the TPD profiles, which correspond to basic sites present in the samples with different strengths [18, 19, 20]. Both fresh NaY and 5 wt%K/NaY showed CO_2 desorption at approximately 195 °C, which can be ascribed to the interaction of CO_2 with sites of weak basic strength. The amount of adsorbed CO_2 in the low temperature region of NaY can be assigned to weak basic sites. A negligible catalytic activity of NaY was observed when it was used as catalysts in the transesterification of palm oil, suggesting that the weak basic sites inadequate promote the transesterification. The number of basic sites of the samples measured by CO_2-TPD and titration methods is in the range of 0.372 to 2.7 mmol/g of catalyst (Table 1). The difference in the number of basic sites for each catalyst indicates that the basic strength and basicity are influenced by the addition of KOH, as revealed in Table 1 and Fig. 3.



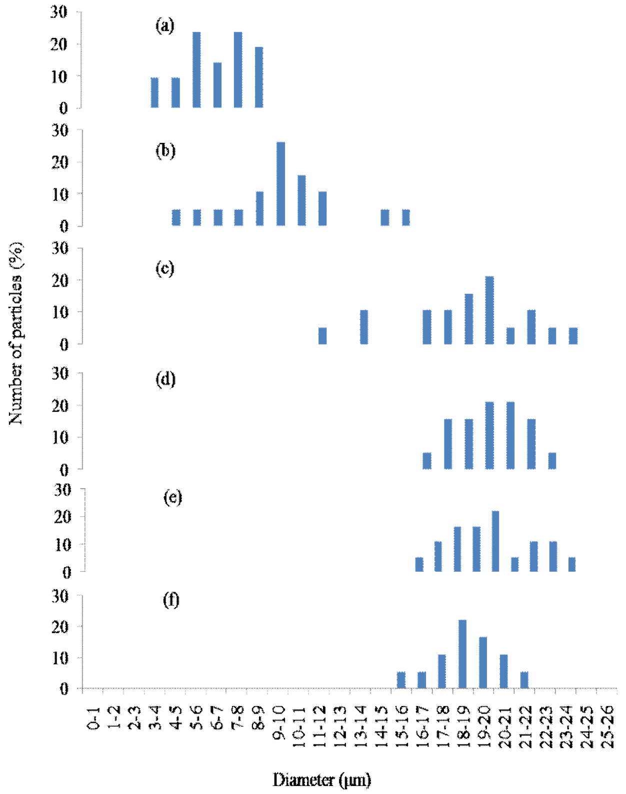


Fig. 2. SEM images and particle size distribution of fresh catalysts: (a) NaY, (b) 5% K/NaY, (c) 10% K/NaY, (d) 15% K/NaY, and (e) 20% K/NaY; and spent catalyst: (f) 15%K/NaY.

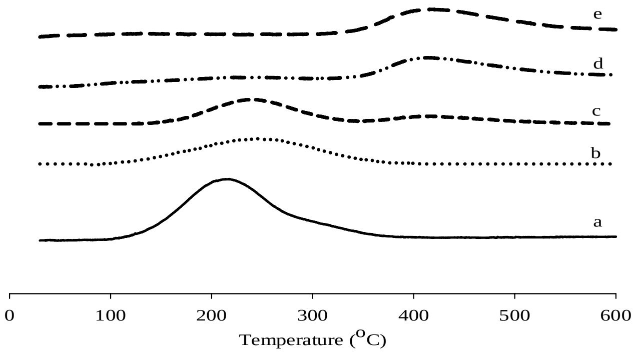


Fig. 3. CO_2-TPD profiles of (a) NaY, (b) 5%K/NaY, (c) 10%K/NaY, (d) 15%K/NaY, and (e) 20%K/NaY.

When the amount of potassium was increased to 10 wt%, two peaks of desorption appear, one at approximately 240 °C, which refers to the weak basic site, and the other peak appears at 400 °C, which refers to the moderate basic sites. Serio et al. [21] reported the presence of these kinds of basic sites as super-basic sites at temperatures of >350 °C. Therefore, this sample would reveal the occluded potassium species to be responsible for the high activity of the impregnated sample with further increasing the amount of potassium from 15 to 20 wt %, only one peak of CO2 desorption appears, at around 400 °C. These catalysts show the presence of more strong basic sites, which resulted in a further increase in the basicity of these samples.

There is a clear relation between the distribution of basic sites and activity, as shown in Fig.4. With the addition of KOH to the NaY, the basicity increases, and hence the catalytic activity for the transesterification increases. Interestingly, it was found that the measured basicity from the CO_2-TPD is less than the titration. Similar results were also found with KNO_3/Al_2O_3 and KNO_3/ZrO_2, and are attributed to the overlapping structure of the basic species form on the sample [14].

The overlapping structure of the basic species covered by upper layers was not exposed to CO_2, but would react with an acidic agent if the top layers were resolved in an aqueous titration process. Therefore, the CO_2-TPD results show the basicity exposed on the top of the structure; however, the basicity result measured by the titration method showed many more basic sites of the catalyst.

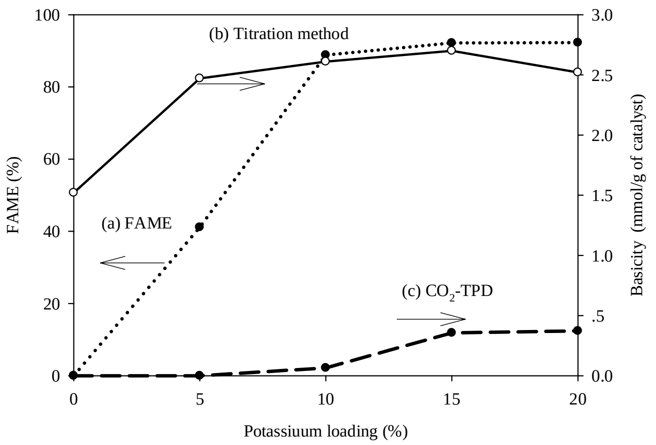


Fig. 4. (a) FAME (%), (b) titration method, and (c) CO2-TPD* (only strong basicity) with varying the potassium loading.

3.2.2. Stability of Catalyst

In order to evaluate the stability of the catalyst, its reusability under optimum conditions was studied. The spent catalyst was separated after each run without pretreatment, followed by the addition of fresh palm oil and methanol. The K/NaY catalyst gave 92.18 %FAME in the first run and a FAME yield of 55.28 % was observed in the second run, as illustrated in Fig. 5. In the fourth cycle, only 15.4 %FAME was obtained. It may be noted that although our FAME yield appears to be quite high in the first run; however, the FAME yield decreased quickly in the fourth cycle. This deactivation might be due to either some molecules poisoning to the catalyst or to the leaching of active species from the solid catalyst.

To reveal the leaching of the active species from the solid catalyst, potassium as the active species was measured using XRD, SEM with EDS, and XRF. The XRD patterns of spent the K/NaY (Fig.1) illustrated that the spent catalysts had the same diffraction peaks as the fresh catalysts and no phase change was observed. The XRD patterns of 15 wt%K/NaY show that the intensity and crystallinity of the spent catalyst (36.62 %) slightly increase from the fresh catalyst (32.80 %). It might be suggested that some molecules were leached from the surface.

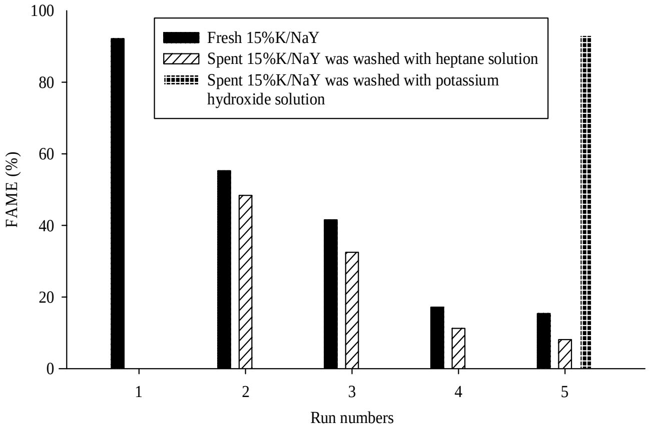


Fig. 5. FAME (%) versus run numbers in the transesterification reaction of palm oil with methanol for the K/NaY catalyst.

The SEM pictures (with scale bar 10 μm) showed that the particles of fresh catalysts are agglomerated and are spherical with an average size in the range of 6.48 to 21.30 μm (Table 1). However, the SEM results are not clearly evident to explain all of the effects of leaching. Therefore, the K species of fresh and spent catalysts was further investigated. The K contents of the fresh catalyst measured by EDS are lower than the expected potassium loading. It could be suggested that some of the potassium is diffused into the pores of the zeolite. After the first run, the K content of the spent catalyst was lower, compared to that of the fresh catalyst. With further increasing the amount of potassium in the sample, the potassium leaching from the surface of the NaY zeolite was clearly observed. For the spent first catalyst at 5 wt %K loading, no significant leaching was observed. However, by increasing the amount of K to more than 10 wt %, it seems that the leaching effect of the potassium was more pronounced, corresponding with the results from the EDS.

To determine whether destruction of the zeolite support or leaching of the active species to the alcoholic phase occurred upon recycling, the K and Si/Al content of fresh and spent catalysts were obtained. It was found that the percentages of potassium remaining in the catalyst decreased by 5.05 % in the first run, and 5.64 % and 10.64 % in third and fourth runs, respectively. The Si/Al ratios also remain at 3.4 in every run of all samples, suggesting that the structure of the zeolite support was not destroyed during the reaction. Our previous work indicated that the amount of potassium leaching on the NaY zeolite is much less than that on the Al_2O_3 support [12], the leached active species could be the homogeneous part which is lost to the liquid phase, and the catalytic activity would certainly be lost. Therefore, preventing the leaching of the active species during the run was responsible for the catalytic activity of the heterogeneous catalyst. We previously found that the type of support strongly affects the amount of leaching of the active species and the percentage leached did not surpass 8 %; therefore, the influence of the leached potassium on K/NaY catalysts is expected to be of little importance. In the present study, we found that leaching of potassium in the prepared catalyst does occur and the leaching of all these catalysts in the ester phase was measured. Therefore, it could be concluded that NaY zeolite can be used as a support that possessed lower leaching than Al_2O_3 catalyst.

At this point, our results indicate that degradation of the catalyst occurs in successive runs, although a relatively low amount of leaching was observed. It would be interesting to investigate the effect of deactivation of the active sites due to poisoning by some molecules (biodiesel and glycerin) in the mixture that might cover the active sites of the catalyst. To reveal the deactivation of the active sites due to the poisoning by some molecule, the catalyst used was washed once for 1 h with heptane to remove the esters. This sample was dried for 24 h at 110 °C. The activity measurement for this reused catalyst was slightly lower than the value obtained in the second run of reutilization (48.3 % FAME), as shown in Fig.5. Consequently, the deactivation of the catalyst during reaction could be caused by glycerol molecules.

In order to investigate the possibility of catalyst regeneration, the deactivated K/NaY catalyst in the fifth run was washed with heptane. Then, the catalyst was washed with a 5.75 M potassium hydroxide solution, the same as the initial impregnated concentration, to remove glycerol and prevent leaching of active species to solute, and was dried at 110 °C for 24 h. The treated almost completely catalyst recovered the activity shown by the fresh catalyst (FAME = 93.10 %). It is possible to regenerate the catalyst by submitting it to a polar solution, like methanol, to remove the glycerol. However, a polar solution might promote the leaching of the active species [21].

To assure the results of this washing procedure, FT-IR was used and the FTIR spectra of the fresh, spent, and treated catalysts are shown in Fig.6. The NaY peak appears at 3500, 1640, and 1030 cm-1, which clearly seen in all samples as the OH stretching band, –Si–O–Si– stretching vibrations, and overlaps with the –Al–O– and –Al–O–Si– stretching vibrations [22], respectively. The fresh 15 wt%K/NaY shows new band at 1455 cm-1, assigned to the bending mode of O–H. The spent 15 wt %K/NaY catalyst shows the FTIR spectrum at 2927, 2845, 1735, 1557, and 1450 cm-1. The peaks at 2927 and 2845 cm-1 reveal C–H stretching of alkane, 1735 cm-1 shows the C=O vibration of carbonyl band, and 1450 cm-1 shows (C=C) unsaturated hydrocarbon band, which were found in the biodiesel solution [23], respectively, and 1557 cm-1 shows the formation of carbonate ions adsorption on zeolite [24]. The 1169 cm-1 band should be observed as a methyl group near carbonyl groups; however, it is not clearly seen because of interfered of spectra between carbonyl groups and framework of zeolite. Therefore, the spent catalysts (spectra c–d) can be identified as adsorbed oxygenated hydrocarbons (CxHyOz), which contained biodiesel, glycerol, and heptane. After the spent catalyst was washed by the potassium solution (curve e), the alkane and carbonyl ion peaks disappear, implying that the unsaturated hydrocarbon and carbonyl group, biodiesel, was washed out. Accordingly, the FT-IR results correspond to the activity result that after washing the spent catalyst with the potassium solution, the activity of the catalyst will be recovered.

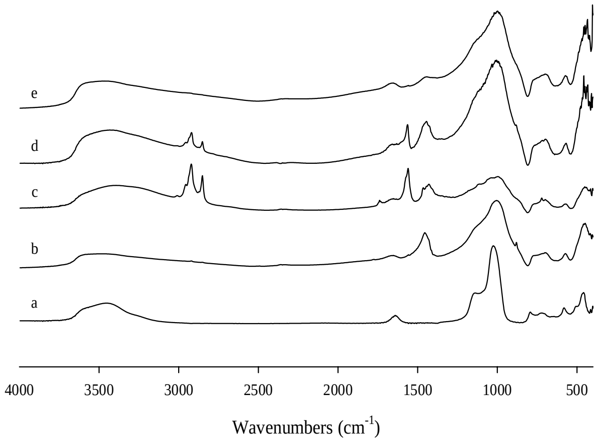


Fig. 6. FTIR spectra of (a) NaY, (b) fresh 15wt%K/NaY, (c) spent 4thrun 15wt%K/NaY, (d) washed with heptane, and (e) washed with potassium solution of spent 4thrun 15wt%K/NaY.

The activity of the K/NaY catalyst was also confirmed by using a methanol solution as the medium reaction in the transesterification, although, this catalyst still has some leaching. Further attention must be paid to the stability (leaching) and to the reutilization of solid catalytic systems when reporting the transesterification reactions by heterogeneous catalysts. These considerations should be extended to other basic catalytic systems, which relate to alkaline and alkaline-earth metal oxides, and other methods to treat used catalysts. From the data reported in Fig. 5, it is clear that at 60 °C we can obtain maximum FAME of 93 %. However, this is not sufficient for biodiesel industrial plants requiring conversions higher than 96 %. To achieve this goal, it is necessary to perform a second transesterification stage after glycerol and catalyst separation. Two transesterification stages, however, have more advantages in that more pure glycerol can be and reusability for the catalyst can be obtained.

4. Conclusions

The FAME yield was studied over KOH/NaY zeolite catalysts for the transesterification of palm oil. The catalytic activities of KOH/NaY relate with the basic properties of the catalysts. A catalyst with 15 wt % K loading on NaY zeolite was found to be the optimum catalyst, which gave the highest basicity and the best catalytic activity. Moreover, leaching of the active species was found over spent catalysts. The amount of leached potassium rises when increasing the potassium loading. The recycle runs reveal that the activity of the catalyst decreases up to five runs due to some poison molecules.

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