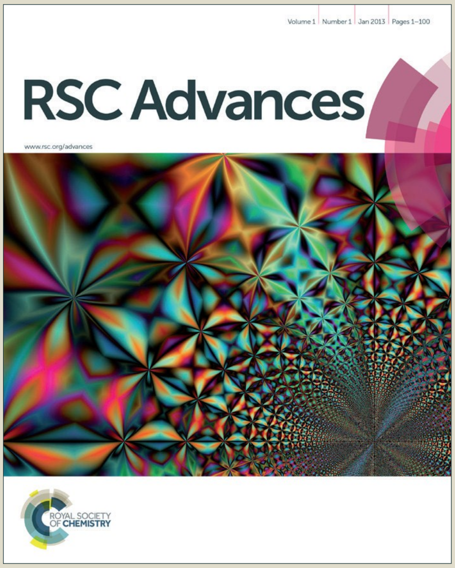
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Synthesis of ethylene glycol monomethyl ether monolaurate catalysed by KF/$NaAlO_2$ as a novel and efficient solid base

Shengfeng Lou[1], Lihua Jia*[1], Xiangfeng Guo*[1], Wenwang Wu[1], Lianbing Gao[1],
Hongyuan Wu[1], Jianjun Wang[2]

[1]College of Chemistry and Chemical Engineering, Key Laboratory of Fine Chemicals of College of Heilongjiang Province, Qiqihar University, Qiqihar 161006, China.

[2] Heilongjiang Haohua Chemical Corporation, Limitd, Qiqihar 161033, China.

*Corresponding author. Email: jlh29@163.com (Jia L.), xfguo@163.com (Guo X.)

Abstract: A novel solid base catalyst of $NaAlO_2$ modified with KF (*x*-KF/$NaAlO_2$) was prepared by wet-impregnation method and used for the synthesis of ethylene glycol monomethyl ether monolaurate (EGMEML) *via* transesterification of ethylene glycol monomethyl ether (EGME) and methyl laurate (ML). The catalyst was characterized by Hammett indicator method, X-ray diffraction, thermogravimetry analysis, Fourier transform infrared spectroscopy, scanning electron microscopy with energy dispersive spectrometer. The effect of the reaction parameters such as the amount of KF loading, molar ratio of EGME to ML, dosage of catalyst, reaction time and temperature on the yield of EGMEML was investigated. These characterizations led to a conclusion that the reaction between $NaAlO_2$ and KF mainly generates fluoroaluminates, which act as the main active sites for the transesterification. The catalyst shows excellent catalytic activity and good stability. The highest yield of 91% was obtained over 30%-KF/$NaAlO_2$ at EGME/ML molar ratio of 3.0, the catalyst amount of 5 wt%, and reaction time of 4 h at 120 ^{o}C. And a yield of 80% was obtained after use for three consecutive rounds without reactivation. Furthermore, a desirable yield of 88.0% of novel biodiesel of ethylene glycol methyl ether soybean oil monoester was obtained with 30%-KF/$NaAlO_2$ as catalyst. Moreover, it was found the reaction follows second-order kinetics, the activation energy (*Ea*) equals 56.54 kJ/mol of the reaction of EGME with ML; and the thermodynamic parameters of activation were evaluated based on activation complex theory of the reaction; and the following datum are obtained, $\Delta G^{\ddagger} > 0$, $\Delta H^{\ddagger} > 0$ and $\Delta S^{\ddagger} < 0$, indicating the unspontaneous and endergonic nature of the reaction of EGME with ML. Koros-Nowak test was conducted and the results confirmed that the diffusion limitations did not affect the catalytic activity. Finally, a few of physicochemical properties of the EGMEML as biodiesel were determined, and the values were within that of European standards.

Keywords: Heterogeneous catalysis; Impregnation; Biomass conversion; Novel biodiesel; Sodium aluminate.

1 Introduction

Energy is an indispensable factor for human to preserve economic growth and maintain standard of living [1]. In recent years, due to the transportation and the basic industry sectors, the increase of energy demand has been supplied using fossil resources (crude oil, natural gas and coal, principally) [2]. Hence, recent interest in alternative sources for petroleum-based fuels has been stimulated. Among many possible resources, biodiesel obtained by the use of oils of plant origin like vegetable oils and tree borne oil seeds has been drew more attention [3]. This kind of fuel is biodegradable and non-toxic, and has similar calorific value as compared to petroleum diesel [4]. Moreover, biodiesel can be mixed with petroleum diesel and the components of the two fuels allow in any proportion [5]. For instance, as inherently biodiesel possesses better lubricity, the lubricity of diesel can be improved with addition of biodiesel [6]. Recently, a kind of novel biodiesel was synthesized by the transesterification reaction of FAMEs with short chain glycol ethers [7,8]. Compared with the conventional biodiesel, novel biodiesel not only has the advantages of traditional biodiesel, but also attempts the introduction of ether groups into the molecules and the amount of oxygen containing can be largely improved. So, engine-out exhaust emissions and combustion are effectively reduced [9]. Guo et al., [10] reported the synthesis of ethylene glycol monomethyl ether palm oil monoester (EGMMEPOM) through transesterification of a refined palm oil and ethylene glycol monomethyl ether. It was found that EGMMEPOM has a maximal reduction of the smoke, NO_x, by 26.3% and 14.0%, CO and HC also significantly reduced compared with diesel fuel. Gao et al., [11] disclosed that the production of ethylene glycol n-propyl ether palm oil monoester (EGPEPOM) through transesterification of refined palm oil and ethylene glycol n-propyl ether with sodium as the catalyst. In comparison to diesel fuel, the emissions of smoke, NO_x, brake-specific CO and HC of EGPEPOM decreased 37.5, 23.7, 66.6 and 27.1%, respectively. Zhang et al., [12] revealed the manufacture of ethylene glycol monobutyl ether palm oil monoester

(EGMEPM) *via* transesterification of palm oil and ethylene glycol monobutyl ether (EGME). Smoke, CO, HC, and NO_x emissions were reduced by 57%, 40%, 75%, and 25% compared to diesel fuel, respectively. Therefore, the novel biodiesel has been regarded as an excellent cleaning energy.

Homogeneous or heterogeneous catalysts are usually used to promote the transesterification reaction rate [13]. Although homogeneous catalysts have high catalytic efficiency in a short time, it also has several drawbacks such as soap formation, catalytic efficiency reduction caused by the consumption of catalyst, the increase of viscosity and gels formation [14]. Moreover, remove of the homogeneous base catalyst after reaction creates large amount of caustic wastewater, contaminating the environment and increasing production costs [15]. The using of heterogeneous solid base catalysts effectively solved the issues in transesterification. Moreover, heterogeneous solid base catalysts can be easily separated from the reaction mixture, conveniently regenerated, and the corrosion of the reactor could be decreased in some degree, leading to operation much safer, cheaper and more environment-friendly [16]. In recent years, our group devoted to the study of solid base catalyst applied in the production of novel biodiesels. Fan et al., [17] used calcined sodium silicate as catalyst for the synthesis of novel biodiesel from soybean oil methyl ester and ethylene glycol monomethyl ether, a maximum yield above 90.0% was obtained. Catalyst preparation process is simple and the separation process becomes easily after reaction. Chen et al., [18] synthesized KF-modified Ca-Al hydrotalcite and used as a catalyst to produce a novel biodiesel of ethylene glycol monomethyl ether monolaurate, the effect of the structure and preparing method of the catalyst on the catalytic activity were discussed. However, developing the excellent activity and handleability of the solid base catalysts is still a challenge in the transesterification.

Sodium aluminate is an important commercial inorganic chemical due to the versatility of its technological applications. Sodium aluminate is mainly applied to effective water treatment systems. It is also used in producers of paper, paint pigments, alumina-containing catalysts, dishwasher detergents, ingot molds, and molecular sieves, concrete, and so on [19]. Normally, $NaAlO_2$ is water soluble and shows strong basicity in water, but insoluble in alcohol. Cobas et al., [20] studied the isomerization of the galactooligosaccharides mixture by the action of sodium aluminate. At the optimal conditions, the isomerization yield was >60%. Mutreja et al., [21] evaluated sodium aluminate as basic catalyst for the transesterification of waste mutton fat with methanol. The conversion to biodiesel could reach 97%, sodium ion concentration in unwashed biodiesel obtained was found to be 5.6 ppm. Bai et al., [22] developed the one-pot synthesis of glycidol from glycerol and dimethyl carbonate by using $NaAlO_2$ as a solid base catalyst. It showed high conversion of glycerol and selectivity to glycidol. The conversion of glycerol and the selectivity to glycidol remain at 87.1% and 68.7% as catalysts used for the next run. Cherikkallinmel et al., [23] used sodium aluminate from waste aluminium source as catalyst for the transesterification of Jatropha oil. A maximum yield of 99% was obtained at 65 ^{o}C. The catalyst kept high catalyst activity after calcinating at 650 ^{o}C. Wan et al., [24] employed sodium aluminate as a heterogeneous catalyst for the production of biodiesel from soybean oil by transesterification. And the yield was 66.2%, 62.9%, and 61.4% as the catalysts used for three cycles.

In order to prepare a base catalyst with high efficiency and stability for the transesterification, KF loading sodium aluminate solid base catalyst by immersion method was synthesized, and used in the production of ethylene glycol monomethyl ether monolaurate and soybeanoil monoester novel biodiesel in this paper. Hammett indicator method, X-ray diffraction (XRD), thermogravimetry analysis (TG-DSC), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy and Energy dispersive spectrometer (SEM-EDS) were performed to characterize the structure of the catalyst, in an attempt to explain the correlation between structure and activity of the catalyst. The different reaction parameters such as temperature, reactant ratio, reaction time and amount of catalyst were optimized. And a desirable yield of 88.0% was obtained as the catalyst was used to the production of ethylene glycol methyl ether soybean oil monoester. At the same time, repeatability and stability of catalyst was investigated. Koras-Nowak criterion tests demonstrated that the mass transport phenomenon did not affect the catalytic activity. Finally, the rate constant and the activation energy were determined from the kinetic study. The values of thermodynamic parameters of Gibbs free energy of activation ($\Delta G^{\ddagger}$), enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were investigated using the activation complex theory.

2 Experimental

2.1 Materials

$KF\cdot 2H_2O$, $NaAlO_2$, methanol, methyl laurate and ethylene glycol monomethyl ether were of analytical grade, all reagents were purchased from Aladdin, China.

2.2 Catalyst characterizations

The basic strength of the sample (H_-) was determined using Hammett indicator. About 20.0 mg of the sample was shaken with 5.00 mL methanol and two or three drops of Hammett indicators-methanol solution (0.1%, w/w) and then left to equilibrate for 2 h when no further color changes were observed [25]. The Hammett indicators used and the corresponding H_- values are listed in Table 1. Alkaline determination was measured by benzoic acid titration method, using 0.02 mol/L benzoic acid-anhydrous ethanol solution as titrant, until the basic color of indicator adsorbed on the surface of solid alkali just disappeared.

Powder XRD diffraction was performed on a Bruker D8 Advance (Germany) diffractometer, using Cu Kα radiation (λ=1.5418 Å) at 40 kV and 50 mA. The scanning speed was 3^{o} min^{-1} and scanned area ranged $2\theta = 5^{o}- 80^{o}$.

Table 1

Thermogravimetric analysis (TG-DSC) was carried out using NETZSCH STA F3. 10 mg of the sample was used and alumina was used as reference. TG and DSC curves were obtained from 25 ^{o}C to 800 ^{o}C under nitrogen atmosphere with a heating rate of 10 ^{o}C min^{-1}.

FT-IR spectra were recorded on an AVATAR370 spectrometer during 4000-400

cm^{-1}, with 4 cm^{-1} resolution. The KBr pellet technique was applied for preparing samples. All measurements were conducted at room temperature.

Morphology of the samples was observed by SEM using a Rigaku S-4300 spectrometer (Japan). The voltage was 20 kV and the vacuum degree of the sample room was better than 10^{-4} Pa.

2.3 Catalyst preparation

The catalyst is prepared through wet impregnation method. Initially, $NaAlO_2$ activated at 400 ^oC for 4 h. Then, 1.00 g $NaAlO_2$ was immersed in 20 mL KF methanol solution with certain amount $KF{\cdot}2H_2O$ and stirred for 4 h at room temperature. And methanol was removed under 80 ^oC. The precursor was dried at 80 ^oC overnight and stored in a vacuum desiccator. Prior to the reaction, the precursor was activated in a muffle furnace at 400 ^oC for 4 h. For convenience, the catalysts were designated as x-KF/$NaAlO_2$, where x stands for the KF loading mass percentage. 30%-KF/$NaAlO_2$ was mean for 30 wt% of KF with respect to $NaAlO_2$.

2.4 Catalytic activity measurements

The transesterification of ethylene glycol monomethyl ether with methyl laurate was carried out in a 50 mL three-necked glass round bottom flask, equipped with a long condenser connected to water circulation and a thermometer. The desired amount of ethylene glycol monomethyl ether, methyl laurate and catalyst were added into the flask. The reaction was carried out on a hot plate with magnetic controlled stirrer until it reached the desired reaction temperature and time. After that, the reaction was stopped by cooling the reactor to room temperature and the catalyst was separated from the liquid phase by filtration. The supernatant liquid was purified in a rotary vacuum evaporator to remove excess EGME and byproduct methanol. All experiments were performed under atmospheric pressure.

2.5 Product analysis

Analysis of the reaction products were conducted by an SP 6890 gas chromatograph equipped with a flame ionization detector and a OV-101 column (30 m × 0.52 mm, film thickness 0.5μm). The GC oven temperature was maintained at 210 °C for 1 min and then increased to 230 °C at a rate of 10 °C/min and held for 1 min, and ramped at 10 °C min^{-1} up to 260 °C, the oven temperature was kept at 260 °C throughout the analysis. The injector temperature was fixed 280 °C and the detector temperature was at 280 °C. The GC was connected to a chemstation which recorded the peak areas and retention times in the chromatogram. The yield (Y) was calculated by the following eqn (1).

$$Y = \frac{m_1 \times w}{m_2} \times 100\% \tag{1}$$

where m_1 is the product actual mass (g), m_2 is the theoretical calculated mass of the target product (g) and w is the mass concentration of the target product determined by GC.

The turnover frequency (TOF) was calculated by the following eqn (2).

$$\text{TOF} = \frac{\text{mol}_{\text{actual}}}{t \times f_m \times m_{cat}} \tag{2}$$

where m_{cat} is the mass amount of the catalyst (g), $\text{mol}_{\text{actual}}$ is the mole amount of target product, t is the desired reaction time (min), and f_m is the amount of basic sites of the 30%-KF/$NaAlO_2$ (mmol/g).

3 Results and discussion

3.1 Characterization of catalyst

Thermal stability of $NaAlO_2$ and as-prepared KF/$NaAlO_2$ were examined by TG-DSC experiments as shown in Figure 1. Three major weight losses for $NaAlO_2$ appeared and lined with the three endothermic peaks in the relevant DSC profile with the transition temperatures at 78^oC, 143 ^oC and 200 ^oC, respectively (Figure 1A). The first weight loss of 2.5% is assigned to the elimination of water, the second weight loss of 3.7% is due to desorption of CO_2 from the basic sites [22], and the last loss of 3.0% is attributed to the decomposition of crystal water of $NaAlO_2$. After loading KF (Figure 1B), the fresh KF/$NaAlO_2$ sample presents three main weight losses in the temperature ranges of 100-150°C, 150-200°C and 320-370°C, respectively. The first weight loss of 3.7% is assigned to the elimination of water adsorbed on the surface, and the second weight loss of 5.6% is due to the remove of CO_2. Compared with that of $NaAlO_2$, the new endothermic peak at 330°C may be assigned to formation of new compounds. Based on these results all the catalysts were activated at 400^oC

Figure 1

XRD patterns of $NaAlO_2$, and KF/$NaAlO_2$ were performed to determine the change of crystal structure of the catalysts as shown in Figure 2A. $NaAlO_2$ calcinated at 400^oC exhibited the typical diffraction peaks of $NaAlO_2$ at 2θ value of 20.7◦, 21.2◦, 21.2◦, 30.3◦, 33.2◦, 34.3◦ and 34.9◦ (JCPDS file 33-1200). With increasing the loading amount of KF, the intensities of the diffraction peaks of $NaAlO_2$ decreased, meanwhile, new peaks appeared. Among of them, the peaks of 30.7◦ and 41.5◦ belong to that of $Na_5Al_3F_{14}$ (JCPDS file 30-1144), and the peaks of 29.7◦, 36◦ and 42◦ correspond to that of K_3AlF_6 [26] (Figure 2B). These demonstrate there is a strong interaction between KF and $NaAlO_2$. The results of XRD patterns are agreement with that of TG-DSC. When the KF amount was up to 40%, another new phase of KF (JCPDS file 36-1458) obviously come out, as well as the intensities of the diffraction peaks of $NaAlO_2$, $Na_5Al_3F_{14}$ and K_3AlF_6 decreased, which may result from the excess of KF covering the active sites [27].

Figure 2

The investigation of KF/$NaAlO_2$ was conducted *via* IR spectroscopy as shown in Figure 3A. It can be seen that there are two bands at 3440 and 1640 cm^{-1}, which are assigned to stretching and bending vibration of the physically adsorbed water, respectively [28]. With the increase of KF loading, the intensities of absorption bands at 3440 and 1640 cm^{-1} enhanced. It indicates the adsorbed O-H band could not entirely belong to water molecular in air but partly assign to surface hydroxyl groups formed by alkaline activity sites. The two bands at 1367 cm^{-1} and 1440 cm^{-1} are attributed to carbonate species [29]. The existence of CO_3^{2-} specie is due to the exposure of catalyst in air for FT-IR analysis [30]. As shown in Figure 3B, the peak at 811 cm^{-1} corresponds to the formation of O-O triangular species bonds, and the peaks at 617 and 558 cm^{-1} belong to the vibrations of Al-O bond [22]. With KF loading amount increased, both of the vibrations of Al-O bond and O-O triangular species bonds existed but receded, which indicates the loading KF acted with $NaAlO_2$. The result is consistent with that of XRD.

Figure 3

The morphological structure unit of $NaAlO_2$ is a rodlike profile which arranged unregularly (Figure 4A), and the rod presents a tetrahedron structure and smooth surface (Figure 4B). After loading KF, the catalyst still kept the rodlike structure, and some new crystalline granules on the surface were observed (Figure 4C). These particles on the rods could be the formed new materials of $Na_5Al_3F_{14}$ and K_3AlF_6, which is in line with the results of XRD, TG-DSC and FT-IR. Figure 5 shows the element mappings of 30%-KF/$NaAlO_2$, confirming the presence of K, Al, F, Na and O and their homogeneous distribution on the surface of the catalyst.

Figure 4

Figure 5

Table 2

Table 2 summarizes the basic strength and basicity of x-KF/$NaAlO_2$. The catalysts could change the color of phenolphthalein ($H_- = 9.8$) from colorless to purple, but failed to convert 2,4-dinitroaniline ($H_- = 15.0$) from yellow to mauve. Therefore, their basic strength could be tentatively denoted as $9.8 < H_- < 15.0$ [31]. As shown in Table 2, the yield of 68% of EGMEML was obtained as $NaAlO_2$ directly used as a catalyst for the transesterification, and it was found the mixture after reaction formed gel, which caused a difficulty in the separation of catalyst from the reaction mixture. When the amount of KF loading increased to 10%, the basicity of catalyst decreased obviously and the EGMEML yield changed slightly compared with that of $NaAlO_2$ as catalyst. With further increase the amount of KF loading, the yield EGMEML first increased then decreased; as loading KF of 30%, the highest yield of biodiesel was obtained. The results line with the change of the total basicity.

After loading KF, the activity of the catalysts may be associated with the formation of basic active sites generated from the preferential attack of F^- ions of KF on the element aluminum of $NaAlO_2$. In this case, the active sites thus generated correspond to the fluoride ions themselves and to the negatively charged oxygen atoms located in their vicinity, and another dominant factor is the presence of K^+ and Na^+ cations highly distributed around the active sites and generated the catalyst's basicity [32-34].

Further increasing the loading amount of KF to 40%, led to a decrease of the basicity and resulted a decrease in the EGMEML yield. It is very likely that the higher amount of KF loading may result in the cover of basic sites by the exceeded KF and/or agglomeration of KF phase occurred during calcination [28]. The fact is the highest yield of novel biodiesel was obtained when 30%-KF/$NaAlO_2$ as catalyst for the transesterification.

3.2 Influence of the reaction parameters

Figure 6

The effect of KF mass content of *x*-KF/$NaAlO_2$ on catalytic performance was investigated as shown in Figure 6. After loading KF, the yield of EGMEML improved obviously. With the increase of KF amount from 10% to 30%, the EGMEML yield changed from 66% to 91%. This may be related to the number of catalyst surface active sites. The more KF amount loads, the more active sites generate. Thus, the yield of EGMEML increases. However, further increased the loading amount of KF to 40%, the yield slightly reduced, it may be due to an excess amount of KF covered active sites. This is consistent with the results of Hammett indicator. So, the best KF loading amount of 30% was chosen.

Figure 7

The presence of catalyst is necessary for transesterification reaction to proceed [4]. The effect of catalyst amount on EGMEML yield was investigated as shown in Figure 7A. With the augment in amount of the catalyst from 2 to 5 %, there was an increase in yield from 60% to 91%, which may due to more catalytic sites available for the reactants [35]. With further increase the amount of the catalyst from 5 to 6 %, the decrease of the EGMEML yield was slightly observed. The reason was possibly due to the high viscosity of the slurry caused a mixing problem involving reactants, products and solid catalyst [36]. Hence, the amount catalyst of 5 % was selected for optimizing other reaction conditions.

As transesterification of EGME with ML is a reversible reaction, a molar ratio higher than the stoichiometric ratio of EGME and ML is required to shift the equilibrium of the reaction towards EGMEML production. The behavior of ML transesterification with EGME at different molar ratio of ML to EGME is shown in Figure 7B. ML and EGME in 1:3 molar ratio resulted in the highest yield of 91%. When the molar ratio of EGME/ML is above 3, the excess amount of EGME may cause the reaction system dilution and reaction rate reduction [37], which resulted in a decrease of the yield of EGMEML, as well as an increase of the cost for excess EGME and its recovery [38]. Thus, ML and EGME in 1:3 molar ratio was used for optimizing other parameters.

In order to evaluate the effect of reaction time on EGMEML yield, reactions were allowed to proceed for variant durations of 2 to 6 h and the obtained results were shown in Figure 7C. At the beginning of EGMEML synthesis, the EGMEML yield increased rapidly from 65% to 90%. The highest transesterification efficiency was reached at reaction time of 4 h. After 4 h, the yield was not significantly increased. It indicates that the reaction reached the equilibrium state.

The effect of various reaction temperatures during the transesterification reaction was also studied with 30%-KF/$NaAlO_2$ as catalyst over the range of 90-130 ^oC as shown in Figure 7D. With the increase of reaction temperature, the yield of EGMEML largely improved. The highest EGMEML yield of 91% was procured at reaction temperature of 120 °C, for the viscosity of the reactants reduced and the interactions of the reactants molecules speeded up by higher amounts of energy [4]. As the temperature further increased to 130 ^oC, the yield decreased clearly, which may due to the EGME vaporization and the bubbles formation, limiting the reaction on the three-phase interface [18].

3.3 Transesterification of Different FAMEs with EGME.

Several fatty acid methyl esters (FAMEs) with different carbon number was selected as raw materials in the production of various ethylene glycol monomethyl ether fatty acid esters by 30%-KF/$NaAlO_2$ as the catalyst. Table 3 shows the yield for the various FAMEs, such as methyl oleate, methyl stearate, methyl palmitate, methyl linoleate and methyl laurate as raw material in the reaction. A maximum yield of 91.0% was obtained for the transesterification of ML and EGME. The results show that 30%-KF/$NaAlO_2$ is an effective heterogeneous catalyst for the reaction of various FAMEs with EGME.

Table 3

3.4 Production of novel biodiesel of ethylene glycol monomethyl ether soybean oil monoester

Based on the optimized conditions of the transesterification of ML with EGME, 30%-KF/$NaAlO_2$ was used as a catalyst in the production of a novel biodiesel of ethylene glycol monomethyl ether soybean oil monoester from the raw material of methyl soybean oil ester biodiesel and EGME. As expected, the novel biodiesel yield of 88.0% was obtained when the soybean biodiesel/EGME molar ratio was 1:6, the reaction temperature was 120 °C, the mass amount of catalyst was 5 %, and the reaction time was 4 h. It can be concluded that 30%-KF/$NaAlO_2$ is an efficacious catalyst for the preparation of soybean oil-base novel biodiesel.

3.5 Comparison of the catalytic activity of KF/$NaAlO_2$ with other basic catalysts

In order to demonstrate the high catalytic activity of KF/$NaAlO_2$, some common base catalysts were used for the transesterification. The results of the transesterification catalyzed by KF, NaF, KOH, *etc.* are summarized in Table 4.

Table 4

It is obviously observed from Table 4, KF/$NaAlO_2$ exhibits the highest activities among of the catalysts, the catalytic activity of NaF is the weakest, and of those $NaAlO_2$, KOH and CaO are medium. However, KOH as catalyst in post-processing generated a lot of waste water from the experimental process, and $NaAlO_2$ was difficult to separate from the product mixture for the gelation, which is same as that of CaO. The yield of EGMEML with KF/$NaAlO_2$ as catalyst is almost same as that of Na_2SiO_3 cacinated [17] and KF/HTL-M [18] in the transesterification of ML with

EGME. Therefore, $KF/NaAlO_2$ could be an efficiently potential solid base catalyst in the production of novel biodiesel.

3.6 Reusability and stability of $KF/NaAlO_2$

FT-IR spectroscopy of fresh catalyst, used and unwashed catalyst, as well as used and washed catalyst are shown in Figure 8. It can be found that the yield of 77% for EGMEML was obtained when the used catalyst without any dispose was directly used in the next round. When the used catalyst washed by acetone, catalytic activity largely improved, the yield of EGMEML increased to 84%. All the characteristic absorption bands of the used catalyst are the same with that of fresh catalyst. However, for the unwashed catalyst, three new bands at 1631-1731cm^{-1}, 2850 cm^{-1} and 2920 cm^{-1} appeared, which attributed to C=O and C-H stretching vibrations, respectively [39]. After the catalyst washing by acetone three times, the new bands disappeared. The phenomena implies that surface of used catalyst may cover by a few of organic oligomers.

Figure 8

Figure 9 shows SEM micrograph of 30%-$KF/NaAlO_2$ of Fresh catalyst (A) and catalyst used 3rd round (B). It can be found the aspect of the particles and agglomerates of fresh 30%-$KF/NaAlO_2$ and the used catalyst are similar, meaning the surface roughness and rodlike structure remained unchanged. The basic strength and basicity of used 30%-$KF/NaAlO_2$ were also determined and listed in Table 5. It showed that the catalyst used three rounds kept the same basic strength with fresh catalyst, but the basicity clearly decreased. EGMEML yields of 90, 84, and 80% were obtained as 30%-KF/$NaAlO_2$ was used for three consecutive reactions.

Figure 9

Table 5

The analysis of EDS for the surface of the fresh 30%-KF/$NaAlO_2$ catalyst and recycled 30%-KF/$NaAlO_2$ catalyst were carried out and the results were listed in Table 6. Each data in Table 6 was the average value determined from three points on the catalyst surface. It can be seen from Table 6, the content of K, Na and F decreased and the basicity and yield decreased after the catalyst was used consecutive three rounds compared with that of fresh catalyst. It may cause by the active sites running off on the surface of the catalyst during the recycle process, leading to the loss of basicity, thereby the catalytic activity of the catalyst decreased.

Table 6

Figure 10

In order to ensure the heterogeneous nature of the catalyst, leaching test was performed under optimized reaction conditions. After reacting 1.0 h, the catalyst was removed by centrifugation and reactants were heated again for additional 4.0 h. As can be seen from Figure 10, no significant gain in EGMEML yield was obtained after removing the catalyst, and the yield of EGMEML increased obviously with the catalyst. It reveals that 30%-KF/$NaAlO_2$ has good stability, and the nature of the transesterification catalyzed by KF/$NaAlO_2$ is a heterogeneous reaction [40].

3.7 Koros-Nowak test

Table 7

To investigate the effect of diffusion limitations on the catalytic activity, the Koros-Nowak criterion test was designed and conducted [41]. In present study, different catalyst dosages of 30%-KF/$NaAlO_2$ were employed with a ML/EGME ratio of 1:3 at 120 °C. EGMEML formed during the course of reaction were quantified with a time gap of 15 min by GC technique. The results in Table 7 showed the TOFs were almost similar with the increase of catalyst amount at same EGMEML yield. Hence, it denotes that the reaction of ML with EGME obeyed the Koros-Nowak criterion and reaction rates were not masked by the rates of transport [42].

3.8 Kinetics and thermodynamics study of transesterification reaction

Figure 11

With the purpose of discover the kinetics of transesterification of ML with EGME over 30%-KF/NaAlO$_2$, the reaction was explored and described as below:

$$\text{ML (A)} + \text{EGME (B)} \rightarrow \text{products}$$

The reaction rate equation can be written [17] as eqn (3).

$$-\mathrm{d}C_A / \mathrm{d}t = \mathrm{k}[C_A]^{\mathrm{a}}[C_B]^{\mathrm{b}} \qquad (3)$$

When EGME was excessive, namely $C_{A0} \ll C_{B0}$, as shown in Figure 11A, the plot of -lg(dC_A/dt) vs. -lg(C_A) shows good linear relationship, the value of slope is found to be 0.97. In a similar way, When ML was excessive, namely $C_{A0} \gg C_{B0}$, the plot of -lg(dC_B/dt) vs. -lg(C_B) also shows good linear relationship and the value of slope is found to be 1.10. It indicates that the grading number *a* and *b* of reactant A and B were 1, respectively. The rate formula of the reaction follows second-order kinetics. To calculate the activation energy, reactions were carried out in temperature range of 105-120°C. The activation energy (Ea) could be calculated [41] based on the Arrhenius equation following eqn(4):

$$ln\mathrm{k} = ln\mathrm{A} - \mathrm{E}_a / RT \qquad (4)$$

where E_a is the activation energy (kJ mol^{-1}), A is the preexponential factor (h^{-1}), R is the gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}) and T is the reaction temperature (K).

The relationship of ln k *vs.* 1/T was discussed, and the scatter plot is shown in Figure 11B. The values of E_a and A from the plot were found to be 56.54 kJ/mol and 3.28×10^{6} h^{-1}. The value of E_a was greater than 25 kJ/mol, the reactions were governed by chemical step. The observed E_a value in the present study (56.54 kJ/mol) was found within the range of the reported values (26-82 kJ/mol) for the transesterification reaction catalyzed by heterogeneous catalysts [43].

Figure 12

For the sake of explaining the behavior of transesterification reactions, thermodynamic analysis was addressed for evaluating the enthalpy of activation ($\Delta H^{\ddagger}$), entropy of activation ($\Delta S^{\ddagger}$), and the Gibbs free energy of activation ($\Delta G^{\ddagger}$) based on the transition state theory (activation complex theory), which was developed by Eyring in 1935 [44] to evaluate thermodynamic parameters of activation from temperature-dependent rate constants. The parameters were calculated from Eyring-Polanyi equation [45]. Eyring-Polanyi equation (eqn (5)) is analogous to the Arrhenius equation.

$$k = \frac{k_B T}{h} \exp(-\frac{\Delta G^{\ddagger}}{RT}) \qquad (5)$$

Taking the natural logarithm of eqn (5) and replacing $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, eqn (6) can be written as:

$$ln(\frac{k}{T}) = -\frac{\Delta H^{\ddagger}}{R}(\frac{1}{T}) + [ln(\frac{k_B}{h}) + \frac{\Delta S^{\ddagger}}{R}] \qquad (6)$$

where R, k_B and h are the universal gas (8.314J mol^{-1}K^{-1}), Boltzmann (1.38×10^{-23} J/K) and Plancks (6.63 ×10^{-34} Js) constants respectively. Eqn (6) describes the mathematical relationship between enthalpy and entropy of activation with rate constant. Thus, the values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ could be calculated from the slope and intercept of the Erying plot between $1/T$ and ln k/T as shown in Figure 12. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found out to be 41.57 kJ/mol and -160.87 J/mol·K respectively. Further, the value of $\Delta G^{\ddagger}$ was calculated as 104.77 kJ/mol at 393 K. A positive value of enthalpy of activation ($\Delta H^{\ddagger}$) indicates raising the energy level and transforming the reactants to their transition state required energy input (heat) from external source [40]. A negative value of entropy of activation ($\Delta S^{\ddagger}$) suggests that reactant species have joined together to form a more ordered transition state [46]. A positive value of Gibbs free energy of activation ($\Delta G^{\ddagger}$) indicates that the reaction was unspontaneous and endergonic in nature [45]. Based on the datum, it could be concluded the reaction of ML with EGME over 30%-KF/$NaAlO_2$ is unspontaneous, endothermic and endergonic in nature.

3.9 Properties of EGMEML

Table 8

The properties of the obtained EGMEML and that of standards of diesel, biodiesels are listed in Table 8. In short, the properties of the obtained EGMEML present many similarities with that of diesel and biodiesel, and therefore, the properties of obtained EGMEML can be deemed as an alternative of diesel.

4 Conclusions

The heterogeneous catalyst KF/$NaAlO_2$ can be used as solid base catalyst for the preparation of the novel biodiesel via transesterification. Analyses by different techniques reveal that KF reacted with $NaAlO_2$ and generated fluoroaluminates as the dominant active sites for the transesterification. The catalysts show excellent catalytic activity and good stability, at the optimum conditions, the highest EGMEML yield of 91% was obtained and a satisfy yield of EGMEML was obtained when KF/$NaAlO_2$ was used for three consecutive rounds without reactivation. And the nature of the reaction is unspontaneous and endergonic; the reaction appeared to be a good fit with the second order reaction kinetics, the activation energy was to be 56.54 kJ/mol; the reaction rate is free from the heat and mass transfer. KF/$NaAlO_2$ as the solid basic catalyst is a promising candidate catalyst for the synthesis of the novel biodiesel via transesterification.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21176125), the Science Research Project of the Ministry of Education of Heilongjiang Province of China (2012TD012, 12511Z030, 12521594, JX201210), the Natural Science Foundation of Heilongjiang province of China (B201313).

References

[1] Lin, L.; Zhou, C.; Vittayapadung, S.; Shen, X.; Dong, M. *Appl. Energy* **2011**, *88*, 1020-1031.

[2] Fattah, I. M. R.; Masjuki, H. H.; Liaquat, A. M.; Ramli, R.; Kalam, M. A.; Riazuddin, V. N. *Renew. Sust. Energ. Rev.* **2013**, *18*, 552-567.

[3] Meher, L.C.; Sagar, D.V.; Naik, S.N. *Renew. Sust. Energ. Rev.* **2006**, *10*, 248-268.

[4] Algoufi, Y.T.; Hameed, B.H. *Fuel Process. Technol.* **2014**, *126*, 5-11.

[5] Silitonga, A. S.; Masjuki, H. H.; Mahlia, T. M. I.; Ong, H. C.; Chong, W. T.;

Boosroh, M. H. *Renew. Sust. Energ. Rev.* **2013**, *22*, 346-360.

[6] Jakeria, M.R.; Fazal, M.A.; Hasee, A.S.M.A. *Renew. Sust. Energ. Rev.* **2014**, *30*, 154-163.

[7] Guo, H.; Xun, Q.; Liu, S.; Wang, X. *SAE Technical Paper* **2015,** DOI: 10.4271/ 2015-01-0955.

[8] Chen, X.; Guo, H.; Zhang, L. *SAE Technical Paper* **2014**, DOI: 10.4271/2014-01-1469.

[9] Jiang, D.; Yun, B. *J. Renewable Sustainable Energy* **2012**, *4*, 053118.

[10] Guo, H.; Liu, S.; Wang, R.; Su, J.; Ma J.; Feng, Y. *Environ. Prog. Sustain. Energy* **2015**, DOI: 10.1002/ep.12191.

[11] Gao, G.; Feng, Y.; Guo, H.; Liu, S. *Energy Fuels* **2011**, *25*, 4686-4692.

[12] Zhang, J.; Wang, X.; Guo, H.; Liu, S.; Ma, J. *Int. J. Green Energy* **2012**, *9*, 573-583.

[13] Borges, M.E.; Díaz, L. *Renew. Sust. Energ. Rev.* **2012**, *16*, 2839-2849.

[14] Veljković, V. B.; Banković-Ilić, I. B.; Stamenković, O. S. *Renew. Sust. Energ. Rev.* **2015**, *49*, 500-516.

[15] Deshmane, V. G.; Adewuyi, Y. G. *Fuel* **2013**, *107*, 474-482.

[16] Dossin, T. F.; Reyniers, M. F.; Berger, R. J.; Marin, G. B. *Appl. Catal. B: Environ.* **2006**, *67*, 136-148.

[17] Fan, F.; Jia, L.; Guo, X.; Lu, X.; Chen, J. *Energy Fuels* **2013**, *27*, 5215-5221.

[18] Chen, J.; Jia, L.; Guo, X.; Xiang, L.; Lou, S. *RSC Adv.* **2014**, *4*, 60025-60033.

[19] Rayzman, V.; Filipovich, I.; Nisse L.; Vlasenko, Y. *JOM* **1998**, *50*, 32-37.

[20] Cobas, A.C.; Corzo, N.; Villamiel, M.; Olano, A. *J. Agric. Food Chem.* **2008**, *56,* 10954-10959.

[21] Mutreja, V.; Singh, S.; Ali, A. *J. Oleo. Sci.* **2012**, *61*, 665-669.

[22] Bai, R.; Zhang, H.; Mei, F.; Wang, S.; Li, T.; Gu, Y.; Li, G. *Green Chem.* **2013**, *15*, 2929-2934.

[23] Cherikkallinmel, S. K.; Gopalakrishnan, A.; Yaakob, Z.; Ramakrishnan, R.M.; Sugunan, S.; Narayanan, B. N. *RSC Adv.* **2015**, *5*, 46290-46294.

[24] Wan, T.; Yu, P.; Wang, S.; Luo, Y. *Energy Fuels* **2009**, *23,* 1089-1092.

[25] Fan, F.; Gao, C.; Jia, L.; Guo, X. *Res Chem Intermed* **2014**, *40*,157-167.

[26] Verziu, M.; Florea, M.; Simon, S.; Simon, V.; Filip, P.; Parvulescu, V. I.; Hardacre, C. *J. Catal.* **2009**, *263*, 56-66.

[27] Jia, L.; Li, Y.; Chen, J.; Guo, X.; Lou, S.; Duan, H. *Res Chem Intermed* **2015**, DOI: 10.1007/s11164-015-2118-y.

[28] Xie, W.; Huang, X. *Catal. Lett.* **2006**, *107*, 53-59.

[29] Sun, C.; Qiu, F.; Yang, D.; Ye, B. *Fuel Process. Technol.* **2014**, *126*, 383-391.

[30] Li, H.; Niu, S.; Lu, C.; Liu, M.; Huo, M. *Energ. Convers. Manage.* **2014**, *86*, 1110-1117.

[31] Liu, H.; Su, L.; Shao, Y.; Zou, L. *Fuel* **2012**, *97*, 651-657.

[32] Boz, N.; Degirmenbasi, N.; Kalyon, D. *Appl. Catal. B: Environ.* **2009**, *89*, 590-596.

[33] Fujita, S.; Bhanage, B.; Aoki, D.; Ochiai, Y.; Iwasa, N.; Arai, M. *Appl. Catal. A: Gen.* **2006**, *313*, 151-159.

[34] Xu, C.; Sun, J.; Zhao, B.; Liu, Q. *Appl. Catal. B: Environ.* **2010**, *99*, 111-117.

[35] Mutreja, V.; Singh, S.; Ali, A. *Renew. Energy* **2014**, *62*, 226-233.

[36] Xie, W.; Peng, H.; Chen, L. *Appl. Catal. A-Gen.* **2006**, *300*, 67-74.

[37] Song, R.; Tong, D.; Tang, J.; Hu, C. *Energy Fuels* **2011**, *25*, 2679-2686.

[38] Wan, L.; Liu, H.; Skala, D. *Appl. Catal. B: Environ.* **2014**, *152-153*, 352-359.

[39] Li, F.J.; Li, H.Q.; Wang, L.G.; Cao, Y. *Fuel Process. Technol.* **2015**, *131*, 421-429.

[40] Kaur, N.; Ali, A. *RSC Adv.* **2014**, *4*, 43671-43681.

[41] Kaur, N.; Ali, A. *Appl. Catal. A-Gen.* **2015**, *489*, 193-202.

[42] Kumar, D.; Ali, A. *Biomass Bioenergy* **2012**, *46*, 459-468.

[43] Kaur, N.; Ali, A. *Fuel Process. Technol.* **2014**, *119*, 173-184.

[44] Eyring, H. *Journal of Chemical Physics* **1935**, *3*, 63-71.

[45] Nautiyal, P.; Subramanian, K. A.; Dastidar, M. G. *Fuel* **2014**, *135*, 228-234.

[46] Ong, L. K.; Kurniawan, A.; Suwandi, A. C.; Lin, C.; Zhao, X.; Ismadji, S. *J. Supercrit. Fluid.* **2013**, *75*, 11-20.

[47] Ozener, O.; Yuksek, L.; Ergenc, A.T.; Ozkan, M. *Fuel* **2014**, *115*, 875-883.

[48] Mofijur, M.; Masjuki, H. H.; Kalam, M. A.; Atabani, A. E.; Shahabuddin, M.; Palash, S. M.; Hazrat, M. A. *Renew. Sust. Energ. Rev.* **2013**, *28*, 441-455.

Figures and Tables

Figure 1 TG-DSC curves of support precursor (A) and 30%-KF/NaAlO$_2$(B).

Figure 2 XRD patterns (A) and their enlarged view (B) of KF/NaAlO$_2$ catalysts. NaAlO$_2$ (a); 10%-KF/NaAlO$_2$ (b); 20%-KF/NaAlO$_2$ (c); 30%-KF/NaAlO$_2$ (d); 40%-KF/NaAlO$_2$ (e).

Figure 3 FT-IR patterns of the catalysts (A) and their enlarged view (B). NaAlO$_2$ (a); 10%-KF/NaAlO$_2$ (b); 20%-KF/NaAlO$_2$ (c); 30%-KF/NaAlO$_2$ (d); 40%-KF/NaAlO$_2$ (e).

Figure 4 SEM images of NaAlO$_2$ support (A), the enlargement of NaAlO$_2$ support (B) and fresh 30%-KF/NaAlO$_2$ catalyst (C).

Figure 5 SEM image of 30%-KF/NaAlO$_2$ catalyst (A) and elemental mapping images of Na(B), Al (C), O (D), K (E) and F (F).

Figure 6 Influence of KF loading amount on the yield of EGMEML. Reaction condition: molar ratio of EGME/ML of 3.0, amount of catalyst of 5 %, reaction time of 4 h, and reaction temperature of 120°C.

Figure 7 Influence of reaction condition on the yield of EGMEML: (A) molar ratio of EGME/ML of 3.0, reaction time of 4 h, and reaction temperature of 120°C; (B) the amount of catalyst 5 %, reaction time 4 h, reaction temperature120°C; (C) the molar ratio of EGME/ML of 3.0, amount of catalyst of 5 %, and reaction temperature of 120°C; (D) molar ratio of EGME/ML of 3.0, amount of catalyst of 5 % and reaction time of 4 h.

Figure 8 FT-IR of fresh catalyst (a), catalyst used and unwashed (b) and catalyst used and washed (c).

Figure 9 SEM micrograph of 30%-KF/$NaAlO_2$ of fresh catalyst (A) and catalyst used 3rd round (B)

Figure 10 Leaching test for 30%-KF/$NaAlO_2$ catalyst.

Figure 11 Transesterification reaction kinetics analysis of ML with EGME over 30%-KF/$NaAlO_2$: (A) plots of $-\lg(\mathrm{d}C_A/\mathrm{d}t)$ vs. $-\lg(C_A)$ (■) and-$\lg(\mathrm{d}C_B/\mathrm{d}t)$ vs. $-\lg(C_B)$(●) (B); (B) plot of ln k vs. $1/T$.

Figure 12 Eyring plot of 30%-KF/$NaAlO_2$ catalyzed transesterification of ML with EGME.

Table 1 Colors and H_- value of some Hammett indicators.

Table 2 Basic strength and basicity of x-KF/$NaAlO_2$ catalysts.

Table 3 Yields of different FAMEs in the transesterification reaction

Table 4 Comparison of the catalytic activity of KF/$NaAlO_2$ with other basic catalysts for the production of novel biodiesel

Table 5 Basic strength and basicity of used 30%-KF/$NaAlO_2$ catalysts.

Table 6 Elemental composition of $NaAlO_2$ and 30%-KF/$NaAlO_2$.

Table 7 Koros-Nowak test for heat- and mass-transfer limitations.

Table 8 Properties of the obtained EGMEML and the standards of diesel, biodiesel in Europe.

Figure 1

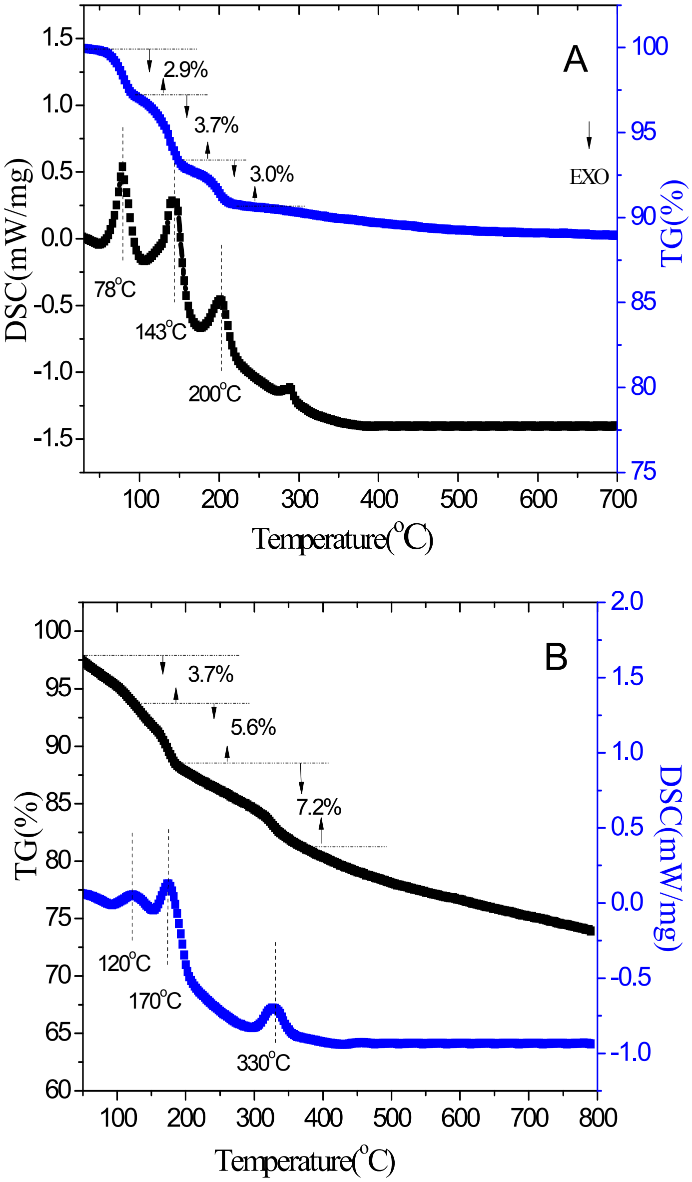

A
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
DSC(mW/mg)
100
95
90
85
80
75
TG(%)
2.9%
3.7%
3.0%
EXO
78°C
143°C
200°C
100
200
300
400
500
600
700
Temperature(°C)
B
100
95
90
85
80
75
70
65
60
TG(%)
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
DSC(mW/mg)
3.7%
5.6%
7.2%
120°C
170°C
330°C
100
200
300
400
500
600
700
800
Temperature(°C)

Figure 2

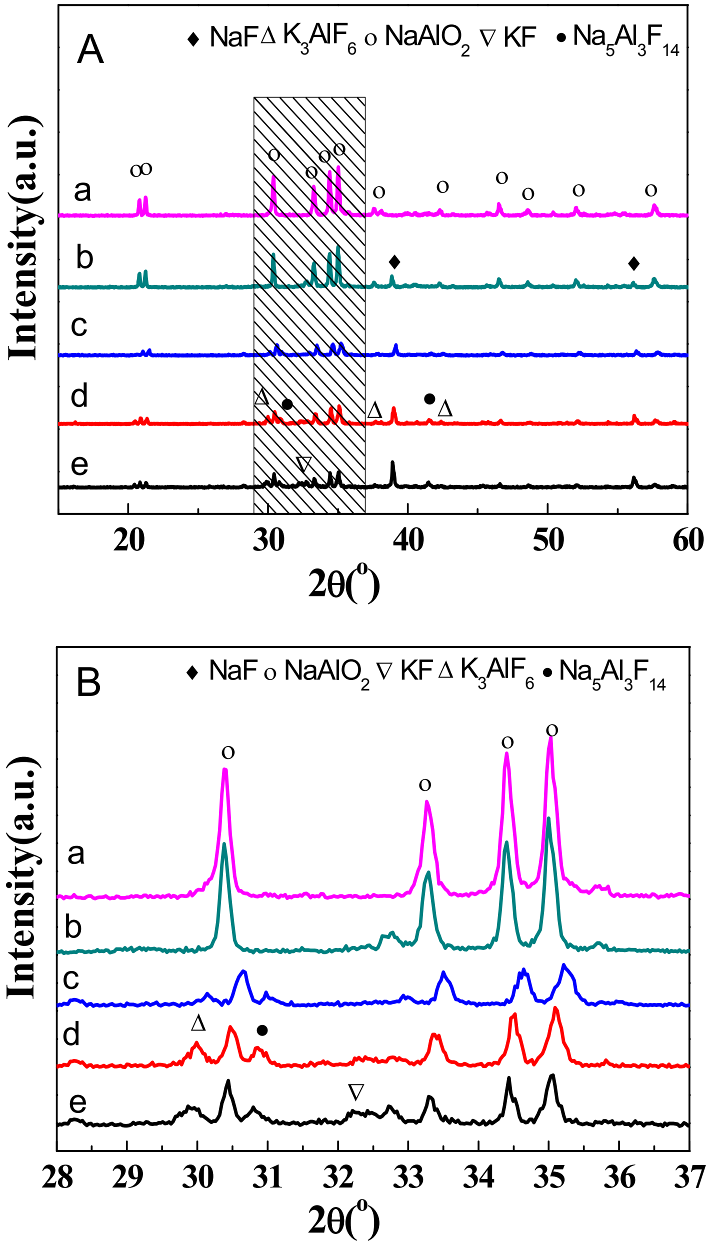
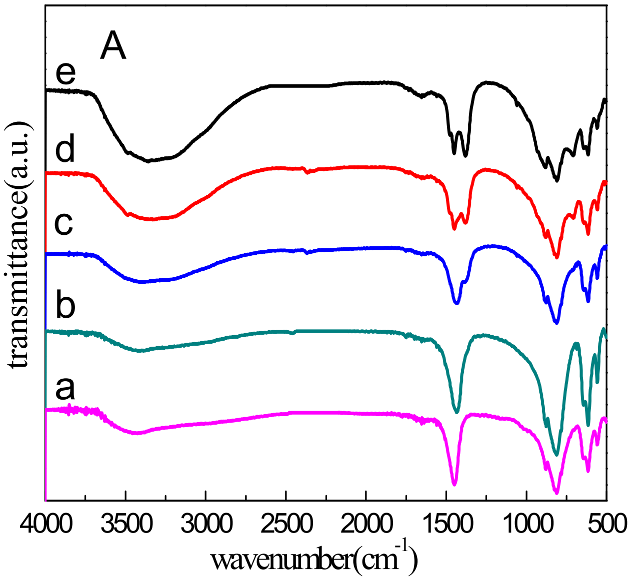

A
◆ NaF Δ K3AlF6 o NaAlO2 ▽ KF ● Na5Al3F14
a
b
c
d
e
Intensity(a.u.)
20
30
40
50
60
2θ(°)
B
◆ NaF o NaAlO2 ▽ KF Δ K3AlF6 ● Na5Al3F14
a
b
c
d
e
Intensity(a.u.)
28
29
30
31
32
33
34
35
36
37
2θ(°)

Figure 3


A
e
d
c
b
a
transmittance(a.u.)
4000
3500
3000
2500
2000
1500
1000
500
wavenumber(cm^{-1})

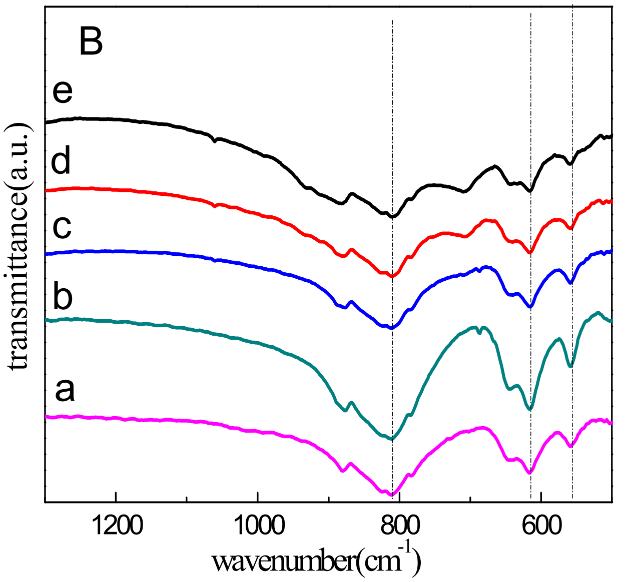

B
e
d
c
b
a
transmittance(a.u.)
1200
1000
800
600
wavenumber(cm^{-1})

Figure 4

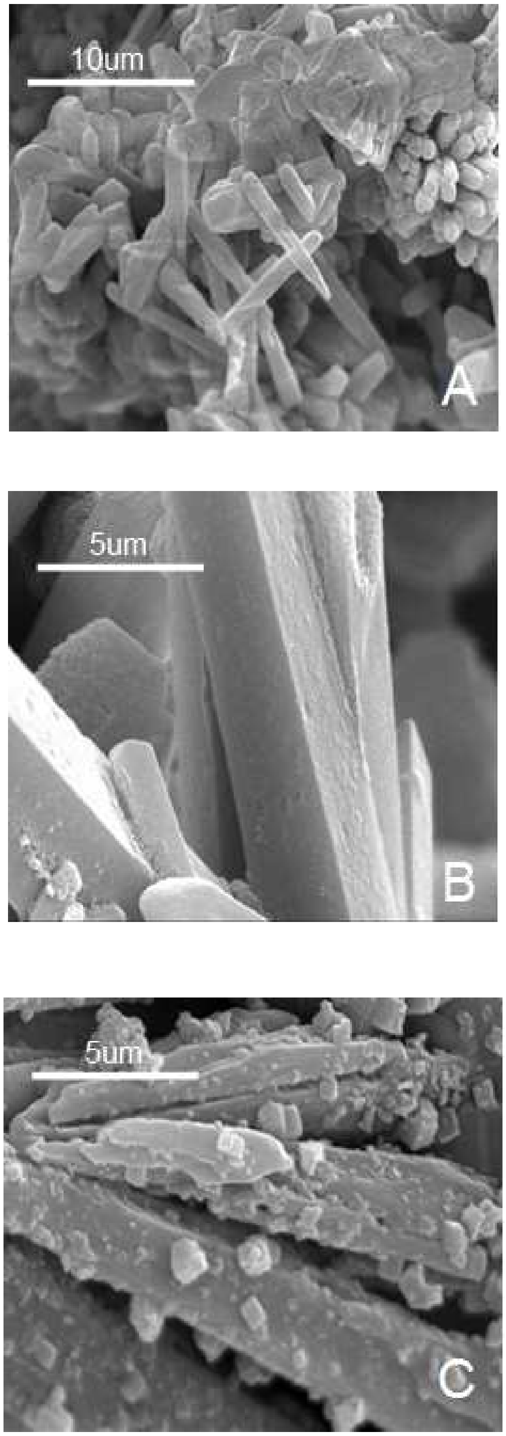


Figure 5

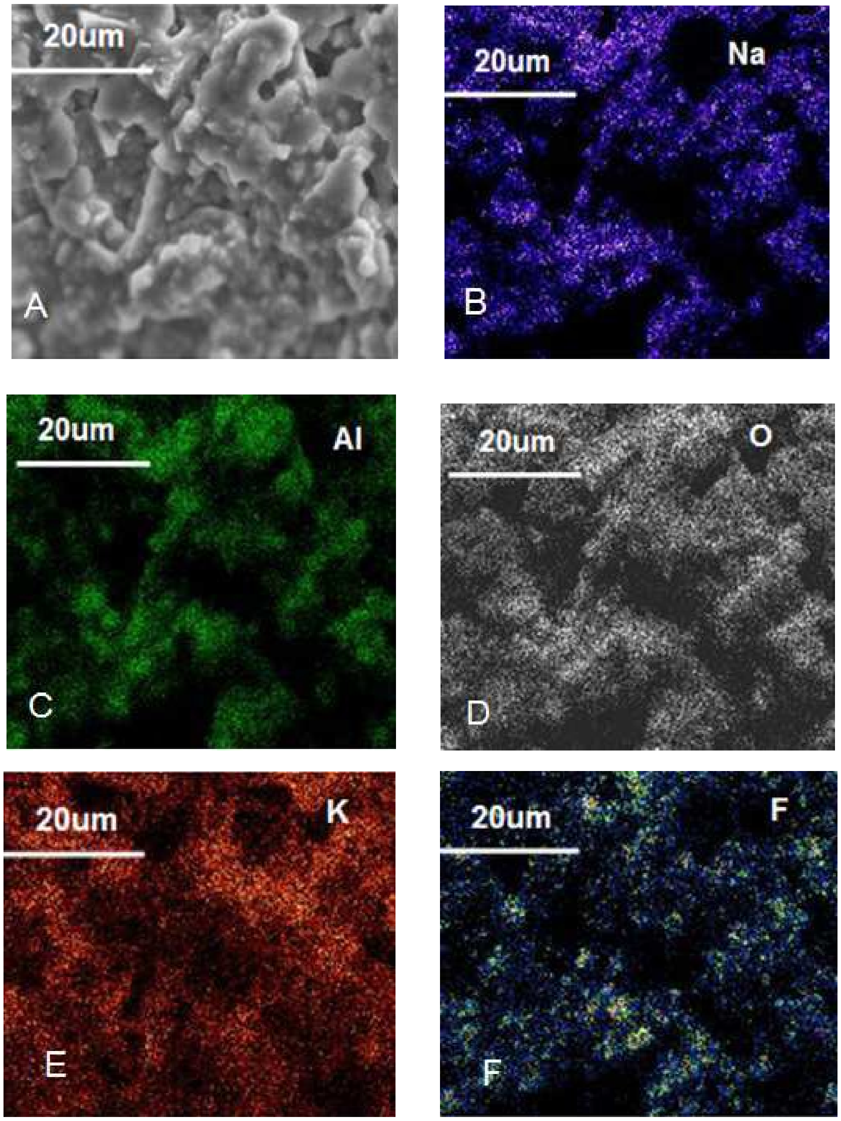


Figure 6

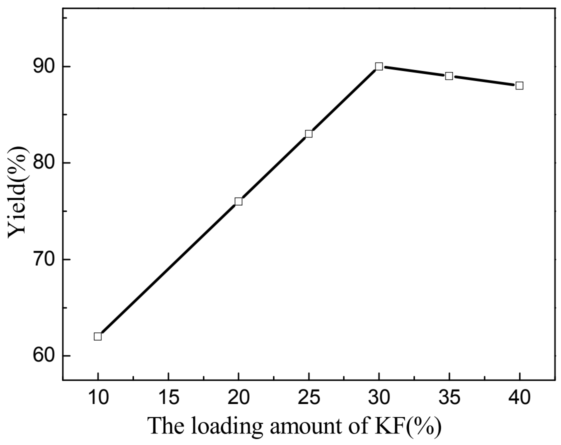


Figure 7

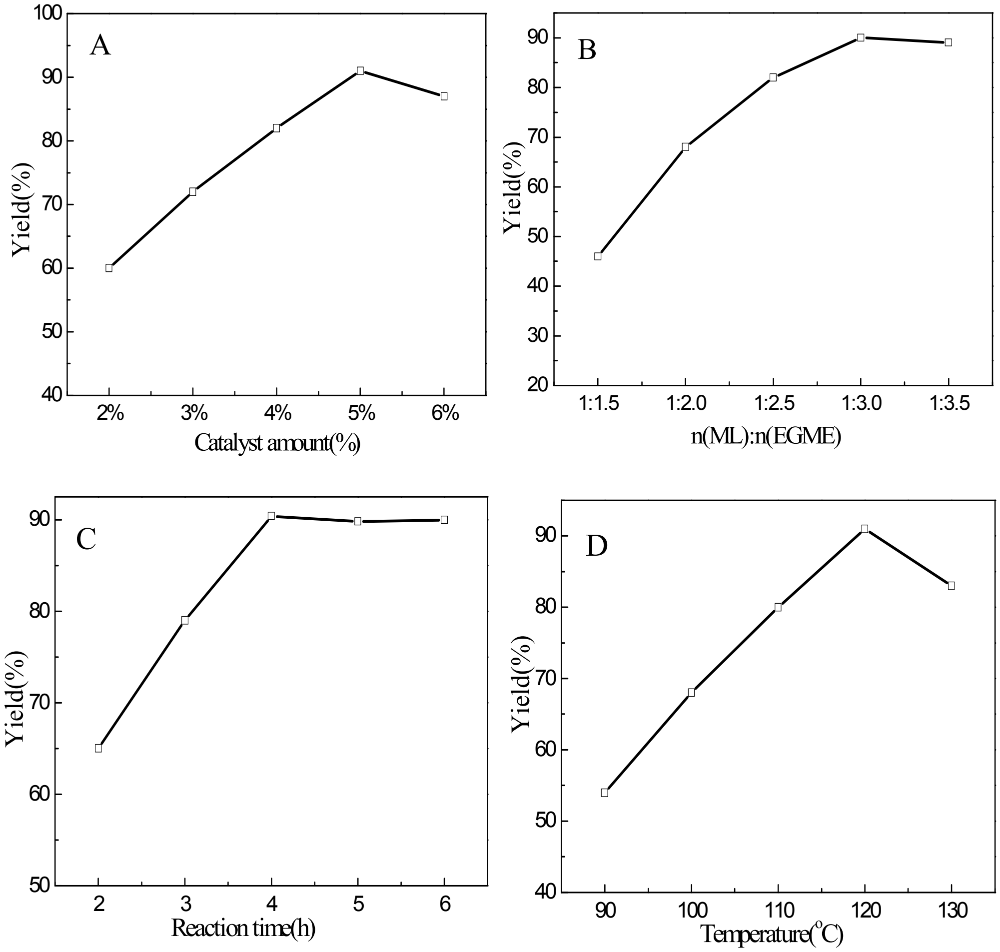

A
Yield(%)
100
90
80
70
60
50
40
2%
3%
4%
5%
6%
Catalyst amount(%)
B
Yield(%)
90
80
70
60
50
40
30
20
1:1.5
1:2.0
1:2.5
1:3.0
1:3.5
n(ML):n(EGME)
C
Yield(%)
90
80
70
60
50
2
3
4
5
6
Reaction time(h)
D
Yield(%)
90
80
70
60
50
40
90
100
110
120
130
Temperature(°C)

Figure 8

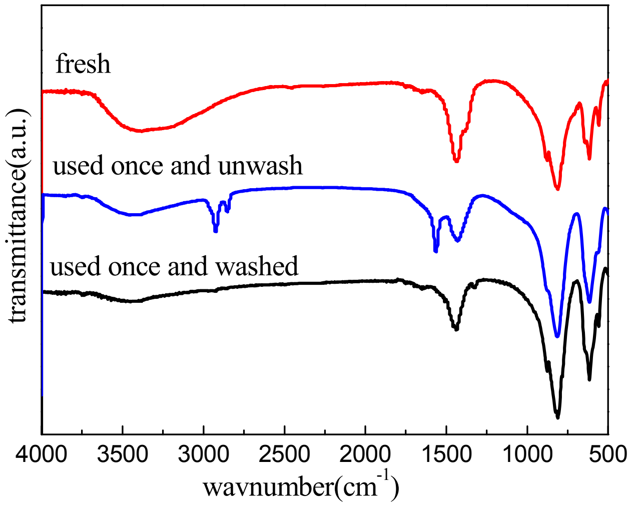

fresh
used once and unwash
used once and washed
transmittance(a.u.)
4000
3500
3000
2500
2000
1500
1000
500
wavnumber(cm^{-1})

Figure 9

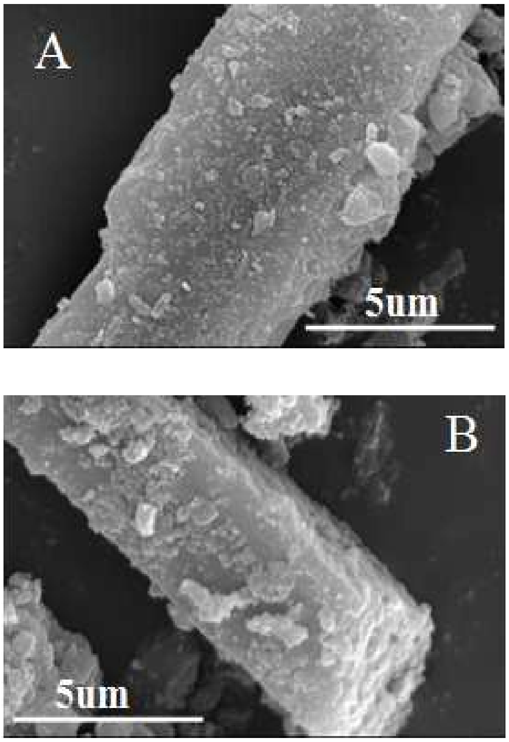


Figure 10

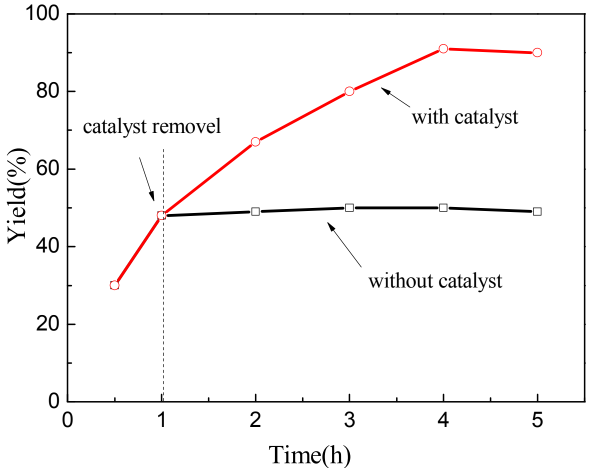

100
80
60
40
20
0
Yield(%)
0
1
2
3
4
5
Time(h)
catalyst removel
with catalyst
without catalyst

Figure 11

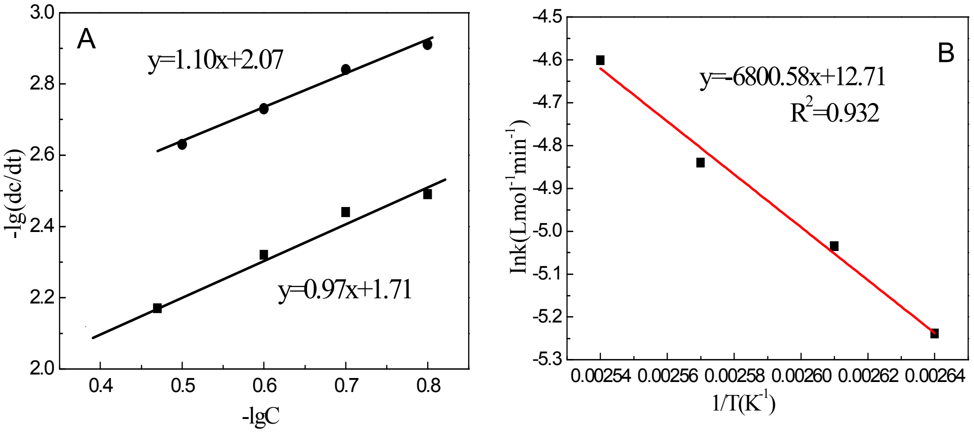

A
y=1.10x+2.07
y=0.97x+1.71
-lg(dc/dt)
-lgC
3.0
2.8
2.6
2.4
2.2
2.0
0.4
0.5
0.6
0.7
0.8
B
y=-6800.58x+12.71
R^2=0.932
lnk(L.mol^{-1}min^{-1})
1/T(K^{-1})
-4.5
-4.6
-4.7
-4.8
-4.9
-5.0
-5.1
-5.2
-5.3
0.00254
0.00256
0.00258
0.00260
0.00262
0.00264

Figure 12

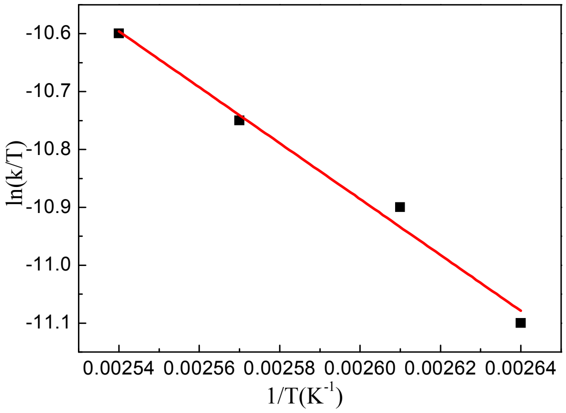

-10.6
-10.7
-10.8
-10.9
-11.0
-11.1
ln(k/T)
0.00254
0.00256
0.00258
0.00260
0.00262
0.00264
1/T(K^{-1})

Table 1

Indicator	Basic color	Acid color	H_-
Bromthymol blue	Yellow	Blue	7.2
Phenolphthalein	Pink	Colorless	9.8
2,4-Dinitroaniline	Red	Yellow	15.0

Table 2

Catalyst	Basic strength(H_-)	Basicity(mmol/g)	Yield(%)*
$NaAlO_2$	$9.8< H_-<15.0$	1.0	68
10%-KF/$NaAlO_2$	$9.8< H_-<15.0$	0.8	66
20%-KF/$NaAlO_2$	$9.8< H_-<15.0$	1.4	76
30%-KF/$NaAlO_2$	$9.8< H_-<15.0$	2.2	90
40%-KF/$NaAlO_2$	$9.8< H_-<15.0$	1.9	85

*Reaction conditions: amount of catalyst 5.0 %, reaction time 4 h, molar ratio of EGME/ML of 3.0, reaction temperature of 120°C.

Table 3

Reactant	methyl oleate	methyl stearate	methyl palmitate	methyl linoleate	methyl laurate
Yield(%)[**]	85.1	81.0	83.7	85.9	91.0

[**] Reaction conditions: molar ratio of EGME/FAME of 3.0, mass amount of catalyst of 5 wt %, reaction time of 4 h, and reaction temperature of 120 °C.

Table 4

Catalyst	Catalyst amount(%)	Reaction temperature(^oC)	EGME / ML	Reaction time(h)	EGMEML Yield(%)
NaF	5	120	3	4	0.8
KF	5	120	3	4	4.3
KOH	5	120	3	4	70
CaO	5	120	3	4	61
$NaAlO_2$	5	120	3	4	68
30%-KF/$NaAlO_2$	5	120	3	4	91

Table 5

Catalyst	Basic strength(H_-)	Basicity(mmol/g)	Yield(%)***
First round	$9.8< H_-<15.0$	2.2	90
Second round	$9.8< H_-<15.0$	1.8	84
Third round	$9.8< H_-<15.0$	1.6	80

***Reaction conditions: the amount of catalyst 5.0 %, reaction time 4 h, molar ratio of EGME/ML of 3.0, reaction temperature of 120°C.

Table 6

Sample	Na	Al	O	K	F	C
$NaAlO_2$	25.34	23.73	44.42	0	0	6.50
30%-KF/$NaAlO_2$	17.39	13.84	34.46	13.49	18.40	2.42
30%-KF/$NaAlO_2$ used 3rd round	13.44	13.52	36.14	11.55	16.56	8.79

Table 7

Catalyst amount (wt%)	3.5	4.0	4.5	5.0
TOF (mol $min^{-1}mol^{-1}$)	0.56	0.55	0.55	0.57

**** Reaction condition: molar ratio of EGME/ML of 3.0, catalyst amount of 5.0%, reaction time of 4 h, reaction temperature of 120°C and the yield of 40%.

Table 8

Specification	Density /g/cm^3 (15^{o}C)	Kinematic viscosity /mm^2/s (40^{o}C)	Flash Point /^{o}C	heating value /kJ/kg	Reference
Diesel	0.838	4.50	64	42.9	[47]
Biodiesel	0.860-0.900	3.5-5.0	>120	35	[48](EN14214)
EGMEPM	0.898	5.98	190	38.2	[10]
EGMEML	0.905	3.60	133	38.4	Experimental data

Graphic Abstract

$NaAlO_2$ modified with KF ($KF/NaAlO_2$) was prepared by wet-impregnation method and used for transesterification of ethylene glycol monomethyl ether and methyl laurate. The catalyst preparation process was simple, and the catalyst showed excellent catalytic activity and good stability.