

Biodiesel production from *Jatropha* oil using mesoporous molecular sieves supporting K_2SiO_3 as catalysts for transesterification

Haitang Wu^{a,*}, Junhua Zhang^a, Yanping Liu^b, Jilu Zheng^a, Qin Wei^a

^a College of Forestry, Northwest A&F University, Yangling 712100, China

^b College of Science, Northwest A&F University, Yangling 712100, China

ARTICLE INFO

Article history:

Received 9 June 2013

Received in revised form 13 October 2013

Accepted 26 October 2013

Available online 22 November 2013

Keywords:

Transesterification

Heterogeneous catalysis

Biodiesel

Solid base catalyst

Jatropha oil

ABSTRACT

A series of solid base catalysts based on potassium salts (K_2CO_3 , K_2SiO_3 and KAc) supported on mesoporous silicas (SBA-15 and AISBA-15) were prepared by impregnation method and used to catalyze the transesterification of *Jatropha* oil with methanol. The prepared catalysts were characterized by several techniques such as X-ray diffraction (XRD), Brunauer–Emmet–Teller method (BET), transmission electron microscopy (TEM) and temperature-programmed desorption of CO_2 (CO_2 -TPD). In addition, various parameters affecting catalytic activity and biodiesel yield were investigated. The results showed that Al element dopant in SBA-15 could protect the pore structure of supported catalyst. The basicity and catalytic activity of AISBA-15 silica were improved significantly after loading potassium compounds. The activity of K_2SiO_3 impregnated catalyst was superior to those of K_2CO_3 and KAc impregnated catalysts. A biodiesel yield of 95% was obtained (using the K_2SiO_3 /AISBA-15 catalyst) with 30 wt.% of K_2SiO_3 loading on AISBA-15 support, methanol/*Jatropha* oil molar ratio 9, reaction temperature 60 °C, reaction time 150 min and catalyst/oil mass ratio 3%. Reuse of the catalyst indicated that the K_2SiO_3 /AISBA-15 had steady catalytic activity compared with traditional KOH and K_2CO_3 catalysts. After being reused for 5 cycles, a modest decrease of its activity led to a reduction of about 6% in the biodiesel yield. This decrease of catalytic activity was mainly caused by the potassium leaching and the adsorption of organic deposits on the catalyst surface.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Biodiesel has recently received great attention as an attractive alternative, biodegradable, non-toxic and renewable diesel fuel. However, the high cost of biodiesel is the major obstacle to its commercialization, so exploring ways to reduce the high cost of biodiesel is very important. It has been reported that approximately 70–95% of biodiesel cost is attributed to raw feedstock cost [1]. Therefore, the cheap and non-edible vegetable oils, animal fats and waste oils are considered as favorable raw materials for biodiesel production especially in developing countries such as China with limited arable land per capita. At present, *Jatropha* trees, as a potential alternative biodiesel crop, are widely cultivated in semi-cultivated tropical or subtropical areas in Central and South America, India, Africa and South China. In China, *Jatropha* seed has an estimated annual production potential of one million metric tons, and it possesses a high oil content of from 45% to 60%, but the presence of some toxic materials makes the oil unsuitable for human consumption [2]. In the near future, it will supply part of resources for commercial biodiesel production in China.

Conventionally the production of biodiesel is through transesterification of crude oil over homogeneous catalysts such as NaOH and KOH [3]. Although homogeneous catalyzed biodiesel production processes are relatively rapid and gain high yields, the removal of base catalysts from products and treatment of alkaline wastewater are costly and non-environmental. In addition, the homogeneous base catalysts require high quality crude oils to prevent undesired side reactions (saponification and hydrolysis). These problems have provided an impetus for the search of effective and eco-friendly heterogeneous catalysts. Nowadays, a wide variety of solid base catalysts have been explored for the biodiesel synthesis, such as alkaline earth oxides [4], modified zeolites [5], hydrotalcites [6] and mixed metal oxides [7]. Moreover, various supported catalysts were prepared such as $Sr(NO_3)_2/ZnO$ [8], KOH/Al_2O_3 [9], $CsNO_3/SBA-15$ [10], CH_3COOK/NaY [11] and magnetic composites $Ca/Al/Fe_3O_4$ [12]. A literature survey shows that solid catalysts functionalized with sodium and potassium compounds appear to be promising for the biodiesel production from vegetable oils [13]. The catalytic activities of supported potassium compounds mainly depend on the loading potassium, the type of the carrier and the conditions of pretreatment. Magnesium oxide [14], calcium oxide [15], zirconia [16], silica [17,18] and oyster shell [19] were modified with sodium or potassium compounds and were used as effective catalyst support materials.

Among these catalyst supports, mesoporous SBA-15 silica has attracted much attention due to its many excellent properties such as

* Corresponding author. Tel.: +86 29 87081511.
E-mail address: haitang345@gmail.com (H. Wu).

good thermal stability, high surface area and unique large pore structure characteristic, which reduce mass transfer limitations and allow high concentration of active sites per mass of material. All these properties seem to meet the requirements for a heterogeneous catalyst to be used in biodiesel production [20]. As the direct loading of strong alkaline usually reacts with silicon element of the silica and results in the structural collapse of the silica, the studies of SBA-15 as solid base carriers are relatively few. However, it is reported that the SBA-15 silica can produce strong base position and avoid destroying the carrier structure by loading weak alkali or neutral salt subsequently through appropriate treatments [21]. These supported solid catalysts are expected to have high catalytic activities in the synthesis of biodiesel.

In the present paper, new types of solid base catalysts were prepared for biodiesel production by loading potassium salts on SBA-15 and AISBA-15 supports. The synthesized solid catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer–Emmett–Teller method (BET) and temperature-programmed desorption of CO_2 (CO_2 -TPD). Then they were tested to catalyze the transesterification of *Jatropha* oil for producing biodiesel in order to compare their activities. The catalyst preparation and transesterification conditions were also investigated to optimize the yield of biodiesel. Furthermore, the possibility of reusing the catalyst in the methanolysis of *Jatropha* oil was investigated.

2. Experimental

2.1. Materials

The refined *Jatropha* oil was provided by a local company located in Xishuangbanna, Yunnan province, China. The acid value (AV) and saponification value (SV) of the *Jatropha* oil were measured as 1.2 mg KOH/g and 193.0 mg KOH/g, respectively. Palmitic acid methyl ester, oleic acid methyl ester, linoleic acid methyl ester, linolenic acid methyl ester, stearic acid methyl ester and heptadecanoic acid methyl ester were purchased from J&K Chemical Ltd and were chromatographically pure. All other chemicals were obtained commercially and of analytical grade.

2.2. Support preparation

Two kinds of supports which were named as SBA-15 and AISBA-15 were synthesized. The synthesis of SBA-15 was carried out as reported in literature [22]. In a typical preparation, 4 g of Pluronic P123 was dissolved in 30 ml water and 120 ml 2 M HCl with stirring at room temperature. Upon complete dissolution, 8.5 g of TEOS (Tetraethylsilicate) was added into the solution with stirring at 35 °C for 20 h. Then the mixture was aged at 80 °C for 48 h without hydrothermal conditions. The solid products were recovered by filtration, washed, dried at room temperature and calcinated at 500 °C for 6 h.

The synthesis of AISBA-15 materials followed a similar procedure to that of SBA-15. According to Si/Al mole ratio of 5, aluminium isopropoxide was simultaneously added into the solution while adding the TEOS, other steps were the same as those in the synthesis of SBA-15. The obtained solid material was named as AISBA-15.

2.3. Catalyst preparation

The base catalysts were prepared by wet impregnation method, using K_2CO_3 , K_2SiO_3 and KAc as active components and SBA-15 or AISBA-15 as support. Firstly, aqueous solutions of potassium salts (K_2CO_3 , K_2SiO_3 and KAc) were prepared. Subsequently, 40 g SBA-15 (AISBA-15) particles was added and impregnated into the required amount of potassium salt aqueous solutions for 12 h at room temperature. The amount of K compound/support was varied from 10 wt.% to 35 wt.%. Then the supports which had absorbed potassium salts were filtered out and dried in a vacuum oven at 100 °C for 12 h. Upon drying,

the solid particles were calcined in the muffle furnace at elevated temperatures (400, 600 and 800 °C) for 2 h, finally the catalysts were prepared.

2.4. Catalyst characterization

Phase composition was identified by XRD (Rigaku, Dmax-rb) using $\text{Cu K}\alpha$ radiation. The microstructure was characterized by TEM (JEOL 2011, Japan). The BET surface area and pore size were measured by the multipoint N_2 adsorption–desorption method at -196 °C with a Micromeritics Tristar 3000 analyzer. To measure the base strength (H_-) and basicity of solid base, the method of Hammett indicator–benzene carboxylic acid (0.02 mol/l anhydrous ethanol solution) titration was used [23]. CO_2 -TPD was performed using a Thermo Electron Corporation TPD/R/O 1100 series catalytic surface analyzer equipped with a TCD detector. The samples were heated to 900 °C at a heating rate of 10 °C/min in flowing He (20 ml/min) after the adsorption of CO_2 at room temperature for 30 min.

2.5. Transesterification reaction and product analysis

The transesterification reaction was carried out in a 200 ml round-bottom flask equipped with a water-cooled condenser and a magnetic stirrer. Firstly, the *Jatropha* oil and catalyst were charged into the flask and heated to the required temperature by water bath. Subsequently, methanol was added into the mixture and the reaction was started with mechanical stirring (about 300 rpm). After reaction, excessive methanol was distilled off under a vacuum condition while the mixture was centrifuged to separate the solid catalyst. After removal of the glycerol layer, the methyl ester contents in the upper layer were quantified using a GC-2010 gas chromatograph (Shimadzu, Japan) connected to a CP-FFAP capillary column (0.32 mm \times 25 m). Heptadecanoic acid methyl ester was used as an internal standard.

In order to quantitatively evaluate the leaching of solid base catalyst under the reaction conditions, the glycerol and methyl ester solutions were analyzed by inductively coupled plasma optical emission spectroscopy (Spectro Genesis) to measure the K concentration.

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of SBA-15, AISBA-15 and supported catalysts with different K_2SiO_3 loadings (10 wt.% and 35 wt.%) are given in Fig. 1. As can be seen, the carrier SBA-15 showed a strong reflection (i.e., $2\theta \approx 0.8^\circ$)

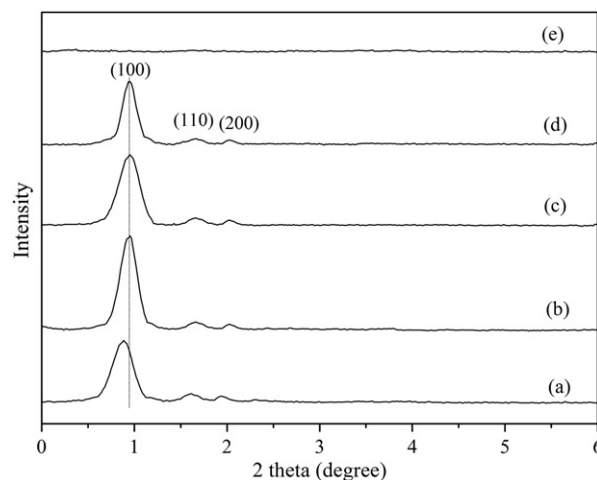


Fig. 1. Small angle XRD patterns of the samples. (a) SBA-15, (b) AISBA-15, (c) K_2SiO_3 (10%)/AISBA-15, (d) K_2SiO_3 (35%)/AISBA-15 and (e) K_2SiO_3 (35%)/SBA-15.

and two small peaks around 1.6° , which were assigned to (100), (110) and (200) reflections of a 2D hexagonal structure [24]. Compared with SBA-15 (100) peak, the (100) plane peak of AISBA-15 shifted to large angle, which was due to the introduction of Al element into the silica framework. However, the AISBA-15 characteristic peaks of (100) lattice plane, (110) lattice plane and (200) lattice plane remained high intensity compared with SBA-15, which indicated that the introduction of Al element did not affect the crystal structure of SBA-15. It was also shown that the XRD patterns of K_2SiO_3 /AISBA-15 catalysts with different K_2SiO_3 loadings were identical to that of AISBA-15. No characteristic peak associated with K_2SiO_3 phase or any new species such as KOH or SiO_2 was observed, indicating the high dispersion of K_2SiO_3 on the AISBA-15 support, and therefore the phase of K_2SiO_3 was undetectable. With the increasing of K_2SiO_3 loading amount, the AISBA-15 characteristic peak intensity decreased gradually, but the major peak of the (100) lattice plane still maintained a relatively high intensity even at a loading of 35 wt.%. This indicated that the AISBA-15 support still retained its structure for these loading amounts. As a comparison, the XRD pattern of SBA-15 with 35 wt.% K_2SiO_3 loading showed almost a straight line paralleled to the X axis, which indicated that the SBA-15 pore structure had been destroyed seriously. It suggested that the addition of Al contributed to the protection of SBA-15 pore structure during the preparation of the catalyst. This could be because the introduction of Al atoms reduced the number of the Si–OH groups of pure silica SBA-15 mesoporous materials and resulted in the generation of Al–O–Si units in the framework of AISBA-15, which could inhibit the condensation of Si–OH in the calcination process and stabilize the framework structure of AISBA-15. Another possible reason was that Al doping could form weak and medium acid sites in the AISBA-15 zeolite [25], which helped to weaken the dissolution of Si atoms by the erosion of K_2SiO_3 base and maintain the pore structure of AISBA-15, thus improving the stability of AISBA-15 support evidently. Accordingly, AISBA-15 was selected as the carrier for the supported catalyst.

Physical properties and catalytic activities of the K functionalized catalysts are summarized in Table 1. The BET surface area of pure AISBA-15 was $654.0 \text{ m}^2/\text{g}$. Upon impregnation with the potassium salt there was a significant reduction of the surface area of the supported catalyst. The surface area of K_2SiO_3 /AISBA-15 decreased with increasing K_2SiO_3 loading, which indicated that the surface and pores of the catalyst carrier were covered during the impregnation process. Nitrogen adsorption isotherms of SBA-15, AISBA-15 and supported catalysts impregnated with different potassium compounds (K_2SiO_3 , K_2CO_3 and KAc) following calcination at 600°C for 2 h, presented a similar changing trend. Among which, the nitrogen adsorption isotherms of SBA-15, AISBA-15 and K_2SiO_3 (35%)/AISBA-15 catalyst are shown in Fig. 2. As can be seen, all the three samples showed the typical Type IV isotherm with an H1 hysteresis loop, a typical feature of SBA-15 silica, indicating that the supports and catalysts were mesoporous and exhibited low energy of adsorption.

The average pore diameter (D_p), BET specific surface area (S_{BET}), and total pore volume (V_p) of AISBA-15 and K_2SiO_3 (35%)/AISBA-15 were

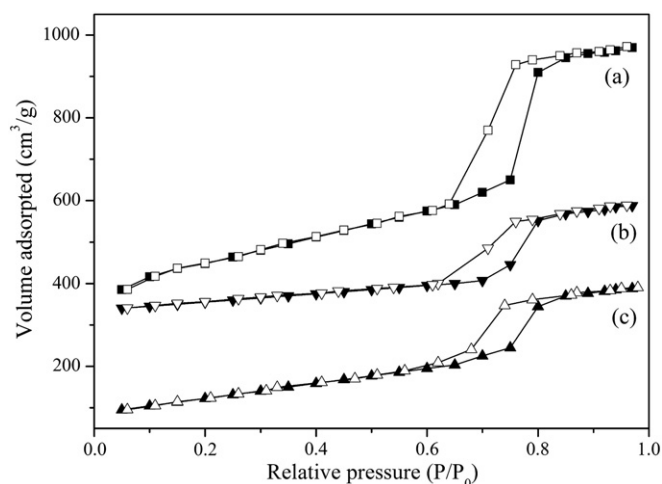


Fig. 2. Nitrogen adsorption-desorption isotherms of different samples. (a) AISBA-15, (b) SBA-15 and (c) K_2SiO_3 (35%)/AISBA-15.

8.3 nm, $654.0 \text{ m}^2/\text{g}$, $1.12 \text{ cm}^3/\text{g}$, and 7.8 nm, $287.1 \text{ m}^2/\text{g}$, $0.45 \text{ cm}^3/\text{g}$, respectively; while for SBA-15 these parameters were 8.1 nm, $597.2 \text{ m}^2/\text{g}$, and $1.04 \text{ cm}^3/\text{g}$, respectively. Compared with AISBA-15, all the textural parameters decreased a little. The enhancement in pore volume and pore diameter of AISBA-15 compared with SBA-15 could be due to the differences in the bond lengths between the cations and oxygen. The Al–O bond length is longer than that of Si–O. This suggested that the incorporation of Al in the AISBA-15 framework improved the pore structure of the support. It has been reported that the dimensions of triglyceride, methyl oleate and glycerin are around 5.8 nm, 2.5 nm and 0.6 nm, respectively [26,27]. The comparison of the mean pore diameter of prepared catalyst with the dimensions of reactant molecules implies that the triglyceride molecules can easily infiltrate into the pores of the catalyst, and most of the active sites will be utilized during the transesterification reaction. Thus it can be expected that the K_2SiO_3 /AISBA-15 catalyst with high surface area of support improves the catalytic activity by two ways: (1) accessibility of reactant molecules to active sites is relatively high on mesoporous AISBA-15, and (2) highly distributed active sites are formed on the support with large mesopore surface area.

Fig. 3 shows the TEM images of SBA-15, AISBA-15 and K_2SiO_3 (30%)/AISBA-15 catalyst. The SBA-15 microcrystals (Fig. 3a) exhibited the morphology of 2D hexagonal arrays of nanochannels with uniform pore size along the [110] direction, which was similar to the microstructure of typical SBA-15 mesoporous silica reported by the literature [28]. Compared with Fig. 3b, it was indicated that the doped Al had no noticeable effect on the morphology of SBA-15, which was in good agreement with the results of XRD. Fig. 3c further suggested that the uniform ordered channel structure of AISBA-15 was maintained well even after loading K_2SiO_3 by 30 wt.%. No aggregated K_2SiO_3 particles were observed and K_2SiO_3 species were found to be highly distributed inside the channels of AISBA-15.

The basicity of the catalyst is an important factor affecting its catalytic performance, and CO_2 -TPD is one of the usual methods of studying basicity distribution for base catalysts. The CO_2 -TPD characterization results are given in Fig. 4. Since the pore size of the SBA-15 (AISBA-15) is much bigger than the molecular diameter of CO_2 , the strength and quantity of the basic sites on the surfaces of the specimens can be determined directly by the areas of the desorption peaks and the desorption temperature of CO_2 [29]. As shown in Fig. 4, the SBA-15 mesoporous molecular sieve exhibited the presence of three CO_2 desorption peaks: about 146°C , 487°C and 725°C , which could correspond to the weak, moderate and strong basic sites, respectively. For the sample AISBA-15 with aluminum-doped, the intensity of the desorption peak of the weak basic sites decreased and shifted to a higher temperature

Table 1

Physical properties of AISBA-15 and K-functionalized AISBA-15 catalysts and biodiesel yields under the same transesterification conditions.

| Sample | BET area (m^2/g) | Basic strength (H-) | Basicity (mmol/g) | Yield of biodiesel (%) |
|---------------------------|------------------------------------|---------------------|-------------------|------------------------|
| AISBA-15 | 654.0 | <7.2 | 0.28 | 7.4 |
| K_2SiO_3 (10%)/AISBA-15 | 498.4 | $7.2 < H- \leq 9.3$ | 0.65 | 24.9 |
| K_2SiO_3 (20%)/AISBA-15 | 444.5 | $7.2 < H- \leq 9.3$ | 1.45 | 53.5 |
| K_2SiO_3 (30%)/AISBA-15 | 374.3 | $7.2 < H- \leq 9.3$ | 1.88 | 95.7 |
| K_2SiO_3 (35%)/AISBA-15 | 287.1 | $9.3 < H- \leq 15$ | 1.94 | 95.3 |
| K_2CO_3 (35%)/AISBA-15 | 341.6 | $9.3 < H- \leq 15$ | 1.81 | 92.8 |
| KAc (35%)/AISBA-15 | 334.2 | $9.3 < H- \leq 15$ | 1.72 | 89.2 |

*Reaction conditions: molar methanol/oil: 6/1, temperature: 65°C , reaction time: 4 h, catalyst amount: 3 wt.%, calcination temperature and time: 600°C and 2 h.

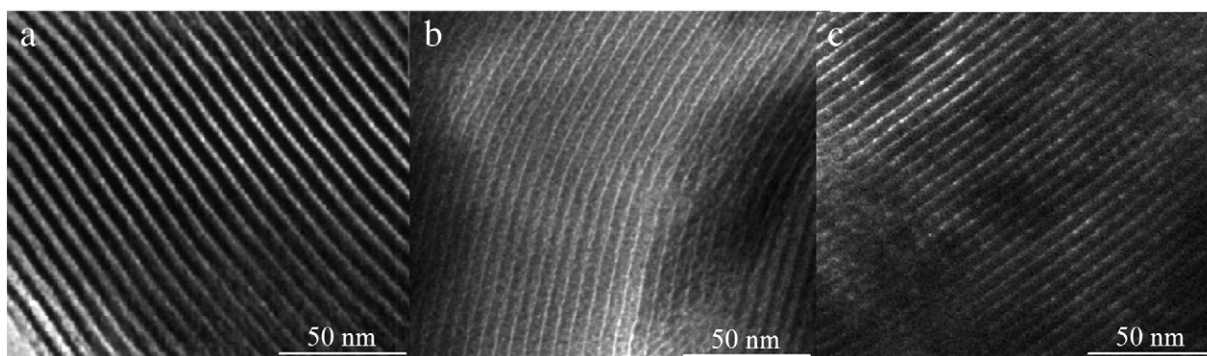


Fig. 3. TEM images of the samples. (a) SBA-15, (b) AISBA-15 and (c) $K_2SiO_3(30\%)/AISBA-15$.

(189 °C) compared with that of SBA-15 silica. A desorption peak for moderate basic sites (496 °C) as well as two for strong basic site at 662 °C and 764 °C was observed, and the intensities of them increased obviously. It is indicated that the basicity of the AISBA-15 was stronger than that of the SBA-15 silica. Similar to the pattern for the SBA-15, the catalyst $K_2SiO_3(30\%)/AISBA-15$ also exhibited only three desorption peaks: about 225 °C, 564 °C and 784 °C, but the desorption peak shifted to a higher temperature and their intensities were stronger than those of SBA-15 and AISBA-15. This suggested that its basicity was enhanced by loading 30 wt.% K_2SiO_3 , which would lead to a better catalytic activity and higher biodiesel yield.

3.2. Catalytic activity and transesterification reaction

High activity of the prepared catalyst can be obtained with a large surface area and strongly basic sites. Three different types of potassium salts functionalized AISBA-15 catalysts $K_2SiO_3(35\%)/AISBA-15$, $K_2CO_3(35\%)/AISBA-15$ and $KAc(35\%)/AISBA-15$ were prepared, and the comparison of their catalytic activities in transesterification reaction is shown in Table 1. For comparison, the same reaction conditions were employed in all experiments. K_2SiO_3 impregnated AISBA-15 catalyst generated a slightly higher biodiesel yield than those using K_2CO_3 and KAc impregnated catalysts. Consistent with our earlier discussion about the influence of basicity on the biodiesel yield, the order of catalytic activities of these three types of supported catalysts was in line with their relative basicity, i.e., basicity of $K_2SiO_3/AISBA-15 > K_2CO_3/AISBA-15 > KAc/AISBA-15$, as shown

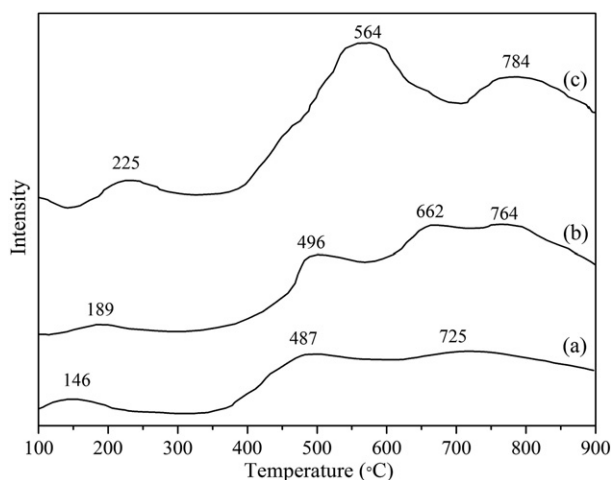


Fig. 4. CO_2 -TPD patterns of the samples. (a) SBA-15, (b) AISBA-15 and (c) $K_2SiO_3(30\%)/AISBA-15$.

in Table 1. The AISBA-15 carrier exhibited weak catalytic activity, most likely due to the lack of strong basic sites on which transesterification reaction could occur. After further loading different potassium compounds (K_2SiO_3 , K_2CO_3 and KAc), the basicity of the AISBA-15 carrier increased. The increasing of basicity in the supported catalysts mainly came from the active ingredients of potassium compounds and the interaction between active components and supports. Further investigation would be needed to explore the mechanism in detail. The $K_2SiO_3/AISBA-15$ after calcination maintained the highest basicity, which might be due to a stronger interaction existed between the K_2SiO_3 active components and AISBA-15 silica. The basicity of $KAc/AISBA-15$ was less than $K_2CO_3/AISBA-15$ because the alkalinity of carbonate calcined product was stronger than that of acetate calcined product [30]. So in the experiment $K_2SiO_3/AISBA-15$ were used as catalysts for further study.

From Table 1, it also can be seen that the yield of biodiesel increased significantly with increasing K_2SiO_3 loading, and the highest yield of 95.7% was obtained at a loading of 30 wt.% K_2SiO_3 . A major reason was the increase of the basicity with increasing K_2SiO_3 content. Compared with surface area, basicity was considered to play an important role in catalytic activity [31]. The increase of the biodiesel yield was most obvious at 30% by weight of K_2SiO_3 of which the basicity was significantly greater than the basicity values at lower K_2SiO_3 concentrations. The increase in the biodiesel yield with increasing basicity of the catalyst was also found in our previous studies on other types of supported catalysts in transesterification reaction [32]. However, when the loaded K_2SiO_3 was over 30 wt.%, the yield did not increase significantly, which could be due to the agglomeration of active K_2SiO_3 phase and the cover of basic sites by the exceeded K_2SiO_3 . Table 1 also shows that the surface area of $K_2SiO_3(35\%)/AISBA-15$ decreased obviously compared with that of $K_2SiO_3(30\%)/AISBA-15$, thus the active sites which reactant molecules could access were reduced. Therefore, the optimum loading amount of K_2SiO_3 was 30 wt.%.

The influence of the calcination temperature on the yield of biodiesel is shown in Table 2. As can be seen, the catalytic activity was increased with increasing calcination temperature from 400 °C to 600 °C. This could be because the active basic sites of K_2SiO_3 increased after activation by heat. However, the calcination procedure at higher temperature (800 °C) decreased catalytic activity. According to the literature [33], deactivation of the catalyst after its calcination at high temperature is probably the result of loss of potassium species, by sublimation and/or

Table 2
Effect of the calcination temperature on the yield of biodiesel.

| Calcination temperature (°C) | Yield of biodiesel |
|------------------------------|--------------------|
| 400 | 81.7 |
| 600 | 95.5 |
| 800 | 56.4 |

its penetration into the subsurface. Moreover, the use of higher temperatures might lead to the modification of catalyst textural properties or the speciation of K atoms. It was also found that the agglomeration of catalyst increased when the calcination temperature exceeded 600 °C, resulting in the calcined catalyst being difficult to remove, which could be due to the structural collapse of the carrier after subjected to high temperature.

To investigate the effects of the methanol to oil molar ratio for $K_2SiO_3/AlSBA-15$ catalyst, the transesterification experiments were conducted by changing the molar ratio from 3:1 to 15:1, while keeping the temperature and the catalyst amount constant at 65 °C and 3 wt.%, respectively. As shown in Fig. 5a, when the molar ratio increased from 3:1 to 6:1, the yield of biodiesel rose significantly from 29.5% to 65.6% after the reaction for 130 min. However, it was observed that altering the methanol/oil molar ratio in the 9 to 15 ratio range had no significant effect on the yield. So the molar ratio of methanol to oil of 9:1 was enough to obtain a high yield of 95% for a relatively short reaction time (around 150 min) when using $K_2SiO_3/AlSBA-15$ catalyst.

Reaction temperature is also an important parameter that influences the biodiesel yield and reaction rate because the intrinsic rate constants are strong functions of temperature. Each experiment was run for 150 min with 3 wt.% (based on oil) catalyst and 9:1 molar ratio of methanol/oil. The results (Fig. 5b) indicated that biodiesel yield was only 52.4% at 30 °C for 150 min, but it increased considerably with increasing reaction temperature and reached 94.7% at 65 °C. Considering that the yield changed little over the 60–65 °C range, the optimized reaction temperature for the transesterification of *Jatropha* oil to biodiesel thus was around 60 °C.

Fig. 5c illustrates the change of yield as a function of catalyst amount with methanol/*Jatropha* oil molar ratio 9:1, reaction temperature 60 °C and reaction time 150 min. The mass ratio of the $K_2SiO_3/AlSBA-15$ catalyst to *Jatropha* oil was varied within the range of 1.0–6.0%. When the catalyst amount increased from 1.0 to 3.0 wt.%, biodiesel yield was raised from 51.3% to a maximum yield of 94.5%, and then reached a plateau value. The reason was that the increase of catalyst amount from 1.0 to 3.0 wt.% could increase the contact between catalyst and reactants and the proton concentration in the interface of oil and methanol. Therefore, the optimum catalyst concentration was 3.0 wt.% in this study.

At the optimum conditions, i.e., methanol/oil molar ratio of 9:1, catalyst amount of 3.0 wt.%, and reaction temperature of 60 °C, three repeated tests were carried out and an average biodiesel yield of $95.1 \pm 1.4\%$ was obtained in 150 min. The yield was higher than previous works reported that were conducted at similar or severer reaction conditions [18,31,33]. The high yield can be attributed to strong basic sites and a large surface area of the $K_2SiO_3/AlSBA-15$ catalyst.

3.3. Catalyst stability

The stability and reusability of the catalyst are very important for the economical application of $K_2SiO_3/AlSBA-15$ as a heterogeneous catalyst for biodiesel production. The reusability of the catalyst was checked by two methods. In the first method, upon the completion of the transesterification reaction the catalyst particles were filtered out, recovered, washed with a mixture of methanol and n-hexane several times, re-calcined at 600 °C for 2 h and then reused as the catalyst of the next run. In the other method, the catalyst was tested by consecutively recovering without any further purification and activation and then was charged for the further run in the batch reactor.

For the reusability analysis the recycling tests were conducted at the optimized reaction conditions with the $K_2SiO_3(30\%)/AlSBA-15$ catalyst. The corresponding results of biodiesel yield as a function of the number of recycling cycles are illustrated in Fig. 6. When using the first regeneration method, the yield of biodiesel reached 95.2% (first use), 92.3% (second use) and 90.4% (third use) at the end of 150 min of reaction

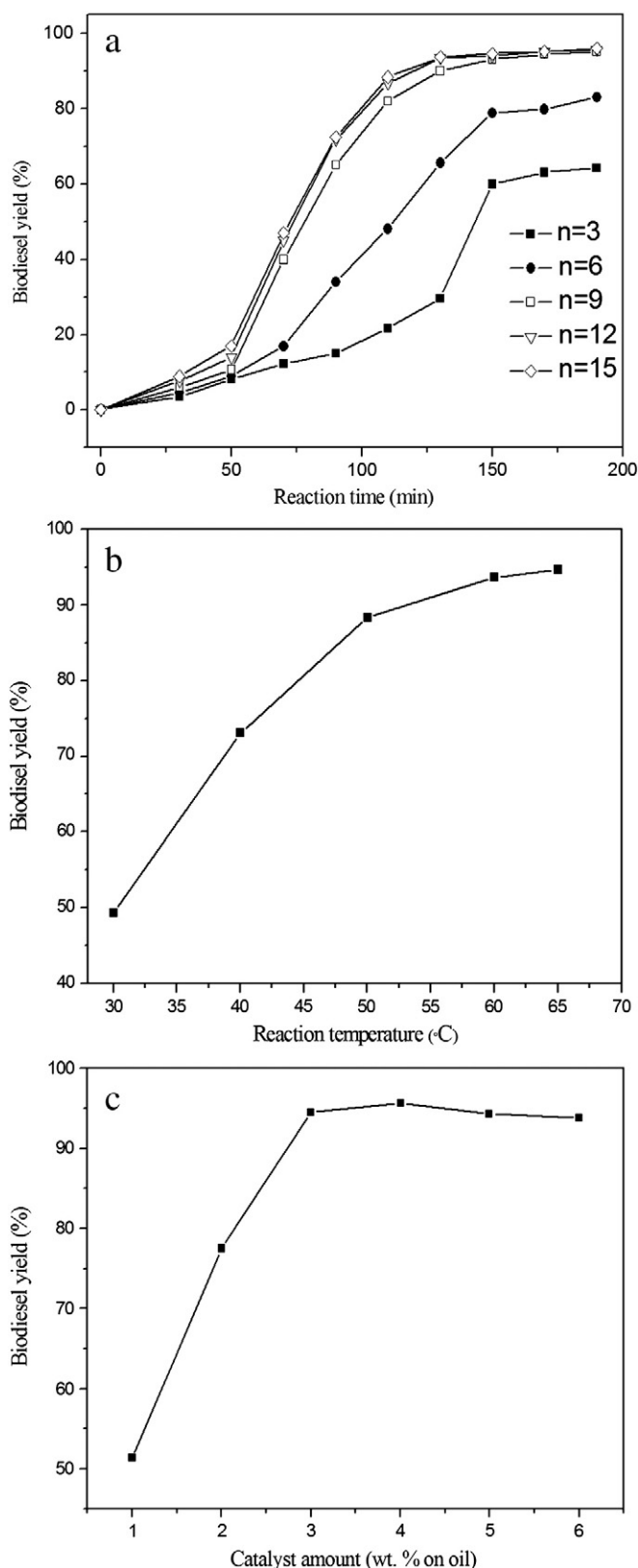


Fig. 5. Effects of variables on biodiesel yield: (a) methanol to oil molar ratio, (b) reaction temperature and (c) catalyst amount.

time. There was no significant decline of yield for the third (90.4%), fourth (89.5%) and fifth (88.7%) runs, which indicated that the $K_2SiO_3/AlSBA-15$ catalyst was relatively stable. Compared with the catalyst using the first regeneration method, a remarkable reduction in the

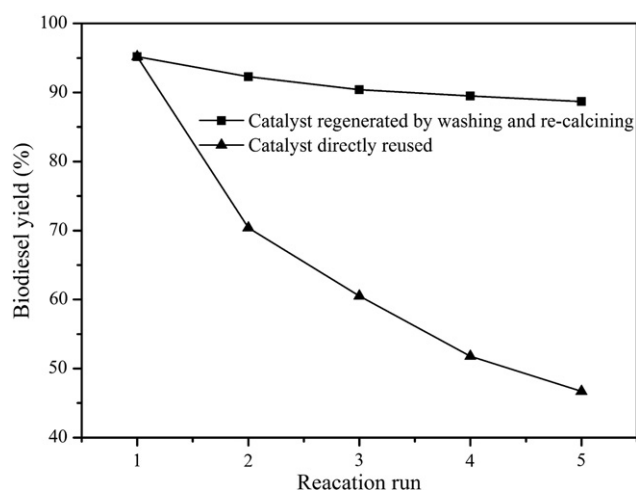


Fig. 6. Conversion of *Jatropha* oil with recycled catalyst. Reaction conditions: methanol/oil molar ratio 9:1, catalyst amount 3 wt%, reaction temperature 60 °C, reaction time 130 min and using $K_2SiO_3(30\%)/AISBA-15$ catalyst.

catalytic activity with the second method took place and the achieved yield of biodiesel was only 46.7% after the fifth run with the same amount of used catalyst.

The adsorption of biodiesel, glycerol and other intermediate products on the surface of the catalyst, which prevented the contact between reactants and basic sites, was considered as one reason for the deactivation of the catalyst. Regeneration of the catalyst was therefore proposed by means of purging or thermal degradation of the organic deposits. Part of these deposits were removed by washing and others were burnt out upon calcination in air, which led to a recovery of the activity of $K_2SiO_3/AISBA-15$ catalyst. The solubility of the catalyst was also an important factor that should be taken into account to correctly assess its performance and practical use. Thus, the leakages of potassium to biodiesel and glycerol phases were investigated. The results showed that after 150 min of reaction the free K^+ concentration in the biodiesel phase and glycerol phase was 9.5 ppm and 22.7 ppm, respectively. Therefore, the leakage of potassium to the organic phase especially glycerol phase was the other reason for the activity loss. However, these

values were much lower compared to K_2CO_3 /cinder [34] and KOH/MgO [14] catalysts. The results indicated that the synthesized $K_2SiO_3/AISBA-15$ catalyst had good potential for the biodiesel production from *Jatropha* oil. Although this catalyst is not perfect which can be used forever, it can be used for several runs efficiently and the activity of the catalyst can be recovered by loading K_2SiO_3 again.

3.4. Biodiesel characteristics

Fig. 7 shows the GC graph for biodiesel from *Jatropha* oil. The produced biodiesel mainly consists of five fatty acid methyl esters: methyl palmitate (C16:0) 9.78%, methyl stearate (C18:0) 4.25%, methyl oleate (C18:1) 24.42%, methyl linoleate (C18:2) 49.91%, and methyl linolenate (C18:3) 3.46%. Its properties such as flash point, viscosity, acid value and cetane number were presented in Table 3, which were close to those of the American standard (ASTM D 751-03). Therefore, it could be concluded that the biodiesel produced from *Jatropha* oil using $K_2SiO_3/AISBA-15$ as a catalyst was qualified as a substitute fuel for diesel engines.

4. Conclusions

Catalysts with different potassium compounds (K_2SiO_3 , K_2CO_3 and KAc) as active components loaded on AISBA-15 mesoporous molecular sieve support were prepared by impregnation method followed by calcination, which were used to catalyze the methanolysis of *Jatropha* oil to biodiesel. The catalyst support showed weak activity, but the basicity and catalytic activity were improved significantly after loading potassium compounds. K_2SiO_3 impregnated AISBA-15 catalyst generated a higher biodiesel yield than those using K_2CO_3 and KAc impregnated catalysts, presumably due to the greater basicity of the catalyst when K_2SiO_3 was utilized. Catalyst characterization showed that K_2SiO_3 was well distributed inside the channels of the AISBA-15 support. The $K_2SiO_3/AISBA-15$ catalyst impregnated with 30 wt.% K_2SiO_3 after calcination at 600 °C was found to be the optimum catalyst. A high biodiesel yield of $95.1 \pm 1.4\%$ could be achieved under the temperature of 60 °C, catalyst loading amount of 3 wt.%, molar methanol/oil ratio of 9:1 and 150 min of reaction time, and the biodiesel properties were close to those of the American standard (ASTM D 751-03). The recycling and reuse of the catalyst up to five times gave rise to a modest decrease of

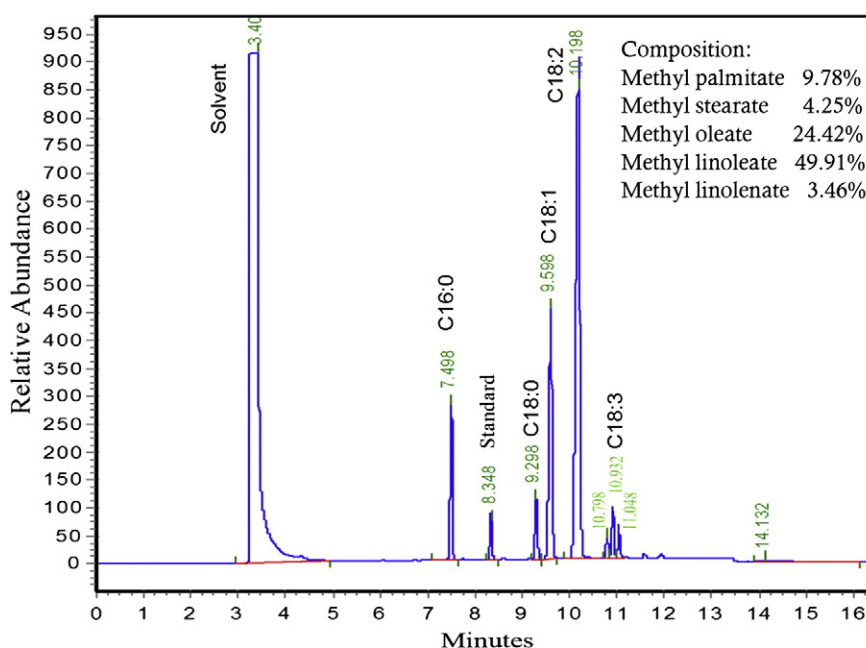


Fig. 7. GC graph for biodiesel from *Jatropha* oil.

Table 3
Properties of biodiesel from *Jatropha* oil.

| Properties | Biodiesel produced | The American Standard (ASTM D 751-03) |
|---------------------------------------|--------------------|---------------------------------------|
| Flash point (°C) | 169 | ≥ 130 |
| Viscosity (mm ² /s, 40 °C) | 5.5 | 1.9–6.0 |
| Acid value (mg KOH/g) | 0.22 | ≤ 0.80 |
| Sulphur content (wt.%) | 0.004 | ≤ 0.05 |
| Cetane number | 62 | ≥ 47 |
| Carbon residue (%) | 0.31 | ≤ 0.05 |
| Calorific value (MJ/kg) | 39.8 | — |

catalytic activity and led to a reduction of about 6% in the biodiesel yield. The main reasons for activity loss were the leaching of some amount of potassium species and the adsorption of organic deposits on the catalyst surface.

Acknowledgments

The authors are grateful to the financial supports of the Fundamental Research Fund for the Central Universities (Grant No. QN2011158) and the Starting Research Fund for the Doctoral Program of Northwest A&F University.

References

- [1] Y. Zhang, M.A. Dubé, D.D. McLean, M. Kates, Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis, *Bioresource Technology* 90 (2003) 229–240.
- [2] X. Deng, Z. Fang, Y.H. Liu, C.L. Yu, Production of biodiesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst, *Energy* 36 (2011) 777–784.
- [3] M. Hájek, F. Skopal, M. Černoch, Effect of phase separation temperature on ester yields from ethanolsysis of rapeseed oil in the presence of NaOH and KOH as catalysts, *Bioresource Technology* 110 (2012) 288–291.
- [4] B. Salamatina, H. Mootabadi, S. Bhatia, A.Z. Abdullah, Optimization of ultrasonic-assisted heterogeneous biodiesel production from palm oil: a response surface methodology approach, *Fuel Processing Technology* 91 (2010) 441–448.
- [5] V. SathyaSelvabala, D.K. Selvaraj, J. Kalimuthu, P.M. Periyaraman, S. Subramanian, Two-step biodiesel production from *Calophyllum inophyllum* oil: optimization of modified β -zeolite catalyzed pre-treatment, *Bioresource Technology* 102 (2011) 1066–1072.
- [6] M.J. Kim, S.M. Park, D.R. Chang, G. Seo, Transesterification of triacetin, tributyrin, and soybean oil with methanol over hydrotalcites with different water contents, *Fuel Processing Technology* 91 (2010) 618–624.
- [7] C. Ngamcharussrivichai, P. Totarat, K. Bunyakit, Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil, *Applied Catalysis A: General* 341 (2008) 77–85.
- [8] Z.Q. Yang, W.L. Xie, Soybean oil transesterification over zinc oxide modified with alkali earth metals, *Fuel Processing Technology* 88 (2007) 631–638.
- [9] K. Noiroj, P. Intarapong, A. Luengnarumitchai, S. Jai-In, A comparative study of KOH/Al₂O₃ and KOH/NaY catalysts for biodiesel production via transesterification from palm oil, *Renewable Energy* 34 (2009) 1145–1150.
- [10] H. Kazemian, B. Turowec, M.N. Siddiquee, S. Rohani, Biodiesel production using cesium modified mesoporous ordered silica as heterogeneous base catalyst, *Fuel* 103 (2013) 719–724.
- [11] N. Supamathanon, J. Wittayakun, S. Prayoonpokarach, Properties of *Jatropha* seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite, *Journal of Industrial and Engineering Chemistry* 17 (2011) 182–185.
- [12] S. Tang, L. Wang, Y. Zhang, S. Li, S. Tian, B. Wang, Study on preparation of Ca/Al/Fe₃O₄ magnetic composite solid catalyst and its application in biodiesel transesterification, *Fuel Processing Technology* 95 (2012) 84–89.
- [13] J.X. Wang, K. Chen, C. Chen, Biodiesel production from soybean oil catalyzed by K₂SiO₃/C, *Chinese Journal of Catalysts* 32 (2011) 1592–1596.
- [14] O. Ilgen, A.N. Akin, Transesterification of canola oil to biodiesel using MgO loaded with KOH as a heterogeneous catalyst, *Energy & Fuels* 23 (2009) 1786–1789.
- [15] L.B. Wen, Y. Wang, D.L. Lu, S.Y. Hu, H.Y. Han, Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil, *Fuel* 89 (2010) 2267–2271.
- [16] F.X. Qiu, Y.H. Li, D.Y. Yang, X.H. Li, P. Sun, Heterogeneous solid base nanocatalyst: preparation, characterization and application in biodiesel production, *Bioresource Technology* 102 (2011) 4150–4156.
- [17] C. Samart, P. Sreetongkittikul, C. Sookman, Heterogeneous catalysis of transesterification of soybean oil using KI/mesoporous silica, *Fuel Processing Technology* 90 (2009) 922–925.
- [18] A.Z. Abdullah, N. Razali, K.T. Lee, Optimization of mesoporous K/SBA-15 catalyzed transesterification of palm oil using response surface methodology, *Fuel Processing Technology* 90 (2009) 958–964.
- [19] S. Jairam, P. Kolar, R. Sharma-Shivappa, J.A. Osborne, J.P. Davis, KI-impregnated oyster shell as a solid catalyst for soybean oil transesterification, *Bioresource Technology* 104 (2012) 329–335.
- [20] J.A. Melero, L.F. Bautista, J. Iglesias, G. Morales, R. Sánchez-Vázquez, Zr-SBA-15 acid catalyst: optimization of the synthesis and reaction conditions for biodiesel production from low-grade oils and fats, *Catalysis Today* 195 (2012) 44–53.
- [21] Y.D. Wei, S.G. Zhang, G.S. Li, S.F. Yin, Z.T. Qu, Research progress on solid superbase catalysts in the last decade, *Chinese Journal of Catalysis* 32 (2011) 891–898.
- [22] D.Y. Zhao, O.S. Huo, J.L. Feng, B.F. Chamelka, G.D. Stucky, Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures, *Journal of the American Chemical Society* 120 (1998) 6024–6036.
- [23] H. Gorzawski, W.F. Hoelderich, Preparation of superbases and their use as catalysts for double-bond isomerization, *Journal of Molecular Catalysis A: Chemical* 144 (1999) 181–187.
- [24] H.J. Wan, X.J. Li, S.F. Ji, B.Y. Huang, K. Wang, C.Y. Li, Effect of Ni loading and Ce_xZr_{1-x}O₂ promoter on Ni-based SBA-15 catalysts for steam reforming of methane, *Journal of Natural Gas Chemistry* 16 (2007) 139–147.
- [25] M.J. Cheng, Z.B. Wang, K. Sakurai, F. Kumata, T. Saito, T. Komatsu, T. Yashima, Creation of acid sites on SBA-15 mesoporous silica by alumination, *Chemistry Letters* 28 (1999) 131–132.
- [26] K. Jacobson, R. Gopinath, L.C. Meher, A.K. Dalai, Solid acid catalyzed biodiesel production from waste cooking oil, *Applied Catalysis B: Environmental* 85 (2008) 86–91.
- [27] M.L. Granados, M.D.Z. Poves, D.M. Alonso, R. Mariscal, F.C. Galisteo, R. Moreno-Tost, J. Santamaría, J.L.G. Fierro, Biodiesel from sunflower oil by using activated calcium oxide, *Applied Catalysis B: Environmental* 73 (2007) 317–326.
- [28] V. Brahmakhatri, A. Patel, 12-Tungstophosphoric acid anchored to SBA-15: an efficient, environmentally benign reusable catalysts for biodiesel production by esterification of free fatty acids, *Applied Catalysis A: General* 403 (2011) 161–172.
- [29] Y.L. Wei, Y. Cao, J.H. Zhu, X.W. Yan, Investigation on new mesoporous solid basic material MgO/SBA-15, *Chinese Journal of Inorganic Chemistry* 19 (2003) 233–239.
- [30] S.L. Yan, H.F. Lu, L.H. Jiang, B. Liang, Solid base catalysts for transesterification of oil with methanol to produce biodiesel, *Journal of Chemical Industry and Engineering (China)* 58 (2007) 2506–2512.
- [31] F.E. Soetaredjo, A. Ayucitra, S. Ismadji, A.L. Maukar, KOH/bentonite catalysts for transesterification of palm oil to biodiesel, *Applied Clay Science* 53 (2011) 341–346.
- [32] H.T. Wu, J.H. Zhang, Q. Wei, J.L. Zheng, J.A. Zhang, Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts, *Fuel Processing Technology* 109 (2013) 13–18.
- [33] I. Lukić, J. Krstić, D. Jovanović, D. Skala, Alumina/silica supported K₂CO₃ as a catalyst for biodiesel synthesis from sunflower oil, *Bioresource Technology* 100 (2009) 4690–4696.
- [34] H. Liu, L.Y. Su, F.F. Liu, C. Li, U.U. Solomon, Cinder supported K₂CO₃ as catalyst for biodiesel production, *Applied Catalysis B: Environmental* 106 (2011) 550–558.