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Production of biodiesel through transesterification of soybean oil using lithium orthosilicate solid catalyst

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ABSTRACT

This study synthesized biodiesel from soybean oil using transesterification over a lithium orthosilicate (Li_4SiO_4) catalyst. Under the optimal reaction condition of a methanol/oil molar ratio of 18:1, a 6% (wt/wt oil) catalyst amount, and a reaction at 65 °C for 2 h, the conversion to biodiesel could achieve 98.1%. The catalyst was prepared using a solid-state reaction. Li_4SiO_4 can be used directly for biodiesel production without being further dried or thermal pretreated, avoiding the usual activation of solid catalysts at high temperature. The effects of the methanol/oil ratio, catalyst amounts, reaction time and reaction temperature on the conversion are also reported in this paper. The solid base catalyst was highly active, air-insensitive and can be reused for at least ten cycles without loss of activity. The catalysts were characterized using XRD, SEM-EDS, FTIR, TGA-DTA, and the Hammett indicator method.

1. Introduction

World energy demand is increasing rapidly because of the excessive use of diesel fuels [1]. Biodiesel fuel, an alternative to classic diesel fuel, is considered an ecological fuel because it consists of methyl esters of fatty acids derived from vegetable oils or animal fats. Conventional processes of biodiesel production involve using homogeneous alkaline catalysts under mild temperatures (60–80 °C) and atmospheric pressure [2]. However, these catalysts require additional neutralization and separation steps for the final reaction mixture, thus leading to a series of environmental problems related to using excessive amounts of water and energy. These problems have provided an impetus to search for solid and more environmentally stable catalysts. The relevant key limitations of using basic solid catalysts, from an industrial perspective, involve the surface active sites being rapidly poisoned upon exposing the catalyst to ambient air. The chemisorption of carbon dioxide and water on the surface sites forms carbonates and hydroxyl groups, respectively [3–10]. Therefore, avoiding direct exposure of the catalyst to room air is critical while handling and transferring the catalyst from the activation unit to the reactor. Calcium oxide (CaO) is a promising basic heterogeneous catalyst for synthesizing biodiesel at mild temperatures (below the boiling point of methanol) and at atmospheric pressure [7], but is rapidly hydrated and carbonated by contact with room temperature air. A few minutes are adequate for CaO to chemisorb a substantial amount of H_2O and CO_2 [9]. Mixing CaO with biodiesel formation of a paste has been reported to protect the activated CaO against the poisoning from ambient H_2O and CO_2 that may occur during handling or storing of the activated solid [3,6]. Approximately 15 g of biodiesel was required to protect each gram of CaO [3]. Previous studies have reported that calcium glyceroxide (calcium oxide combined with the by-product glycerol following the transesterification reaction) is an air-exposure tolerant catalyst, but is a weaker base than calcium oxide, thus decreasing the reaction efficiency [8,10]. Li-impregnated CaO and MgO catalysts for transesterification reactions were reported in the literature [11–14]. These catalysts appeared to be promising candidates to replace conventional homogeneous catalysts for biodiesel production because the reaction times are low enough to be practical in continuous processes and the preparations are neither difficult nor costly. The objective of this study was to investigate solid Li_4SiO_4 catalysts use in biodiesel production, examine the optimum conditions of the methanol/oil ratio, catalyst amounts, reaction time and reaction temperature. Moreover, the Li_4SiO_4 catalyst was highly active, air-insensitive and can be reused for at least ten cycles without loss of activity.

2. Experimental

2.1. Catalyst preparation

Soybean cooking oil (Great Wall Enterprise Co., Taiwan), methanol (ACS grade, ECHO Chemical Co., Taiwan), reagent grade $LiNO_3$ (Katayama Chemical Co., Japan), SiO_2 (0.12 μm, Shimakyu's Pure Chemicals, Osaka, Japan), Li_2CO_3 (Shimakyu's Pure Chemicals, Osaka,

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Japan) and $LiOH \cdot H_2O$ (Chameleon Reagent, Osaka, Japan) were used as received. The Li_4SiO_4 was prepared using a solid-state reaction. A 0.133 mole amorphous SiO_2 powder was added to an aqueous solution containing 0.532 moles of $LiNO_3$. The as-prepared solution was dried at 120 °C for 24 h. Finally, the SiO_2 and $LiNO_3$ mixing powder was thoroughly ground and calcined at 800 C in air for 4 h. The as-prepared sample was washed with 700 ml of anhydrous methanol and dried at 95 °C under a vacuum for 1 h to remove absorbed base sites from the catalyst surface.

2.2. Catalyst characterization

The base strength of the samples (H_) was determined using Hammett indicators [6]. Approximately 50 mg of the sample was shaken with 1 ml of a methanol solution of the Hammett indicator. A duration of 2 h was allowed to elapse to achieve equilibrium after which no additional change of color occurred. The basic strength is defined as being stronger than the weakest indicator that exhibits a color change, and weaker than the strongest indicator that produces no color change. Bromthymol blue (H_ = 7.2), phenolphthalein (H_ = 9.8), indigo carmine (H_ = 12.2), 2,4-dinitroaniline (H_ = 15.0), and 4-nitroaniline (H_ = 18.4), at a concentration of 0.02 mol/L, were used as Hammett indicators. The characterization of catalysts was performed using a powder X-ray diffractometer (XRD, MAC MXP18), with Cu Kα radiation, over a 2θ range from 5 to 90° with a step size of 0.04°, and a scanning speed of 3° min^{-1}. The morphology and chemical composition of Li_4SiO_4 catalysts were investigated by using a JEOL JSM-7401 F Field Emission SEM-EDS. For FTIR spectroscopy, samples were prepared as KBr pellets and the analyses were performed on a Spectrometer NICOLET 380. The infrared spectra were collected and analyzed using a data acquisition computer and OMNIC 4.1b software (Nicolet Corp.). The background and spectral measurements were averaged against 32 scans with a resolution of 4 cm^{-1}. Thermogravimetric analyses were carried out with a Seiko SSC 5000 instrument. The samples (10.6 mg) were heated from room temperature up to 1000 °C, with a scan rate of 5 °C min^{-1}, and under an air atmosphere stream (air flow = 80 ml min^{-1}) to ensure water desorption. The samples were analyzed as received (i.e. without any vacuum pre-treatment or special heat conditioning).

2.3. Reaction procedures

The conversion of soybean oil to biodiesel was performed in a 250 ml flat-bottomed flask, equipped with a reflux condenser and a magnetic stirrer. The reactor was initially filled with 12.5 g of soybean oil, which was heated to 65 °C for 2 h while stirring at 300 rpm. The reactant was stirred evenly to avoid splashing in the flask at the stirring speed. The timing of the reaction was initiated as soon as the mixture of the methanol and catalyst was added into the reactor. The effects of the molar ratio of methanol to oil (6:1–30:1) and catalyst/oil weight ratio (2–10 wt.%) on the conversion of triglycerides to biodiesel were investigated. All of the experiments were performed at atmospheric pressure. After the transesterification reaction, DI water was added into the reaction mixture to stop the reaction [15]. The water contents have a significant inhibiting effect on the transesterification of glycerides with alcohols that use alkaline or acid catalysts, because water causes the reaction change to saponificate. The biodiesel and glycerol layers were easily separated because of differing densities of 0.86 and 1.126 g/cm^3, respectively. A supernatant was filtered through a common paper filter, and excess methanol and water were then evaporated before to fatty acid methyl ester (FAME) analysis.

2.4. Analytical methods

Fatty acid methyl ester concentrations, expressed as the biodiesel purity of the product, were determined using a gas chromatography system (Thermo trace GC ultra, Thermo Co.), equipped with a flame ionization detector, a capillary column (Tr-biodiesel (F), Thermo Co., 30 m in length with 0.25 mm i.d. and 0.25 μm film thickness), a programmed column oven, and a programmed temperature injector. The oven temperature program consisted of the following steps: start at 120 °C (maintain for 1 min); increase at a rate of 30 °C min^{-1} to 220 °C (maintain for 1 min); then increase at a rate of 10 °C min^{-1} to 250 °C (maintain for 1 min). The temperature of the programmed temperature injector was 90 °C for 0.05 min, and programmed to 260 °C, at a rate of 10 °C min^{-1}. Nitrogen was used as a carrier gas with a flowrate of 2 ml min^{-1}. The amounts of FAME were calculated using the internal standard (methyl heptadecanoate) method, according to the method prescribed by the Chinese National Standard 15051.

To evaluate quantitatively the leaching of the solid base catalyst under reaction conditions, some of the samples removed from the reactor were filtered, and the residual methanol was then evaporated in a rotary evaporator to leave the FAME and glycerol as separate phases. After evaporating, the dry fraction was treated with 0.1 N hydrochloric acid [16]. The resulting solution was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES, spectro genesis) to determine the Li concentration.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of the as prepared sample, samples exposed to air for 24 h before and after used. The XRD peaks were mainly consistent with the JCPDS file 37–1472, whose space group was $P2_1/m$ and lattice parameters were $a = 5.303$ Å, $b = 6.113$ Å, $c = 5.154$ Å, and $\beta = 90.33$. The intensity of Li_2SiO_3 peaks in the diffractogram was very weak, indicating that the content of Li_2SiO_3 was very low in the product. Reused Li_4SiO_4 was washed with anhydrous methanol and then subjected to a vacuum drying process to remove absorbed resultants from the catalyst surface prior to XRD and SEM. After exposure to air, the crystalline phase of the Li_4SiO_4 was stable. However, it is uncommon for CaO to chemisorb a substantial amount of H_2O quickly in the air and be converted into $Ca(OH)_2$ following a loss of catalytic activity.

Fig. 2 shows the FTIR spectra of the Li_2CO_3, $LiOH \cdot H_2O$, and Li_4SiO_4 synthesized using asolid-state reaction with and without exposure to air. The FTIR spectrum of Li_4SiO_4 that was unexposed to air (Fig. 2a) shows a sharp band of isolated OH stretching vibration at 3562 cm^{-1} and a broad band of OH stretching vibrations of hydrogen-bonded for LiOH in 3530–2800 cm^{-1} [17]. The peaks at

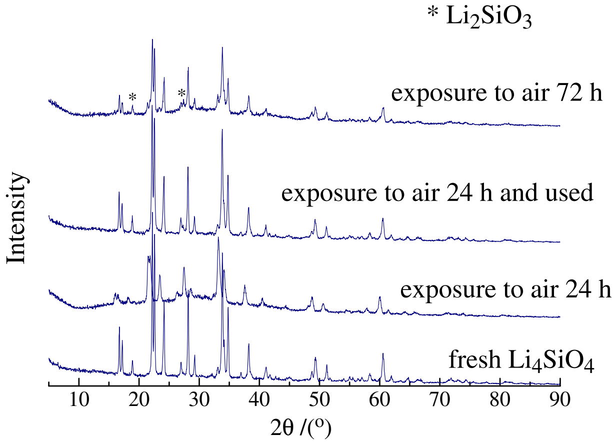

Fig. 1. XRD patterns of samples.

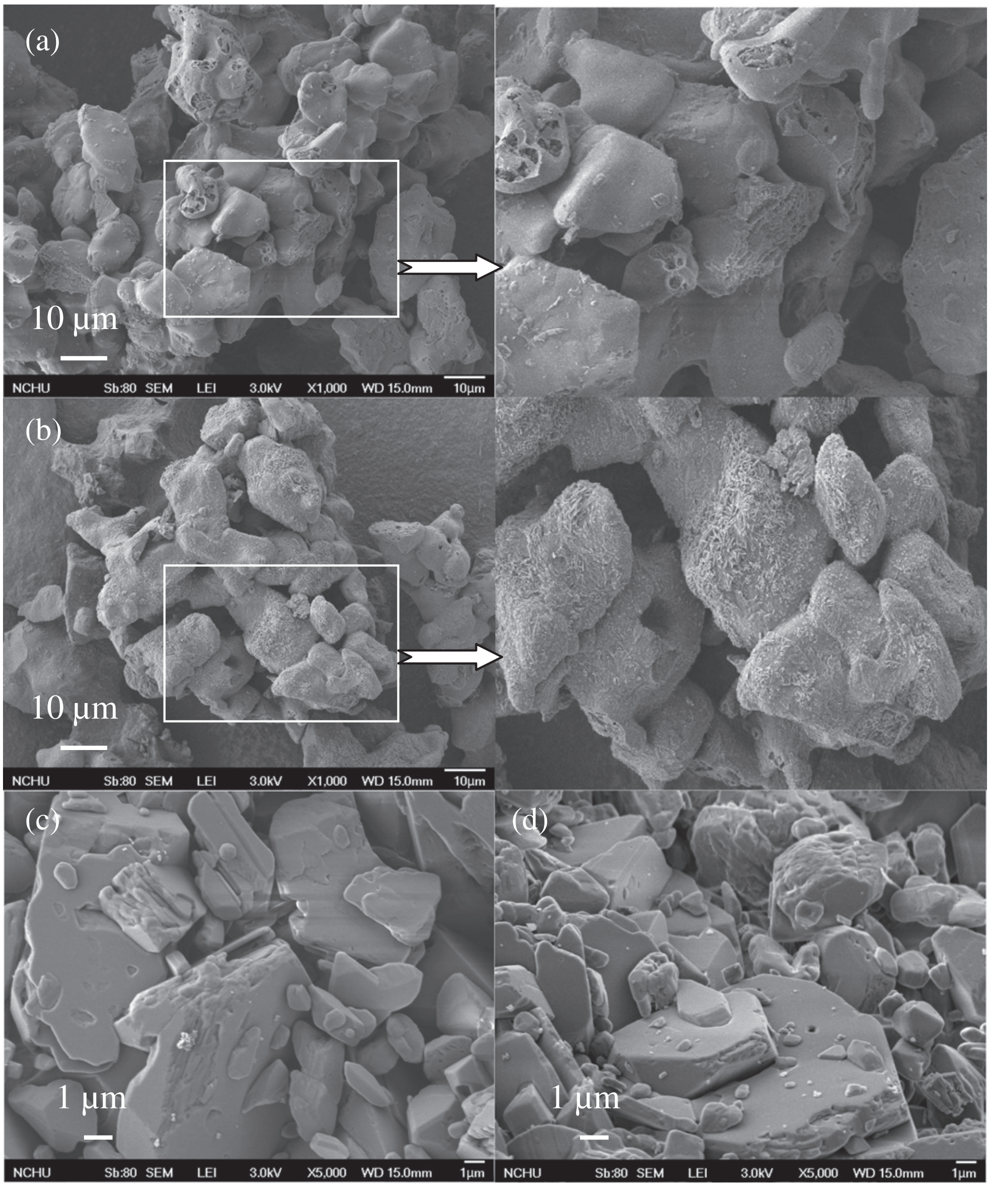

Fig. 2. SEM micrograph of (a) as-prepared Li_4SiO_4, (b) Li_4SiO_4 exposure to air for 24 h, (c) fresh Li_2CO_3, (d) Li_2CO_3 exposure to air for 24 h.

1490 cm^{-1} and 1445 cm^{-1} are the C–O asymmetric and symmetric stretching modes of Li_2CO_3, respectively. The CO_3 group-bending mode creates a peak at 871 cm^{-1} [18–23]. The CO_3^{2-} anions formed on the surface of the samples probably by absorbing CO_2 molecules from the air after calcining. The absorption bands originating from the Li–O–group were located at 985 cm^{-1} [23]. In addition, bands associated with vibrations of O–Si–O and Si–O–Si bridges occurred at 802 and 830 cm^{-1}, respectively. The bands located at 962 cm^{-1} and 906 cm^{-1} were due to the asymmetric stretching vibration of Si–O-H silanol groups and bending vibration of O-Si-H, respectively [23,24]. The free NO^{3-} anion originating from decomposed $LiNO_3$ in the solid-state reaction yields a vibration mode of anti-symmetric stretching at approximately 1386 cm^{-1} [25]. The FTIR spectra of Li_4SiO_4 exposed to air for 72 h (Fig. 2b) were similar to those unexposed to air, but no obvious OH stretching vibration was observed. The FTIR results are in accordance with the formation of LiOH, SiOH, and Li_2CO_3 species over the surface of the Li_4SiO_4 [23]. After exposure to air for 24 h, LiOH reacted with CO_2 in the air to form Li_2CO_3 over the surface of the Li_4SiO_4, and the OH stretching vibration characteristic disappeared.

The FTIR spectra of Li_2CO_3 (Fig. 2c) shows that the peaks at 1487 cm^{-1} and 1439 cm^{-1} are the C–O asymmetric and symmetric stretching modes, respectively. The CO_3 group-bending mode creates a peak at 869 cm^{-1} [18–23]. The FTIR spectra of $LiOH \cdot H_2O$ (Fig. 2d) show a single sharp band of isolated OH stretching vibration for free LiOH at 3563 cm^{-1} [17], a broad band of OH stretching vibrations of hydrogen-bonded for LiOH in 3510–2800 cm^{-1}. The broad peaks at 1540 cm^{-1} and 1442 cm^{-1} are the C–O asymmetric and symmetric stretching modes of Li_2CO_3, respectively. The CO_3 group-bending mode creates a peak at 870 cm^{-1} [17–23]. The absorption bands originating from the Li–O-group were located at 985 cm^{-1} [23]. In contrast to the FTIR spectra of $LiOH \cdot H_2O$ and Li_2CO_3, no obvious OH stretching vibration was observed for Li_2CO_3. This result corresponds to the $LiOH \cdot H_2O$ reacted with CO_2 to form Li_2CO_3 on the surface of the Li_4SiO_4 catalyst in the air for 24 h, and the OH stretching vibration of LiOH was disappeared (Fig. 2a,b).

Table 1
Base strengths (H_) of $Li_4SiO_4$and CaOafter exposing to air.

Exposure time (h)	Li_4SiO_4	conversion*	CaO	conversion**	Li_2CO_3	conversion***
0	12.2–15.0	98.6	15.0–18.4	95.2	9.8–12.2	95.5
24	12.2–15.0	98.1	7.2–9.8	2.9	9.8–12.2	98.6
48	12.2–15.0	95.8	7.2–9.8	2.5	9.8–12.2	95.5
72	12.2–15.0	96.6	7.2–9.8	1.3	9.8–12.2	95.1
used	12.2–15.0	97.3			9.8–12.2	93.9

* Reaction conditions: methanol to oil molar ratio = 18:1; catalyst amount = 6 wt.%; reaction temperature = 65 °C; reaction time = 2 h.
** Reaction conditions: methanol to oil molar ratio = 12:1; catalyst amount = 3 wt.%; reaction temperature = 65 °C; reaction time = 2 h.
*** Reaction conditions: methanol to oil molar ratio = 30:1; catalyst amount = 10 wt.%; reaction temperature = 65 °C; reaction time = 3 h.

Table 1 shows the basic strength of Li_4SiO_4, CaO and Li_2CO_3 after different exposure times to ambient air (temperature 25 ± 2 °C, relative humidity: 50 ± 5%). The effect of exposure to air on the catalytic activity of the transesterification reaction was examined. CaO appeared to exhibit more initial basic strength ($15.0<H\_<18.4$) than Li_4SiO_4 ($12.2<H\_<15.0$) did. However, the basic strength of CaO deactivated obviously following the exposure of the catalysts to air ($7.2<H\_<9.8$), thus influencing the conversion to FAME. This deactivation was probably due to the hydration, followed by carbonation on the surface, even after a 3 min exposure to air, when the CaO was appreciably deactivated [8]. This severely limited its practical application due to the need for inert atmosphere during handling, storage, reactor loading, and use.

The basic strength (H–) of Li_4SiO_4 was maintained in the range of 9.8–12.2, even after exposure to air for 72 h; therefore, no obvious differences manifested in the soybean oil conversion between the air-exposed Li_4SiO_4 catalyst (24 to 72 h) (97.0 ± 1.1%) and the as-prepared Li_4SiO_4 catalyst (98.6%), which verified that the catalytic sites of Li_4SiO_4 tolerated the CO_2 and H_2O contained in the air. Li_4SiO_4 was the solid base catalyst with the advantage of tolerance to air-exposure, which facilitated the operation of the catalytic reaction. The basic strength (H_) of Li_2CO_3 was also maintained in the range of 9.8–12.2, even after exposure to air for 72 h; therefore, no obvious differences manifested in the soybean oil conversion between the air-exposed Li_2CO_3 catalyst (24 to 72 h) (97.1 ± 1.1%) and the fresh Li_2CO_3 catalyst (95.5%). This implied that the catalytic activity of Li_4SiO_4 catalyst was not obviously deactivated than CaO due to the hydration, followed by carbonation in the air on the catalyst surface.

Lithium orthosilicate (Li_4SiO_4) has been widely studied as a promising carbon dioxide (CO_2) absorbent [23]. The process of CO_2 capture, using Li_4SiO_4 as a solid absorbent, occurs according to the following reaction [26]:

$$Li_4SiO_{4(s)} + CO_{2(g)} \leftrightarrow Li_2CO_{3(s)} + Li_2SiO_{3(s)} \tag{1}$$

Kato and Nakagawa [27] used a thermogravimetric instrument to analyze the CO_2 absorption of Li_4SiO_4 in dry, pure CO_2 gas, with a flow rate of 300 ml/min; the clear weight increase was observed at approximately 720 °C. The weight change was approximately 35 mass%, which responded to the amount of CO_2 absorption; however, the absorption rate is extremely slow (below 200 °C). The XRD patterns (Fig. 1.) correspond with this view, because the Li_4SiO_4 did not obviously decompose to Li_2CO_3 and Li_2SiO_3 by absorbing CO_2 in the air at room temperature. The Li_2CO_3 species were observed in the FTIR spectrum of Li_4SiO_4 (Fig. 2), indicating a favorable dispersion of a small amount of Li_2CO_3 on the surface of Li_4SiO_4, but no obvious catalytic degradation in the transesterification reaction (Table 1).

Feng Guo et al. used Na_2SiO_3 as an efficient solid base catalyst in the transesterifying soybean oil with methanol [28]. Na_2SiO_3 was hygroscopic and easy to deliquesce in the air [29]. In contrast to Na_2SiO_3, Li_4SiO_4 was a more anti-deliquescent catalyst in the air. The SEM patterns (Fig. 3.) correspond with this view, because no further particle adhesion was apparent, indicating that Li_4SiO_4 was not easily deliquesced in air for at least 24 h. Ortiz-Landeros et al. examined the hydration process of Li_4SiO_4 [23] to elucidate water absorbed by Li_4SiO_4 particles, using a TGA method. In their report, only approximately 0.045% (wt/wt Li_4SiO_4) water adsorption on the Li_4SiO_4 surface was observed at 26 °C and 60% RH. The CaO catalyst was easy to chemisorb H_2O and transform to $Ca(OH)_2$ in the air. Fig. 2 displays the FTIR spectrum of Li_4SiO_4 exposed to air for 24 h, and the residual LiOH that reacted with CO_2 in the air to form Li_2CO_3 over the surface of the Li_4SiO_4. Because Li_2CO_3 was an efficient solid base catalyst in the transesterification reaction, Li_4SiO_4 stably maintained its catalytic activity.

Fig. 3 shows the typical SEM images of the as-prepared Li_4SiO_4 and Li_4SiO_4 exposed to air for 24 h. All Li_4SiO_4 catalysts particles show obvious agglomeration and nonhomogeneous polyhedral crystals with a side length of approximately 10–50 μm. Fig. 3b shows a great amount of the small particles cohered on the surface of Li_4SiO_4 catalyst after exposureto air for 24 h which caused by Li_4SiO_4 hydration, followed by carbonation in the air on the catalyst surface. Fig. 3 also shows the typical SEM images of the fresh Li_2CO_3 and Li_2CO_3 exposure to air for 24 h. There were no obvious small particles cohered on the surface of Li_2CO_3 after exposure to air for 24 h, implying that the hydration and carbonation reaction in the air on the Li_2CO_3 surface was slight.

TGA curve (Fig. 4) for the as-prepared Li_4SiO_4 catalyst, produced by the solid state method, showed that the first reduction of weight was produced between room temperature and 65 °C, and it was attributed to a evaporation process of residual methanol. The second weight loss, which occurred between 130 and 250 °C, was attributed to the dehydration of the sample. A large mass loss, corresponding to two united endothermic peaks, was detected between 490 and 750 °C. It might be resulted from the complicated reactions between the lithium compounds and silicon compounds [30], which might be divided into two steps [31]:

$$515–565^\circ C: Li_2CO_3 + SiO_2 \rightarrow Li_2SiO_3 + CO_2$$

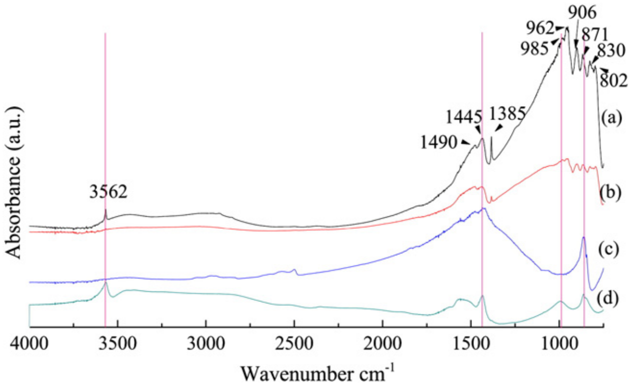

Fig. 3. FTIR spectra of the (a) Li_4SiO_4 exposure to air for 24 h, (b) Li_4SiO_4, (c) Li_2CO_3 and (d) $LiOH \cdot H_2O$.

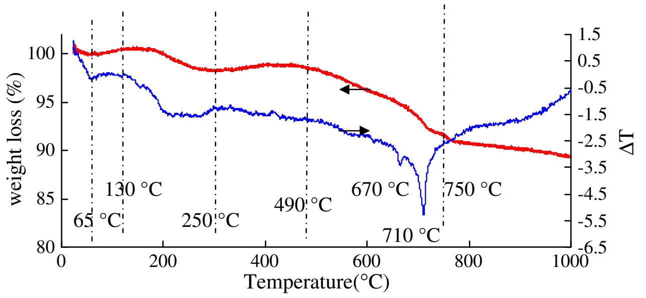

Fig. 4. TG-DTA curves for the as-prepared Li_4SiO_4 sample.

$$565\text{–}730^{\circ}\mathrm{C} : Li_2CO_3 + SiO_2 \rightarrow Li_2SiO_3 + CO_2$$

$$\text{and then } Li_2SiO_3 + Li_2CO_3 \rightarrow Li_4SiO_4 + CO_2 \quad (2)$$

Although the XRD analyses did not show the presence of impurities (Li_2CO_3 and SiO_2), which might be formed after the experiment from a decomposition reaction of Li_4SiO_4 with moisture and CO_2 in the air, the thermal analyses demonstrated that both materials contained some minor impurities. Note that the lower limit detection by XRD technique depends on the scattering properties of the components of the materials. Silicates, typically, are detected when the concentration is higher than 3%, and the size crystal is bigger than 3 nm [32]. The phase transition of Li_4SiO_4 into a pseudo-orthorhombic structure was observed by differential thermal analysis (DTA) during heating at 670 and 710 °C [33]. After the third change, the weight kept decreasing slowly with an endothermic signal, showing the vaporization of $Li_2O_{(s)}$ being able to easily take place [34].

3.2. Optimization of transesterification reaction conditions

This study also investigated the effects of catalyst amount on conversion. The catalyst amount was varied in the range of 2–10 wt.% (catalyst/oil weight ratio). As shown in Fig. 5, the conversion was increased as the catalyst amount increased from 2 to 4 wt.%. The conversion reached a plateau value at the catalyst weight percentage between 4 and 10%. Additional catalysts increased the contact opportunity of the catalyst and the reactant, which directly influenced the reaction speed and the conversion. In heterogeneous catalysis, mass transfer and reactant adsorption on the catalyst are extremely crucial; therefore, a molar ratio higher than the stoichiometric molar ratio of methanol is required to shift the equilibrium for the reaction [35]. As shown in Fig. 5, with an increase in the methanol-loading amount, the conversion was increased considerably. The maximal conversion ratio was 98.1% at the methanol/oil molar ratio of 18:1. Fig. 6 displays the effects of reaction time and reaction temperature on conversion. The conversion was increased steadily within the reaction time range of 1 h, and thereafter remained nearly constant as a result of a nearly equilibrium conversion. For the transesterification of refined soybean oil with methanol (1:18) using 6 wt.% Li_4SiO_4, five different temperatures were used. After 2 h, conversions were 99.1, 98.4, 95.0, 95.6 and 59.4% for 65, 55, 45, 40 and 25 °C, respectively. Temperature clearly influenced the reaction rate and the biodiesel purity.

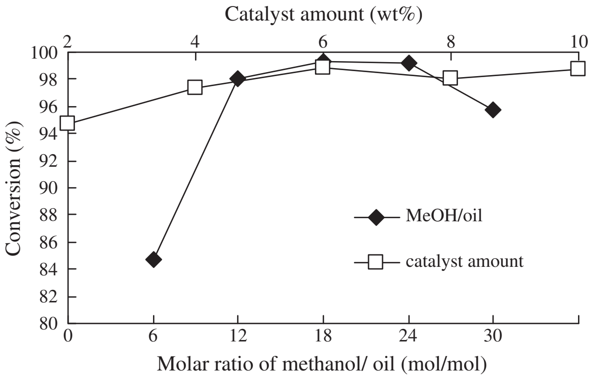

Fig. 5. Influence of catalyst amount (reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 18:1, reaction time 2 h, reaction temperature 65 °C) and methanol/oil molar ratio on the conversion (reaction conditions: 12.5 g soybean oil, catalyst amount 6 wt.%, reaction time 2 h, reaction temperature 65 °C).

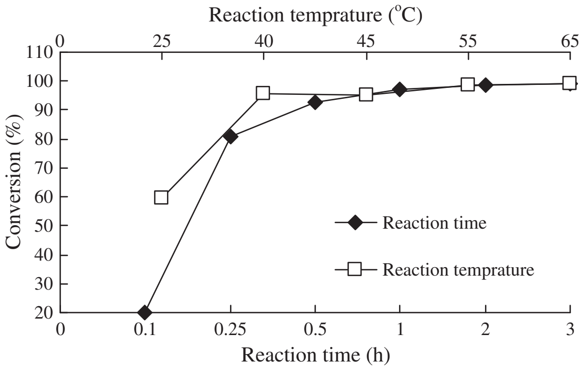

Fig. 6. Influence of reaction time (reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 18:1, catalyst amount 6 wt.%, reaction temperature 65 °C) and reaction temperature on the conversion (reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 18:1, catalyst amount 6 wt.%, reaction time 2 h).

3.3. Reusability of the catalyst

After the transesterification was completed, the samples were recovered using simple decantation. The remaining catalyst in the reactor was used to catalyze the next batch of transesterification. In Fig. 7, 96.1% of the FAME purity could be obtained even after recycling six times. The FAME purity was slightly reduced to 94.6 ± 0.5% when Li_4SiO_4 was reused seven to ten times (Fig. 7), because the amount of catalyst used in the next run was lower than that in the initial run, which might partly be responsible for the reduced biodiesel purity during the subsequent run. Glycerol covering the surface of the catalyst was also considered as the reason for activity loss. To maintain a fixed oil/catalyst mass ratio in all successive cycles, the amount of oil and methanol was reduced appropriately to make a better comparison. The catalysts were washed with anhydrous methanol and dried at 95 °C (water bath) for 1 h under a vacuum (water-pump

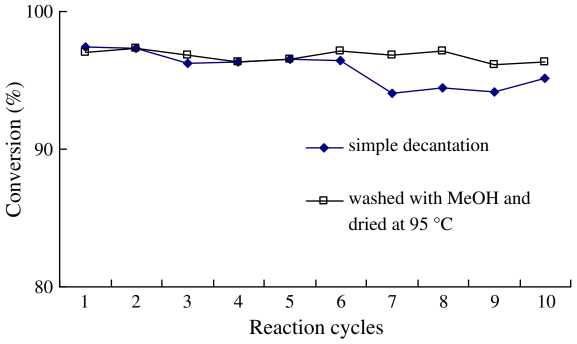

Fig. 7. Reusability study after seven reaction cycles for Li_4SiO_4catalyst, reaction conditions: catalyst amount 6 wt. %, methanol/oil molar ratio 18:1, reaction time 2 h, reaction temperature 65 °C.

suction). As shown in Fig. 7, 96.3% of the FAME purity was obtained after recycling ten times.

In contrast to Na_2SiO_3 [36] and Li_2SiO_3 catalysts [28] being obviously degradable before eight recycling, Li_4SiO_4 catalyst was more stable for recycling process in the transesterification reaction. Of the alkali and alkali earth oxides, CaO is one of the solids that demonstrate higher transesterification activities [9]. The glycerol released during the transesterification reaction reacts with CaO forming Ca glyceroxides [7]. In the present study, after catalyst regeneration, the crystalline phase of the Li_4SiO_4 catalyst remained unchanged (Fig. 1), indicating that Li_4SiO_4 has greater stability than CaO in the transesterification reaction and can recover its activity following a suitable catalyst regeneration process.

The solubility of the catalysts was also a critical factor to consider for correct interpretation of their performances and assessment of their potential practical application. This was a significant issue because the presence of metal would necessitate neutralization and washing steps in the production process, thus nullifying the possible advantage of using these compounds as heterogeneous catalysts. The first transesterification reaction produced oil containing 0.4 ppm of lithium and glycerol containing 147.0 ppm of lithium. As shown in Table 2, repeating the process one to three times maintained the conversion ratio to FAME at 97.1 ± 0.4%, and exposure to air from 24 to 72 h maintained the conversion ratio at 97.2 ± 1.3%. These results demonstrated that extremely small quantities (free Li^+ concentration of less than 1 ppm) existed in the biodiesel. The obtained results indicated that the prepared Li_4SiO_4 catalyst was stable for use in biodiesel production from soybean oil (Table 3).

3.4. Comparison of the activity with CaO and Li/CaO catalysts

Calcium oxide (CaO) as a catalyst has received attention among researchers worldwide for the development of biodiesel because of its low cost and simple preparation process. Granados et al. [9] used the activated calcium oxide as a solid base catalyst in the methanolysis of sunflower oil to avoid reduction of CaO catalytic activity. The catalyst was thermally treated at 700 °C to chemically desorb CO_2 prior to being used in the reaction. After a 100 m reaction time, 94% conversion was obtained at 60 °C with alcohol/oil molar ratio of 13:1 and catalyst content of 3 wt.% based on the weight of the oil. Huaping et al. [37] used CaO as a heterogeneous catalyst for biodiesel synthesis from Jatropha curcas oil. The base strength of calcium oxide increased to 26.5 (grouped in the category of super base) following treatment with ammonium carbonate solution and further calcination. Calcination at 900 °C resulted in a 93% conversion of jatropha oil to FAME in optimized conditions (70 °C temperature, 2.5 h reaction time, 1.5 wt.% catalyst amount, and 9:1 methanol to oil molar ratio). Calcium oxide impregnated with Li_2CO_3 was shown to be effective for the complete transesterification of used cottonseed oil at 65 °C with an oil/methanol molar ratio of 1:12, even in the presence of (i) 15 wt.% moisture in 2.5 h, (ii) 6 wt.% of free fatty acid in 2.5 h, (iii) 5 wt.% moisture and 2 wt.% free fatty acid content in 4 h [11]. Calcium oxide impregnated with 1.75 wt.% of lithium was used as a solid catalyst for the transesterification of karanja and jatropha oil, containing 3.4 and 8.3 wt.% of free fatty acids, respectively [12]. The complete transesterification of karanja and jatropha oils was achieved in 1 and 2 h, respectively, at 65 °C, utilizing a 12:1 molar ratio of methanol to oil and 5 wt.% (catalyst/oil, w/w) of catalyst. Transesterification of soybean oil with methanol has been studied in a heterogeneous system on Li-doped MgO catalysts [13]. The catalyst with a Li/Mg molar ratio of 0.08 and calcined at 550 °C displays the highest FAME yield of 93.9% at 60 °C with a molar ratio of methanol/soybean oil of 12 and the catalyst amount of 9 wt. %. Table 3 shows the CaO, Li/CaO, Li/MgO and Li_4SiO_4 catalysts and their reaction conditions.

Table 2
Metal leaching of the Li_4SiO_4 upon reuse and air exposure.

	Biodiesel conversion (%)	Li leaching (ppm)
First use	97.5	0.4
Second use	97.3	0.3
Third use	96.7	0.6
Exposure to air 24 h	98.5	0.3
Exposure to air 48 h	95.8	0.4
Exposure to air 72 h	96.6	0.4

Table 3
CaO, Li/CaO, Li/MgO and Li_4SiO_4 used as heterogeneous catalysts.

Catalyst	Catalyst preparation	Feedstock	Operation conditions	Conversion (C)/yield (Y) (%)	Ref.
CaO	Calcined at 1000 °C	Sunflower oil	T = 60 °C, t = 100 min, alcohol/oil = 13:1, catalyst content = 3%	C = 94%	[9]
CaO	Treatment with ammonium carbonate and calcined at 900 °C	Jatropha oil	T = 70 °C, t = 150 min, alcohol/oil = 9:1, catalyst content = 1.5%	C = 93%	[32]
Li/CaO	Impregnated with 1.5 wt.% of lithium and heated at 120 °C for 24 h	Used cottonseed oil with 15 wt.% moisture	T = 65 °C, t = 150 min, alcohol/oil = 12:1, catalyst content = 5%	C > 99%	[11]
Li/CaO	Impregnated with 1.75 wt.% of lithium and heated at 120 °C for 24 h	Karanja oil with 3.4 wt.% FFA	T = 65 °C, t = 60 min, alcohol/oil = 12:1, catalyst content = 5%	C > 99%	[12]
Li/CaO	impregnated with 1.75 wt.% of lithium and heated at 120 °C for 24 h	jatropha oil with 8.3 wt.% FFA	T = 65 °C, t = 120 min, alcohol/oil = 12:1, catalyst content = 5%	C > 99%	[12]
Li/MgO	Li/Mg molar ratio of 0.08 and calcined at 550 °C for 10 h in a flowing He	Soybean oil	T = 60 °C, t = 120 min, alcohol/oil = 12:1, catalyst content = 9%	Y = 93.9%	[13]
Li_4SiO_4	Li/Si molar ratio of 4 and calcined at 900 °C for 4 h	Soybean oil	T = 65 °C, t = 120 min, alcohol/oil = 18:1, catalyst content = 6%	C = 98%	

3.5. Properties of biodiesel

To confirm the quality of the final product obtained under the optimal conditions, a certified authority analyzed the biodiesel samples for characteristics of commercial biodiesel fuels (Chinese Petroleum Corporation, Chiayi Laboratory). Table 4 summarizes the resulting properties of biodiesel, such as ester content, free glycerol, total

Table 4
Comparison of properties of the obtained biodiesel and the standards of biodiesel in the United States and Europe.

Property	Unit	Value	ASTM D-6751	EN 14214
Esters content	wt.%	98.1		> 96.5
Free glycerol	wt.%	0.008	< 0.02	
Total glycerol	wt.%	0.12	< 0.24	
Density at 15 °C	kg/m^3	889		860–900
Flash point	°C	161	> 130	> 120
Sulfur content	mg/kg	2.4	15	10
kinematic viscosity at 40 °C	cSt	4.1	1.9–6.0	3.5–5.0
Copper corrosion		1A	NO.3 max	Class 1
Cetane number		54	> 47	> 51
Iodine number	g I_2/100 g	115		< 120
Acid value	mg KOH/g	0.10	< 0.5	

glycerol, density, flash point, sulfur content, kinematic viscosity, copper corrosion, cetane number, iodine value, and acid value. The testing results revealed that the present study's biodiesel/FAME product fulfilled most of the criteria assigned by international standards.

4. Conclusions

This study developed a Li_4SiO_4 catalyst for application to the biodiesel production. The following conclusions were drawn:

(1) The experimental results show that Li_4SiO_4 demonstrated excellent catalytic activity and stability because of its basic strength above 12.2 and because it is stable in transesterification reactions. Li_4SiO_4 is easy to synthesize using a solid-state reaction and can be used for biodiesel production directly without further catalyst synthesis processes, involving either drying or thermal treatment.

(2) For many base-catalyzed reactions, solid base catalysts are easily poisoned by carbon dioxide and water. The high sensitivity to these molecules has prevented the solid base catalysts from being used in a practical process. However, the Li_4SiO_4 catalysts are tolerant to water and carbon dioxide and the catalytic activity of transesterification reactions were not reduced. Moreover, the favorable lifetime of the reuse characteristics of Li_4SiO_4 catalysts is appropriate for industrial production.

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