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Short communication

Synthesis and characterization of magnetic $LiFe_5O_8$-$LiFeO_2$ as a solid basic catalyst for biodiesel production

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ABSTRACT

This study is focused on the transesterification of the soybean oil into biodiesel using magnetic based solid catalysts ($LiFe_5O_8$-$LiFeO_2$). The catalyst was prepared through a simple solid-state reaction that involved mixing and grinding iron oxide (Fe_2O_3) and Li_2CO_3. The results demonstrated that the catalyst was ferromagnetic. Under the optimal reaction conditions, the highest FAME conversion in the transesterification of soybean oil can reach 96.5% by using $LiFe_5O_8$-$LiFeO_2$ catalyst. The $LiFe_5O_8$-$LiFeO_2$ demonstrates excellent catalytic activities and it could be recovered by magnetic separation. The $LiFe_5O_8$-$LiFeO_2$ can be easily recovered and reused without significant deactivation.

1. Introduction

There is an increasing demand for discovering alternative energy sources to meet the increasing energy needs in the world [1]. Therefore, many scientists strongly suggest replacing fossil fuel with biofuel in the future. Among biofuel sources, animal and plant oils have attracted considerable attention as the potential resources for producing an alternate petroleum-based diesel fuel [2–4].

Nowadays, the homogeneous basic catalysts are most preferred in the commercial production of biodiesel due to the low cost and availability [5–7]. Although homogeneous catalyst is the most common catalysts for the transesterification of animal or plant oil catalyzed into biodiesel, they possess serious problems such as the catalyst cannot be recovered or reused, and high cost, low efficiency and generates large amounts of wastewater [8]. In addition, general a large amount of water is required for the subsequent purification of the biodiesel. The use of heterogeneous catalysts could definitely improve the processes and alleviate these problems associated with the use of homogeneous catalyst. Heterogeneous solid base catalysts are advantageous because they can be easily separated and are recyclable, ecofriendly, and environmentally benign [9].

In recent years, it is interesting to modify the structures of surface metal oxide species in order to improve their catalytic properties for specific applications. Modifying catalyst on a suitable is considered desirable owing to its several advantages of repeated use, ease of separation from the product, manipulation of catalyst properties, improved stability, and easy storage. Modified catalyst as host material are associated with mainly two unique properties, such as (1) easy separation from the reaction medium during processing and (2) large specific surface area enabling high loading of base sites. In this context, the recently developed Li-based catalysts proved to display unexpected catalytic properties and stability [10–12]. Dai et al. [13] reported that solid base catalyst, prepared by solid-state reaction, enhanced the conversion. Chen et al. [14] reported that the significant enhancement of catalytic activity was achieved by using SiO_2 and Li_2CO_3, loading to a high amount of basic site.

Furthermore, magnetic materials have a new developing direction due to the applications of nanotechnology [15].In catalysis research, the magnetic materials can act as promising solid-base catalysts, because the magnetic structure manipulation provides catalysts obtaining with a larger amount of active base sites, thereby promoting a high surface area. Especially, some solid magnetic catalysts are convenient for magnetic separation, generally avoid the loss of catalyst and increase its recovered in comparison to filtration or centrifugation [16,17].

In our previous study, we applied Li_2CO_3 to transesterification and demonstrated that Li_2CO_3 catalysts had a high conversion for transesterification. However, usually catalysts are separated from the reaction means by filtration steps, thereby, much research has been devoted to the development of easily separable catalysts where in this item the magnetic $LiFe_5O_8$-$LiFeO_2$ become even more attractive and preponderant. The components of these solid catalysts were identified as lithium–iron oxide, namely $LiFe_5O_8$-$LiFeO_2$.

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2. Materials and methods

2.1. Materials

Soybean oil (Great Wall Enterprise Co., Taiwan), methanol (ACS grade, ECHO Chemical Co., Miaoli, Taiwan), reagent grade Li_2CO_3 (Shimakyu's Pure Chemicals, Osaka, Japan), reagent grade Fe_2O_3 (Panreac Quimica, S.L.U.) was used as received.

2.2. Catalyst preparation

The $LiFe_5O_8$-$LiFeO_2$ was synthesized by the simple solid-state reaction. A stoichiometric amount of Fe_2O_3 and Li_2CO_3 were homogeneously mixed with water. Fe_2O_3 was added to an aqueous solution containing Li_2CO_3 (Li_2CO_3/Fe_2O_3 molar ratio of 1) were well homogeneously mixed into crucible was calcination temperatures (600 °C, 700 °C, 800 °C, 900 °C) in muffle furnace, and then cooled to room temperature.

2.3. Reaction procedures

Soybean oil was converted to biodiesel in a flat-bottom flask equipped with a refluxed condenser and a magnetic stirrer. The reactor was initially filled with 12.5 g of soybean oil, which was heated to 65 °C while stirring at 300 rpm. The reactant was stirred evenly in the flask to avoid splashing. The effects of the methanol/oil molar ratio and catalyst loading on the conversion of triglycerides to biodiesel were investigated. All experiments were performed at atmospheric pressure.

2.4. Catalyst characterization

The basic strength of the as-prepared catalyst (H_) was determined using Hammett indicators. About 100 mg of the sample was shaken with 2 mL of Hammett indicators and then left to equilibrate for 2 h when no further color changes were observed. X-ray diffraction (XRD) data for the products were measured at 295 K on a powder diffractometer (AC MXP18, Tokyo, Japan, λ = 1.54056 Å). For phase identification, XRD data were collected in a range 2 from 20^o to 80^o with a step interval 0.02. The microstructure of the as-prepared catalyst was observed using a Field emission scanning electron microscopy energy dispersive spectroscopy, (FESEM-EDS, JEOL, JSM-7401, Tokyo, Japan). The specific surface areas (BET) of the particles were measured by nitrogen adsorption on the basis of the Brunauer–Emmett–Teller equation with a surface area analyzer (BET; Micromeritics, Gemini 2370C). The magnetization curves and hysteresis loop of the sample were characterized with a model 4HF vibrating sample magnetometer (ADI) with a maximum field of 18 kOe at room temperature.

2.5. Analytical methods

FAME concentrations, expressed as the biodiesel purity of the product, were determined using a gas chromatography system (Thermo Trace GC Ultra, Thermo Co., Austin, Texas, USA) equipped with a flame ionization detector, a capillary column (Tr-biodiesel (F), Thermo Co., length: 30 m; internal diameter: 0.25 mm; and film thickness: 0.25 μm), a programmed column oven, and a programmed temperature injector. The oven temperature was programmed as follows: starting at 120 °C, an increase to 220 °C at a rate of 30 °C/min, and an increase to 250 °C at a rate of 10 °C/min. The temperature of the programmed temperature injector was 90 °C for 0.05 min and increased to 260 °C (programmed temperature) at a rate of 10 °C/min. Nitrogen was used as the carrier gas at a flow rate of 2 mL/min. The conversion was determined according to the following equation.

$$\text{Conversion\%} = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times A_{EI}}{m} \times 100\%$$

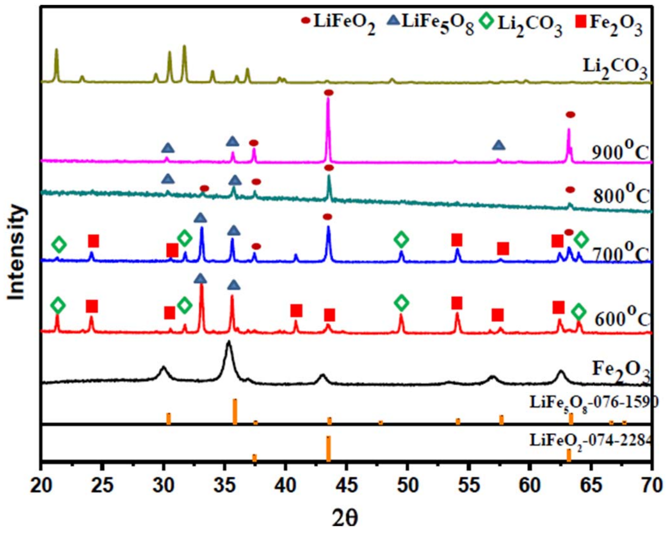

Fig. 1. XRD patterns of the $LiFe_5O_8$-$LiFeO_2$ prepared using various calcination temperatures.

ΣA: Sum of areas of all peaks ranging from C14:0 and C24:0, A_{EI}: Heptadecanoic acid methyl ester IS area, C_{EI}: Concentration (mg/mL) of Heptadecanoic acid methyl ester solution, V_{EI}: Volume of Heptadecanoic acid methyl ester solution added to sample, m: Mass of the sample (mg).

3. Results and discussion

Fig. 1 shows the XRD patterns of Li_2CO_3, Fe_2O_3, and $LiFe_5O_8$-$LiFeO_2$ with 2θ scanning from 20° to 80°. When calcination occurred at 600 °C, the Fe_2O_3 and Li_2CO_3 underwent decarbonization and dehydration processes that led to the formation of $LiFe_5O_8$. Upon the calcination at 800 °C, this is possibly resulted from the complex reactions between Li and Fe compounds. The increasing calcination temperature leads to the crystallization of the catalyst into a new structure. Li^+ is sucked into the gap in the Fe compound crystal layers and reacts with Fe to produce mixture of crystalline $LiFe_5O_8$ and $LiFeO_2$. The conversion equations in calcination were described as follows:

$$Li_2CO_3 + Fe_2O_3 \rightarrow 2LiFeO_2 + CO_2 \quad 600 - 700^{\circ}C \tag{1}$$

$$Li_2CO_3 + 5Fe_2O_3 \rightarrow 2LiFe_5O_8 + CO_2 \quad 700 - 800^{\circ}C \tag{2}$$

Therefore, mixture of crystalline $LiFe_5O_8$ and $LiFeO_2$ is the major active site for the reaction.

The physical and chemical properties of $LiFe_5O_8$-$LiFeO_2$, including basic strength, surface area, and pore size, are summarised in Table S1. From this Table, it can be seen that the specific surface area are between 1.18 and 5.32 $m^2\,g^{-1}$, but basic strength has significant variation after Li replaces Fe. It is determined that the conversion is not directly related to the surface area and pore volume, but the conversion agrees well with the basic strength generated during a large amount active Li–O sites with the calcination temperature. The weak and broad peaks can be observed in pore size distributions of the 100 nm (see Fig. S2), the enhancement of pore size represents more active Li–O sites.

$LiFe_5O_8$-$LiFeO_2$ can be characterized by FT-IR spectrum. $LiFe_5O_8$-$LiFeO_2$ was prepared by Fe_2O_3 and Li_2CO_3 using a simple solid-state reaction method at different calcination temperature, as shown in Fig. 2. The peaks at 1411 cm^{-1} and 857 cm^{-1} are assigned to stretching the vibration of C—O and the deformation vibration of C—O—C, respectively. It shows that the main IR bands at 526 and 447 cm^{-1}, which are attributed to Fe—O stretching modes. With the increasing calcination temperature, the peak intensity of the phase of C—O decreases. Upon calcination temperature at 800 °C, Fe_2O_3 and Li_2CO_3 undergoing decarbonization and dehydration processes leads to

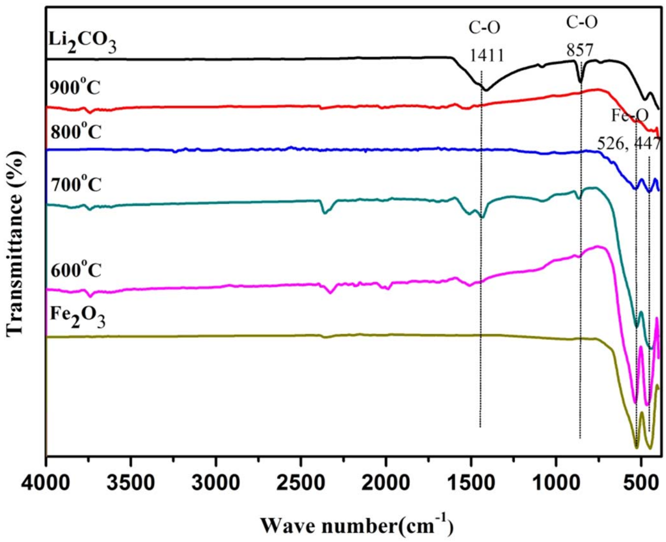

Fig. 2. FTIR patterns of the $LiFe_5O_8$-$LiFeO_2$ prepared using various calcination temperatures.

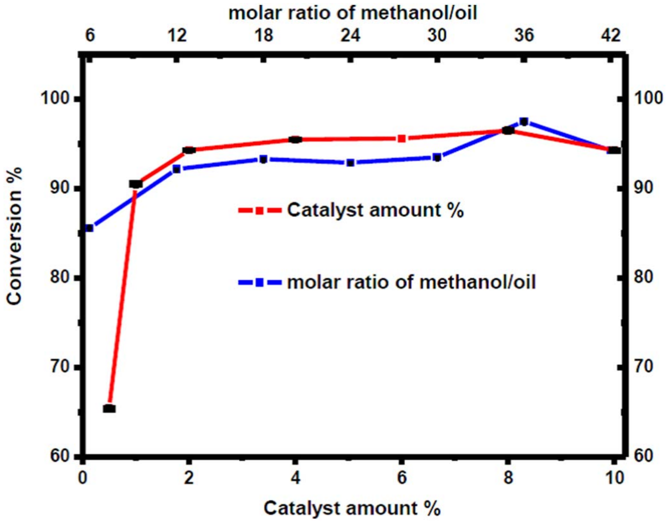

Fig. 4. Influence of calcination temperature and time on the conversion reaction on the conversion rate (reaction conditions: soybean oil; 12.5 g, reaction temperature; 65 °C, and reaction time; 2 h).

the formation of $LiFe_5O_8$-$LiFeO_2$. It is consistent with the XRD result.

Fig. S1 shows the FE-SEM image with different calcination temperature of $LiFe_5O_8$-$LiFeO_2$. The catalyst is prepared with homogeneously mixing Fe_2O_3 and Li_2CO_3 by the simple solid-state reaction. Fig. S1(a), Fe_2O_3 and Li_2CO_3 calcined at 600 °C, a lot of Li_2CO_3 still exist and keep their microstructure. Some homogeneous small mineral aggregates have very rough surface. Fig. S1(b) sheet needle aggregates and agglomerated particles were present when the calcination temperature increased because of the formation of $LiFe_5O_8$ phase. Fig. S1(c) shows the FE-SEM images of mixture of crystalline $LiFe_5O_8$-$LiFeO_2$ with impermeable porous surface. The temperature exceeded 800 °C because many of the s sheet needle aggregates and flakes cohered on the surface entered a molten state formation with very smooth surface. Fig. S1(d) presents FE-SEM images at 900 °C. While at calcination temperature 900 °C, the particles show the obvious agglomeration and gradually shape lumps.

Magnetic solid alkaline catalysts are convenient to be separated from the biodiesel by a magnet [17,18]. Magnetic hysteresis measurement for magnetic solid alkaline catalysts is carried out in applied magnetic field at 298 K, with the field sweeping from − 15 to 15 kOe. The hysteresis loop (Fig. 3) of the sample does not reach the saturation up to the maximally applied magnetic field. The magnetization measurement of the sample exhibits a hysteretic feature with the coercivity (Hc) and remanent magnetization (Mr) being determined to be 1000 Oe and 0.64 emu/g, respectively, suggesting that $LiFe_5O_8$-$LiFeO_2$ exhibits ferromagnetic characteristic at 298 K. It shows that $LiFe_5O_8$-$LiFeO_2$ can be easily separated from the biodiesel using an external magnet.

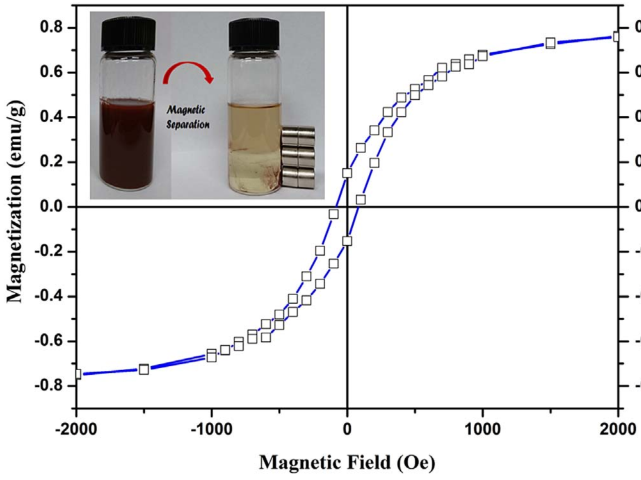

Fig. 3. Hysteresis loop of $LiFe_5O_8$-$LiFeO_2$ measured at 298 K.

3.1. Reaction studies

Fig. 4 shows the conversion at different calcination temperature of $LiFe_5O_8$-$LiFeO_2$ through the transesterification process. In order to investigate the effects of the calcination conditions, several calcination temperatures (600 °C, 700 °C, 800 °C, and 900 °C) were considered, the conversion increased and the optimal calcination temperature for the catalyst was at 800 °C. At this temperature, the highest conversion of 96.5% was achieved, the conversion rate decreased when the temperature was 900 °C, and a further increase in the calcination temperature suppressed the catalytic activity of $LiFe_5O_8$-$LiFeO_2$. As can be seen, the deactivation of the $LiFe_5O_8$-$LiFeO_2$ after its calcination at high temperature is probably the result of the loss of basic sites, by the sublimation and agglomeration into the structure [6]. Therefore, the optimal calcination temperature is 800 °C in this study. Enough calcination time is required to obtain a complete decomposition of Fe_2O_3 and Li_2CO_3 in preparation for $LiFe_5O_8$-$LiFeO_2$. Fig. 4 shows effects of calcination time on conversion rate. The calcination time significantly influences the transesterification reaction, where the conversion increased with an increase in calcination time. The increasing calcination time leads to obtain a complete decomposition into a new structure. It is possible that the presence of $LiFe_5O_8$-$LiFeO_2$ structure, where the $LiFe_5O_8$-$LiFeO_2$ are in close interaction, results in a more active sites of surface, which in turn leads to higher conversions rate [9]. This also agrees with the base strength of the samples in Table S1. It was suggests that the $LiFe_5O_8$-$LiFeO_2$ contained a large amount basic sites of $9.8 < H\_ < 15.0$ on the $LiFe_5O_8$-$LiFeO_2$, causing the catalysts for the high activity towards transesterification reaction.

The effect of methanol to oil molar ratio on the transesterification was also investigated. One of the important variables affecting the biodiesel is the molar ratio of methanol to triglyceride [19]. However, the methanol to oil molar ratio should be higher than that of the stoichiometric molar ratio in order to drive the reaction towards the completion and shift it to the right hand side to produce more biodiesel [12]. The excess methanol can be collected and recycled. As is evident from Fig. 5, when the molar ratio was increased from 12, the conversion increased. The maximum conversion rate was obtained when the methanol/oil molar ratio was 36. These results indicate that the maximum

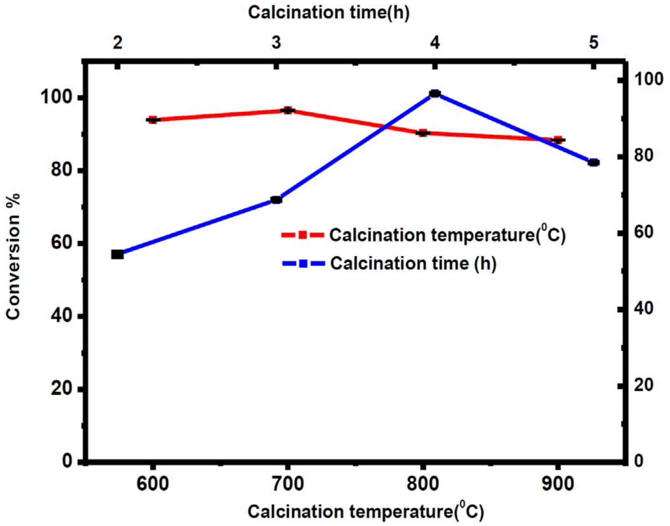

Fig. 5. Influence of the methanol/oil molar ratio and catalyst amount on the conversion rate (reaction conditions: soybean oil; 12.5 g, reaction temperature; 65 °C, and reaction time; 2 h).

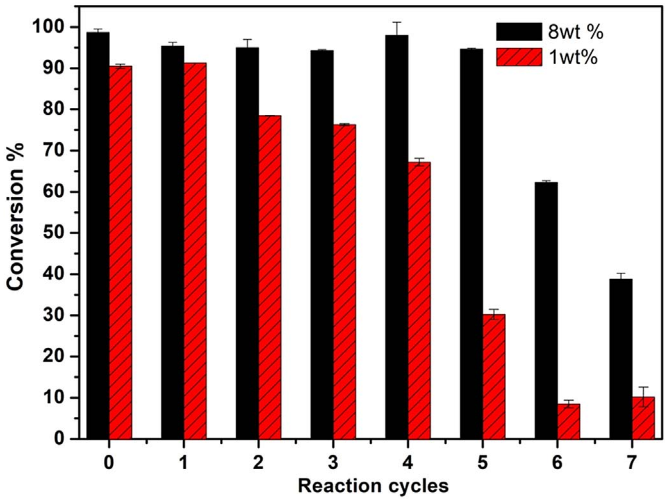

Fig. 6. Reusability study after 5 reaction cycles for $LiFe_5O_8$-$LiFeO_2$ catalyst. (Reaction conditions: methanol /oil ratio 36:1, catalyst amount 8 wt%, reaction temperature 65 °C and reaction time 2 h).

conversion is 96.5% for $LiFe_5O_8$-$LiFeO_2$.

Moreover, the effect of catalyst loading on the transesterification was also investigated. As shown in Fig. 5, the conversion rate was increased considerably with the catalyst loading increasing from 2 to 10. However, the further increase of catalyst loading higher than 8 showed very limited effect on the conversion rate. Wang et al. [20] also observed similar results, when the conversion increased with an increase in the $LiFe_5O_8$-$LiFeO_2$ loading. So, the excess of mass transfer content might affect the catalyst and catalytic conversion performance [21]. Therefore, 8 is the appropriate catalyst loading for this reaction.

3.2. *Reusability of the catalyst*

Maintains a high recovery of catalysts was also a critical factor in appropriately interpreting their performance and assessing their potential practical application. The catalytic results revealed that $LiFe_5O_8$-$LiFeO_2$ maintained its activity after 7 catalytic runs (Fig. 6). After the fifth catalytic run, the biodiesel yield remained close to 94%. As shown the results, indicating the current $LiFe_5O_8$-$LiFeO_2$ can be separated by magnetic separation technology. The decrease in recovery is probably related to both facts: the solubility of catalyst and the loss of catalyst of the collecting operation.

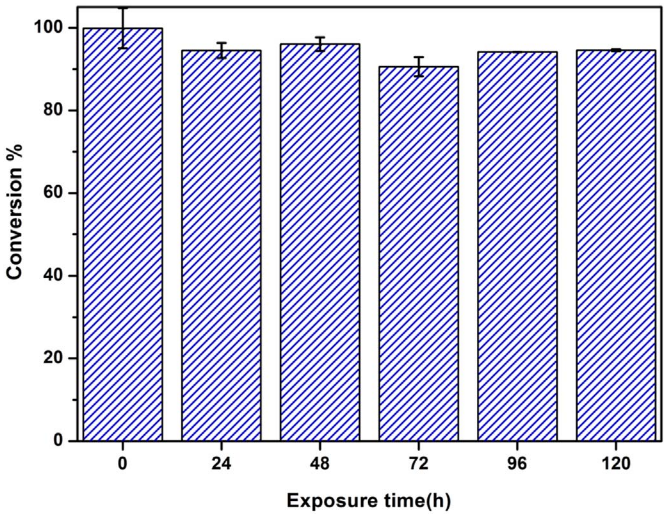

Fig. 7. Influence of $LiFe_5O_8$-$LiFeO_2$ exposed to air for 0–120 h on the conversion rate (Reaction conditions: methanol /oil ratio 36:1, catalyst amount 8 wt%, reaction temperature 65 °C and reaction time 2 h).

The used $LiFe_5O_8$-$LiFeO_2$ was also examined using XRD and no apparent difference was observed between the as-prepared and used samples (Fig. S3). Fig. 7 shows the effect of exposure to air of $LiFe_5O_8$-$LiFeO_2$. According to Fig. 7, the conversion rate (94.4%–95.8%) between the air-exposed catalyst $(0-120\text{h})$ and fresh $LiFe_5O_8$-$LiFeO_2$ (96.5%) was observed, verifying that the activity sites of $LiFe_5O_8$-$LiFeO_2$ are tolerant towards H_2O and CO_2 contained exposure to air [22]. Thus, $LiFe_5O_8$-$LiFeO_2$ is air- resisting, resulting in easy transesterification reaction.

4. Conclusion

An effective magnetic $LiFe_5O_8$-$LiFeO_2$ is successfully synthesized from Li_2CO_3 and Fe_2O_3 and shows catalytic activities towards triglyceride transesterification. In the results, it is found that the utilization of methanol to oil molar ratio 36, with 8% catalyst loading, gives an optimum biodiesel yield of 96.5 ± 0.5%. Moreover, the magnetic $LiFe_5O_8$-$LiFeO_2$ can be reused, without activation, for at least 5 catalytic runs, maintaining the biodiesel yields close to 94%. $LiFe_5O_8$-$LiFeO_2$ demonstrates excellent catalytic activities and could be separated from the biodiesel by a magnet.

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Appendix A. Supplementary data

Supplementary data of XRD patterns and FE-SEM Images to this article can be found online at https://doi.org/10.1016/j.catcom.2017.12.002.

References

[1] T.H. Dang, B.H. Chen, D.J. Lee, Application of kaolin-based catalysts in biodiesel production via transesterification of vegetable oils in excess methanol, Bioresour. Technol. 145 (2013) 175–181.
[2] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, Appl. Energy 87 (2010) 1083–1095.
[3] J.F.P. Gomes, J.F.B. Puna, L.M. Goncalves, J.C.M. Bordado, Study on the use of MgAl hydrotalcites as solid heterogeneous catalysts for biodiesel production,

Energy 36 (2011) 6770–6778.

[4] Y.M. Dai, K.T. Chen, C.C. Chen, Study of the microwave lipid extraction from microalgae for biodiesel production, Chem. Eng. J. 250 (2014) 267–273.

[5] M. Hájek, F. Skopal, M. Černoch, Effect of phase separation temperature on ester yields from ethanolysis of rapeseed oil in the presence of NaOH and KOH as catalysts, Bioresour. Technol. 110 (2012) 288–291.

[6] M.Y. Chen, J.X. Wang, K.T. Chen, B.Z. Wen, W.Y. Lin, C.C. Chen, Transesterification of soybean oil catalyzed by calcium hydroxide which obtained from hydrolysis reaction of calcium carbide, J. Chin. Chem. Soc. 59 (2012) 170–175.

[7] L.C. Meher, D. Vidya-Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification: a review, Renew. Sust. Energ. Rev. 10 (2006) 248–268.

[8] A. Kawashima, K. Matsubara, K. Honda, Development of heterogeneous base catalysts for biodiesel production, Bioresour. Technol. 99 (2008) 3439–3443.

[9] Y.M. Dai, I.H. Kao, C.C. Chen, Evaluating the optimum operating parameters of biodiesel production process from soybean oil using the Li_2TiO_3 catalyst, J. Taiwan Inst. Chem. Eng. 70 (2017) 370–376.

[10] Y. Ding, H. Sun, J. Duan, P. Chen, H. Lou, X. Zheng, Mesoporous Li/ZrO_2 as a solid base catalyst for biodiesel production from transesterification of soybean oil with methanol, Catal. Commun. 12 (2011) 606–610.

[11] N. Hindryawati, G.P. Maniam Rezaul, M. Karim, K.F. Chong, Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst, JESTECH 17 (2014) 95–103.

[12] J.X. Wang, K.T. Chen, J.S. Wu, P.H. Wang, S.T. Huang, C.C. Chen, Production of biodiesel through transesterification of soybean oil using lithium orthosilicate solid catalyst, Fuel Process. Technol. 104 (2012) 167–173.

[13] Y.M. Dai, J.S. Wu, C.C. Chen, K.T. Chen, Evaluating the optimum operating parameters on transesterification reaction for biodiesel production over a $LiAlO_2$ catalyst, Chem. Eng. J. 280 (2015) 270–376.

[14] K.T. Chen, J.X. Wang, P.H. Wang, C.Y. Liou, C.W. Nien, J.S. Wu, C.C. Chen, Rice husk ash as a catalyst precursor for biodiesel production, J. Taiwan Inst. Chem. Eng. 44 (2013) 622–629.

[15] Y. Gao, B.H. Chen, H.L. Lin, Y.X. Ma, Preparation and characterization of a magnetically separated photocatalyst and its catalytic properties, Mater. Chem. Phys. 80 (2003) 348–355.

[16] S. Tang, L. Wang, Y. Zhang, S. Li, S. Tian, B. Wang, Study on preparation of Ca/Al/Fe_3O_4 magnetic composite solid catalyst and its application in biodiesel transesterification, Fuel Process. Technol. 95 (2012) 84–89.

[17] H. Wu, Y. Liu, J. Zhang, G. Li, In situ reactive extraction of cottonseeds with methyl acetate for biodiesel production using magnetic solid acid catalysts, Bioresour. Technol. 174 (2014) 182–189.

[18] M. Feyzi, L. Norouzi, Preparation and kinetic study of magnetic Ca/$Fe_3O_4SiO_2$ nanocatalysts for biodiesel production, Renew. Energy 94 (2016) 579–586.

[19] X.Y. Liao, Y.L. Zhu, S.G. Wang, Y.W. Li, Producing triacetylglycerol with glycerol by two steps: esterification and acetylation, Fuel Process. Technol. 90 (2009) 988–993.

[20] S.H. Wang, Y.B. Wang, J.M. Jehng, Preparation and characterization of hydrotalcite-like compounds containing transition metal as a solid base catalyst for the transesterification, Appl. Catal. A Gen. 439-440 (2012) 135–141.

[21] G. Arzamendi, I. Campo, E. Arguinarena, M. Sanchez, M. Montes, L.M. Gandia, Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH, Chem. Eng. J. 134 (2007) 123–130.

[22] N. Pasupulety, K. Gund, Y.Q. Liu, G.L. Rempel, F.T.T. Ng, Production of biodiesel from soybean oil on CaO/Al_2O_3 solid base catalysts, Appl. Catal. A Gen. 452 (2013) 189–202.