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Application of Li_2SiO_3 as a heterogeneous catalyst in the production of biodiesel from soybean oil

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Abstract

Biodiesel was synthesized from soybean oil by transesterification over Li_2SiO_3 catalyst. The Li_2SiO_3 can be used for biodiesel production directly without further drying or thermal pretreatment, no obvious difference in the FAME conversion (92.4–96.7%) between the air-exposed catalyst (24–72 h) and the fresh one (94.2%). This leads to important benefits when considering industrial applications of Li_2SiO_3 as a solid catalyst for storing and handling catalyst without taking special actions.

Keywords: Biodiesel; Solid catalyst; Li_2SiO_3; Transesterification; Triglyceride

Biodiesel fuel, an alternative to classic diesel fuel, belongs to ecological fuels because it consists of methyl esters of fatty acids, derived from vegetable oils or animal fats. The relevant key limitations for the use of basic solid catalysts from an industrial point of view are the surface active sites which are rapidly poisoned upon exposing the catalyst to ambient air because of the chemisorption of carbon dioxide and water on the surface sites to form carbonates and hydroxyl groups, respectively [1–8]. Therefore, it is critical to avoid the catalyst direct exposure to room air while handling and transferring the catalyst from the activation unit to the reactor. CaO is a promising basic heterogeneous catalyst for the synthesis of biodiesel at mild temperatures (below the boiling point of methanol) and at atmospheric pressure [5], but it is rapidly hydrated and carbonated by contact with room air. Few minutes are enough for CaO to chemisorb significant amount of H_2O and CO_2 [7]. CaO mixed with biodiesel formation of a paste had been reported in a remarkable protection of the activated CaO against the poisoning by ambient H_2O and CO_2 that may occur during handling or storing of the activated solid [1,4]. Approximately 15 g of biodiesel was needed to protect per gram of CaO. Calcium glyceroxide (calcium oxide combined with the by-produced glycerol under the transesterification reaction and turned into calcium glyceroxide) had been reported as a air-exposure tolerant catalyst, but it was weaker base than calcium oxide and brought a decrease in the reaction efficiency [6,8]. The objective of the present work is to investigate solid Li_2SiO_3 catalysts used for biodiesel production. The effects of methanol/oil ratio, catalyst amounts, and reaction time on the conversion were also studied. The catalytic activity of solid base catalysts was not affected by exposure of the catalyst to air before use for the reaction.

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1. Experimental

Li_2SiO_3 was prepared by solid-state reaction. A 0.133 mol amorphous SiO_2 powder was added (0.12 μm, Shimakyu's Pure Chemicals, Osaka, Japan) to an aqueous solution containing 0.266 mol $LiNO_3$ (Katayama Chemical Co., Japan). The as-prepared solution was dried at 120 °C for 24 h. Finally, SiO_2 and $LiNO_3$ mixing powder was well grinded and calcined at 900 °C in air for 4 h.

The conversion of soybean oil to biodiesel was performed in a 250 mL flat bottom flask equipped with a reflux condenser and a magnetic stirrer (340 rpm). The base strength of the samples (H_) was determined by using Hammett indicators [6]. The characterization of catalysts was performed on a MAC MXP18 Powder X-ray diffractometer. The FAME concentration expressed as the biodiesel purity of the product was determined by gas chromatography according to Chinese National Standard 15051.

2. Results and discussion

Fig. 1 shows the XRD patterns of the sample and sample exposure to air for 24–72 h, the main crystalline phase of Li_2SiO_3 is identified to consist with the JCPDS file 74-2145. After exposing to air, the crystalline phase of Li_2SiO_3 was stable, it is unlike CaO to convert into $Ca(OH)_2$ in the air quickly.

Lithium orthosilicate (Li_4SiO_4) has been widely studied as a promising carbon dioxide (CO_2) absorbent [9]. The process of CO_2 capture, using Li_4SiO_4 as a solid absorbent, takes place according to the reaction [9]:

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

In contrast to Li_4SiO_4, Li_2SiO_3 was rather unsensible to capture CO_2 [10] and was a candidate air-exposure tolerant catalyst. In fact, Kato and Nakagawa [11] tested Li_2SiO_3 for the CO_2 capture and did not observe any weight increment.

Table 1 shows the basic strength of Li_2SiO_3 and CaO after different exposure times to ambient. Li_2SiO_3 and CaO appear the same initial basic strength. But the basic strength of CaO was changed obviously by exposure of the catalysts to air, even after the 3 min exposure to air, CaO was appreciably deactivated [8]. On the other hand, Li_2SiO_3 was more stable after exposure to air, and therefore Li_2SiO_3 appears higher basic strength after exposing to air.

The effect of the catalyst amount on the conversion was also investigated. The catalyst amount was varied in the range of 2–10% (catalyst/oil weight ratio). As shown in Fig. 2, the conversion was increased as the catalyst amount increased from 2 to 8%. The conversion reached a plateau value at the catalyst weight percent between 8 and 10%. More catalyst

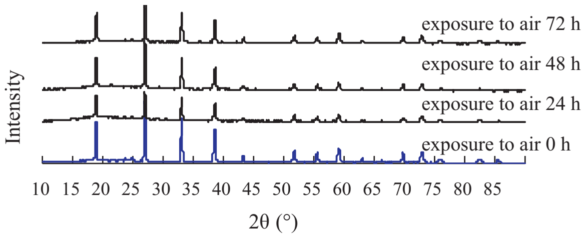

Fig. 1. XRD patterns of samples.

Table 1
Base strengths of Li_2SiO_3 and CaO after exposing to air.

Exposure time (h)	Li_2SiO_3	CaO
0	15.0 <H_ < 18.4	15.0 < H_ < 18.4
24	9.8 <H_ < 15.0	7.2 < H_ < 9.8
48	9.8 <H_ < 15.0	7.2 < H_ < 9.8
72	9.8 <H_ < 15.0	7.2 < H_ < 9.8

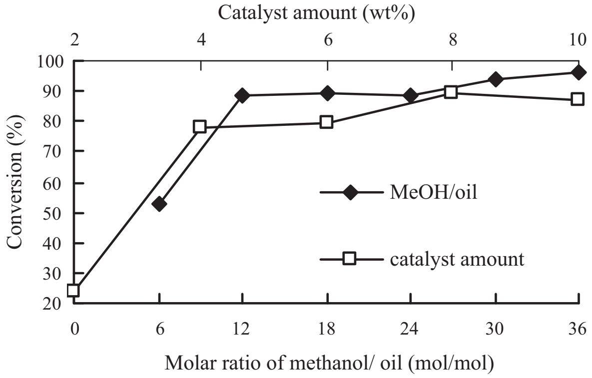

Fig. 2. Influence of catalyst amount (reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 18:1, reaction time 3 h, reaction temperature 65 °C) and methanol/oil molar ratio on the conversion (reaction conditions: 12.5 g soybean oil, catalyst amount 10 wt%, reaction time 3 h, reaction temperature 65 °C).

increased the contact opportunity of the catalyst and the reactant, which directly influenced the reaction speed and the conversion. Stoichiometrically, the transesterification of soybean oil requires 3 mol of methanol for each mole of oil. Since transesterification reaction is a reversible reaction, excess methanol would shift the equilibrium towards the direction of FAME formation. As shown in Fig. 2, with an increase in the methanol-loading amount, the conversion was increased considerably. The maximum conversion ratio was 96.1% at the methanol/oil molar ratio of 36/1.

Effect of reaction time and exposure time to air of catalyst on biodiesel conversion is shown in Fig. 3. The conversion was increased steadily within the reaction time range within 0.5 h, and thereafter remained nearly constant as a result of a nearly equilibrium conversion. The effect of exposure to air on the catalytic activity of transesterification reaction was examined for Li_2SiO_3 and CaO. Fig. 3 shows no obvious difference in the FAME conversion (92.4–96.7%) between the air-exposed Li_2SiO_3 catalyst (24–72 h) and the fresh one (94.2%), which verified that the catalytic sites of Li_2SiO_3 was tolerant to CO_2 and H_2O contained in air. Under the reacting condition, it was inferred that CO_2 and H_2O interacting with the catalytic sites were eliminated due to the acidic property of methanol [6]. Li_2SiO_3 was the solid base catalyst having the advantage of tolerance to air-exposure, which will cause easy operation of the catalytic reaction. On the other hand, CaO exposure to air for 24 h invited serious decrease in the conversions of FAME from 95.2% to 2.5%.

After the transesterification was completed, the samples were recovered by simple decantation. The remaining catalyst in the reactor was used to catalyze the next batch of transesterification. In Fig. 4, 93.7% of the biodiesel purity could be obtained even after recycling for 4 times. The biodiesel purity was reduced to 50.3% when Li_2SiO_3 was reused for 6 times (Fig. 4), because the amount of catalyst used in the next run was lower than it in the initial run that might partly be responsible to the reduced biodiesel purity during the subsequent run. Glycerol covering the surface of catalyst was also considered as the reason for activity loss. After recycling for 6 times, the catalyst was washed

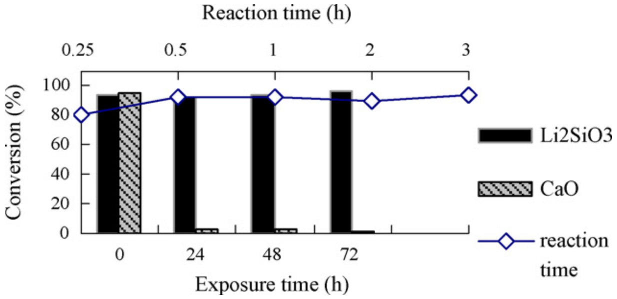

Fig. 3. Influence of reaction time and exposure time to air (reaction time 2 h) on the conversion. Reaction conditions: methanol to oil molar ratio = 30:1 (Li_2SiO_3), 12:1 (CaO); catalyst amount = 10 wt% (Li_2SiO_3), 3 wt% (CaO); reaction temperature = 65 °C.

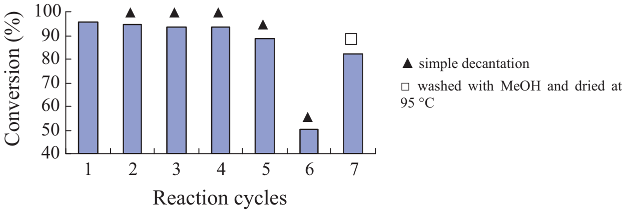

Fig. 4. Reusability study after seven reaction cycles for Li_2SiO_3 catalyst, reaction conditions: catalyst amount 10 wt%, methanol/oil molar ratio 30:1, reaction time 3 h, reaction temperature 65 °C.

thoroughly with anhydrous methanol and dried at 95 °C under vacuum for 1 h. In the seventh recycling, the amount of feedstock and methanol was equivalently reduced to the collected catalyst amount. Furthermore, by reacting under the same conditions, the biodiesel purity was recovered to 82.4%.

3. Conclusions

This study developed a Li_2SiO_3 catalyst and application to the biodiesel production. The following conclusions have been made:

(1) The experimental results show that Li_2SiO_3 demonstrated excellent catalytic activity and stability due to its basic strength and because it is insoluble in methanol. Li_2SiO_3 is a common compound and easy to be obtained, it can be use for biodiesel production directly without further catalyst synthesized process, dried 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_2SiO_3 catalysts are tolerant to water and carbon dioxide and the catalytic activity of transesterification reaction has not reduced, which enables the Li_2SiO_3 catalysts to be used in a biodiesel production process without pretreatment and/or prevention procedures in catalyst preparation.

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