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Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate

Feng Guo [a,b], Ning-Ning Wei [a], Zhi-Long Xiu [a,*], Zhen Fang [b]

[a] *School of Life Science and Biotechnology, Dalian University of Technology, Linggong Road 2, Dalian 116024, PR China*
[b] *Chinese Academy of Sciences, Biomass Group, Laboratory of Tropical Plant Resource Science, Xishuangbanna Tropical Botanical Garden, Xuefu Road 88, Kunming 650223, PR China*

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ABSTRACT

Solid calcined sodium silicate (CSS) was successfully used to produce biodiesel from vegetable oil, but its transesterification mechanism is still not well-understood. In this work, stability tests confirmed that some active basic species were leached into methanol from CSS. FT-IR spectra and density functional theory were employed to deduce the mechanistic route of transesterification reactions catalyzed with CSS. It was confirmed that alkaline active species were formed from the ion-exchange between CSS and CH_3OH. Deactivated CSS can be reused by regenerating the active sites using a simple method found by us.

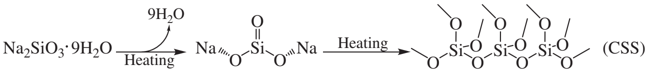
1. Introduction

During the past decades, biodiesel has become more and more important as one of alternative liquid fuels due to the high oil demand from China and India, and limited petroleum resources [1,2]. Biodiesel is usually produced from renewable vegetable oils or animal fats through transesterification with methanol in the presence of catalysts. The commonly used catalysts are base, acid and lipase [3–5]. Homogeneous liquid base catalysts, such as alkaline metal alkoxides (CH_3ONa and CH_3OK) and alkaline hydroxides (NaOH and KOH), are effective [6–9]. However, soaps are usually formed when free fatty acids (FFAs) and water existed in crude oil, resulting in the catalyst deactivation and productivity reduction [3,10].

Many solid catalysts were studied for the triglyceride transesterification due to their better recovery and recycling, such as alkaline earth metal oxides, Mg–Al hydrotalcites, supported solid base catalysts, anion-exchange resins and salt catalysts [3,11–16]. Most of the catalysts were sensitive to water and FFAs. It is difficult to avoid the formation of soaps if water and FFAs exist in the feedstocks. Catalysts that are water- or FFAs-tolerant are needed since removal of the impurities will increase the cost. Alkali metal carbonates were used as catalysts for the transesterification of crude oil with high moisture that was removed by the formation of bicarbonate [17]. However, carbonates exhibited weak basic activity and gave low reaction rate at higher temperature. Sodium silicate is similar to Na_2CO_3 and could also react with H_2O to form NaOH for biodiesel production. Additionally, it is immiscible with triglyceride and alcohol, and exhibited high catalytic activity after calcination [18]. In the presence of water, NaOH and Si–O–H are formed by the hydrolysis of sodium silicate [19–21] according to the following equation:

$$\mathrm{Na{-}O{-}\overset{\overset{\displaystyle O}{\|}}{Si}{-}O{-}Na} + H_2O \longrightarrow \mathrm{Na{-}O{-}\overset{\overset{\displaystyle O}{\|}}{Si}{-}O{-}H} + NaOH \qquad (1)$$

In our previous work [18], we found that the hydrolysis reaction avoids the formation of soap as water content was less than 4 wt.%. The produced NaOH is also an efficient catalyst for transesterification reaction. However, the transesterification mechanism catalyzed by sodium silicate is still not clear. Compared with sodium silicate, calcined sodium silicate (CSS) had more regular crystalline phase, and Si–O–Si extension was formed between adjacent SiO_4^{4-} (Eq. (2)), which changed the structure of sodium silicate [18].



(2)

In CSS, Na^+ ions were distributed in random combinations around non-bridging oxygen [22].

In this study, the stability of CSS was studied firstly. A mechanism was then proposed for the transesterification of soybean oil based on the catalyst structures identified by Fourier-Transform Infrared (FT-IR). Finally, the used catalyst was regenerated and tested for biodiesel production.

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[*] Corresponding author. Tel./fax: +86 411 84706369.
E-mail address: zhlxiu@dlut.edu.cn (Z.-L. Xiu).

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2. Experimental

2.1. Preparation and characterization of catalyst

Sodium silicate (19.3–22.8 wt.% Na_2O) and dehydrated methanol (purity 99.5%) used in this study were obtained from Kermel Corp., Tianjin, China. Refined soybean oil was purchased from Fuhong Corp., Liaoning, China. In catalyst preparation, sodium silicate was dehydrated at 200 °C for 15–20 min, and then calcined in a muffle furnace at 400 °C for 2 h. The CSS was milled and passed through a 120 mesh sieve. Prior to the transesterification, the CSS was further calcined at 400 °C in air for 2 h.

FT-IR (EQUINOX55, GER) and IR (SHIMADZU, JPN) spectrometers were used to characterize the changes of chemical structure of CSS. The scanning range was set from 400 to 4000 cm^{-1}.

2.2. Transesterification reaction

A 250 mL three-necked round-bottomed flask equipped with a reflux condenser was charged with 30.0 g of soybean oil. The transesterification was performed at the optimized condition obtained in our previous work [18], i.e., CSS of 3.0 wt.%, methanol/oil molar ratio of 7.5/1, reaction time of 60 min, reaction temperature of 60 °C, and stirring rate of 250 rpm. After reaction, catalysts and excess methanol were recovered by centrifugation and vacuum distillation, respectively.

2.3. Stability test of the CSS

Stability tests were performed using the same instruments in the above transesterification reaction. After temperature reached 60 °C, freshly prepared CSS and anhydrous methanol were added in the flask. After agitated for 60 min, the suspended mixture was filtrated via a funnel (with a 5–15 μm pore-size filter). The percolated liquid was further centrifugated at 12,000 r/min for 15 min to recover the smaller sized CSS. The basicity of recovered CSS was measured using the method of Hammett indicator–benzene carboxylic acid titration [13]. Leached basicity from the CSS into methanol was determined as the basicity difference between the fresh and recovered CSS. The washed CSS was dried at 105 °C for 3 h to remove absorbed methanol, and characterized by FT-IR. It was then used to catalyze the next batch of transesterification.

2.4. Analysis method

The composition of reaction mixture was determined by Gas Chromatography (GC; GC-14B, Shimadzu, Japan) with capillary column of PONA (50 m × ∅ 0.25 mm × 0.5 μm). Heptadecanoic acid methyl ester was used as the internal standard to analyze biodiesel yield. The temperature for column was 270 °C, and for injector and detector was 290 °C.

2.5. Comparison of ability to provide protons

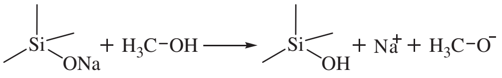
In order to compare the ability of methanol and sodium silicate to provide protons, geometric optimizations of methanol, $NaHSiO_3$ and $NaHSi_2O_5$ were performed using the density functional theory (DFT) with Becke's three-parameter hybrid exchange function, Lee–Yang–Parr gradient-corrected correlation function (B3-LYP function) and 6-31+G(d,p) basis set. The vibrational frequencies of methanol and $NaHSiO_3$ molecules were also calculated using the same theory. All the calculations were carried out with the Gaussian 03 package.

3. Results and discussion

3.1. Stability of catalyst

The total basicity of the CSS was 16.16 mmol/g, determined by Hammett indicator–benzene carboxylic acid titration. Fig. 1 shows the change of leached basicity from the CSS into methanol during the stability tests, indicating the methanol solution contains base species. The amount of leached alkali content reduced as washing batches increased, which confirmed that some base ingredients of CSS were dissolved into methanol. Fig. 2a shows effect of the base lose on catalytic activity. After washed for five times, the CSS is still highly active. The recovered methanol was also used to catalyze the transesterification. Fig. 2b shows that the first recovered methanol performed best in catalytic activity. As washing batches rose, biodiesel yield dropped. Compared with the washed solid CSS, the corresponding recovered methanol had a higher initial reaction rate due to lower mass transfer resistance. The above results indicated that the basic species of CSS leached into methanol during the methanol washing process, which confirmed by improvement of the transesterification reaction with pre-mixture of methanol with the CCS (Fig. 2c).

Structural changes of the CSS during washing process were analyzed by FT-IR (Fig. 3). All the samples had similar absorption bands. Table 1 shows the wave numbers attributed to Si–O–Si, and Si–O–H. Silicon–oxygen tetrahedral structure formed a piece of a three dimensional (3D) random network by means of the Si–O–Si bridging units. This interconnection of 3D networks would be terminated where the alkali concentration was very high. Because there is no difference in wave-number for FT-IR absorptions, absorbance (A) was introduced to evaluate the amount of the corresponding functional groups (Table 1). Compared with the fresh CSS, $A_{Si-O-Si}$ and $A_{Si-O-Na}$ in the washed catalysts decreased. However, A_{Si-O-H} and A_{OH} (~3500 cm^{-1}) showed the opposite trend, indicating the hydration of Si–O–Si and Si–O–Na. This proved the following reaction taking place:



(3)

The formed CH_3O^- initialized the transesterification reaction. Eq. (3) also explained why the recovered methanol had catalytic activity after the washing procedure.

3.2. Transesterification mechanism catalyzed by the CSS

The transesterification reactions started on the surface of the CSS. Fig. 4 shows the mechanistic route. First, ion-exchange proceeded after methanol absorbed on the surface of the CSS, and the catalytic

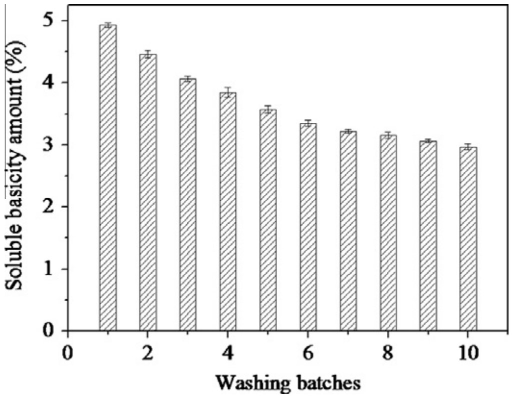


Fig. 1. Basicity amount of the CSS leached in methanol.