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## Original Research Paper

# Facile synthesis of layered sodium disilicates as efficient and recoverable nanocatalysts for biodiesel production from rapeseed oil

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### ARTICLE INFO

#### Article history:

Received 21 November 2017  
Received in revised form 13 February 2018  
Accepted 15 February 2018  
Available online xxx

#### Keywords:

Sodium disilicates  
Biodiesel  
Transesterification  
Recoverable catalyst

### ABSTRACT

In this study,  $\alpha$ ,  $\beta$  and  $\delta$  phases of layered sodium disilicates were synthesized and used as heterogeneous catalysts for transesterification of rapeseed oil with methanol to methyl esters (biodiesel). The catalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) technique, Fourier transform infrared spectroscopy (FT-IR),  $N_2$  adsorption-desorption, and thermogravimetric analysis (TGA-DTA).  $\delta$ - $Na_2Si_2O_5$  showed better catalytic efficiency than the other two phases of sodium disilicate, and showed excellent activity at the optimized conditions. The transesterification conditions, such as the catalyst dosage, molar ratio of methanol to oil, reaction temperature and reaction time were investigated. The results revealed that with a catalyst loading of 4 wt%, methanol to oil ratio of 30:1, reaction temperature of 65 °C and reaction time of 3 h, conversion of biodiesel reached 97.8%.

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## 1. Introduction

In recent years, the use of biodiesel as a replacement of fossil fuels has drawn great attention due to diminishing petroleum reserves and environmental concerns [1–3]. Biodiesel, a mixture of mono alkyl (normally methyl) ester of long chain fatty acids, is a clean, renewable, biodegradable and non-toxic fuel. Biodiesel is usually produced through transesterification of edible or non-edible vegetable oils with methanol in the presence of an appropriate catalyst. The transesterification reaction can be catalyzed by an acid, a base or an enzyme [4,5]. Basic catalysts including homogeneous and heterogeneous catalysts are more widely used due to their better catalytic performance compared to acid and enzyme catalysts [6]. Homogeneous liquid base catalysts, such as alkaline metal alkoxides ( $CH_3ONa$  and  $CH_3OK$ ) and alkaline hydroxides ( $NaOH$  and  $KOH$ ) have shown high catalytic activity under mild reaction conditions. However, these catalysts require additional neutralization and separation steps from the final reaction mixture, thus leading to a series of environmental problems related to using excessive amounts of water and energy [7,8].

On the other hand, heterogeneous catalysts can be easily separated by filtration, reused and recycled several times and require no neutralization processes. In addition, they can also produce a high purity glycerol by-product. Hence, heterogeneous-catalysis

is an efficient and more cost-effective tool to produce biodiesel [9,10]. A lot of research has been done in this direction. Commonly used solid base catalysts are alkaline earth metal oxides, Mg-Al hydrotalcites, supported solid base catalysts and anion-exchange resins [11–15]. The relevant key limitations of using these catalysts, from an industrial perspective, involve the surface active sites being rapidly poisoned upon exposing the catalysts to ambient air. Few minutes are enough for CaO to chemisorb significant amount of carbon dioxide and water to form carbonates and hydroxyl groups. Therefore, it is critical to avoid the catalyst direct exposure to air while handling and transferring the catalyst from the activation unit to the reactor [16,17].

Alkaline metasilicates i.e.  $Li_2SiO_3$ ,  $Na_2SiO_3$  and  $K_2SiO_3$ , and  $Li_4SiO_4$  orthosilicate have been previously used as solid base catalysts for biodiesel production. They have appeared to be promising candidates to replace alkaline earth oxides due to their low reaction times and air-insensitivity [18–24]. Layered sodium disilicates ( $Na_2Si_2O_5$ ) have a polymeric layered bidimensional crystal structure. At least six different modifications have been reported as a function of temperature, pressure, and synthesis conditions, though the common framework phases are  $\alpha$ ,  $\beta$  and  $\delta$  [25]. Their foundations are built from the condensation of silicate tetrahedral into a single sheet, with interlamination achieved through sodium cations. This makes them structurally similar to the natural mineral bentonite, and they therefore have the potential for application as an adsorbent, ion exchanger, or catalyst/catalyst support [26,27].

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In this study, we report the synthesis of  $\alpha$ -,  $\beta$ -, and  $\delta$ -phase layered sodium disilicates. The effect of changing the reaction time and temperature is studied. Structure and morphology of the as-synthesized disilicates are investigated, and then the catalytic performances of these solid base catalysts are evaluated for transesterification of rapeseed oil with methanol.

## 2. Experimental

### 2.1. Materials

Commercial edible rapeseed oil was obtained from a local grocery store. Methanol, sodium hydroxide, silicon dioxide and n-heptane were purchased from Merck chemical company. Methyl heptadecanoate as the standard of GC was purchased from Sigma-Aldrich. All chemical materials were used without further purification.

### 2.2. Catalyst preparation

Layered sodium disilicates were prepared by modifications of the method described by Beneke and Lagaly [28]. In a typical experiment, 0.2 mol  $\text{SiO}_2$  was dispersed in 30 mL methanol and then cold NaOH solution (0.2 mol NaOH in 7 mL  $\text{H}_2\text{O}$ ) was slowly added. The mixture was stirred for 5 h. The resulting slurry was dried at 100 °C for 24 h. Crystallization was achieved by calcination at various temperatures (500–800 °C) for different periods of time (30–300 min). A representative diagram is shown in Scheme 1.

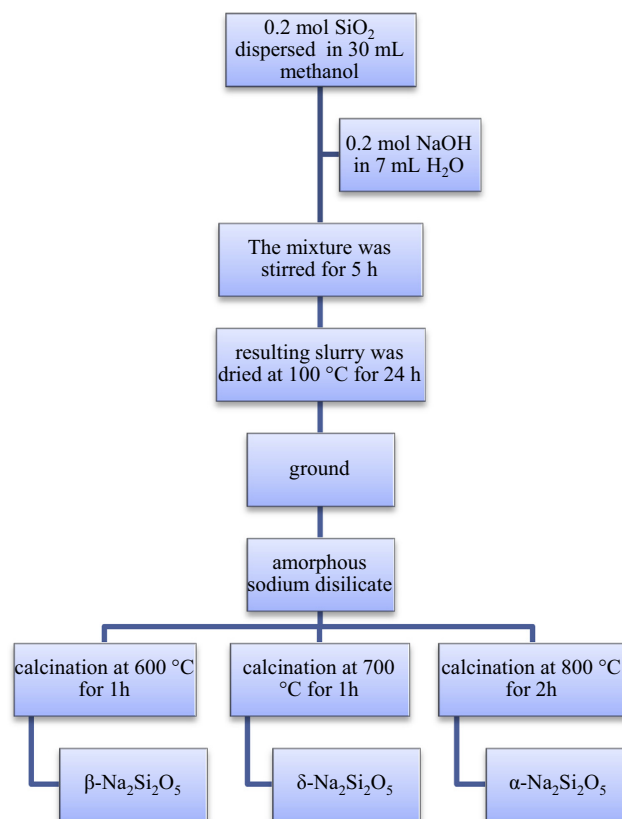
### 2.3. Catalyst characterization

The X-ray diffraction (XRD) patterns were obtained using a Philips X-ray diffractometer (model D8 Bruker) with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Morphological characterization was performed by scanning electron microscopy (SEM, TESCAN MIRA 3). Textural analyses were carried out with a BELSORP mini apparatus by determining the nitrogen adsorption/desorption isotherms at  $-196 \text{ }^\circ\text{C}$ . Prior to the measurements, the samples were outgassed for 3 h at 300 °C. The specific surface area was determined by the BET method. The total pore volume and the pore size distribution were assessed by BJH method. FT-IR spectra of the samples were collected on a Bruker FT-IR instrument using KBr pellet technique in the range of  $4000\text{--}400 \text{ cm}^{-1}$ . Thermogravimetry analyses (TGA) and differential thermal analyses (DTA) were carried out on a LINSEIS model STA PT 1600 instrument under air atmosphere at a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ .

### 2.4. General procedure for transesterification reaction

Transesterification reactions were carried out in a 50 mL flask equipped with a reflux condenser. The catalyst was dispersed in the desired amount of methanol with magnetic stirring. The rapeseed oil was then added and the mixture was heated at reflux for appropriate time. The average molecular weight of the used rapeseed oil ( $872 \text{ g mol}^{-1}$ ) was calculated from the saponification value (s.v. =  $193 \text{ mg KOH/g}$ ) (ASTM D94). After the reaction, the catalyst was separated by filtration and then methanol was recovered by rotary evaporator at 60 °C. At last, the biodiesel and glycerol were separated within a separation funnel.

The FAME content of the prepared biodiesel sample was quantified by GC-17A Shimadzu gas chromatography equipped with a BP10 capillary column ( $25 \text{ m} \times 0.32 \text{ mm}$ ; phase thickness:  $0.5 \text{ }\mu\text{m}$ ) and FID detector according to the standard test methods EN 14103. Methyl heptadecanoate was used as the internal standard.



Scheme 1. Preparation process for different polymorphs of  $\text{Na}_2\text{Si}_2\text{O}_5$ .

The conversion of the produced biodiesel was calculated with the following Eq. (1):

$$\text{conversion}(\%) = \frac{(\sum A) - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100 \quad (1)$$

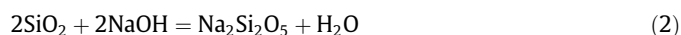
where  $\sum A$  is the total peak area of rapeseed oil methyl esters,  $A_{IS}$  is the peak area of internal standard,  $C_{IS}$  is the concentration of the internal standard solution,  $V_{IS}$  is the volume of the internal standard solution and  $m$  is the mass of sample [29]. Scheme 2 shows a representative illustration of the transesterification reaction.

## 3. Results and discussion

### 3.1. Catalyst characterization

#### 3.1.1. Thermogravimetric analysis

Thermogravimetric analysis and differential thermal analysis were conducted on the amorphous sodium disilicate precursor to find suitable calcination temperature for the synthesis of  $\alpha$ -,  $\beta$ -, and  $\delta$ -phase sodium disilicate, and the results are shown in Fig. 1. The first mass loss ( $\sim 9\%$ ) occurs below  $120 \text{ }^\circ\text{C}$ , and a corresponding endothermic peak is observed on the DTA curve, which is caused by the dehydration of sample. Upon heating the sample further from  $120 \text{ }^\circ\text{C}$  to  $350 \text{ }^\circ\text{C}$ ,  $\sim 10\%$  weight lost was observed, consistent with the theoretical weight loss calculated from the following formula:



The DTA curve presents an exothermic peak around  $670 \text{ }^\circ\text{C}$ , attributed to the crystallization of  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$  and an endothermic effect around  $850 \text{ }^\circ\text{C}$ , corresponding to the melting of silicate [26,30].

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