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# Transesterification of canola oil as biodiesel over Na/Zr-SBA-15 catalysts: Effect of zirconium content

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## ARTICLE INFO

### Article history:

Received 31 May 2014

Received in revised form

25 August 2014

Accepted 26 August 2014

Available online 16 October 2014

### Keywords:

Biodiesel

Transesterification

Acidic catalyst

Zr-SBA-15

## ABSTRACT

A series of mesoporous Zr-SBA-15-supported Na catalysts was prepared and applied to the heterogeneous catalysis of canola oil transesterification. The effects of Si/Zr ratio, reaction time, and percentage of Na loading on the conversion to fatty acid methyl esters (FAME) were studied. The dependence of the textural structure and chemical properties of Zr-SBA-15 supports on Zr content was investigated using small-angle X-ray diffraction, Brunauer–Emmett–Teller analysis, transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) spectroscopy. The results obtained from FTIR and TEM indicate that the incorporation of Zr atoms into the SBA-15 structure facilitated the formation of Brønsted acid sites and decreased the particle size of Na species. Catalysts with a higher Zr content enhanced the FAME yield. The optimum conditions determined were as follows: reaction temperature of 70 °C, 15 wt.% Na, reaction time of 6 h, and 12% catalyst content (wt.% oil) with a methanol/oil molar ratio of 6:1. The optimum conditions resulted in a FAME yield of up to 99%.

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## Introduction

The continuous consumption of traditional fossil energy resources and increasing environmental concerns have prompted extensive research on renewable fuels. According to a recent study from the International Energy Agency, only energy produced from renewable sources and waste has the highest potential to replace fossil fuels, especially for transportation. Among such sources, combustible fuels and waste accounted for 10% of the world's total energy supply from fuel

[1]. Hence, renewable energy from combustible energy, such as biodiesels, is predicted to enter the energy market in the near future to diversify the global energy source.

Biodiesel, which is an alternative, non-toxic, and eco-friendly diesel fuel, was developed to ensure energy availability at an affordable price and to prevent environmental damage [2–4]. The triglyceride transesterification of edible oils with methanol to obtain biodiesel in the form of fatty acid methyl ester (FAME) is a commonly used method. Biodiesel can be obtained from the transesterification of vegetable oil or animal fats in the presence of short-chain alcohols and

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<http://dx.doi.org/10.1016/j.ijhydene.2014.08.154>

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catalysts. However, vegetable oil and animal fat contain numerous free fatty acids (FFA) and water, resulting in soap formation that significantly affects conversion during the transesterification reaction. The transesterification of edible oils can be catalyzed by a homogeneous or heterogeneous base and acid catalysts [4]. Among these catalysts, heterogeneous acid catalysts can simultaneously esterify FFA and transesterify triglycerides, even in the presence of 9% FFA [5–7]. Therefore, both vegetable and waste oils can be used in transesterification when acid catalysts are applied to reduce production costs [8].

Ordered mesoporous zeolites, such as SBA-15, MCM-41, and hexagonal molecular sieves (HMS), have recently received considerable attention in industrial applications involving catalysis and organic transformations because of their large surface area and controllable pore size [9,10], which enable reactions to involve larger molecules. Among these zeolites, silica SBA-15 shows higher thermal and hydrothermal stabilities than MCM-41 or HMS [11]. However, the pure-silica SBA-15 lacks Brønsted-acid sites and usually exhibits only mild Lewis-acid sites and low catalytic activity due to absence of heteroatom active sites. Thus, the acidity and activity of silica SBA-15 requires further enhancement and modification when applied in catalytic reactions [12,13]. Many studies have been conducted on improving the surface acidity of silica SBA-15 by substituting other metals, such as Al, Ti(IV), Sn(IV), or Zr(IV), in the silica matrix. This substitution mainly creates Brønsted acidic sites [14] or Lewis acidic sites [8], depending on the synthesis conditions. Generally, the heteroatom can be substantially incorporated through post-synthesis or direct-synthesis (also called one-pot synthesis) method. This process of incorporation grafts the heteroatom onto a calcined sample or copolymerizes a metal precursor in the presence of an organosilane solution [15]. Although the heteroatom-containing SBA-15 is mainly prepared using the post-synthesis method to achieve high heteroatom loading, this method usually destroys the framework of SBA-15, especially at high heteroatom loadings, because of a complicated synthetic process that uses solvent in a strict condition for preparation [11,16]. For example, Kao et al. synthesized Al-SBA-15 using aqueous  $(\text{NH}_4)_3\text{AlF}_6$  as the aluminum source and by adjusting the pH of the solution to 9.3 to avoid a condition with strongly acidic reactions [17]. Another disadvantage of these post-synthetic methods is the tendency of metal oxides to appear in the channel or on the external surface of the pore wall, which would negatively affect the catalytic activity [17,18].

Among these zeolites, mesoporous Zr-SBA-15, which functions as a beneficial catalyst and a suitable catalytic support [19], has received considerable attention for its acidity-generating characteristics. Ijlesias et al. [20] reported that the synthesis of Zr-SBA-15 materials results in highly acidic properties and reveals high catalytic activity in transesterification, with the FAME yield reaching over 70%. However, further incorporation of titanium, molybdenum, and tungsten as doping metals does not translate into higher catalytic activity.

Based on this premise, we present the synthesis of Zr-SBA-15 materials using the direct-synthesis method and the coating active site using the impregnation method. The use of

Zr-SBA-15 as support resulted in high catalytic activity in the transesterification reaction compared with previous studies. The effect of different experimental parameters such as reaction time, Na catalyst loading weight, and reusability were also investigated.

## Experimental

### Catalyst preparation

A series of Zr-SBA-15 supports was synthesized according to a previously described method [4,21]. In a typical procedure, 5 g of a pluronic triblock copolymer P123 was dissolved in 2 M HCl solution at room temperature for 1 h. After the copolymer was completely dissolved, 11.5 ml of tetraethyl orthosilicate was added drop wise to the synthesis medium. An appropriate amount of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was added to achieve the desired Si/Zr molar ratios: 10, 30, or 50. The suspension was then stirred for 3 h and aged at 110 °C for 24 h. The solid product was collected through filtration, washed with acetone, and air-dried at 110 °C overnight. Calcination was performed in air at 500 °C for 6 h, and the product was denoted as Zr-SBA-15(X), where X is the Si/Zr molar ratio in the initial gel. For comparison, the Zr-free SBA-15 sample was synthesized using the same procedure but without the introduction of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and denoted as SBA-15.

The active site of Na was deposited on the surface of Zr-SBA-15 support using a conventional impregnation method. The Zr-SBA-15 support was introduced to various calculated amounts of NaOH aqueous solution, which were 5, 12, and 15 wt.% of the loading weight in the supported catalyst. After 24 h, the catalyst was dried at 105 °C overnight, followed by calcination at 400 °C in air for 4 h. The obtained sample was denoted as YNa/Zr-SBA-15(X), where Y represents loading weight. The ordered structure of Na-loaded Zr-SBA-15 was further analyzed with low-angle XRD to confirm that it can withstand the impregnation solution treatment. For the sample loaded with Na, a well-resolved XRD pattern with a prominent peak (100) and two weak peaks (110 and 200) were observed at around  $2\theta = 1^\circ$  and  $2\theta = 2^\circ$ , which is consistent with the XRD patterns of silica Zr-SBA-15 (Fig. 1).

### Characterization

Small angle X-ray diffraction (SAXRD) data were obtained using a Siemens D5005 (40 kV, 30 mA) with a nickel-filtered Cu-K $\alpha$  radiation and a wavelength of 0.15406 nm. The diffraction patterns were collected under ambient conditions in the  $2\theta$  range between 0.2° and 5° at a scanning rate of 1°/min. The  $a_0$  unit-cell parameter was estimated from the position of the (1 0 0) diffraction line ( $a_0 = d_{100} \times 2/\sqrt{3}$ ) [22]. Inductively coupled plasma with atomic emission spectroscopy (ICP-AES) technique was used to determine the actual Zr and Na contents in the catalysts on a Varian Vista-PRO AX CCD-simultaneous ICP-AES spectrophotometer. Previously, solid samples were digested with acid solution.

Nitrogen adsorption–desorption isotherms were obtained at –196 °C using a surface area analyzer. The surface area values were calculated using the Brunauer–Emmett–Teller

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