



Research article

Mild synthesis of biofuel over a microcrystalline $S_2O_8^{2-}/ZrO_2$ catalyst

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ABSTRACT

A solid super acid catalyst, $S_2O_8^{2-}/ZrO_2$, was prepared by a new synthesis route of one-pot method with ammonium persulfate via vapor phase hydrolysis to improve biodiesel production using expired soybean oil as reactant. Catalysts were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), and NH_3 -temperature programmed desorption (NH_3 -TPD) to determine the optimum pretreatment conditions and understand the role of the active sites for transesterification. $S_2O_8^{2-}/ZrO_2$ calcined at 500 °C, which showed an amorphous phase by XRD characterization, was identified as composed of tetragonal phase ZrO_2 microcrystallites by TEM examination. The microcrystallites which anchored more $S_2O_8^{2-}$ had abundant super acid and displayed high catalytic activity in the transesterification under mild reaction conditions. The reaction parameters over the catalyst were optimized and both the conversion of soybean oil and selectivity of biofuel reached 100% under the conditions of 110 °C of reaction temperature, 4 h of reaction time and 20:1 of methanol to oil molar ratio. Moreover, the catalyst showed high stability in the reactions and no sulfur leaching was found in the biodiesel products in cyclic utilization.

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1. Introduction

Biodiesel has been recognized as a clean and renewable fuel. The promising biodiesel of fatty acid methyl esters (FAMES) has received much attention in recent years [1]. FAMES can be produced from the transesterification and esterification with short-chain alcohol in the presence of acid or base catalysts [2–4].

In the processes of biodiesel production, the homogeneous acid and alkaline catalysts are often hindered by corrosion and additional purification [5]. Meanwhile, with a heterogeneous catalytic system, the catalysts are recyclable and easily separable, which simplify the steps of biodiesel purification [6,7]. In addition, solid acid catalysts are excellent alternatives to other catalysts, owing to their simultaneously catalyzing the esterification and transesterification reactions with low-grade, highly-acidic and water-containing oils without soap formation [8,9]. It is observed that solid acid-catalyzed biodiesel production reactions are slow and need a longer reaction time and a higher temperature to obtain relatively high reaction rate and better biodiesel yield [10,11]. However, the application of heterogeneous acidic catalysts in industrial production of biodiesel is limited by minimal energy consumption principle in manufacturing. Thus, the preparation of highly active heterogeneous acidic catalysts under moderate catalytic conditions is critical for the efficient application.

Recently, many types of heterogeneous acidic catalysts, such as heteropolyacids, ion exchange resins, zeolites and sulfated metal oxide etc. [8,12], have been developed to meet requirements as described.

Among the solid acid catalysts, sulfated zirconia showed superior performance in biodiesel production with its plenty of strong acid sites [13]. Conventional sulfated zirconia has been usually prepared by two-step (precipitation-impregnation) method with the sulfating agent of sulfuric acid or $(NH_4)_2SO_4$ solution [14]. The conventional sulfated zirconia is commonly used by many researchers as heterogeneous catalyst in the production of biodiesel. For example, Kiss et al. [15] reported the esterification of dodecanoic acid with 2-ethylhexanol catalyzed by the sulfated zirconia. It exhibited the best esterification conversion of 70% at 160 °C. Jitputti et al. [16] also reported the transesterification of crude palm kernel oil with methanol catalyzed by the catalyst. The highest fatty acid methyl ester yield was over 90% at 200 °C. Obviously, the conventional sulfated zirconia has displayed good catalytic performance on relatively high reaction temperature. In addition, Zhang et al. [17] studied the activity of modified sulfated zirconia prepared by chlorosulfonic acid impregnation, showing complete conversion of simulated crude rice bran oil into FAMES biodiesel at low reaction temperature (120 °C). However, the catalyst was synthesized by complicated multi-step and hazardous chemical.

Recently, one-pot modified preparation method has attracted considerable attention, due to its simple and facile synthesis procedure. Sang et al. [18] reported that a one-step route was used to synthesize the mesoporous sulfated zirconia nanoparticles using the aqueous solution of sodium dodecyl sulfate and $Zr(OC_3H_7)_4$. The catalyst exhibited the highest yield of fatty acid esters (98%) in transesterification of soybean oil with methanol at 120 °C. However, it is an intricate process, which involves the hydrolysis of organic zirconium in the precursor solution. Lately, we have reported effect of a simple one-pot route of synthesizing nanocrystal zirconia [19]. The preparation of the nanocrystal

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zirconia was obtained by vapor phase hydrolysis using anhydrous alcohol solvent, which could efficiently control the hydrolysis of organic zirconium precursor. However, whether the corresponding modified sulfated zirconia can be directly synthesized by one-pot route with an effective sulfated agent - ammonium persulfate [20] is still to be discussed. What is more, the catalytic activity of this catalyst in the conversion of expired oil to biodiesel under mild conditions has not been explored.

In this work, a direct synthesis of solid super acid catalyst ($S_2O_8^{2-}/ZrO_2$) by one-pot method is proposed. The X-ray diffraction (XRD), transmission electron microscope (TEM), and NH_3 -temperature programmed desorption (NH_3 -TPD) analyses have been employed to connect the physical characteristics and acid property of the catalysts with their performance in the transesterification of expired oil. The best performance of the solid acid catalyst was also studied by optimizing the reaction parameters, including those of reaction temperature, reaction time and molar ratio of oil to methanol. Finally, recyclability of the catalyst was evaluated under the determined optimum conditions.

2. Materials and methods

2.1. Materials

Zirconium n-propoxide ($Zr(OC_3H_7)_4$) with 80 wt.% in n-propanol was purchased from Aladdin. Benzyl alcohol, methanol, ethanol and ammonium persulfate ($(NH_4)_2S_2O_8$) were supplied by Tianjin Guangfu Fine Chemical Institute.

2.2. Catalyst preparation and characterization

2.2.1. Catalyst preparation

$S_2O_8^{2-}/ZrO_2$ used in this study was prepared in a modified method based on the procedure reported by Shi et al. [19], but with the addition of ammonium persulfate as sulfur source. In a typical procedure, 0.959 g zirconium n-butoxide was dissolved into a 12 mL benzylalcohol and stirred for a while. Then the solution was poured into the weighing bottle with 1.14 g ammonium persulfate, which was placed in a Teflon-lined stainless steel autoclave with deionized water and heated to 140 °C for 24 h. On completion of the synthesis period, the precipitate was obtained using centrifuge, washed twice with ethanol and dried in an oven at 60 °C overnight. The samples were calcined in muffle furnace at various temperatures (500 °C, 600 °C and 700 °C) for different calcination duration (1 h, 3 h and 5 h) to determine the optimum calcination condition. The catalysts were labeled as S_2Zx-y , where “x” stands for the calcination temperature and “y” the calcination duration. For example, $S_2Z500-1$ stands for the catalyst calcined at 500 °C for 1 h.

2.2.2. Catalyst characterization

The XRD patterns of sulfated zirconia catalysts were recorded on Shimadzu XRD-6000 with $Cu K\alpha$ radiation at 20°–70°, 2θ in steps of 8°. TEM images were taken on a JEM-2100F high resolution transmission electronic microscope at an accelerating voltage of 200 kV. The acidity of the catalyst was measured with NH_3 -TPD experiment. Thermal conductivity detector (TCD) was used for the ammonia desorption profile. In a typical run, 0.1 g of the catalyst was heated in an helium flow at 300 °C for 1 h and then cooled down to 120 °C. Next, the sample was allowed to saturate with NH_3 at 120 °C. Subsequently, it was treated with dry helium for 30 min to eliminate the weakly adsorbed NH_3 until then the temperature increased to 600 °C at a rate of 10 °C·min⁻¹ and kept constant for a given time period. The total sulfur content was measured by using a YX-DL 8300 type compact sulfur detector (Youxin Equipment Manufacture Co., Ltd., China) with measuring accuracy of 0.001%.

2.3. Catalytic activity measurement

The reactions were performed according to batch catalytic experiment in a 50 mL stainless steel autoclave with Teflon wall and autogenous pressure with constant stirring (600 rpm). The total volume of the reaction mixture and typical catalyst concentration were kept constant, being at 20 mL and 3 wt.% of the weight of the oil, respectively. The predetermined amounts of catalysts, the commercial edible grade oil (an expired soybean oil) and methanol were sealed in the reactor. When the set temperature was reached, the stirrer began working and it was timed. After a preset reaction time, the reaction mixture was cooled to room temperature and filtered to separate the solid catalyst. The methanol was then removed by a rotary evaporator, so glycerol could be separated by gravity filtration. Consequently, the remaining liquid was diluted with pyridine and analyzed for its compounds content.

To optimize the reaction condition, parameters such as reaction time, reaction temperature and molar ratio of the reactants were adjusted. Studies of the processes were conducted in the reaction time from 1 h to 6 h, at temperature ranging from 90 °C to 150 °C, by varying the molar ratio of methanol to oil in the range of 6:1 to 30:1 (with excess of methanol).

The reference products were analyzed and quantified using gas chromatograph equipped with an AS-200 automatic injection, a flame ionization detector and an Agilent DB 5ht capillary separation column. The column oven temperature was programmed from 70 to 190 °C (at the rate of 15 °C·min⁻¹) and then raised to 260 °C at 7 °C·min⁻¹ and to 380 °C at 30 °C·min⁻¹ and maintained at this temperature for 6 min. The injector and detector temperatures were set at 360 °C and 380 °C, respectively. In this experiment, the conversion of oil based on the amount of the oil collected in the product was calculated according to the following formula:

$$\text{Conversion of oil (\%)} = 100 - \frac{\text{mass of unreaction oil}}{\text{initial mass of oil}} \times 100$$

3. Results and discussion

3.1. Characterization

The XRD patterns of the sulfated zirconia prepared with different calcination processes were shown in Fig. 1. Clearly, the XRD pattern of $S_2Z500-1$ presented broad peaks in the 2θ regions of 20°–40° and 40°–70°, indicating the existence of amorphous structure, which were

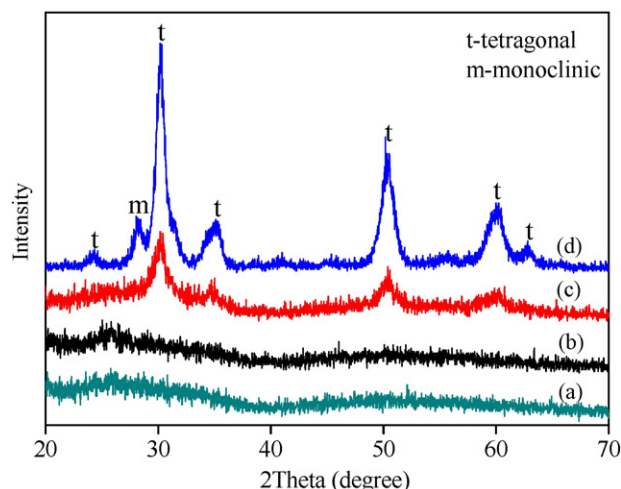


Fig. 1. XRD patterns of (a) $S_2Z500-1$ (b) $S_2Z500-5$ (c) $S_2Z600-1$ and (d) $S_2Z700-1$.

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