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Synthesis of mesoporous sulfated zirconia nanoparticles with high surface area and their applies for biodiesel production as effective catalysts

Yongming Luo[a], Zhanqiang Mei[b], Nengsheng Liu[c], Hua Wang[c], Caiyun Han[a], Sufang He[a,b,*]

[a] *Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, PR China*
[b] *Research Center for Analysis and Measurement, Kunming University of Science and Technology, Kunming, 650093, PR China*
[c] *Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, PR China*

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ABSTRACT

Sulfated zirconia (SZ) was employed as solid acid catalyst for biodiesel production via the transesterification of soybean oil with methanol. The effects of synthesis method, template/sulfonating agent and calcination temperature were investigated. Compared to conventional two-step route, one-step liquid-crystal template (LCT) method achieved the successful synthesis of mesoporous SZ nanoparticles (MNSZ) with larger surface area, favored the more acid sites, stronger acidity and smaller tetragonal ZrO_2 (t-ZrO_2). Sodium dodecyl sulfate (SDS), both as template/sulfonating agent, was superior to Hexadecylsulfonic acid sodium salt (CSS) in retarding the grain growth of t-ZrO_2, formation of monoclinic ZrO_2 phase and loss of sulfated groups. High calcination temperature resulted in the serious loss of acid sites, decrease of surface area and increase in crystal size of t-ZrO_2, accelerated the transformation of active t-ZrO_2 into monoclinic ZrO_2, thus leaded to severe decline in catalytic activity. MNSZ, prepared via one-step LCT method at 550 °C using SDS as template/sulfonating agent, was found to be the best catalyst. Over this catalyst of 4 wt%, approximately 100% of soybean oil conversion and FAME yield of 94.9% could be achieved at 120 °C in 4 h, using the feedstock with methanol/soybean oil molar ratio of 12:1.

1. Introduction

Compared to the petroleum-derived diesel fuel, biodiesel is advantageous in terms of biodegradability, less toxicity, renewability, high combustion efficiency, as well as the much easier and safer handling, storage, and transportation [1–3]. In the current situation that a series of serious social and environmental problems caused by the use of fossil fuel [1], including dwindling reserves of crude oil, oscillating petroleum fuel prices, and the overconsumption of liquid fuels, large greenhouse gas emissions, acid rain, and also global warming, biodiesel is consistently gaining attention as a viable substitute for petroleum diesel in a near future [1,4].

Biodiesel, a mixture of fatty acid methyl esters (FAME), is usually derived from the alcoholysis of vegetable oils or animal fats with an excess of a primary alcohol (most commonly methanol) in the presence of a catalyst. The catalysts typically used in these industrial units are NaOH and KOH homogeneous base catalysts [5,6]. Unfortunately, production of biodiesel catalyzed by such base catalysts has many shortcomings. The presence of free fatty acids (FFAs) and water facilitate the hydrolysis reaction of esters to form the more FFA on one hand, and promote the undesirable saponification reactions of FFA with base catalysts on the other hand. These always result in the catalyst deactivation and productivity reduction [7,8], moreover, lead to the difficulties in the separation and purification of biodiesel from the post-reaction mixture, and disposal issues of the generated waste water stream [1]. To overcome these problems, one of the widely recommended alternatives is the usage of acid catalysts, which are able to simultaneously catalyze the transesterification of triglycerides and the esterification of FFAs without the formation of soaps [9–14], and thus can help in processing inexpensive feedstocks containing FFAs and water. Compared to the unrecyclable homogeneous catalysts, the heterogeneous catalysts can be easily separated from the reaction medium, and then be regenerated and recycled [14]. In addition, it is beneficial to minimizing the corrosion, environmental and toxicity problems [3,14,15–19]. In this regards, biodiesel production by the heterogeneous acid-catalyzed alcoholysis reaction is a good choice. Recently, various solid acidic catalysts have been comprehensively tested for biodiesel production, such as silica, zeolites, zirconia and carbon materials [9,20–24]. Among them, zirconia materials [9,12,13,24–28] are reported as a family of the efficient heterogeneous catalysts, in particular, sulfated zirconia (SZ) is the widely used one [9,12,13,29–31]. Nevertheless, the conventional sulfated zirconia (CSZ)

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* Corresponding author at: Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, PR China.
E-mail address: shucai1983@163.com (S. He).

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is known to suffer lower reaction rates and significant deactivation during liquid-phase transesterification, possibly due to poor porosity and low surface area [32,33] which are the essential assets for obtaining large number of accessible active sites and minimizing the diffusional issues [34–36]. In this situation, mesoporous sulfated zirconia (MSZ), which is reported to possess uniform pore size, large surface area and high porosity [37–39], is considered to be an ideal solid acid catalyst for biodiesel production.

The MSZ synthesis strategy, which will result in diverse structural, textural and acidic properties, plays an important role in the catalytic behaviors [29]. Numerous methods [40–49] have been employed to improve the textural properties and acidity of MSZ. These methods are generally classified into one-step and two-step. Owing to the advantages of avoiding the impregnation (sulfating) step and simplifying the overall synthesis procedure to a great extent [46], one-step synthesis route has recently attracted considerable attention [45–49].

In this paper, the mesoporous nanosized sulfated zirconia (MNSZ) were prepared via one-step liquid-crystal template (LCT) method by employing SDS both as a template and a sulfonating agent, and used as heterogeneous catalyst in the soybean oil transesterification reaction with methanol for biodiesel production. In the attempt to identify the correlation among synthesis parameters, surface properties and catalytic data, XRD, N_2 absorption-desorption isotherms, FT-IR, TEM, XPS and NH_3-TPD were employed to characterize the SZ catalysts. In addition, the influence of different experimental parameters, such as methanol/oil molar ratio, catalyst concentration, reaction temperature and time, on the catalytic behavior had been also evaluated in order to optimize experimental conditions for biodiesel production.

2. Experimental

2.1. Materials

Zirconium *n*-propoxide solution ($Zr(OC_3H_7)_4$, 70 wt.% in *n*-propanol) was purchased from Sigma–Aldrich. Sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$, SDS, CP, 95 wt.%), Hexadecylsulfonic acid sodium salt ($C_{16}H_{33}NaO_3S$, CSS, AR, 99 wt.%), concentration hydrochloric acid (c-HCl, 36 wt.%) and anhydrous methanol were obtained from Shanghai chemical regent company of China. Soybean oil was purchased from Kunming Chang-feng Company.

2.2. Synthesis of catalysts

The mesoporous nanosized sulfated zirconia (MNSZ) samples were prepared according to our previous works [49], which is introduced briefly as following procedures. 13.5 g of SDS (or 14.7 g of CSS) was added into 200 ml of deionized water with vigorously stirring at room temperature (RT). After complete dissolution of SDS/CSS, 20 ml $Zr(OC_3H_7)_4$ was added into the mixture solution to keep the molar ratio of Zr/S at 1:1. Next, the pH value of mixture solution was adjusted to 3.0 by 1.0 M HCl and the mixture solution was continuously stirred for 0.5 h. Then, the mixture was aged at RT for 20 h and thermally treated at 80 °C for 5 days under static conditions. Subsequently, the reaction product was filtered, washed with the deionized water/isopropanol solution, and dried at 110 °C for 12–24 h. Finally, the sample was calcined at different temperature in air for 3 h. The sulfated zirconia sample synthesized by this route was designated as $MNSZ_{\text{-x-y}}$, where 'y' is calcination temperature. 'x = 12′ represents SDS, 'x = 16′ represents CSS.

For comparison, sulfated zirconia was synthesized by conventional two step method. $Zr(OH)_4$ was prepared as the above procedure except the addition of SDS/CSS and calcinations, using $Zr(OC_3H_7)_4$ as zirconium source. Subsequently, the dried zirconium hydroxide was ground and was added into 1 M H_2SO_4 solution with stirring (20 ml/g $Zr(OH)_4$) for 2 h. Then, the sulfated product was filtered and dried again at 110 °C for 12–24 h. Finally, the sample was then calcined at 550 °C in air for 3 h. The sulfated zirconia sample synthesized by this route was designated as $CSZ_{\text{-550}}$.

ZrO_2 was also prepared using similar method except sulfating.

2.3. Characterization

X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-1200 diffractometer using Cu K_α radiation ($\lambda = 1.5406$ A°), operating at 40 kV and 30 mA. BET surface area and N_2 adsorption–-desorption isotherms were carried out on a Micromeritics-ASAP-2000 apparatus at −196 °C. All samples were degassed at 250 °C for 2 h prior to analysis. The BET specific surface area was calculated from adsorption data in the relative pressure range from 0.05 to 0.25.

TEM and HR-TEM images were obtained on a JEM-2010 HR transmission electron microscope, operating with an accelerate voltage of 200 kV.

FT-IR spectra of the samples in the form of KBr pellets were recorded by using a Nincolet 560 IR spectrometer with a DTGS detector.

The NH_3 temperature programmed desorption (NH_3-TPD) measurements were carried on an on-line Autochem 2910 instrument with TCD analyzing the evolved ammonia. The samples were pretreated at 400 °C for 1 h, and then cooled to 100 °C in He flow (40 ml/min), next, saturated with 10% NH_3/He (60 ml/min) at 50 °C for 2 h and subsequently flushed with He (60 ml/min) at 100 °C for 2 h to remove the physisorbed ammonia. Finally, the desorption of samples was performed from 100 °C to 700 °C with a ramp of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) analyses were performed on a PHI 5000 Versa Probe II spectrometer using Al Ka radiation as (1486.6 eV) the excitation X-ray source. The binding energies were calibrated by using the adventitious carbon (C1s at 284.6 eV) to account for charging effects.

The content of each species of SZ was evaluated by means of a Sequential X-ray Fluorescence spectrometer (Shimadzu 1800) on solid samples, and also by ICP-OES (Leeman Prodigy) after the complete dissolution of solid samples.

2.4. Transesterification of soybean oil with methanol

The performance of sulfated zirconia catalysts was evaluated in the transesterification of soybean oil with methanol. Briefly, soybean oil, methanol and sulfated zirconia catalysts (MNSZ and CSZ) were mixed in a batch reactor, and then this mixture was heated to a certain temperature under the vigorous stirring of 400 rpm for a required reaction time. To optimize the reaction conditions, the transesterification experiments were performed by varying reaction parameters such as methanol/oil molar ratio, catalyst concentration, reaction temperature and time. After reaction, the mixture was cooled to room temperature, and then centrifuged to separate the solid catalyst. The upper layer was taken out for gas chromatographic analysis after phase separation. Prior to analysis, methanol and water were removed by vaporization and dry. The yield of fatty acid methyl esters (FAME) was determined by a flame ionization detection (FID) of gas chromatography (GC) equipped with a capillary column (Agilent DB-5HT, 30 m × 0.32 mm × 0.10 μm).

3. Results and discussion

3.1. The optimization of synthesis parameters

3.1.1. Effect of preparation method

X-ray diffraction (XRD) and FT-IR spectra of sulfated zirconia prepared with one-step LCT and conventional two-step methods were compared in Fig. 1, in which ZrO_2 was included as a reference. Only the peaks (2θ at 30.3°, 34.9°, 50.4°, 60.3° and 62.9°) assigned to tetragonal phase zirconia (t-ZrO_2) were detected for both of the SZ samples from the XRD patterns, with higher peak intensity for $CSZ_{\text{-550}}$ and lower peak