



Mesoporous nanocrystalline sulfated zirconia synthesis and its application for FFA esterification in oils

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ABSTRACT

Mesoporous nanocrystalline sulfated zirconia catalyst has been prepared from zirconium hydroxide synthesized at different digestion/hydrothermal treatment times. Sulfuric acid and chlorosulfonic acid were used as two different sulfonating agents. The effect of digestion time, sulfonating agent and the calcination temperature on structural, textural and catalytic properties of the prepared catalyst were investigated in details using nitrogen adsorption–desorption (BET), ammonia temperature programmed desorption (NH₃-TPD), X-ray diffraction (XRD), thermogravimetry and differential scanning calorimetry (TGA–DSC), and Fourier transform infrared spectroscopy (FTIR). The sulfated zirconia prepared at various digestion times and two different sulfonating agents were tested for the esterification of free fatty acid (FFAs) in soybean oil (prepared by mixing oleic acid in soybean oil) as model reaction. Sulfated zirconia catalyst prepared with 3 h digestion time and 600 °C calcination temperature using chlorosulfonic acid showed the highest catalytic activity with about 85% conversion in just 80 min of esterification time at 60 °C reaction temperature.

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1. Introduction

Biodiesel also called fatty acid methyl ester is a clean-burning, renewable fuel produced from vegetable oils, animal fats and recycled cooking oil and greases, etc. It is not only biodegradable but also free of sulfur, making it a cleaner burning fuel than petroleum diesel with reduced emission of SO_x, CO, unburnt hydrocarbons and particulate matter [1]. Excellent lubricating properties that extend engine life, superior cetane number, flash point compared to conventional diesel and acceptable cold filter plugging point (CFPP) are some of the attributes that make biodiesel very attractive alternative fuel [2,3].

The major hurdle in the use of biodiesel for replacing conventional petroleum fuels is its higher cost. The two main factors that affect the cost of biodiesel are the cost of raw materials and the processing cost such as catalysts and equipments [4]. The raw materials account for over 60–75% of the biodiesel production expenses. The potential solution to this problem is the utilization of low value alternative feedstocks of varying type, quality and cost. For example, the cost of waste cooking oil is 2–3 times lower than virgin oils. Thus the utilization of less expensive feedstocks such as animal fat, waste cooking oil, yellow and brown grease is expected to

appreciably reduce the biodiesel cost [5]. However, many of these alternative feedstocks may contain high levels of free fatty acids (FFA), water, or insoluble matter, which affect biodiesel production [6]. Synthesis of biodiesel via transesterification reaction with feedstocks having higher FFA and moisture is complicated. During the reaction, the feedstocks undergo saponification reaction leading to soaps formation resulting in reduced biodiesel yields, especially when alkaline catalysts are used. Furthermore, the soap formation also leads to the catalyst consumption, lowering catalytic efficiency and increase in the viscosity of reaction mixture and gel formation requiring additional purification steps [5]. These problems could potentially be eliminated via the use of heterogeneous acid catalysts due to their lower susceptibility to FFAs and moisture content in the oil [7]. Also, catalysts can be easily separated from the reaction products with much more simplified product separation steps resulting in high yields of methyl esters and decrease of catalyst cost due to the possibility of catalyst regeneration.

To date, several solid acid catalysts have been reported for biodiesel synthesis, including zeolites (e.g. H-ZSM-5, Y and Beta), ion exchange resins (e.g. Amberlist 12, a styrene based sulfonic acid and Nafion-NR-50, a copolymer of tetrafluoroethylene and perfluoro-2-(fluorosulphonylthoxy) propyl vinyl ether) and metal oxides modified with sulfate ions (SO₄^{2−}/M_xO_y, such as SO₄^{2−}/ZrO₂, SO₄^{2−}/SnO₂, SO₄^{2−}/TiO₂, SO₄^{2−}/WO₃, etc. [8,9]. Zeolite catalysts with small (micron-sized) pores are not suitable for biodiesel manufacture because of the diffusion limitations induced

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by the large fatty acid molecules. Ion-exchange resins are active strong acids, but have a low thermal stability which is problematic as the esterification reaction might require high temperatures. Metal oxides modified with sulfate ions and especially sulfated zirconia, has high boiling point, strength, toughness, good corrosion resistant in acidic and alkaline environment. In addition sulfated zirconia has very high activity, selectivity and stability making it a promising candidate not only for the esterification reaction but also for number of industrially important reactions such as hydrocarbon isomerization, methanol conversion to hydrocarbons, alkylation, acylation, etherification, condensation, nitration, cyclization and Fisher–Tropsch synthesis [10–12]. However, the catalytic and structural properties of the sulfated zirconia depends on number of factors including $\text{Zr}(\text{OH})_2$ preparation method, precursor used, precipitation pH, precursor concentration, type of sulfonating agent, catalyst pretreatment, and calcination [13–15].

In an earlier work, nanocrystalline mesoporous $\text{Zr}(\text{OH})_2$ powder with very high surface area was synthesized using ethylene diamine and zirconyl chloride octahydrate. Ethylene diamine used as precipitating agent also acted as a colloidal protecting agent. The results of the effects of various process parameters such as precipitation pH, precursor concentration, time of hydrothermal treatment and calcination temperature on the structural and textural properties of zirconium oxide were discussed in detail [16].

Yadav and Murkute [17] previously reported the use of chlorosulfonic for the sulfonation of zirconia powder. It was showed that the chlorosulfonic acid treated zirconia possesses more sulfate ions, stability and activity compared to the sulfated zirconia synthesized using sulfuric acid. In this study we report the synthesis of mesoporous nanocrystalline sulfated zirconia with high surface area and acidity. Mesoporous zirconium hydroxide prepared at different digestion times of 0, 1, 3, 6, 12, 24 and 48 h were sulfonated by wet impregnation method using sulfuric acid and chlorosulfonic acid as two different sulfonating agents. To the best of our knowledge, no studies have been reported in the literature showing the effect of digestion/hydrothermal treatment on the sulfonation process and acidity of final sulfated zirconia catalyst. The effect of preparation conditions such as digestion time, sulfonating agent and the calcination temperature on the structural phases, textural characteristics and the number and types of available active acidic sites on the surface of the final sulfated zirconia were investigated using nitrogen adsorption–desorption (BET), ammonia temperature programmed desorption (NH_3 -TPD), X-ray diffraction (XRD), thermogravimetry and differential scanning calorimetry (TGA–DSC), and Fourier transform infrared spectroscopy (FTIR). The sulfated zirconia prepared at the best synthesis conditions was tested for the esterification of free fatty acid in soybean oil (prepared by mixing oleic acid in soybean oil) as model reaction.

2. Experimental

2.1. Chemicals

Zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), 98+ % pure, ethylenediamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), 99%, extra pure, sulfuric acid, 97%, ethylene dichloride were purchased from Acros Organics, NJ, USA. Chlorosulfonic acid, 99% was obtained from Alfa Aesar, Ward Hill, USA. The water used at all stages of the experiments was purified using a Mill-Q Advantage A10 with Elix 5 system obtained from Millipore Corporation (Bedford, MA, USA).

2.2. Catalyst synthesis

The method for the synthesis of zirconium hydroxide (80–90% yield) has been discussed in details previously [16]. Zirconyl

chloride octahydrate and ethylene diamine are used as zirconium precursor and precipitating agent, respectively, as reported by D'souza et al. [18]. Sulfated zirconia was prepared from this material using two different methods based upon two different sulfonating agents, i.e., sulfuric acid and chlorosulfonic acid. In the case of sulfuric acid, 1 g of the dried again as prepared zirconium hydroxide power was mixed with 15 ml of 1 N H_2SO_4 and then stirred with magnetic stirrer for about 10 min followed by the filtration and air drying. The air dried material was then dried in oven for 24 h at 110 °C. In the case of chlorosulfonic acid, 1 g of dried as prepared zirconium hydroxide power was immersed in 15 ml, 0.5 M solution of chlorosulfonic acid in ethylene dichloride. After about 30 min, ethylene dichloride was evaporated in an oven at 80 °C for 20 h and then dried completely for 24 h at 110 °C. The samples prepared by using both methods were then calcined at 600 °C and 650 °C temperature for 2 h with controlled heating and cooling rates of 0.5 °C/min and 1 °C/min respectively, in the presence of air. The two different samples were denoted as SZ and CSZ for sulfated zirconia prepared using sulfuric acid and chlorosulfonic acid, respectively. Finally, the prepared samples were characterized by using different analytical and instrumentation techniques described in the following section.

2.3. Catalyst characterization

The BET surface area, total pore volume and pore size distribution of the catalyst were determined with AUTOSORB-1C, Chemisorption–Physisorption analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Surface area was calculated by using BET equation from the adsorption branch of the isotherm in a relative pressure range of 0.07–0.3. The pore size distribution was calculated from desorption branches using the Barrett–Joyner–Halenda (BJH) method [19]. The total pore volume was derived based on the amount of N_2 adsorbed at a relative pressure close to unity. The acidity of the sulfated zirconia catalyst was measured by using ammonia temperature programmed desorption (NH_3 -TPD) experiments. Thermal conductivity detector (TCD) connected to the AUTOSORB-1C was used to measure the ammonia desorption profile. In a typical run, 0.25 g of the catalyst (sandwiched between two small wads of glass wool) was placed into the chemisorptions cell and heated to 140 °C at 20 °C/min under the helium flow for 30 min to remove adsorbed components. Later the sample was cooled to 100 °C and saturated with ammonia by exposing the sample to 100% NH_3 for 10 min. Physisorbed ammonia was removed by purging the sample with helium gas for 30 min. Finally, the temperature was ramped to 600 °C at a rate of 20 °C/min and evolved ammonia was quantified by thermal conductivity detector.

Thermo-gravimetric (TGA) and differential scanning calorimetry analysis (DSC) were carried out using a SDT Q600 V20.4 Build 14 system (TA Instruments, New Castle, DE, USA). The heating was carried out in an air environment. The air flow rate was maintained at 100 ml/min and the heating rate was 10 °C/min.

Infrared absorption–transmission spectra were obtained using an FTIR spectrometer (SENSOR 27, Bruker Optics, Inc., Billerica, MA) with HeNe laser source and a room-temperature deuterated L-alanine triglycine sulfate detector (DLATGS detector). The FTIR was equipped with an ATR sampling accessory, MIRacle ATR set with Diamond crystal assembly from PIKE Technologies (PIKE Technologies, Inc., Madison, WI). All spectra were collected at 20 ± 1 °C using an average of 16 scans and with a spectral resolution of 2 cm^{-1} . The background spectra were obtained using a clean ATR accessory with a continuous dry, CO_2 -free air purge from a laboratory generator (Parker–Balston, Haverhill, MA) to remove moisture. During the analysis, a small amount of powdered sample was placed on the crystal and pressured with high pressure clamp to get the intimate contact between the sample and crystal surface.

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