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Sono-sulfated zirconia nanocatalyst supported on MCM-41 for biodiesel production from sunflower oil: Influence of ultrasound irradiation power on catalytic properties and performance

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ABSTRACT

Sono-sulfated zirconia nanocatalyst supported on MCM-41 was prepared by an ultrasound-assisted impregnation/hydrothermal hybrid method. The effect of irradiation power was studied by changing power of the sonication (30, 60 and 90 W) during the synthesis which led to different physiochemical properties of the nanocatalyst. XRD, FESEM, EDX, FTIR and BET analyses exhibited smaller particles with higher surface area and less population of particle aggregates at highly irradiated nanocatalysts. The nanocatalyst irradiated at 90 W for 30 min showed a very narrow particle size distribution. About 59% of nanocatalyst particles were in the range of 1–30 nm. The performance of investigated nanocatalysts in biodiesel production from sunflower oil showed ultrasound-assisted synthesized nanocatalysts had higher conversion in comparison to non-sonicated catalyst. Biodiesel conversion in catalyst with 90 W and 30 min ultrasonic irradiation exceeded 96.9% under constant condition at 60 °C reaction temperature, methanol/oil molar ratio of 9:1 and 5% catalyst concentration. After five cycles, biodiesel conversion of non-sonicated catalyst was well maintained in a high extend (71.4%) while biodiesel conversion of non-sonicated catalyst barely reached to 43.5%. Among sonicated nanocatalysts, with increasing power of irradiation, the nanocatalyst represented higher conversion and reusability.

1. Introduction

Biodiesel also called fatty acid methyl ester is a clean-burning renewable fuel produced from vegetable oils [1,2], animal fats [3,4], recycled cooking oils [5,6] and triglyceride sources [7,8]. It is not exclusively biodegradable but also free of sulfur, making it a cleaner burning fuel than petroleum diesel with reduced emission of SOx, CO, unburned hydrocarbons and particulate matter [9]. Excellent lubricating properties that extend engine life, superior cetane number, flash point compared to conventional diesel and suitable cold filter plugging point (CFPP) are some of the attributes that make biodiesel very attractive alternative fuel [10,11].

The major barrier in the use of biodiesel for replacing conventional petroleum fuels is its high cost [12,13]. The two main factors that affect the cost of biodiesel are the raw materials cost and the processing cost like catalysts and equipments [14]. The use of cheaper and recycled feedstocks, such as inedible animal fats and waste cooking oils, allows for increases in the production and improvement in the biodiesel economic outlook [15,16]. Also, heterogeneous catalysts can be easily separated from the reaction products with much more simplified product separation steps resulting in high yields of methyl esters and decreasing catalyst cost due to the possibility of catalyst reusability [17–19]. Among solid acid catalyst, metal oxides modified with sulfate ions and particularly 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 favourable candidate for the esterification reaction. However, it has been reported that these catalysts suffer from a serious deactivation after several reaction cycles, for which several explanations have been suggested, as the intermediate or product molecules blocking the catalyst pores [20], or their anchorage to acidic centres [21], the irreversible bonding of water

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molecules generated as product of the esterification reaction to the acidic centres [22], and the leaching of sulfur species to the reaction medium; the latter being proposed as the most important one for many authors in the light of reported experimental results, as the loss of sulfur content of the spent catalysts with respect to the fresh ones, or the detection of sulfuric acid or sulfuric acid-derived species in the reaction medium. Thus, closely all catalytic activities reported in the first reaction cycle appear to be due to homogeneous rather than heterogeneous catalysis [23–25]. Moreover, leaching of sulfur species deactivates the catalyst in an irreversible way. Although re-impregnation with sulfuric acid has been proposed as a solution [20], this method rises the catalyst cost and, what is more important, may be undesirable for produced biodiesel to meet the sulfur content recommendations regarding the environmental concerns. Thus, Garcia et al. found that amorphous sulfated zirconia has a much more quantity of acid sites that are active for transesterification of vegetable oil, for example, tetragonal sulfated zirconia phases [25]. With these antecedents, it would be so interesting to explore the possibilities of a highly dispersed zirconia as carrier of sulfate species, which could be achieved by employing a zirconium doped mesoporous MCM-41 silica as support, since it has been demonstrated that these solids give rise to amorphous and very well-dispersed zirconia-like species on the pore walls of the silica matrix [26], which are likely to strong interact with the following supported sulfate species.

The physicochemical properties of the synthesized nanocatalyst can be affected by hybrid synthesis methods [27–29]. Arena et al. used a hybrid sonochemically synthesis method for high dispersion of active site on support [30]. Although they found that the ultrasound improved the physiochemical properties of the catalyst, however, the effect of ultrasound was not considered in details. When a liquid is irradiated by ultrasound, acoustic cavitation will begin to appear [30–33]. After bubbles are collapsed in solution as a result of acoustic cavitation, high temperatures, high pressures and very short lifetimes are observed; these transient, localized hot spots facilitate chemical reactions during synthesis procedure [34–36]. Therefore, the nucleation rate and dispersion of the fine particles on the carrier enhanced [37–39].

In the present work, we report the effect of ultrasonic power on properties of a sulfate mesoporous zirconium doped MCM-41 silica (with Zr/Si molar ratio = 0.2) prepared by ultrasound assisted impregnation hybrid synthesis method on the esterification of free fatty acids (FFA) in sunflower oil (Fig. 1). The characterization of the synthesized catalysts is studied using various methods containing the nitrogen adsorption Brunauer-Emmett-Teller (BET), the X-ray diffraction (XRD), the Fourier-transformed infrared (FTIR), the field emission scanning electron microscopy (FESEM) and the energy dispersive X-ray (EDX). Additionally, the reusability of catalyst will be investigated in order to leaching of sulfur-containing species to the reaction medium.

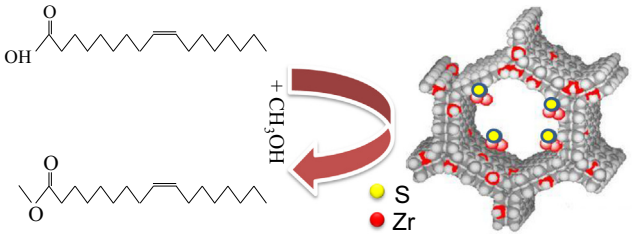

Fig. 1. Reaction pathway for biodiesel production from sunflower oil over sono-sulfated zirconia nanocatalyst supported on MCM-41.

2. Materials and methods

2.1. Materials

Cetyltrimethyl-ammonium bromide ($C_{19}H_{42}BrN$, Merck, extra pure), sodium metasilicate (Na_2O_3Si, Aldrich, 99.9%) and Zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$, Aldrich, 99%), were used as the sources of the template and support, respectively. Sulfuric acid (H_2SO_4, Merck, 98%) was applied as the source of sulfate phase.

2.2. Nanocatalysts preparation and procedure

ZrO_2-MCM-41 mesoporous support was synthesized by hydrothermal method according to the reported methods in the literature [26]. Fig. 2 shows schematically the methodology of the preparation method of S-ZrO_2/MCM-41 nanocatalyst. Appropriate amounts of cetyltrimethyl-ammonium bromide, sodium metasilicate and Zirconyl chloride octahydrate were dissolved in water and stirred and then pH was adjusted to 10.5 with 4 N sulfuric acid. The resulting homogenous solution was transferred into an autoclave and then heated in an oven at 120 °C for 12 h. The solid product was filtered, washed and dried at 110 °C for 6 h and calcined at 600 °C for 6 h to remove the surfactant.

The incorporation of sulfate was performed by incipient wetness impregnation under ultrasound irradiation using aqueous solutions of sulfuric acid. The sonication was carried out using a SONOPULS HD 3200 system and the slurry was irradiated with high intensity ultrasonic radiation by employing a direct immersion titanium horn (1 cm^2, 20 kHz). The concentration of the precursor solution was adjusted to give rise to catalysts with sulfate loadings of 10 wt%. The resulting solution was dried at 110 °C for 6 h and then calcined at 600 °C for 3 h to remove the surfactant. The catalysts were labelled as SZM(P = x), where x is the ultrasonic irradiation power. Different power outputs (30, 60 and 90 W) were applied for synthesis of SZM catalysts. A schematic diagram of the experimental setup is illustrated in Fig. 3.

2.3. Nanocatalysts characterization techniques

Laboratory X-ray powder diffraction (XRD) patterns were gathered on a PAN analytical X'Pert Pro automated diffractometer. Powder patterns were recorded in Bragg-Brentano reflection configuration by applying a Ge (1 1 1) primary monochromator (Cu Kα1) and the X'Celerator detector with a step size of 0.02° (2θ). The powder patterns were recorded at low angles between 1 and 10° in 2θ with an equivalent counting time of 203.6 s/° and at high angles between 10 and 70° in 2θ with an equivalent counting time of 27.8 s/°. The diffraction peaks of the crystalline phase were compared with compounds reported in the Joint Committee of Powder Diffraction Standards (JCPDS) database file. The microstructure and morphology of nanocatalysts were studied by FESEM (HITACHI S-109 4160). EDX-Dot Mapping analysis was performed by VEGA//TESCAN, BSE DETECTOR for elemental analysis. The BET specific surface area of the samples was carried out by using a Quantachrome CHEMBET-3000 apparatus. FTIR of the powders was recorded using UNICAM 4600 Fourier spectrometer in a range of 400–4000 cm^{-1} by KBr pellet method at 25 °C room temperature.

2.4. Catalytic performance test

The catalytic activity/performance of prepared SZM catalysts was determined by testing them for the esterification of oleic acid in soybean oil (10% oleic acid) as reactant model for used oil. The reaction was carried out in a cylindrical jacketed glass reactor with

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