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Biodiesel production by esterification of free fatty acid over sulfated zirconia

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ABSTRACT

Sulfated zirconia was synthesized and characterized by various physico-chemical techniques such as EDS, Thermal analysis (TGA & DTG), FT-IR, XRD, BET surface area measurement, SEM and n-butyl amine acidity determination. The use of synthesized catalyst was explored for biodiesel production by esterification of (free fatty acid) oleic acid with methanol. Influence of various reaction parameters (catalyst concentration, acid/alcohol molar ratio, catalyst amount, reaction temperature and reaction time) on catalytic performance was studied to optimize the conditions for maximum yield of methyl oleate. Also the catalyst was regenerated and reused. As an application, preliminary study was carried out for biodiesel production by transesterification of waste cooking oil and Jatropha oil, as feedstock without any pretreatment, with methanol.

1. Introduction

Biodiesel is a renewable, biodegradable and non-toxic fuel. Biodiesel production has become a very intense research area due to rapidly depleting energy reserves and fluctuating petroleum prices [1]. Fatty acid methyl ester (FAME) commonly known as biodiesel can be a potential renewable energy fuel which can replace petroleum-derived diesel [2–5].

The conventional biodiesel production process based on the use of alkaline catalyst, such as sodium hydroxide or sodium methoxide, for transesterification of triglyceride posed serious separation problem. The presence of water and/or free fatty acids (FFA) in the reaction system leads to saponification [3,6,7]. A homogeneous acid catalyst, such as sulfuric acid or hydrochloric acid can also be used [8,9], which does not produce soap and increase the fuel production. However, corrosiveness and the down-streaming separation are the main problems. To avoid these problems, heterogeneous acid catalysts could be used. Also working with heterogeneous acid catalysts improves economic issues and better profitability of the biodiesel production process [10].

Among the various available heterogeneous acid catalysts, sulfated zirconia finds enormous applications in biodiesel production, especially due to its high catalytic activity and selectivity towards the ester when fatty acid reacts with a large variety of alcohols [2,8,9,11].

Rothenberg and co-workers have reported the use of sulfated zirconia, titania and stannia esterification reactions of free fatty acids, but the former was still the most active [3]. Jitputti and co-workers have reported that sulfated zirconia can give promising results in transesterification of palm kernel oil and crude coconut oil with methyl ester yield reaching as high as 90.3% and 86.3%, respectively [11]. Chen and his group had also evaluated the catalytic activity of SO_4^{2-}/ZrO_2 for transesterification of cotton seed oil, rich in free fatty acid content to produce fatty acid methyl esters [12]. Meunier and co-workers have reported a study focused on the esterification of a synthetic mixture of palmitic acid in sunflower oil with methanol over sulfated zirconia [13]. Lee and co-workers have also reported the use SO_4^{2-}/ZrO_2 for the esterification of free fatty acids present in used vegetable oils, waste cooking oil (WCO) with methanol [14]. Xiao and co-workers have used sulfated zirconia as catalysts for the transesterification of waste cooking oil with methanol [15].

Sulfated zirconia has also been reported for biodiesel production by esterification of free fatty acids such as dodecanoic acid with 2-ethyl hexanol [16,17] and for palmitic acid with methanol [13]. Recently K. T. Lee and co-workers have reported transesterification of *Jatropha curcas* oil by SO_4^{2-}/ZrO_2 and studied the effect of interaction between process variables [18]. Dussadee Rattanaphra and co-workers have reported esterification of myristic acid with methanol in presence of triglycerides over sulfated zirconia [19]. At the same time there are no reports on the esterification of oleic acid for biodiesel production using sulfated zirconia as catalyst.

Therefore, it was thought of interest to explore the catalytic activity of sulfated zirconia for biodiesel production by esterification

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of oleic acid. In the present work, sulfated zirconia was synthesized and characterized by various physico-chemical techniques such as EDS, Thermal analysis (TGA & DTG), FT-IR, XRD, BET surface area measurement, SEM and n-butly amine acidity determination. The effect of various reaction parameters such as catalyst concentration, acid/alcohol molar ratio, catalyst amount, reaction temperature as well as reaction time were studied to optimize the conditions for maximum yield for fatty acid methyl ester (FAME). Also the catalyst can be regenerated and reused. As an application, preliminary study was carried out for biodiesel production by transesterification of waste cooking oil and Jatropha oil, as feedstock without any pretreatment, with methanol over the present catalyst.

2. Experimental

2.1. Materials

All chemicals were of A.R. grade. Zirconium oxychloride was obtained from Loba chemie, Mumbai, and used as received. Methanol, Oleic acid and liquor ammonia were obtained from Merck and used as received.

2.2. Synthesis of hydrous zirconia

Hydrous zirconia was prepared by adding an aqueous ammonia solution to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ upto pH 8.5. The resulted precipitates were aged at 100 °C in a water bath for 1 h, filtered, washed with conductivity water until chloride free water was obtained and dried at 100 °C for 10 h. The obtained material was designated as ZrO_2.

2.3. Synthesis of the catalysts

A series of catalysts were synthesized by the wet impregnation of 1 g of ZrO_2 with 15 ml aqueous solution of 0.1, 0.2, 0.3 and 1 N sulfuric acid for 10 h with occasional stirring. The solution was then filtered and the obtained materials were dried at 120 °C for 10 h. The resulting materials were designated as 0.1 N SO_4^{2-}/ZrO_2, 0.2 N SO_4^{2-}/ZrO_2, 0.3 N SO_4^{2-}/ZrO_2 and 1.0 N SO_4^{2-}/ZrO_2 respectively. The filtrates solutions were analyzed for SO_4^{2-} and the remaining sulfate was subtracted from the total sulfate, which gives the weight % of SO_4^{2-} supported to ZrO_2. The selected catalyst i.e. 1 N SO_4^{2-}/ZrO_2 was calcined at 600 °C for 4 h. The obtained material was designated as C SO_4^{2-}/ZrO_2.

2.4. Characterization

Elemental analysis was carried out using JSM 5910 LV combined with INCA instrument for EDS- SEM. Thermal analysis of the sample was obtained by using the INKARP Thermal Analysis System (TG/DTA 6300). FT-IR spectra of the samples were obtained using KBr pellet on Perkin-Elmer. The structural information was carried out by the XRD pattern using PHILIPS PW-1830. The conditions used were: Cu Kα radiation (1.5417 Å), scanning angle from 5° to 60°. The surface morphologies of the support and catalyst were studied by SEM using a Jeol SEM instrument (model-JSM 5610 LV) with scanning electrode at 15 kV. Adsorption–Desorption isotherms of samples were recorded on a micromeritics ASAP 2010 surface area analyzer at −196 °C. From the Adsorption–Desorption isotherms specific surface area was calculated using BET method.

2.5. n-butyl amine acidity determination

The total acidity for all the materials was determined by n-butyl amine titration [20]. A 0.025 M solution of n-butyl amine in toluene was used for estimation. The catalyst weighing 0.25 g was suspended in this solution for 24 h and excess base was titrated against trichloroacetic acid using neutral red as an indicator. This gives the total acidity of the material.

2.6. Catalytic reaction

The esterification of oleic acid with methanol was carried out in a 100 ml batch reactor provided with a double walled air condenser, magnetic stirrer and a guard tube. The reaction mixture was diluted to 100 ml with methanol up to the mark; 5 ml of diluted solution was taken for the determination of unreacted acid. This was titrated against 0.1 M standardized methanolic NaOH solution. Blank reading was found out by diluting the definite quantity of oleic acid to 100 ml using methanol. 5 ml of this solution was titrated against 0.1 M standardized methanolic NaOH solutions using phenolphthalein indicator. Difference between the blank reading and reading for reaction mixture was used for finding out the % yield of ester.

3. Results and discussion

As shown in Table 1, 1.0 N SO_4^{2-}/ZrO_2, containing maximum weight % SO_4^{2-}, was selected for detailed study. For convenience, it was once again coded as SO_4^{2-}/ZrO_2. Table 2 shows the elemental analysis (EDS) for 1 N SO_4^{2-}/ZrO_2 and C SO_4^{2-}/ZrO_2. The observed values of elemental analysis were in good agreement with theoretically calculated values.

The TGA and DTG for the SO_4^{2-}/ZrO_2 is shown in Fig. 1. TGA showed that SO_4^{2-}/ZrO_2 was thermally stable. There was an initial weight loss observed from room temperature to 150 °C due to adsorbed water, after that there was negligible weight loss up to 350 °C and 550 °C, which indicates that the material was stable up to 600 °C. It is known that at higher temperature hydrous zirconia undergoes a phase change and it was clearly observed from DTG curve. The DTG curve showed the phase change of ZrO_2 which started at 400 °C indicating the phase change from monoclinic to tetragonal. Hence, the sample SO_4^{2-}/ZrO_2 was calcined at 600 °C for 4 h.

FT-IR spectra of SO_4^{2-}/ZrO_2 (Fig. 2), shows a broad band at 3391 cm^{-1} corresponding to the OH stretching vibration and also the band at 1631 cm^{-1} corresponding to δ HOH [21]. The bands at 1235, 1132, 1054 and 987 cm^{-1} indicated the presence of SO_4^{2-}, and were in good agreement with the reported one [22]. FT-IR spectra of C SO_4^{2-}/ZrO_2 (Fig. 2), shows that the calcination, at 600 °C modify the position of SO_4^{2-} bands and shift towards higher wave number. The SO_4^{2-} bands were replaced by a very broad band with a shoulder at 1379, 1233 and 1042 cm^{-1}. The OH stretching band at

Table 1
Weight % of SO_4^{2-} onto ZrO_2.

Catalyst	Weight % of SO_4^{2-}
0.1 N SO_4^{2-}/ZrO_2	5.0
0.2 N SO_4^{2-}/ZrO_2	26.3
0.3 N SO_4^{2-}/ZrO_2	40.0
1.0 N SO_4^{2-}/ZrO_2	68.5

Table 2
Elemental analysis (EDS).

Materials	Elements (Weight %)			
	O	Zr	S	
			Analytical	Theoretical
SO_4^{2-}/ZrO_2	49.12	47.98	2.90	1
C SO_4^{2-}/ZrO_2	39.62	58.96	1.42	1