Esterification of Free Fatty Acids (FFA) in used oil using a lab-synthesized mesoporous nanocrystalline sulfated zirconia

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Introduction

The utilization of less expensive feedstocks such as animal fat, waste cooking oil, yellow and brown grease is expected to appreciably reduce the cost of production of biodiesel (also called fatty acid methyl ester (FAME)), a clean-burning, renewable fuel. However, many of these alternative feedstocks may contain high levels of free fatty acids (FFA), which affect biodiesel production. Sulfated zirconia, has very high activity, selectivity and stability making it a promising candidate for the esterification of FFAs in oils to produce FAME.

In this study, 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 (H_2SO_4) and chlorosulfonic acid (CSA) as two different sulfonating agents. The synthesized sulfate zirconia catalysts were evaluated using BET, NH_3-TPD, XRD, TGA-DSC, and FTIR. The sulfated zirconia prepared at the best synthesis conditions was tested for the esterification of FFA in soybean oil (prepared by mixing oleic acid in soybean oil) as model reaction.

Materials and Methods

The sulfated zirconia was prepared from synthesized zirconium hydroxide (ZH) using H_2SO_4 and CSA as sulfonating agents. With H_2SO_4, 1 g of the dried as-prepared ZH 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. With CSA, 1 g of dried as prepared ZH power was immersed in 15 ml, 0.5 M solution of CSA 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 then calcined at 600 °C and 650 °C for 2 h in the presence of air. The two samples were denoted as SZ and CSZ for sulfated zirconia prepared using H_2SO_4 and CSA, respectively.

Results and Discussion

The surface area, pore volume and average pore sizes of the SZ and CSZ prepared with various digestion times calcined at 600 °C are given in **Table 1**. A slightly higher surface area was observed upon sulfonation using H_2SO_4 compared to the non-sulfated zirconia. The surface area was also observed to increase with increase in digestion time. Thus it can be concluded that the time of digestion certainly has the influence on the number of active sulfate sites on the zirconia surface. A drastic reduction in the surface area and pore volume and increase in the average pore size was observed upon sulfonation using CSA. Figure 1(a) is the conversion vs time plot for SZ prepared at different digestion times for oleic acid esterification reaction with: methanol/acid oil: 9/1, temperature: 60 °C, catalyst loading: 2 % (wt % of acid oil). Figure 2b is the conversion vs time plot for CSZ prepared at different digestion times for oleic acid esterification reaction with: methanol/acid oil: 9/1, temperature: 60 °C, catalyst loading: 2 % (wt % of acid oil). The CSZ catalyst prepared with 3 h digestion time and calcined at 600 °C showed the highest catalytic activity of about 85 % conversion in just 80 min at 60 °C for the esterification reaction. The higher catalytic activity of CSZ with significantly lower surface area compared to SZ is attributed to the presence of higher surface superacidic sites compared with SZ.

Table 1. Textural properties of the SZ and CSZ calcined at 600°C temperature

Material	Digestion time (h)	Surface area (m^2/g)	Pore volume (cm^3/g)	Avg. pore size (nm)
Zirconia	3	141.6	0.1415	3.996
SZ	1	114.1	0.0965	3.381
	3	149.0	0.1306	3.507
	6	165.5	0.1492	3.606
	12	158.8	0.1546	3.892
	24	177.6	0.1845	4.157
	48	176.5	0.1807	4.096
CSZ	1	18.02	0.0664	14.74
	3	20.93	0.0778	14.71
	6	23.73	0.0881	14.85
	12	18.90	0.0516	10.91
	24	20.98	0.0523	9.982
	48	20.07	0.0478	9.528

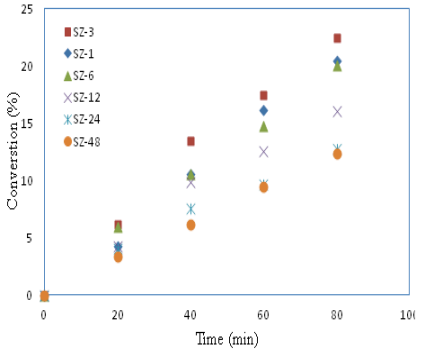

Figure 1a

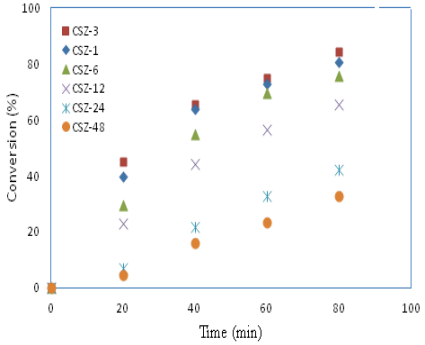

Figure 1b

Significance

The digestion time and the type of sulfonating agents have significant influence on structural, textural and catalytic properties of sulfated zirconia catalyst.

References

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