

Evaluation of Catalytic Activity of Two Forms of Synthesized Sulphated Zirconia for Triglyceride Cracking

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Abstract

Conventional wet-precipitation method was used to synthesis sulphated zirconia using two different molar ratios of sulphating agents. (1) the first was using a molar ratio of 1: 45 of $ZrOCl_2 \cdot 8H_2O$ impregnated with 1 M H_2SO_4 , (wp) and (2) a molar ratio of 1: 6 was used for the modified conventional wet-precipitation method, (mwp). The properties of both catalysts were examined by various techniques: EDX, XPS, FTIR, SEM, XRDP, Py-DRIFTS and BET nitrogen adsorption techniques. The variation in the molar ratio of the sulphating agent used during preparation led to sulphated zirconias that exhibited different properties in terms of specific surface areas, acid sites, thermal stability and surface sulphate. Both catalysts were catalytically active for triglycerides cracking for fatty acid methyl esters in a thermocatalytic reaction. The SZ1 not only exhibited higher conversion of triglycerides but higher FAMES yield, approximately 50% after 3 h, as compared to SZ2 (39%). Interestingly, SZ1 was selective towards unsaturated esters whereas SZ2 was towards saturated esters.

Keywords: conventional method, sulphated zirconia, saturated and unsaturated FAMES, thermocatalytic cracking

Introduction

Transesterification of triglycerides using monohydric alcohols is the most common process for biodiesel production. This process has a number of limitations, due to the use of homogeneous catalysts and alcohol. An alternative method of production is to use solid acid catalyst in thermocatalytic cracking. This would remove the need for alcohols altogether, reduction of downstream processes, and simplified flow sheet, thereby removing a substantial capital cost.

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Thermocatalytic cracking of triglycerides could fit into existing infrastructure; the main problem is finding a solid acid catalyst that is active, selective, and stable under the process conditions. Sulphated zirconia is a super-acid catalyst; but its catalytic properties are string function of the preparation method. Therefore, its preparation and catalytic performance have drawn much attention among researchers. In the present study, two types of sulphated zirconias were synthesized via conventional wet-precipitation method and modified wet precipitation method and their activity compared for biodiesel production.

Experimental

In the first instance sulphated zirconia was prepared by precipitation of zirconium oxychloride hydrate with ammonium hydroxide at pH 9. This was followed by impregnation of 1 gram of the resulting zirconium hydroxide with 15 ml of 1 M H_2SO_4 and calcination for 3 hours at $650^\circ C$; designated as 'wp'. The second was by using 2 ml of 1 M H_2SO_4 per gram of zirconium hydroxide and calcined for 3 hours at $650^\circ C$, it is designated 'mwp'. The catalysts were characterised using surface techniques, and their catalytic activities were investigated using triglycerides oil in a batch reactor at $270^\circ C$.

Results and discussion

XRDP indicates similarity in the morphology of both catalysts; they were found to be crystalline with 'wp' having a crystallite size of 10.42 nm and 17.51 nm for 'mwp' catalyst. However 'mwp' catalyst exhibited both tetragonal and monoclinic phases whereas 'wp' catalyst was only tetragonal in nature. The IR spectra of the catalysts exhibited strong absorptions of sulphate ions coordinated to the zirconium cation between 1297 cm^{-1} and 896 cm^{-1} region. The frequencies from both catalysts were similar, suggesting that the sulphur species in both samples are similar; however the intensity of absorption for 'mwp' catalyst is higher (16%) than 'wp' catalyst (13%). Elemental analysis (EDX) and X-ray photoelectron spectroscopy reveal similar results of higher retention of sulphur on the 'mwp' catalyst (13 wt %); almost double the weight percentage found on the 'wp' catalyst. The XPS also revealed consistency in O 1s spectra of both catalysts showing oxide oxygen at 530.6 eV and sulphate oxygen at 532 eV. The data showed that the sulphate species are S^{6+} of SO_4^{2-} . This is in agreement with [1]. The infrared spectra of the adsorbed pyridine on both catalysts, confirmed the presence of Bronsted and Lewis acid sites at 1544 cm^{-1} and 1440 cm^{-1}

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respectively. However the 'wp' has more Lewis acid as observed on the catalyst; (75%) and less of Bronsted acid sites (25%). The reverse is the case with the 'mwp' catalyst, approximately 58% of Bronsted acidity was observed; despite lesser amount and same source of acid used for impregnation of 'mwp' catalyst. The BET surface areas were $65\text{m}^2/\text{g}$, and $101\text{m}^2/\text{g}$, for 'wp' and 'mwp' respectively. Both catalysts were found to be active for triglyceride cracking; however the 'mwp' catalyst exhibited greater activity for fatty acid methyl esters ~30% after $2\frac{1}{4}$ h and 20% for 'wp' after 2 h. Interestingly the fatty acid methyl esters profile from modified wet-precipitated catalyst ('mwp') showed more selectivity for saturated fatty acid methyl esters compared to unsaturated.

Conclusion

The higher surface area and Bronsted acid sites of the 'mwp' sulphated zirconia resulted in increased catalytic activity and selectivity. From the elemental analysis there is an indication of loss of sulphur in the 'wp' catalyst, as more sulphate was used during preparation yet the post calcination analysis revealed less than half of the sulphate on the surface of the catalyst. The poor performance of 'wp' catalyst could be due to suppression of acidity by excess sulphate loading [2] as well as leaching during reaction because the EDX analysis of post reaction characterization of the catalysts showed no presence of sulphur on the 'wp' catalyst.

Justification for Acceptance

Selective cracking of triglycerides, using solid acid catalysts could revolutionise the economics of biodiesel production. The modified wet-precipitated catalyst investigated in this work is more active and more environmentally-friendly than the conventional wet-precipitated catalyst. Thermocatalytic cracking process removes the need for alcohols altogether and no glycerol in the product stream.

References

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