Using Calcium Oxide Based Catalysts in Transesterification of Soybean Oil with Methanol

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Introduction

Biodiesel, a renewable fuel with similar combustion properties to fossil diesel, is normally produced by the transesterification of highly refined oils with short-chain alcohols. Conventionally, some homogeneous base catalysts such as NaOH and $NaOCH_3$ were employed. However, these homogeneous catalysts are corrosive. And removal of these catalysts after reaction causes a large amount of waste wash water and a long time for phase separation. Moreover, traditional base catalysts can react with water and free fatty acids (FFA) in feedstocks to form soap which will greatly decrease the catalyst activity. Therefore, highly refined acid-free oil (FFA content < 0.5 %, water content < 0.06%) and anhydrous alcohol should be used for homogeneous base catalysts. However, that leads to a high feedstock cost. Thus, new catalytic processes are desirable for the development of an environmentally benign process, which can utilize low cost unrefined and waste oils directly.

Heterogeneous basic catalysts such as supported alkaline metal hydroxide catalysts [1] and alkaline earth metal oxide catalysts[2] have been studied. However, most of the reported heterogeneous catalysts show a much lower activity than traditional homogeneous base catalysts. Recently Yan et al. [3] reported a supported CaO catalyst have a high activity and an improved tolerance to water (2 %) and FFA (3 %). However, effects of water and FFA on catalyst structure and the catalytic performance in unrefined and waste oils were not fully elucidated. In this study, a lanthanum modified CaO catalyst was prepared and used in unrefined and waste oil system for biodiesel production. The effects of catalyst structure and reaction parameters (water and FFA content, oil feedstock types, water and CO_2 in air, molar ratio of methanol to oil, reaction temperature, activation temperature and catalyst dosage) on the yield of fatty acid methyl esters (FAME) were studied.

Materials and Methods

A sol-gel method was used to prepare calcium oxide based catalysts (Ca3La1, Ca1La0 and Ca0La1). Catalysts were characterized by XRD, XPS, SEM and EDS measurements. Reaction was performed in a batch reactor. In most studies, 10.0 g of soybean oil and 7.6 g of methanol and 0.5 g activated oxide catalyst were used.

Results and Discussion

Table 1 shows that Ca3La1 is a mixture of CaO, La_2O_3 and $La(OH)_3$ phases. And the average crystal size of CaO is about 57.2 nm. Ca3La1 has a stronger base strength and a higher amount of basicity than Ca1La0 and Ca0La1. Moreover, Ca3La1 has the highest specific BET surface area and FAME yield.

Crude soybean oil, crude palm oil and waste cooking oil without any pretreatment were converted to FAME directly using Ca3La1 catalyst (Figure 1). The average yield of these oils was about 96 % at 3 hours.

Table 1. Specific surface areas, XRD, basicity and catalytic activity of Ca1La0, Ca0La1, Ca3La1

Catalyst	BET Area m^2/g	X-ray Structure	Basicity mmol/g					Yield of FAME % [1]
			$4.2<H_-<6.8$	$6.8<H_-<7.2$	$7.2<H_-<9.8$	$9.8<H_-<15$	Total Basicity mmol/g	
Ca1 La0	10.4	$Ca(OH)_2$	0.3	0.1	\	\	0.4	18.7
Ca0 La1	9.9	$La(OH)_3$	0.1	\	\	\	0.1	3.2
Ca3 La1	62.6	CaO, La_2O3, $La(OH)_3$	0.6	2.0	10.4	1.0	14.0	95.3

Significance

This class of catalysts can directly utilize waste or unrefined oils and it provides a potential to decreases the production cost and feedstock cost of biodiesel.

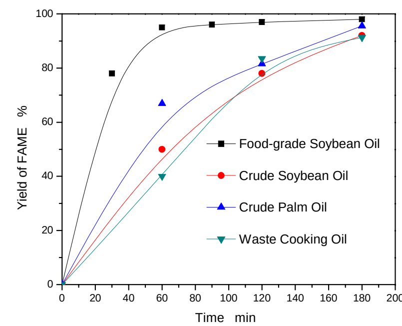

Figure 1. FAME yield of crude palm oil, crude soybean oil, waste cooking oil, food-grade soybean oil

References

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