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Transesterification of rapeseed oil under flow conditions catalyzed by basic solids: M—Al(La)—O (M = Sr, Ba), M—Mg—O (M = Y, La)

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ABSTRACT

Binary composites on basis of M—Al—O (M = Sr, Ba), M—Mg—O (M = Y, La), M—La—O (M = Sr, Ba) prepared by precipitation and calcined at 700–1200 °C were characterized by thermal analysis (TG–DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy of adsorbed probe molecule $CDCl_3$ (FTIR), low temperature nitrogen adsorption and heat desorption of argon and their catalytic activity towards the transesterification reaction of rapeseed oil was studied in the flow fixed bed reactor at 200 °C and 20 atm. The phase composition, texture and surface composition of the catalysts are determined by their chemical nature and calcination temperature. The performance of the catalysts calcined at 700–750 °C diminishes in the order of Sr—La—O > Ba—La—O > La—Mg—O ≥ Y—Mg—O > Ba—Al—O^{700} > Sr—Al—O^{700} and is in a straight correlation with the integrated intensity of absorption of surface carbonate species representing the amount of the strong basic sites on the surface of the catalysts. Thermal treatment of M—Al—O (M = Sr, Ba) catalysts at 1200 °C exerts minor influence on their performance.

1. Introduction

Nowadays, biodiesel composed by mono-alkyl esters of long chain fatty acids obtained from renewable sources such as vegetable oils or animal fats has gained significant attention as an environmentally benign substitute for petroleum-based fuels [1]. Moreover biodiesel is nontoxic and biodegradable [2].

Biodiesel is commonly produced *via* transesterification reaction of vegetable oils. In the course of this process one mole of triglyceride, the major component of vegetable oils, reacts with three moles of a short chain alcohol, preferably methanol, to produce one mole of glycerol and three moles of methyl esters. Traditionally, homogeneous base catalysts KOH, NaOH, sodium methoxide and potassium methoxide, providing high rate of the reaction under mild conditions (65 °C and 1 atm), are used for the production of biodiesel [2–10]. However, a significant drawback of the homogeneous process is the necessity of introduction of an additional technologically complex stage of the catalyst removal from the reaction products. Consequently, a considerable amount of waste water is inevitably produced and a long time is required for phase separation [11]. Moreover the application of homogeneous alkaline catalysts imposes strong restrictions on the water and free fatty acids (FFAs) content in oil feedstock. High amount of FFAs deactivates homogeneous base catalysts [1]. In particular, the total FFA content in the lipid feedstock must not exceed 0.5 wt%. Total water content must be not higher than 0.1–0.3 wt%, since its presence promotes hydrolysis of the alkyl esters to FFAs and consequent soap formation [4,7].

Saka and coworkers [12,13] and later Demirbas [14] proposed a non-catalytic method of the transesterification of rapeseed oil in supercritical methanol. Under these conditions, a rapeseed oil conversion of 95% is achieved during 5 min (for 6 ml of reaction mixture), and the catalyst separation step is not required. However, the process must be carried out at very high pressures (200–450 atm) and temperatures (300–400 °C). Recently, Tan et al. [15] described the transesterification of palm oil in the presence of heptane which was used as a co-solvent in order to increase the mutual solubility between methanol and triglycerides. The addition of heptane results in the decrease of the required reaction temperature from 360 °C to 280 °C and pressure from 220 atm to 150 atm, but the yield of fatty acid methyl esters (FAMEs) decreases from 80% to 66% as well.

Another way to overcome the drawbacks of homogeneous base catalysts is the application of heterogeneous catalytic systems, which are less corrosive and environmentally benign and can be

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