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Biodiesel production from soybean oil and methanol using hydrotalcites as catalyst

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ABSTRACT

Esters of fatty acids, derived from vegetable oils or animal fats, and known as biodiesel, are a promising alternative diesel fuel regarding the limited resources of fossil fuels and the environmental concerns. In this work, methanolysis of soybean oil was investigated using Mg–Al hydrotalcites as heterogeneous catalyst, evaluating the effect of Mg/Al ratio on the basicity and catalytic activity for biodiesel production. The catalysts were prepared with Al/(Mg + Al) molar ratios of 0.20, 0.25 and 0.33, and characterized by X-ray diffraction (XRD), textural analysis (BET method) and temperature-programmed desorption of CO₂ (CO₂-TPD). When the reaction was carried out at 230 °C with a methanol:soybean oil molar ratio of 13:1, a reaction time of 1 h and a catalyst loading of 5 wt.%, the oil conversion was 90% for the sample with Al/(Mg + Al) ratio of 0.33. This sample was the only one to show basic sites of medium strength. We also investigated the reuse of this catalyst, the effect of calcination temperature and made a comparison between refined and acidic oil.

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1. Introduction

Biodiesel is defined as alkyl esters of fatty acids produced from vegetable oils and animal fats. There has been an increasing interest in biodiesel as a green and alternative fuel as a result of recent legislations that require a major reduction of vehicle emissions, as well as the soaring price of petroleum [1].

Most biodiesel is produced today by transesterification of triglycerides to methyl esters using homogeneous basic catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides. However, the use of homogenous base catalysts for transesterification is problematic because the alkali can produce large amounts of unwanted soap by-product, which creates serious problems of product separation and ultimately decreases substantially the yield [2,3].

In contrast, heterogeneous catalysts are easily removed from the reaction mixture, making the purification step easier. Biodiesel production costs could certainly be reduced by using a heterogeneous catalyst for transesterification reaction instead of a homogeneous catalyst. The heterogeneous process provides higher quality esters and glycerol, which are more easily separated and further expensive refining operations are not needed [4–6].

The development of heterogeneous catalysts for transesterification of vegetable oils has also industrial interest, as can be seen by the large number of published patents. In these patents, mixed oxides and/or spinels of aluminum and a second transition metal are claimed as active catalysts for transesterification of vegetable oils and animal fats with several alcohols, particularly methanol and ethanol. However, high methyl ester yields and the production of high purity glycerin are associated to the reaction occurring in at least two stages, at high temperatures and pressures (170–250 °C, 30–70 atm), in continuous or batch reactors [7]. These researches lead to the development of a commercial process (Esterfip-H Trade Mark-Axens, France) for biodiesel production from methanolysis of vegetable oils, using a Zn-containing spinel derived from hydrotalcites as solid catalyst [8].

Hydrotalcites (HTs), a family of anionic clays, present positively charged brucite-like layers $(Mg(OH)_2)$ in which some of Mg^{2+} is replaced by Al^{3+} in octahedral sites of hydroxide sheets. The electrical neutrality is attained by compensating anions located in the interlayer space along with water molecules [9]. Decomposition of Mg–Al hydrotalcite yields a high surface area Mg–Al mixed oxide, which presumably exposes strong Lewis basic sites. The basic properties of these sites depend on the Mg/Al ratio in the hydrotalcite precursor. Interestingly, the reconstruction of decomposed Mg–Al hydrotalcite by rehydration at room temperature has been reported to enhance the catalytic activity [10].

Some authors have reported that the hydrotalcites, in the absence of calcination, present no catalytic activity for transesterification reaction [11,12]. On the other hand, Cantrell et al. [13] successfully used calcined hydrotalcites in promoting the transesterification of glyceryl tributyrate with methanol at 60 °C. The reaction rate increased steadily with Mg content and the most active catalyst (with Al/(Mg + Al) ratio of 0.25) was an order of magnitude more active than MgO. Xie et al. [11] also found that the most active calcined hydrotalcite has an atomic ratio Al/(Mg + Al) of 0.25, in soybean oil

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