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Transesterification of canola oil catalized by calcined Mg–Al hydrotalcite doped with nitratine

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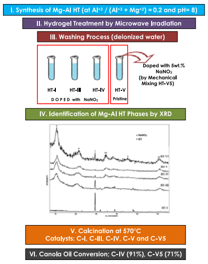
HIGHLIGHTS

- Hydrotalcite doped with 7 wt% NaNO3 converts canola oil to biodiesel up to 91%.
- The activity of hydrotalcite-NaNO3 is due to Mg^{2+}–O^{2-} pairs and Na_2O phase.
- $NaNO_3$ promotes the regeneration of hydrotalcite catalysts.
- Na_2O induces the conversion of canola oil to biodiesel as MgO provides active sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Mg–Al hydrotalcite substrates having an $X = Al^{+3}/(Al^{+3} + Mg^{+2})$ metal molar ratio equal to 0.2, were synthesized at pH=8 from a coprecipitation method combined with microwave radiation exposure to induce the crystalline network growth of the precursory hydrogel. The hydrotalcite materials were obtained either pristine or with the inclusion of nitratine at different amounts; this compound being added during the washing procedure of the hydrogel. The hydrotalcite substrates were calcined in air at 570 °C for 18 h, thus generating the corresponding mixed metal oxides. The final substrates were characterized by infrared spectroscopy, while also displaying the characteristic X-ray diffraction patterns of the hydrotalcite phase before calcination. The mixed metal oxide solids were used as catalysts (C_I–C_V) and were tested in the transesterification reaction of canola oil. It was found that the conversion to biodiesel increased, depending on the nitratine content existing in hydrotalcite as well as on the extension of the formed periclase phase. Among all catalysts, one of the substrates (containing 7 wt% of nitratine) exhibited the highest conversion of canola oil to biodiesel (91%), which, in this material, can be attributed to the preponderant presence of periclase and promoting effect of Na_2O. The latter material and a catalyst with no nitratine content were characterized by scanning electron microscopy, and their elemental surface composition was evaluated by Energy Dispersive X-ray Spectroscopy; in turn, their basic character was assessed by CO_2 Temperature Programmed Desorption. The conversion of synthesized Fatty Acid Methyl-Esters was calculated from the area under the signal peaks registered by Nuclear Magnetic Resonance spectroscopy.

1. Introduction

Since the invention and operation of the internal combustion engine, carried out by Rudolf Diesel in 1893 by employing fuel oil,

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all vegetable and edible oils, animal fat, and oil frying waste have been the main source for obtaining first-generation biofuels. Because of the large boom, and excessive use of fossil fuels, particularly of petroleum oil and its derivatives, that took place during the 20th century, serious environmental pollution problems were originated. This fact, coupled with the imminent decline of global oil reserves, has caused that researchers have focused their work on finding alternative sources of clean and renewable energy. Among these sources, biodiesel outstands as an oxygenated fuel which contains 10–15% oxygen by weight as well as of being a sulfur-free fuel. These facts lead biodiesel to undertake complete combustion and to generate lower exhaust emissions than diesel fuel. Biodiesel can help to reduce the world dependence on fossil fuels. It also involves a significant environmental benefit that classifies it as a clean source of energy that can replace the conventional diesel in devices such as heaters and domestic appliances, as well as in those involved in internal combustion engines with no further adjustment (Carreto et al., 2004).

Up till now, most conventional production of biodiesel from vegetable oil feedstocks involves the use of homogenous basic catalysts, such as sodium or potassium hydroxides, or alkoxides, which are very active, but they involve corrosion and separation problems, as well as emanating important effluent contaminants into the environment. Moreover, solid catalysts can be potentially used for long periods of time thus allowing for a technology easy to adjust under continuous processing, and improving the economics of biodiesel production.

Different types of heterogeneous catalysts endowed with basic properties have been developed for the transesterification reaction of vegetable oils to biodiesel (Marchetti and Errazu, 2008; Narasimharao et al., 2007; Palligarnai et al., 2008; Park et al., 2008; Talebian-Kiakalaieh et al., 2013). The basic properties of alkaline and alkaline-earth metals have been evaluated (Arzamendi et al., 2008) with respect to the transesterification of refined sunflower oil with methanol at 50 °C. Catalytic runs were performed under a molar methanol/oil ratio of 12:1 in a batch reactor. The considered catalysts were Li, Na, K, Rb, Cs, and Ca hydroxides, Na, K, Ca and Mg carbonates, Na and K bicarbonates, sodium phosphates as well as Ca and Mg oxides. These authors concluded that the catalytic behavior mainly depended on the homogeneous or heterogeneous character of each substance; i.e. on their solubility in methanol. Additionally, the researchers also studied the chemical stability under reaction conditions of the most active heterogeneous catalysts by assessing the presence of metals in the reaction mixture.

Recently, it has been reported the employment of calcined Mg–Al hydrotalcite (HT) substrates (mixed oxides) as catalysts (Cantrell et al., 2005; Wenlei et al., 2006; Gao et al., 2010; Shumaker et al., 2007). Structure-reactivity relationships have been involved in the design of useful HT catalysts for the synthesis of fine chemicals, especially in the area of green chemistry (these materials being sustainable-renewable). A more recent application of HT substrates has been made in the transesterification of vegetable oils to biodiesel since the steps of the synthesis and their related parameters can be varied ad-libitum. For instance, the molar Mg/Al metal ratio, the concentration, and the type of bimetallic and trimetallic cations that can partially replace the Mg or Al atoms in the HT network, can be selected in order to modulate the basic properties of mixed oxides after calcinations (Rekha et al., 2009; Wen et al., 2010; Di Serio et al., 2008; Li et al., 2009; Zabeti et al., 2009).

Kotwal et al., 2009 studied a flash-based catalyst for the transesterification of sunflower oil with methanol to methyl esters. These researchers correlated the displayed esterification activity with the characteristics of the catalysts. Catalyst preparation variables, such as KNO_3 amount and calcination temperature were optimized. The catalysts were prepared by loading 5 wt% of KNO_3 on flash followed by calcination at 500 °C, at which temperature the catalysts exhibited maximum oil conversion (i.e. 87.5 wt%). The catalysts were characterized by powder XRD. The above authors also investigated the influence of diverse reaction parameters, such as wt% of catalyst loading, methanol to oil molar ratio, reaction time, temperature, catalyst reusability on the catalytic activity.

A new heterogeneous catalyst for the esterification of free fatty acids and the transesterification of vegetable oils was reported by Cordeiro et al. (2008), and Vyas et al. (2009). The layered zinc hydroxide nitrate compound ($Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$) resulted very effective in the alcoholysis of palm oil and the esterification of lauric acid with methanol, even when hydrated ethanol was used. The catalytic properties of calcined Li–Al, Mg–Al and Mg–Fe layered double hydroxides (LDHs) were examined in two transesterification reactions; namely, the reaction of glyceryltributyrate with methanol and the reaction of soybean oil with methanol (Shumaker et al., 2008). While the Li–Al catalysts showed high activity in these reactions at methanol reflux temperature, the Mg–Fe and Mg–Al catalysts exhibited lower methyl ester yields.

In the present work, we synthesized Mg–Al HT catalysts using microwave irradiation for developing the growing process of the crystalline network (Fetter et al., 1997) while varying the nitratine ($NaNO_3$) content through washing treatments of the formed hydrogels. The calcined HT (mixed oxide) materials were used as catalysts (C_I–C_V) to study the transesterification of canola oil to biodiesel. Additionally, through mechanical mixing, it was doped pure synthesized HT with the target to test the effect of the nitratine load on the selectivity and conversion of canola oil to biodiesel.

2. Materials and methods

2.1. Synthesis of hydrotalcite and mixed oxide substrates

The HT synthesis was carried out by the coprecipitation method under a molar metal ratio $X = Al^{+3}/(Al^{+3} + Mg^{+2}) = 0.2$ at pH=8 and using NaOH (Fermont) as the precipitating agent. The $Mg(NO_3)_2 \cdot 6H_2O$ (Fermont) and $Al(NO_3)_3 \cdot 9H_2O$ (Fermont) precursory solutions were added simultaneously (dropwise) under constant agitation and maintaining a constant pH during the reaction. The growth process of the crystalline network of the precursory hydrogels was accelerated by subjecting the reaction system to microwave radiation, inside an LG (1000 W) oven at 80% power for 5 min. The procedure for obtaining hydrotalcite compounds with (and without) different contents of nitratine was as follows: the 500 mL of formed hydrogels were treated in the microwave oven, followed by an aging step for 48 h at 25 °C, in order to create the hydrotalcite compounds. Subsequently, hydrogel samples of 100 mL were washed with deionized water every 24 h. The different hydrotalcite compounds obtained were labeled as HT-I, HT-III, and HT-IV according to their different nitratine contents and HT-V for the pristine (no nitratine) HT (see Fig. 1). Finally, all samples were dried in an oven at 100 °C and the resultant solids were sieved to 80 mesh. Afterwards, the HT substrates were transformed into their respective mixed oxide (MO) counterparts through calcination in a tubular furnace, under an air flow of 110 mL/min at 570 °C for 18 h. The resultant C_I, C_{III}, C_{IV}, and C_V solids were used as catalysts for the transesterification reaction of canola oil to biodiesel.

The pristine HT-V catalyst was doped with two different amounts of nitratine (Fermont), i.e. at in 1 and 5 wt%. relative to the HT-V mass. The created solids were homogeneously mixed in an agate mortar and the corresponding C_{V1} and C_{V5} catalysts were