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Full Length Article

Outstanding performance of rehydrated Mg-Al hydrotalcites as heterogeneous methanolysis catalysts for the synthesis of biodiesel

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ABSTRACT

There is still a need for active, selective and stable heterogeneous catalysts for the synthesis of biodiesel. In this work, magnesium-aluminium hydrotalcites with Mg/Al molar ratios within the 1.5–5 range were synthesized by coprecipitation and used as transesterification catalysts for the synthesis of biodiesel. The mixed oxides obtained after calcination recovered the hydrotalcite structure in the form of meixnerite after rehydration in boiling water. The solids were characterized by XRD, TGA, N_2 adsorption-desorption, and SEM. Basic properties were assessed by means of Hammett indicators and CO_2-TPD. Rehydrated materials with the highest Mg/Al ratios showed some distinctive features: low surface area, well defined flake-like crystals, high basicity and strong basic sites with $H\_$ values above 11. They were also the most active catalysts allowing to achieve 51–75% sunflower oil methanolysis conversion after 8 h of reaction under mild conditions (60 °C, 1 atm), methanol/oil molar ratio of 12 using between 2 and 6 wt% of catalyst. The conversion increased up to 96% (92% fatty acid methyl esters yield) using 2 wt% catalyst and methanol/oil molar ratio of 48. Catalyst leaching was not a serious problem with these solids that could be reutilized maintaining very good activities. A general accordance between solids basic properties and their catalytic performance has been observed. These results are among the best reported in the literature for heterogeneous methanolysis catalysts and have been attributed to the high basicity of the rehydrated solids and the presence of strong and accessible basic sites probably consisting in interlayer hydroxide anions at the edges of the crystals.

1. Introduction

Transesterification with methanol (methanolysis) of the triglycerides present in vegetable oils catalyzed by homogeneous Na or K hydroxides or methoxides in batch or flow reactors is the most common method for the industrial production of biodiesel [1]. This process suffers from several drawbacks mainly because the catalyst cannot be reutilized and it is required the neutralization and washing of the produced biodiesel and glycerol which generates large volumes of wastewater. With the aim of helping to overcome these problems, great efforts are currently being devoted to develop active and stable heterogeneous catalysts for biodiesel production. A variety of basic and acid solids have been considered for the transesterification of triglycerides and the esterification of free fatty acids (FFA) with variable degrees of success [2]. As concerns the methanolysis of vegetable oils, it can be mentioned the use of alkaline-earth metals oxides and hydroxides [3,4], supported alkaline and alkaline-earth metals compounds [5,6], and hydrotalcites [7–10]. In spite of the great effort devoted to this task there is still a need for active, selective and stable catalysts for improving the synthesis of biodiesel through the heterogenization of the catalyst.

Due to their tunable properties and promising performance, hydrotalcites are among the materials that have attracted more attention in the recent years as transesterification catalysts. Hydrotalcites belong to the layered double hydroxides (LDHs) family. These minerals are described by the formula $[M_n^{2+}M_m^{3+}(OH)_{2(n+m)}]^{m+}[A^{x-}]_{m/x}\cdot yH_2O$, where M^{2+} is a divalent metal (*e.g.* Ca^{2+}, Mg^{2+}, Zn^{2+}), M^{3+} is very frequently Al^{3+}, A^{x-} an anion (*e.g.* $CO_3{}^{2-}$, $NO_3{}^{-}$, Cl^{-}) and x is within the 0.1–0.5 range. More specifically, hydrotalcites are Mg-Al-LDHs that can be viewed as brucite, $Mg(OH)_2$, with partial substitution of Mg^{2+}

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by Al^{3+}. This results in net positive charge in the layers that is balanced by anions located, together with water molecules, in the interlayer space [11–14].

It is well-known that the oxides obtained after the calcination of hydrotalcites at moderate temperatures can recover the original layered structure when exposed to water [15]. These reconstructed Mg-Al LDHs (meixnerite) contain hydroxyde anions in the interlayer space and Brønsted basic sites active in a variety of base-catalyzed reactions. However, there are very few reports on the use of rehydrated hydrotalcites in methanolysis reactions. Xi and Davis [16,17] studied the methanolysis of tributyrin, a model triglyceride, catalyzed by hydrotalcites with Mg/Al molar ratios of 2 and 4. These authors found that the rehydrated solids were significantly more active than the calcined ones. Kim et al. showed a positive effect of rehydration on the activity of a hydrotalcite with Mg/Al molar ratio of 2.8 in the methanolysis of soybean oil [10].

In previous studies by our group with commercial Mg-Al hydrotalcites it was found that the original solids were inactive for methanolysis of sunflower oil. Among the calcined solids only one mainly consisting of MgO was active whereas rehydration significantly improved the activity of the solids with the highest Mg/Al ratios [7]. In this work, the investigation is extended to a series of Mg-Al hydrotalcites synthesized considering different Mg/Al ratios that were characterized by means of several techniques. The performance as transesterification catalysts of the calcined and rehydrated materials was tested in the methanolysis of sunflower oil. Takehira has reviewed the recent developments of LDH-derived catalysts, with emphasis on the performance of rehydrated hydrotalcites [18]. In spite of the abundant literature existing, to our knowledge, there is no a study equivalent to this one reporting on the results of a systematic investigation on the combined effects of the rehydration and composition of Mg-Al hydrotalcites on their performance as methanolysis catalysts.

2. Experimental

2.1. Catalysts preparation

The hydrotalcites were prepared by coprecipitation from two aqueous solutions, one of them containing $Mg(NO_3)_2 \cdot 6H_2O$ (Aldrich) and $Al(NO_3)_3 \cdot 9H_2O$ (Aldrich) and the other NaOH 2.3 M (Scharlau) and Na_2CO_3 0.6 M (Aldrich). The concentrations of the metallic solutions were adjusted to obtain Mg/Al nominal molar ratios of 2, 3, 4, 5, 6 and 7 with aluminum concentrations in the range between 0.27 and 0.5 M. Both solutions were simultaneously added dropwise into a jacketed glass flask of 500 cm^3 at room temperature under vigorous stirring. The addition rate was controlled to maintain the pH between 10 and 11 until putting out the metallic solution after about 3 h. The resulting suspension was stirred for 20 h at 65 °C, and then filtered to recover a white precipitate that was thoroughly washed with deionized water until achieving a pH of 7 to remove sodium ions. The solids were dried at 100 °C for 24 h to give the as-synthesized hydrotalcites (HT) that will be denoted as HTx-as, where x is the nominal Mg/Al molar ratio employed for the synthesis.

The solids were calcined at 500 °C (1.3 °C/min) for 6 h to give the calcined materials that will be referred to as HTx-ca. To obtain the rehydrated hydrotalcites, calcined samples were immersed into boiling deionized water until total liquid evaporation after about 15 min. The resulting solids were rapidly removed from the hot vessel and dried under vacuum at 65 °C for 5 h to give the rehydrated hydrotalcites that are denoted as HTx-rh. The degree of rehydration of the several solids was similar, resulting in a weight increase of about 36 wt%. Solids with other percentages of rehydratation were prepared varying the immersion time (1–30 min) of the calcined hydrotalcites into boiling deionized water.

2.2. Catalysts characterization

Elemental analyses were performed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a VISTA-MPX (VARIAN) spectrophotometer. The catalysts were characterized by N_2 adsorption-desorption at −196 °C with a static volumetric apparatus (Micromeritics ASAP 2000 adsorption analyzer). Prior to the measurements, samples were degassed for 5 h at 80 °C. Specific surface areas (S_{BET}) were calculated using the BET method from the nitrogen adsorption isotherms taking a value of 0.162 nm^2 for the cross-sectional area of the adsorbed N_2 molecule. Specific total pore volumes were assessed from the amount of nitrogen adsorbed at a relative pressure of 0.99, assuming that the density of the nitrogen condensed in the pores is equal to that of liquid nitrogen at −196 °C (1.547 g/cm^3). X ray powder diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using Cu Kα (40 mA, 40 kV) radiation ($\lambda = 1.5418$ Å) and a range of 2θ angles between 20 and 80° (scan step size of 0.05°). Thermogravimetric analyses (TGA) were performed in a Seiko Exstar 6000 thermobalance under oxygen flow and heating rate of 5 °C/min. The morphology of the samples was examined with a scanning high-resolution field-emission electron microscope (HITACHI S-5200).

The basic properties of the solids were determined through temperature programmed desorption of CO_2 (CO_2-TPD) and tests with Hammett indicators. CO_2-TPD experiments were carried out using a Micromeritics AutoChem II apparatus equipped with a TCD detector and a programmable furnace with temperature control. Typically, 50 mg of the sample were placed in a quartz tube over quartz wool and pretreated at 50 °C for 30 min under flowing Ar. Afterwards the sample was saturated at room temperature with a CO_2 stream (10 vol% CO_2 in Ar). CO_2 desorption was registered from room temperature to 1000 °C at a heating rate of 10 °C/min. In order to calculate the basicity (basic sites density) it was assumed that one CO_2 molecule is adsorbed on one surface basic site.

The basic strength ($H\_$) was determined according to the method based on the color change of Hammett indicators [15]. The value of $H\_$ is approximately given by the pK_a of the acid indicator showing upon adsorption a color intermediate between those of the acidic and basic forms. The indicators employed in this work were (pK_a values are given between parentheses): bromothymol blue (7.2), phenolphthalein (9.3), thimolphthalein (9.9), alizarine yellow (11.0) and indigo carmine (12.2). The determination of $H\_$ was carried out placing about 100 mg of the solid in a test tube, adding about 2 cm^3 of a solution of the indicator in toluene and shaking vigorously. After equilibration, the suspension was examined for color change.

2.3. Transesterification reactions

Transesterification reactions were carried out in a Radleys Carousel Tornado IS6 system with capacity for carrying out simultaneously up to 6 catalytic tests. Each reaction was performed in a 100 cm^3 round bottomed flask closed hermetically and with mechanical stirring to obtain a good suspension of the catalysts particles. The flasks are directly heated by the hotplate where they lean which allows a temperature control within ± 0.5 °C. The sidearm of the flasks was adapted to fit a type K thermocouple and the inlet and outlet sides of a recirculation loop made of 1/8″ Teflon tubing and comprising a diaphragm-type metering pump (ProMinent Gugal type G) and a stainless steel three-way ball valve for sampling purposes. Reactions were carried out with HPLC grade methanol (Scharlau) and refined sunflower oil (Urzante, Navarra, Spain; acid value of 0.07 mg KOH/g); a molecular weight of 879.5 g/mol was assumed for the oil. Reference reaction conditions were 1 atm, 60 °C, 2 wt% of catalyst referred to the oil loaded into the reactor, and methanol/oil molar ratio of 12. When using the calcined samples as catalysts, the solids were used immediately after calcination, being weighted and transferred still hot into the reaction flask containing the oil to minimize the interaction with ambient