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Catalytic fast pyrolysis of biomass over Mg-Al mixed oxides derived from hydrotalcite-like precursors: Influence of Mg/Al ratio

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ABSTRACT

In this work we examine a series of Mg-Al mixed oxides derived from hydrotalcite-like precursors prepared with different Mg/Al ratios i.e. Mg/Al = 2, 3, and 4, as catalysts for the catalytic fast pyrolysis (CFP) of wheat straw. Characterization of the Mg-Al mixed oxides by N₂ adsorption, X-ray diffraction and CO₂ temperature programmed desorption revealed a decrease in the surface area and a higher number and proportion of basic sites corresponding to an increase in the Mg concentration in the hydrotalcite precursors. The Mg-Al mixed oxides derived from hydrotalcite precursors are active materials for the catalytic fast pyrolysis of biomass. The removal of oxygen during the catalytic fast pyrolysis of biomass over the Mg-Al-mixed oxides depends on their Mg/Al ratio, and an increase in gas production with a strong improvement in the decarboxylation capacity as the Mg concentration in the mixed oxides decreased, was observed. The Al-Mg mixed oxide catalyst with the lowest Al concentration (Mg/Al = 4.0) maintained the deoxygenation and bio-oil energy yield at levels comparable to those achieved over an acidic ZSM-5 zeolite widely used in the CFP of biomass. A moderate increment in ketone formation for the catalyst with Mg/Al = 4.0 suggests that these basic materials promote the aldol condensation and ketonization of pyrolytic compounds by removing the oxygen in the form of H₂O and CO₂.

1. Introduction

Several biomass conversion technologies are used in the production of fuels, including thermochemical, biochemical, mechanical or physical and chemical processes. The pyrolysis of biomass is one of the most studied biomass conversion platforms/technologies, because it has the advantage of producing liquid, solid and gaseous products similar to those of the oil and gas industry, depending on the conditions used [1]. Research into biomass pyrolysis is extensive and has attracted many initiatives in recent years [1–6]. Thermochemical conversion of lignocellulosic biomass into liquids (bio-oils) by fast pyrolysis is an attractive method for the production of renewable fuels taking into account its high efficiency in the transformation [7]. Bio-oils are interesting carbon sources which can be used as crude for the production of fuels. However, bio-oils contain a high concentration of oxygenated compounds that limit their applicability because the high oxygen content implies corrosiveness, non-volatility, and thermal instability [8]. For this reason the removal of oxygen from bio-oils is a key factor in improving its usability and stability. The removal of oxygen during pyrolysis can be effectively achieved using catalytic systems that

selectively remove the oxygen from oxygenate compounds in the form of CO₂ (decarboxylation), CO (decarbonylation) or H₂O (dehydration) [9–14]. In addition to these basic reactions, other reactions such as cracking and polymerization can also take place, taking into account the complexity of the organic compounds formed during the pyrolysis of biomass. In the CFP the removal of oxygen in the form of CO₂ is preferred because it maximizes the elimination of system oxygen per carbon atom while maintaining the hydrogen content in the bio-oil [15]. Accordingly, the materials used in the CFP should promote the decarboxylation reactions and the extent of dehydration reactions should be controlled to preserve the H/C ratio of the bio-oil as high as possible.

Catalysts of different natures have been tested for the upgrading of bio-oils produced in the CFP of biomass. Acid catalysts, such as γ -Al₂O₃ [16], silica-alumina [11] or zeolites [9], supported noble metals [10,16] or sulfides [11], mesoporous materials such as MCM-41, SBA-15 or MSU-J [17,18], or natural minerals such as sepiolite or bentonite [19] have all been studied. Among these the best results have been obtained using zeolites H-Beta (BEA), H-Y (FAU) and ZSM-5 (MFI). These zeolites are used either without modification [9,16] or modified with basic oxides

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[14]. ZSM-5 is one of the most frequently used zeolites in fast pyrolysis of biomass due its optimal acidic strength and topology, particularly when it is obtained with a hierarchical structure [9,14,16,18,20–22]. ZSM-5 shows an optimum pore size of 0.55 nm, which minimizes extensive coking without restricting the access of the large molecules involved in the pyrolysis [16,18]. However, the high acidity of the zeolites favours the formation of coke and the consequent catalyst deactivation [11,16]. Basic catalysts such as oxides [11,18,23,24], salts and hydroxides [18] of alkaline and alkaline earth metals, mixed oxides minerals such as serpentine [25] or co-precipitated mixed oxides [13,15,26,27] have also been studied as candidates for the CFP of biomass in order to minimize the deactivation by coke formation. In general, using basic catalysts for CFP produces lower bio-oil yields but achieves a better oxygen quality by comparison with the zeolites [18]. For the basic catalysts the removal of oxygen during CFP is mainly related to the ketonization of carboxylic acids, and the aldol condensations of ketones and aldehydes [28,29]. Some of the basic materials, e.g. the mixed oxides derived from hydrotalcites, possess a combination of basic sites, as well as some acid sites [20,29] which could additionally [30–32], favour deoxygenation activity during CFP because they can act as bifunctional catalysts, as well as minimising the formation of gases by controlling the cracking processes on the acid sites [14,18,24]. Therefore, basic catalysts based on mixed Mg-Al oxides derived from hydrotalcite-like precursors could be of interest for the removal of oxygen during the CFP of biomass because they exhibit a high specific surface area, a high thermal stability, and a controllable basic character [26,30]. However, although these mixed oxides have been proposed for the gasification of tar generated in the pyrolysis of biomass [30] they have not been assayed directly as a CFP catalyst.

Hydrotalcite-like compounds (HT) are layered double hydroxides derived from brucite layers (MgOH). Hydrotalcite-like compounds have the formula $[M_{(1-x)}^{2+}M_x^{3+}(OH)_2] \cdot [A^{n-}]_{x/n} \cdot mH_2O$ in which M^{2+} and M^{3+} occupy the octahedral interstitial sites six-coordinated to the hydroxyl groups forming brucite-like sheets which stack to create a layered structure. The brucite-like sheets are positively charged due to the partial substitution of magnesium by trivalent cations, thus, balancing anions (A^{n-} : NO_3^- , CO_3^{2-} , Cl^- , ...) intercalated in the inter-layer space to compensate the positive charge [31]. When heated the hydrotalcite structure collapses forming an amorphous mixture of metal oxides, with the general formula $M^{2+}M^{3+}(O)$, with a very small crystal size and high thermal stability. The basicity of the mixed metal oxides derived from HT depends on the nature and ratio of the divalent and trivalent metal cations used in the formulation. In the case of Mg-Al mixed oxides derived from HT the number and strength of basic sites depends on the Mg/Al ratio, and shows an increase in the basicity in parallel with the decrease in the concentration of Al^{3+} in the HT precursor [26,32,33]. The basicity of the mixed oxides also depends on the nature of the anions in the interlayer region and the thermal treatment applied to decompose the HT structure [34,37].

Arising from this background, the present study has been aimed at investigating the influence of the chemical composition of Mg-Al hydrotalcite-like compounds at ratios of Mg/Al = 2.0, 3.0 and 4.0, on the activity of basic Mg-Al mixed oxides derived from them and used as catalysts for biomass fast pyrolysis. Wheat straw was selected as the feedstock for this study because it is representative of those agriculture residues which are abundant and which do not compete, but are complementary to, food production. A careful investigation into the physicochemical properties of the Mg-Al mixed oxides was performed in an attempt to understand the relationship between their activity and their structural, textural and surface characteristics.

2. Experimental

2.1. Preparation of the hydrotalcite-like precursors and the Mg-Al mixed oxide catalysts

Hydrotalcite-like precursors (HT) with different Mg/Al ratios i.e.

2.0, 3.0 and 4.0, were selected in order to have a wide basicity range in the derived Mg-Al oxides taking into account the Mg/Al interval (1–7) able to form hydrotalcite structures [26,32,33]. In the case of Mg-Al mixed oxides derived from HT the number and strength of basic sites depends on the Mg/Al ratio, showing an increase in the basicity in parallel with the decrease in the concentration of Al^{3+} in the HT precursor.

The hydrotalcite-like precursors (HT) with different Mg/Al ratios (2.0, 3.0 and 4.0), were synthesized by simultaneous co-precipitation of Mg^{2+} (aqueous solution 0.5 M $MgCl_2$) and Al^{3+} (aqueous solution 0.5 M $AlCl_3$) using ammonium carbonate generated in situ by controlled hydrolysis of urea (1.5 M) at 90 °C [30,36]. After co-precipitation, the precipitates were aged by stirring at 90 °C, for 72 h. After the aging process the precipitates were filtered and subsequently washed with ice-cooled distilled water until the pH of the filtrate became neutral. After washing, the filtrates were finally dried at 80 °C under air for 12 h. The hydrotalcite precursors were labelled as HT x (x = Mg/Al ratio = 2, 3 and 4). The Mg-Al mixed oxide catalysts were obtained by the thermal decomposition of the corresponding HT-x precursors. Thermal decomposition of the HT precursors was performed under air-flow at 500 °C for 15 h, this temperature was achieved by a heating rate of 1.5 °C min^{-1} . The Mg-Al mixed oxidecatalysts obtained were labelled as Mg-Al x (x = Mg/Al ratio = 2, 3 and 4). In addition, a commercial ZSM-5 sample (Si/Al = 42; S_{BET} = 452 m^2/g), provided by Clariant was also used as a reference catalyst for comparison purposes. This catalyst is widely used in pyrolysis because it provides good deoxygenation selectivity and can promote the formation of aromatics [13–15,38]. The best balance between bio-oil yield and the removal of oxygen are obtained with moderate acidity, therefore we selected a zeolite with a Si/Al = 42 as the benchmark catalyst for wheat straw pyrolysis.

2.2. Physicochemical characterization

The chemical composition of the HT precursors and Mg-Al mixed oxide catalysts were determined by measuring the concentration of Mg and Al in the solutions following solid acid digestion by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using an Optima 3300DV (Perkin Elmer) spectrometer.

A gravimetric analysis during the thermal decomposition of the HT precursors was studied from room temperature to 900 °C, at a heating rate of 10 °C min^{-1} , under O_2/N_2 flow (20% vol, 25 $mL\ min^{-1}$) using a TGA/SDTA 851 (Mettler, Toledo) thermal analyzer.

The textural properties of the Mg-Al mixed oxide catalysts were determined from the N_2 adsorption-desorption isotherms. The isotherms were acquired at –196 °C in an ASAP 2100 (Micromeritics) surface area measurement analyzer, over de-gassed samples (10^{-5} mbar at 120 °C for 20 h). Specific surface areas were calculated using the BET method within the P/P₀ range from 0.05 to 0.30, and taking a value of 0.162 nm^2 for the cross-section of the adsorbed N_2 molecule.

X-ray diffraction (XRD) studies of the HT precursors and Mg-Al mixed oxide catalysts were carried out using a X'Pert Powder (PANalytical) diffractometer equipped with Cu K α radiation of wavelength λ = 1.54 Å. The scanning range was established between Bragg angles 10 ° and 70° (2 θ) with a step size of 0.02° (40 s/step) during a continuous scan. The estimation of the size of the crystalline domains of the HT precursors (D_p) was determined by applying the Scherrer equation from the broadening of the (003), and the (110) reflections of the rhombohedral layered double hydroxide phase.

The basicity of the Mg-Al mixed oxide catalysts was determined by temperature programmed desorption of chemisorbed carbon dioxide (CO₂-TPD) carried out in an Autochem II 2920 (Micromeritics) analyser. The CO₂ desorption was monitored using a thermal conductivity detector. The amount of desorbed carbon dioxide was determined by the calibration of the intensity of the TCD response. Prior to carbon dioxide chemisorption, the Mg-Al mixed oxidecatalysts were pre-treated under He flow (50 $mL\ min^{-1}$) at 500 °C for 1 h (heating rate:

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