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Infrared analysis of methanol adsorption on mixed oxides derived from Mg/Al hydrotalcite catalysts for transesterification reactions

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ABSTRACT

Mixed oxides derived from hydrotalcites by thermal decomposition are promising catalysts for transesterification reactions. To gain insight into its action mechanism, methanol O—H bond activation was analyzed over Mg—Al mixed oxides using in-situ DRIFT spectroscopy to follow adsorbed species. After methanol adsorption, non-dissociative and dissociative species were identified. Dissociative adsorption resulted in two types of methoxy groups, type I or monodentate methoxy species and type II or bridging methoxy species. Catalytic tests of methanolysis of triacetin have shown a trend where, the higher the amount of adsorbed monodentate methoxy species the higher the catalytic activity of transesterification reaction.

1. Introduction

Biodiesel is an alternative fuel produced by transesterification of oils; this reaction consists of transforming triglycerides into fatty acid alkyl esters, in the presence of an alcohol, such as methanol, and a catalyst, with glycerol as co-product [1,2]. Commercial biodiesel is mainly produced by means of homogeneous catalysts as sodium and potassium hydroxide. However, the use of this kind of catalysts is a drawback requiring, for high yields, the use of refined oils as raw material to avoid saponification. In this way, the research of heterogeneous catalysts useful for transesterification reaction has increased. Between the solids that have gained attention in the last few years as transesterification catalysts are hydrotalcites.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are a group of both naturally occurring and synthetic lamellar compounds with general formula $[M^{2+}_{1\text{-}x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$. These materials consist of a positively charged brucite-like metal hydroxide layers containing divalent and trivalent metal cations. The positive charge of the hydroxyl layers results from the isomorphous replacement of a fraction of the divalent cations, M^{2+}, by trivalent cations M^{3+}. This net positive charge is compensated by interlayer anions A^{n-}, where water molecules are located as well [3–5].

LDHs materials have attracted attention because of their interesting properties and applications as catalysts, catalysts support, ion-exchange materials, adsorbents and drug storage-delivery agents [6–9]. Thermal decomposition of hydrotalcite-like compounds leads to formation of mixed oxides which are characterized by the presence of acid–base pairs [5,10,11], these pairs could be characterized by means of a protic molecule as water or methanol [12–15]. The contact between a protic molecule and an oxide surface eventually provokes its deprotonation; according to Chizallet et al. [13]. the deprotonation ability of an oxide surface probes not only the ability of oxide ions O^{2-} to share an electron pair to stabilize the proton from the adsorbate, but also probes the ability of the surface metallic cation to accept the electron pair from the alcoxi species stabilizing it [13].

Several reactions require the activation of an alcohol as a nucleophilic reactant, for example, transesterification reaction requires the deprotonation of an alcohol such as methanol to generate surface OH and methoxy species, the latter which are believed to be responsible for the nucleophilic attack to the carbonyl group on esters (triglycerides) [16]; therefore the study of the formation of this kind of species would contribute to understand the mechanism of different reaction processes where alkoxy species are involved.

In this way, several authors have made different efforts to gain insight the mechanism of activation of methanol over the surface of mixed oxides derived from hydrotalcites. Montanari et al. [16] obtained a mixed oxide from an hydrotalcite material of Zn—Al molar ratio of 2. This material was constituted by a poorly crystallized ZnO phase. By IR analysis, the authors observed the presence of spinel-like domains and determined that the catalyst dissociative adsorb methanol giving rise to two types of methoxy species. One, named type **A**, corresponding to bridging methoxy on Al or Zn ions, which was more stable to

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desorption. The other one, named type **B**, was more labile to temperature desorption, and were, according to the authors, those involved in transesterification reaction and polyethoxylation reactions.

Navajas et al. [14] analyzed the adsorption of methanol on a series of commercial hydrotalcites (calcined and rehydrated) by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). They found different species after methanol adsorption including molecular and dissociated species, the total quantity of methoxy species being related to the basic character of the solids. A linear correlation between the amount of adsorbed monodentate methoxy species and the catalytic activity in biodiesel production was found.

In the present work, we prepared a series of mixed oxides derived from hydrotalcites with Mg/Al molar ratio of 2, 3 and 5. The adsorption of methanol over these solids was followed using in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique. The aim was to gain insight into the activation process of this probe molecule over Mg-Al mixed oxides and analyze if, as said in literature [17,18] the presence of a high quantity of strong basic sites is determinant in transesterification reaction or if by the contrary, the presence of different species such as acid-base pairs, is related with the mentioned reaction.

2. Experimental

2.1. Catalyst preparation

A set of Mg-Al hydrotalcite-like precursors with Mg/Al molar ratio of 2 (HM2), 3 (HM3) and 5 (HM5) were synthesized by coprecipitation method as described by Tsyganok et al. [17,18]. For this purpose, an aqueous solution of the metal nitrates $Mg(NO_3)_2·6H_2O$ (Merck, > 99%) and $Al(NO_3)_3·9H_2O$ (Panreac, > 98%) containing the desired Mg/Al ratio with individual cation concentration of 1.0 M, and an aqueous solution of NaOH 2.0 M were simultaneously introduced by dropwise addition into a stirred beaker containing an aqueous solution of Na_2CO_3 (J.T. Baker, ≥99.5%, carbonate ions at 2.5 times in excess) held at 65 °C. The addition of the NaOH solution was controlled in order to hold a constant pH of 10. When the nitrates solution was completely added, the obtained slurry was stirred at 65 °C for 1 h, followed by aging without stirring for 24 h at the same temperature. The precipitate was then separated by centrifugation, washed until neutral pH of the filtrate and dried at 90 °C for 24 h. The solids were calcined in static air by heating at 1.5 °C/min up to 500 °C over 6 h to obtain the corresponding mixed oxides. These calcined samples will be referred as CHM*x*, where *x* is the Mg/Al molar ratio: 2, 3, 5.

2.2. Catalyst characterization

Mg and Al elemental analyses were performed by atomic absorption spectroscopy (AAS) using a Thermo Scientific Series 3000 after dissolution of the samples in aqueous HNO_3. X-ray diffraction (XRD) patterns of the powdered samples were obtained using an Empyrean (PANalytical) diffractometer operating with Cu Kα radiation ($\lambda = 1.5406$ Å) at 40 mA, 45 kV, data were collected in the 2θ range of 5°–90° and scan step size of 0.0530°. Thermogravimetric analyses (TGA) were performed in a TA Instruments TGA Q500 thermobalance under air flow and heating rate of 10 °C/min until 900 °C. N_2 adsorption-desorption isotherms at −196 °C were measured on a Micromeritics® ASAP 2020 analyzer. Prior to the measurements, the samples were degassed under vacuum at 400 °C for 1 h. Specific surface areas (S_{BET}) were calculated using the BET method. The basic and acid properties of the solids were carried out by temperature-programmed desorption of CO_2 (CO_2-TPD) and NH_3 (NH_3-TPD) using a Micromeritics® Autochem 2920 analyzer equipped with a TCD detector. Typically, ca. 150 mg of sample was placed in a U-shaped quartz reactor, the sample was pre-treated under helium at 500 °C during 60 min and then cooled to 50 °C and contacted with a 5% CO_2/He or 5% NH_3/He flow for 60 min. Physically adsorbed CO_2 or NH_3 was firstly removed by flushing helium at 50 °C. Desorption was measured by heating the sample from 50 °C to 500 °C at 10 °C/min. The number of basic or acid sites was calculated by deconvolution of the CO_2 or NH_3 peaks with the software of the instrument assuming Gaussian and logarithmic distributions and a calibration made diluting the mixture (5% CO_2/He or 5% NH_3/He) at different concentrations. The surface composition of hydrotalcites was measured by X-ray photoelectron spectroscopy (XPS) using a PHI spectrometer and the areas corresponding to the O 1s, Mg 1s, Al 2p in the case of CHM2 and O1s, Mg 1s and Al 2s in the case of CHM3 and CHM5.

2.3. DRIFT analysis

In-situ DRIFT spectra were collected for samples placed in a high pressure/high temperature chamber (Thermo Spectra-Tech) with ZnSe windows coupled to a Thermo Nicolet 6700 infrared spectrometer using KBr optics and a MCT detector. The samples were diluted at 50 wt% with KBr. Spectra were obtained co-adding 96 scans at 2 cm^{-1}. In order to clean the surface of the samples, a pre-treatment was made under Ar flow (50 cm^3 STP/min) at 500 °C and kept at this value for 1 h. Methanol adsorption was carried out at two different temperatures, 30 °C and 250 °C for 30 min using a stream of Ar saturated with methanol vapor at −10 °C. The purpose of carry out the adsorption of methanol at high temperature was to analyze its partial decomposition and to evaluate which of the adsorbed species were the most stable. Desorption was made using an Ar flow (50 cm^3 STP/min) from adsorption temperature to 350 °C. DRIFT spectra were collected at different temperatures. A KBr spectrum was used as background. An experiment using pure KBr was developed under the same conditions using and adsorption temperature of 30 °C, to verify if methanol is adsorbed in such conditions over pure KBr. There was no evidence of the presence of methanol adsorption bands over pure KBr at the conditions analyzed in the present paper.

2.4. Catalytic activity

Triacetin (Alfa Aesar, 99%) and methanol (Merck ≥ 99%) were selected as reactants. All catalytic tests were carried out with a methanol/triacetin molar ratio of 10, catalytic concentration of 10 wt % referred to triacetin mass, atmospheric pressure and 60 °C. In a typical run, 5.0 g of triacetin, 7.3 g of methanol and 0.5 g of catalyst tested as fine powders (No. 325 mesh) were charged in a two-neck round bottomed flask equipped with a condenser and magnetic stirring. The catalysts were activated before the reaction at 500 °C and were transferred immediately over the methanol to be used in the reaction to avoid contact with ambient water and CO_2. The mixture methanol-catalyst was added over the triacetin that was at the reaction temperature. Samples were withdrawn for analysis at reaction times 0 min, 5 min, 60 min, 120 min, 180 min, 240 min, 300 min and 360 min. Samples were quenched with ice-water, centrifuged and analyzed by gas chromatography using a GC–MS QP2010 Plus Shimadzu, equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.10 μm) and a FID detector. A blank reaction was carried out under the same conditions without catalyst.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Characterization of structure and textural properties

The successful incorporation of Mg and Al within hydrotalcite structure, and therefore in mixed oxides, was first verified by elemental analysis. Table 1 shows AAS results for bulk $r = Al/(Al + Mg)$ in mixed oxides. Upon calcination at 500 °C, the hydrotalcite-like solids suffered decarbonation and dehydration processes that led to the formation of