

Research Article

Influence of the Incorporation of Transition Metals on the Basicity of Mg,Al-Mixed Oxides and on Their Catalytic Properties for Transesterification of Vegetable Oils

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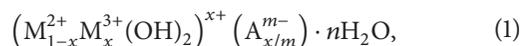
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The transesterification of vegetable oils produces fatty acid methyl esters (biodiesel). Biodiesel is a nonpolluting alternative fuel produced from renewable resources whose chemical and physical properties closely resemble those of the petroleum diesel fuel and does not contribute to the greenhouse effect. The use of solid catalysts makes biodiesel production processes environmentally friendly. In this work, Mg,Al-mixed oxides derived from Mg,Al-hydrotalcite-like compound with an $M^{3+}/(M^{2+} + M^{3+})$ molar ratio of 0.25, in which Mg or Al was partially replaced by Co^{2+} , Cu^{2+} , Cr^{3+} , or Fe^{3+} , were prepared, characterized, and evaluated as catalysts for the transesterification of soybean oil with methanol. The results have indicated that the incorporation of transition metal influenced both textural and base properties. All the evaluated catalysts were active for the studied reaction. The catalytic activity followed the order $Cr-MO < Co-MO < Cu-MO < Fe-MO < MO$ and could be explained by mesoporous volume.

1. Introduction

Hydrotalcite-like compounds (HTLCs) are layered double hydroxides (LDHs) that have been investigated during the last two decades as adsorbents, anion exchangers, and catalysts or catalyst precursors for different types of chemical reactions. The general formula of the HTLCs is



where the divalent ion can be Mg^{2+} , Ca^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} , or Ni^{2+} , the trivalent ion can be Al^{3+} , Fe^{3+} , or Cr^{3+} , the compensation anion can be OH^- , Cl^- , NO_3^- , CO_3^{2-} , or SO_4^{2-} , and x can take values between 0.17 and 0.33 [1].

Mg,Al-hydrotalcite is the most common LDH, and it can also be synthesized in a ternary form in which Mg

or Al is partially replaced by a transition metal cation. Thermally treating HTLCs induces dehydration, dehydroxylation, and loss of compensation anions, forming mixed oxides/hydroxides with basic properties and a poorly crystallized structure [2]. These oxides present small particle size, large specific surface area, and basic properties attributed to hydroxyl groups, different $O^{2-}-M^{2+}$ acid-base pairs, and O^{2-} anions [3–6]. The acid-base properties and, as a consequence, the catalytic activity and selectivity of these Mg,Me,Al-mixed oxides depend on chemical composition (type of Me cation and Mg/Me/Al molar ratio) and on the conditions of the thermal treatment used to decompose the hydrotalcite precursor. So, they can be tailored to the process under study aiming at increasing their activity and/or selectivity. Their main applications as basic catalyst include aldol, nitroaldol, Knoevenagel, and Claisen-Schmidt condensations, alkylation

of ketones and phenols, Michael additions, glycerolysis of fats for the manufacture of monoglycerides, selective reduction of unsaturated ketones/aldehydes by hydrogen transfer from alcohols, and more recently transesterification of vegetable oils for biodiesel production [2, 4–10].

Biodiesel is a nontoxic, biodegradable, and renewable fuel which use has a beneficial impact on the environment. When compared to conventional fossil diesel, it offers many advantages such as high cetane number, high lubricity, high flash point, low viscosity, and lower emissions of CO, SO₂, unburned hydrocarbons, polyaromatic hydrocarbons, and particulate matter [11].

The conventional process of biodiesel production is the transesterification of vegetable oils with a short carbon-chain alcohol (methanol or ethanol) in the presence of homogeneous basic catalysts. However, these catalytic systems have some technological problems, such as removal of basic catalysts after reaction, production of a large amount of wastewater, and emulsification. Besides, the growing concern about the environment is leading the chemical industry to develop less pollutant and more selective chemical processes. So, solid basic catalysts have received increasing attention as a substitute for the highly pollutant liquid homogeneous catalysts in organic reactions because they reduce or eliminate the problems cited previously, and can be reused and adapted to continuous processes in fixed bed reactors.

In this context, several studies related to the use of basic solids such as oxides or hydroxides of alkali metals supported on silica or alumina [12, 13], mixed oxides derived from hydrotalcite [9, 10, 14–18], and other oxides [19–21] as catalysts for biodiesel production are found in the literature. Concerning the mixed oxides derived from HTLCs, different authors reported that the chemical composition has a significant influence on the basic properties and consequently on the catalytic activity in transesterification reactions [9, 10, 15, 22, 23].

The use of commercial calcined Mg,Al-hydrotalcite in the transesterification of rapeseed oil, at 60°C with methanol/oil molar ratio of 275, was first reported by Leclercq et al. [14] with poor results (conversion of 35% after 22 h of reaction). On the other hand, Zeng et al. [22] studied the same reaction using Mg,Al-hydrotalcites with different Mg/Al molar ratios. According to them, the hydrotalcite catalyst calcined at 500°C with Mg/Al molar ratio of 3.0 exhibited the highest catalytic activity in the transesterification. In addition, the optimized parameters (methanol/oil molar ratio = 6:1, catalyst content = 1.5 wt.% related to oil amount, stirring speed = 300 rpm, reaction temperature = 65°C, and reaction time = 4 h) gave a maximum ester conversion of 90.5%.

The application of Mg,Al-hydrotalcite for biodiesel production from soybean oil was claimed by Siano et al. [17] which found that the activity of the catalyst was affected by the ratio of Mg/Al, and the most active catalyst was obtained with Mg/Al ratio of 3 to 8. The catalyst was suitable for oils with a high amount of water content (10,000 ppm), and a conversion of 92% was obtained after 1 h of reaction time using catalyst content of 5 wt.% and alcohol/oil weight ratio of 0.45 at reaction temperature of 180°C.

The use of MgO (obtained from different precursors) and calcined hydrotalcite [Al/(Al + Mg) = 0.20] as catalysts for the transesterification of soybean oil with methanol was compared by Di Serio et al. [16]. The results showed a correlation not only with the catalyst basicity, but also with its textural properties, which was dependent on both precursor and preparation method. The calcined hydrotalcite showed the best performance among the studied catalysts, and for the reaction performed at 215–225°C using catalyst content of 1 wt.% and methanol/oil weight ratio of 0.45 the biodiesel yield of 94% was obtained.

An environmentally benign process for the methanolysis of soybean oil to methyl esters using calcined Mg,Al-hydrotalcites as solid base catalysts in a heterogeneous system was developed by Xie et al. [15]. When the reaction was carried out at reflux of methanol, with a molar ratio of soybean oil to methanol of 15:1, a reaction time of 9 h, and a catalyst amount of 7.5 wt.%, the oil conversion was 67%. The calcined hydrotalcite with an Mg/Al ratio of 3.0 obtained by calcination at 500°C was found to be the optimum catalyst that presents the highest basicity and the best catalytic activity for this reaction. The activity of the catalysts for methanolysis reaction was correlated closely with their basicity as determined by the Hammett method.

Antunes et al. [10] used MgO, ZnO, Al₂O₃, and mixed oxides derived from hydrotalcites-like compounds (Mg/Al and Zn/Mg/Al) as basic solid catalysts on the transesterification of soybean oil with methanol. The results indicated that both MgO and mixed oxides were efficient to catalyze the reaction with a fatty acid methyl esters yield higher than 60% at 130°C. The catalytic performance of the studied catalysts was influenced by their relative basicity, which is affected by the chemical composition. They found methyl esters yields of 70 and 85% to MgO and Mg,Al-mixed oxides, respectively, at 130°C using an alcohol/oil molar ratio of 55:1 and after 7 h.

The catalytic properties of calcined Li-Al, Mg-Al, and Mg-Fe layered double hydroxides (LDHs) were examined by Shumaker et al. [9] for two transesterification reactions, namely, the reaction of glyceryl tributyrates with methanol and the reaction of soybean oil with methanol. Calcined [LiAl₂(OH)₆](CO₃)_{0.5} · nH₂O was an effective catalyst for the transesterification of soybean oil with methanol in which a methyl ester yield of over 80% was produced when the catalyst was calcined at 450°C, and the reaction was conducted at a methanol/oil ratio of 15:1 with a catalyst loading of 1 wt.% at reflux temperature for 1 h. While Li-Al catalysts showed high activity in these reactions at reflux temperature of methanol, Mg-Fe and Mg-Al catalysts exhibited much lower methyl ester yields. Temperature-programmed desorption of CO₂ measurements revealed the presence of sites of weak, medium, and strong basicity on both Mg-Al and Li-Al catalysts, the latter showing higher concentrations of medium and strong base sites; by implication, these are the main active sites in transesterification catalyzed by calcined Li-Al LDHs. Maximum activity was observed for the Li-Al catalysts when a calcination temperature of 450–500°C was applied, corresponding to decomposition of layered double hydroxide to mixed oxide without formation of crystalline lithium aluminate phases.

The incorporation of Fe, Cr, and Ga into Mg,Al-hydroxalite structure was studied by Macala et al. [23] in order to synthesize mixed oxide catalysts with appropriated basicity and activity for the transesterification reaction of glyceryl tributyrate or soybean oil with methanol. Among the catalysts, Fe-doped materials were much more active than the other catalysts for both transesterification reactions. For the transesterification of soybean oil, a conversion of 38% after 40 min on-stream at 80°C using 1 wt.% of catalyst was obtained. The presence of strong basic sites was observed on Fe,Mg,Al-mixed oxides using a Hammett indicator.

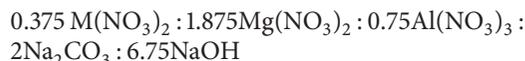
Mixed oxide catalysts derived from Mg-Co-Al-La layered double hydroxide with various Mg:Co:Al:La ratios were prepared by coprecipitation and calcination by Li et al. [18]. Their catalytic performance as heterogeneous base catalysts for the transesterification of canola oil with ethanol to produce biodiesel was compared over 5 h in a batch reactor at 200°C. Amending the catalyst by the addition of La, a possible stabilizer and catalyst, and an increase in Mg, which provides the main base catalyst sites, did not seem to affect the catalytic activity. Experiments using Mg₂CoAl catalyst are reported, showing the effects of reaction temperature, ethanol/oil molar ratio, particle size, and catalyst stability in the transesterification of canola oil. This material was active for the transesterification of canola oil with ethanol and also stable maintaining its activity after 7 cycles. The kinetics of the transesterification of canola oil catalyzed by Mg₂CoAl may be modeled as a first-order reaction.

The previous results show that the substitution of Mg and Al for other different cations in Mg,Al-hydroxalite structure is very interesting due to the possibility of tailoring the acid-base properties of the materials in order to improve its catalytic performance. So, in this work mixed oxides of Mg and Al derived from Mg,Al-HTLCs, with molar ratio $M^{3+}/(M^{2+} + M^{3+}) = 0.25$, in which the Mg or Al was partially replaced by Co, Cu, Cr, or Fe were comparatively evaluated in the transesterification of soybean oil with methanol to produce biodiesel. The results were interpreted according to the basic and textural properties of these materials.

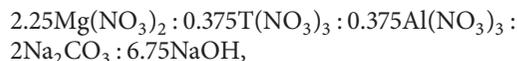
2. Experimental

2.1. Catalyst Preparation. A coprecipitation method was used to synthesize hydroxalite-like compounds with an $(Al + T^{3+})/((M^{2+} + Mg) + (Al + T^{3+}))$ molar ratio of 0.25. The synthesis gel was prepared by mixing an aqueous solution of metallic cations (solution A) with a highly basic carbonate solution (solution B), under vigorous stirring. Solution A was prepared by dissolving metal nitrates in distilled water in order to obtain total metal cations concentration of 1.5 mol L⁻¹. In the preparation of solution B, sodium carbonate and sodium hydroxide were dissolved in distilled water so as to obtain a carbonate concentration of 1 mol L⁻¹ and an amount of OH⁻ sufficient to keep the pH during gel aging at 13. The gel was aged for 18 h at 60°C (exception for the Cr-containing sample, which was aged for 7 days). The solid obtained was filtered, washed with distilled water (90°C) until

pH 7, and dried at 80°C overnight. The gel composition is the following:



or



where M refers to the divalent cation (Co²⁺ or Cu²⁺) that partially replaces Mg²⁺ cations and T refers to trivalent cation (Fe³⁺ or Cr³⁺) that partially replaces Al³⁺ cations. The molar ratios M²⁺/Mg (0.20) and T³⁺/Al (1.0) were selected in order to reach a transition metal content close to 11% (molar base) [24]. An Mg,Al-hydroxalite with an Al/(Mg+Al) molar ratio of 0.25 was also synthesized as reference material using similar procedure (M²⁺ or T³⁺ cations were not present in solution A).

The precursors samples were named HT (Mg,Al-hydroxalite), M-HT, or T-HT, where M or T is the cation that partially replaces Mg or Al, respectively. The mixed oxides were obtained by calcining HTLCs precursors under dry air from room temperature to 450°C, at a 1°C min⁻¹ heating rate, and keeping at this temperature for 10 h. The calcined samples were named MO, M-MO or T-MO, (M and T defined previously).

2.2. Physicochemical Characterization. The chemical composition of the HTLCs samples was determined by X-ray fluorescence spectrometry using a Rigaku RIX 3100 spectrometer. In order to identify the crystalline phases formed on both the HTLCs and the mixed oxides, X-ray powder diffractograms were recorded in a Rigaku X-ray diffractometer equipped with a graphite monochromator using Cu Kα, 40 kV and 40 mA, in the range 2θ from 5° to 80°. The software Unit-Cell [25] was employed for structural refinement aiming at calculating the lattice parameters, *a* and *c*. The textural characteristics such as specific surface area (BET) and pore volume (BJH) were determined by N₂ adsorption-desorption at -196°C in a Micromeritics ASAP 2000. The HTLCs and mixed oxides samples were previously outgassed at 200 and 450°C, respectively, overnight.

2.3. Basicity Characterization. The basic properties of the studied catalysts were determined by temperature-programmed desorption of CO₂ in a unit TPD/TPR equipped with thermal conductivity detector. This technique allows evaluating the distribution of relative strength and density of basic sites present on the materials. The catalysts (400 mg) were pretreated under a flow of helium (30 mL min⁻¹), starting from room temperature up to 450°C at a heating rate of 1°C min⁻¹, and then kept at this temperature for 10 h. After activation, the catalysts were cooled down to 100°C and treated with a gas mixture containing 4% CO₂ in He (30 mL min⁻¹). Desorption profiles of chemisorbed CO₂ were obtained by heating the sample from 100 to 450°C under He (30 mL min⁻¹) using

a heating rate of $10^{\circ}\text{C min}^{-1}$. The basic sites density was determined according to the ability of the material to retain CO_2 molecules during chemical adsorption. The amount of CO_2 chemically adsorbed was calculated as the difference between the total and the physically amount adsorbed.

The acid-base properties of the prepared mixed oxides were also determined by the 2-propanol transformation reaction, which was carried out in vapor phase at atmospheric pressure. 2-propanol was fed to the reactor through a saturator held at 20°C using N_2 as carrier gas. Samples were thermally treated in situ from room temperature up to 450°C , using a heating rate of $1^{\circ}\text{C min}^{-1}$, and then kept at this temperature for 10 h. The reaction temperature was 350°C and $\text{N}_2/2\text{-propanol}$ molar ratio equal to 23. Two sets of experiments were carried out. Firstly the weight hourly space velocity (WHSV, gram of 2-propanol per hour per gram of catalyst) was kept constant at 13.0 h^{-1} , whereas in the second it was varied in order to reach initial isoconversion of 50%. The reaction products were analyzed by online gas chromatography using a CHROMPACK 9000 gas chromatograph, equipped with a 50 m capillary CPSil5CB and a flame ionization detector.

2.4. Catalytic Tests. The methanolysis of soybean oil was carried out in liquid phase, under autogenous pressure using a 50 mL stainless steel batch reactor magnetically stirred and heated with a thermostatic bath. Immediately before the runs, the catalysts were calcined according to the procedure previously described in order to obtain mixed oxides. After activation, they were rapidly transferred to the reactor containing the mixture of soybean oil and methanol. Then, the system was heated to reaction temperature, reaching this value quickly. The catalytic performance of the different studied catalysts was evaluated at the following reaction conditions: reaction temperature = 130°C ; methanol/soybean oil molar ratio = 75; reaction time = 7 h; 5 wt.% of catalyst (referred to the amount of soybean oil). At the end of each test, the system was rapidly cooled down to room temperature, and the catalyst was separated by centrifugation. The phase with lower density, which contains the methyl ester mixture, was removed, and after methanol elimination it was analyzed by gas chromatography using a VARIAN 3800 chromatograph equipped with a 30 m Carbowax 20 M capillary column and a flame ionization detector. Methyl heptadecanoate was used as internal standard for the determination of methyl esters yield that is expressed in terms of weight percentage, as described in the European Norm EN14103.

3. Results and Discussion

3.1. Physicochemical Characterization. Figure 1 shows the X-ray diffractograms of the as-synthesized HTLC materials in which the crystallographic planes associated with the main peaks are highlighted. Except for the Cu-containing sample, the characteristic pattern of pure hydrotalcite in carbonate form was observed for samples HT, Co-HT, Fe-HT, and Cr-HT, suggesting the complete incorporation of the transition metals into the crystalline structure. For sample

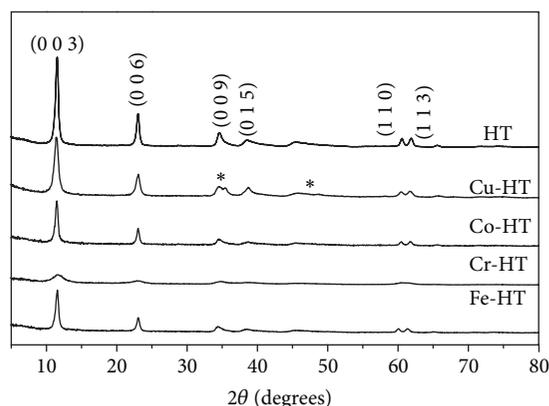


FIGURE 1: X-ray diffraction patterns of the as-synthesized HTLCs precursors. (*) CuO-tenorite.

Cu-HT, diffraction lines at 2θ equal to 35.45° and 48.75° , corresponding to CuO-tenorite (*) [26] were observed along with the hydrotalcite pattern. Although a large aging time (7 days) was used to synthesize the chromium-containing sample (Cr-HT), a very low crystallinity was noted indicating slower crystallization kinetics when compared to the other samples.

The peaks associated to planes (0 0 3), (0 0 6), (1 1 0), and (1 1 3) were used to calculate the lattice parameters, a and c , typical of hydrotalcite structures with rhombohedral 3R symmetry. These parameters and the ionic radius of the cations present in each HTLC structure are shown in Table 1. Comparing the values of parameter a , which is a function of the cation-cation distance in the hydroxide layers [27], it can be observed that their differences are compatible with those existent between Mg^{2+} or Al^{3+} ionic radius and those of the transition metal di- or trivalent cations. This indicates that these transition metal cations have isomorphously replaced Mg^{2+} or Al^{3+} in the HTLC structure. On the other hand, the values of parameter c , which is related to the layer thickness (brucite-like sheet plus an interlayer), probably reflect the influence of various factors such as the amount of interlayer water, the size of the interlayer anion and of M^{2+} - M^{3+} cations, and the strength of electrostatic attractive forces between layer and interlayer [27, 28]. As to the crystallite size, estimated using Scherrer equation considering the line broadening associated to (0 0 3) basal reflection, the results in Table 1 confirm the lower crystallite size of sample Cr-HT which can be related to the lower crystallization rate of this sample.

The chemical composition and textural properties of as-synthesized HTLCs are shown in Table 2. The metallic cations incorporation has occurred as expected, since the chemical composition of the samples was quite similar to that of the corresponding synthesis gel. Concerning the textural characteristics, the partial replacement of Mg or Al by Cu, Co, or Fe did not have a significant effect on BET specific surface area when compared to that of pure Mg,Al-hydrotalcite (sample HT), but mesoporous volume has increased. On the other hand, the highest surface area of

TABLE 1: Lattice parameters of the as-synthesized HTLCs.

Sample	a	c	Crystallite size (Å)	Ionic radius (Å) [1]
HT	3.0536	23.1392	178	$Mg^{2+} = 0.65$ $Al^{3+} = 0.50$
Cu-HT	3.0602	23.3020	124	$Cu^{2+} = 0.69$
Co-HT	3.0596	23.2677	176	$Co^{2+} = 0.74$
Fe-HT	3.0791	23.0999	178	$Fe^{3+} = 0.64$
Cr-HT	—	—	52	$Cr^{3+} = 0.69$

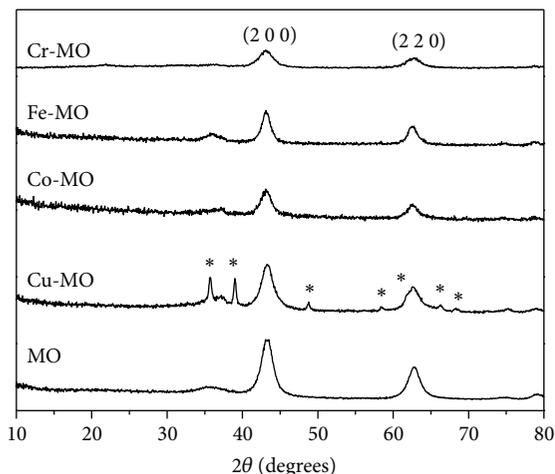
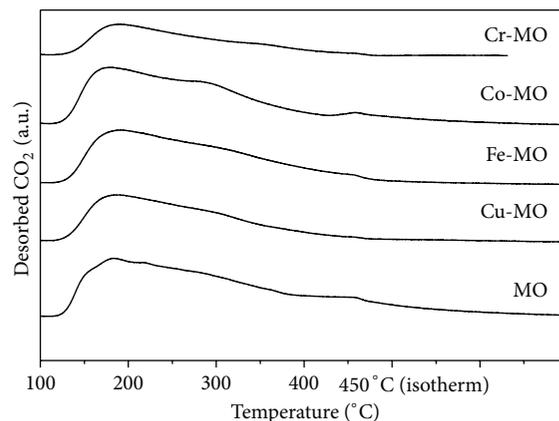


FIGURE 2: X-ray diffraction patterns of the mixed oxides derived from HTLCs after calcination at 450°C. (*) CuO-tenorite.

sample Cr-HT, compared to the other synthesized materials, could be reflecting its smallest crystallite size.

Upon calcination at 450°C, a poorly crystallized Mg(Al)O with a periclase-type structure ($2\theta = 43.40^\circ$ and 62.90° , corresponding to the (2 0 0) and (2 2 0) reflections) [26] in which the oxides of the transition metals were dispersed was observed due to the collapse of the layered structure of HTLCs. No spinel-type phase was detected in the X-ray diffractograms (Figure 2). For sample Cu-MO, characteristic peaks associated to the CuO-tenorite phase were observed along with the Mg(Cu,Al)O-periclase phase. The oxide phase was already present in the precursor material and became more evident after thermal treatment at 450°C. This result differs from those of Chmielarz et al. [29] which studied a Cu,Mg,Al-hydrotalcite with similar composition and detected the segregation of a CuO-phase only for the sample calcined at 1000°C. On the other hand, X-ray diffractograms of samples Co-MO, Cr-MO, and Fe-MO indicate that cobalt, chromium, and iron oxides are well dispersed in the Mg(Al)O phase.

Textural analysis of the samples calcined under air at 450°C indicated that they are mesoporous mixed oxides whose main textural properties are shown in Table 3. The incorporation of Cu, Co, and Fe in the HTLC structure originated mixed oxides with smaller BET specific area and pore volume than those of the corresponding Mg,Al-mixed oxide (MO). Similar trends are reported by Chmielarz et al.

FIGURE 3: Desorption profiles of chemisorbed CO₂ (CO₂-TPD).

[29]. However, for Cr-mixed oxide sample the specific area is higher and the pore volume is smaller than those of Mg,Al-mixed oxide. The incorporation of Cu led to the sample with the lowest values of specific area and mesopores volume which could be associated to a partial blockage of the pores due to the presence of the segregated phase coexisting with the periclase-type phase.

3.2. Basicity Characterization. The profiles of CO₂ temperature-programmed desorption are shown in Figure 3. It is observed that all profiles are characterized by the presence of a broad peak covering a wide range of temperatures, suggesting a wide distribution of basic strength of surface sites. Therefore, it can be concluded that the partial substitution of Mg or Al for different ions of transition metals had no significant effect on the distribution of strength of basic sites. Valente et al. [30] observed similar CO₂ profiles for Mg,Al-mixed oxides where Mg or Al were substituted for Ni, Zn, Cu, and Fe indicating a wide strength distribution of basic sites.

The total basic site density of the studied catalysts was determined by temperature-programmed desorption of CO₂ and expressed as the amount of chemisorbed CO₂. The results are shown in Figure 4. It is observed that, while the incorporation of Co and Fe slightly decreased the basic site density, the presence of Cu and Cr produced samples with much lower basicity. The reduction in total basic sites density upon the replacement of Mg and/or Al by transition metal was also reported in the literature [30, 31]. However, the magnitude of the observed effect varies depending on the metal content and methodology of sample preparation.

Considering that the incorporation of transition metals also influenced BET specific area and volume of mesopores, attempts were made to correlate the density of basic sites with textural properties. As shown in Figure 5, there is a direct correlation between the volume of mesopores and the density of basic sites.

The transformation of 2-propanol is often used as a model reaction for the determination of the acid-base properties of solid catalysts. This transformation occurs via elimination reactions, dehydration, and dehydrogenation, for example,

TABLE 2: Chemical composition and textural characteristics of HTLCs.

Sample	Molar composition		S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$) ^a
	Gel	Sample		
Mg/Al	6.0/2.0	6.06/1.94	71	0.378
Cu/Mg/Al	1.0/5.0/2.0	0.81/5.25/1.94	76	0.413
Co/Mg/Al	1.0/5.0/2.0	0.95/5.11/1.94	69	0.489
Cr/Mg/Al	1.0/6.0/1.0	0.88/6.12/1.00	170	0.190
Fe/Mg/Al	1.0/6.0/1.0	0.91/6.12/0.97	71	0.490

^a Calculated by BJH method.

TABLE 3: Textural characteristics of mixed oxides.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$) ^a
MO	213	0.747
Cu-MO	114	0.495
Co-MO	179	0.656
Cr-MO	253	0.163
Fe-MO	140	0.617

^a Calculated by BJH method.

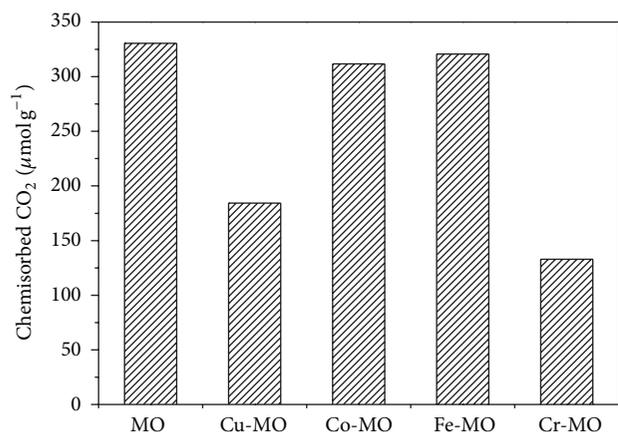


FIGURE 4: Basic site density of studied catalysts measured by CO₂-TPD.

which can occur through different mechanisms depending on the nature of the studied materials [32]. However, the presence of redox sites can also promote dehydrogenation of 2-propanol. Concerning the dehydration reaction, most primary and secondary alcohols react through an E2 concerted mechanism, involving both acid and basic sites of the solid, and leading to olefin and ether formation. However, alcohol dehydration can also proceed through the E1b mechanism involving an intermediate carbanion on strong basic solids which possess acid/base sites with imbalanced strength. On the other hand, the dehydrogenation reaction occurs over strongly basic solid catalysts through an E1b mechanism involving the same intermediate carbanion that forms olefins, but in this case, the ketone is formed by an α -hydrogen abstraction. Another alternative mechanism for dehydrogenation is an oxidative process in which redox centers and molecular or lattice oxygen are required. When

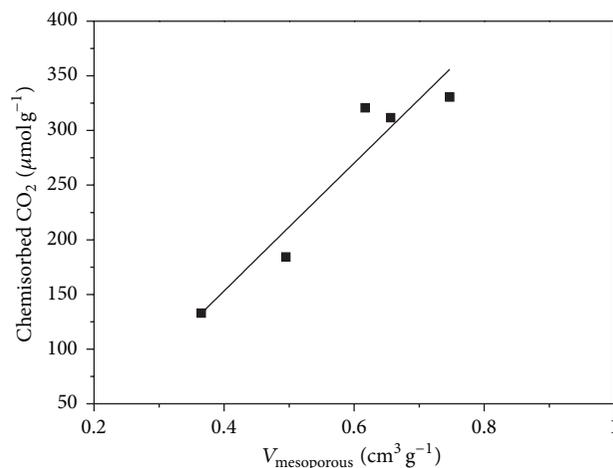


FIGURE 5: Relationship between basic site density measured by CO₂-TPD and mesoporous volume.

2-propanol is used as a model probe, the possible reaction products are propene, di-isopropyl ether, and acetone.

Figure 6 shows 2-propanol conversion behavior with time-on-stream for the mixed oxides obtained after calcination at 450°C. For the experimental conditions used in this work, all samples were active and showed a slight deactivation. According to these results, Cu-MO presents the higher density of sites capable of catalyzing the reactions of 2-propanol, and the following sequence of activity could be established: Cu-MO > Cr-MO > Co-MO > Fe-MO. This trend differs significantly from that found by TPD of CO₂ reinforcing the difficulty in the selection of an appropriate technique to characterize the basic properties of solid catalysts.

In order to investigate the influence of the presence of transition metals on the nature of surface sites, the selectivity of the catalysts was analyzed in a second set of experiments carried out at initial isoconversion conditions (Figure 7). Only acetone and propene were detected as reaction products, and their selectivities were determined at 2-propanol conversion of approximately 50%. Over Cu-MO and Co-MO the selectivity to acetone was very high mainly indicating the presence of strong basic sites and/or redox centers. In the case of Cr-MO and Fe-MO both acetone and propene were observed showing that these samples presented strong basic sites, acid sites, and possibly redox centers. Our results are in agreement with those of Valente et al. [30] that have studied

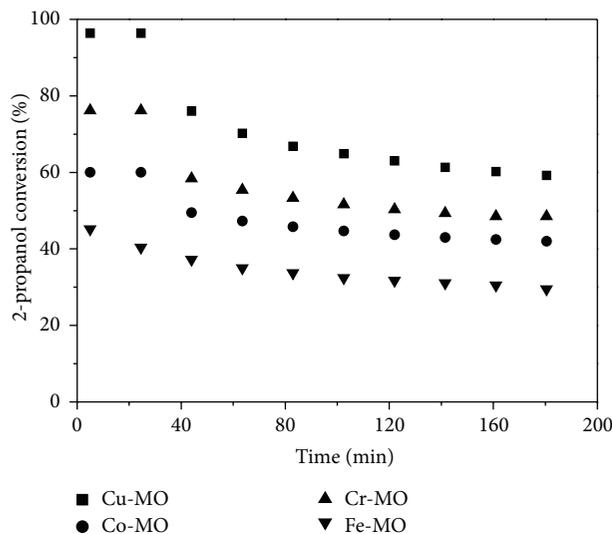


FIGURE 6: Conversion of 2-propanol as a function of time-on-stream for the mixed oxides obtained after calcination to 450°C (atmospheric pressure, $T = 350^\circ\text{C}$; $\text{N}_2/2\text{-propanol} = 23$; $\text{WHSV} = 13.0\text{ h}^{-1}$).

the conversion of 4-methylpentan-2-ol into 4-methylpentan-2-one (MIBK) and olefins via dehydrogenation and dehydration, respectively, over MgZnAl-, MgCuAl-, MgNiAl-, and MgFeAl-mixed oxides. They verified that MgCuAl produced only MIBK, while MgFeAl catalyzed the formation of olefins and MIBK. Although the transformation of 2-propanol is largely used as a model reaction to study acid-base properties, it is not easy to clearly identify the nature or strength of the acid-base sites, especially when reducible metals are present in the sample. The elucidation of the role of basic or redox sites on the dehydrogenation of 2-propanol is still difficult and not deeply studied. Carriazo et al. [33] have studied the acid-base and redox properties of amorphous magnesium and zinc molybdates derived from Mg,Al- and Zn,Al-heptamolybdate layered double hydroxides using Fourier transform infrared spectroscopy (FTIR) to monitor the adsorption of 2-propanol, acetic acid, and acetone on those materials. According to their results a distinction between the acid-base mechanism and the redox one for 2-propanol dehydrogenation could not be achieved.

3.3. Catalytic Results. Methyl esters of palmitic (C16), stearic (C18), oleic (C18:1), and linoleic (C18:2) acids were the main products formed in the soybean oil transesterification with methanol. The reaction scheme is shown in Figure 8. The transesterification process is a sequence of three reversible consecutive reactions in which mono- and diglycerides are intermediates. According to the stoichiometry, the reaction occurs between 1 mol of triglyceride and 3 mol of alcohol. However, an excess of alcohol is generally used to increase the esters yield and to facilitate glycerol separation.

The catalytic performance of the studied solids was compared at 130°C using a methanol/oil molar ratio of 75. The results, expressed as fatty acid methyl esters (FAME) yield

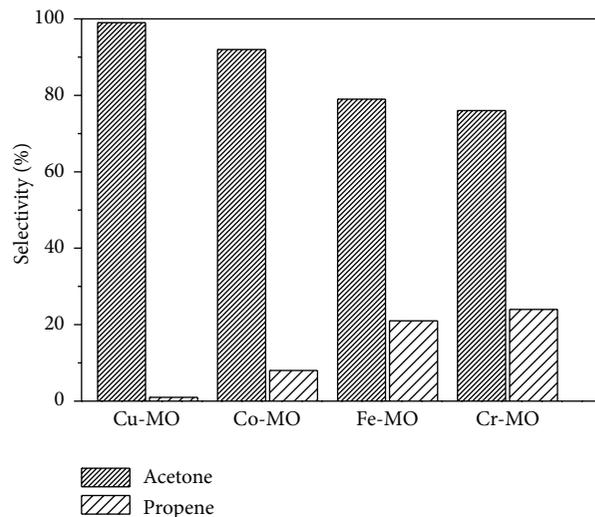


FIGURE 7: Selectivity results for 2-propanol transformation at iso-conversion of 50% (atmospheric pressure, $T = 350^\circ\text{C}$; $\text{N}_2/2\text{-propanol} = 23$; reaction time = 5 min).

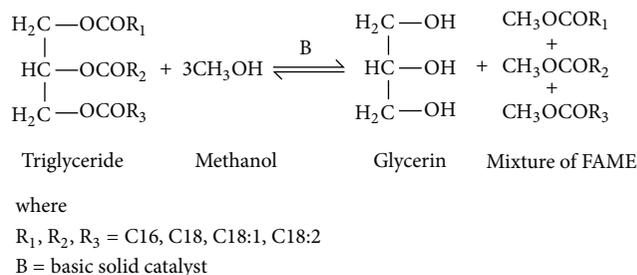


FIGURE 8: Reaction scheme for the transesterification of soybean oil with methanol.

(%), are presented in Figure 9. No reaction was observed in the absence of catalyst at 130°C . These results indicate that the mixed oxides samples are active in the transesterification of soybean oil with methanol; that is, they have sufficient basicity to catalyze the reaction. The following sequence of catalytic activity could be observed: $\text{Cr-MO} < \text{Co-MO} < \text{Cu-MO} < \text{Fe-MO} < \text{MO}$. The methyl esters yield correlated well to the volume of mesopores variation as shown in Figure 10. However, the attempt to correlate the catalytic performance of the transition metal-mixed oxides for transesterification reaction and their basic properties failed. Thus, for the basic site density measured by $\text{CO}_2\text{-TPD}$ the results presented in Figure 11 only suggest a slight trend of increase in biodiesel yield with increasing density of basic sites, while no clear correlation was observed between the catalytic behavior of the transition metal mixed oxides studied in this work for the 2-propanol transformation and the transesterification of soybean oil and methanol. This fact could be related to the influence of the redox mechanism on 2-propanol transformation but not on the transesterification reaction. The characterization of basic properties is still a challenge due to the difficulty of selecting the appropriated technique,

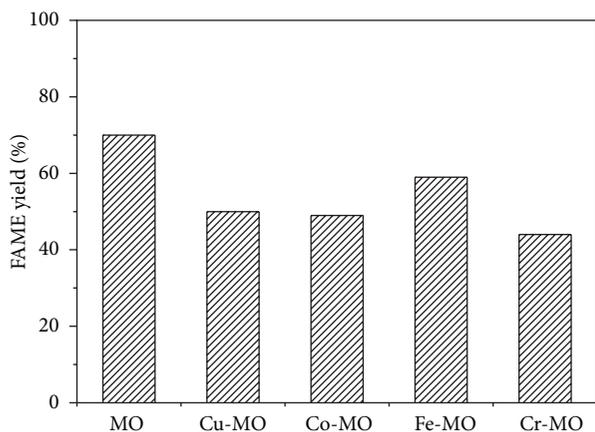


FIGURE 9: Methyl esters yield for the studied catalysts ($R_{\text{CH}_3\text{OH}/\text{oil}} = 75$; $T = 130^\circ\text{C}$; $t = 7$ h; 5 wt.% of catalyst).

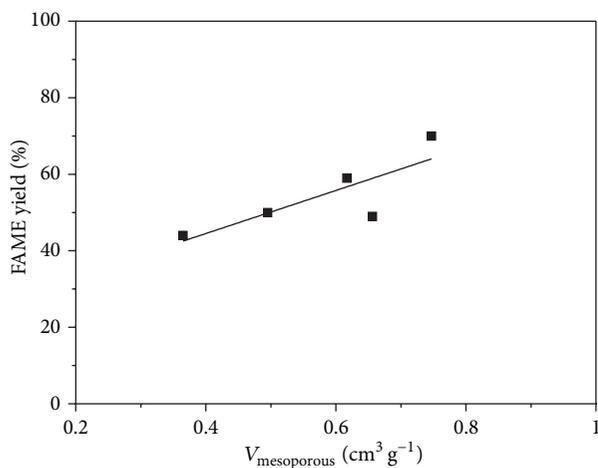


FIGURE 10: Relationship between the activity (expressed by methyl esters yield) and mesoporous volume.

probe molecule, or model reaction that can represent the same catalytic mechanism of the studied reaction.

The comparison of the catalytic results for the transesterification of soybean oil and methanol obtained in this study with those recently reported is not easy because just a few published results using Mg,Al-mixed oxides containing transition metals for transesterification reaction are available. Macala et al. [23] have depicted that the partial substitution of Al by Fe generates a mixed oxide more active than an Mg,Al-mixed oxide for the reaction between glyceryl tributyrate and methanol at 60°C using 1 wt.% of catalyst and a methanol to glyceryl tributyrate molar ratio of 6. However, the authors have highlighted the low activity achieved by their Mg,Al-mixed oxide. It is also necessary to point out that the transesterification of glyceryl tributyrate and methanol is a model reaction using a simpler ester to model triglycerides. A good performance of a Co,Mg,Al-mixed oxide (M^{2+}/M^{3+} molar ratio = 3) has been described by Li et al. [18] in the transesterification of canola oil and ethanol, but in this case a comparison with the results of the present work is

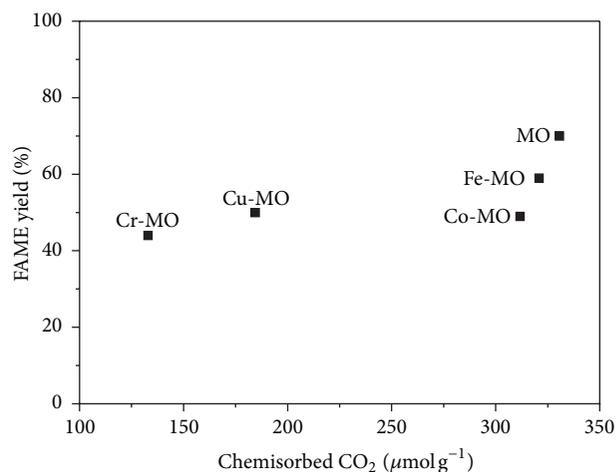


FIGURE 11: Relationship between the activity (expressed by methyl esters) and basic site density of the catalysts.

hampered by the fact that the Mg,Al-mixed oxide prepared by the authors turned into a gel-like phase in the presence of the reaction medium making the catalyst recovery difficult. Although these authors [18, 23] mentioned a better catalytic behavior for Mg,Al-mixed oxides containing transition metals, both of them reported unusual performance for their Mg,Al-mixed oxides. On the other hand, Pavel et al. [31] have synthesized MMgAlO mixed oxide catalysts ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{and Zn}$) derived from the corresponding layered double hydroxide by thermal decomposition. These mixed oxides were tested as catalyst for cyanoethylation of methanol, which first reaction step is the abstraction of a proton from the hydroxyl group of methanol by basic sites producing an alkoxide anion. The authors reported that reaction conversion decreased after introduction of transition metal cations. This is the same trend observed in our work. Although Pavel et al. [31] have studied a different reaction, the first step of both cyanoethylation of methanol and transesterification of soybean oil and methanol is the same.

4. Conclusions

The mixed oxides derived from Mg,Al-HTLC in which the Mg or Al was partially replaced by a transition metal (Cu, Co, Fe, or Cr) were prepared, characterized, and tested as catalysts for the transesterification of soybean oil with methanol. The results showed that the incorporation of transition metal influences both the textural characteristics and the density of basic sites present in catalysts, although not having a significant effect on the distribution of basic strength of these sites. All tested catalysts were active in the reaction studied, and the following sequence of catalytic activity was found: $\text{Cr-MO} < \text{Co-MO} < \text{Cu-MO} < \text{Fe-MO} < \text{MO}$. The incorporation of transition metal did not improve the catalytic activity of Mg,Al-mixed oxide. When the catalytic performance is analyzed according to physicochemical characterization, it appears that these results can be explained by catalyst texture and expressed by the volume of mesopores.

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