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Transesterification of soybean oil with methanol catalyzed by basic solids

Wallace Magalhães Antunes, Cláudia de Oliveira Veloso,
Cristiane Assumpção Henriques *

Programa de Pós-graduação em Engenharia Química, IQ/UERJ, Rua São Francisco Xavier, 524,
CEP 20559-900 Rio de Janeiro, RJ, Brazil

Abstract

The fatty acid methyl esters prepared by transesterification of vegetable oils with methanol are products of commercial interest due to their use as raw materials for chemical, pharmaceutical and food industries and also as biodiesel. Biodiesel is a non-polluting alternative fuel produced from renewable resources whose chemical and physical properties closely resemble those of the petroleum diesel fuel. This work studied the transesterification of soybean oil with methanol over basic solid catalysts such as: MgO, ZnO, Al_2O_3, and mixed oxides derived from hydrotalcite-like compounds (Mg/Al and Zn/Mg/Al). The influence of the catalyst basicity on their catalytic performance was also evaluated. The results indicated that both MgO and mixed oxides were efficient to catalyze the reaction under study with a fatty acid methyl esters yield higher than 60% at 130 °C. The influence of chemical composition on catalytic performance was closely related to the density of basic sites of the samples. The fatty acid methyl esters yield was favored by the increase on reaction temperature.

Keywords: Biodiesel; Transesterification; Basic solid catalysts; Methanolysis; Mixed oxides; Hydrotalcites

1. Introduction

Hydrotalcites are layered double magnesium–aluminum hydroxides with general formula $[Mg_{8-x}Al_x(OH)_{16}(CO_3^{2-})_{x/2}]\cdot nH_2O$, whose structure consists of brucite-like layers, where partial substitution of Al^{3+} for Mg^{2+} cations originates an excess of positive charges which are compensated by carbonate anions located along with water molecules in the interlayer space [1,2]. The Al/(Al + Mg) ratio in pure hydrotalcites can take values between 0.20 and 0.34. Both Mg^{2+} and Al^{3+} can be total or partially substituted by di- and trivalent cations forming a class of important compounds named hydrotalcite-like compounds (HTLCs) or layered double hydroxides (LDHs) [2].

Thermally treated HTLCs induces dehydration, dehydroxylation, and loss of compensation anions, forming mixed oxides/hydroxides with basic properties and a poorly crystallized structure [1]. These oxides present small particle size, large specific surface area, and basic properties attributed to hydroxyl groups, different O^{2-}–M^{n+} acid–base pairs and O^{2-} anions [3–6]. So, they are potentially useful as adsorbents and as heterogeneous base catalysts and catalytic supports. As shown by different authors [4,5,7,8], the surface basic properties and consequently the catalytic performance depend on the chemical composition and on the method of preparation of the parent hydrotalcite, the optimum Mg/Al ratio depending on the basic site density and strength required to activate the reactant of the reaction under study. The catalytic applications of mixed oxides obtained from HTLCs include base-catalyzed reactions such as aldol, nitroaldol, Knoevenagel and Claisen–Schmidt condensations [1,3,5,6,9–15], Michael additions [16], alkylation of di-ketones and phenols [8,17], and more recently transesterification of vegetable oils [18–20].

Transesterification of vegetable oils or animal fats with short carbon-chain alcohols (methanol or ethanol), catalyzed by strong acids or bases, produces a mixture of fatty acids esters also known as biodiesel, which is non-toxic, biodegradable, and an excellent substitute for conventional diesel fuels [21].

Biodiesel can be considered a renewable and practically inexhaustible source of energy. Their physico-chemical properties such as energy content, cetane number, and viscosity are

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* Corresponding author. Fax: +55 21 2587 7227.
E-mail address: cah@uerj.br (C.A. Henriques).

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similar to those of petroleum-based diesel fuels. Thus, biodiesel can be used in compression–ignition (diesel) engines with little or no modifications. Moreover, recent regulations have restricted sulfur content in diesel fuel, so reducing its lubricity. The biodiesel addition in diesel blends is an interesting option to enhance the engine performance (higher cetane number) restoring its lubricity. In addition to this, the use of biodiesel has a beneficial impact on the environment, since it decreases the emissions of CO, SO_2, unburned hydrocarbons, polyaromatic hydrocarbons (PAHs), and particulate matter [22].

The conventional process of biodiesel production is the transesterification of vegetable oils with methanol in the presence of homogeneous basic catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides [23–25]. However, these catalytic systems have some technological problems, such as the difficulty for removal of the basic catalysts after reaction, the large amount of wastewater produced, and emulsification. The latter is associated to the soaps that are known to emulsify the biodiesel with glycerin, especially if ethanol is used. Furthermore, the growing concern about the environment is leading the chemical industry to develop less pollutant and more selective chemical processes. In this context, solid catalysts have received increasing attention as substitutes for the highly pollutant liquid homogeneous catalysts in organic reactions. The replacement of the homogeneous catalysts for heterogeneous ones has several technical advantages, such as little or no corrosion, easy handling and separation, catalysts reutilization, and reduction of the amount of toxic wastes. Moreover, the use of heterogeneous catalysis in transesterification reactions prevents the undesirable saponification and allows the process simplification and the reduction of the processing costs by eliminating the additional steps associated with homogeneous catalysts.

Several researches on transesterification of vegetable oils with methanol at laboratory scale have reported the use of heterogeneous catalysts. Leclercq et al. [18] studied rapeseed oil transesterification with methanol in the presence of zeolites (CsNaX) and commercial hydrotalcite. Conversions of 70% and of 35% in the presence of Cs-exchanged zeolites and calcined hydrotalcite, respectively, were observed after 22 h at methanol reflux using a methanol/oil molar ratio of 275. The use of ETS-4 and ETS-10 (titanosilicalites) was patented by Bayense et al. [26] that have obtained conversion of 85.7% and 52.6%, respectively, at 220 °C after 1.5 h. Good performance of the molecular sieves NaX impregnated with Na_2O and ETS-10 was reported by Suppes et al. [27] that observed conversions up to 90% in methyl esters at temperatures between 120 and 150 °C after 24 h of reaction. In another work, Suppes et al. [28] observed a conversion of 78% and ethyl esters selectivity greater than 95% at 260 °C after 18 min of reaction using calcium carbonate as catalyst. More recently, Kim et al. [29] reported the excellent performance of Na/NaOH/–Al_2O_3 catalyst when comparing to NaOH (homogeneous catalysis) whereas Xie et al. [22,30–32] investigated the performance of different basic solids as catalysts for the methanolysis of soybean oil. When the reaction was studied over calcined Mg, Al-hydrotalcites at reflux of methanol with a methanol/oil molar ratio of 15:1, the mixed oxide with a Mg/Al = 3 was found to be the optimum catalysts with an oil conversion of 67% [22]. Good performances were also reported for K_2O/Al_2O_3 [31,32] (oil conversion equal to 87%, when KNO_3 was the precursor of K_2O, and equal to 96%, when it was KI) and for KF/ZnO [30] (oil conversion = 87%) as catalysts on the transesterification reaction carried out at similar conditions (reflux of methanol, methanol/oil = 15). For all the studied catalysts, their activities correlated well with their corresponding basic properties.

The development of heterogeneous catalysts for transesterification of vegetable oils has also industrial interest, as can be seen by the large number of published patents [33–40]. In these patents, mixed oxides and/or spinels of aluminum and a second transition metal are claimed as active catalysts for transesterification of vegetable oils and animal fats with several alcohols, particularly methanol and ethanol. However, high methyl esters yields and the production of high purity glycerin are associated to the reaction occurring in at least two stages, at high temperatures and pressures (170–250 °C; 30–70 atm), in continuous or batch reactor. These researches lead to the development of a commercial process (Esterfip-H Trade Mark-Axens, France) for biodiesel production from methanolysis of vegetable oils, using a Zn-containing spinel derived from HTLCs as solid catalyst [41].

Taking into account the promising results claimed in several patents for Zn-containing catalysts in vegetable oils transesterification with short carbon-chain alcohols we decide to continue our study in the production of fatty acids methyl esters from the methanolysis of soybean oil comparing the catalytic performance of Zn, Mg, Al-mixed oxide and ZnO with that of Mg, Al-mixed oxide, MgO and Al_2O_3, at different temperatures. The influence of the relative basicity of these materials on the FAME yield was also investigated.

2. Experimental

2.1. Reagents

Commercial soybean oil and methanol (VETEC, 99.8%) were used without any previous treatment in the transesterification reaction. The catalysts were prepared using technical grade reagents.

2.2. Catalysts preparation

Mg, Al-hydrotalcite and Zn, Mg, Al-HTLC were prepared by coprecipitating, at room temperature, an aqueous solution of metallic cations (solution A) with a highly basic carbonate solution (solution B). Solution A, containing $Zn(NO_3)_2\cdot 4H_2O$, $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ or $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ dissolved in distilled water was 1.5 M in $(M^{3+} + M^{2+})$ with an $Al/(Al + M^{2+})$ molar ratio equal to 0.25 and a Zn/Mg molar ratio of 0.20. Solution B was prepared dissolving appropriate amounts of Na_2CO_3 and NaOH in distilled water in order to obtain a $[CO_3{}^{2-}]$ equal to 1.0 M and a pH equal to 10 during the aging of the gel. In the synthesis procedure, solution A was slowly dropped (60 mL/h) under vigorous stirring to a B solution placed in a 150 mL PTFE reactor. The gel formed was aged under constant pH 13 for 18 h at 60 °C. Afterwards, the solid obtained was filtrated and washed with hot distilled water until neutral pH. Then, it was dried at 90 °C for 12 h. Mg, Al-hydrotalcite and Zn, Mg, Al-HTLC were named MgHT and ZnMgHT, respectively. In order to obtain the mixed oxides the samples were calcined under dry air flow (100 mL/min) from room temperature to 450 °C at a 1 °C/min heating rate and held at this temperature for 12 h. The mixed oxides so obtained were named MgMO and ZnMgMO.

The precursors of the magnesium oxide (MgO) and of the aluminum oxide (Al_2O_3) were prepared as described above, except that aluminum or magnesium were absent of the synthesis gel, respectively. The oxides were obtained by the same thermal treatment described above.

The ZnO was obtained through the calcination of a commercial zinc carbonate under air flow (40 mL/min) from room temperature to 350 °C at a 10 °C/min heating rate and held at this temperature for 4 h. This procedure was used aiming at obtaining a material with a higher specific surface area than that of the commercial ZnO (<10 m^2/g).

2.3. Physico-chemical characterization

The chemical composition of the original hydrotalcite samples was determined by X-ray fluorescence (XRF) using a Rigaku RIX3100 spectrometer whereas their thermal decomposition was evaluated by thermogravimetric analysis (TGA) and derivative thermal analysis (DTA) carried out in a Rigaku Thermobalance TAS 100 operating under a flow of air at a 10 °C/min heating rate up to 900 °C.

X-ray powder diffractograms were recorded in a Rigaku Miniflex X-Ray Diffractometer equipped with a graphite monochromator using Cu Kα radiation, 30 kV and 15 mA, in order to identify the crystalline phases present in the samples.

Textural characteristics such as specific surface area (BET), microporous volume (*t*-plot), and mesoporous volume (BJH) were determined by N_2 adsorption–desorption at −196 °C in a Micromeritics ASAP 2000. Before the analysis, the samples were pretreated under vacuum overnight at 450 °C.

2.3.1. Basicity characterization—model reaction of diacetone alcohol retroaldolization

Diacetone alcohol (DAA) retroaldolization reaction was carried out in vapor phase at atmospheric pressure. The reactant was fed to the reactor through a saturator held at 30 °C, using nitrogen as carrier gas. Before the reaction, the samples were calcined "*in situ*" under the conditions presented before (item 2.2). The experimental conditions used were the following: reaction temperature = 40 °C; N_2/DAA molar ratio = 244; and a proper weight hourly space velocity (WHSV, gram of DAA per hour per gram of catalyst) for each sample. The reaction products were analyzed by on-line gas chromatography (CHROMPACK 9000) using a 50 m CP-Sil 5CB capillary column and a flame ionization detector.

2.4. Catalytic tests

The transesterification reaction of soybean oil with methanol was carried out in liquid phase, under autogenous pressure employing a 50 mL stainless steel batch reactor magnetically stirred and heated with a thermostatic bath. Immediately before the runs, the hydrotalcites were calcined according to the procedure described in item 2.2 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 catalysts studied was evaluated at the following reaction conditions: reaction temperature = 70, 100, and 130 °C; methanol/soybean oil molar ratio = 55 (18 times higher than the stoichiometric amount); reaction time = 7 h; 5% w/w of catalyst (referred to the amount of soybean oil). At the end of each test, the system was rapidly cooled to room temperature and the catalyst was separated by centrifugation. The less dense phase, which contain 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. Physico-chemical characterization of the catalysts

The results of chemical analysis of the as-synthesized samples, expressed by their Al/(M^{2+} + Al) and Zn/Mg molar ratios, are shown in Table 1. For both samples, the chemical composition was quite similar to that of the corresponding

Table 1
Chemical analysis, cell parameters and thermogravimetric analysis of the as-synthesized hydrotalcites

Sample	Al/(Al + M^{2+})		Zn/Mg		*a* (Å)	*c* (Å)	Loss of interlayer water		Dehydration/ decarbonation	
	Gel	Sample	Gel	Sample			(wt.%)	T_{max} (°C)	(wt.%)	T_{max} (°C)
MgHT	0.25	0.25	–	–	3.0536	23.1392	18.8	203	24.6	398
ZnMgHT	0.25	0.26	0.20	0.16	3.0573	23.0037	15.5	198	25.7	386

T_{max} is the "maximum" temperature of the corresponding peak in the DTA profile.

synthesis gel, indicating that the metallic cations were incorporated at the expected levels.

The X-ray diffractograms of the as-synthesized materials are presented in Fig. 1. Samples MgHT and ZnMgHT show the characteristic pattern of pure hydrotalcite in carbonate form, whose main planes are marked in the figure, indicating that pure samples were obtained. These results suggest the complete incorporation of Zn^{2+} cations into the layered structure. The lattice parameters, *a* and *c*, typical of hydrotalcite structures with rombohedral 3R symmetry were calculated from the peaks associated to planes (0 0 3), (0 0 6), (1 1 0) and (1 1 3) using the software UnitCell and are shown in Table 1. The values of parameter *a*, which is a function of the cation–cation distance in the hydroxyde layers, is higher for sample ZnMgHT, which confirms the isomorphic substitution of Zn^{2+} (0.74 Å) for Mg^{2+} (0.65 Å). Parameter *c*, which is related to the layer thickness (brucite-like sheet plus an interlayer), is lower for the Zn-containing sample. Since it depends upon several factors such as the amount of interlayer water, the size of the interlayer anion and of the M^{2+}–M^{3+} cations, and the strength of the electrostatic attractive forces between the layer and the interlayer [42,43], this result must probably reflect the influence of these various factors.

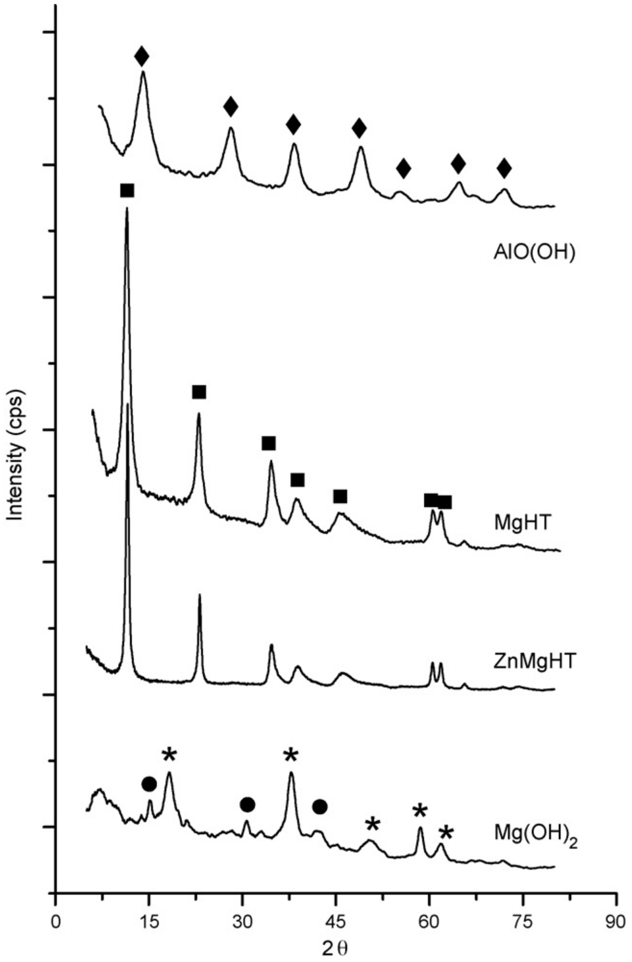

Fig. 1. X-ray diffraction patterns of the synthesized materials (■, Hydrotalcite; ◆, AlO(OH) bohemite; *, $Mg(OH)_2$ brucite; ●, hydromagnesite).

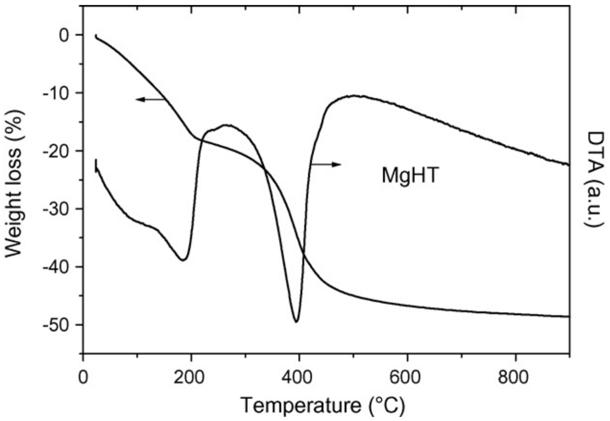

Fig. 2. TGA and DTA profiles of sample MgHT.

Fig. 1 also shows that a mixture of $Mg(OH)_2$–brucite (main) and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) phases was the precursor of MgO, while Al_2O_3 was obtained from AlO(OH)–bohemite.

The TGA and DTA profiles of the as-synthesized samples, MgHT and ZnMgHT, are shown in Figs. 2 and 3, respectively. Both samples show the two typical weight losses of HTLCs in carbonate form associated to endothermic transformations. The first weight loss, with a maximum rate at near 200 °C, corresponds to the loss of interlayer water, and the second, with a maximum rate in the range 385–400 °C, is due to dehydroxylation and decarboxylation. As can be seen in Table 1, the losses of weight related to both transformations were slightly influenced by the chemical composition of the samples.

Taking into account the general formula of HTLCs, the results of chemical analysis (Al/(Al + Mg) molar ratio) associated to those of TGA (weight loss associated to interlayer water) allowed the calculation of the chemical formula of the hydrotalcite samples, which are presented in Table 2.

Fig. 4 shows the X-ray diffractograms of the calcined samples. It can be observed that the thermal treatment of the MgHT and ZnMgHT samples, at 450 °C, results in the collapse of the lamellar structure and in the formation of a poorly

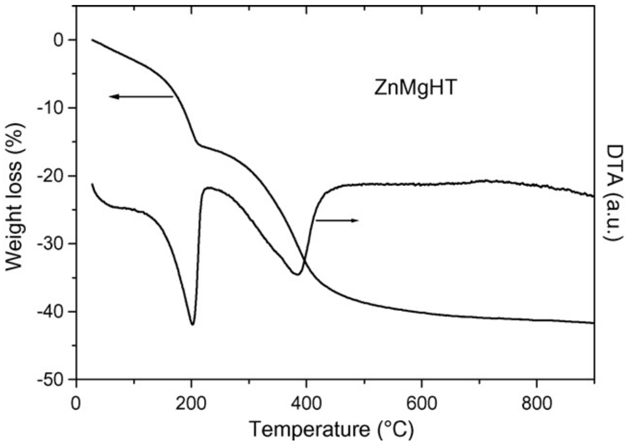

Fig. 3. TGA and DTA profiles of sample ZnMgHT.

Table 2
Chemical formula of the synthesized HTLCs

Sample	Chemical formula
MgHT	$Mg_6Al_2(CO_3)(OH)_{16}\cdot 6.8H_2O$
ZnMgHT	$Mg_{5.08}Zn_{0.83}Al_{2.09}(CO_3)_{1.05}(OH)_{16}\cdot 5.2H_2O$

crystallized Mg(Al)O and Mg(Zn,Al)O mixed oxides, in which the zinc and/or aluminum oxides are perfectly dispersed in the magnesium oxide matrix. These mixed oxides present an MgO–periclase structure with characteristic peaks at $2\theta \approx 35.7^\circ$, 43° and 63°. The same structure was observed for MgO.

The thermal treatment of bohemite and zinc carbonate originated γ-Al_2O_3 and ZnO, respectively. The intense and narrow peaks observed in the ZnO diffractogram reflect the high crystallinity of this material compared to the other samples.

The main textural characteristics of the studied catalysts were determined by nitrogen adsorption and are shown in Table 3. Except for ZnO, the catalysts are mesoporous materials with BET specific surface area in the range 160–280 m^2/g. The low specific surface area of ZnO could be associated to its larger crystallite size, as suggested by X-ray diffraction. As reported in the literature [44], incorporation of Zn in hydrotalcite structure produces mixed oxides with smaller specific surface area.

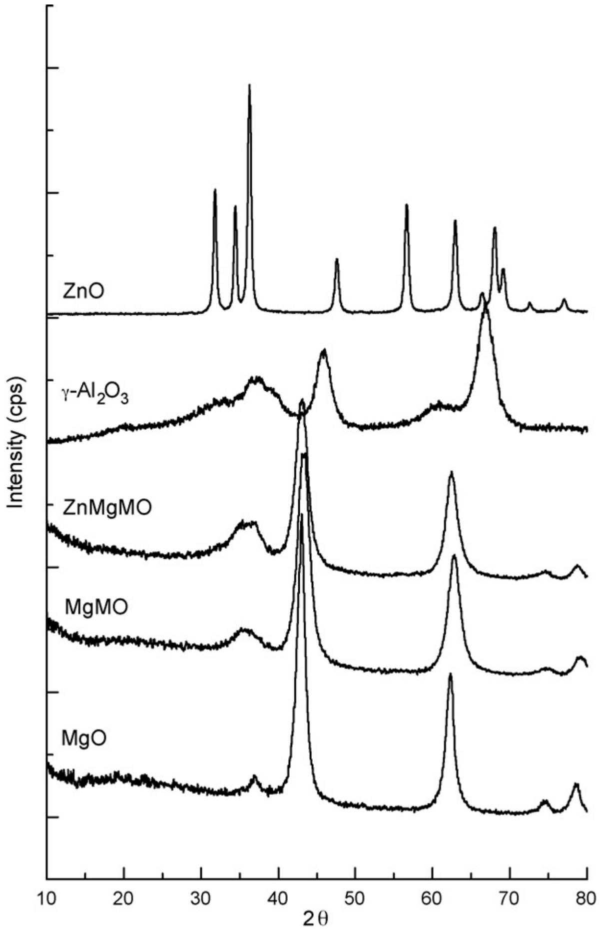

Fig. 4. X-ray diffractograms of the bulk oxides and mixed oxides catalysts.

Table 3
Textural characteristics of the studied catalysts

Sample	S_{BET} (m^2/g)	V_{meso}[a] (cm^3/g)	$S_{external}$[b] (m^2/g)	V_{micro}[b] (cm^3/g)
MgO	281	0.580	281	–
MgMO	232	0.302	197	0.014
ZnMgMO	159	0.774	159	–
ZnO	26	0.108	21	0.002
Al_2O_3	254	0.310	254	–

[a] BJH method.
[b] *t*-plot method.

3.2. Basicity characterization

The relative basicity of the samples was evaluated by means of the DAA retroaldolization (Fig. 5). This is a promising model reaction for the characterization of the basicity of solid materials, since the acetone formation is catalyzed only by basic sites and the DAA molecule is small enough to be used in the presence of materials with small pores.

Preliminary tests indicated that the studied samples could be classified in two distinct groups according to their basicity. So, for a better comparison each group was tested using an adequate space velocity.

Fig. 6 shows the evolution of acetone molar fraction during the reaction time for the oxides Al_2O_3, MgO, and ZnO (WHSV = 2.7 h^{-1}). As observed, MgO is much more active than ZnO and Al_2O_3, which present similar DAA conversions. Since the specific surface area of ZnO was smaller than that of the other samples, the activity of these materials was calculated on the basis of their specific surface area, using the conversion of acetone after 10 min of reaction time. The obtained results were: 3.97×10^{-5} mol DAA/s m^2 for Al_2O_3 and 3.73×10^{-4} mol DAA/s m^2 for ZnO indicating that ZnO presents a larger basic site density than Al_2O_3.

Due to their higher catalytic activity, the DAA retroaldolization over the mixed oxides (MgMO and ZnMgMO) and over MgO were carried out using a space velocity of 20.0 h^{-1}. The results are shown in Fig. 7. It was observed that the Zn-containing mixed oxide shows the lowest basic sites density regarding MgO and MgMO samples.

According to the results presented in Figs. 6 and 7 the following sequence of relative basicity can be proposed: $MgO \approx MgMO > ZnMgMO > ZnO > Al_2O_3$.

These results agree with the electronegativities of the metals present in the bulk oxides and indicate that Mg partial substitution by Zn in hydrotalcite decreases the basicity of the mixed oxide formed. The same behavior was previously reported [44,45] by other authors using different techniques to evaluate basic properties.

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 Fig. 8.

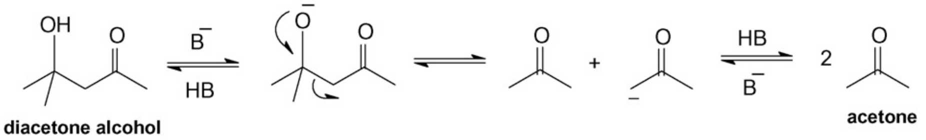

Fig. 5. Reaction scheme for the retroaldolization of DAA.

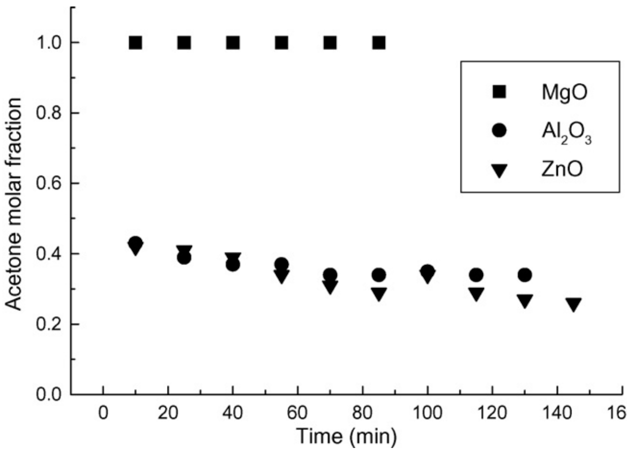

Fig. 6. Acetone molar fraction as a function of the reaction time for the samples MgO, Al_2O_3 and ZnO (WHSV = 2.7 h^{-1}).

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 the alcohol. However, an excess of alcohol is generally used to increase the esters yield and to facilitate glycerin separation [21,23,24].

The catalytic performance of the studied solids was compared at 130 °C using a methanol/oil molar ratio equal to 55. The results, expressed as yield in methyl esters (percent basis), are presented in Fig. 9. As previously reported [19], no reaction was observed in the absence of catalyst at 130 °C.

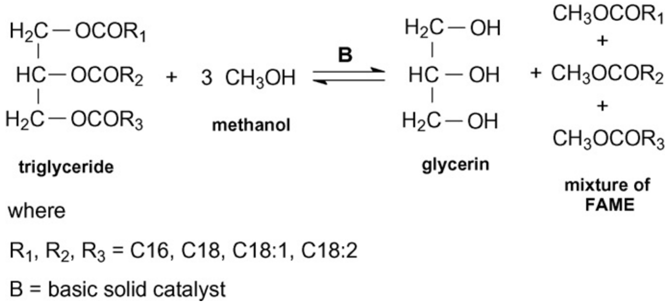

Fig. 8. Reaction scheme for the transesterification of soybean oil with methanol.

Fig. 9 shows that MgO and the mixed oxides derived from hydrotalcites are active in the transesterification of soybean oil with methanol. The yields in methyl esters reach values greater than 60%, indicating the presence of sites with basic strength sufficient to abstract protons whose pK_a is 16.7, as is the case of the proton of the hydroxyl group of methanol.

No evidences of the formation of metal soaps or metal glycerates were observed in this work.

As to the influence of the catalyst chemical composition, the methyl esters yields reflect the relative basicity of the catalysts, as determined by the DAA retroaldolization. However, the low yield obtained for ZnO can be related to both its lower basicity and specific surface area.

The influence of the reaction temperature is also shown in Fig. 9. As expected, the production of fatty acid methyl esters was favored by the increase in the temperature.

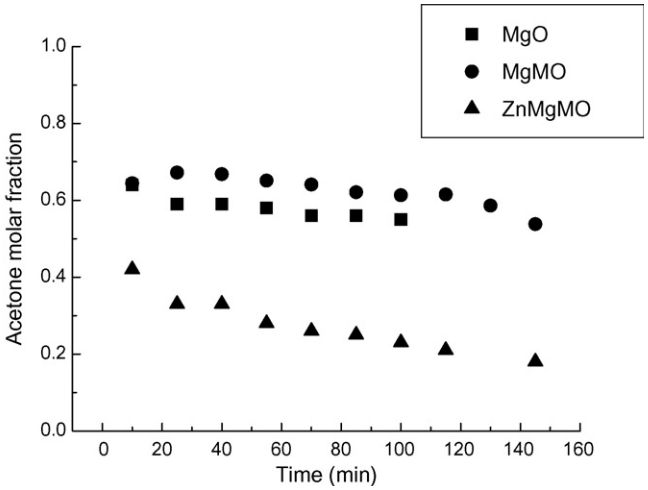

Fig. 7. Acetone molar fraction as a function of the reaction time for the samples MgO, MgMO and ZnMgMO (WHSV = 20.0 h^{-1}).

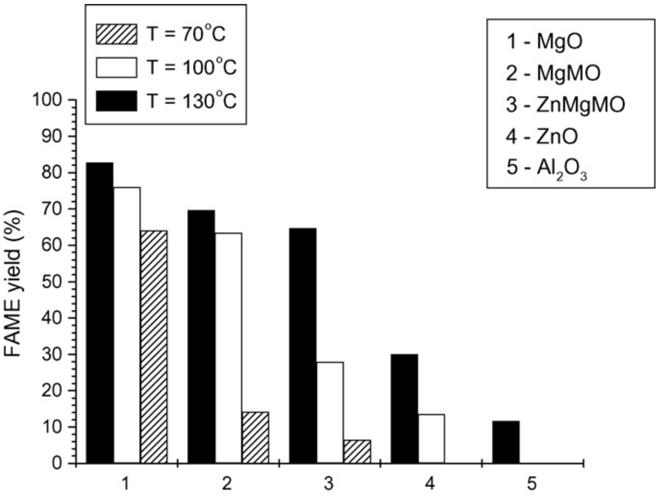

Fig. 9. Methyl esters yield for the catalysts at different temperatures ($R_{CH_3OH/oil}$ = 55; reaction time = 7 h).

The best performance of MgO in comparison to the mixed oxides derived from hydrotalcites was also observed by Leclercq et al. [18] and Corma et al. [46] in the methanolysis and glycerosis of rapeseed oil, respectively. On the other hand, the poor performance of the catalyst ZnMgMO, which presented low methyl esters yields than MgMO particularly at lower temperatures, suggests that the Zn-containing catalyst requires more severe reaction conditions to achieve similar yields. These results are in accordance with those reported in the literature for similar reactions catalyzed by Zn-containing mixed oxides/spinels, which were carried out at higher temperature and pressure.

4. Conclusions

The mixed oxides derived from hydrotalcites/HTLCs and MgO present basic sites strong enough to abstract the proton from the hydroxyl group of methanol ($pK_a = 16.7$). So, they show potential for use as catalysts in the transesterification of soybean oil with methanol in a heterogeneous reaction system.

The catalytic performance of the studied catalysts was influenced by their relative basicity, which is affected by the chemical composition. The increase in reaction temperature increased the fatty acid methyl esters (biodiesel) yield.

A preliminary evaluation of the results indicates that additional researches either on new basic solid catalysts or on the optimization of the experimental conditions aiming at the improvement of the biodiesel production are still necessary. The major drawback is to obtain high methyl esters yields under reaction conditions appropriate for the development of the process in a commercial scale. Although there is no expectation of reaching high yields in heterogeneous media using experimental conditions as soft as those employed with homogeneous catalysis, the reduction of the processing costs due to the process simplifications along with the minimization of the environmental problems justify the use of basic heterogeneous catalysts.

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