Transesterification of Soybean Oil to Biodiesel by Using Heterogeneous Basic Catalysts

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Biodiesel production has increased greatly in recent years, because of the less-detrimental effects of this fuel on the environment, compared to a conventional diesel obtained from petroleum. This work investigates the possibility of using MgO and calcined hydrotalcites as catalysts for the transesterification of soybean oil with methanol. The achieved experimental data show a correlation not only with the catalysts basicity, but also with its structural texture. However, the structural texture of the examined catalysts is dependent on both the precursor and the preparation method. At least four different types of basic sites have been individuated on the surface of MgO and calcined hydrotalcite catalysts. The strongest basic sites (super-basic) promote the transesterification reaction also at very low temperature (100 °C), while the basic sites of medium strength require higher temperatures to promote the same reaction. Ultimately, all the tested catalysts are resistant to the presence of moisture in the reaction environment.

1. Introduction

The Kyoto Protocol signed in 1997 requires, from the European Union (EU), a commitment to reduce, between 2008 and 2012, greenhouse gas emissions by 8% from their 1990 level. One of the instruments chosen by the EU Commission to achieve these results is reported in the Directive 2003/30/EU, which states that, starting from 2010, at least 5.75% of the fuel used for driving engines in member states should come from renewable sources. For this reason, biodiesel production is constantly growing: EU production increased by almost 35% between 2002 and 2003 (Source: European Biodiesel Board). The current production capacity in the EU is 2.2 Mt/yr.

Biodiesel is a nonpetroleum-based fuel that generally consists of fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), derived from the transesterification of triglycerides (TG) with methanol or ethanol, respectively. The occurring reaction is
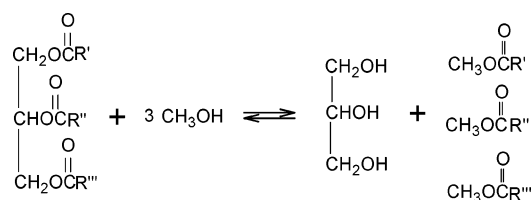
As can be seen, glycerol is a byproduct of the reaction.

The present day high price of petroleum notwithstanding, biodiesel is not competitive with petroleum diesel without subsidies or tax incentives. There are two main factors that affect the cost of biodiesel: the cost of raw materials (fats or oil and alcohols) and the cost of processing.[1]

The most commonly used technology for TG transesterification is based on the use of batch plants, in which a basic homogeneous catalyst is used (NaOH or NaOCH$_3$) and, at the end of the reaction, the catalyst is neutralized with acetic acid

or a mineral acid. A continuous transesterification process would be a good opportunity for reducing the production costs.[1] However, this technology has different unavoidable drawbacks. In the presence of moisture or free fatty acids (FFAs), soaps are formed that favor emulsion between glycerol and oil. Emulsion is also favored by the presence of unreacted monoglycerides and diglycerides. Therefore, a long settling time is necessary for the separation of the two emulsioned phases. Moreover, the recovered glycerol is, normally, impure, because of the presence of salts, soaps, monoglycerides, and diglycerides, and purification represents an additional cost. The cost of biodiesel could certainly be reduced through the use of a heterogeneous catalyst, instead of a homogeneous one, providing for higher-quality esters and glycerol, which are more easily separated, and there is no need for further expensive refining operations.[2]

To this end, the French Institute of Petroleum (IFP) has recently announced the construction of a new 160 000 t/yr biodiesel plant that is based on the use of an heterogeneous catalyst.[3] The catalyst proposed by the IFP is a Lewis acid catalyst based on a zinc compound (zinc aluminate[4]). Many other heterogeneous catalysts that are based on both acid[5,6] and basic[6−12] solids have recently been proposed in the literature.

In particular, the Mg−Al calcined hydrotalcites, derived from hydrotalcites of general formula $[Mg^{2+}_{(1-x)}Al^{3+}_x(OH)_2]^{x+}$-$(CO_3)^{2-}_{x/n}$, are solids with interesting basic properties[13] that have shown good activity in transesterification reactions.[12,14−18]

Corma et al.,[14] for example, in a patent mainly devoted to the transesterification of triglycerides with glycerol to prepare monoglycerides, also claimed the possibility to use calcined hydrotalcites and magnesium oxides in promoting the transesterification of triglycerides with monoalcohols, even if no examples or experimental data for this reaction are reported in the patent.

Leclerq et al.[7] tested the use of commercial calcined hydrotalcites in the transesterification of rapeseed oil, at 60 °C, with poor results for this catalyst, probably because of the very low temperature adopted in the performed runs. Cantrell et al.,[12] on the contrary, successfully used calcined hydrotalcites in promoting the transesterification of glycerol-tributirrate with methanol.

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Table 1. Fatty Acids Composition of the Used Soybean Oil, Determined by Gas Chromatography (GC) Analysis

fatty acid	content (%)
palmitic	11
stearic	4
oleic	23
linoleic	56
linolenic	5
others	1

More recently, we have confirmed, in an Italian patent application,[18] the good performances of calcined hydrotalcites and magnesium oxide in promoting the transesterification reactions that occur in biodiesel preparation.

In this paper, a deeper study of the performances of calcined hydrotalcite and MgO catalysts in the transesterification of soybean oil with methanol is reported.

The performances of magnesium oxide (obtained with different methods) and calcined hydrotalcite are compared in an attempt to correlate the activity data with the basicity and structural properties of these solids.

2. Experimental Section

2.1. Materials. A calcined AlMg hydrotalcite (calcined hydrotalcite, CHT) with an Al/(Al + Mg) theoretical atomic ratio of ∼0.20 and one of the type of MgO (named MgO(I)) were prepared following the methods described by McKenzie and Fishel.[19] The hydrotalcite and MgO(I) catalysts were prepared mixing two solutions, A and B: solution A contained a combination of aluminum and magnesium ($Mg(NO_3)_2$ 0.8 M and $Al(NO_3)_3$ 0.2 M) such that the Al/(Al + Mg) atomic ratio was 0.2 for hydrotalcite preparation, whereas only 1.0 M $Mg(NO_3)_2$ was used for (MgO(I)) preparation; solution B was prepared by dissolving NaOH and Na_2CO_3 (see McKenzie and Fishel[19] for more details).

Solution A was fed at a rate of 1 cm³/min for 4 h under vigorous stirring, while solution B was fed over time, when necessary, to maintain a pH value of 10. The obtained gels were aged at 65 °C for 24 h, and then filtered and washed to pH 7. After drying, at 85 °C for 14 h, the catalysts were obtained by calcination at 500 °C in air for 14 h.

We have prepared a calcined Al−Mg hydrotalcite with an Al/(Al + Mg) theoretical atomic ratio of ∼0.20, because it was the best one in regard to the transesterification of rapeseed oil with glycerol[15] and was also active in the glycerolysis of fatty methyl esters.[17]

Other two magnesium oxides have then been prepared MgO-(II) and MgO(III), by calcinating for 18 h at 400 °C $Mg(OH)_2$ and $(MgCO_3)_4*Mg(OH)_2$, respectively. Other proven catalysts include a commercial MgO (hereafter referenced as MgO(c)) and γ-alumina. The former catalyst has been supplied by Merck, and the latter by Dutral. All of the catalysts have been dried, at 200 °C in air for 2 h, before their use.

Soybean oil was purchased in a local food store (the fatty acids composition of the soybean oil, as determined by gas chromatography (GC) analysis, is reported in Table 1). All other used reagents (when not specified) were supplied by Aldrich and used as received, without further purification.

2.2. Catalyst Characterization. The composition of the CHT catalyst has been determined by dissolving the catalyst and analyzing the obtained solution by atomic absorption, using a Varian Spectra 220 apparatus.[16]

The textural properties of the obtained solids were determined using nitrogen adsorption−desorption isotherms, at liquid nitrogen temperature, by means of a Sorptomatic model 1990 instrument. Surface areas were determined by the Brunauer−Emmett−Teller (BET) procedure, while the total volume and pore size distribution were determined using the Dollimore−Heal method. X-ray investigation of the solids was performed using a Philips model 1887 diffractometer. The patterns were obtained using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA; the diffraction angle 2θ was scanned at a rate of 2°/min. Finally, the basic properties of the solids were determined using the temperature-programmed desorption of carbon dioxide (CO_2-TPD), which was used as the probe molecule[20−22] in a TPD/R/O 1100 TermoQuest instrument. The catalysts were degassed by heating, at 500 °C, under helium and then treated, at room temperature, with the probe gas stream. Physically adsorbed CO_2 was first removed by flushing helium at 40 °C. The basic strength distributions were evaluated by observing the capacity of the material to retain the probe molecules during the desorption that occurs at increasing temperatures (10 °C/min).

2.3. Transesterification. The screening of the different prepared catalysts has been performed in small stainless steel vial reactors. The reaction has been made by introducing reagents (methanol and soybean oil) together with a weighed amount of catalyst in each reactor.

The reactors (four or five) then were heated in a ventilated oven. To minimize mass-transfer limitations, the reactors were constantly agitated inside the oven.

The temperature of the oven was initially fixed at 50 °C for 14 min and then increased at a rate of 20 °C/min until to reach the reaction temperature for runs with final temperature equal to 100 °C and 180 °C. In the case of runs performed with a final temperature of 200 °C, the oven temperature was fixed at 50 °C for 2 min and then it was increased at a rate of 15 °C min. Then, after a pre-fixed reaction time, the samples were quickly cooled by putting the vials in a cold bath. Experimental runs have, normally, been performed with pure methanol, but some runs have also been made with the addition of water to the reactants.

The CHT, the four samples of magnesium oxide with different characteristics (MgO(c), MgO(I), MgO(II), and MgO(III)), and the γ-alumina were all tested as catalysts and their activities were compared.

The FAME yields, in the catalytic tests, were determined using a H NMR technique[23] (Bruker, 200 MHz), i.e., measuring the area of the H NMR signal relative to the methoxylic (A_1) and methylenic groups (A_2), respectively:

$$Y_{FAME} = \frac{A_1/3}{A_2/2}$$

The composition of the obtained methylester phase was determined by flame ionization detection−gas chromatography (FID−GC) analysis.[24]

To confirm the results obtained in the vials, the catalysts with the best performance (CHT) were also tested in a 1 dm³ autoclave reactor at 215−225 °C. These runs were performed by introducing both the reactants and the catalyst into the autoclave and heating them until the reaction temperature was achieved. The heating temperature profiles were approximately linear with time, and the reaction temperature was reached within ∼80 min. Samples of the reaction mixture were withdrawn at different times and analyzed. To evaluate the effect of the catalyst on the reaction rate, a run has been performed under the same conditions but without a catalyst, and the obtained results were compared.

Table 2. Characterization of the Used Catalysts and Their Effect on the Brunauer−Emmett−Teller (BET) Surface Area, Pore Volumes, Dimension of Crystallites, and Basic Sites Density

catalyst	surface area (m^2/g)	crystallite dimension (Å)	pore volume (cm^3/g)	specific basicity (CO_2 μmol/g)	intrinsic basicity (CO_2 μmol/m^2)
γ-Al_2O_3	174	20		155	0.86
CHT(I)	144	29	0.94	369	2.6
MgO(c)	36	115	0.15	266	7.2
MgO(I)	134	77	0.44	361	2.7
MgO(II)	214	110	0.59	756	3.5
MgO(III)	229	65	0.61	893	3.9

3. Results and Discussion

3.1. Catalyst Characterization. The Al/(Mg + Al) atomic ratio of the prepared CHT was 0.18 from chemical analysis, which is quite similar to the atomic ratio of the initial solution.
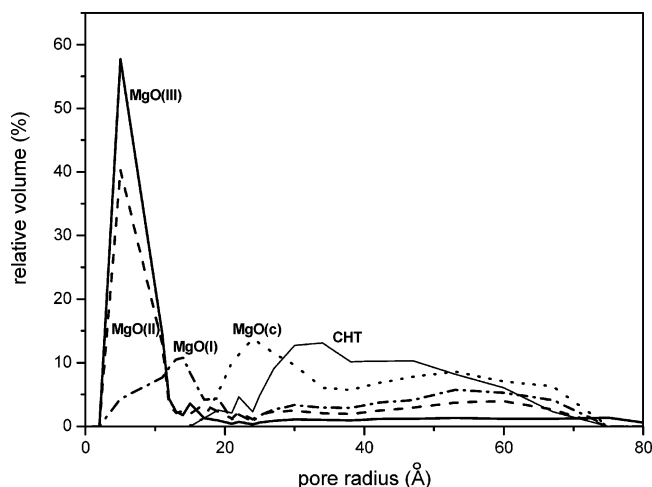
From the data reported in Table 2, it can be observed that CHT and MgO(I) have approximately the same surface area, whereas MgO(II) and MgO(III) that were obtained by calcination of two different precursors, at 400 °C instead of 500 °C, have higher surface area. At last, the commercial magnesium oxide MgO(c) has the lowest surface area.

CHT shows the greatest value of pore volume and MgO(c) gives the lowest value. A large portion of the pores of magnesium oxides with the higher surface area (MgO(II) and MgO(III)) are micropores, whereas, for MgO(c), MgO(I), and CHT, we have a preeminence of mesopores (see Figure 1).

In the X-ray diffraction (XRD) patterns of the CHT only the presence of an MgO-like phase has been observed.[22] The average crystallite size was determined using the XRD signal width, and we can see from the data reported in Table 2 that smaller crystallites are favored by the aluminum content in the CHT sample, with respect to magnesium oxide obtained under the same conditions (MgO(I)), in agreement with data reported by Di Cosimo et al.[20] MgO(c) and MgO(II) have crystallites of similar size, whereas MgO(III) has a higher dispersion.

CO_2-TPD profiles for all the tested catalysts of Table 2 are shown in Figure 2. The complex desorption profiles, reported in Figure 2, are due to the presence of basic sites of different strengths. In particular, all solids show a desorption peak at temperatures of ~100 °C, which can be attributed to the interaction of CO_2 with sites of weak basic strengths.[20−22] It has been proposed in the literature that these sites correspond to OH⁻ groups on the surface (see Bolognini et al.[21] and references therein). This peak, which is observed for all the examined solids, is the only one present on the γ-alumina surface.

A second desorption peak, which appears at higher temperatures (~200 °C), that is predominant for the MgO samples

can be attributed to basic sites of medium strength related to oxygen in both Mg^{2+}−O^{2-} and Al^{3+}−O^{2-} pairs. Some of the magnesium oxides and the CHT both show another desorption peak at a higher temperature range that can be attributed to stronger basic sites corresponding to isolated O^{2-} anions (250−300 °C). Finally, only the CHT and MgO(III) samples show a broad desorption area at temperatures of >350 °C. These very high desorption temperatures could be due to the presence of much stronger basic sites (superbasic), probably corresponding always to isolated O^{2-} but located in a particular position of the surface.

The specific and intrinsic basicity calculated for all the tested solids are reported in Table 2. It is interesting to observe that the intrinsic basicity increases as the MgO surface area decreases,[16,25] in agreement with previous results reported in the literature. The previous results clearly show that the textural properties of the MgO solid surfaces are affected by both the precursors and the preparation procedure, and this is in agreement with the findings of other authors.[25−27] These differences in textural properties strongly affect the catalytic performances as it will be seen in the next session.

3.2. Transesterification Reaction. All the catalysts reported in Table 2 have been tested, first of all, in the transesterification of a soybean oil (FFA concentration of 0.1% w/w), at 100 °C, and the obtained yields with the related operative conditions are reported in Figure 3.

As can be seen, CHT and MgO(III) are the most active catalysts at this temperature, whereas the other MgO catalysts

Figure 1. Pore volumes distribution for the catalysts reported in Table 2.
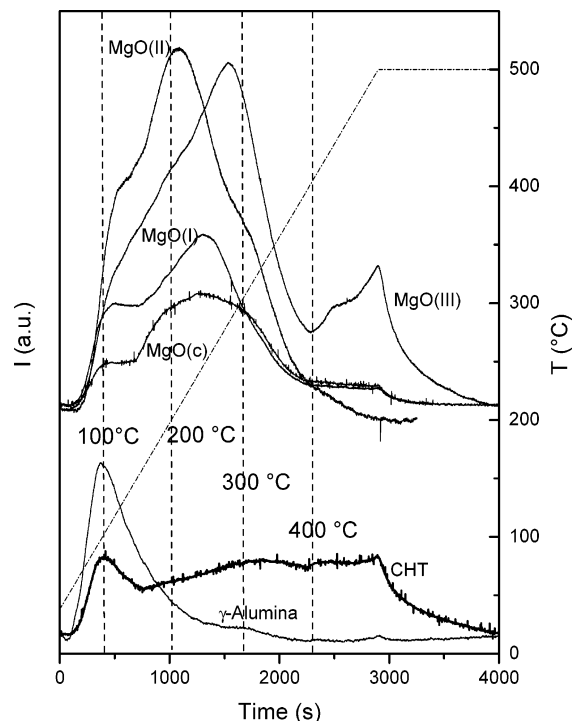
Figure 2. Temperature-programmed desorption of carbon dioxide (CO_2-TPD) profiles of the different proven catalysts.
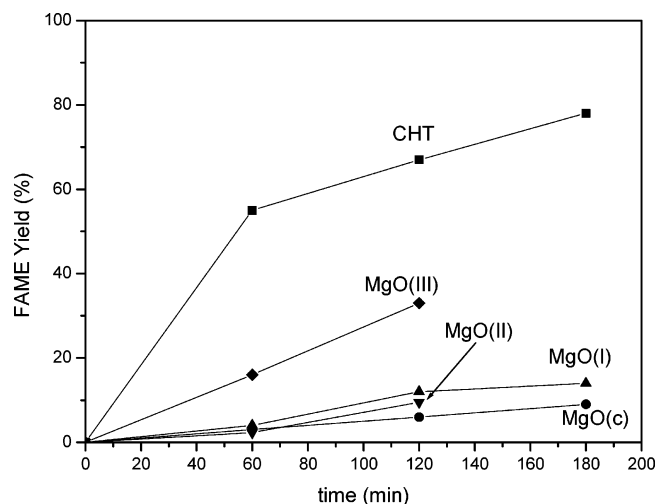
Figure 3. Yields of obtained biodiesel as a function of the reaction time in transesterification of soybean oil with methanol using the catalysts reported in Table 2. Reaction conditions: $T = 100$ °C, 2.0 g of oil, 0.44 g of methanol, and 0.2 g of catalyst.

Figure 4. Yields of obtained biodiesel in transesterification of soybean oil with methanol using the catalysts reported in Table 2 for a reaction time of 1 h. Reaction conditions: $T = 180$ °C, 2.0 g of oil, 0.88 g of methanol, 0.1 g of catalyst, and a reaction time of 60 min.

Figure 5. Yields of obtained biodiesel in transesterification of soybean oil with methanol using the catalysts reported in Table 2 for a reaction time of 1 h. Reaction conditions: $T = 200$ °C, 2.0 g of oil, 0.88 g of methanol, 0.1 g of catalyst, and a reaction time of 60 min.
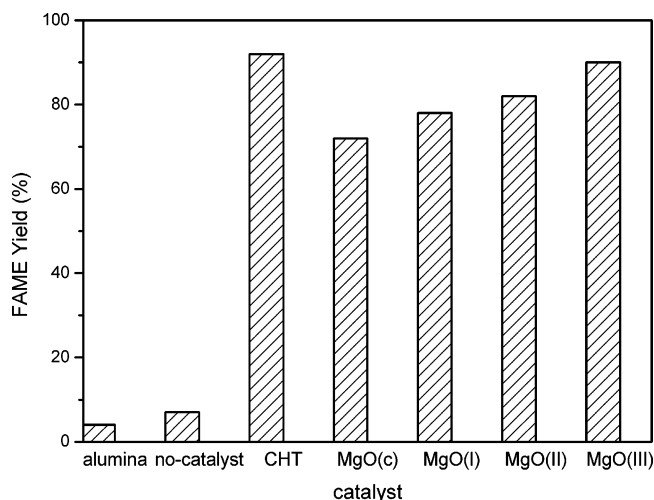
have very low performances, in agreement with the data of both Cantrell et al.[12] and Gryglewicz,[29] who reported low or no activity using MgO in transesterification reactions performed at 60 °C. The greater activity of MgO(III), with respect to other MgO catalysts, can be justified by the presence on this solid of a higher concentration of very strong basic sites (super-basic sites, that is, those desorbing CO_2 at temperatures of >350 °C). On the other hand, although calcined CHT has a comparable concentration of these basic sites (see Figure 2), its activity is higher than that of MgO(III). The higher activity of CHT, compared to MgO(III), can be explained by considering the physical structure of the two catalysts. As a matter of fact, very narrow micropores are predominant in MgO(III) catalysts (radius of <10 Å), while CHT has pores of greater radius (≫20 Å). The presence of large pores in the CHT favors the reaction by rendering the active sites more accessible to the bulky triglyceride molecules.

The catalysts also have been tested at 180 °C, i.e., a temperature level normally adopted for acid catalysts.[4,5] At such very high temperatures, an uncatalyzed reaction contribution could be operative, or the internal stainless steel surface of the vials can catalyze the reaction,[28] therefore, a run has also been performed in the absence of the catalyst. All the obtained results for the reaction activities with the related operative conditions are reported in Figure 4.

As can be seen, γ-Al_2O_3 shows negligible catalytic activity in the transesterification reaction also at such high temperatures, whereas CHT, and all MgO catalysts, give high FAME yields. Therefore, we can conclude that, while at 100 °C, only the strongest basic site are involved, at 180 °C, the sites of medium strength are also operative. CHT and MgO(III) show similar activities at this temperature, because the effect of the narrower size of the pores of MgO(III) is balanced by its higher specific basicity, with respect to CHT.

The product distribution in the esteric phase for the run performed at 180 °C in the presence of CHT, determined by GC analysis, resulted as follows: methylesters, 95.5% w/w; glycerol, 0.4% w/w; and nonidentified compounds, 0.6% w/w.

By observing the data reported in Figure 4, the FAME yields obtained using different MgO catalysts approximately increase as the specific basicity of the catalysts increases. But again, this parameter is not the only one to be considered. As a matter
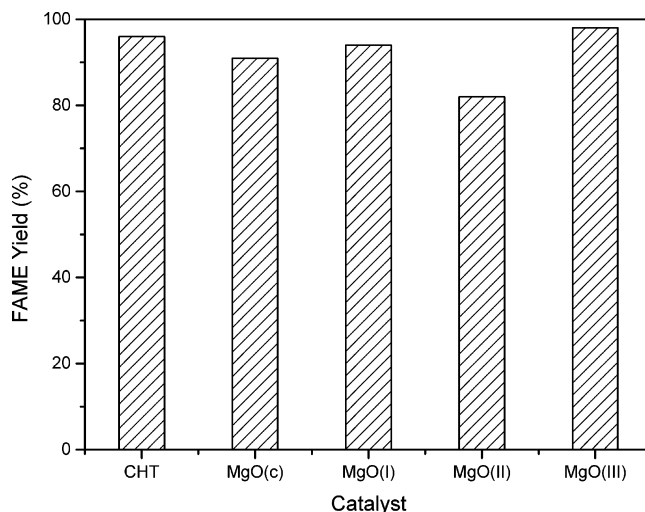
of fact, the difference in the yields can also be affected by the physical structure of the catalysts. MgO(I), for example, has a much lower specific basicity than MgO(II) (see Table 2) but the obtained conversions are comparable. However, MgO(I) has a much more favorable pore distribution (see Figure 1).

The influence of porosity (and of pore size distribution) becomes much more visible by observing the data collected in the runs performed at 200 °C and reported in Figure 5. By increasing the temperature, the reaction rate obviously increases and, after 60 min of reaction, all the catalysts, except MgO(II), give FAME yields of >90%. The activity of MgO(II) is less than the activities of MgO(c) and MgO(I), despite its higher specific basicity (see Table 2). This result can be explained by considering that the greater mean size of the pores of MgO(c) and MgO(I), compared to MgO(II) (see Figure 1), which make the sites more accessible and, therefore, makes the catalyst more active.

As mentioned previously, one of the best catalysts (CHT) has also been tested in an autoclave of 1 L, using 250 g of soybean oil, 114 g of methanol and 2.5 g of CHT catalyst. The autoclave was heated to 215−225 °C. The yields obtained at
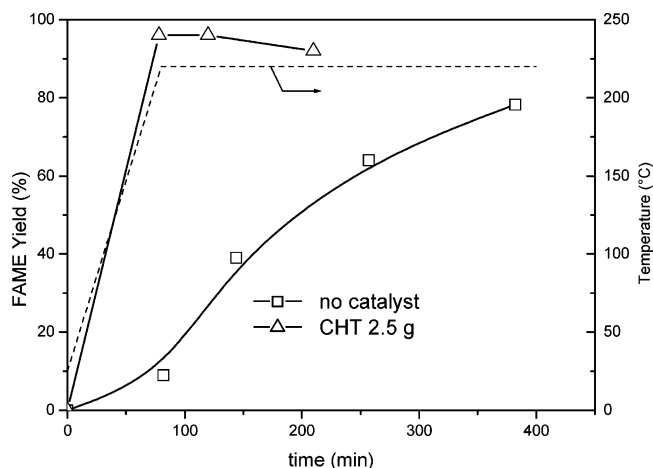
Figure 6. Yields obtained for different reaction times in the soybean oil transesterification with methanol performed in an autoclave, respectively, in the presence of CHT catalyst and in the absence of catalyst. Conditions: 250 g of oil and 114 g of methanol.

Table 3. Influence of Water on the Performance of MgO(I) and CHT Catalysts[a]

water content (ppm)	biodiesel yield (%)
MgO(I) Catalyst	
0	78
10000	77
CHT Catalyst	
0	92
10000	92

[a] Reaction conditions: $T = 180$ °C, 2.0 g of oil, 0.88 g of methanol, 0.1 g of catalyst, and a reaction time of 60 min.

different reaction times are reported in Figure 6. The same figure also reports data obtained in a run performed under the same conditions but in the absence of a catalyst.

As can be seen, the catalytic effect of CHT is very high, considering the very low catalyst concentration (ratio of catalyst/oil = 0.01 by weight). The reaction products were cooled and discharged, and the catalyst was filtered and recovered. After methanol distillation, the two resulting liquid phases (glycerol and esteric phase) were easily separated by settling.

The esteric phase then was analyzed by GC, and the following results were obtained: methylesters, 94.0% w/w; monoglycerides, 4.2% w/w; diglycerides, 0.9% w/w; triglycerides, 0% w/w; gs, glycerol 0.3% w/w; and nonidentified products 0.6% w/w. Also, in this case, the analysis shows good selectivity of the CHT catalyst with a low concentration of diglycerides (<1%) and an absence of triglycerides.

Because vegetable oils, animal fats, and alcohols usually contain water,[11] the influence of the presence of water on MgO-(I) and CHT performances has also been investigated in the present work. It is well-known, in fact, that the presence of water can affect the performances of many heterogeneous catalysts. For example, the activity of the catalyst used in IFP technology is strongly reduced by the presence of water and a water concentration of <1000−1500 ppm must be used.[30]

To test the effect of water in the transesterification of soybean oil with methanol, some runs have been performed at 180 °C in the presence of high water concentration (10 000 ppm). The obtained results, reported in Table 3, show that the activity of both magnesium oxide and calcined hydrotalcite is not affected by the presence of an excess of water. This open the possibility to use not refined bio-ethanol as a transesterification reagent.[18]

3. Conclusions

As has been seen, two different activity levels can be observed for all the tested catalysts: one at 100 °C, for calcined hydrotalcite (CHT) and MgO(III), and another one that gives high performances at temperatures of >180 °C for all the other basic catalysts. It is reasonable to assume that super-basic sites observed in the TPD runs (i.e., basic sites that desorb CO_2 at a temperature of $T > 350$ °C) are responsible for the catalytic activity observed at 100 °C, whereas, at higher temperatures, the basic sites of medium strength are also involved.

However, in both cases, we observed differences in the catalytic activity also as a consequence of the textural properties of the proven catalysts. In particular, mesoporous catalysts are more active than catalysts containing many micropores for the difficulty of the bulky triglyceride molecules to reach the basic catalytic sites inside the micropores.

Finally, both CHT and MgO catalysts are poorly affected by the presence of water. This last finding is relevant from the economic point of view, because, to operate in an imperfectly dried reaction environment reduces the raw material pretreatment costs and open the possibility to use not refined bio-ethanol.

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