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Lewis and Brönsted basic active sites on solid catalysts and their role in the synthesis of monoglycerides

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Abstract

Solid Brönsted base catalysts show higher activity and much higher specific rate than reported Lewis basic hydrotalcite catalyst for transesterification of oleic acid methyl ester with glycerol. The selectivity of the former for monoglycerides is higher because of the lower deactivation of the catalyst, which allows the transesterification of diglycerides to occur at longer reaction times. Calcined Li–Al hydrotalcites give higher activity than MgO or Al–Mg hydrotalcites because of the stronger Lewis basicity of the former. All of the solid Lewis basic catalysts have the same selectivity to monoglyceride regardless of the base strength, a selectivity lower than that of Brönsted basic solid catalysts.

Keywords: Hydrotalcite; Glycerolysis: Lewis and Brönsted sites; Solid catalyst; Regeneration

1. Introduction

In the last decade, renewable raw materials have become very important in the search for a sustainable chemistry. Vegetable oils and fats are the largest source of renewable raw materials used in the chemical industry. The most important benefits from oleochemicals are their biodegradability and nontoxic character, which allow the preparation of environmentally friendly surfactants. More specifically, the fatty acid monoesters of glycerol are valuable compounds with wide applications as emulsifiers in food, pharmaceutics, and cosmetics [1–3]. There are two main synthetic routes for obtaining monoglycerides: direct esterification of glycerol with fatty acids and transesterification of glycerol with triglycerides or fatty acid methyl esters. In both routes the commercial processes use homogeneous catalysts. For the first route, an acid catalyst (e.g., sulfuric, phosphoric, or organic sulfonic acid) is required [4,5], whereas the transesterification process involves a base-catalyzed reaction with a strong base such as KOH or $Ca(OH)_2$ and high temperatures [6]. These industrial processes lead to a mixture of mono-, di-, and tri-esters with monoglyceride content of 40–60%, and a molecular distillation is necessary to obtain greater (∼80%) monoglyceride enrichment. A drawback associated with using homogeneous catalysts is the need for a neutralization step with the formation of soaps and a high salt content. Alternative methods for the preparation of monoglycerides include the enzymatic alcoholysis of triglycerides [7] and the enzymatic esterification of glycerol and fatty acids [8]. The drawbacks of the enzymatic methods are low space velocity and a relatively complex workup of the reaction mixture.

Glycerolysis of fatty methyl esters is an interesting route for monoglyceride synthesis. Using methyl esters instead of the corresponding fatty acids and glycerol in the preparation of monoglycerides has several advantages. For instance, methyl esters that are prepared from fats by energy-preserving fat methanolysis reactions are easily purified and less corrosive. Furthermore, glycerolysis of fatty acids occurs more rapidly than esterification of fatty acids with glyc-

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erol [9]. In addition, because of the lower hydrophobic character, fatty acid methyl esters exhibit higher miscibility with glycerol, and the process can be carried out at lower temperatures (between 393 and 503 K) than required for transesterification of fats (533 K).

The substitution of homogeneous catalysts by heterogeneous catalysts not only offers advantages in process design (i.e., easy separation of the products from the catalyst, avoiding neutralization and extraction steps, reducing the waste formation, and recycle of the catalyst), but also may improve yield and selectivity to the desired product by designing a specific solid catalyst for the particular process. In this respect, Barrault el al. [10–12] showed that basic solid catalysts such as MgO, CeO_2, and La_2O_3, as well as alkali-doped MgO (Li/MgO and Na/MgO), were active catalysts for the transesterification of methylstearate with glycerol. These authors noted that in this process, the nature of the oxide has a small effect on monoester selectivity, and that the distribution of the esters obtained was similar to that obtained with homogeneous basic catalysts.

Hydrotalcites and hydrotalcite-like compounds are layered double hydroxides (LDHs), which have the general molecular formula $M_x^{2+}M_y^{3+}(OH)_{2(x+y)}A_{y/n}^{n-}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively, and A^{n-} is an intercalated anion. Structurally, these have brucite-like $[Mg(OH)_2]$ sheets where isomorphous substitution of Mg^{2+} by a trivalent cation like Al^{3+}, occurs. The resulting excess of positive charge in the layered network is compensated for by anions, which occupy the interlayer space along with water molecules [13]. Through controlled thermal decomposition, LDHs are converted to mixed oxides with high specific surface areas and strong Lewis basic sites. In particular, calcined Al–Mg hydrotalcites with different Al/Mg ratios have been used for the glycerolysis of triolein and rapeseed oil [14].

It has been recently reported that the catalytic activity of calcined hydrotalcites can be enhanced by rehydration at room temperature under exclusion of CO_2 [15]. This treatment results in restoration of the original layered structure, with OH^- as the compensating anions in the interlayer. This material is very active in catalyzing the self-condensation of acetone yielding diacetone alcohol [16], the condensation of benzaldehyde with acetone at 273 K [15,17], aldol condensations of citral with acetone [18,19] and ethyl methyl ketone [20], Knoevenagel condensations [21], cross-aldol condensation of aldehydes [22], and Michael additions [23].

It is clear that with rehydrated hydrotalcites, strong Brönsted basic sites are now available whose activity could be comparable with that of the homogeneous catalysts. We report on this here. However, suitable transesterification catalysts also could be prepared by synthesizing solid Lewis bases with a basicity stronger than that of conventional Mg–Al hydrotalcites. We have done this by preparing a crystalline Al–Li hydrotalcite. In this material, Li can occupy octahedral positions in the structure, which may result in increased hydrotalcite basicity. Calcination of the structure is expected to give the corresponding mixed oxides where Li will be highly dispersed in the form of Li_2O.

2. Experimental

2.1. Materials

Glycerol (99.5%) and methyl oleate (MeO) (90%) were purchased from Aldrich and used without further purification. The solvents, acetone, isopropyl alcohol, hexane, and ethanol of HPLC grade, were purchased from Merck.

Al–Mg hydrotalcite was prepared from a gel produced by mixing two solutions, A and B. Solution A contains $(3-x)$ mol of $Mg(NO_3)_2\cdot 6H_2O$ and x mol of $Al(NO_3)_3\cdot 9H_2O$ in the (Al + Mg) concentration of 1.5 mol/l for an Al/(Al + Mg) ratio of 0.20. Solution B is formed by $(6+x)$ mol of NaOH and 2 mol of Na_2CO_3 dissolved in the same volume as in solution A. Both solutions were co-added at a rate of 1 ml/min under vigorous mechanical stirring at room temperature. The suspension was left for 12 h at 333 K. The hydrotalcite was filtered and washed until it reached a pH 7, and the solids were dried at 333 K.

The Al–Li layered double-hydroxy carbonate ($[Al_2Li(OH)_6]_2CO_3\cdot nH_2O$) with a Al/(Al + Li) molar ratio of 0.33 was prepared as described previously [24]. A hexane solution of aluminum-tri-(*sec*-butoxide) (17 wt%) was added dropwise to a lithium carbonate aqueous solution (0.55 wt%) under vigorous mechanical stirring at room temperature. The suspension was left for 24 h at 333 K. The Al–Li hydrotalcite was filtered and washed until it reached a pH 7, and the solid was dried at 333 K.

The hydrotalcites were activated by heating at 723 K in a dry flow of N_2. The temperature was raised at a rate of 2°/min to 723 K and maintained for 8 h. The solid was then cooled to room temperature in N_2.

Rehydrated Al–Mg calcined hydrotalcites (HTr) were prepared at room temperature under a flow of nitrogen (40 ml/min) saturated with water vapor, free of CO_2, during different times. Analyses of Mg and Al were performed using atomic absorption.

The MgO sample was prepared by thermal decomposition of magnesium oxalate at 873 K in vacuum for 6 h [25]. A 40 wt% KF impregnated on alumina was obtained from Aldrich. The main characteristics of the catalysts are summarized in Table 1.

X-Ray diffraction measurements were recorded with a Philips X'Pert (PN 3719) diffractometer (Cu-K_α radiation

Table 1
Main characteristics of the base catalysts

Catalyst	BET surface ($m^2 g^{-1}$)	Pore volume area ($cc\,g^{-1}$)
MgO	246	0.384
HTc	220	0.627
HTcLi	240	0.657
KF/Al_2O_3	14.8	–

provided by a graphite monochromator) equipped with an automatic variable divergence slit and working in the constant irradiated area mode.

N_2 and Ar adsorption/desorption isotherms were performed at 77 and 87 K, respectively, in an ASAP 2010 apparatus (Micromeritics) after pretreating the samples under vacuum at 673 K overnight and the (BET) surfaces were obtained using the BET methodology.

2.2. Reaction procedure

The transesterification reactions were performed in a glass batch reactor equipped with a condenser system. Glycerol, the fatty acid methyl ester, and catalyst (4 wt%) were mixed under stirring at 500 rpm and heated in a silicone bath to the required temperature in absence of solvent, under nitrogen atmosphere. A Dean–Stark instrument was adapted to the glass batch reactor to remove the methanol formed during the reaction. Samples were periodically taken out of the reactor and separated from the catalyst by filtration using pyridine as a solvent. The reaction products were converted to volatile trimethylsilylether derivatives with N,N-bis(trimethylsilyl)-trifluoroacetamide following a derivatization method described previously [26]. A known amount of tricaprin was added as an internal standard, and the products dissolved in hexane were analyzed by gas chromatography (GC). On completion of the reaction, the product was dissolved in isopropyl alcohol and filtered. The organic solution was evaporated in vacuum and submitted to extraction with hexane to separate the fatty products from the free glycerol. Finally, the hexane layer was evaporated in vacuum, and the extracted products were weighted and analyzed.

The GC analyses were performed with a Fisons Instruments GC 8000 gas chromatograph, equipped with an on-column injector, flame ionization detector, and 15 m × 0.32 mm × 0.25 µm fused silica capillary column (SGE HT5 aluminum-clad; SUPELCO). The analytical conditions were as follows: direct injection (splitless, hold for 1 min), on-column injector temperature 337 K; column initial temperature 433 K; first program rate 10°/min; final temperature 643 K, hold 7 min; detector temperature 643 K; carrier gas pressure 10 kPa.

The fatty methyl ester conversion to the different reaction products is given by the following equation:

$$\text{Molar conversion (\%)} = \frac{A_{\text{mono}}/rF_{\text{mono}} + 2A_{\text{di}}/rF_{\text{di}} + 3A_{\text{tri}}/rF_{\text{tri}}}{A_{\text{mono}}/rF_{\text{mono}} + 2A_{\text{di}}/rF_{\text{di}} + 3A_{\text{tri}}/rF_{\text{tri}} + A_{\text{ME}}/rF_{\text{ME}}} \times 100,$$

where A_{mono}, A_{di}, A_{tri}, and A_{ME} are the respective areas of the peaks corresponding to monoglycerides, diglycerides, triglycerides, and fatty acid methyl esters and rF are their respective response factors.

The selectivity to monoglycerides was calculated according the following equation:

$$\text{Selectivity to monoglycerides (\%)} = \frac{A_{\text{mono}}/rF_{\text{mono}}}{A_{\text{mono}}/rF_{\text{mono}} + 2A_{\text{di}}/rF_{\text{di}} + 3A_{\text{tri}}/rF_{\text{tri}}} \times 100.$$

3. Results and discussion

3.1. Transesterification of methyl oleate with glycerol using Al–Mg calcined-rehydrated hydrotalcite as a Brönsted base catalyst

Despite the fact that the transesterification of fatty acid methyl esters with glycerol is carried out industrially using Brönsted basic catalysts in the homogeneous phase, we have found that studies with solid catalysts have been carried out using Lewis basic catalysts [10,12]. It certainly will be of interest to see whether Brönsted solid bases can also selectively catalyze the transesterification reaction, and how they compare with analogous solid Lewis bases.

It has been shown that it is possible to generate Brönsted basic sites in a hydrotalcite, by rehydrating the mixed Al–Mg oxides obtained by previous calcination of a conventionally prepared hydrotalcite [15]. But for other reactions, such as aldol condensations [16,18,20,27] and cyanoethylation of alcohols [28], it has been shown that controlling the water on the catalyst in a calcined-rehydrated hydrotalcite is of paramount importance in achieving the optimum catalytic activity. In fact, excess water poisons the stronger basic sites, which may cause hydrolysis of the different esters yielding the corresponding fatty acids as byproducts. Thus, to optimize the amount of water on the catalyst surface, we prepared three calcined-rehydrated samples by contacting the calcined solid (an Al–Mg mixed oxide with an $\text{Al}/(\text{Al}+\text{Mg})$ molar ratio of 0.20) with a flow of N_2 saturated with decarbonated water during 12, 24, and 48 h, resulting in a total water content of 32, 38, and 67 wt%, respectively. The samples were labeled $\text{HTr}_{12\text{ h}}$, $\text{HTr}_{24\text{ h}}$, and $\text{HTr}_{48\text{ h}}$, respectively. Fig. 1 presents the X-ray diffraction patterns of hydrotalcites after synthesis, calcination, and rehydration. The figure shows that the layered crystalline structure of hydrotalcite disappears during calcination at 723 K and is converted to a mixed oxide of the Mg(Al)O type. The original layered structure is restored to a great extent by rehydration of the calcined solid, giving a meixnerite-like structure in which the weak base carbonate anions are replaced by strong Brönsted OH^- sites.

These different rehydrated hydrotalcites were tested in the transesterification of methyl oleate (MeO) with glycerol, using a glycerol:MeO molar ratio of 6:1 at 473 K in the absence of solvent. In the glycerolysis of fatty acid methyl esters, monoglycerides appear as the only primary products. Thus the glycerol and the fatty acid methyl ester react initially to yield a mixture of monoesters (1- and

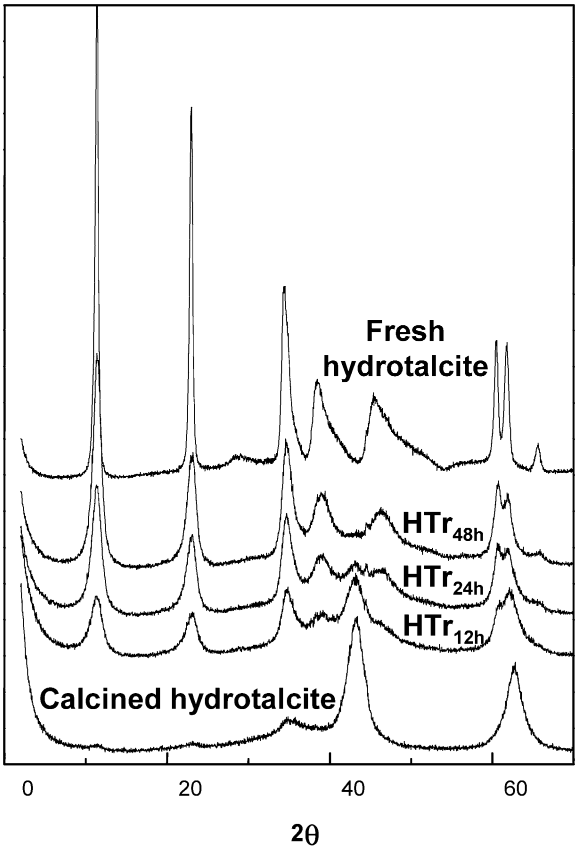
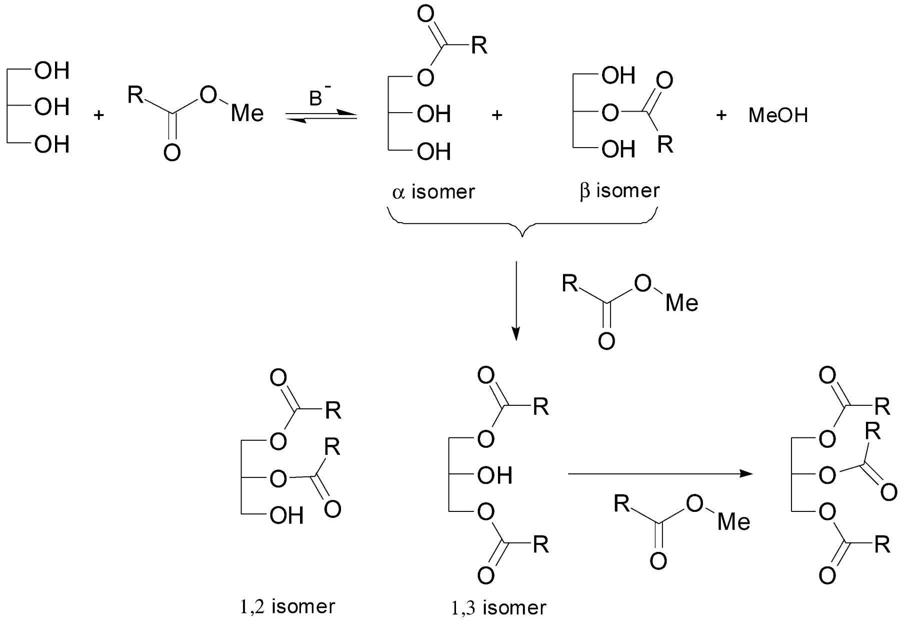


Fig. 1. XRD patterns of hydrotalcites after synthesis, calcination and rehydration.

2- or α and β monoglyceride isomers, respectively) plus methanol. But further transesterification of the monoesters with the fatty methyl ester and/or with the previously formed monoglycerides leads to the formation of diglycerides (1,2- and 1,3-isomers) and even triglyceride as secondary products (Scheme 1).

Fig. 2 illustrates the evolution of the reactant and products obtained at different reaction times using Lewis [calcined Al–Mg hydrotalcite (HTc)] and Brönsted base catalysts [calcined-rehydrated hydrotalcite $HTr_{12\,h}$)] samples are compared. It can be seen that the initial activity (i.e., initial rate for the disappearance of MeO) for the rehydrated sample is higher than that for the calcined HTc sample (BET = 220 m^2/g), despite the lower surface area (48 m^2/g) of the $HTr_{12\,h}$ sample. Comparing the selectivity to monoesters (Fig. 3) demonstrates that for conversions close to 100%, the $HTr_{12\,h}$ sample exhibits slightly higher selectivity than the calcined sample. As shown in Fig. 2, these results are due mainly to the ability of the rehydrated sample to catalyze the transesterification of the diglycerides when practically the total conversion of MeO is achieved, but also to the lower triester formation on this catalyst.

The increased transesterification rate in the rehydrated sample must be related to the presence of Brönsted basic sites in the restored hydrotalcite, which appear to be more active for the transesterification than the Lewis basic sites in the mixed oxides, as has been observed for other reactions [18,20,23,27,29,30]. Rao et al. [15] reported that both the number and strength of sites measured by adsorption of CO_2 decrease in the Al–Mg rehydrated sample outgassed at 373 K compared with the mixed oxide. Then, taking this into account, the larger initial activity observed for the Brönsted catalyst cannot be related with a higher basicity of the Brönsted sites, but was probably related to changes in the adsorption properties of these catalysts. Thus a favored adsorption of glycerol on the hydrophilic rehydrated catalyst surface improves the glycerolysis rate at the initial stage of the reaction. Furthermore, this different behavior with re-



Scheme 1.

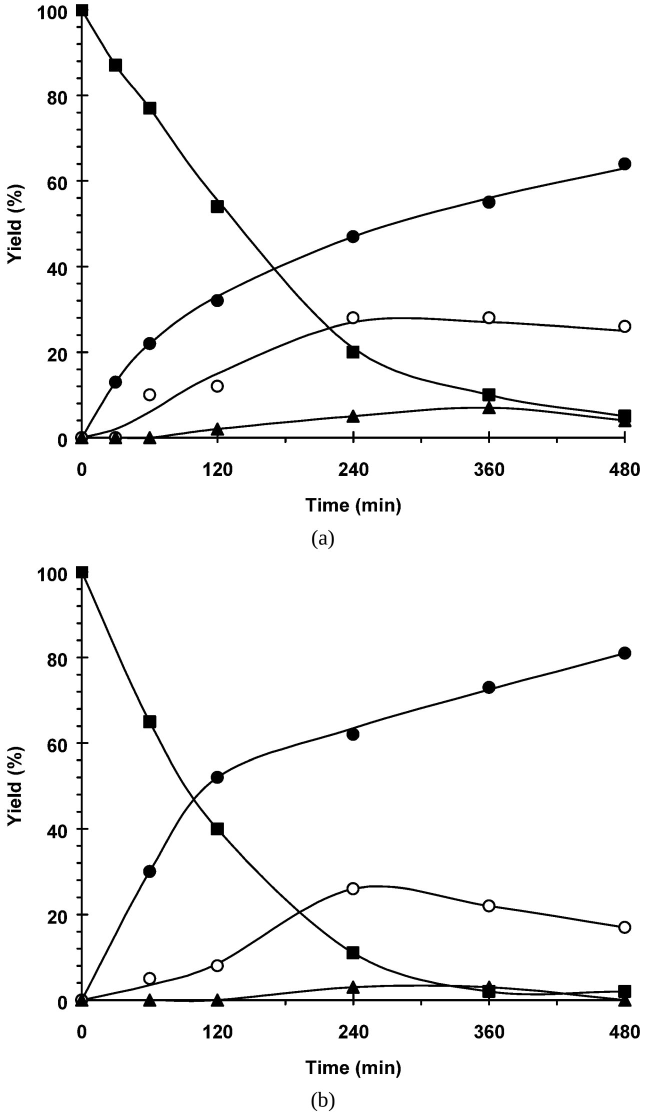


Fig. 2. Results of the transesterification of MeO (methyl oleate) with glycerol at 473 K using as base catalyst: (a) HTc; (b) $HTr_{12\,h}$, (■) MeO, (●) monoesters, (○) diesters, (▲) triester.

spect to activity and selectivity to monoesters also could be influenced by a lower deactivation rate of the rehydrated sample with respect to the calcined hydrotalcite. To check this possibility, the HTc and $HTr_{12\,h}$ samples used earlier in the reaction were separated from the reaction mixture, washed thoroughly with acetone and then with ethanol, and reused again as catalysts. Fig. 4 displays the kinetic behavior of reused samples and shows that HTc exhibits some higher deactivation rate than $HTr_{12\,h}$. The greater deactivation observed here may be responsible for the lower activity of the calcined sample in performing subsequent transesterification of the diglycerides formed during the reaction, and thus it is responsible for the slightly lower selectivity to monoesters achieved by the calcined material during its first cycle of reaction.

To study the influence of the water content in the rehydrated hydrotalcites, $HTr_{24\,h}$ (38 wt% of water) and $HT_{48\,h}$ (67 wt% of water), on catalytic behavior, samples were tested under the same reaction conditions as before. Oleic acid was not detected in any case, and the amount of triglyceride formed was very low and similar for the three samples (∼1%). Fig. 5 compares the activities for the conversion of MeO obtained with these rehydrated hydrotalcite samples. As can be seen, an increase in water content >32 wt% causes a decrease in catalytic activity, which may indicate that an excess of water can cause catalyst decay or active site inhibition. To test this possibility, used $HTr_{24\,h}$ and $HTr_{48\,h}$ samples were separated from the reaction mixture, washed with acetone and ethanol, and reused again. Fig. 6 shows that the catalytic activity of the reused HTr samples is the same regardless of the initial water content. However, the reused HTc sample exhibits lower catalytic activity, indicating that for calcined hydrotalcites, deactivation is more severe than for the rehydrated samples. Thermogravimetric studies were performed to estimate the relative amount of organic retained on the different samples (calcined and calcined-rehydrated hydrotalcites). We observed a weight loss of around 70 wt% for the HTc sample (calcined sample) and 60 wt% for the rehydrated materials. The loss of physically adsorbed and interlayer water molecules (at temperatures <473 K) was very similar for all samples (3%). The second weight loss (473–773 K) originates from dehydroxylation of the brucite-like sheets (which must be occurring in higher extent on the rehydrated samples) plus decomposition of organic material. Taking into account the greater weight loss of the calcined hydrotalcite, we can conclude that the higher amount of organic retained on this material is responsible for the higher deactivation rate observed. It is important to point out that the reused $HTr_{24\,h}$ and $HTr_{48\,h}$ samples exhibit higher catalytic activity than their corresponding fresh samples. This can be clearly observed in Fig. 7, which compares the catalytic activity of the reused $HTr_{48\,h}$ sample with

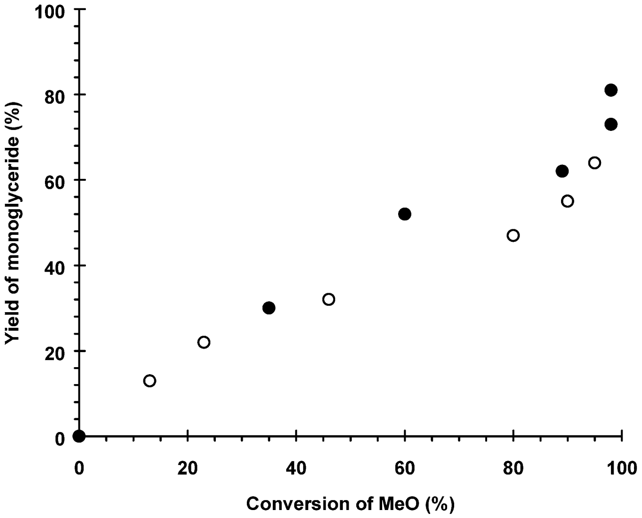
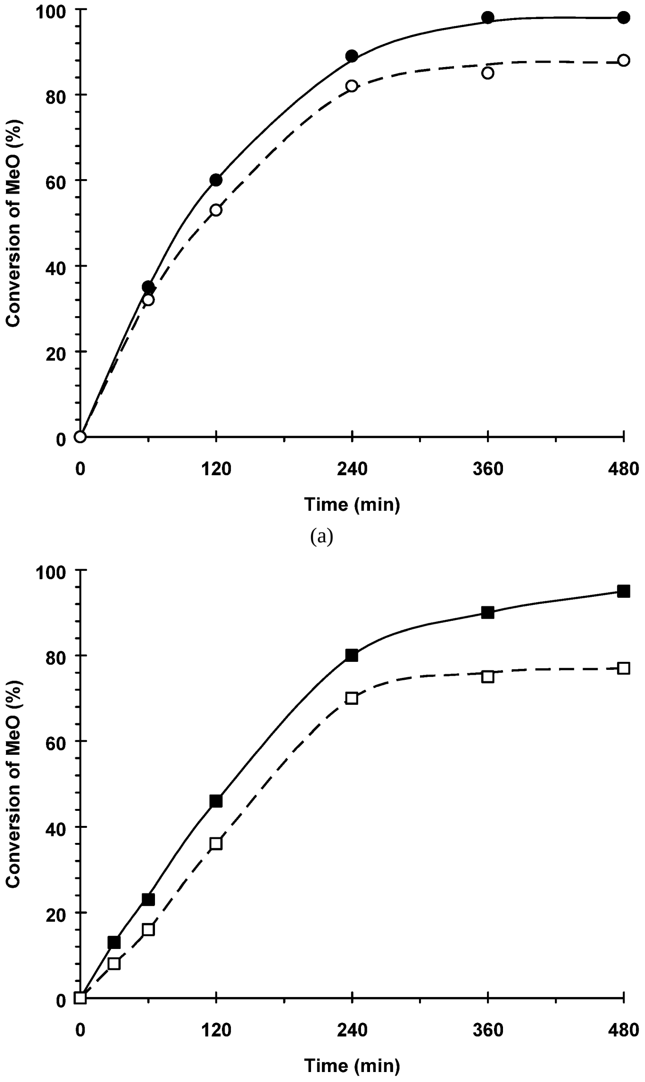


Fig. 3. Results of Yield of monoglycerides versus conversion of MeO (methyl oleate) obtained in the transesterification of MeO using: (●) $HTr_{12\,h}$ and (○) HTc as catalysts.



(a)

(b)

Fig. 4. Conversion of MeO (methyl oleate) versus reaction time plot (a) using $HTr_{12\ h}$ sample: (●) first cycle, (○) second cycle; (b) using HTc sample: (■) first cycle, (□) second cycle.

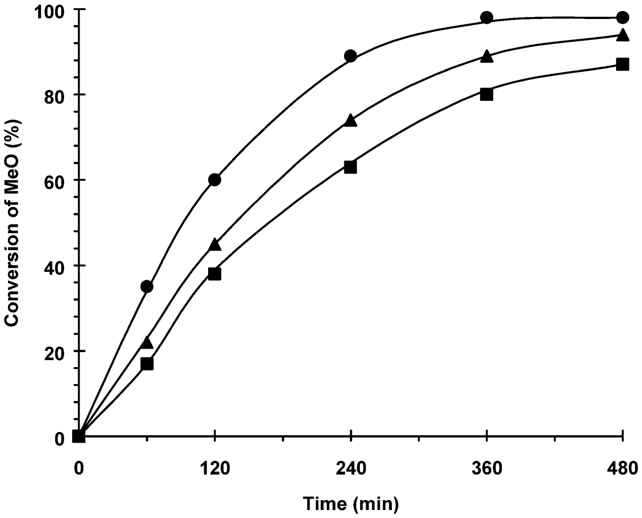


Fig. 5. Results of conversion of MeO (methyl oleate) versus reaction time obtained using HTr samples with different water contents: (●) $HTr_{12\ h}$, (▲) $HTr_{24\ h}$, (■) $HTr_{48\ h}$.

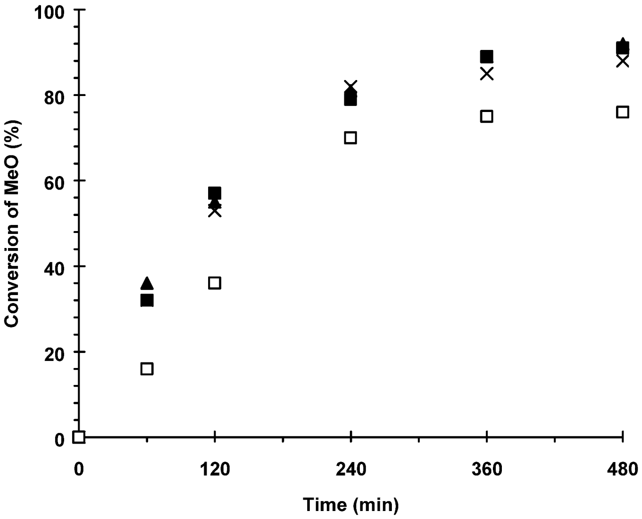


Fig. 6. Results of conversion of MeO (methyl oleate) versus reaction time obtained in the reuse (second cycle) of the HT samples: (×) $HTr_{12\ h}$, (▲) $HTr_{24\ h}$, (■) $HTr_{48\ h}$, (□) HTc.

the catalytic activity of this sample obtained during its first use. The results indicate that the catalyst decay observed for the samples with water content >32% should be due mainly to the excess water that can adsorb on active OH^- sites, decreasing their basicity. Thus it is not unreasonable to believe that the excess of the adsorbed water will be lost during the reaction, resulting in a catalyst surface with similar basicity-adsorption properties regardless of the initial water content. This assumption would agree with the fact that all of the reused HTr samples exhibit the same catalytic activity (Fig. 6). When rehydrated catalysts were reused in a third cycle, all catalysts displayed similar activities as in the second cycle.

From these results, we can conclude that at low conversion levels the mixed oxide and the rehydrated sample have similar selectivity to monoglycerides (see Fig. 3), but at high conversion levels the $HTr_{12\ h}$ sample has a slightly higher selectivity to monoglycerides. This behavior can be attributed mainly to the capability of the rehydrated sample to perform subsequent transesterification of the diglycerides remaining in the reaction mixture. This can be a consequence of their different adsorption properties as well as of their lower deactivation rate with respect to the calcined hydrotalcite. We have also shown that for the rehydrated samples there is an optimum water content that provides the optimum properties of basicity-adsorption of the catalyst surface, leading to maximum activity and selectivity to monoglycerides. Finally, rehydrated samples can be reused several times without loss of activity or selectivity.

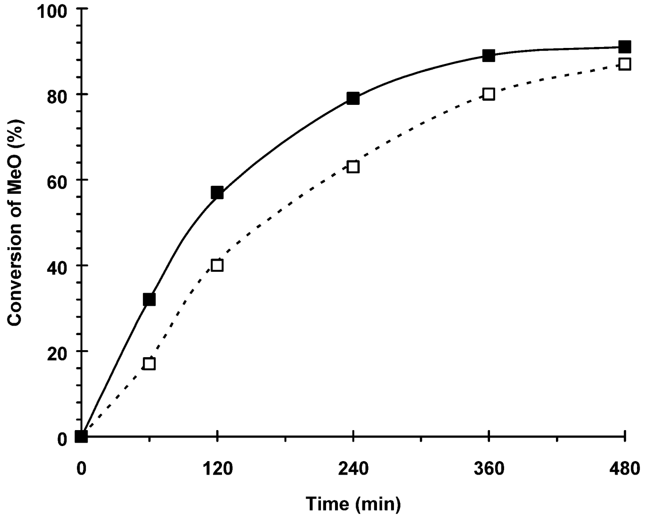


Fig. 7. Results of conversion of MeO (methyl oleate) versus reaction time obtained when the transesterification is carried out using $HTr_{48\,h}$: (□) first cycle, (■) second cycle.

3.2. Transesterification of methyl oleate using strong Lewis basic catalysts

We have shown that controlled rehydration of the calcined Al–Mg hydrotalcite notably enhances the catalytic activity of the corresponding Al–Mg mixed oxide for the transesterification of methyl oleate with glycerol. However, it clearly should be possible to increase the catalytic activity of the mixed oxide by increasing the intrinsic Lewis basic strength of the sites. The global basicity of the mixed oxide can be modified by changing its chemical composition. Thus we must expect that in a hydrotalcite, when Mg^{2+} is substituted with a more electropositive ion, such as Li^+, the negative charge density on the oxygen will increase, leading to increased basicity of the resulting mixed oxide. To check this, we synthesized an Al–Li mixed oxide with an $Al/(Al+Li)$ molar ratio of 0.33 and compared its activity for the glycerolysis of methyl oleate with that of Al–Mg mixed oxide and other strong Lewis solid base catalysts, such as MgO and KF on alumina (Fig. 8).

As can be seen from this figure, the order of activity for the Lewis catalysts is KF/alumina > HTcLi > MgO > HTc. This order should be related to the different global basicity of these materials. Thus KF/alumina exhibits the highest basic character, whereas the Al–Li mixed oxide performs transesterification more efficiently than the Al–Mg mixed oxide. But MgO, which has a higher concentration of basic sites than Al–Mg mixed oxide although of lower basic strength, exhibits high activity for this process. For comparison purposes, Fig. 8 also shows the kinetic behavior of the $HTr_{12\,h}$. As can be seen, this catalyst gives lower conversion than the Lewis base HTcLi and much lower than the KF/alumina catalyst. Table 2 gives the yields and selectivity to monoglycerides obtained working at 473 K after a 6-h reaction time on the different catalysts. This table shows that all Lewis base catalysts exhibit similar selectivities, indicating that selectivity depends on conversion and not on the nature of the Lewis basic catalyst. These results are in good agreement with those reported by Barrault et al. [10] for the glycerolysis of methyl stearate using metallic oxides as a base catalyst. However, the Brönsted base catalyst obtained by rehydrating a calcined hydrotalcite, although less active than HTcLi or KF/alumina, gives a higher selectivity to monoesters.

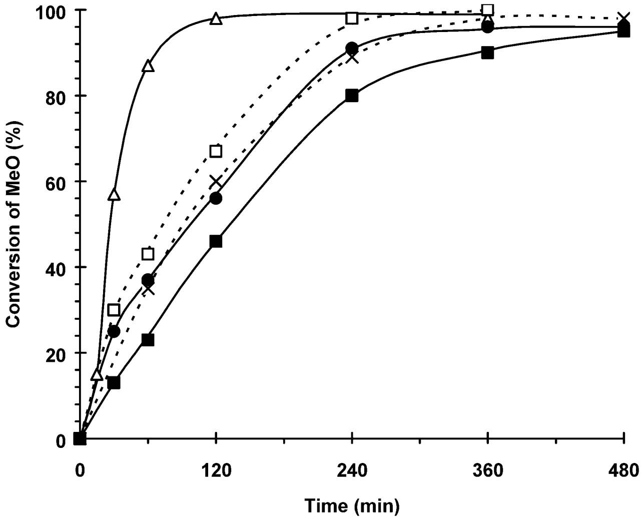


Fig. 8. Results of conversion of MeO (methyl oleate) versus reaction time obtained when the transesterification is carried out using Lewis base catalysts: (△) KF/Alumina, (□) HTcLi, (●) MgO, (×) $HTr_{12\,h}$, (■) HTc.

Table 2
Transesterification of methyloleate using different basic catalysts[a]

Catalysts	MeO conversion (%)	Yield[a] (%)			Selectivity to monoesters (%)
		Monoester	Diester	Triester	
$HTr_{12\,h}$	98 (8 h)	80	17	1	80
HTc	95 (8 h)	64	27	4	67
HTcLi	98 (4 h)	69	27	2	70
MgO	96 (6 h)	70	25	1	73
KF/Al_2O_3	98 (2 h)	68	28	2	69

[a] Reaction conditions: molar ratio glycerol/MeO = 6; 4 wt% of catalyst at 473 K.

Finally, we explored the transesterification of palmitic and lauric acid methyl esters (saturated acids with 12 and 16 carbon atoms, respectively) with glycerol and we found that the reactions with these esters are more facile than the one reported in this work.

4. Conclusions

Rehydrated Al–Mg mixed oxides that exhibit Brönsted basic sites are effective catalysts for the transesterification of fatty acid methyl esters with glycerol, giving excellent selectivity to monoglycerides. This selectivity is higher than that obtained with a large variety of solid Lewis base catalysts. The higher monoester selectivity achieved with the rehydrated hydrotalcite sample is due mainly to this catalyst's ability to perform the subsequent transesterification of the diglycerides formed during the reaction. This can be a consequence of different adsorption characteristics of the mixed oxides derived from hydrotalcites and the rehydrated samples, as well as the lower deactivation rate of the rehydrated sample. In contrast, Al–Li mixed oxide resulted in an active Lewis base catalyst with better performance that MgO and HTc. Thus we can conclude that Al–Li mixed oxide and rehydrated Al–Mg mixed oxides appear to be promising catalysts for such reactions and could replace homogeneous catalysts, avoiding the formation of wastes and washing steps entailed in the usual process that uses homogeneous catalysts such as alkaline hydroxides.

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