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Catalysts for the Production of Fine Chemicals

Production of Food Emulsifiers, Monoglycerides, by Glycerolysis of Fats with Solid Base Catalysts

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Glycerolysis of triolein and rapeseed oil were carried out with base catalysts such as Cs-MCM-41, Cs-Sepiolite, MgO, and calcined hydrotalcites with different Al/Al + Mg ratios. A wide range of basicities were covered in order to extract active hydrogens with pKa values from 9 to 16. MgO and hydrotalcites with low Al content, basic enough to extract protons from aliphatic alcohols such as glycerol, are active and selective catalysts for glycerolysis. By optimizing the main process variables, such as temperature and the glycerol/oil ratio it is possible to obtain a high yield of monoglycerides as well as to meet the quality requirements established by the European Union.

INTRODUCTION

Food emulsifiers are indispensable ingredients in most processed food containing fats and oils. Edible and surface active monoesters and diesters of fatty acids and glycerol are the major emulsifiers used in food products as well as in the pharmaceutical and cosmetic industries (1–4).

The two most important industrial processes for the preparation of mono- and diglycerides are the glycerolysis of animal and vegetable fats or oils and the direct esterification of fatty acids and glycerol. The former method represents a special case of the transesterification reaction which has been studied extensively (5–8); several patents exist for commercial processes (9–13). Glycerolysis involves a reaction between oil or fat and glycerol at high temperatures in the presence of a basic catalyst. Industrial glycerolysis was carried out at temperatures above 473 K, with NaOH or KOH as the catalysts. In the case of monoglycerides used in the food industry, hydrated lime, $Ca(OH)_2$, is preferred because of a low color development in the final product.

When the reaction is finished the catalysts must be neutralized to prevent the reversion of the reaction, which can occur to an extent of about 30%, and also to avoid undesirable characteristics of the final mixture such as a soapy taste, unstable color, and foaming due to the presence of the catalyst. Thus, at the end of the reaction, phosphoric acid is usually added to the system to neutralize the catalyst. Thereafter, the products are filtered onto clays, and even when a large amount of solvent is used, a considerable proportion of fatty monoglycerides remains adsorbed on the clay. Moreover, undesirable by-products are formed during the neutralization of the hydrated lime, thus making the filtering problematic (14).

This paper describes the preparation of monoglycerides by transesterification in the presence of heterogeneous basic catalysts such as Sepiolite-Na–Cs, MCM-41-Cs, high surface area MgO, and hydrotalcites. These catalysts are easy to separate from the reaction media by filtering, avoiding the formation of by-products and the neutralization step. The influence of the basic strength of the catalysts and the reaction conditions were studied; it is shown that MgO and hydrotalcites are potential catalysts for the production of monoglycerides by transesterification between glycerol and triglycerides.

EXPERIMENTAL

Materials

A series of solid catalysts with different basicities, i.e., Na–Cs sepiolite MCM-41-Cs, MgO, and Al–Mg hydrotalcites, were prepared as catalysts, by means of the following procedures.

The sepiolite Na–Cs was prepared from a natural sepiolite of the "Vallecas" type (15). The sodium form of the sepiolite was exchanged using an aqueous solution of CsCl at room temperature. The final sepiolite, containing 1.7 wt% of Cs and 6.3 wt% of Na, both located in the channels of the sepiolite, was dried at 373 K for 16 h and calcined at 573 K.

The MCM-41-Cs was prepared starting with a MCM-41 with a Si/Al ratio of 13 and a pore diameter of 30 Å. The protons compensating the negative charge on the tricoordinated aluminiums were exchanged in a 1 M aqueous solution of CsCl at 353 K according to the procedure reported

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TABLE 1

Synthesis Composition of Hydrotalcites

Sample	Gel composition	Al/(Al + Mg)
HT1	$2.4Mg(NO_3)_2 : 0.6Al(NO_3)_3 : 2Na_2CO_3 : 6.6NaOH$	0.20
HT2	$2.25Mg(NO_3)_2 : 0.75Al(NO_3)_3 : 2Na_2CO_3 : 6.75NaOH$	0.25
HT3	$2.1Mg(NO_3)_2 : 0.9Al(NO_3)_3 : 2Na_2CO_3 : 6.9NaOH$	0.30
HT4	$2Mg(NO_3)_2 : 1Al(NO_3)_3 : 2Na_2CO_3 : 5NaOH$	0.33

in reference (16). The final MCM-41 contained 7.87 wt% of Cs.

Al–Mg hydrotalcites were prepared from the gel produced by mixing two solutions: A, containing $Mg(NO_3)_2$ and $Al(NO_3)_3$ 1.5 M in Al + Mg, with Al/(Al + Mg) atomic ratios equal to 0.20, 0.25, 0.30, and 0.33 (Table 1); B, prepared by dissolving Na_2CO_3 and NaOH to achieve a Na_2CO_3 concentration equal to 1 M at 60 $ml \cdot h^{-1}$ addition rate for 4 h under vigorous stirring. The concentration of NaOH was adjusted to obtain $pH = 13$ (Table 1). The gels were aged at 473 K for 18 h and then filtered and washed to $pH = 7$. After drying the solids at 353 K for 12 h, the hydrotalcites were calcined at 723 K in air in order to obtain mixed Mg–Al oxides (17). The surface areas of these oxides are presented in Table 2.

The preparation of the magnesium oxide was based on a slight modification of the method described by Putanov *et al.* (18) to obtain a high surface magnesium oxide (Table 2). The MgO was obtained by calcination of a magnesium oxalate at 973 K for 3 h. The magnesium oxalate was prepared at 313 K by adding a solution of oxalic acid (2 M) to a magnesium acetate solution (2.5 M). Before calcination, the magnesium oxalate was filtered, washed, and dried overnight at 353 K.

The crystal sizes, the volume, and diameter pore sizes of the catalyts presented above are given in Table 2.

TABLE 2

Compositions, Surface Areas, Mesoporous Volumes, and Particle and Diameter Pore Sizes of the Basic Catalysts

Catalysts	Surface (m^2/g)[a]	Al/(Al + Mg)	Pore volume (cc/g)	Diameter pore size[b] (Å)	Particle size (μm)
Sepiolite-Cs	160	—	0.27	20	5–10
MCM-41-Cs	830	—	0.53	37	>0.1
MgO	200	0	0.61	122	—
HT-1	211	0.20	0.84	160	≈0.4
HT-2	251	0.25	0.87	138	<0.5
HT-3	262	0.30	0.83	126	0.4
HT-4	246	0.33	0.66	107	0.4

[a] Determined by N_2 physisorption and following the BET procedure.
[b] Average pore diameter calculated by BET.

Glycerine (Aldrich) and tricaprin (Fluka) with a normal purity of 99%, were used without further purification. Triolein with a purity >99%, was obtained from Aldrich, and the rapeseed oil was kindly provided by Robbe S.A.

Analytical Methods

The elemental composition of the catalysts was analyzed by atomic absorption using a Varian Spectra A-10 plus apparatus. The surface area measurements were made on an ASAP-2000 apparatus following the BET procedure.

The GC analyses were performed with a Fisons Instruments GC 8000 gas chromatograph. This instrument was equipped with an on-column injector and a flame ionization detector and was fitted with a 1.5 m × 0.53 mm ID guard column (J&W Scientific), connected in series with a 12 m × 0.53 mm ID fused silica capillary column (SGE HT5 Aluminium Clad) from Supelco. The analytical conditions were the following: direct injection (splitless, hold for 1 min); on-column injector temperature, 337 K; column initial temperature, 437 K; first program rate, 10°/min; intermediate temperature, 573 K; second program rate, 5°/min; final temperature, 633 K; hold, 7 min; detector temperature, 643 K; carrier gas pressure, 10 KPa.

Figure 1 presents a typical chromatogram obtained during the transesterification of triolein with glycerol.

Reaction Procedure

The transesterification reaction was performed in a glass batch reactor equipped with a condenser system. Glycerine and the corresponding triglyceride were stirred at 400 rpm and heated in a silicone bath to the required temperature. When the reaction temperature was stabilized the catalyst was added and the reaction started. In order to follow the progress of the reaction, samples were periodically

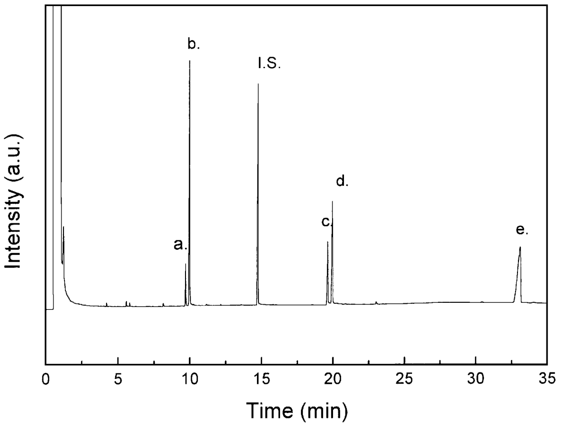


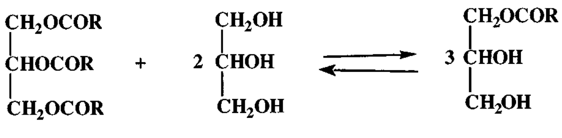
FIG. 1. Gas chromatogram of silylated products, with tricaprin as the internal standard (i.s.), obtained during the transesterification of triolein with glycerol at 513 K and MgO as the catalyst (a) β-monoolein, (b) α-monoolein, (c) 1,2-diolein, (d) 1,3-diolein, (e) triolein.

removed from the reactor and separated from the catalyst by filtering, using pyridine as the solvent. The reaction products were converted to volatile trimethylsilylether derivatives with N-methyl-N-(trimethylsilyl)-trifluoroacetamide, following the method described in Ref. (19). After 15 min at room temperature, a known amount of tricaprin was added as the internal standard, and the products dissolved in hexane were analyzed by gas chromatography (GC).

At the end of the reaction, the reaction mixture was dissolved in isopropyl alcohol and filtered. The organic solution was evaporated in vacuum and was submitted to extraction with hexane in order to separate the fatty products from the free glycerol. After that, the hexane layer was evaporated in vacuum and the extracted products weighed and analyzed. On the other hand, the filtered catalyst was submitted to continuous solid-liquid extraction using a microsoxhlet equipment and dichloromethane as the solvent; the extracted products were also analyzed, weighed, and included in the mass balance. Only the experiments with mass balances better than 95 wt% with respect to the esters were considered.

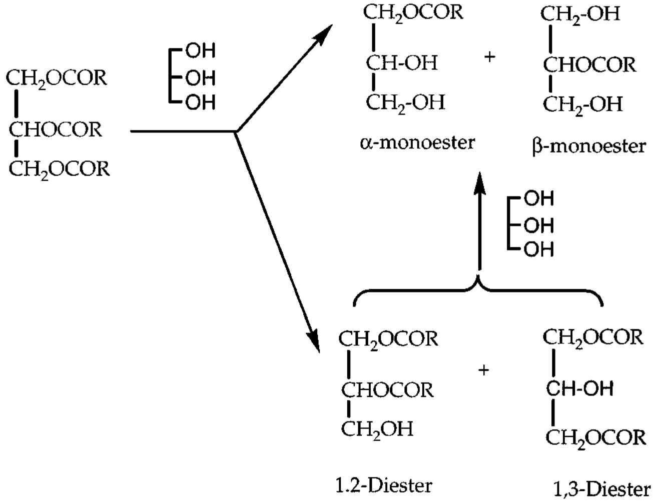
RESULTS AND DISCUSSION

For a specific base catalyzed reaction, the strength and number of active sites are of paramount importance for the control of activity and selectivity. Basic solid catalysts such as zeolites (16), sepiolites (20), and hydrotalcites (21), allow the exploration of the influence of basicity in a wide range of basic strengths. Basic Faujasites, MCM-41 (22), and sepiolite can be obtained by fully exchanging the materials with alkaline cations. The amount and nature of these will determine the final basicity. In the case of hydrotalcites, the number and strength of the basic sites depend on the chemical composition and the activation conditions of the sample (17). Taking advantage of these properties with the aim of selecting the most appropriate catalyst for the transesterification of vegetable oil with glycerol,



we chose four catalysts covering a wide range of basicities: MCM-41-Cs, sepiolite-Cs, Mg–Al hydrotalcite, and MgO.

Concerning the chemical process, fat glycerolysis involves a reaction between triglyceride and glycerol and requires two moles of glycerol per mole of triglyceride to yield three moles of fatty monoester (see the scheme above). However, one should take into account that the chemical equation for fatty glycerolysis represented above is a simplification, since it considers the formation of the predominant monoglyceride only. Thus, even though this equation suggests a trimolecular process, the reaction occurs stepwise in a series of two steps represented by two successive equations with different reaction rates. Indeed, the glycerol and the fat react initially to the separate 1,3- and 1,2-diglyceride isomers, and these, through a second reaction step, generate the α and β (or 1- and 2-) monoglycerides.



This reaction involves only one catalytic active site per reaction step, and therefore, a first-order kinetic equation with respect to the concentration of active sites can be expected.

On the other hand, it should be taken into account that fat glycerolysis is a reversible reaction and, therefore, an excess of glycerol over the two moles theoretically required should be used in order to shift the equilibrium toward the formation of monoglycerides. However, although the stoichiometry and thermodynamics for transesterification are understandable, the experimental procedure may present a problem which can limit the success of the process. It requires a sufficient degree of homogeneity or mutual solubility of the hydrophilic glycerol in the initial hydrophobic triglyceride fat or in subsequent fat-like phases. In fact, only 4% of the glycerol is soluble in common fats at room temperature. Thus, an excess of glycerol to force the reaction to completion cannot be reached when working at room temperature. Therefore, temperatures must be high enough to increase the solubility of glycerol in the fat phase. Thus, the activity of the catalysts was tested by conducting the transesterification of pure triolein with glycerol at 513 K with glycerol/triolein molar ratios of 12 and 4 wt% of catalyst. The final distribution of the products obtained after 5 h of reaction time in the presence of the different basic catalysts and without catalyst is shown in Table 3. Figures 2a and 2b show the plotted yields of monoglycerides and diglycerides in the presence of MgO and HT-1.

Glycerolysis is a slow reaction in the absence of the catalyst. After 5 h of reaction, the yields and conversion were still very low, and, consequently, we can ignore the interference of the blank reaction with the catalytic glycerolysis.

TABLE 3

Total Conversions, Rates, Yields, and Selectivities to Monoolein Obtained in the Glycerolysis of Triolein with Glycerol at 513 K and in the Presence of Different Solid Catalysts Using a Gly/Tr Molar Ratio of 12 and a 4 wt% of Catalyst

Catalysts	Total conversion[a] (X) (%)	ro[b]/S[c] · 10^5 $(\mathrm{mol} \cdot \mathrm{h}^{-1} \cdot \mathrm{m}^{-2})$	Yield (%)				Selectivity to monoolein (%)
			βMono-	αMono-	1,2-Di-	1,3-Di-	
None	13	—	1	6	2	4	53
MCM41-Cs	26	0.09	2	10	5	9	46
Sepiolite-Cs	45	0.77	4	30	4	7	75
HT-1	92	2.55	9	63	8	12	78
MgO	97	3.00	8	65	9	15	75

[a] After 5-h reaction time.
[b] ro (initial rate calculated at conversions below 15%).
[c] Surface area of the catalyst.

MCM-41-Cs, sepiolite-Cs, hydrotalcite, and MgO are quite active for the transesterification reaction, the order of reactivity being MgO > HT > Sepiolite-Cs > MCM-41-Cs. However, when the surface area is taken into account (Table 3), the activity of MCM-41-Cs is much lower than that of the other three catalysts. These results agree with previous work in which the basicity of alkaline Sepiolite, measured as the capacity for abstracting the acidic hydrogens in activated methylenic compounds, was found to be higher (pKa up to 13.3) than that of exchanged zeolites (pKa 10–10.7) (23). It was also higher than alkaline exchanged MCM-41, which is very active for Knoevenagel condensation involving activated methylenic compounds with pKa 9–11, but shows low activity for Claisen condensation which involves the extraction of protons with a pKa $\sim$ 16 (22). Therefore, the relatively low activities obtained for cesium-exchanged sepiolite and MCM-41 are not surprising, considering that the hydrogens to be extracted in aliphatic alcohols, such as glycerol, have a pKa close to 16 (24).

On the other hand, the aluminum magnesium mixed oxides derived from the hydrotalcite, and the magnesium oxide are sufficiently basic for carrying out the transesterification with yields higher than 90% conversion and more than 75% selectivity to monoglyceride. These results are consistent with the observation that MgO and Mg−Al hydrotalcite have basic sites, strong enough for proton abstraction in cases where the pKa is close to 16 (21, 23, 25).

Transesterification of Rapeseed Oil with Glycerol

From an industrial point of view, an investigation of an inexpensive and widely available natural animal or vegetable oil as the triglyceride source, instead of triolein, would give more representative results. Therefore, we studied and optimized the reaction conditions for the fat glycerolysis of rapeseed oil (RO) with glycerol which, apart from being cheap, has a high content ($\sim$63%) of oleic fatty acid esters (26). In Fig. 3, we present a typical chromatogram of the transesterification of rapeseed oil with glycerol obtained after a 1-h reaction in the presence of 4 wt% MgO, with a glycerol/rapeseed oil molar ratio of 12. In this chromatogram we can define three distinct zones corresponding

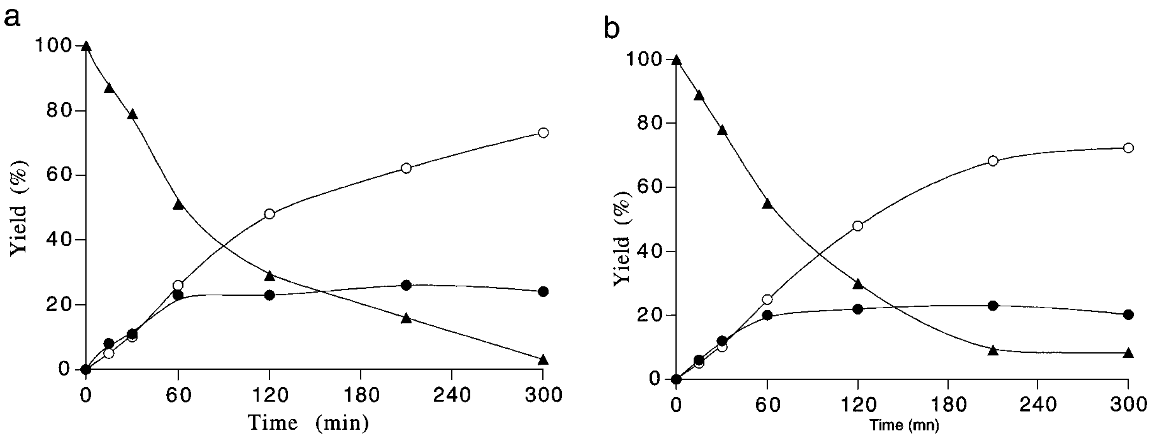


FIG. 2. Transesterification of triolein with glycerol at 513 K and a glycerol/triolein molar ratio of 12: Yields of monoolein (○), diolein (●), and triolein (▲); (a) with 4 wt% MgO and (b) with 4 wt% of HT-1 as catalyst.

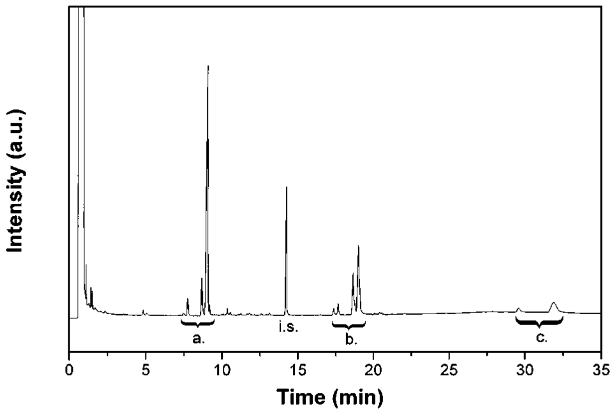


FIG. 3. Typical gas chromatogram of silylated products, with tricaprin as the internal standard (i.s.), obtained during the transesterification of rapeseed oil (RO) with glycerol at 513 K and MgO as the catalyst: (a) monoglycerides, (b) diglycerides, (c) triglycerides.

to the three groups of lipids: (a) monoglycerides (between 7 and 9.5 min), (b) diglycerides (between 17 and 19.5 min), and (c) triglycerides (between 29 and 32.5 min) (19). In order to quantify the different fatty esters, we used the same response factors as for the transesterification of pure triolein, with tricaprin as the internal standard (IS). To calculate the rapeseed oil molar conversion and the yields of monoesters and diesters, we considered that the rapeseed oil was composed exclusively of triesters of the oleic acid.

When rapeseed oil was used, it was found that the activities of the MgO and HT catalysts are very similar to those obtained with the pure triglyceride (triolein). After 5 h, the conversion and selectivity to monoesters achieved with the two feeds are practically the same. Thus, based on the study of triolein, we selected magnesium oxide (MgO) as the catalyst to optimize the reaction parameters for the transesterification of rapeseed oil.

The Influence of the Amount of Catalyst and of the Reaction Temperature

The reaction should be first order with respect to the catalyst concentration; i.e., the same active site should be involved in both steps. Indeed, working at 513 K with a glycerol/rapeseed oil ratio of 6, the initial rate of disappearance of the tryglyceride reactive doubled, but the selectivity remained the same, with 4 instead of 2 wt% catalyst.

The reaction temperature also allows for an increase in the reaction rate, while at the same time causing changes in selectivity. However, for the production of commercial products, the practical temperature limit for fat glycerolysis is 533 K. For the production of food monoglycerides, the temperature must remain at around 528 K, because taste, aroma, and color of the products begin to deteriorate at higher temperatures (14).

To study the influence of the reaction temperature, we worked with temperatures ranging from 473 to 513 K. The results obtained after 5-h reaction time are listed in Table 4.

The apparent activation energy was calculated by fitting the initial rate values to the Arrhenius equation and results in a value of 85 $\mathrm{kJ \cdot mol^{-1}}$. This value seems to indicate that the reaction is not controlled by mass transfer limitations and, consequently, that the differences observed among the different catalysts and reaction conditions are due to differences in the number of active sites and to the intrinsic rate constants. From a practical point of view, we conclude that, in order to obtain a good conversion in the transesterification of rapeseed oil with glycerol, using realistic amounts of catalyst, temperatures should be above 473 K. We conclude, from the results given in Table 4, that the selectivity to the monoester increases with temperature. However, when the yields are compared at the same level of conversion (Figs. 4a–b), no effect of reaction temperature on selectivity to monoester is found.

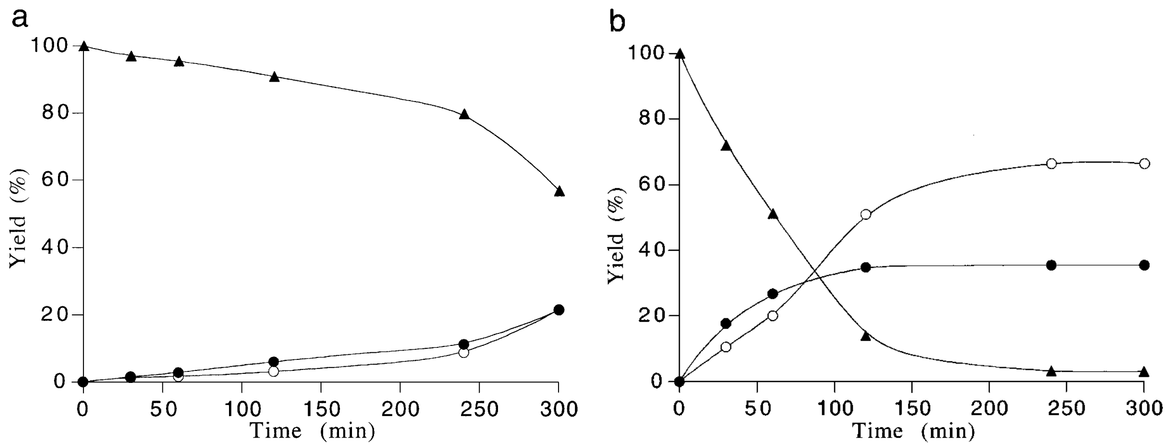


FIG. 4. Yields of monoglycerides (○), diglycerides (●), and triglycerides (▲), obtained in the glycerolysis of rapeseed oil (RO), using MgO (2 wt%) as the catalyst and a glycerol/rapeseed oil molar ratio of 6 at (a) 473 K and (b) 513 K.

TABLE 4

Influence of Temperature on the Initial Rate (mol · h^{-1} · g^{-1}), Total Conversions, Yields, and Selectivity to Monoesters in the Transesterification Reaction of Rapeseed Oil with Glycerol Using MgO as the Catalyst (2 wt%) with a Reactant Molar Ratio Gly/RO = 6

Temperature (K)	Initial rate 10^3 (mol · h^{-1} · g^{-1})	Total conversion[a] (%)	Yield (%)		Selectivity to monoesters (%)
			Monoesters	Diesters	
473	2.81	44	22	22	50
493	6.33	83	43	40	52
513	21.12	96	63	33	66

[a] After 5 h of reaction time.

Besides the typical kinetic influence, the reaction temperature can also have an important effect on the solubility of the two reaction phases, i.e., rapeseed oil and glycerol and this, together with the oil to glycerol ratio, are probably important process variables (14).

Influence of the Glycerol/Oil Ratio

In order to establish the practical limits of the molar excess of glycerol and its possible effect on the selectivity to monoester, the reaction was carried out at 513 K, with 4 wt% of magnesium oxide and a glycerol to rapeseed oil molar ratio between 3 and 18. After 5 h, we obtained the results presented in Table 5.

Our results suggest that, for maximum conversion and selectivity to monoester, ratios between 6 and 12 are necessary. In fact, at lower values, a 20% reduction in the selectivity to monoesters is observed, and ratios greater than 12 do not increase the yields but complicate ester and glycerol recovery, thus increasing the cost of the process.

Influence of the Chemical Composition of the Catalyst

Since the MgO and MgO−Al_2O_3 systems appear to be promising catalysts for the transesterification reaction, we optimized the composition of the catalyst, going from pure MgO to the MgO/Al_2O_3 series with Al/Al + Mg ratios from 0.20 to 0.33.

TABLE 5

Influence of the Glycerine/Rapeseed Oil Molar Ratio on the Glycerolysis Reaction Using MgO as the Basic Catalyst (4 wt%) at 513 K

Ratio Gly/RO	Total conversion[a] (%)	Yield (%)		Selectivity
		Monoesters	Diesters	
3	93	39	54	41
6	97	67	30	69
12	96	65	31	68
18	96	65	31	68

[a] After 5 h reaction time.

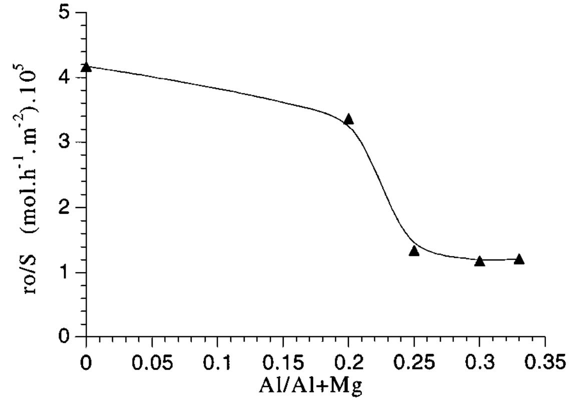


FIG. 5. Influence of the Al/(Al + Mg) ratio of the starting hydrotalcites on the initial rate of disappearance of the triglycerides per unit surface area (ro/S) during the glycerolysis of rapeseed oil at 513 K, using a glycerol/rapeseed oil molar ratio of 12.

When the initial rates are plotted against the Al/Al + Mg ratio (Fig. 5) the catalyst activity is highest for the MgO catalyst. It is believed (27) that, by adding Al_2O_3 in to MgO, the total number of basic sites decreases, even though stronger basic sites appear. Thus we conclude, in this reaction, the basic sites present in MgO are already active enough for carrying out the reaction and that the formation of stronger sites, formed in the hydrotalcite derived oxides, does not compensate for the decrease in the total number of sites produced in the MgO upon the addition of Al_2O_3.

With respect to the selectivity, the results presented in Table 6 and the observations reported here, show that the differences found for the selectivity to monoglycerides are not due to the nature of the catalyst but to differences in the level of conversion.

It seems that higher activities and selectivities will be achieved only when a better mixture of the two phases is

TABLE 6

Influence of the Chemical Composition of the Catalyst on the Total Conversions, Yields, and Selectivity to Monoesters in the Trans esterification Reaction of Rapeseed Oil with Glycerol, Using a Reactant Molar Ratio of Gly/RO = 12 and 4 wt% of Different Oxides at 513 K

Catalysts	Total conversion[a] (%)	Yield (%)		Selectivity to monoesters
		Monoesters	Diesters	
MgO	96	65	31	68
HT-1	95	64	31	67
HT-2	89	52	37	58
HT-3	84	53	31	63
HT-4	70	39	31	56

[a] After 5 h of reaction time.

TABLE 7

Characteristics of the Final Product Obtained by the Transesterification of Rapeseed Oil with Glycerol with 4 wt% MgO as Catalyst and a Molar Ratio of the Reactants Gy/RO = 12 at 513 K

Sample composition		Limits according to European standards
Mono plus diesters[a]	89	>70
Acids free[a,b]	2	<3
Glycerol[a]	3	<7
Polyglycerols[a]	0	<4% total glycerol
Water[c]	1	<2

Note. The results (wt%) are compared with the requirements established by the E.U.

[a] Quantified by GC.

[b] Determined by titration (official methods of analysis A.O.A.C., 28. 029 (1980)).

[c] Determined by Karl–Fischer method.

obtained. The patent literature reports the use of NaOH, KOH, CO_3K_2, or alcoholates as base catalysts for the glycerolysis of different types of fat at the optimum reaction temperature. The yield of monoglyceride was never better than 75% (14), and yields of 90% are achieved only when glycerolysis is carried out in solvents such as pyridine (28) or in the presence of soap as an emulsifier (9, 10). However, a clear drawback of both methods is that the solvent or the soap must be completely removed from the products at the end of the reaction.

Comparing the results of experiments under the above conditions and our results obtained with MgO, we conclude that having obtained similar results, our method clearly presents the advantage of being far less complicated. An analysis of the final product characteristics obtained on the MgO catalyst (29) and the product quality requirements established by the European Union shows that the final ester mixture obtained easily meets those requirements (Table 7).

In conclusion, basic catalysts with basic sites strong enough to abstract a proton from an active methylenic group with pKa = 16 are efficienty in the transesterification between triglycerides and glycerol and produce high yields and selectivities to monoglycerides. With optimized reaction conditions and catalyst composition the final results are as good as those obtained using the less attractive and more costly processes reported in the patent literature. Moreover, the final reaction product, without further purification meets the quality requirements established by the European Union.

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