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Combined Alkyl and Sulfonic Acid Functionalization of MCM-41-Type Silica

Part 2. Esterification of Glycerol with Fatty Acids

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The esterification of glycerol with lauric and oleic acids (1 : 1 molar ratio) has been carried out by using hybrid MCM-41 materials containing simultaneously alkyl (methyl or propyl) and sulfonic acid groups as catalysts. It has been found that for each fatty acid the catalyst activity is affected by the concentration of methyl groups, and maximum activity per sulfonic acid group is achieved by tuning the methyl/sulfonic acid ratio. A monolaurin yield of 63% is obtained with the most active catalyst, whereas for oleic acid the maximum monoolein yield was 45%. Reduction of the average pore size (determined by N_2 adsorption) from 14 to below 10 Å has a detrimental influence on the catalyst activity for both acids. © **2000 Academic Press**

Key Words: **MCM-41; mesoporous acid catalysts; sulfonic acid; fatty acids; selective esterification; monoglyceride.**

INTRODUCTION

Recently, the synthesis of mesoporous materials containing immobilized sulfonic acid groups which behave as active and selective catalysts of the esterification reaction of polyols with fatty acids has been reported (1–3). The improved catalytic performance of these materials as compared with zeolites has been attributed to their larger pore size and increased hydrophobicity (3), inherent to the presence of the alkyl chain belonging to the propylsulfonic group anchored on the surface.

The benefits of adjusting the catalyst hydrophobicity to that required to balance the differences in polarity of the reactants have already been reported for Ti–MCM-41 materials. Indeed, it has been shown that the introduction of trimethylsilyl groups by postsynthesis procedures improves the catalyst activity as well as the selectivity in the epoxidation of cyclohexene with peroxides (4, 5). Therefore, the esterification of glycerol with fatty acids, which also involves the interaction on the catalyst surface of molecules of very different polarities, could be expected to be influenced by alterations of the catalyst hydrophobicity, in addition to those produced by the chemical nature of the alkylsulfonic group of the SO_3H–MCM-41 materials.

Following this strategy, in Part 1 of this work (6), the synthesis and characterization of well-ordered, hybrid MCM-41 materials containing simultaneously alkyl (either methyl or propyl) and sulfonic acid groups has been reported. In Part 2 of this work the application of these hybrid materials as catalysts for the esterification of glycerol with lauric and oleic acids is described. The influence of some catalyst properties, such as the alkyl/sulfonic acid ratio, pore size, and nature of the anchored alkyl group, will be discussed.

EXPERIMENTAL

Catalytic Tests

The reagents used for catalytic tests were glycerol (Fluka, 99 + %), lauric acid (Fluka, 99.9 + %), oleic acid (Aldrich, 90 + %), hexadecane (J.T. Baker, 99 + %), and tetradecane (Aldrich, 99 + %). The esterification reaction of glycerol with each acid was accomplished in the liquid phase (without solvent), in a stirred four-opening flask heated in an oil bath under atmospheric pressure. An N_2 steady flow of 10 ml min^{-1} was passed over the reaction mixture through one flask opening, in order to eliminate the water formed during the esterification, which was adsorbed by means of a glass elbow-shaped tube packaged with zeolite A. The reaction temperature was controlled to ±1 K by using a thermometer immersed in the reactant mixture. Tetradecane and hexadecane (20 wt% in the reaction mixture) were used as internal standards in the reactions with lauric and oleic acids, respectively. The reaction mixture was sampled for time intervals ranging between 1 and 24 h, counted since the reaction stabilized at the working temperature.

The range of reaction temperatures studied was 363–393 K. A molar ratio of fatty acid to glycerol of 1 (typically

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0.025 mol each) was used and the amount of catalyst, previously dried at 383 K overnight, was 5.0 wt%.

In order to evaluate the extent of the homogeneous reaction, experiments with no catalyst were carried out under the same experimental conditions as those described above.

Experiments using *p*-toluenesulfonic acid (PTSA, 0.5 wt%) were also performed with oleic acid and glycerol in order to compare the activity of the mesoporous materials with that of a conventional homogeneous catalyst.

Identification and Analysis of Reaction Products

The direct analysis of the products of this reaction by using gas chromatography has been previously described in the literature (1). However, by using those experimental conditions described, we did not obtain a good reproducibility of the analyses. The silanization of compounds with –OH groups is widely used in order to obtain more volatile derivatives which are easy to analyze by GC. In order to get better analytical conditions we developed a method involving the derivatization of the products and reagents to render more volatile the mono- and diesters formed and the reactants not transformed. The derivatization was accomplished as follows: 100 μl of pyridine (>99%, Fluka), 200 μl of *N*,*O*-bis(trimethylsilyl) acetamide (BCA, ca. 97%, Fluka), and 100 μl of trimethylchlorosilane (TMCS, >99%, Fluka) were added to a 2-ml vial containing 10 mg of each reaction sample. Vials were encapsulated, agitated, and placed in a sand bath at 373 K for 20–30 min. Finally, 2 μl of each sample was analyzed by GC.

Reaction products were identified and analyzed using a FISONS HGC 8000 gas chromatograph coupled to a FISONS MD-800 mass spectrometer and a flame ionization detector. Products obtained in the reaction with lauric acid were separated by passing through a 15-m-long capillary column with 0.32-mm internal diameter and a 0.10-μm-thick methylsilicone layer (TRACER TRB-1). In the reaction with oleic acid, a 12-m length capillary column with 0.23-mm i.d. and a 0.10-μm-thick phenylpolycarborane–siloxane (SGE HT-5) layer was used. After identification, reaction products were analyzed by means of a flame ionization detector fitted to the chromatograph. Products yields were calculated taking into account the response factors of each compound, which were determined experimentally, and the selectivity to glycerol esters was calculated according to the ratio between the quantity of esters formed and the total quantity of products yielded at each time. No reaction products other than the glycerol esters were observed under the experimental conditions used. In order to calculate the monoglyceride yield both the 1- and the 2-substituted compounds (the former one being the major product in all the reactions) have been taken into account.

RESULTS AND DISCUSSION

Lauric Acid

(a) Influence of the content of methyl groups. The conversion of lauric acid as a function of time for the esterification reaction of this acid with glycerol at 373 K is plotted in Fig. 1 for several $[Me/SO_3H]$–MCM-41 catalysts. It can be seen in the figure that although the blank reaction is not negligible, the reaction is much faster when these catalysts are used, in such a way that conversion higher than 90% is obtained after 24 h in most cases, while less than 20% conversion is attained in the absence of catalyst. Nevertheless, significant differences in reaction rate are observed among the catalysts.

It has to be taken into account that the catalysts have different concentrations of sulfonic acid (Table 1), and therefore a more appropriate comparison of catalyst activity should be done on the basis of turnover number (TON).

The turnover numbers, expressed as the conversion of fatty acid per milliequivalent of sulfonic acid group, after 8 h of reaction are plotted as a function of the concentration of methyl groups in Fig. 2. It can be seen in the figure that the activity increases rapidly by a factor of 3 as the Me concentration in the catalyst approaches 2 mequiv g^{-1}, and remains nearly constant for higher Me loading.

The variation of the turnover numbers with the concentration of alkyl groups could be attributed to the depletion of the hydrophilic character of the catalysts. As shown in Table 1, the amount of water desorbed at T lower than 393 K as determined by TG measurement (6) decreases as the Me content of the catalyst increases, this variation being more abrupt in the Me content interval 0.3–1.8 mequiv g^{-1}. This increase of the hydrophobic character of MCM-41

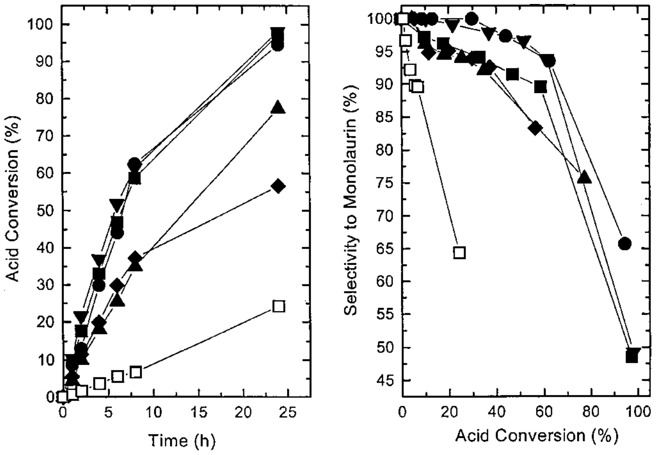

FIG. 1. Conversion of lauric acid vs reaction time and selectivity to monolaurin vs acid conversion for $[Me/SO_3H]$–MCM-41 catalysts compared with the blank test at 373 K: blank (□), M0H (▲), M5H (■), M10H (●), M40H (▼), and M60H (◆).

TABLE 1

Catalyst Properties

	Catalysts							
	M0H	M5H	M10H	M40H	M60H	Ms10H	Mt10H	Mp10H
SO_3H (mequiv g^{-1})	1.58	1.38	1.44	0.89	0.54	1.33	1.32	1.25
Me (mequiv g^{-1})	0	0.2	0.3	1.8	4.5	—	—	—
g_{H_2O}/g_{SiO_2}	0.11	0.11	0.11	0.06	0.04	—	—	0.11

materials containing anchored organic groups has been also reported in Refs. (5, 7).

The influence of the anchored Me groups on the catalyst performance in the esterification reaction is not restricted to the co-condensation synthesis procedure used to prepare the catalyst precursor. A sample of pure silica MCM-41 was treated with 3-mercaptopropyl trimethoxysilane (sample F-1), and a portion of the resulting product was further reacted with methyltrimethoxysilane (sample F-1-Me). After oxidation with nitric acid, the methyl-containing (F-1-Me) catalyst exhibited a 3-fold increase of activity as compared with the nonmethylated material (Table 2).

The methylation of the catalysts also shows benefits in the selectivity to the monoester. It can be seen in Fig. 1 that the incorporation of Me groups allows the selective synthesis of glycerol monolaurin. For the more active catalysts, those with 0.3 and 1.8 mequiv g^{-1} of Me groups, yields of the monoderivative higher than 60% were obtained. Figure 1 also shows a remarkable drop in monoglyceride selectivity for conversions higher than 60%. Thus, prolonged contact of the reaction products with the catalyst would equilibrate the glyceride derivatives, decreasing the monoester concentration.

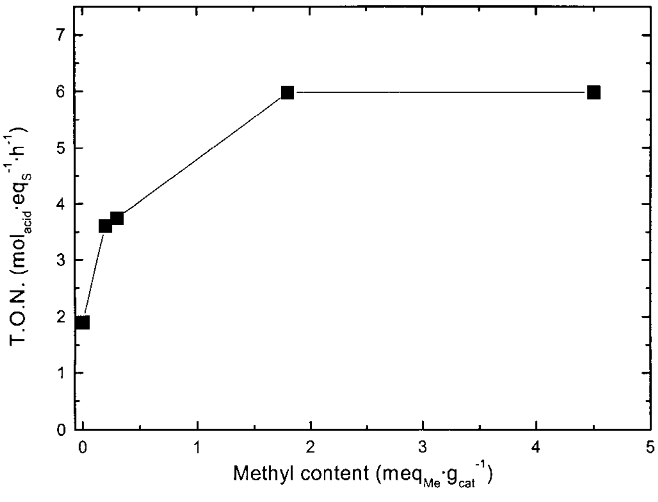

FIG. 2. Turnover number in the esterification of lauric acid with glycerol at 373 K after 8 h of reaction vs concentration of methyl groups in the [Me/SO_3H]–MCM-41 catalysts.

(b) Influence of the pore size. The influence of the pore size of the catalyst on the lauric acid conversion is illustrated in Fig. 3 for two materials (Ms10H and M10H) with roughly the same sulfonic acid concentration (Table 1). A decrease of the pore size from 14 Å (sample M10H) to below 10 Å (sample Ms10H) (see Table 1 in Part 1 of this work) substantially diminishes the reaction rate. Moreover, the selectivity to the monolaurin also decreases as the pore size is reduced (Fig. 3). The results for the small-pore sample suggest that diffusional limitations influence the reaction rate, which is in agreement with the reported relatively low activity of zeolite materials for this reaction (8, 9). Thus, the higher contribution of the nonselective reaction on the external surface to the overall activity makes the selectivity to the monoglyceride drop.

The catalyst synthesized from a trimethylbenzene-containing gel (Mt10H), which shows practically the same pore size as the regular one (M10H), also shows a similar reaction rate. The selectivity of both catalysts is also very similar, although the one prepared from trimethylbenzene is slightly more selective at high conversion.

(c) Influence of the alkyl group. The influence of the nature of the anchored alkyl group, either methyl or propyl, on the catalyst activity and selectivity is plotted in Fig. 4 as a function of time. The catalytic activity is slightly higher for the Me-containing sample, but taking into the account the differences in SO_3H content (Table 1), the TONs for both

TABLE 2

Physical Properties and Catalytic Activity of the Pure Silica MCM-41 Catalysts Functionalized with Mercaptopropyl Trimethoxysilane and Methyltrimethoxysilane

	Catalysts	
	F-1	F-1-Me
SO_3H (mequiv g^{-1})	0.37	0.23
Lauric acid conversion[a]	12.5	22.1
TON (mol_{acid} eqS^{-1} h^{-1})	2.89	8.21

[a] After 8 h of reaction; temperature of reaction, 373 K; lauric acid, 0.025 mol; glycerol, 0.025 mol; catalyst, 0.365 g; internal standard, tetradecane, 1.45 g.

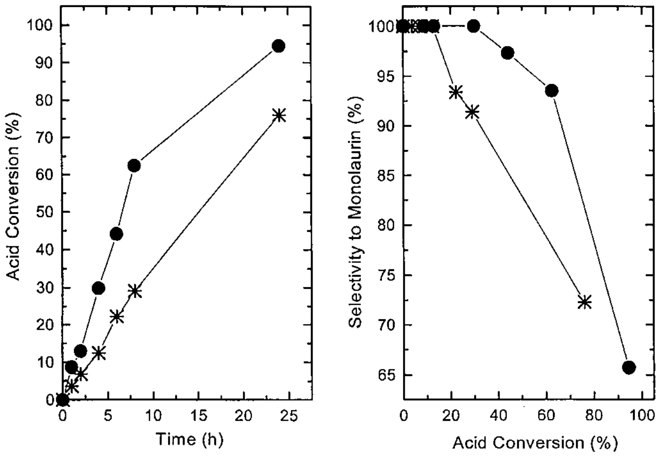

FIG. 3. Influence of the pore size of two [Me/SO_3H]–MCM-41 with the same methyl content on the activity and selectivity of the esterification of lauric acid with glycerol at 373 K: M10H (●) and Ms10H (✳).

catalysts are very similar. Indeed, both catalysts exhibit a similar hydrophilic character, as evidenced by the amount of water adsorbed (Table 1). Nevertheless, the methylated catalyst is more selective than the Pr-containing material.

(d) Yield to monolaurin vs lauric acid conversion. The monolaurin yields as a function of the lauric acid conversion are displayed in Fig. 5A for all the catalysts at 373 K. For the most active and selective materials, yields above 60% are obtained at lauric acid conversion levels close to 95%. For the catalyst prepared from a TMB-containing gel (Mt10H), a glycerol monolaurin yield of 70% is obtained at 95.5% conversion. On the other hand, trilaurin is detected only for conversion higher than 90%, with a selectivity below 1%. These values demonstrate that the incorporation of the methyl groups to the SO_3H–MCM-41 materials improves the monoester selectivity of the catalysts by more than 15% compared with the results previously described in the literature (1).

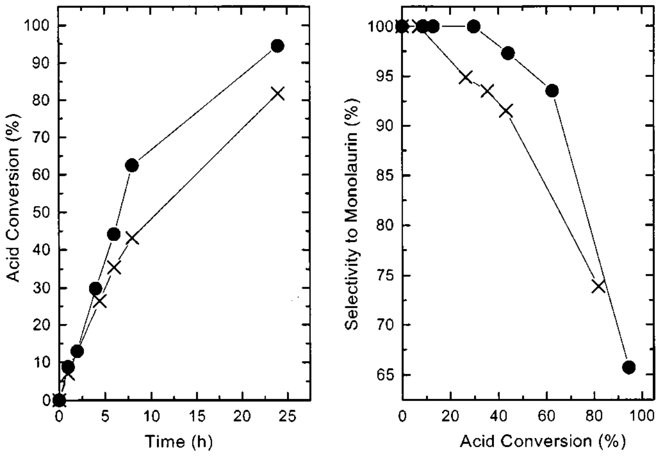

FIG. 4. Influence of the nature of the alkyl group of two [R/SO_3H]–MCM-41 with the same alkyl content on the activity and selectivity of the esterification of lauric acid with glycerol at 373 K: M10H (●) and Mp10H (×).

(e) Effect of the reaction temperature. The influence of the reaction temperature on the fatty acid conversion is shown in Fig. 6 for the M10H catalyst and the blank reaction. The conversion of lauric acid in the homogeneous reaction without catalyst at 373 K is quite low—below 8%—at short reaction times and it becomes significant after 24 h of reaction—23%. When the temperature increases to 393 K, the homogeneous reaction becomes important in only 6 h of reaction and after 24 h the conversion reaches a value above 50%. The selectivity to monolaurin in both cases is related to the conversion and it drops very quickly when the conversion increases due to the formation of diesters in the consecutive esterification of the monolaurin with another molecule of acid.

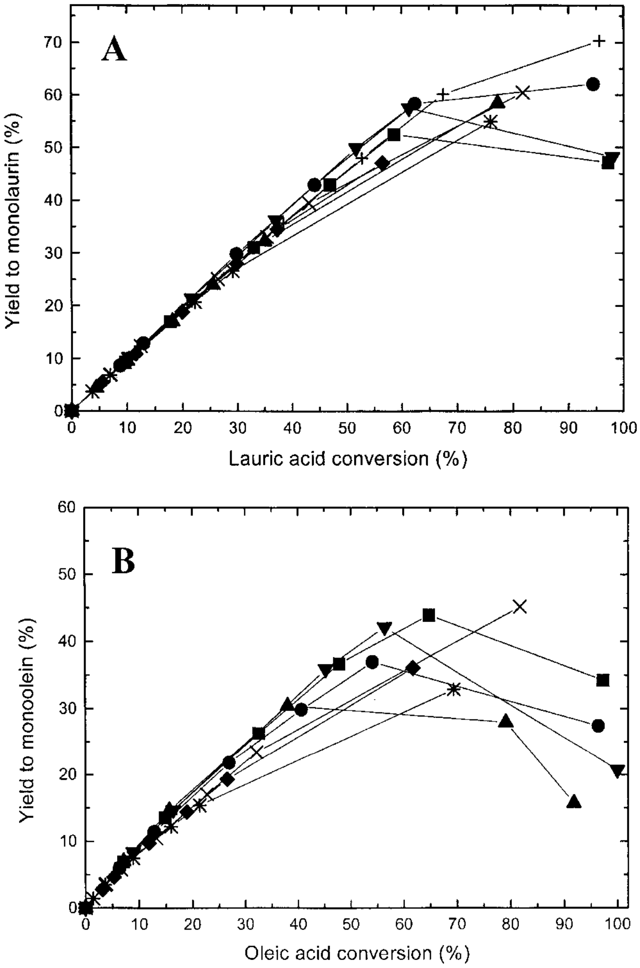

FIG. 5. Monolaurin (A) and monoolein (B) yield vs acid conversion for the different catalysts used in the esterification of lauric and oleic acids with glycerol at 373 K: M0H (▲), M5H (■), M10H (●), M40H (▼), M60H (◆), Ms10H (✳), Mp10H (×), and Mt10H (+).

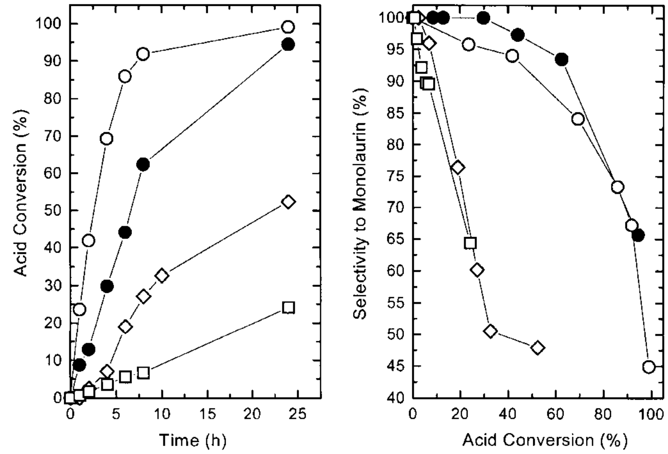

FIG. 6. Effect of the temperature on the activity and selectivity in the esterification of lauric acid with glycerol. Blank reaction: 373 K (□) and 393 K (◇). Catalyst M10H: 373 K (●) and 393 K (○).

In the presence of the catalysts M10H, at 393 K, a conversion of 70% is obtained after 4 h and increases to more than 90% after 8 h, while a 60% conversion is reached at 373 K after 8 h of reaction. Therefore, the contribution of the homogeneous reaction in both cases becomes significant at the longer reaction times. In this sense, the selectivity to the monoglyceride in the catalyzed reactions decreases more rapidly at 393 K, probably due to the increased contribution of the homogeneous reaction. In spite of this, a high monolaurin yield—62% at 92% conversion—is obtained at 393 K after only 8 h of reaction.

Oleic Acid

(a) Effect of the Me content. The esterification of glycerol with oleic acid has been carried out by using the same catalysts previously described for lauric acid, and the results are plotted in Fig. 7. Differences in activity are found among the catalysts tested, obtaining an acid conversion higher than 90% after 24 h of reaction for most of them. As it was discussed before, the reaction rate is expected to be influenced by the sulfonic acid and methyl groups concentrations in the catalyst. When the catalyst activities per mole of sulfonic acid are compared, variations in activity are found, which nevertheless show no clear dependence on the Me content of the material.

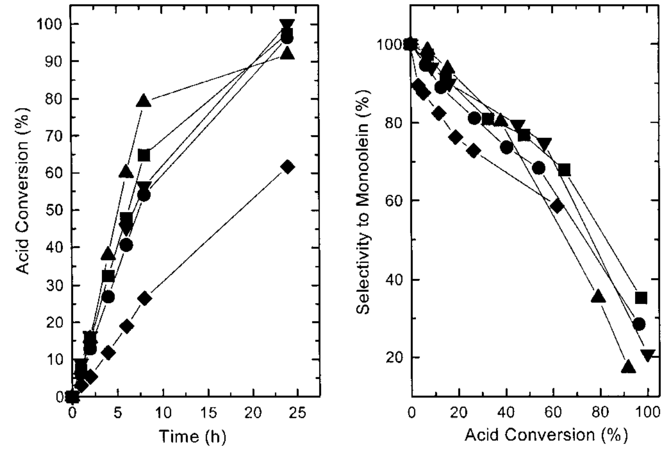

FIG. 7. Conversion of oleic acid vs reaction time and selectivity to monoolein vs acid conversion for [Me/SO$_3$H]–MCM-41 catalysts at 373 K: M0H (▲), M5H (■), M10H (●), M40H (▼), and M60H (◆).

The methylation of the catalyst improves in general the selectivity to glycerol monoolein, which is better than 80% at 40% conversion for the most selective one. After 24 h, conversion higher than 95% is obtained with most of the catalysts, whereas the selectivity to the monoester drops to 30%. The maximum yield of monoolein is close to 45% at 60% conversion (Fig. 5B).

When the activity patterns of the different catalysts in the esterification of glycerol with the two fatty acids, lauric and oleic, are compared, it can be noticed that both the esterification rate and the selectivity to the monoester decrease as the hydrocarbon backbone of the fatty acid increases in length. In order to understand this difference, the esterification reaction has been carried out by using *p*-toluenesulfonic acid (PTS, 0.5 wt%) as a homogeneous catalyst, and the reaction rate per equivalent of SO$_3$H (obtained from the slope of the conversion plot vs time) has been calculated.

It has been pointed out (1) that the physical conditions of the reaction mixture influence the esterification rate, which increases as the mixture of fatty acid and glycerol is emulsified by the monoglyceride formed in the reaction. For this reason, the reaction rate as defined above has been calculated from conversions in the range 15–30%, where enough monoester is formed that we may safely assume that good emulsifying conditions are achieved.

The reaction rates obtained in this way for the most active heterogeneous catalyst and the PTS homogeneous catalyst are collected in Table 3 for lauric and oleic acids. The PTS possesses an intrinsic activity higher than those of the heterogeneous catalysts for both esterification reactions, the activity for lauric acid esterification being higher than that of oleic acid by 40% at 373 K. However, it is interesting to observe that whereas the rate of the heterogeneous catalyzed esterification of lauric acid decreases by a factor

TABLE 3

Reaction Rate for the Esterification of Fatty Acids with Glycerol Catalyzed by M40H and *p*-Toluenesulfonic acid[a]

Catalyst	Lauric acid, 373 K	Oleic acid 373 K	Oleic acid 393 K
M40H	1.7	0.6	1.3
PTS	6.0	4.6	7.2

[a] Grams of fatty acid converted per milliequivalent of S per hour.

of 3 as compared with that of PTS at 373 K, it is 8 times (at 373 K) and 6 times (at 393 K) lower for the oleic acid reaction. These results strongly support that the esterification of glycerol with oleic acid catalyzed by these acidic MCM-41-type materials could be affected by diffusional limitations that would also decrease the monoglyceride selectivity, as in this case the contribution of the nonselective, external surface to the overall catalytic reaction would also gain in importance. Diffusional constraints could also eventually affect the lauric acid reaction, but these effects would be in any case less severe than those for oleic acid. Nevertheless, it has also to be considered that both acids differ in their hydrophobic character and, therefore, this could also affect the adsorption on the catalyst pores.

(b) Influence of pore size. The influence of the pore constraints which affect the reaction rate can be clearly observed as the average pore size of the catalyst is reduced (Fig. 8). In this case the reaction rate decreases by a factor of 2, whereas lower selectivity to monoolein is also obtained when the pore size decreases from 14 to less than 10 Å.

(c) Influence of the alkyl group. The replacement of Me by Pr groups in the catalyst reduces the reaction rate of the glycerol esterification with oleic acid (Fig. 9). As has been discussed before, both catalysts (M10H and Mp10H) have different contents of sulfonic acid groups and, therefore, the activities per acid group should be compared. It is observed that the concentration of sulfonic groups in the Pr-containing catalyst is 20% lower than that of the Me material, but nevertheless the activity decreases by nearly 50% and the selectivity to glycerol monoolein is also lower. This result suggests that there is an increasing steric constraint for this reaction as the methyl group is replaced by the bulkier propyl fragment. It is worth mentioning that with lauric acid, having less steric requirement than oleic acid, the reaction rate is hardly affected by changing the nature of the alkyl group (Fig. 4).

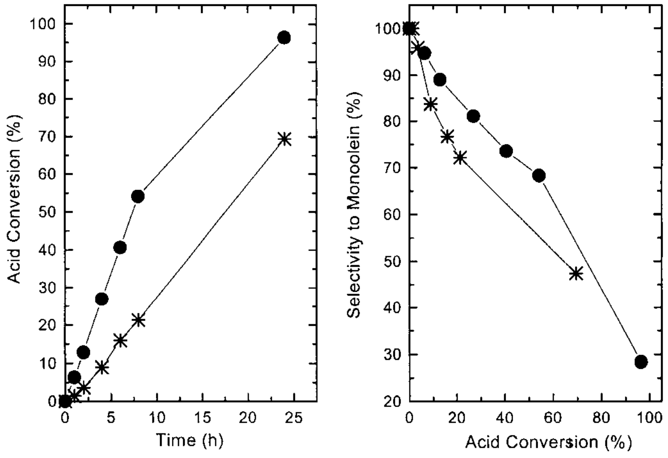

FIG. 8. Influence of the pore size of two [Me/SO$_3$H]–MCM-41 with the same methyl content on the activity and selectivity of the esterification of oleic acid with glycerol at 373 K: M10H (●) and Ms10H (✳).

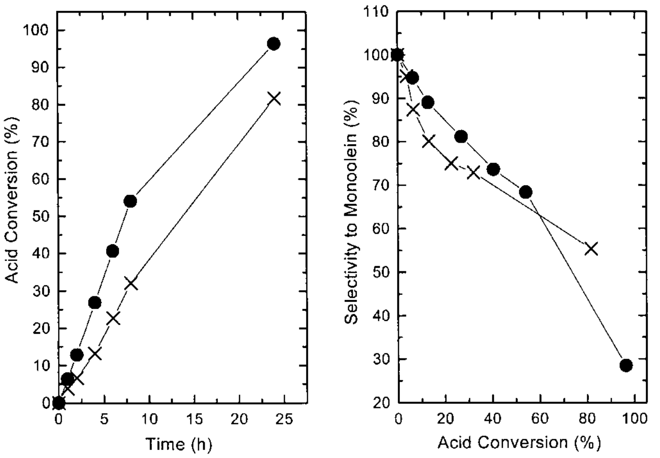

FIG. 9. Influence of the nature of the alkyl group of two [R/SO$_3$H]–MCM-41 with the same alkyl content on the activity and selectivity of the esterification of oleic acid with glycerol at 373 K: M10H (●) and Mp10H (×).

(d) Yield to monoolein vs oleic acid conversion. The monoglyceride yields as a function of the oleic acid conversion have been displayed in Fig. 5B for all the catalysts at 393 K. First of all, it can be noticed that, in the reaction with oleic acid, the yield of the monoester is lower than that of the reaction with the lauric acid (Fig. 5A). The maximum yield obtained is ∼45% for the M5H and the Mp10H catalysts at conversions of the oleic acid above 60%. These results also improve significantly the ones obtained with nonmethylated catalysts previously described in the literature (1). The maximum monoester yields are reached at intermediate conversions. At longer reaction times, the reaction mixture tends to approach to the equilibrium among the mono-, di-, and (at very high conversions) triglycerides due to the esterification of the monoglycerides with the remaining oleic acid (1).

(e) Influence of the reaction temperature. The effect that the temperature in the interval 373–423 K has on the conversion of oleic acid as a function of time has been plotted in Fig. 10 for the catalysts M40H and M10H and the blank reaction. Like in the esterification of lauric acid, the contribution of the homogeneous reaction is important only after 24 h at the higher temperature tested, 393 K. In the blank reaction the selectivity to monoglyceride decreases rapidly when the acid conversion increases. This effect is not observed in the experiment at 373 K due to the low conversion (less than 5% after 24 h).

A strong enhancement of the esterification rate takes place for the catalyst M40H by increasing the reaction temperature from 373 K to 423 K. At the highest temperature tested, a conversion of 96% is obtained after 6 h. It is also interesting to observe that the selectivity to the monoester also increases slightly upon increasing the reaction temperature. Thus, a yield of glycerol monoolein of 43% was obtained in only 2 h. After 4 h, the yield is 40% at 88% conversion.

The catalyst M10H, with a lower Me content than M40H, shows the same relative increase in activity as a function of temperature in the range 373–393 K. Indeed, the selectivity plots of Figs. 6 and 10 show that the monoglyceride yield is more affected by the nature of the catalyst than by the reaction temperature. Indeed, the selectivity increases with the Me loading of the catalyst at the two temperatures tested.

Catalyst Stability

The TG plots of the oxidized catalysts discussed in Part 1 of this work show that a notorious weight loss takes place as the [Me/SO$_3$H]–MCM-41 catalysts are heated in air at T higher than 473 K. However, inspection of the TG curves suggests that some volatile compounds could be released at lower temperatures. Therefore, the sulfur content of the products after reaction has been determined, as it could be an important property of the glycerides mixture for commercial applications.

Table 4 collects the sulfur content of the reaction mixture and the percentage of sulfur leached from the catalysts after different reaction times for some selected experiments and reaction temperatures. The percentage of the sulfur leached has been calculated on the basis of the total sulfur—not only the –SO$_3$H analyzed by titration—presents in the catalyst. It can be observed in the table that in the reaction of lauric acid at 373 K, only a small amount of the S is leached from the catalysts to the liquid phase, except in the sample M40H, which after 24 h of reaction loses almost 8 wt% of the initial sulfur. The leaching of the S increases with the reaction temperature, for both lauric and oleic acids, and it seems more pronounced at longer reaction times, particularly at high temperature. The data collected in Table 4 from the ICP analyses do not confirm the provenance of the leached sulfur, either from sulfonic groups or from partially oxidized (nonacidic) sulfur species.

TABLE 4

ICP Analyses of the Sulfur Present in the Products Mixture during the Reaction, in ppm (Values in Parentheses Correspond to the Percentage of the Initial S Leached from the Catalysts[a])

		Lauric acid, 373 K	
Catalyst		8 h	24 h
M5H			29 (0.6%)
M10H		45[b] (1.1%)	72 (2.0%)
M40H		76 (2.6%)	201 (7.9%)
		Lauric acid, 393 K	
		8 h	24 h
M10H		150 (4.6%)	287 (9.2%)
		Oleic acid, 393 K	
		8 h	24 h
M5H			99 (3.1%)
M10H		80 (2.4%)	130 (4.1%)
M40H			89 (3.5%)
		Oleic acid, 423 K	
	4 h	8 h	24 h
M40H	137 (5.5%)	165 (6.7%)	241 (9.9%)

[a] Sulfur content in the reagents: lauric acid, 22 ppm; oleic acid, 10 ppm. In a typical experiment 0.025 mol of each of the reagents and 0.365 g of catalyst are used.

[b] Four hours of reaction.

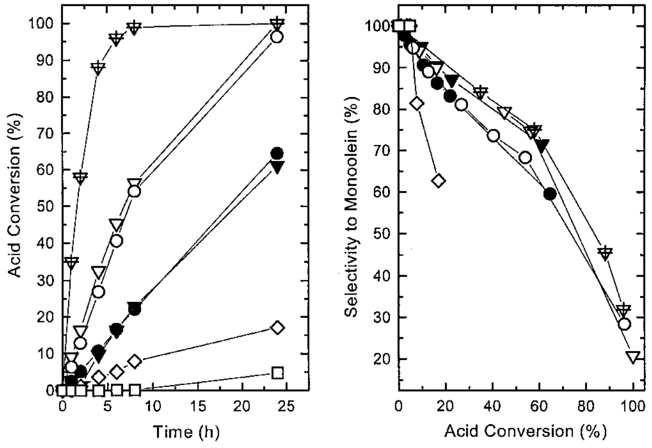

FIG. 10. Effect of the temperature on the activity and selectivity in the esterification of oleic acid with glycerol. M10H: 373 K (●) and 393 K (○). M40H: 373 K (▼), 393 K (▽), and 423 K (⊽). Blank reaction: 373 K (□) and 393 K (◇).

CONCLUSIONS

Well-ordered, hybrid MCM-41 materials containing alkyl (methyl or propyl) and sulfonic acid groups are efficient catalysts for the esterification of glycerol with lauric and oleic acids. For lauric acid, the activity per sulfonic acid group increases strongly with the concentration of methyl groups, until a steady level is reached above 1.8 mequiv of Me per gram of catalyst. This behavior parallels the changes in the hydrophobicity of the catalysts. The selectivity to glycerol monolaurin also improves upon partial functionalization of the catalyst surface with alkyl groups, and a maximum monolaurin yield of 63% is obtained.

For the esterification with oleic acid, similar effects are found, although the influence of the methylation of the catalyst is less pronounced. Indeed, the optimum monoglyceride yield, 45%, is lower than that for lauric acid.

The reduction of the average pore size below the 14 Å of the standard catalyst has a detrimental influence on the catalyst performance for both acids. It is probable that the reaction of oleic acid is diffusion limited even for the catalyst with 14 Å of pore aperture.

In summary, highly active and selective SO_3H–MCM-41 catalysts for the esterification of glycerol can be obtained by appropriate tuning of the catalyst hydrophobicity and pore size to those required by the polarity and steric constraints of the reactants. Further improvement of catalyst performance would rely upon fine control of those properties, as well as on the contribution of the external surface to the overall reaction.

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