

Mesoporous Sulfonic Acids as Selective Heterogeneous Catalysts for the Synthesis of Monoglycerides

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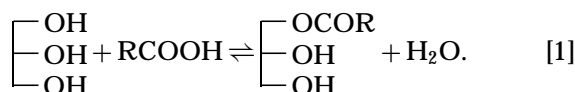
Glycerol was esterified with an equimolar amount of lauric acid to monolaurin using zeolites, sulfonic resins, and sulfonic mesoporous materials as catalysts. The latter were obtained by immobilization of 3-mercaptopropyl groups and oxidation with H₂O₂. In particular, fatty acid conversions, monoglyceride yields, and selectivities obtained with mesoporous (ordered, amorphous) sulfonic catalysts were compared with those of other heterogeneous or homogeneous catalysts. When using silica gel coated with propylsulfonic acids, high reaction rates are coupled to high monoglyceride yields, e.g., 53% mono yield for a 1:1 glycerol:lauric acid ratio. Minimizing the autocatalytic contribution of the fatty acid reactant is a critical issue. The influence of a number of reaction parameters is investigated. The mesoporous sulfonic catalysts are also employed in the esterification of propanediols and *meso*-erythritol, and for reactions with other fatty acids. © 1999 Academic Press

Key Words: esterification; monoglycerides; mesoporous materials; sulfonic acids.

INTRODUCTION

Monoglycerides (MG) consist of a hydrophilic head and a hydrophobic tail, which give them detergency characteristics. Therefore monoglycerides and their derivatives have a wide application as emulsifiers in food, pharmaceutical, and cosmetic industries (1, 2). They increase skin permeability and thus facilitate percutaneous drug absorption. At the moment they are also being considered for use in low-calorie margarines.

There are two major industrial routes to monoglycerides (3, 4). First, they are manufactured by glycerolysis, i.e., a base-catalyzed transesterification of triglycerides with glycerol at elevated temperature (e.g., 528 K). Second, monoglycerides may be produced by a direct, single esterification of glycerol with a fatty acid:



In order to lower the temperature of the latter process, an acid catalyst is required, e.g., sulfuric acid, phosphoric acid, or organic sulfonic acids such as Twitchell-type reagents (5).

However, as the three hydroxyl groups in glycerol do not strongly differ in reactivity, mixtures of mono-, di-, and even triglycerides are obtained with acid and base catalysis. Techniques for purification of monoglycerides, e.g., distillation, are limited to food applications since such process steps are expensive. Therefore it is highly desirable to improve the monoester yield by choosing favorable reaction conditions and designing an appropriate solid catalyst.

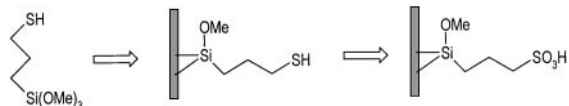
Acid 12-membered ring zeolites such as USY have been frequently used in this context (6–9). Even if such catalysts may exhibit a high monoester selectivity, the activity and consequently monoglyceride yield are sometimes low. Mesoporous silicas are more easily accessible for large reactants such as fatty acids and their esters; moreover, they can be modified in order to obtain specific properties, e.g., in redox or base catalysis (10–13). Recently, hybrid organic–inorganic silicas with immobilized sulfonic acids were used in acid-catalyzed reactions, such as the condensation of 2-methylfuran with acetone, and the esterification of D-sorbitol with lauric acid (14). By tuning the hydrophobic–hydrophilic balance of the mesoporous surface, major improvements of activity and selectivity were realized.

In this paper, we describe the synthesis of monolaurin via direct esterification of glycerol with lauric acid by means of siliceous mesoporous materials (silica gel, MCM-41, HMS) with Brønsted propylsulfonic acid groups. Such organofunctionalized mesoporous catalysts can be obtained via various routes (15–20), and the influence of the different methods on catalytic performance is described. The best mesoporous sulfonic catalysts offer a unique combination of high activity and high selectivity, which is not obtained with homogeneous or traditional heterogeneous catalysts. Finally, the applicability of the new catalysts to reactions of other polyols is demonstrated.

EXPERIMENTAL

Catalyst Preparation and Characterization

Synthesis of MCM-41. Siliceous MCM-41 was synthesized according to the literature (21). The starting



SCHEME 1

components include Ludox AS 40, 25% cetyltrimethylammonium chloride (CTMACl, Aldrich), and 20 wt% tetraethylammonium hydroxide (TEAOH, Aldrich). In the standard procedure 19.43 g TEAOH, 16.16 g CTMACl, and 20 ml H₂O were added to 19.27 g Ludox AS 40 under stirring (200 rpm). After 15 min, 32.33 g CTMACl and 20 ml H₂O were added to the reagent mixture. The synthesis gel was agitated for another 15 min and divided over two autoclaves. The hydrothermal step was carried out dynamically at 383 K. The resulting white product was filtered, washed extensively with hot H₂O and EtOH, dried at 333 K in air, and finally calcined at 823 K for 12 h.

Propylsulfonic acid mesoporous silicas. Mesoporous silicas were modified with a 3-mercaptopropyl group using (3-mercaptopropyl)trimethoxysilane (MPTS, Fluka) as the organosulfonic acid precursor (see Scheme 1). Deposition of MPTS in toluene onto a support with controlled water content results in a “coated” material with a monolayer of MPTS moieties, while less-covered “silylated” materials are obtained in dry conditions. Alternatively, in the synthesis of a HMS (hexagonal mesoporous silica), organofunctional groups are directly incorporated by “co-condensation” of MPTS and the main Si source (TEOS) in the presence of a neutral surfactant. Representative recipes for the different synthesis procedures are based on literature examples (14, 15, 18, 19) and are given below.

Coated MCM-41-SH. Calcined MCM-41 (3.5 g) is hydrated by refluxing for 3 h in 500 ml water and removed from the suspension by filtration. The wet filter cake is suspended in toluene (300 ml) in a Dean Stark apparatus, and H₂O/toluene is removed until a translucent suspension is obtained (approximately 100–150 ml). An excess of MPTS (20.0 g) is added and after stirring overnight without heating, the suspension is refluxed for 3 h. The coated material is then washed in a soxhlet extractor with CH₂Cl₂/Et₂O (50/50) for 24 h and air-dried.

Silylated MCM-41-SH. Calcined MCM-41 (3.5 g) is evacuated (overnight, 393 K, <10 Pa) and added to a solution of MPTS (7.4 g) in 300 ml toluene. Toluene was dried over zeolite 4A before use. After 4 h refluxing, the powder is collected and subjected to the same soxhlet purification as the previous material.

Coated silica gel-SH. This was prepared by modifying a chromatographic silica gel 60 (70–230 mesh, Fluka) with MPTS following the same method as used to coat MCM-41.

HMS-SH by co-condensation. HMS-SH was synthesized at room temperature from a gel containing 0.8 TEOS, 0.2 MPTS, 0.275 *n*-dodecylamine, 8.9 EtOH, 29.4 H₂O. The amine was first dissolved in the alcohol–water mixture. Then the TEOS-MPTS mixture was added and the mixture was stirred for 24 h. The amine template was extracted from the as-synthesized HMS-SH with boiling EtOH.

Oxidation procedure and acidification. Materials with immobilized mercaptopropyl groups were oxidized with H₂O₂ in a methanol–water mixture. Typically, 2.04 g of aqueous 35% H₂O₂ dissolved in three parts of methanol was used per g of material. After 24 h, the suspension was filtered, and washed with H₂O and EtOH. The wet material was resuspended (1 wt%) in acidified H₂O (H₂SO₄; 0.1 M) for another 4 h. Finally, the materials were extensively rinsed with H₂O, dried at 333 K, and stored in a desiccator. These acid-activated materials are denoted with the suffix -SO₃H. The oxidation procedure is slightly different from the one published previously (14). ¹³C-MAS-NMR proves that the current procedure leaves no -SH or -S-S- groups on the surface; the only signals are those of heterogenized -(CH₂)₃SO₃H.

Catalyst recuperation for reuse. After reaction the catalyst was allowed to sink to the bottom of the reactor at 333 K. After 5 h, the reaction liquor was decanted. The catalyst was resuspended in EtOH and centrifuged. This washing procedure was repeated five times, and the catalyst was finally dried at 333 K.

Characterization. XRD analyses were performed with a Siemens D5000 diffractometer. Loadings with organic groups (meq g⁻¹) were routinely determined from thermogravimetric analysis and were calculated based on the weight loss between 423 and 573 K. A Coulter Omnisorp 100 apparatus was employed for N₂ sorption experiments. A combination of XRD and sorption experiments was used throughout to evaluate the materials after modification or after reaction. XRD proved that the hexagonal structure of the ordered mesoporous materials did not undergo major changes. Some sorption characteristics are included in Table 1.

Other solid Brønsted acid catalysts. H-USY (CBV 720 from PQ; Si/Al = 14.5) was activated in a quartz tube under an air flow. The zeolite was heated with a slope of 1 K min⁻¹ and kept at 773 K for 12 h. Amberlyst-15 was a commercial product from Fluka (4.6 meq g⁻¹). This sulfonic acid resin was thoroughly washed with H₂O to remove all residual homogeneous acid and dried after Dean Stark extraction with toluene.

Esterification Procedures

First, 12.6 g glycerol and 27.4 g lauric acid (molar ratio = 1:1) were added to a 100-ml round bottom flask. After

TABLE 1
Esterification of Glycerol with Lauric Acid: Characteristics of the Catalysts, and Maximum Monoglyceride Yield with Homogeneous and Heterogeneous Catalysts^a

| Catalyst | Surface loading (meq g ⁻¹) | S_{BET}^b (m ² g ⁻¹) | V_p^b (ml g ⁻¹) | t (h) | Monoglyceride yield (%) |
|-------------------------------------|---|---|----------------------------------|------------|----------------------------|
| Coated silica gel-SO ₃ H | 0.7 | 240 | 0.48 | 8 | 51 |
| HMS-SO ₃ H | 1.8 | 943 | 0.32 | 10.2 | 52 |
| Silylated MCM-41-SO ₃ H | 0.7 | 650 | 0.38 | 24 | 53 |
| Coated MCM-41-SO ₃ H | 1.7 | 398 | 0.19 | 24 | 47 |
| Amberlyst-15 | 4.6 | — | — | 11.8 | 44 |
| H-USY | 1.1 | 757 | 0.49 | 23.5 | 36 |
| <i>p</i> TSA ^c | — | — | — | 4 | 44 |
| Blank | — | — | — | 22.3 | 24 |

^a Glycerol : lauric acid = 1 : 1, $T = 385$ K, 5 wt% catalyst relative to glycerol.

^b S_{BET} , BET surface, determined in a P/P_0 range between 0.05 and 0.2. V_p , volume of micro- and mesopores, determined from t -plots. For ordered mesoporous materials, V_p was calculated by extrapolation of the linear part of the t -plot between $t = 0.65$ and 0.95 nm. For silica gel, the t -interval 1.0–1.3 nm was used. For US-Y, micropores amount to 0.27 ml g⁻¹, and mesopores to 0.22 ml g⁻¹.

^c *p*-Toluenesulfonic acid; 0.5 wt% relative to glycerol.

heating to 385 K, the catalyst (typically 0.630 g, or 5 wt% with respect to glycerol) was added. The reaction mixture was stirred magnetically at 200 rpm. The temperature was held at 385 ± 1 K with a Eurotherm controller. Application of vacuum or flushing with nitrogen did not accelerate the esterification; apparently, water evaporation is facile at this high surface/volume ratio. Samples were taken every hour from the top fat layer and diluted into tetrahydrofuran (THF, 5 wt%) for chromatographic analysis. Simultaneously a second sample was diluted into CDCl₃ for NMR characterization.

Catalyst mass effects were investigated by stepwise decreasing the catalyst weight, while keeping all other parameters constant. The glycerol : lauric acid reactant ratio was raised by using 25.2 or 73.2 g glycerol (for 2 : 1 and 6 : 1 ratios) with the same amount of lauric acid (27.4 g) and catalyst (0.63 g). A 1 : 2 reactant ratio was achieved by doubling the lauric acid mass.

1.73 g 1,2-propanediol or 1,3-propanediol and 4.56 g lauric acid (molar ratio = 1 : 1) were reacted in a 25-ml round bottom flask in a heated oil bath. The temperature was brought at 385 K and 0.105 g catalyst was added, resulting in the same catalyst weight per mole of polyol as in the case of glycerol. In the case of *meso*-erythritol, an identical procedure was used, except for 2.84 g of the polyol and a reaction temperature of 403 K. Sample dilution was in THF for 1,3-propanediol, and in CDCl₃ for 1,2-propanediol and *meso*-erythritol.

Product Analysis

Gas chromatographic analyses were performed on a BPX-5 column (SGE) with an HP-5890 instrument with FID detector. Samples were injected "on-column" at 363 K.

The column was held at this temperature for 2 min and then heated to 613 K at a rate of 10 K min⁻¹. Standard compounds were from Larodan Lipids. ¹H-NMR was used to identify ester isomers and to determine ester distribution. Routine analyses were performed on a 300-MHz AMX-Bruker spectrometer. For better resolution, a 400-MHz spectrometer was occasionally used.

¹H-NMR shifts for reaction of lauric acid and 1,2-propanediol (only protons on C-1 and C-2): 1,2-diol: 3.91 (1, m), 3.63 (1, dd), 3.40 (1, dd); 1-laurate: 4.10 (1, dd), 4.03 (1, m), 3.93 (1, dd); 2-laurate: 4.98 (1, quintet of doublets), 3.67 (1, dd), 3.59 (1, dd); 1,2-dilaurate: 5.13 (1, quintet of doublets), 4.16 (1, dd), ~3.8–3.9 (1, dd). For reaction of glycerol and lauric acid: see Table 3.

RESULTS AND DISCUSSION

Influence of Catalyst Type on Glycerol Esterification; Catalyst Regeneration

In Fig. 1 the fatty acid (FA) conversion is plotted vs time for the reaction of glycerol and lauric acid. At the reaction temperature of 385 K, the blank reaction is not negligible. This is due to autocatalysis by the lauric acid reagent. The contribution of this spontaneous reaction is known to increase with temperature (9). Note, however, that even for monophasic reaction mixtures, e.g., oleyl alcohol and oleic acid, catalytic studies have been performed at much higher temperatures (22, 23). With the H-USY catalyst, the reaction is already appreciably faster. H-USY has been reported previously to be superior among zeolite catalysts (6–9). However, the mesoporous sulfonic acids are far more active materials. With a coated silica gel-SO₃H, the fatty acid is completely converted within 12 h. As

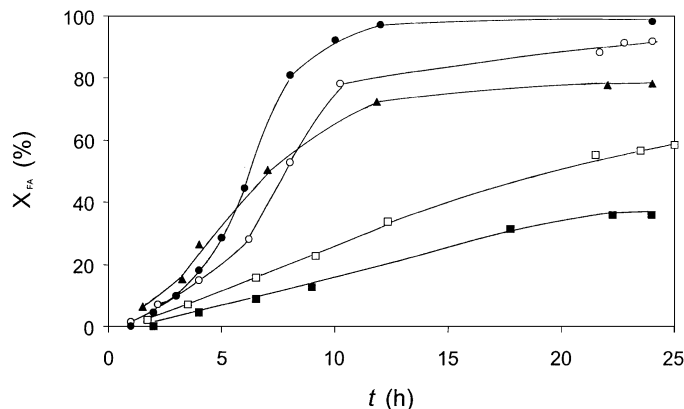


FIG. 1. Esterification of glycerol with lauric acid (385 K; glycerol:lauric acid = 1:1; 5 wt% catalyst): fatty acid conversion (X_{FA}) vs time for (●) coated silica gel-SO₃H, (○) HMS-SO₃H, (▲) Amberlyst-15, (□) H-USY (Si/Al = 14.5), and (■) blank reaction.

reported by Barrault *et al.* (24), commercial sulfonic resins such as Amberlyst-15 display a remarkable activity, even if the activity is somewhat lower than for the silica-gel-based catalyst.

Among the functionalized materials, the coated silica gel-SO₃H is the more active catalyst on a weight basis, followed by the HMS-SO₃H material prepared by co-condensation (Fig. 2). Activities of coated MCM-41-SO₃H and silylated MCM-41-SO₃H are lower. Loadings, BET surfaces, and pore volumes are given in Table 1. The pore volumes V_p , as determined by the t -plot method, include the primary mesopores and some microporosity for the ordered mesoporous materials. For silica-gel-based materials, V_p includes all, mostly noncylindrical mesopores. There is no clear relation between the concentration of -SO₃H groups and the activity. However, it is striking that the catalyst with the

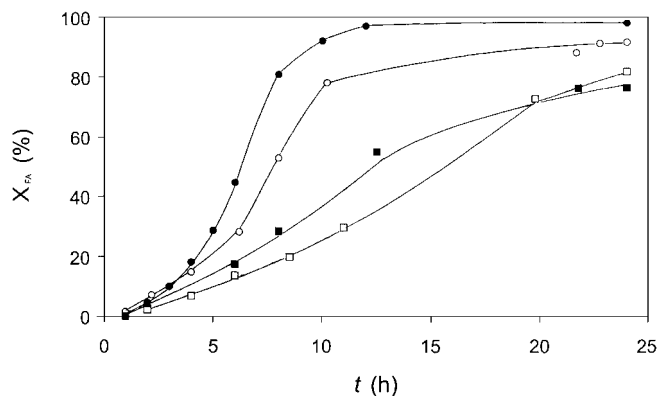


FIG. 2. Esterification of glycerol with lauric acid (385 K; glycerol:lauric acid = 1:1; 5 wt% catalyst): fatty acid conversion (X_{FA}) vs time for (●) coated silica gel-SO₃H, (○) HMS-SO₃H, (■) coated MCM-41-prop-SO₃H, and (□) silylated MCM-41-prop-SO₃H.

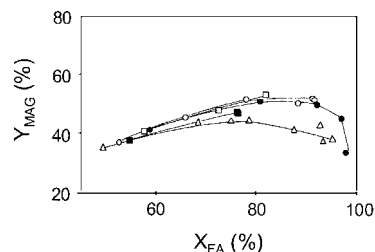


FIG. 3. Esterification of glycerol with lauric acid (385 K; glycerol:lauric acid = 1:1; 5 wt% catalyst): monoglyceride yield (Y_{MAG}) vs fatty acid conversion (X_{FA}): (●) coated silica gel-SO₃H, (○) HMS-prop-SO₃H, (■) coated MCM-41-prop-SO₃H, (□) silylated MCM-41-prop-SO₃H, and (△) PTSA (0.5 wt%).

most open structure, i.e., with the smallest S_{BET}/V_p ratio, has the highest activity (coated silica gel-SO₃H).

When the MG yields of the different catalysts are examined, it is found that they are determined by conversion as well as by catalyst type. Maximum MG yields are shown in Table 1, together with the reaction times needed. Plots of the MG yield as a function of conversion are given in Fig. 3. For each catalyst type, maximum yields are reproducible within 1–2% for consecutive experiments. This proves that there is a statistically highly significant difference between the functionalized mesoporous materials on the one hand and the homogeneous reference catalyst (*p*-toluenesulfonic acid, *p*TSA) on the other hand. MG yields only start to decrease at a point close to complete conversion. This maximum is caused by subsequent esterification of MG with remaining FA, and by the tendency of the reaction mixture to equilibrate between mono-, di-, and triglycerides. The latter element is a reasonable assumption as transesterification is known to be acid catalyzed (4).

In the blank reaction and in the presence of H-USY, a maximum MG yield is not obtained within 24 h. This is due to the low FA conversions; even with H-USY, selectivity after 24 h (58% conversion) still amounts to 62%. *p*TSA is a highly active homogeneous catalyst, but the eventual MG yield (44%) is lower than for sulfonic mesoporous materials. The latter all give reproducible MG yields between 51 and 53%. Only the coated MCM-41-SO₃H is an exception, probably because of lower activity or desactivation. Thus a maximum yield is not reached, implying that the contribution of the less selective blank reaction gets more important.

In order to investigate catalyst stability and heterogeneity, the organomodified catalysts were reused. A typical result is given in Fig. 4, for a coated MCM-41-SO₃H. For the regenerated catalyst, conversion and MG selectivity are practically indistinguishable from those of a freshly synthesized material. Such results strongly argue against a contribution of leached sulfonic acid groups or sulfuric acid to the observed catalytic activity.

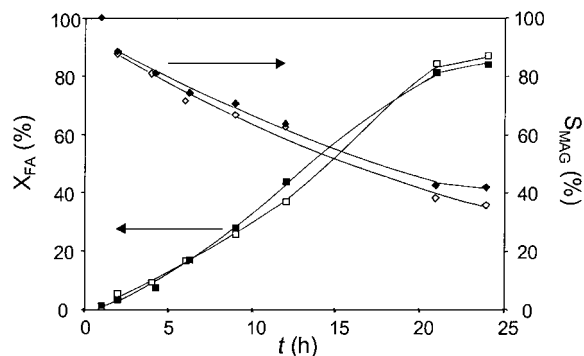


FIG. 4. Catalyst reuse in reaction of glycerol with lauric acid (5 wt% coated MCM-41-SO₃H): conversion (X_{FA}) vs time for (■) fresh catalyst and (□) reused catalyst; monoglyceride selectivity (S_{MAG}) for (◆) first and (◇) second run.

Influence of Reaction Parameters

Some reaction parameters were examined, with an emphasis on those that may influence the MG yield or may decrease the required reaction time.

Effect of catalyst concentration. The amount of catalyst was varied stepwise between 0 and 5%, for a 1 : 1 glycerol : lauric acid ratio. Typical data are presented in Fig. 5, for a silylated MCM-41-SO₃H. If the blank contribution to the reaction is subtracted, a monotonous increase of the conversion with the catalyst concentration is observed. This implies that transfer of reactants from one liquid phase to another is not rate limiting; in such a case, the rate would be independent of catalyst mass.

Effect of the glycerol : lauric acid ratio. Doubling the initial amount of lauric acid (1 : 2 ratio) does not have a major effect on the acid conversion percentage as a function of time, implying that ultimately twice as many moles of fatty

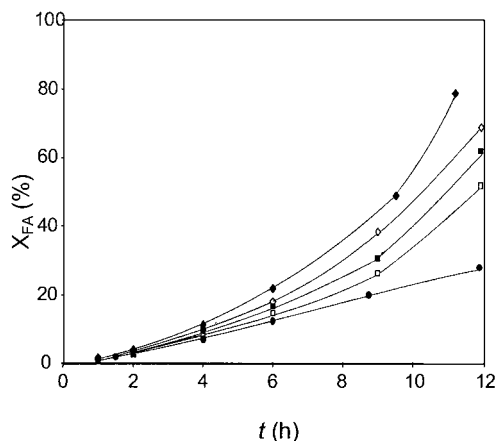


FIG. 5. Esterification of glycerol with lauric acid: influence of the catalyst mass (wt% silylated MCM-41-SO₃H) on fatty acid conversion (X_{FA}): (◆) 5 wt%, (◇) 3.75 wt%, (■) 2.5 wt%, (□) 1.25 wt%, and (●) blank reaction.

acid are converted (Fig. 6a). However, a marked decrease in MG selectivity is observed (Fig. 6b). On the contrary, when alcohol : acid ratios are raised, there is a larger chance that a fatty acid reacts with glycerol than with a monoglyceride, and this should increase the MG selectivity. As anticipated, a steady selectivity increase is observed when going from a 1 : 1 to 6 : 1 reactant ratio. Simultaneously, the FA conversion rate decreases, probably because of a shift in the adsorption equilibrium at the active site.

Effect of reaction temperature. Temperature effects on FA conversion and MG yield are illustrated for silylated MCM-41-SO₃H in Fig. 6. At 385 K the reaction is completed after 15 h, while this takes up to 48 h at 363 K. Effects on MG selectivity are minor. Nevertheless, the lighter color of the reaction mixture at 363 K suggests that at lower temperature, fewer degradation products are formed from glycerol.

Addition of an emulsifier. Even with coated silica gel-SO₃H, FA conversion is slow, unless a sufficient amount of emulsifying monoglyceride is present. This is proved by starting the reaction with 90 mol% lauric acid and 10 mol% monolaurin (385 K, 5 wt% catalyst). The conversion–time and selectivity–conversion plots can be perfectly superimposed on those of the standard reaction when the x -axes for time or conversion are shifted with 3 h or with 10%, respectively. Note nevertheless that conversion of the first 60 mol% of fatty acid only takes 5 h, as opposed to 7.5 h in the absence of emulsifier. In terms of applicability, the addition of a limited amount of MG product has the prime advantage that the slow initial phase in the reaction with the organomodified material is substantially shortened.

Detailed Analysis of Conversion and Selectivity for Different Catalysts

In order to rationalize activities and selectivities in glycerol esterification, one should consider the physical behaviour of the reaction mixture. Glycerol and lauric acid are immiscible, and their mutual solubilities are low. As soon as the esterification has formed enough emulsifying monoglycerides, a w/o-emulsion is formed, resulting in an abrupt visual homogenization and a sudden increase of the interfacial area A_i (25). This homogenization occurs at a FA conversion between 15 and 20%.

When the reaction mixture is considered to consist of an oil phase, a (solubilized) glycerol phase, and an interface, the reaction rate R_{tot} (mol% FA reacted h⁻¹) is

$$R_{tot} = R_o + R_g + R_i, \quad [2]$$

where R_o , R_g , and R_i are the contributions by the fatty acid phase, glycerol phase, and interface. R_i is only significant after micellization. Besides the activity of the heterogeneous catalyst or the $pTSA$ (R_{cat}), the presence of catalytic carboxylic acid groups in one of the reactants causes

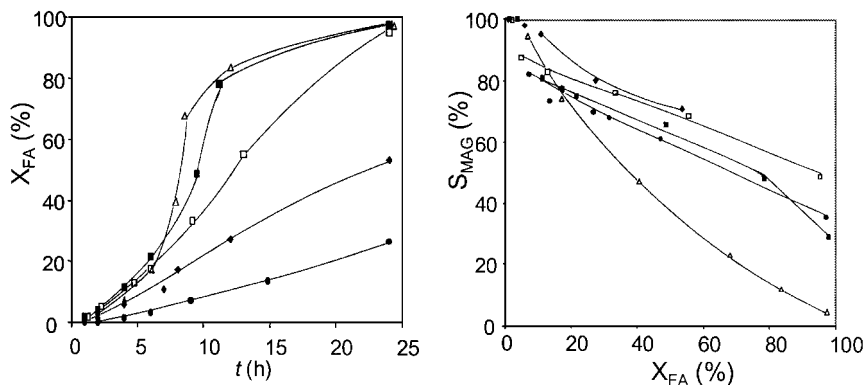


FIG. 6. Influence of glycerol : acid ratio and temperature on glycerol esterification with lauric acid: (left) acid conversion (X_{FA}) and (right) mono-glyceride selectivity (S_{MAG}). (Δ) 1 : 2, 385 K; (\blacksquare) 1 : 1, 385 K; (\square) 2 : 1, 385 K; (\blacklozenge) 6 : 1, 385 K; and (\bullet) 1 : 1, 363 K. Catalyst: 5 wt% silylated MCM-41-SO₃H.

spontaneous reaction (R_{self}) (26). Activity due to acid leached from the heterogeneous catalyst can be excluded based on the regeneration experiment of Fig. 4. Thus each term in (2) can be written as

$$R_x = R_{cat,x} + R_{self,x}. \quad [3]$$

Expressions for such terms may be found in the literature (26–28). Because the solubility of the autocatalytic lauric acid in the glycerol phase ($[FA]_g$) is very low, spontaneous reaction mainly occurs in the fat phase or at the interface ($R_{self,g} \approx 0$). In Fig. 7, the contribution of $R_{self,o}$ to the blank reaction (labeled A) is easily recognized at the start of the reaction. Spontaneous reaction increases only slightly after micellization, indicating that $R_{self,i}$ is small.

Visual control in the early phase of the reaction proves that all heterogeneous catalysts, including the sulfonic mesoporous materials, are dispersed in the polar glycerol phase. Therefore only three significant terms remain for a

heterogeneously catalyzed reaction,

$$\begin{aligned} R &= R_{self,o} + R_{cat,g} + R_{cat,i} \\ &= k_{self,o} \cdot [\text{glycerol}]_o \cdot [FA]_o^2 V_o \\ &\quad + k_{cat,g} \cdot [\text{catalyst}]_g \cdot [\text{glycerol}]_g \cdot [FA]_g \cdot V_g \\ &\quad + k_{cat,i} \cdot [\text{catalyst}]_{i,S} \cdot [\text{glycerol}]_{i,S} \cdot [FA]_{i,S} \cdot A_i, \quad [4] \end{aligned}$$

where V_o and V_g are the volumes of the fat and glycerol phases. Before the CMC is reached, the conversion increases linearly with time within experimental error for all catalysts. At this stage, the activity of the organomodified materials is almost twice as high as that of the H-USY zeolite (Table 2). However, the major difference between the zeolite and the organomodified materials only becomes apparent after micellization. With a coated silica gel-SO₃H, the rate (i.e., the slope of the conversion–time plot) more than triples after reaching the CMC! (Table 2; Fig. 7C). This indicates that the organomodified material is particularly capable of catalyzing the reaction at the interface. A zeolite such as H-USY only displays a slight rate increase at the CMC (Table 2). This suggests that the zeolite catalyst is less active at the phase boundary, which might be related to a smaller hydrophobicity (Figure 7B).

TABLE 2

Esterification of Glycerol with Lauric Acid Catalyzed by Different Heterogeneous Catalysts: Initial Fatty Acid Conversion Rates (mol% h⁻¹) and Conversion Rates after Emulsification^a

| Catalyst | Initial rate (mol% h ⁻¹) ^b | Rate after emulsification (mol% h ⁻¹) |
|-------------------------------------|---|---|
| Coated silica gel-SO ₃ H | 4.8 | 14.8 |
| HMS-SO ₃ H | 4.6 | 12.6 |
| Amberlyst-15 | 4.5 | 7.7 |
| H-USY | 2.8 | 2.9 |
| Blank | 1.8 | 2.0 |

^a 385 K; glycerol : lauric acid = 1 : 1; 5 wt% catalyst.

^b Rate below 10% fatty acid conversion.

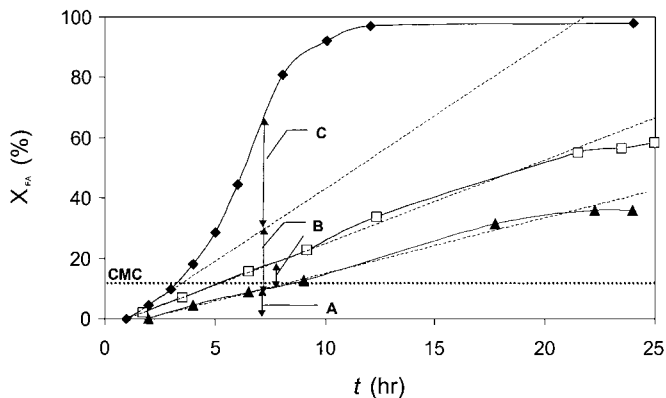


FIG. 7. Esterification of glycerol with lauric acid (385 K; glycerol : lauric acid = 1 : 1; 5 wt% catalyst). Kinetic analysis: (\blacklozenge) coated silica gel-SO₃H, (\square) H-USY, and (\blacktriangle) blank reaction: (A) blank reaction in the fatty acid phase; (B) contribution of catalyst to conversion in the glycerol phase; (C) catalytic contribution at the interface.

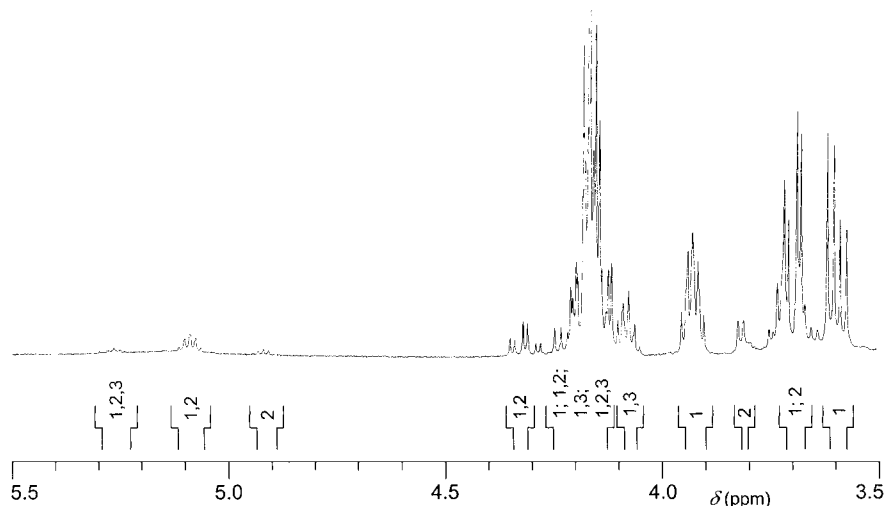


FIG. 8. $^1\text{H-NMR}$ -spectrum of glyceride backbone with typical shifts (ppm) for a mixture of mono-, di-, and triglycerides: 1-mono-: 3.59, 3.70, 3.92, 4.14, 4.20; 2-mono-: 3.82, 4.93; 1,2-di-: 3.72, 4.32, 5.08; 1,3-di-: 4.09, 4.13–4.28; tri-: 4.15, 4.30, 5.26.

Such observations also allow us to rationalize the selectivity differences of Fig. 3. A homogeneous organic catalyst such as *p*TSA dissolves well in the fat phase ($R_{\text{cat,o}} \neq 0$). Consequently reaction of the residual FA in the fat phase with the MG in the same phase is stimulated at the expense of reaction of FA from the fat phase with glycerol from the polar phase. Thus the presence of acid *p*TSA catalyst in the fat phase leads to more pronounced formation of diglycerides and even triglycerides. For analogous reasons, the blank reaction has a similar, rather low MG selectivity. In contrast, higher MG selectivities can be obtained with heterogeneous catalysts, as these are only catalytically active at the interface or in the glycerol phase, where the MG concentration is low.

Detailed $^1\text{H-NMR}$ Analysis of the Glycerol-Lauric Acid Reaction

While GC is an excellent routine technique, it does not allow us to fully identify different ester isomers nor to esti-

mate reliably their distribution. $^1\text{H-NMR}$ signals of alcohol α -hydrogen atoms shift downfield upon esterification, and signals arising from secondary carbon atoms appear downfield in comparison to those of primary carbons. Therefore NMR was employed to study in detail the fate of the polyol backbone during the formation of mono- and polyesters.

A typical 400-MHz $^1\text{H-NMR}$ spectrum of a late sample from the glycerol-lauric acid reaction shows signals of α - and β -monoglycerides; 1,2- and 1,3-diglyceride; and triglyceride (Fig. 8). Characteristic shifts in the glycerol backbone corresponding to each isomer are given in Table 3. It is seen that esterification not only affects the α -hydrogens, but also causes a slight shift increment for β -hydrogens. Note also that the two α -hydrogen atoms at position 1 (or at 3) are often not chemically equivalent. This is nicely illustrated in the spectroscopic fingerprint of α -monoglyceride, which contains four doublets of doublets and one quintet. Comparison between GC and integrated $^1\text{H-NMR}$ spectra shows excellent agreement, even if it is observed that NMR offers better accuracy at low conversions.

TABLE 3

$^1\text{H-NMR}$ Signals of the Polyol Residue in Esterification of Glycerol with Lauric Acid^a

| δ (ppm) | Glyceride | | | | |
|----------------|--------------|--------------|---------------|--------------|--------------|
| | 1-mono- | 2-mono- | 1,2-di- | 1,3-di- | tri- |
| <3.65 | 3.59 (1, dd) | | | | |
| 3.65–3.80 | 3.70 (1, dd) | | 3.72 (2, d) | | |
| 3.8–3.88 | | 3.82 (4, d) | | | |
| 3.88–4.0 | 3.92 (1, qi) | | | | |
| 4.0–4.4 | 4.14 (1, dd) | | ~4.25 (1, dd) | 4.07 (1, qi) | 4.15 (2, dd) |
| | 4.20 (1, dd) | | 4.32 (1, dd) | 4.17 (4, m) | 4.30 (2, dd) |
| >4.8 | | 4.93 (1, qi) | 5.08 (1, qi) | | 5.26 (1, qi) |

^a d, doublet; dd, doublet of doublets; qi, quintet; m, multiplet.

TABLE 4

Esterifications of Various Polyols and Fatty Acids Catalyzed by Coated Silica Gel-SO₃H^a

| Polyol | Fatty acid | <i>t</i> (h) | FA conversion | Monoester(s) selectivity | Other products |
|--------------------------------------|-------------|--------------|---------------|--------------------------|----------------|
| 1,2-Propanediol | Lauric acid | 1 | 16 | 100 | — |
| | | 3 | 68 | 83 | 1,2-Diester |
| | | 6 | >99 | 63 | 1,2-Diester |
| 1,3-Propanediol | Lauric acid | 1 | 95 | 60 | 1,3-Diester |
| | | 3 | >99 | 47 | 1,3-Diester |
| | | 5 | >99 | 37 | 1,3-Diester |
| <i>meso</i> -Erythritol ^b | Lauric acid | 4 | 10 | 85 | Diesters |
| | | 11 | 70 | 55 | Diesters |
| Glycerol | Oleic acid | 13 | 32 | 55 | Diesters |
| | | 16 | 39 | 49 | Diesters |
| | | 23 | 68 | 45 | Diesters |

^a Polyol : fatty acid = 1 : 1; *T* = 385 K; 4.6 g of catalyst per mol of polyol. For further details, see Experimental.

^b *T* = 403 K.

The composition of the monoglyceride pool in reactions at 385 K is 91 ± 1% α and 9 ± 1% β , whatever the catalyst or progress of the esterification. Even the initial sample in the reaction with 10% added pure α -monolaurin immediately displays this α - β distribution, which is in agreement with literature data on the temperature-dependent equilibrium between α - and β -monoglycerides (4). Analogous observations hold for the distribution over 1,2- and 1,3-dilaurins, with a 1,2 : 1,3 ratio of 0.4. Under standard reaction conditions (385 K; glycerol : lauric acid = 1 : 1; 5 wt% catalyst), formation of trilaurin (δ = 5.26) is negligible even after 24 h.

Esterification with Other Poly-alcohols, or Fatty Acids

Several other esterifications were performed using the most active catalyst, coated silica gel-SO₃H. 1,2-Propanediol reacts to form mono- and diesters (Table 4). The α : β monoester ratio is 10 throughout the reaction, indicative of intramolecular transesterification. The eventual monoester yield is 63%. With 1,3-propanediol, the reaction is complete already after 3 h. The propanediols are expected to be more soluble in the FA phase, and this explains the higher rates than for glycerol. Reaction of *meso*-erythritol gives a complex reaction mixture. Based on NMR, dominant products are 1- and 2-monoesters, but the different isomeric diesters are also formed.

When oleic acid was used in a 1 : 1 ratio with glycerol, a conversion of 68% was obtained after 23 h, while the monoglyceride yield was 31%. Again a constant α - to β -monoglyceride ratio of 10 was observed. As oleic acid has even less affinity for glycerol than lauric acid, not only the background reaction but also the micellization-dependent catalyzed reaction is slower. The ¹H-NMR spectrum remained identical in the domain between 5 and 6 ppm,

proving that the catalyst does not effect any *cis-trans* isomerization.

GENERAL DISCUSSION

Direct esterification of glycerol with higher fatty acids is usually conducted at high temperatures, in order to increase the mutual solubilities of the immiscible reactant phases. The resulting gain in conversion, however, is counterbalanced by a selectivity loss. This problem can be circumvented by working at relatively low temperature and with an active catalyst, under the condition that the catalytic activity resides in the glycerol phase. Thus, in order to maximize the MG yield, it is essential to keep the catalyst out of the fatty acid phase before as well as after micellization.

Zeolites such as USY produce virtually exclusively MG in the initial stage of the reaction, but their activity is low (9). This is a serious drawback, as the eventual monoglyceride yield is evidently the product of conversion and selectivity. A high activity is, moreover, desirable to overcome the background reaction with its intrinsically low MG selectivity. The best sulfonic mesoporous material, coated silica gel-SO₃H, has an activity that is far superior to that of USY, while preserving an excellent selectivity. This is largely due to the capability of this material to increase the reaction rate after micellization, as illustrated in Fig. 7. This rate increase is not due to acid leaching, as was shown in Fig. 4. Recent literature reveals at least two other examples of organomodified surfaces that efficiently catalyze reactions between two immiscible phases. Pinnavaia describes the use of quaternary ammonium-exchanged hectorite, which functions as a phase transfer catalyst in halide exchange reactions (29). A silica surface with bound polyoxyethylene chains was

employed as a catalyst support in the epoxidation of olefins with H_2O_2 (30).

Regarding the relation between activity and structure of the mesoporous material, higher concentrations of surface groups do not necessarily lead to the highest conversions; in fact, the most active catalyst (coated silica gel- SO_3H) has only 0.7 mmol SO_3H groups g^{-1} , as estimated by TGA. Rather a good accessibility of the active sites seems important. Even if the average pore diameter decreases gradually upon going from an amorphous structure to a silylated or a coated ordered mesoporous material, we have not been able to observe effects of product shape selectivity, mainly because the less selective background reaction becomes more important as the catalysts' activity decreases.

In conclusion, sulfonic mesoporous materials catalyze the biphasic glycerol esterification, coupling large conversion rates to high monoglyceride yields. With the same catalysts, a wide range of esters can be synthesized starting from various polyols and acids.

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