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Direct esterification of olive-pomace oil using mesoporous silica supported sulfonic acids

F. Alrouh [a,*], A. Karam [b], A. Alshaghel [a], S. El-Kadri [a]

[a] Department of Chemistry, Faculty of Sciences, University of Aleppo, P.O. Box 8276, Aleppo, Syria
[b] Department of Chemistry, Faculty of Sciences, University of Al-Baath, P.O. Box 77, Homs, Syria

Abstract Mesoporous silica MCM-41 and SBA-15 containing propyl sulfonic acid groups were synthesized according to the literature and were characterized by X-ray diffraction, N$_2$ adsorption and the H$^+$ exchange capacities of the sulfonic acid groups were titrated. The esterification reaction of glycerol with olive-pomace oil has been carried out by using prepared functionalized mesoporous silica (MCM-41 and SBA-15) as catalysts. It has been monitored by GC two fatty acids (palmitic and oleic acids) as reactants in olive-pomace oil and their related monoacylglycerols (Glycerol monopalmitate GMP and monooleate GMO) as reaction product. The catalytic activities of the functionalized mesoporous silica were compared with commercial catalysts, these included homogeneous catalysts (p-toluenesulfonic acid) and heterogeneous catalysts (Amberlyst-15). The total yield of monoacylglycerols (GMO + GMP) was nearly 40%. Remarkably, we found that MCM-41-SO$_3$H was recycled at least 3 times without any loss of activity.

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1. Introduction

There are several reasons for the global interest in the chemical industry based on vegetable oils as alternative raw materials that replace the fossil oil: – The low toxicity and the fully biodegradability of vegetable oils are exact opposite to the raw materials from fossil oil that are contained in their structure cycles of benzene, phenols or substituted chains which are difficult to biodegrade, are leading to increase the pollution of the environment with a various industrial wastes. – An inexhaustible source for the preparation of raw materials for the industry, on the contrary, declining the global stocks of fossil oil with the time and we have to wait to compensate it for thousands of years (Scrimgeour, 2005; Clark and Deswarte, 2008; Eissen et al., 2002; Barrault et al., 2002; Clark and Macquarrie, 2002; Clark, 1999; Anastas and Warner, 1998).

One of the vegetable oil is the olive oil. In fact, Syria is a rich country in olive oil. In 2005, it was classified as the sixth in the world (International Olive Oil Council). The production of olive oil produces olive "pomace" as by-product which contains oil. This olive-pomace oil is distinguished by high acidity ($\approx$50.0 w/w%). The production of this oil in Syria is about 14 thousand tons per year.

* Corresponding author. Tel.: +963 933 12 34 80; fax: +963 21 26 33 136.
E-mail addresses: fadirouh@hotmail.com (F. Alrouh), akaram@al-baath-univ.edu.sy (A. Karam).
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Glycerol is industrially available in large scale as a by-product from the production of biodiesel. The glycerol esters of fatty acids are valuable chemical compounds that find important applications in pharmaceutics, foods, cosmetics and detergent industries. Commercial production of glycerol monoesters is achieved by acid catalyzed esterification of glycerol with fatty acids, involving the use of p-toluenesulfonic acid (p-TSA) or sulfuric acid as catalysts, or by base catalyzed triglycerides transesterification. Mixtures of mono-, di- and triglycerides are usually obtained with different compositions depending on process constraints and on the chemical properties of the reagents. Recently, alternative methods involving immobilized enzymes were also reported and seemed to be an available process despite a relatively complex work up.

To put in use the olive-pomace oil and glycerol, there are two methods: the first one is the reducing of the free fatty acid in oil by enzymatic glycerolysis to use it as olive oil (Fadiloğlu et al., 2003), and the second one is the production of monoacylglycerols of the fatty acid from the olive-pomace oil (Shrestha et al., 2010; Moquin and Temelli, 2008).

We are now reporting an environmentally friendly direct esterification of olive-pomace oil with glycerol in the presence of acid homogeneous and heterogeneous catalysts. We are also describing the preparation of a series of catalysts contained of sulfonic group constructed on mesoporous SBA-15 and MCM-41 silica.

2. Experimental procedure

2.1. Material and methods

Glycerol (purity > 99%) was supplied by BDH. Silica precursors, tetraethoxysilane (TEOS) and mercaptopropyltrimethoxysilane (MPTMS), hexadecylammonium bromide, Pluronic 123 were provided by Merck, Sigam–Aldrich and Alfa-aeser. olive-pomace oil was provided by Bouchra for detergents.

2.2. Treatment of olive-pomace oil

The treatment of olive-pomace oil was realized according to the literature (FIRESTONE, 2005) 100 g of olive-pomace oil were taken and washed two times with a 100 ml solution of (10%) phosphoric acid and after each time, centrifugation of mixture was got rid of the gums. Then, the saponification of the resulting mixture was realized by 200 ml of 12% potassium hydroxide solution. The solution was stirred mechanically for 24 h at 60–70 °C. After the confirmation of the medium alkalinity, the fatty acids were liberated by adding 200 ml of 2 N HCl, the mixture was stirred for 2 h and then the oily layer

was separated and the acidity is removed by washing with a saturated saline solution containing (1%) sodium bicarbonate for several times. Then, 200 ml of diethylether were added to the resulting oil, and were dried by anhydrous sodium sulfate, and after filtration, the diethylether was evaporated, the resulting material was kept in an opaque flacone under an atmosphere of nitrogen in the fridge until use.

2.3. Catalyst Preparation

2.3.1. Synthesis of MCM-41-SO₃H

Siliceous MCM-41 was synthesized according to the literature (Dîaz et al., 2001; Dîaz et al., 2000; Mbaraka et al., 2003). In a typical synthesis procedure, an aqueous solution of cetyltrimethylammonium bromide (C_{16}-TMA, 3.33 g) in 200 ml of mixture (MeOH:H_2O, 70:30), (Solution A), is prepared at room temperature. To this solution, a mixture of Tetraethylorthosilicate (TEOS, 18.7 g, 90 mmol) and 3-mercaptopropyltriethoxysilane (MPTS, 1,96 g, 10 mmol, 10% molarity of silica precursor) was added slowly with violent stirring for 1 h. Then, 10 ml of 2.7 N NaOH (pH 10) were added to the mixture, a white precipitate was formed with the violent stirring at room temperature for 24 h. The final gel was transferred into Teflon autoclave and put in an oven at 105–110 °C for four days, the precipitate was filtrated, was washed with distilled water for several times and was dried at 40 °C for 24 h. The surfactant inside the pores of these materials was completely removed by stirring the precipitate with 225 ml of HCl/EtOH (1:10) mixture for 1.5 g precipitate under reflux for 24 h, the precipitate then was washed for several times with a hot distilled water until having a filtrate without surfactant (verified by dimidium bromide indicator). This procedure is summarized in Fig. 1.

The thiol-functionalized samples were then converted into the sulfonic acid groups by oxidation of –SH groups with aqueous H_2O_2 as an oxidant with a ratio of 20:1 liquid to solid at room temperature for 24 h. The precipitate was filtrated, was treated with 50 ml of 0.055 N H_2SO_4 for 30 min, was washed with distilled water for several times and was dried at 40 °C for 2 days (Fig. 2).

2.3.2. Synthesis of SBA-15-SO₃H

Pluronic (4 g) was dissolved in 125 g of aqueous HCl (1.9 M) and stirred at room temperature. The solution was then heated at 40 °C before addition of (7.7 g, 37 mmol) TEOS. After stirring for 30mn, MPTS (0.74 g, 3.7 mmol) and (3.8 ml) of 35% H_2O_2 were added. The solution was then stirred for 24 h at 40 °C and aged into a Teflon autoclave for an additional 24 h at 100 °C. The resulting solid was finally collected by filtration
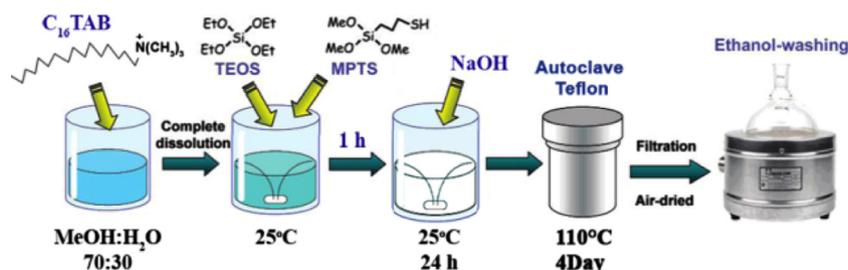
Figure 1   Preparation of MCM-41-SH.
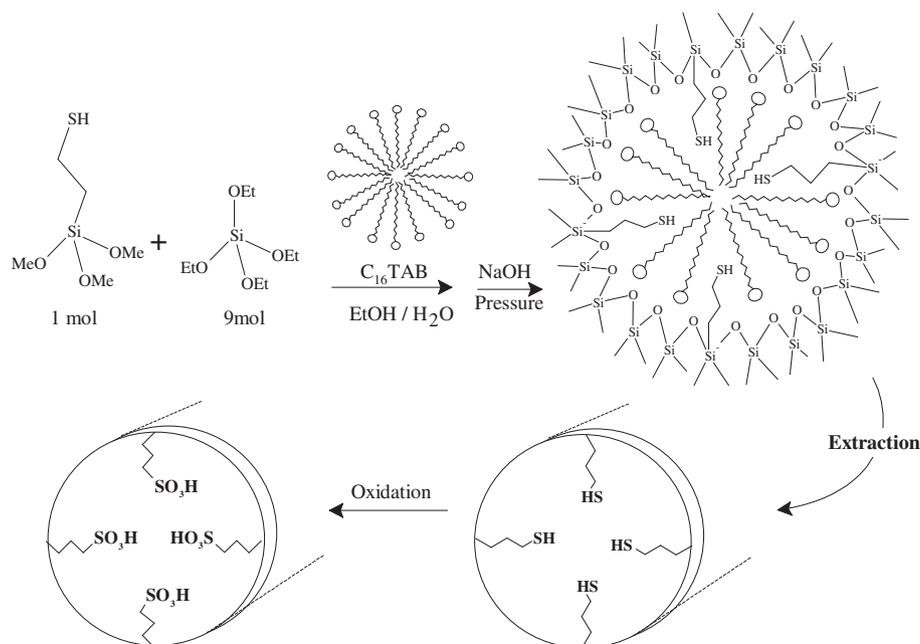
Figure 2   Preparation of MCM-41-SO$_3$H.
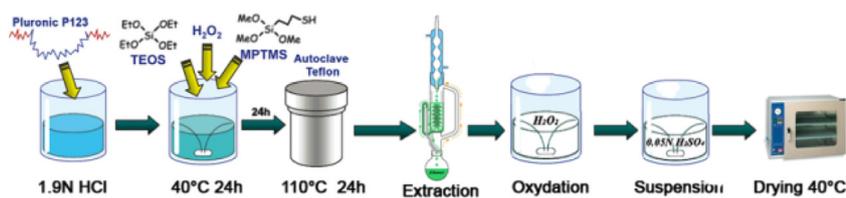
Figure 3   Preparation of SBA-15-SO$_3$H.

and thoroughly washed with water. The recovered SBA-15-SO$_3$H was dried in an oven at 50 °C (10–1 mm Hg) for 18 h.

Removal of the Pluronic P123 was carried out by soxhlet extraction over boiling ethanol for 24 h affording the hybrid organic–inorganic SBA-15-SO$_3$H. The resulting solid was washed for several times with distilled water until having a filtrate without surfactant (verified by potassium ferrocyanide). To be sure of the oxidation of all thiol groups, the same procedure in MCM-41 was applied (Fig. 3).

2.4. Characterization of solids

The properties of the extracted and oxidized catalysts (MCM-41, SBA-15) were examined by X-ray diffraction, N$_2$ adsorption and the ion capacities of the sulfonic acid groups.

Low angle XRD was used to determine the structure of the materials, with BRUKER AXS D5005 apparatus by employing Cu $K\alpha$ radiation. The textural properties (surface area and pore diameter) of the extracted and oxidized catalysts were determined by the adsorption/desorption of nitrogen which was carried out at 77 K using a MICROMERITICS TRI-STAR apparatus.

The titration of the sulfonic acid groups in catalysts was carried out with METROHM 794 BasicTitrino. Infrared spectra of the prepared catalysts were recorded (using KBr) in the range 4000–400 cm^{-1} using a JASCO 4100 FTIR spectrometer.

3. Results and discussion

The X-ray diffraction (XRD) patterns (Fig. 4) of two prepared oxidized catalysts showed an intense diffraction peak corresponding to the d_{100} reflection at 2θ 2.01° and 0.99° for prepared MCM-41 and SBA-15, respectively, which is accompanied by weaker reflections at 2θ close to 4.0° for
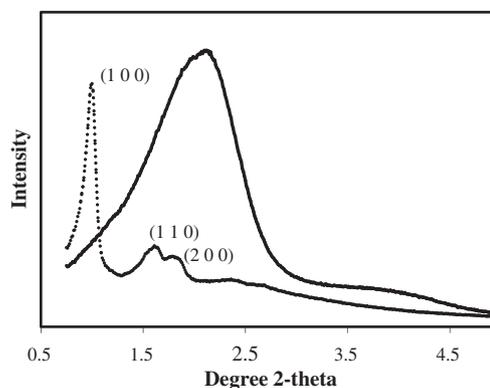
Figure 4   XRD patterns of the prepared catalysts (–) MCM-41-SO$_3$H, (. . .) SBA-15-SO$_3$H.

Table 1   Textural and physicochemical properties of the functionalized mesoporous catalysts.

Sample	BET surface area $m^2 g^{-1}$	Unit cell parameter (XRD) Å	Pore diameter (BJH) Å	H^+ exchange capacity $mmolH^+/g$
MCM-41	833.7	48.31	32.2	0.504
SBA-15	726.1	102.44	70.4	0.698

MCM-41 and 1.56–1.75°, corresponding to the d_{110} and d_{200}, which are the spacing of the hexagonal symmetry *p6mm* of MCM-41 and SBA-15 (Dinnebier and Billinge, 2008; Dîaz et al., 2000). This indicates that only one phase was obtained and the unit cell parameter $(a_0 = 2d_{100}/3^{1/2})$ of these materials is shown in (Table 1).

Nitrogen adsorption and desorption isotherms were described in Fig. 5, showed typical IV isotherm type according to IUPAC. (Sing et al., 1985) Monolayer adsorption on the walls of the mesopores is responsible for N_2 uptake at low relative pressures ($P/P_0 < 0.3$), so specific surface areas were calculated following the BET procedure using P/P_0 at this area of isotherms, and pore size distribution was obtained by using the BJH pore analysis applied to the desorption branch of the nitrogen adsorption /desorption isotherm. As shown in (Fig. 5), narrow pore size distributions were obtained.
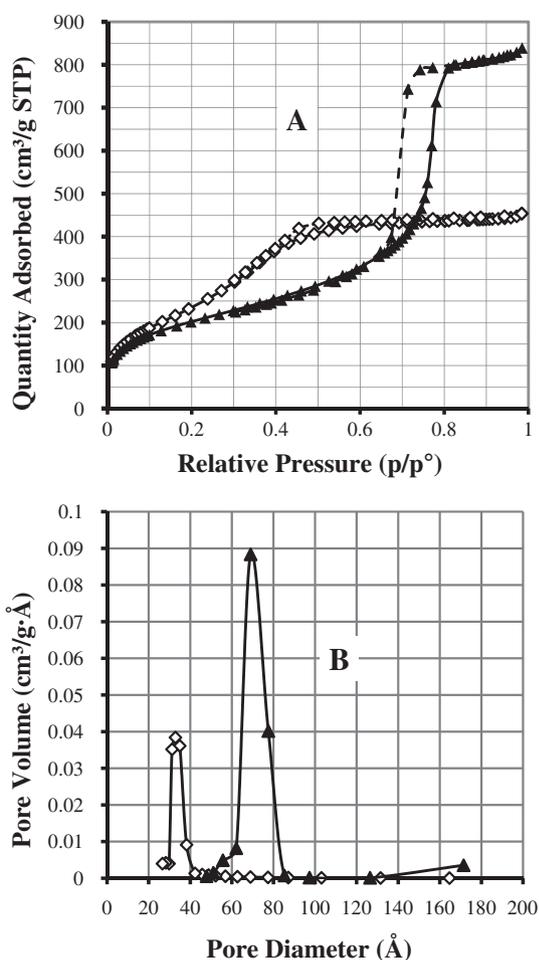
The H^+ exchange capacities of the sulfonic acid groups in the functionalized mesoporous silica were determined quantitatively using acid–base titration using 0.1 N KCl (aq) as the ion-exchange agent. Approximately 0.2 g of the sample was added to 20 ml of the salt solution and allowed to equilibrate for 30 min. Thereafter, it was titrated by 0.02 N KOH (aq). The numbers of sulfonic acid groups in the mesoporous silica are given in (Table 1).

The IR spectra (Fig. 6) showed that no traces of the template remain in the samples after the extraction. There were two bands at 1490 and 1480 cm^{-1} that can identify the presence of asymmetric head group methyl (CH_3–N^+) of the cetyltrimethylammonium ion which was not observed, so the use of reagents (dimidium bromide) to verify the absence of the filtrate from surfactant was activated. (Dîaz et al., 2001; Dîaz et al., 2000; Mbaraka et al., 2003).

The catalytic activities of the functionalized mesoporous silica were compared with commercial catalysts. These included homogeneous catalysts (*p*-toluenesulfonic acid, *p*-TSA, Merck) and heterogeneous catalysts (Amberlyst-15, 53 m^2g^{-1}, Pore diameter = 300 Å, H^+ capacity = 4.7 meq/g, Rohm and Haas Co., USA).

3.1. Procedure of the esterification olive-pomace oil with glycerol

Treated olive-pomace oil (in considering which olive-pomace oil contains 100% oleic acid) (1 mmol), glycerol (6 mmol) and 2 mol % (relatively to oleic acid) of supported sulfonic groups were mixed in an open flask and stirred at the (110 °C) temperature under air. At the end of the reaction, reaction products were directly extracted from the crude with ethyl acetate (2×3 mL) then the organic layer was evaporated.

Figure 5   (A) N_2 isotherms of the prepared catalysts; (B) pore size distribution following the BJH method ($\diamond$) MCM-41-SO$_3$H, ($\blacktriangle$) SBA-15-SO$_3$H.
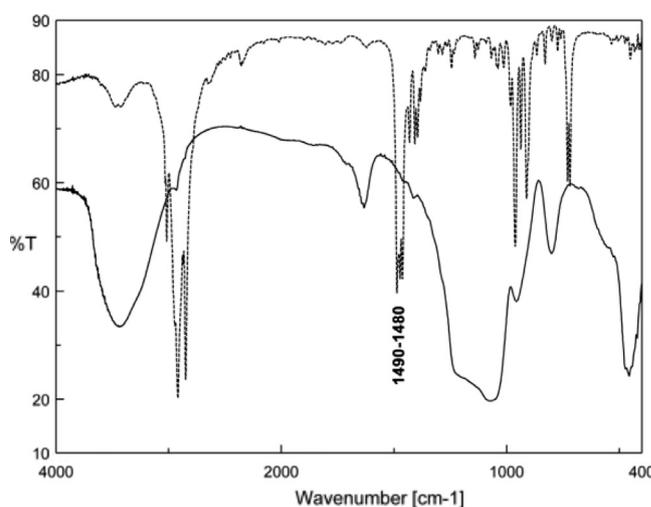
Figure 6   IR spectra for MCM-41 after extraction of surfactant (–) MCM-41, (. . .) C$_{16}$TAB.
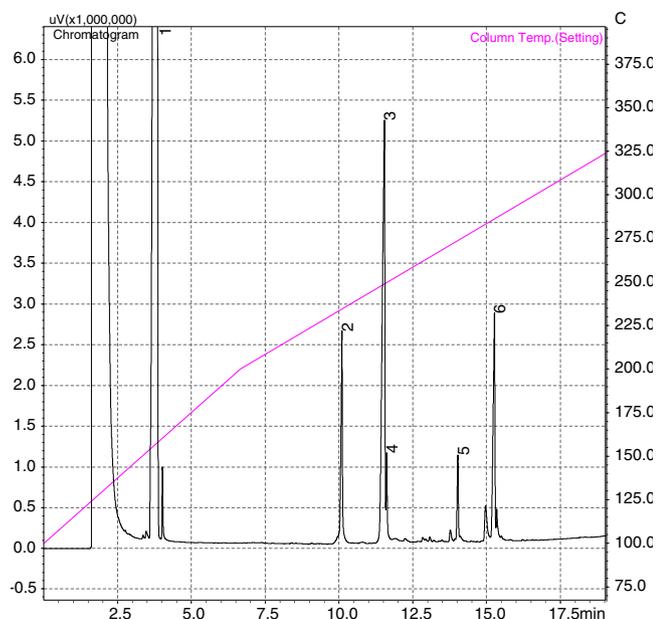
Figure 7 Chromatogram of a sample esterification reaction of olive-pomace oil using a dodecane as internal standard, 1-dodecane, 2-palmitic acid, 3-oleic acid, 4-stearic acid, 5-monopalmitate (GMP), 6-monooleate (GMO).

The reaction progress was monitored by Shimadzu 2010 GC equipped with a BPX5 column (12 m × 0.22 mm; phase thickness: 0.25 μm) supplied by SGE, The detector was an FID at 270 °C and the injection system splitless. The carrier gas was Nitrogen and the flow rate 1 mL/min. Prior analysis; products were silylated according to the Sahasrabuhde method

(Sahasrabudhe, 1967). Yields and reaction progress were determined by internal calibration with dodecane. The GC operating conditions were as follows: The GC column oven temperature was 100 °C, raised at 15 °C/min to 200 °C, then raised at 10 °C/min to 360 °C, and maintained at that temperature for 10 min.

The conversion and the selectivity were expressed with regard to the oleic acid transformation using the reaction coefficients for the formation of mono-, di- and triglycerides, where S is the chromatographic surface corrected by response factor of different products. We can apply the same equations for the palmitic acid transformation: (Pouilloux et al., 1999) Fig. 7.

$$\text{Conversion } (\%) = \frac{S_{monooleate} + 2\, S_{dioliate} + 3\, S_{trioleate}}{S_{monooleate} + 2\, S_{dioleate} + 3;\, S_{trioleate} + S_{acid}} \times 100$$

$$\text{Selectivity of Monooleate} = \frac{S_{monooleate}}{S_{monooleate} + 2\, S_{dioleate} + 3\, S_{trioleate}} \times 100$$

First, esterification of glycerol with treated olive-pomace oil (oleic acid and palmitic acid together) was studied at 110 °C in the presence of 2 mol % of *p*-toluene sulfonic acid (*p*-TSA) as reference homogeneous catalyst. Indeed, after a 24-h reaction, the conversion of oleic acid 70%. As expected, using *p*-TSA, the yields of both monoacylglycerols were 30% (glycerol monooleate, GMO, and glycerol monopalmitate, GMP) at conversion nearly was 70% of the both acids (Fig. 8), these lower the selectivity probably due to the more solubility of *p*-TSA in the layer of oil than in the layer of glycerol.
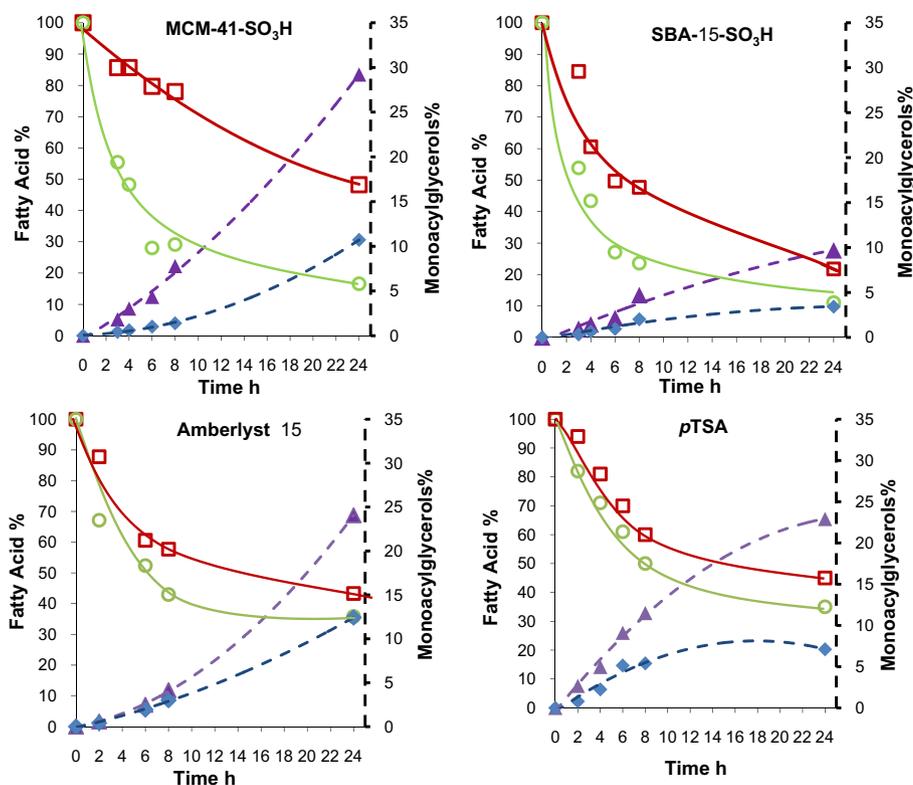
Figure 8 The conversion of olive-pomace oil and the yield of monoacylglycerols, ■ palmitic acid, ● oleic acid, ▲ GMP, ◆ GMO.

In order to increase the selectivity of this reaction, we used heterogeneous catalysts immobilized sulfonic groups like as Amberlyst 15 that is a polystyrenic resin (highly non-polar structure) which is commonly used in esterification reactions, (Pouilloux et al., 1999), and SBA-15-SO₃H and MCM-41-SO₃H that are known to be porous, highly polar and strong hydrophilic interactions between the silica framework and glycerol are expected to favor a rapid desorption of the targeted amphiphilic monomer from the catalytic surface. (Dinnebier and Billinge, 2008; Dîaz et al., 2000).

Amberlyst 15 with non-polar structure and pore diameters 250 Å appeared to be the same activity and selectivity as homogeneous p-TSA relatively to oleic acid (Fig. 6). Furthermore, both the fatty acid diffusion and the accessibility to active sites decrease and become the limiting steps of the esterification. Moreover, we believe that glycerol adsorption on active sites weakens the acid strength of the resin. Using mesoporous silica catalyst with hydrophilic surface such as SBA-15-SO₃H (pores diameters 70 Å) and MCM-41-SO₃H (pores diameters 32 Å). After nearly total consumption of starting materials, the yield of monoacylglycerols increased to 40% in the case of MCM-41-SO₃H. Comparing with Ambrlyst 15, the production of GMO is more selective (12% of GMO at 90% conversion of oleic acid), on the other hand, the yield of GMP nearly identical in the two casees, it may be due to the blocking of acid inside the pores in an intermediate form which prevents it not to produce co-products. In the case of SBA-15-SO₃H, we can apply the same explication, the activity of SBA-15 is the same for each acid, but due to the large pores diameter, the acids probably stayed blocking the acid inside the pores in an intermediate form. On the other hand, the low selectivity in GMO and GMP is due to the poisoning of the active site in the catalyst.

Next, we studied the stabilities of MCM-41-SO₃H. To this end, recycling experiments were undertaken Fig. 9. After the first catalytic run, the monoacylglycerols were selectively extracted from the media of reaction with ethyl acetate. Note that the solid catalysts remained in suspension in glycerol and no reactivation or purification of the catalyst was performed between each cycle. The olive-pomace oil and the consumed glycerol were then reloaded for another catalytic cycle. As shown in (Fig. 9), cycle after cycle, remarkably, no drop of yield of monoacylglycerols was observed since, after 3 successive catalytic cycles, 11% yield of GMO and 26% yield of GMP (37% total yield of monoacylglycerols) were still recovered.
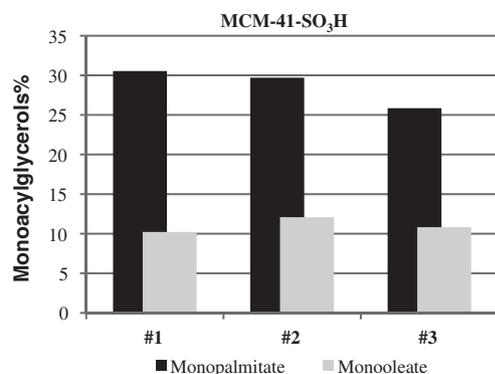
Figure 9 Catalytic recycling over MCM-41-SO₃H.

4. Conclusions

In conclusion, we report here that acid mesoporous silica MCM-41-SO₃H is more selective than homogeneous or usual solid acid catalysts for the direct transformation of olive-pomace oil substrate. The total yield of monoacylglycerols (GMO + GMP) was nearly 40%. Remarkably, we found that MCM-41-SO₃H was recycled at least 3 times without any loss of activity and selectivity of monoacylglycerols.

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