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Synthesis of Monoglycerides by Esterification of Oleic Acid with Glycerol in Heterogeneous Catalytic Process Using Tin–Organic Framework Catalyst

Lik H. Wee · Tristan Lescouet · Julia Fritsch · Francesca Bonino ·
Marcus Rose · Zhijun Sui · Eva Garrier · Dirk Packet · Silvia Bordiga ·
Stefan Kaskel · Moti Herskowitz · David Farrusseng · Johan A. Martens

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Abstract Selective synthesis of monoglycerides by esterification of glycerol with fatty acids is a difficult reaction because of immiscibility of reagents and the formation of di- and tri-glyceride by-products. In this work a heterogeneous catalytic process was conceived in which the reactant mixture was homogenized using *tert*-butanol solvent. Candidate catalysts were screened in the reaction of oleic acid with glycerol. While under such reaction conditions zeolites were rather inactive, metal–organic

frameworks and, especially, tin–organic frameworks were found promising. A tin–organic framework (Sn–EOF) was most active and achieved ≥ 98 % monoglyceride selectivity at 40 % conversion in catalyzing esterification of oleic acid with glycerol at a low reaction temperature of 150 °C. Leaching of tin from Sn–EOF catalyst was suppressed by limiting the amount of oleic acid in the starting mixture. Characterization of the acid sites of Sn–EOF by pyridine-chemisorption and FTIR revealed Lewis acidity to be responsible for the catalytic activity.

L. H. Wee · J. A. Martens (✉)
Centre for Surface Chemistry and Catalysis, KU Leuven,
Kasteelpark Arenberg 23, Heverlee B3001, Belgium
e-mail: johan.martens@biw.kuleuven.be

T. Lescouet · D. Farrusseng
Institut de Recherche sur la Catalyse et l'Environnement
de Lyon (IRCELYON), CNRS, University Lyon 1,
2 Av. Albert Einstein, 69626 Villeurbanne, France

J. Fritsch · M. Rose · S. Kaskel
Department for Inorganic Chemistry, Dresden University
of Technology, 01062 Dresden, Germany

F. Bonino · S. Bordiga
Department of Chemistry, NIS Centre of Excellence,
University of Turin, Via P. Giuria 7, 10125 Turin, Italy

F. Bonino · S. Bordiga
Department of Chemistry, INSTM Reference Center,
University of Turin, Via Quarellino 11, 10135 Turin, Italy

Z. Sui · M. Herskowitz
Blechner Center for Industrial Catalysis and Process
Development, Ben-Gurion University of the Negev,
Beer-Sheva, Israel

E. Garrier · D. Packet
Novance, Rue les rives de l'Oise, Venette,
B.P. 20609, 60206 Compiègne Cedex, France

Keywords Tin–organic framework · Esterification ·
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1 Introduction

Monoglycerides are renewable surfactant molecules finding application in food and pharmaceutical formulations, cosmetics and detergents [1]. The synthesis of monoglycerides on industrial scale is achieved mainly via two routes: (1) direct esterification of glycerol with fatty acid [2] and (2) transesterification of tri-glycerides with glycerol, both catalyzed by homogeneous strong acid or base catalysts such as H_2SO_4 , H_3PO_4 , KOH, NaOH, or $\text{Ca}(\text{OH})_2$. The reaction typically is carried out at relatively high temperatures of 220–250 °C. These conventional processes involving the use of homogeneous catalysts typically lead to low monoglycerides selectivity (40–50 %) due to di- and tri-glyceride side products formation and undesired formation of soap. For monoglyceride synthesis, dissolved transition metal complexes with Lewis acid properties based on Sn are highly active and more selective [3], but the elimination of the transition metal from the monoglyceride product is problematic. In addition to

chemical contamination by the catalyst, for human consumption such as in food and pharmaceutical products, limitation of by-product formation is essential. High-temperature processes also bear the risk of deterioration of taste, aroma and color. In addition, techniques for separation of monoglycerides from di- and tri-glycerides via distillation are technically complicated, and energy consuming. For all these reasons the development of an efficient monoglyceride production process taking advantage of heterogeneous catalysis under mild reaction conditions with convenient catalyst recovery and recycling is a scientific challenge of practical interest. For the targeted reaction several types of heterogeneous catalysts have been investigated in literature [4–13]. For example, 3-mercaptopropyltrimethoxysilane functionalized-MCM-41 has been tested for the esterification of glycerol with lauric or oleic acid [4, 5]. Oleic acid conversion up to 89 % was achieved with 40 % monoglycerides selectivity at 120 °C after 8 h. The use of short chain fatty acid (lauric acid) resulted in higher monoglyceride selectivity (59 % at 85 % lauric acid conversion) [5]. Corma et al. [9] investigated the glycerolysis of the triolein or rapeseed oil with glycerol over solid basic catalysts such as sepiolite-Cs, MCM-41-Cs, MgO and hydrotalcites. MgO was found to be the better catalyst achieving 97 % triolein conversion and 75 % monoglyceride selectivity after 5 h reaction at 240 °C. Zeolites with different framework topology catalyzed esterification of lauric acid with glycerol [10]. Monolaurate selectivity up to 69 % at 50 % lauric acid conversion was reached using an acid Y type zeolite at 112 °C [11]. Generally the monoglyceride selectivity of the investigated heterogeneous catalysts were not significantly better than in the homogeneous catalytic processes. The development of a heterogeneous catalytic process for monoglyceride synthesis is complicated by the immiscibility of glycerol and fatty acid, and the autocatalytic activity of the fatty acid [4].

In the 1990s, a new class of nanoporous materials known as metal–organic frameworks (MOFs) emerged [14]. MOFs are organic–inorganic hybrid materials constructed from organic linkers of metal centers. MOFs offer outstanding physical properties such as high surface area, tunable porosity, and functionality [15]. An ever increasing number of MOFs containing Al, Mg, Mn, Fe, Ti, Zn, Cr or Zr with potential Lewis type acidity are being reported. The metal atoms in the framework can serve as active Lewis acid catalytic centers. Moreover, the organic linkers of MOF structures are amenable and can be foreseen with amine or amide basic catalytic functions. MOFs can encapsulate guest species with catalytic activity such as polyoxometalates or porphyrins [16] and such species can be released and recovered again by encapsulation in the MOF after reaction [17]. MOFs have been evaluated for a

vast range of catalytic applications with variable success [18–21]. MOFs show great promise for esterification reactions involving short alcohols with acetic acid and fatty acids performed in monophasic liquid phase [17, 22, 23], but to our knowledge the potential of MOFs for monoglycerides synthesis has not yet been explored. Here, we report a convenient reaction procedure enabling screening of MOFs for monoglycerides synthesis through esterification of oleic acid with glycerol. An amorphous tin based organic framework with pore size of ca. 1 nm enabled synthesis of monoglycerides with high selectivity and minimum leaching of tin into the reaction product.

2 Experimental

2.1 Preparation of MOFs

$\text{Cu}_3(\text{BTC})_2$ encapsulated Keggin phosphotungstic acid (HPW) or silicotungstic acid (HSiW) denoted as HPW/ $\text{Cu}_3(\text{BTC})_2$ or HSiW/ $\text{Cu}_3(\text{BTC})_2$ (BTC benzene-1,3,5-tricarboxylic acid), respectively, was prepared from 12 g of copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (99–104 %, Sigma-Aldrich) and 8.0 g of HPW ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$) (for microscopy, Fluka) dissolving in 100 ml of distilled water. 5.8 g of BTC was dissolved in 140 ml of absolute ethanol (BDH). Both the synthesis solutions were mixed under vigorous stirring for 5 min and transferred into a 1 l round bottom flask and heated to 110 °C for 24 h under reflux. The solid product was washed with distilled water: ethanol mixture (1:1, v/v), recovered by filtration and dried in an oven at 60 °C. Nanosized HPW/ $\text{Cu}_3(\text{BTC})_2$ was synthesized via the freeze drying approach as previously reported [22]. The synthesis of Sn–EOF was performed according to the previous reported method by Fritsch et al. [24] 7.8 g (25 mmol) of 4,4'-dibromobiphenyl (99 %, Acros Organics) was dissolved in 500 ml of dry tetrahydrofuran (THF) (VWR) under argon atmosphere. After cooling the solution to -78 °C, 20 ml (50 mmol, 2.5 M, Sigma-Aldrich) of *n*-butyllithium (CAUTION: *n*-butyllithium is explosive when exposed to air and water) was added slowly under vigorous stirring with controlling the temperature via a syringe pump (40 ml/h). Afterwards, 3.26 g of (12.5 mmol, 1.44 ml) SnCl_4 (98 %, Fisher Scientific) was added dropwise under vigorous stirring. The mixture was slightly warmed to room temperature and stirring under argon was continued overnight. The resulting precipitate was filtered and washed twice with THF, distilled water and ethanol. After drying under vacuum at room temperature the product was obtained as light beige powder. The specific surface area of Sn–EOF was determined using nitrogen physisorption. The sample was outgassed at 80 °C overnight under vacuum. The BET surface area was

consistent with earlier work [24]. Al-MIL-53-NH₂ was prepared and purified according to the synthesis protocols introduced by Stock et al. [25]. Suspension containing stoichiometric amount of aluminum chloride hexahydrate (965.7 mg, 4 mmol) and 2-aminobenzene-1,4-dicarboxylate (ABDC) (724.6 mg, 4 mmol) in 20 ml deionized H₂O was introduced in a 23 ml Teflon-lined autoclave. The mixture was heated at 150 °C for 9 h. After cooling the product was separated from water by centrifugation. In order to remove the incorporated ABDC, the as-synthesized product was placed in an autoclave with anhydrous dimethylformamide (DMF) and heated at 150 °C for a day. Then the solvent was substituted by fresh DMF and the solvothermal treatment was repeated twice. Afterwards the DMF was evacuated by Soxhlet-extraction using dichloromethane (DCM) for 20 h. Finally, solid was dried under reduced pressure for 9 h to obtain activated, fine powdered Al-MIL-53-NH₂. In-MIL-68-NH₂ was synthesized and activated following the published procedures [26, 27]. Indium nitrate (1,203.3 mg, 4 mmol) and ABDC (724.6 mg, 4 mmol) were dissolved in DMF (30 ml). The reaction mixture was stirred for 5 min, and then a solution of 4-diazabicyclo[2.2.2] octane (DABCO) (897.4 mg, 8 mmol) in DMF (10 ml) was added. The reaction mixture was stirred for 120 min at room temperature. The obtained precipitate was washed with DMF in an autoclave at 150 °C overnight followed by Soxhlet extraction with DCM for 24 h. UiO-66-NH₂ and UiO-66 were synthesized by solvothermal method in a Teflon-lined autoclave [28]. ZrCl₄ (600 mg), ABDC or benzene-1,4- dicarboxylic acid (BDC) (480 mg) and water (50 µl) were added to 40 ml of DMF. The mixture was heated at 120 °C for 6 h. The obtained precipitate was washed with DMF in an autoclave at 150 °C overnight followed by a DCM Soxhlet for 24 h. Zinc triazolate with amine substituents ZnF(TAZ-NH₂) was synthesized by solvothermal method in a Teflon-lined autoclave [29]. ZnF₂·4H₂O (1.05 g) and 3,5-diamino-1,2,4-triazole (0.6 g) were added to 30 ml of water. The mixture was heated at 160 °C for 3 days. The obtained precipitate was washed with water and dried at 90 °C overnight. Ultrastable Y zeolite (CBV-720) was supplied by Zeolyst International and used without further treatment.

2.2 Esterification Reactions

The screening of MOF catalysts for esterification of oleic acid with glycerol was performed using glass vials and mini stainless steel autoclaves (both 12 ml) magnetically stirred at 1,000 rpm and heated in a temperature controlled copper block. Alternatively the esterification reaction was carried out using a reflux system consisting of a 1 l four-necked flask equipped with Teflon shaft stirrer, a thermocouple, air and water condensers and an inert gas (nitrogen)

inlet tube. The reaction mixture was stirred at 400 rpm. Conversion of oleic acid and selectivity of monoglyceride were determined using gas chromatography (GC). GC analyses were performed on a high-temperature apolar column DB5 (Agilent J&W, 30 m × 0.53 mm, 1.50 µm) with an HP-6890 instrument equipped with flame ionization detector (FID). The content of leached Sn was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (VARIAN 725 S instrument).

2.3 Characterization of Acid Sites by Pyridine Adsorption Monitored by Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were collected on a Vertex 70 Bruker spectrophotometer equipped with a MCT detector, at 2 cm⁻¹ resolution, on a thin self-supported wafer. The sample was activated in a home-made cell under high vacuum (residual pressure <10⁻⁴ mbar) at 120 °C for one night. At RT pyridine vapor was dosed on the sample and then progressively outgassed.

3 Results and Discussion

3.1 Esterification of Glycerol with Oleic Acid in Absence of Solvent

Oleic acid and glycerol are immiscible liquids. The monoglyceride reaction product acts as an emulsifier and, upon stirring, the two liquid layers become an emulsion and after sufficient conversion, a homogeneous liquid phase was obtained. The reaction of an equimolar mixture of oleic acid and glycerol was run first in absence of catalyst in a closed glass vessel at 120 °C (blank, Table 1). After 3 h, 30 % oleic acid conversion was reached, and 75 % monoglyceride selectivity. After 8 h the conversion was increased to 45 % while the monoglyceride selectivity was decreased to 63 %. Diglycerides and triglyceride were the observed as side products. The esterification reaction under these conditions is catalyzed by the oleic acid itself. Similar autocatalytic effects have been previously reported [4].

All the MOFs used in this studies were synthesized according to the previously reported methods and the synthesis procedures were presented in details in the experimental section. Phase purity, crystallinity and microporosity of the MOFs were verified and confirmed by XRD and N₂ adsorption (not shown). The esterification reaction in absence of solvent was performed using HPW/Cu₃(BTC)₂ catalyst, a copper benzene tricarboxylate MOF having encapsulated Keggin HPW in the pores of HKUST-1 framework structure [30]. HKUST-1 framework has two

Table 1 Esterification of oleic acid with glycerol in the absence of solvent

Catalysts	Catalyst loading (wt%)	Reaction time (h)	Oleic acid conversion (%)	Selectivity (%)		
				Mono	Di	Tri
Blank	–	3	30	75	24	1
		8	45	63	34	3
HPW/Cu ₃ (BTC) ₂	1	3	30	77	22	1
	1	8	45	62	35	3
	2	3	28	76	23	1
	5	3	31	75	24	1
Ultrastable Y zeolite	1	3	33	78	21	1
	1	8	45	63	34	3
	2	3	32	77	22	1
	5	3	29	76	23	1

Molar ratio of oleic acid: glycerol = 1:1, 120 °C, copper block reactor. Catalyst loading was based on added oleic acid

types of pores with free diameters of 1.3 and 1.0 nm, respectively, connected through accessible windows of 1.1 and 0.9 nm. The largest cage accommodate the Keggin anions [30]. HPW is well known for its strong Brønsted acidity and HPW/Cu₃(BTC)₂ MOF has been reported as active heterogeneous catalyst for ester hydrolysis [30], and esterification of acetic acid with 1-propanol [23, 31]. Ultrastable Y zeolite was used as a reference. It has micropores with 0.7 nm windows and a secondary mesoporosity that should be wide enough to accommodate the reagent and product molecules [32]. Ultrastable Y zeolite has been reported to be superior among other zeolite catalysts in the investigated reaction [33].

Esterification of oleic acid with glycerol in 1:1 molar ratio was performed in closed glass vessels at 120 °C using catalyst contents of 1, 3 and 5 wt% based on oleic acid, and reaction times of 3 or 8 h (Table 1). The catalytic activity of HPW/Cu₃(BTC)₂ and ultrastable Y zeolite in this reaction was negligible since the conversion obtained in presence and in absence of these catalysts was similar (Table 1). Increasing the catalyst content from 1 to 5 wt% did not improve conversion. The autocatalytic effect of the oleic acid reagent was responsible for the conversion.

In an alternative experimental setup water produced by the esterification reaction was evacuated. The reflux reactor consisted of a glass stirring shaft with a Teflon stirring paddle for efficient mixing of the reaction mixture and a condenser connected to the reactor for collecting water vapor formed during reaction. The esterification reaction of oleic acid with glycerol was carried out at 180 °C for 3 h departing from an equimolar mixture of oleic acid and glycerol. The tested MOF catalysts were nanosized and micron-sized HPW/Cu₃(BTC)₂, HSiW/Cu₃(BTC)₂, homogeneous HPW, Sn–EOF and ultrastable Y zeolite. The results (Table 2) show that even without catalyst a high oleic acid conversion (89 %) was obtained. In presence of the majority of tested catalysts the oleic acid conversion was further enhanced. Under these

reaction conditions, a catalytic effect was superimposed on an autocatalytic contribution. HPW converted the glycerol into polyglycerol and produced little monoglyceride. While polyglycerol formation was also observed when using HWP encapsulated in nanopowder of Cu₃(BTC)₂, it was absent on larger particles of this catalyst formulation. Visual inspection revealed a color change indicating that the MOF catalysts were degraded after 3 h at 180 °C (photographs of Fig. 1). It was clear such reaction conditions are less suitable for Cu₃(BTC)₂ type catalysts. The highest conversion of oleic acid (100 %) was obtained using Sn–EOF catalyst. Sn–EOF is an elemental-organic framework (EOF) material constructed from Sn⁴⁺ ions connected to 4,4'-dibromobiphenyl organic linker via element-carbon bondings. Sn–EOF is an amorphous microporous material with a BET surface area of 445 m² g^{−1} and pore size around 1 nm [24]. It is thermally stable up to 200 °C in air [24]. A full characterization of the material could be obtained from ref. 24. The monoglyceride selectivity in these experiments at high conversion was below 50 %. Such experimental setup with continuous elimination of water by evaporation appeared unsuited.

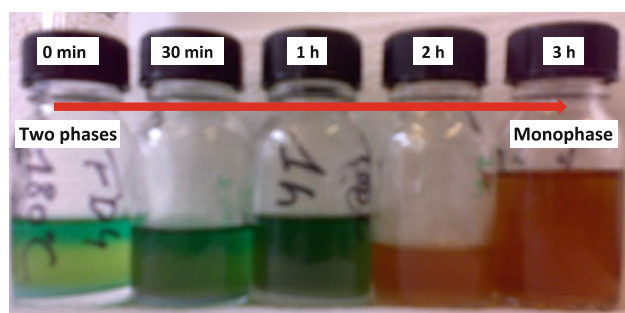
3.2 Esterification of Glycerol with Oleic Acid in Presence of Solvent

When esterification of oleic acid with glycerol is performed at high reaction temperature (200–260 °C) and pressure (30–100 psig) a monophasic reaction phase is obtained with water addition [34]. Such conditions likely are not suitable for MOFs. Alternatively, for homogenizing the starting mixture a solvent can be used. The selection of an appropriate solvent was not obvious, however. The solvent should have high boiling point to limit vaporization, and provide high solubility of both oleic acid and glycerol. Five candidate solvents emerged from our search: diglyme, dimethylsulfoxide (DMSO), DMF, monoolein and

Table 2 Esterification of oleic acid with glycerol with water evacuation in reflux reactor

Catalysts	Reaction time (h)	Oleic acid conversion (%)	Selectivity (%)			
			Mono	Di	Tri	Polyglycerol
Blank	3	89	51	40	9	
HPW	2	95	2	12	13	73
Ultrastable Y zeolite	3	92	47	43	10	
HPW/Cu ₃ (BTC) ₂	3	97	39	49	12	
Nano HPW/Cu ₃ (BTC) ₂	3	99	21	35	9	35
HSiW/Cu ₃ (BTC) ₂	3	88	50	43	7	
Sn-EOF	3	100	48	42	10	

Molar ratio of oleic acid: glycerol = 1:1, 180°C, reflux reactor. 1 wt% catalyst loading based on added oleic acid

**Fig. 1** Photograph showing initial biphasic reaction mixture becomes monophasic. HPW/Cu₃(BTC)₂ degradation gives rise to colour change from greenish to brownish

tert-butanol. Except for diglyme both oleic acid and glycerol were soluble in these solvents.

The esterification reaction was performed using DMSO, DMF, and monoolein solvent. The solvent was added in a weight proportion of solvent to reaction mixture of 2:1. Sn-EOF was chosen for further investigation as its catalytic activity was already superior in absence of solvent (Table 2). In the presence of DMSO and DMF solvent, high oleic acid conversion (70–80 %) together with higher selectivity for monoglyceride (>90 %) were reached. Furthermore, conversion and selectivity in presence and absence of catalyst were similar, showing that the autocatalytic effect predominated. The same observation was made with ultrastable Y zeolite catalyst. Furthermore, Sn-EOF catalyst was unstable in these solvents, leading to dissolution at the end of the experiment. The use of monoolein solvent was also investigated. Since monoolein is a monoglyceride, the consecutive reaction to diglycerides was enhanced, which is undesired.

In another series of experiments, *tert*-butanol solvent was used (Table 3). MOF candidate catalysts grafted with amino functions (Al-MIL-53-NH₂, In-MIL-68-NH₂, UiO-66-NH₂ and ZnF (TAZ-NH₂), UiO-66 in addition to Sn-EOF were investigated. These esterification reactions were performed at 150 °C for 20 h. MOFs with amino group

were found less active for catalyzing esterification of oleic acid with glycerol. Sn-EOF was a superior catalyst achieving 26 and 40 % conversion after 8 and 20 h, respectively, which was higher than in the absence of catalyst (16 and 23 % conversion, respectively). The monoglyceride selectivity exceeded 98 %. A drawback was that Sn-EOF catalyst was partially dissolved. To trace the origin of the solubility, Sn-EOF catalyst was suspended in glycerol, monoglyceride, oleic acid or *tert*-butanol and the suspension heated. Oleic acid was found responsible for degradation of the Sn-EOF catalysts upon heating above 150 °C. Thus, subsequent esterification reactions were conducted using a lower concentration of oleic acid. Experiments were run with 1, 0.4, 0.3 and 0.2 mol oleic acid per mol glycerol in the starting mixture. The stability of Sn-EOF catalyst was improved at reduced concentration of oleic acid as evidenced from visual inspection of the amount of catalyst that precipitated after reaction (Fig. 2). A further esterification experiment was performed at 150 °C for 20 h using *tert*-butanol solvent and an oleic acid to glycerol molar ratio of 0.1:1 in the starting mixture (Fig. 3). The oleic acid conversion reached up to 40 and 98 % monoglyceride selectivity was achieved. High selectivity clearly is reached with the presence of a homogeneous liquid phase, independent of catalyst. Under similar reaction conditions, the selectivity of monoolein achieved was limited at 60 % at 40 % oleic acid conversion in the absence of *tert*-butanol. The Sn-EOF catalyst could be recovered and recycled. However, a gradual loss of the catalytic activity was noted in the second run, where 30 % oleic acid conversion and >90 % monoglyceride selectivity were obtained. Chemical analysis of the reaction product from which Sn-EOF catalyst was removed through centrifugation revealed a residual tin concentration of 700 ppm. Although the solubility of the Sn-EOF catalyst was significantly suppressed, some leaching could not be avoided. The presence of solvent is a handicap if the monoglyceride products were to be used in food or pharmaceutical application. Given the large difference in volatility, the monoglyceride could be easily purified by

Table 3 Esterification of oleic acid with glycerol in *tert*-butanol solvent

Catalysts	Reaction time (h)	Oleic acid conversion (%)	Selectivity to Mono (%)
Blank	8	16	100
Blank	20	23	100
Sn-EOF	8	26	99
Sn-EOF	20	40	98
Al-MIL-53-NH ₂	8	11	100
Al-MIL-53-NH ₂	20	23	100
In-MIL-68-NH ₂	8	14	100
In-MIL-68-NH ₂	20	22	99
UiO-66	8	17	100
UiO-66	20	29	99
UiO-66-NH ₂	20	18	100
ZnF(TAZ-NH ₂)	20	25	100

Molar ratio of oleic acid: glycerol = 1:1, 150 °C, stainless steel autoclave reactor. Total reaction mixture: solvent = 1:2(w/w). 1 wt% catalyst loading based on added oleic acid

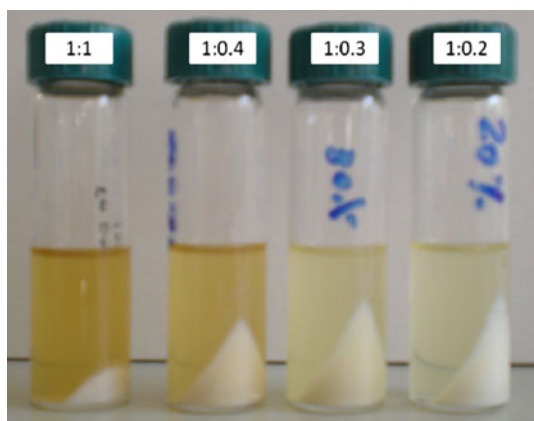


Fig. 2 Photographs of reaction product with sedimented Sn-EOF catalyst obtained using different starting glycerol:oleic acid molar ratio's indicated on the vials. The increasing amount of catalyst precipitate and reduction of coloration from *left to right* reveal the decrease of catalyst solubility at lower oleic acid concentration. *Reaction conditions:* *tert*-butanol solvent; reaction temperature of 150 °C; reaction time of 24 h, 4.64 g of *tert*-butanol added to 0.57 g of glycerol, 0.2 g of Sn-EOF

distillation. There exist applications where the presence of residual solvent is less critical.

3.3 In Situ FTIR Spectroscopy Analysis by Pyridine Adsorption

The acid sites in Sn-EOF were characterized by FTIR and pyridine adsorption (Fig. 4). Sn-EOF itself has some vibrational modes overlapping with pyridine (e.g. ring modes) [24]. The spectral features ascribed to pyridine appear in the

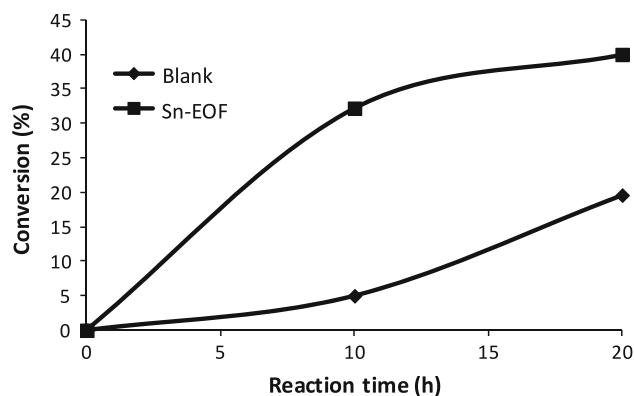


Fig. 3 Esterification of oleic acid with glycerol catalyzed by Sn-EOF. *Reaction conditions:* temperature of 150 °C, starting mixture composed of 0.175 g oleic acid, 0.57 g glycerol, 4.64 g *tert*-butanol and 0.2 g Sn-EOF catalyst

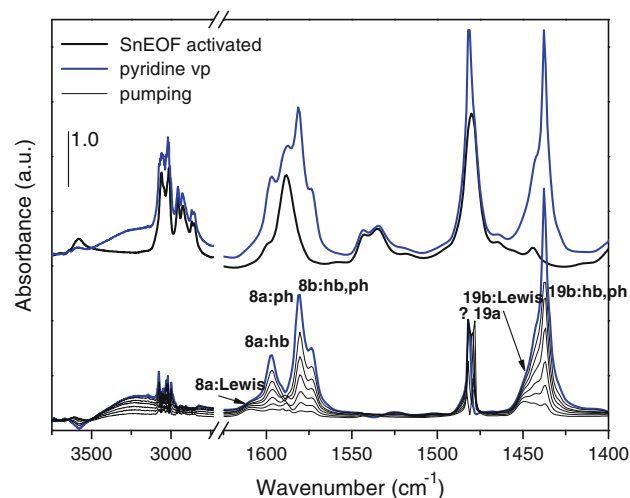


Fig. 4 FTIR spectra of Sn-EOF catalyst after pyridine vapor adsorption (blue curve, upper part); Sn-EOF activated in vacuo at 120 °C for 1 night (black curve, upper part). Bottom part reports difference spectra (in respect to the activated sample) obtained at decreasing coverages (black curves) in respect to the highest one (blue curve)

difference spectra (bottom part of Fig. 4) showing positive bands due to species formed upon pyridine adsorption, and negative bands due to consumed species. Bands in the 3,100–3,000 cm⁻¹ range were ascribed to pyridine ν(C–H) stretching modes, while the negative band at 3,580 cm⁻¹ was due to the consumption of some Sn–OH species, assumed to be present in defects. In the 1,625–1,400 cm⁻¹ range based on literature on pyridine adsorption on different materials [35–39], all the emerging bands were attributed to pyridine interacting with a Lewis site, hydrogen-bonded (hb) or physisorbed (ph). In particular the assignment can be done in the following way: 1610 8a Lewis, 1597 8a hb, 1580 8a ph or 8b hb, 1573 8b ph, 1480 19a ph or hb (probable artifact due to subtraction hb (probable artifact due to subtraction marked

with a question mark), 1450 19b Lewis, 1443 19b hb, 1437 19b ph. It is evident that in some cases there is the superposition of some components due to the frequency closeness of the different species. In particular, for instance, for some modes the perturbation induced by Lewis sites is definitely smaller and these bands are, therefore, superimposed to those of hydrogen-bonded species. The identification of Lewis moieties is supported by comparison with IR experiments of pyridine dosed on γ -Al₂O₃ (a solid characterized by strong Lewis acid sites), where four bands, respectively at 1620 (8a), 1578 (8b), 1492 (19a), and 1450 (19b) cm⁻¹, are observed [38, 39]. Sn-beta zeolite is known as a Sn-based Lewis acid, catalyzing a variety of green chemical reactions [40, 41]. We tested a reference Sn-beta zeolite under the same reaction conditions as Sn-EOF and observed a black colouring. The Sn-beta zeolite was inactive with an oleic acid conversion of 4 % only after 20 h, even below the conversion in absence of catalyst (20 %).

4 Conclusions

Selective esterification of oleic acid with glycerol to monoglyceride is a demanding reaction. The catalytic activity of MOFs including HPW/Cu₃(BTC)₂, HSiW/Cu₃(BTC)₂, Al-MIL-53-NH₂, In-MIL-68-NH₂, UiO-66, UiO-66-NH₂ and ZnF(TAZ-NH₂) hardly exceeds the autocatalytic activity of the fatty acid. On top of limited activity, there is a MOF stability issue, oleic acid being responsible for the degradation of MOFs. Solvents in which both glycerol and oleic acid can be dissolved in high quantity were identified: *tert*-butanol, DMF, DMSO and monoolein. *tert*-Butanol was identified as the optimum solvent. In this solvent MOF catalysts and especially Sn-EOF are catalytically active. In a catalytic experiment using Sn-EOF catalyst departing from a mixture with molar ratio of oleic acid to glycerol of 0.1:1 in *tert*-butanol solvent, Sn-EOF was most effective and showed limited tin leaching. The use of *tert*-butanol solvent and reaction conditions with low concentration of oleic acid are recommended for further MOF catalyst screening programs.

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