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Short communication

One-pot microwave assisted catalytic transformation of vegetable oil into glycerol-free biodiesel

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HIGHLIGHTS

- Direct transformation of triglycerides into FAMEs and glycerol ether derivatives.
- Application of microwave irradiations for sustainable biofuel production.
- Useful soybean oil conversion into biodiesel, without glycerol byproduct.
- The chosen catalyst is able to promote simultaneously three different reactions.
- The heterogeneous one-pot transesterification/esterification catalysis was assessed.

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ABSTRACT

The present study is our attempt to develop a first robust protocol for one-pot transformation of vegetable oils, such as soybean oil, to a mixture of FAMEs and glycerol ether derivatives as final potential biofuel. The reaction is catalyzed by amorphous silica oxide functionalized with 10 wt% of sulfonic groups. The best performance was observed when a mixture of substrate/tert-butyl-methyl ether in 1:10 ratio and almost 1% catalyst was treated under microwave conditions fixed at 20 W.

1. Introduction

Biodiesel is a non-toxic and biodegradable alternative fuel obtained from renewable sources and is currently used for diesel engines. In combustion the exhausts contain less particulate matter [1,2] and sulfur species are absent; consequently, it is a potentially important component to mitigate greenhouse gas emissions and substitute fossil fuels. Biodiesel is a mixture of methyl esters of fatty acids (FAMEs) obtained by the transesterification reaction of vegetable oils with methanol in presence of an acid or basic catalyst [3,4] or by using an enzymatic catalyst [5].

Recently, Melero and co-workers have reported various interesting examples for biodiesel production starting from crude vegetable oils with methanol in presence of different kinds of solid materials, opportunely functionalized with sulfonic acid groups, as catalysts [3,6,7].

However, there are several key challenges arising with biodiesel optimization processes which must still be addressed efficiently. The foremost problem is the inevitable production of glycerol as the co-product (about 10% of produced biodiesel), which must be removed and whose formation impacts on the expense of the entire process.

The glycerol could be efficiently utilized to make valuable chemicals, whereas the majority of it is currently burned as a poor heat source. Among the different alternatives, the use of glycerol-derivatives that may be exploited as biodiesel additives is being explored [8,9]. In this context, direct acetylation has been developed to improve the volatility of glycerol, using as acid catalyst Amberlyst-15® [10], sulfonic acid-functionalized amorphous and mesoporous silica materials [11,12], hydroxylated magnesium fluorides [13], in order to satisfactorily yield di- and triacetylglycerol. However, etherification of glycerol appears to be the better

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solution for production of "clean" additives both for diesel and internal combustion engines. The etherification of glycerol by isobutene gives a mixture of mono-, di- and tri-t-butyl ether, GBTEs, though the most desirable molecules are di-ethers. As a matter of fact, mono-ethers are less soluble in fuels, while tri-ethers are not economically convenient for the high content of isobutene required [14]. It is known that acidity of catalyst is a key factor for the etherification of glycerol by isobutene or using tert-butanol, hence catalysts such as sulfuric acid or sulfuric acid-functionalized mesoporous silicas have been considered [15–17]. The reaction occurs in a complex multiphase system because although isobutene is insoluble in the glycerol phase, its solubility increases during the reaction progress proportionally to the glycerol ethers formation as products, where it is highly soluble. Thus isobutene solubility plays a fundamental role both in the kinetic and efficiency of the reaction.

Recently, Gowda et al., have reported an efficient synthesis of tert-butyl ethers using tert-butyl metyl ether (TBME) under mild reaction conditions using sulfuric acid as catalyst [18]. In this context, it has been observed that methyl tert-butyl ether alone decomposes to give isobutene and methanol in the presence of acid catalyst (Scheme 1).

Considering all the literature data above reported, we focused our attention on developing a robust protocol for one-pot microwave assisted transformation of vegetable oils to a mixture of FAMEs and glycerol ether derivatives, using the commercially available tert-butyl metyl ether as single source both as transesterification and transetherification reagent. The final mixture could be exploited to make biofuels. The process developed offers practical and cost-saving advantages since it enables performing the production of FAMEs without requiring steps to remove free glycerol and given that all the final products may be used in the energy chain.

2. Methods

All the chemical reagents used were of analytical grade and used as received.

Purifications were carried out by flash chromatography Silica Gel 60 (70–230 mesh) using the specified eluents.

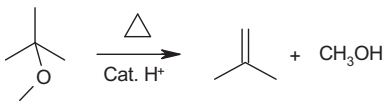
GC analyses were carried out in a Shimadzu® Fast-GC-17A equipped with a FID detector and an Agilent® capillary column (30 m × 0.250 mm, 0.25 μm). GC conditions: isotherm at 100 °C (1 min), ramp at 10 °C/min to 180 °C, isotherm at 180 °C (1 min) ramp at 5 °C/min to 250 °C, isotherm at 250 °C (5 min). The injector and detector temperatures were set respectively at 250 °C and 280 °C.

HPLC analyses were performed using a Varian® HPLC instrument equipped with an Alltech® 300 ELSD detector and a C18 LUNA analytical Phenomenex® column (250 × 4.60 mm; 5 μm). HPLC eluant conditions: Isocratic at 80% MeOH and 20% DCM (3 min), ramp to 30% MeOH and 70% DCM (15 min). Isocratic at 30% MeOH and 70% DCM (5 min); Flowrate 1 mL/min.

The acid-catalyzed reactions were performed using a CEM Discover microwave reactor.

2.1. Synthesis of the propyl-SO_3H amorphous SiO_2

The propyl-SO_3H (10 wt%)/silica was synthesised by sol–gel technique by improving a published procedure [12]. Tetraethyl orthosilicate (TEOS) (7.5 ml, 0.034 mol, Aldrich) was dissolved in ethanol (5 ml) and stirred at 45 °C for 15 min. Then, 5 ml of aqueous solution of acetic acid at pH 5 was added to the mixture, followed by 3-mercaptopropyltrimethoxy silane (MPTMS) (0.625 ml, 0.0034 mol, Aldrich) and hydrogen peroxide (33% w/v solid:liquid ratio of 1:18). The solution was stirred under reflux at 45 °C overnight; the temperature was then increased to 80 °C and kept constant for 4 h. Formation of the gel was achieved by heating up to 100 °C. Thereafter, the obtained wet gel was dried at 120 °C overnight.



Scheme 1.

2.2. Catalyst characterization

Characterizations of the propyl-SO_3H (10 wt%)/silica oxide were carried out as reported elsewhere [12], in order to measure the acid capacity (by titration with 0.01 M NaOH), BET surface area and porosity, structure (by X-ray diffraction, XRD), surface chemical content of sulfonic groups (by X-ray photoelectron spectroscopy, XPS).

2.3. General experimental procedure

In a typical experiment, the selected substrate and the appropriate amount of TBA (*tert*-butyl alcohol) and/or TBME (*tert*-butyl methyl ether) were mixed in a microwave tube in the presence of the opportune amount of the solid acid catalyst. The reaction mixture was irradiated in a microwave reactor pre-set to the desired temperature/power and reaction time. Upon completion of the reaction for the set reaction time, samples of the reaction mixture were opportunely analyzed by GC–FID or HPLC–DR.

The catalyst concentration in the reaction mixture was used in a 1–5 wt% range.

2.4. Procedure for the acid-catalyzed transformation of glyceryltripalmitate

Glyceryltripalmitate (500 mg; 0.619 mmol) was dissolved in TBME (1.6 mL, d 0.744 mg/mL; 24.5 mmol) in a microwave tube and the propyl-SO_3H (10 wt%) amorphous silica (30 mg) was added to the resulting solution. The reaction mixture was irradiated in a microwave reactor, pre-set at 20 W and monitored by HPLC–DR until the complete conversion of the substrate (3 h). The reaction mixture was concentrated under reduced pressure and the crude product was purified by flash chromatography (eluent condition from 95% hexane and 5% EtOAc to 30% hexane and 70% EtOAc), to give methyl palmitate. 96% yield (481 mg; 1.78 mmol) as an amorphous white solid. 1,3-di-*tert*-Butyl-glycerol ether 28% yield (35 mg; 0.171 mmol) as a colorless oil. 1-*tert*-Butyl-glycerol ether 64% yield (60 mg; 0.404 mmol) as a colorless oil. All the NMR analyses of the obtained products were in agreement with literature [19].

3. Results and discussion

The XRD pattern of the propyl-SO_3H functionalized silica showed only a broad peak at $2\theta = 22°$ attributable to the amorphous framework of SiO_2 phase. The N_2 adsorption–desorption isotherm was of type IV, typical of mesoporous oxides. Accordingly, the sulfonic silica showed high specific surface area of 540 m^2/g, mean diameter equal to 5 nm and total pore volume of 0.4 cm^3/g. The acid capacity of the catalyst, determined by titration with 0.01 M NaOH (aq), was equal to 2.2 mmol $H^+ g^{-1}$, according to the acidic properties of similar silica functionalized samples [12]. The presence of SO_3H groups at the surface of the catalyst,