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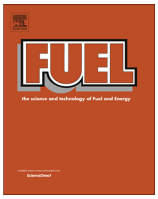

Short communication

A novel and robust homogeneous supported catalyst for biodiesel production

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HIGHLIGHTS

- A homogeneous supported catalyst based on Zn(II) was prepared.
- The catalyst is able to promote esterification and transesterification of acidic vegetable oils.
- The catalyst can be easily recovered and recycled.

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ABSTRACT

A homogeneous supported catalyst based on Zn(II) was prepared by anchoring complex [Zn(OAc)$_2$(N,N′-chelate)] on silica, where N,N′-chelate is a suitably functionalised di-imine ligand. The complex was able to promote the esterification and transesterification of acidic vegetable oils at 160 °C within two hours. The catalyst could be also easily recovered and immediately re-cycled.

1. Introduction

Transesterification and esterification are fundamental reactions within synthesis (Scheme 1) [1].

They have a central role in various fields, comprising the production of polymers, the synthesis of highly functionalized molecules for pharmaceutical uses, and the production of biodiesel.

Examples of polymers resulting from transesterification are polyesters, obtained from the reaction between dimethyl terephthalate and ethylene glycol [1].

Transesterification is of primary importance in the synthesis of polyphosphoesters (PPEs), suitable for biological applications due to their biocompatibility and similarity to biopolymers [2].

Transesterification is also useful for preparing many fine chemicals, *e.g.* macrolides, that are natural compounds obtained by lactonization of ω-hydroxyesters [1].

However, within the various applications of esterification and transesterification, the production of biodiesel is plausibly the most difficult to optimize and one of the current challenges in the field of chemical synthesis [3].

Vegetable oils consist of a mixture of esters of glycerol with fatty acids of different lengths and diverse degrees of unsaturation. They can be used to synthesize chemicals, such as surfactants and lubricants, or to produce biodiesel, *i.e.* a mixture of methyl esters of fatty acids, generally indicated with the acronym FAME's (Fatty Acid Methyl Esters) [3].

The production of FAME's acquires added value when the oil is produced from waste materials (80% of biodiesel costs derive from the raw material), such as frying oils or residues of other productions [4–7].

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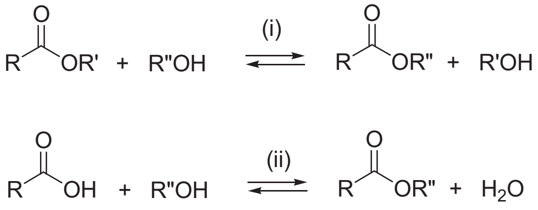


Scheme 1. Transesterification (i) and esterification (ii) reactions.

Industrially, FAME's are typically produced by transesterification of triglycerides (TG) promoted by alkaline catalysts (i in Scheme 2). One of the limits of this approach is their neutralization in the presence of acidic feedstock. In this case, transesterification must be anticipated by the esterification step (ii), in which the free fatty acids (FFA) are converted into their methyl esters using a Brønsted acid catalyst [4–7].

A more efficient procedure can involve the use of acid catalysts, which promote both esterification and transesterification [5–7]. Homogeneous Lewis acids have been proposed [8,9], which are capable of promoting simultaneously the two reactions in mild reaction condition ($T < 180$ °C). However, there are issues to be solved, mainly due to the difficult separation of the catalyst from the products. On the other hand, alternative heterogeneous Lewis acids (metal oxides, metal salts) require high reaction temperatures ($T > 180$ °C) and consequently elevated reaction pressures. Furthermore, they often undergo fast deactivation [7,10]. The consequence of these drawbacks is that no new technology has substituted the two steps approach in the production of biodiesel from waste oils [11].

The present study fits in this context, and proposes a new catalyst for the simultaneous esterification and transesterification, that (i) efficiently promotes the problematic conversion of acidic vegetable oils, (ii) is readily separated from the reaction mixture, (iii) can be immediately recycled.

2. Experimental section

2.1. General considerations

All reagents were purchased from Sigma–Aldrich and used without further purification. The silica AEROLIST (surface area, 150 m^2/g) in pellets was activated by heating in oven at 300 °C for 5 h. The complexes were characterized by NMR spectroscopy, using Varian VXR 200 and Varian Gemini 200 spectrometers. ^{1}H NMR data are reported in ppm and the shifts were referenced to the resonance of the residual protons dmso-d$_6$ (2.55 ppm). Abbreviations used in NMR data: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; m, multiplet; app, apparent. The Zn content in the supported catalyst was determined by ICP (inductively coupled plasma) analysis on Aurora M90 Bruker spectrometer. TGA analysis were performed with Perkin Elmer ST6000, heating the sample from 25 °C to 900 °C, at 10 °C min^{-1} in N_2 stream (20 mL/min). Elemental analysis have been carried out in a LECO CHN analyzer, operated up to 850 °C under O_2/He flow.

2.2. Synthesis of **5**

The ligand was prepared by mixing 10.7 g (0.100 mol) of pyridine-2-carboxaldehyde (**3**) and 22.1 g (0.100 mol) of 3-(triethoxysilyl)propane-1-amine (**4**) in 200 mL of diethyl ether. After 18 h of stirring, the solution was dried over sodium sulfate and then filtered. The product was obtained in quantitative by removing the solvent under vacuum. ^{1}H NMR (dmso-d$_6$) δ: 8.59 (d, ^{3}J = 5.8 Hz, 1H), 8.30 (s, 1H), 7.95 (d, ^{3}J = 7.2 Hz, 1H), 7.80 (app t, ^{3}J = 7.2 Hz, 1H), 7.38 (dd, ^{3}J = 7.2 Hz, 3 J = 5.8 Hz, 1H), 3.70 (q, ^{3}J = 6.9 Hz, 6H), 3.59 (t, ^{3}J = 6.3 Hz, 2H), 1.70 (m, ^{3}J = 6.3 Hz, 2H), 1.10 (t, ^{3}J = 6.9 Hz, 9H), 0.57 (m, ^{3}J = 6.3 Hz, 2H).

2.3. Synthesis of **6**

The complex was prepared by mixing 31.0 g (0.100 mol) of **5** and 18.3 g (0.100 mol) of zinc acetate in 200 mL of dry THF. After one hour of stirring, the volume of the solution was reduced at 50 mL under vacuum. The complex was crystallized by addition of 200 mL of hexane. The yellow product was collected by filtration, washed three time with 50 mL of hexane and dried under vacuum (yield: 45 g, 91%). The compound was stored in a dessiccator.^{1}H NMR (dmso-d$_6$) δ: 8.69 (d, ^{3}J = 5.5 Hz, 1H), 8.64 (s, 1H), 8.21 (app t, ^{3}J = 7.9 Hz, 1H), 8.01 (d, ^{3}J = 7.9 Hz, 1H), 7.78 (dd, ^{3}J = 7.9 Hz, ^{3}J = 5.5 Hz, 1H), 3.75 (q, ^{3}J = 6.7 Hz, 6H), 3.57 (t, ^{3}J = 6.3 Hz, 2H), 1.80 (s, 6H), 1.72 (m, ^{3}J = 6.3 Hz, 2H), 1.14 (t, ^{3}J = 6.7 Hz, 9H), 0.57 (m, ^{3}J = 6.3 Hz, 2H).

2.4. Synthesis of **2**

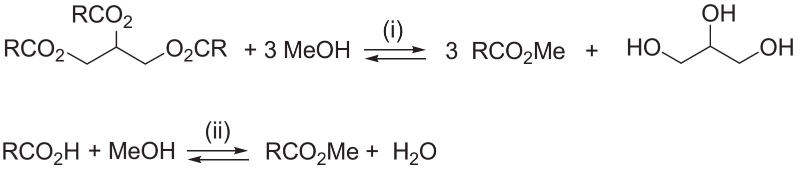
The commercial silica was pre-treated at 300 °C for 5 h, obtaining a silica with a specific area of 163 m^2/g and pores volume of 0.81 cm^3/g (B.E.T.). The catalyst was prepared by adding the silica (80 g) to a solution of 24.7 g (0.0500 mol) of complex **6** in 1.0 L of dry toluene. The mixture was refluxed 20 h under stirring. The solid was filtered, washed with dichloromethane for 16 h in a Soxhlet apparatus, and then dried under vacuum (88 g).

2.5. Catalytic runs

Oil, methanol and the supported catalyst **2** were stirred (rate 500 rpm) in a Parr Instrument® steel reactor in the proportions indicated in the Tables. The temperature in the reactor was increased from room temperature to 160 °C in 35 min. After 2 h the reactor was cooled and the reaction mixture was separated from the catalyst and analyzed. Fresh oil and methanol were added to the residual catalyst for successive runs. The Fame yields were determined by NMR spectroscopy [12] and the residual FFA concentration by titration [13].

3. Results and discussion

This approach refers to the so-called *homogeneous supported catalysis* [14]. In this methodology, the active complex is typically linked to an inorganic oxide or an organic polymer by means of a



Scheme 2. (i) Transesterification of vegetable oils; (ii) esterification of fatty acids.