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Short Communication

Direct aminolysis of triglycerides: A novel use for heterogeneous catalysts

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ABSTRACT

The aminolysis of triglycerides of *Passiflora edulis* oil was investigated using heterogeneous catalysts previously reported for biodiesel production. High rates of conversions (88–100%) to fatty ethanolamides were obtained with all the catalysts when the described transesterification conditions of reaction were used. $ZnO.La_2CO_5.LaOOH$ (2.3%, w/w) was the most efficient, reaching 100% conversion after 8 h at 100 °C.

1. Introduction

The preparation of amides from amines usually results from their reaction with a carboxylic acid or one of its more reactive derivatives [1,2], and methods involving the use of metallic catalysts [3–5], biocatalysis or microwave irradiation [6–11] have been described.

Synthetic fatty amides are used as ingredients for detergents, lubricants and other products [12,13]. They are usually obtained in two steps through the amidation of fatty methyl esters (Fig. 1). The less common direct aminolysis of vegetable oils, performed using enzymes [14–16] or microwave irradiation in the presence of an homogeneous catalyst [17], produces the amide surfactant with less separation steps and by-products than the usual methods.

In the last years, the formation of amides under green conditions and atom economy has become a priority of research for the industry [18]. Heterogeneous catalysts are suitable reagents for this purpose, as they are lesser consumption, environment-free, they can be usually filtered from the reaction by filtration and recycled. Their applications in the production of biodiesel are well known [19–21], but their use in the aminolysis reaction of vegetable oil has not been investigated yet. We report in this work the synthesis of fatty amides through the aminolysis of passion fruit oil in monoethanolamine over heterogeneous catalysts known to efficiency to catalyze transesterification reactions.

2. Experimental

2.1. Materials and instruments

Infrared spectra (FT-IR) were obtained by the KBr disc technique and were performed on a Bomem FT IR MB-102 spectrometer.

Low angle X-ray diffraction (XRD) analyses were performed on a Bruker-D4 Endeavor, using Co Kα radiation in the 2θ range of 5–80°. The qualitative interpretation of the spectra were done by comparison with standards contained in the PDF02 (ICDD, 1996) data bank using a Bruker DiffracPlus software. The morphology of the samples was observed on a LEO S440 transmission electron microscopy. NMR spectra were recorded on a Bruker AVANCE DRX 300 MHz, using deuterated solvents and trimethylsilane as internal reference. Reagents were purchased from Sigma Aldrich and used without purification. Solvents were purchased from VETEC QUÍMICA and used without further purification.

Zn quantifications were performed by Flame Atomic Absorption Spectrometry (F AAS), using the AA240FS FAST SEQUENTIAL AAS (Varian).

2.2. Catalysts preparation and characterization

The catalysts ($Ce[OSO_3C_{12}H_{25}]_3$. $3H_2O$, $K_4Zn_4[Fe(CN)_6]_3$. $6H_2O$. 2(*terc*-butanol), $[Al_2Li(OH)_6](CO_3)_{0.5}$. nH_2O, $ZnO.La_2CO_5.LaOOH$, and *poly*-SDVB) were synthesized according to the literature procedures [22–27] and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and/or nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. The bulk density and cation exchange capacity were determined for poly-SDVB.

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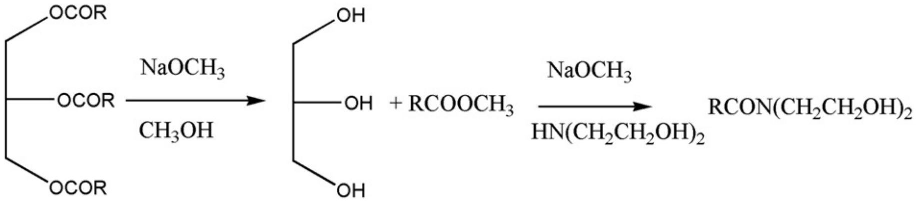

Fig. 1. Industrial synthesis of fatty amides from triglycerides.

2.3. Reaction procedure

2.4. Aminolysis

The first set of reactions was performed using oil (0.5 g), ethanolamine (3–10 mol equivalent) and the catalyst (2.3–50 wt% of oil). In the first experiment, the oil:amine:catalyst ratios (Table 1) used were the same described in the literature for the transesterification reactions [22–26].

The catalysts were removed from the reactions by filtration and the mixtures were partitioned between brine and dichloromethane. The concentrated organic phase was analyzed by ^{1}H NMR to calculate the conversion rate of ester to amide.

In view of the homogenization of reaction conditions a second series of experiments was conducted in the presence of 3 mol equivalent of amine and 2.3% (w/w) of each catalyst, under conventional heating at 100 °C for 8–12 h.

2.5. Influence of the reaction parameters

2.5.1. Determination of $ZnO.La_2CO_5.LaOOH$ (Zn-La) minimal concentration

The reaction was performed at 100 °C for 8 h using 0, 1.6 or 2.3% of the catalyst.

2.5.2. Kinetic of the reaction

The reactions were performed using 0.5 g of the oil, 3 mol equivalent of ethanolamine and 2.3% (w/w) of the catalyst. Aliquots of the reaction were taken at 3, 6 and 8 h and the conversion rate of triglycerides to amide was calculated.

2.6. Catalyst reusability and leaching

The catalyst was filtered from the reaction mixture and reused without any further treatment. Leaching of the catalyst into the reaction mixture was also investigated: the catalyst was filtered at the end of 1 h and the reaction was monitored for another 7 h.

3. Quantification of Zn

The samples (0.5 g) were mixed with 6 mL of concentrated HNO_3 and 1.9 mL of (30% w/w) H_2O_2 and the mixtures were subjected to digestion at 25 °C for 12 h and then under heating (100 °C, 12 h). After digestion, the solutions were diluted in deionized water (resistivity of 18.2 MΩcm) to 25 mL for analysis.

Table 1
Aminolysis of passion fruit oil over heterogeneous catalysis.

Catalyst (%)	Monoethanolamine (mol eq)	Time/Temperature	Conversion (%)
–	3	168 h/150 °C	<1%
$Ce[DS]_3$ (10%)	6	28 h/150 °C	100
Zn-Fe (3%)	10	8 h/25–180°C*	88
Al.Li (3%)	6	18 h/150 °C	97
Zn-La (2,3%)	3	3.2 h/25–180°C*	100
Poly-SDVB (50%)	3	16 h/150 °C	100

* Reaction performed in a hydrothermal reactor.

4. Results and discussion

4.1. Catalysts characterization

The IR spectra of the heterogeneous catalysts synthesized in this work are shown in Fig. 2 and confirmed their structure (more details in the Supplementary Data file).

The bulk density of poly-SDVB (0.33 g/mL), determined according to modified ASTM D-1895, was found to be lower than that described by Rezende et al. [28], which implies a higher porosity of the catalyst and a greater interaction with triglycerides. The cation exchange capacity of the sulfonated polymer was determined as 1.96 meqSO_3H/g catalyst, which is below the described value (3.4 meqSO_3H/g catalyst [28]), suggesting a lower concentration of cationic ions in the medium.

The scanning electron microscopy images for Fe-Zn, Zn-La, poly-SDVB and Al-Li shown in Fig. 1 are consistent with previous literature [22–26].

Fe-Zn (Fig. 2A) revealed a spherical morphology and an average particle size of 1.14 μm. La-Zn catalyst (Fig. 2B) appeared in the form of small particles and some big aggregations. The image of the internal surface of the catalyst produced from poly-SDVB (Fig. 2C) showed large agglomerates with large voids. The morphology of Al-Li consisted in platelets (Fig. 2D), many of which hexagonal, typical of crystallized hydrotalcite-type compounds.

The chemical characteristics of for Fe-Zn, Zn-La, $Ce[DS]_3$ and Al-Li were investigated using X-ray diffraction (XRD) and showed good agreement with the literature.

Double-metal cyanide complexe, Fe.Zn, displayed sharp and dense peaks, at $2\theta = 18.9°$; 22.9°; 25.4°; 28.7° and 29.9° exhibiting higher crystallinity [29].

The XRD pattern of $Ce[DS]_3$ is characteristic of lamellar arrangements and show strong reflections at lower diffraction angles at $2\theta = 6.5°$, 13.0° and 14.8°.

The diffractogram of $[LiAl_2(OH)_6](CO_3)_{0.5}$. nH_2O was consistent with the presence of a crystalline complex and showed reflections at diffraction at $2\theta = 13.8°$; 23.5°; 27.8°; 41.9°; 55.9° and 75.1°. The shape of the diffraction features around 20°, 40°, and 50° is characteristic of turbostratic disorder [30].

4.2. Aminolysis reaction

The ^{1}H NMR spectra of the crude products of the aminolysis reaction of passion fruit oil in monoethanolamine (Fig. 3), were compared to the ^{1}H NMR spectrum of the oil. No signal from the four methylene hydrogens of the glycerol at 4.2 ppm was observed after the completion of the reaction. The remaining resonance signal of at 5.35 ppm was attributed to the olefin protons of the unsaturated portions of the aliphatic chains. The conversion rate was obtained from the signal integration of the protons at 2.28 ppm, corresponding to the hydrogens of the α carbonyl moiety of the oil, in relation to the signal integration of the two amide