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Biodiesel production over lime. Catalytic contributions of bulk phases and surface Ca species formed during reaction

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ABSTRACT

Lime is pointed out as an effective catalyst for biodiesel production by oil methanolysis. Several Ca phases are formed during reaction. Each Ca phase has different contribution to the catalyzed process.

Using CaO as a catalyst, S shape kinetics curve was observed and the induction period can be ascribed to the $Ca(OH)_2$ formation. When $Ca(OH)_2$, prepared by contacting CaO with H_2O, is used as catalyst the initial period with a slow rate of transesterification has almost vanished. Besides, if the catalyst surface is totally converted into methoxide species the induction period is longer than the analogous obtained with CaO. This is an indication that the methoxide species strongly bonded to Ca are less reactive.

The calcium diglyceroxide material (CaO_diglyc), prepared by contacting CaO with a mixture of methanol and glycerol, displays a totally different kinetics curve with no induction period. The faster kinetics and the Ca species detected in the glycerin phase seem to underline a non-negligible homogeneous process contribution.

The characterization of the post-reaction catalysts underlines the relevance of the surface and bulk catalyst modifications. Calcium hydroxide can be pointed out as the active phase whereas calcium diglyceroxide is responsible for the catalyst deactivation due to calcium leaching.

1. Introduction

Fuels production from renewable materials has been attracting increasing interest over the last few decades as they are considered to be part of the solution for some of the most important challenges of modern life, which include concerns over energy security and the need to mitigate climate changes [1]. Despite the problems associated with first generation biofuels like the fuel versus food debate and land use, first generation biodiesel, a mixture of long chain fatty acids methyl or ethyl esters, is the presently available and feasible alternative to substitute fossil diesel in internal combustion engines [2]. There are a large number of commercial plants producing biodiesel by transesterification of vegetable oils and fats using homogenous basic catalysts [3]. However, homogeneous processes have several drawbacks related to phases separation and washing steps and to the impossibility of catalyst reutilization. Therefore, the substitution of homogeneous catalysts by heterogeneous ones may allow to achieve more efficient and economical biodiesel production processes [4,5]. Several materials are referred in the literature as potential catalysts for transesterification reactions, including biodiesel production from vegetable oils or fats [6,7]. Among them, lime, a low cost material, is indicated as presenting interesting catalytic performances for the methanolysis of vegetable oils [8]. When lime is used as catalyst, several Ca phases might be formed in the reaction medium (calcium hydroxide, calcium diglyceroxide and calcium methoxide) and these phases may have different contributions to the catalytic process [9]. Raafat [10] stated that the reactivity order $Ca(OH)_2 < CaO < Ca(OCH_3)_2$ agrees with the Lewis basic theory: the methoxides of alkaline earths metals are more basic than their oxides which are more basic than their hydroxides.

The high reactivity of methanol with calcium oxide, even at room temperature, compelled Kouzu et al. [11] to argue that calcium methoxide is the active phase, instead of CaO, during oil methanolysis. Other researchers also studied the oil methanolysis over calcium methoxide and underlined its excellent catalytic

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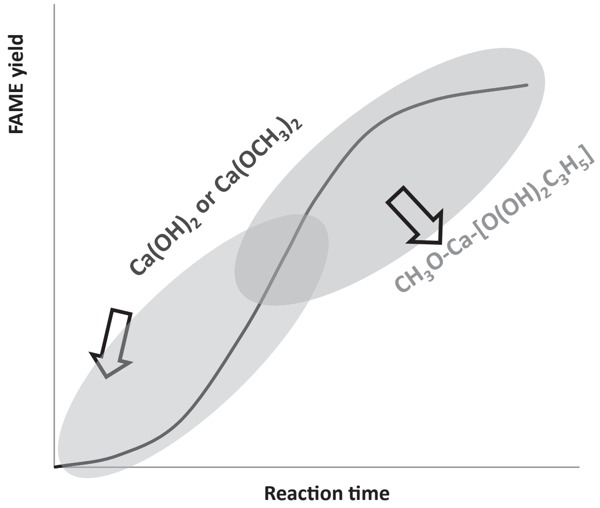

Fig. 1. Typical kinetics curve of oil methanolysis over lime catalyst (adapted from Ref. [6]).

behavior [12]. Calcium hydroxide was also referred to be active for biodiesel production through a mechanism involving the H^+ abstraction of CH_3OH by surface −OH groups [10]. Some authors [13] reported a positive effect for small water contents which can be endorsed by an improvement of surface −OH group availability. Higher water contents promote undesirable soap formation.

A new Ca phase, calcium glycerolate, with excellent catalytic performances was recently reported by Rayero et al. [14].

The existence of several Ca species in the reaction medium, with dissimilar catalytic behavior, potentially contributes to the S-shape kinetics curves (Fig. 1) observed when oil methanolysis is carried out over lime catalysts [15]. Most of the researchers ascribed the sigmoid kinetics curves to the existence of mass transfer limitations for the initial reaction period followed by a kinetics control for the later period. Recently Csernica and Hsu [16] reported, for homogeneous catalyzed oil methanolysis, that the S-shape kinetics curve, usually ascribed to a transition from a mass transfer controlled regime, is, in fact, ascribable to the transition from two-phases to a single phase system. Analogous results, for homogenous catalysis, were reported by Likosar and Levec [17] and Likosar et al. [18].

In order to clarify the sigmoid form of the kinetic curve, the rapeseed oil methanolysis was carried out over CaO, $Ca(OH)_2$ and calcium diglyceroxide. The catalysts, fresh and post-reaction, were characterized by XRD and HATR-FTIR in order to identify the bulk and surface Ca species formed. The role of each Ca phase in the catalytic behavior during biodiesel production and in the quality of the glycerin phase is discussed in the following sections.

2. Experimental

Methanol (≥99%) and the rapeseed oil (average composition Table 1) were supplied by Iberol S.A., a Portuguese biodiesel producer. The oil is used as raw-material in the industrial process and it is therefore semi-refined with an acidity of 0.55 mg KOH/g oil and a water content of 334 mg/kg.

2.1. Preparation of the catalysts

Commercial CaO, from a local producer (Lusical), was used as raw material for catalysts preparation. The “as received material”, a chalky-white material with a wide granulometric distribution, was grounded in a pyrex mortar and dried at 120 °C overnight. The calcium diglyceroxide was prepared by contacting (5 h) the CaO with a mixture containing equal amounts of glycerin and methanol (methanol reflux temperature). A calcium methoxide sample was prepared contacting CaO with methanol in analogous conditions. A similar procedure was used to obtain calcium hydroxide samples, where a water suspension of the grounded CaO was stirred during 5 h at 62 °C. For each catalyst batch 20 g of raw CaO (dried overnight at 120 °C) and 150 mL of liquid (water, methanol or methanol/glycerin) were used.

All the prepared samples were dried overnight at 120 °C before the catalytic tests. The post reaction catalysts (named in the next sections as “PR” or PR#batch number) were washed with methanol (around 20 mL during filtration) and dried overnight at 120 °C.

2.2. Characterization of the catalysts

The surface area (BJH isotherm) of the raw CaO was assessed by N_2 physisorption, at 77 K, using a Micromeritics ASAP 2010 apparatus. Particles size distributions of the fresh and post reaction catalysts were assessed by laser diffraction (blue radiation, 455 nm) based on Lorenz Mie law using a Malvern Mastersizer 2000 equipment. Water dispersions (with 10–20% of obscurity) of the materials were prepared using ultrasound. The granulometric distributions were computed taking into account the refractive index of CaO (1.838). The external surface areas of the catalysts were computed considering spherical particles.

The surface basicity was assessed using basic Hammett indicators in methanolic solutions. Experimental details are given elsewhere [19].

The XRD patterns of fresh and post reaction (PR#*batch number*) catalysts were recorded with a Rigaku Geigerflex diffractometer with Cu K_α radiation at 40 kV and 40 mA (2°/min).

In order to identify the reaction species (hydroxyl, methoxide and others) on the catalysts surface infrared spectra were collected, for fresh and post reaction catalysts, with a resolution of 16 cm^{-1}, using a FT-MIR equipment from BOMEN (FTLA2000-100, ABB) with a DTGS detector. A horizontal total attenuated reflection accessory (HATR), from PIKE Technologies, with a ZnSe crystal was used. Sixty-four scans were accumulated for each spectrum to obtain an acceptable signal-to-noise ratio. Furthermore, the spectra were recorded in duplicate for each sample and the average of the two measurements was used for analysis.

2.3. Methanolysis tests

The methanolysis of rapeseed oil tests were carried out in a 500 mL three-neck round bottom flask equipped with a

Table 1
Characteristics of the rapeseed oil provided by Iberol (local biodiesel industry).

FFA (%)											
C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C24:0	C24:1
0.1	4.2	0.3	2.1	62.8	19.2	9.0	0.7	1.2	0.3	0.2	0.1
Iodine value: 112											
Acidity: 0.55 mg KOH/g oil											
Water: 334 ppm											