Vanadium phosphate catalysts for biodiesel production from acid industrial by-products

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A B S T R A C T

Biodiesel production from high acidity industrial by-products was studied using heterogeneous acid catalysts. These by-products contain 26–39% of free fatty acids, 45–66% of fatty acids methyl esters and 0.6–1.1% of water and are consequently inadequate for direct basic catalyzed transesterification. Macroporous vanadyl phosphate catalysts with V/P = 1 (atomic ratio) prepared via sol–gel like technique was used as catalyst and it was possible to produce in one reaction batch a biodiesel contain 87% and 94% of FAME, depending on the by-product used as raw material. The initial FAME content in the by-products had a beneficial effect on the reactions because they act as a co-solvent, thus improving the miscibility of the reaction mixture components. The water formed during esterification process seems to hinder the esters formation, possibly due to competitive adsorption with methanol and to the promotion of the FAME hydrolysis reaction.The observed catalyst deactivation seems to be related to the reduction of vanadium species. However, spent catalysts can be regenerated, even partially, by reoxidation of the reduced vanadium species with air.

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1. Introduction

Energy is a crucial component of modern life. Sources of energy can be classified into three groups: fossil, renewable and nuclear (Demirbas, 2009). Nowadays, fossil fuels account over 80.3% of the primary energy consumed in the world and 57.7% of that amount is used in transportation sector (Lam et al., 2010). Road, sea and air transportation are the major consumer of fossil energy thus constituting one of the economic sectors with the highest carbon footprint (Piecyk and McKinnon, 2010).

Biofuels are pointed out as feasible substitutes of fossil fuels for the transportation sector (Demirbas, 2007). As produced from biomass, they are expected to provide a renewable and sustainable source of energy with lower GHG emissions (Lapuerta et al., 2008; Jørgensen et al., 2012). Among these, first generation biodiesel, a mixture of long chain fatty acids methyl (FAME) or ethyl esters (FAEE), present combustion characteristics similar to those of petroleum diesel thus being an alternative to fossil fuel. It can be used as pure or mixed with petroleum diesel. European governments aim the incorporation of 10% of biofuels, for the global target of 20% of renewable energy by 2020 (Directive 2009/28/EC, 2009).

Today's commercial production of biodiesel is based on homogeneous catalysts. The cost of biodiesel production is high, i.e., 1.5–3 times more expensive than conventional diesel (Endalew et al., 2011). According to Di Serio et al. (2008), the replacement of the homogeneous catalysts by heterogeneous catalysts could reduce the production costs, thus making biodiesel competitive with petroleum diesel from an economic point of view. Acid, basic and enzyme solid catalysts are referred to alternative as active for biodiesel production (Zabeti et al., 2009).

Vegetable oils used for first generation biodiesel are expensive. Thus it is important to be able to use low costs feedstocks to produce biodiesel, such as high acidity oils that do not allow the use of the conventional basic catalysts (Marchetti and Errazu, 2008). In a recent review, Lam et al. (2010) pointed out the advantages and disadvantages of different catalytic systems (homogeneous, heterogeneous and enzymatic) to convert low grade oils into biodiesel In this case, heterogeneous acid catalysts have the unique advantage related to the fact that they can simultaneously promote esterification and transesterification reactions, allowing the use of high acidity oils as feedstock for biodiesel production thus contributing to economic viability of biodiesel (Sharma et al., 2011).

Different types of heterogeneous acid catalysts have been tested in the biodiesel production. In the literature, the catalytic

performances for resins, tungstated and sulfated zirconia, polyaniline sulfate, heteropolyacids, metal complexes, sulfated tin oxide, vanadium phosphate and zeolites, among others, are described (Di Serio et al., 2007, 2008; Melero et al., 2009). Kiss and Rothenberg (2006) reported that acid catalyst must have a hydrophobic surface, with multi Brönsted acid sites, in order to avoid both water adsorption and the adsorption of the hydrophobic carbon chain of the fatty acids that occur when isolated sites are available. Chen et al. (2007) studied the methanolysis reaction over acid catalysts (sulfated materials) and concluded that Brönsted sites exhibit an important role on catalytic performances. Recent findings (Shi et al., 2012) showed that Brönsted sites are active in esterification, whereas Lewis acid sites are more active in transesterification.

Vanadium phosphorus oxides (VPOs) are known as catalysts for the mild oxidation of hydrocarbons and alcohols (Ennaciri et al., 1999) and they are industrially used to produce maleic anhydride from n-butane (O'Mahony et al., 2004). They possesses simultaneously Brönsted (P—OH) and Lewis acid sites (V=O) (Busca et al., 1989), so they can promote simultaneously esterification and transesterification reactions. The strength and the nature, of the acid sites strongly depend on the preparation procedure (Kamiya et al., 2003). The existence of strong Brönsted acid sites was proven by the large amounts of dimethyl ether obtained during methanol oxidation (Ennaciri et al., 1999).

Excellent performances of vanadium phosphorus catalysts for biodiesel production were reported by Di Serio et al. (2007), despite their low specific surface. Lately, Behera and Parida (2012) successfully used analogous catalysts for the esterification of oleic acid. They also studied the esterification of acetic acid with the VPO catalysts (Parida and Behera, 2010). Published results indicate that vanadium phosphorus oxides will be able to catalyze the methanolysis of acid raw oils, which contain simultaneously triglycerides and fatty acids.

The present research work reports the catalytic behavior of VPO catalysts for biodiesel production from high acidity industrial by-products. Additionally, data for rapeseed oil and oleic acid were also presented, for comparison purposes.

2. Experimental

2.1. Preparation of the catalysts

Several methods are available in the literature to prepare vanadyl phosphate catalysts. The most common procedures usually involve long contact times, under reflux, between powder V_2O_5 and an aqueous solution of o-phosphoric acid (Parida and Behera, 2010).

A novel method involving a sol–gel like procedure, based on the Pechini method (Pechini, 1967; Dias et al., 2010) was used. Batches of 20 g of vanadium phosphorus catalysts with V/P = 1 (atomic ratios) were prepared. All the used chemicals were *pro analysis* grade. Briefly aqueous solutions (100 mL each) of ammonium vanadate and ammonium phosphate were prepared separately adding citric acid as complexation agent (molar ratio citric acid/ammonium salt = 1). The hot solution of phosphate salt was slowly added to the vanadium hot solution under vigorous stirring. After this step the liquid mixture, intense blue, was slowly evaporated at ≈80 °C under stirring and the resulting viscous xerogel was dried overnight at 120 °C. The dried material was, low density foam with green shade, was crushed in a Pyrex mortar and the obtained powder was calcined in a muffle during 5 h at 500–700 °C. More details on the preparation procedure are given elsewhere (Dias, 2012).

2.2. Characterization of the catalysts

The BET surface areas were obtained by N_2 physisorption using ASAP 2010 Micromeritics equipment. The particles size distributions, for fresh catalysts, were assessed by laser diffraction (blue radiation, 455 nm) based on Lorenz Mie law. Malvern Mastersizer 2000 equipment was used. The morphology of fresh and post reaction samples was examined using a JOEL JSM7001F FEG-SEM microscope with an Oxford energy dispersive X-ray high vacuum detector (E = 20 kV) for elemental microanalysis. X-ray diffraction patterns were recorded with a Rigaku Geigerflex diffractometer with Cu K_α radiation at 40 kV and 40 mA (2°/min).

The diffuse reflectance UV–vis spectra, of fresh catalysts, were collected using a Cary 5000 Varian equipment with a DRA 2500 diffuse reflectance accessory (integration sphere). The spectra were deconvoluted using symmetric Gaussian shape lines.

The reactivation procedure was studied by thermogravimetry using a TG-DTA-DSC LabSys, from Setaram, equipment. The catalyst reactivation temperature was selected from TG mass loss/gain profile.

2.3. Raw materials

The rapeseed oil, the industrial by-products and the methanol were supplied by Iberol S.A., a Portuguese biodiesel producer. The commercial oleic acid (p.a. grade) was used as raw material, for comparison purposes. The two acidic raw materials used in this work, identified as P1 and P2, are produced in the plant of Iberol by mixing the glycerol phases obtained after the two reaction batches with the washing waters of the biodiesel purification step. This mixture contains methanol, glycerol, catalyst, soaps, water and the entrained oil and biodiesel and the by-products were produced after methanol and glycerol recovery, by acidulation of the soaps to free fatty acids (soap splitting). Thus, after water removal, the products used in the experiments have a high content of free fatty acids and methyl esters as shown in Table 2. Additionally, the initial content of glycerides (GL) in these two products may be estimated by a mass balance giving a content of 7.8% for P1 and 15.1% for P2.

2.4. Catalytic tests

The methanolysis reactions were carried out at temperatures higher than the refluxing temperature of the methanol using a high pressure stainless steel reactor equipped with mechanical stirrer (600 rpm). The standard procedure for each catalytic test involves the mixture of 100 g of oil with 5% (w/w) of powder catalyst and with methanol (0.55 g/1 g oil that, for the soybean or rapeseed oils corresponds to a molar ratio of methanol:oil of 15/1). After 6 h, at 125 °C, the reactor was cooled down and the catalyst was removed by vacuum filtration and the liquid mixture was transferred into a decantation funnel. After phase separation, the methyl ester layer was washed with water, centrifuged and dried at 80–90 °C under vacuum (0.05 bar) with a rotary evaporator (RE-111, Büchi). Additionally, several experiments were carried out with the industrial by-product P2 to test other reaction conditions such as the use of a different temperature (60 °C and 150 °C), smaller catalyst concentration (2.5% and 1.25%), reaction time (3 h) and weight ratio of methanol to by-product (0.30 g/g). In order to evaluate the deactivation of catalysts several reaction batches were performed with the same catalyst sample, with and without intermediate activation step consisting in recalcination in a muffle (as described above).

The FAME content of the purified crude biodiesel samples was evaluated using near infrared spectroscopy (NIR), against previously developed calibration (Baptista et al., 2008). The spectra, of the liquid samples, were acquired using an ABB BOMEM MB160