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Vanadyl phosphate catalysts in biodiesel production

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Abstract

The possibility of using vanadyl phosphate (VOP)-based catalysts in biodiesel production has been investigated. Vanadium phosphate catalysts resulted very active in the transesterification reaction of triglycerides with methanol, despite their low specific surface area. A slow deactivation of the catalysts has been experimentally detected under the reaction conditions, but the catalyst can easily be regenerated by calcinations in air. The influence of the calcination treatment on the surface structure and, consequently, on its catalytic performances was deeply investigated. Both fresh and used catalysts were characterized by using several techniques, such as BET, X-ray diffraction (XRD), UV–vis diffuse reflectance (DRUV) and laser-Raman (LRS). The characterization results showed that the deactivation is due to a progressive reduction of vanadium (V) species from V^{5+} to V^{4+} and V^{3+} by methanol. By comparing the obtained performances of VOP catalysts with the ones of other heterogeneous catalysts reported by the literature, it is possible to conclude that VOP catalysts can already be used industrially for biodiesel production but their performances can probably be greatly improved in perspective.

Keywords: Transesterification; Biodiesel; Vanadyl phosphate; Heterogeneous catalysis

1. Introduction

Biodiesel is a renewable diesel fuel obtained by the transesterification of vegetable oils or animal fats with methanol. Most biodiesel is currently produced by transesterification of triglycerides of refined/edible oils with methanol in the presence of homogeneous basic catalyst, such as sodium or potassium hydroxides, carbonates or metal alkoxides [1,2]. The main drawback in biodiesel production is the high cost compared with the cost of diesel obtained from petroleum. However, the cost of biodiesel could certainly be lowered by improving the production processes [1]. The first step in this direction could be represented by the use of heterogeneous catalysts instead of homogeneous ones. Heterogeneous catalysts can be more easily separated and give place to higher quality of ester products and glycerol by product. Pure high grade glycerol can be obtained, in this case, without expensive refining operations [3,4]. For these reasons, many heterogeneous catalysts, based on both basic [5–9] and acid [4,10–14] solids, have recently been proposed in the literature.

Catalysts based on vanadyl phosphate ($VOPO_4{\cdot}2H_2O$), mainly used in hydrocarbon oxidation catalytic reactions [15,16] but also active in some other reactions involving Brönsted and Lewis acid sites, such as dehydration [17] and isomerization [18], have never been used in transesterification reactions. These catalysts have shown interesting behaviour in vegetable oil transesterification with methanol, and preliminary results were recently published in a patent [19].

In the present work the catalytic performances of some vanadyl phosphate (VOP) catalysts in the transesterification reaction of soybean oil with methanol have been studied in different operative conditions. Notwithstanding, the catalysts were subjected to a slow deactivation process; the reaction yield in the temperature range 150–180 °C was about 80% in less than 1 h. The catalysts deactivation process has been studied by using different techniques and is due to the progressive reduction of vanadium (V) by methanol. In fact, calcination in air completely restores the initial activity. On the basis of the

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experimental data obtained it is possible to define the most convenient way for a profitable use of the catalyst in an industrial plant. At last, a comparison of the performances obtained with VOP catalysts with the ones obtained with other heterogeneous catalysts conclude the paper.

2. Experimental

2.1. Materials

Soybean oil was purchased in a local food-store (the fatty acid composition of used soybean oil determined by gas chromatographic analysis (%, w/w): palmitic = 11, stearic = 4, oleic = 23, linoleic = 56, linolenic = 5, others = 1). All other employed reagents (when not specified) were supplied by Aldrich and used as received without further purification.

$VOPO_4{\cdot}2\ H_2O$ (VOP) was prepared according to the literature by refluxing a suspension of V_2O_5 in diluted phosphoric acid for 16 h [22]. The obtained compound was then dried in air.As the acid properties of the VOP catalyst change as a function of thermal treatments [20,21], calcined materials were also prepared. The duration of calcinations was 2 h. In the text, the acronyms used for the calcined catalysts are based on the temperature of calcination. For example, $VOPO_4{\cdot}2H_2O$ calcined at 500 °C for 2 h is indicated with the following acronym VOP_{500}.

In order to investigate the deactivation/reactivation mechanisms, the VOP_{500} catalyst was put in contact with pure methanol at $T = 180$ °C for two different times, 15 and 60 min, and then dried by using the rota-vapor. The solids obtained with this procedure are indicated in the text as $VOP(R)_{t_{reax}=15\,min}$ and $VOP(R)_{t_{reax}=60\,min}$, respectively. The samples regenerated by submitting a fraction of VOP(R) catalysts to a calcination treatment in air at $T = 500$ °C for 2 h have been named VOP(C).

2.2. Catalyst characterization

Catalysts were characterised by using different techniques, such as BET, X-ray diffraction (XRD), UV–vis diffuse reflectance (DRUV) and laser-Raman (LRS) spectroscopies.

Textural analyses were carried out by using a Thermoquest Sorptomatic 1990 Instrument (Fisons Instruments) and by determining the nitrogen adsorption/desorption isotherms at 77 K. The samples were thermally pretreated under vacuum overnight up to 473 K (heating rate = 1 K/min). Specific surface area and pore distributions were determined by using the BET and Dollimore-Heal methods [23,24].

XRD analyses were carried out by using a Philips diffractometer. The scans were collected at the range of 5–80° (2θ) using Cu Kα radiation with a rate of 0.02° (2θ)/s.

Diffuse reflectance spectra were obtained on a UV–vis scanning Jasco spectrometer V-550, equipped with an integrating sphere, using $BaSO_4$ as reference, under ambient condition. UV–vis spectra were recorded in the diffuse reflectance mode (R) and transformed by a magnitude proportional to the extinction coefficient (K) through a Kubelka–Munk function ($F(R)$).

Raman spectra were recorded, at room temperature, by using a confocal Raman microscope (Jasco, NRS-3100). The 488-nm line of an air-cooled Ar^+ laser (Melles Griot, 35 LAP 431-220), 125 mW, was injected into an integrated Olympus microscope and focused to a spot size of approximately 2 μm by a 100× or 20× objective. A holographic notch filter was used to reject the excitation laser line. Raman scattering was collected by a peltier-cooled 1024 × 128 pixel CCD photon detector (Andor DU401BVI). For all systems, it takes 10–20 s to collect a complete data set.

2.3. Catalytic experiments

The catalytic screening was performed in small stainless steel vial reactors. The reactors were heated in a ventilated oven. In order to minimize mass transfer limitation, the reactors were constantly agitated inside the oven. The temperature of the oven was initially fixed at 50 °C for 14 min, and then increased at a rate of 20 °C/min until a prefixed reaction temperature was reached. Then, after a fixed reaction time, the temperature was quickly diminished by putting the vials in a cold bath.

According to this procedure, two different sets of kinetic runs were performed. A set of experiments was conducted at $T = 180$ °C by keeping constant the reaction time (60 min) and by using 0.1 g of catalyst, 0.88 g of methanol and 2 g of soybean oil.

Another set of kinetic runs was performed by varying both the reaction temperature (120–150–180 °C) and the reaction time (30–60–90 min) and by using 0.1 g of catalyst, 1.55 g of methanol and 1.55 g of soybean oil.

In all cases, the fatty acid methyl ester (FAME) yields were determined by using an H NMR technique [25] (Bruker 200 MHZ), i.e., measuring the area of the H NMR signal related to the methoxylic (A_1) and methylenic groups (A_2), respectively:

$$Y_{FAME} = \frac{A_1/3}{A_2/2}$$

3. Results and discussion

3.1. Characterization of fresh and calcined catalysts

Specific surface areas determined with the BET procedure for the tested catalysts resulted in the range of 2–4 m^2/g, according to the literature [17].

Both fresh (VOP) and calcined (VOP_{500}) catalysts were submitted to XRD measurements in order to provide information about the structural properties of the samples investigated. In Fig. 1, XRD plots for VOP and VOP_{500} are reported. As can be seen, the catalysts showed XRD patterns with different reflections. In particular, the VOP catalyst showed peaks attributable to crystallographic α form of $VOPO_4{\cdot}2H_2O$ [26] while the same material calcined at 500 °C for 2 h gave signals corresponding to another crystalline form of $VOPO_4$, and more specifically the α_{II} form [26].

Interesting information was also obtained by DRUV analyses that were performed to provide information about