Applied Catalysis B: Environmental 221 (2018) 158–168

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Research paper

Effect of the treatment with H_3PO_4 on the catalytic activity of Nb_2O_5 supported on Zr-doped mesoporous silica catalyst. Case study: Glycerol dehydration

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ARTICLE INFO

Keywords:
Niobium
Phosphoric acid treatment
Glycerol
Acrolein

ABSTRACT

We have previously demonstrated the influence of the niobium species over the glycerol dehydration reaction and how the catalyst regeneration by thermal treatment modified the catalytic performance due to the transformation of superficial niobium species. This experimental conclusion encouraged us to find a way to maintain and even improve the catalytic behavior of these Nb-based catalysts. Thus, herein, it is reported the influence of phosphoric acid treatment on 8 wt% Nb_2O_5 supported on a zirconium doped mesoporous silica (Si/Zr = 5 molar ratio) catalyst, varying the Nb/P molar ratio between 0.1 and 1. Catalysts were full characterized and tested in the glycerol dehydration at 325 °C. This acid treatment modifies the nature of species present on the catalyst surface, as inferred from ^{31}P NMR data, where the presence of zirconium hydrogenphosphate was detected. A comprehensive study of the influence of acid properties on the catalytic activity has been carried out. Thus, the selectivity to acrolein was improved, which was attributed to this hydrogenphosphate phase and the catalyst stability was associated to the existence of acid sites of low and moderate strength. The best catalyst was studied at higher reaction temperatures, showing the highest glycerol conversion and achieving an acrolein selectivity of 74%, at 350 °C. This catalyst was also regenerated, maintaining its catalytic activity.

1. Introduction

In the last years, the development of new catalytic processes for the production of fuels and chemicals from renewable feedstock has been greatly encouraged due to the depletion of fossil resources and environmental concerns. In this context, biodiesel is considered as a promising alternative fuel, with a lower environmental impact than conventional fuels. It is mainly produced from transesterification of vegetable oils and animal fats with short-chain alcohols, mainly methanol and ethanol, obtaining glycerol as by-product [1–3]. Thus, about 1 kg glycerol is roughly obtained per each 10 kg of biodiesel, so that large amounts of glycerol surpluses are generated, causing a drop in its price [4,5]. Therefore, glycerol has become an interesting feedstock for the synthesis of high value-added products, which in some cases are currently produced in the petrochemical industry from oil. Thus, new uses of glycerol are being researched to attain a sustainable biodiesel production.

One of the most promising routes for glycerol valorization lies in its catalytic dehydration to acrolein, which is an important intermediate for the chemical industry and it is employed for the synthesis of acrylic acid and its esters, D,L-methionine, glutaraldehyde, polyurethanes and polyester resins [6]. Although industrial acrolein production is based on partial oxidation of propylene, coming from fossil fuels, catalyzed by multicomponent $BiMoO_x$ based catalysts, there is a growing interest to transform acrolein into glycerol [6,7]. The catalytic conversion of glycerol to acrolein, by a double–dehydration reaction, is an acid-catalyzed process. In this sense, several solid acid catalysts have been proposed for the gas-phase selective conversion of glycerol into acrolein, including heteropolyacids [8–12], zeolites [13–16], metal and mixed oxides [17–20], phosphates and pyrophosphates [21–24], sulfated zirconia [25,26] and sulfonic-functionalized SBA-15 [27]. Different authors have confirmed that the catalytic activity depends strongly on the textural, mainly the pore size, and acid properties of solid catalysts [7,28].

It has been recognized in the literature that niobium oxide exhibits excellent acid properties and hydrothermal stability [29,30]. Chai et al.

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http://dx.doi.org/10.1016/j.apcatb.2017.09.016
Received 23 April 2017; Received in revised form 26 July 2017; Accepted 5 September 2017
Available online 06 September 2017

[31] showed that niobium oxide is an effective catalyst for the gas-phase dehydration of glycerol and studied the influence of calcination temperature. Likewise, different mixed metal oxides, containing niobium, have been tested for this reaction, such as $WNbO_x$ [32] and $ZrNbO_x$ [33,34]. As niobium oxide possesses a low specific area, high-surface area supports are often employed to enhance the dispersion of active phases and increase the number of available active sites. Thus, Shiju et al. [19] prepared a series of silica-supported niobia catalysts for the dehydration of glycerol to acrolein. They stated that the catalytic performance was strongly influenced by the total acidity, which depended on the niobia loading and calcination temperature. Moreover, niobium and tungsten mixed oxides have been evaluated over different supports, such as ZrO_2, Al_2O_3, SiO_2 and TiO_2 [4,35], obtaining high acrolein yields in presence of these catalysts.

On the other hand, the type of acid sites is a key parameter influencing the catalytic performance. It is generally accepted that Brönsted acid sites are more selective to acrolein than Lewis acid sites [15,36–38]. In addition, Lauriol-Garbay et al. [33] confirmed that a reduction of the number of Lewis acid sites improved the stability of catalysts. Moreover, it is known that niobium oxide possesses both Lewis and Brönsted acid sites when is supported on silica [30,39,40]. Furthermore, several authors have demonstrated that when Nb_2O_5 is treated with phosphoric acid, the total acidity and strength of acid sites are enhanced [41–44]. Hence, Lee et al. [45] evaluated the incorporation of different amounts of phosphate to Nb_2O_5, in such a way that this treatment ameliorated its acidic properties. In this sense, the greater the phosphate loading, the higher the amount of acid sites detected on the catalyst surface, improving consequently the glycerol conversion and acrolein selectivity. Likewise, a mesoporous siliconiobium phosphate, prepared by Choi et al. [46], was employed as Brönsted acid catalyst for glycerol dehydration to acrolein. This material displayed high activity and stability attributed to the nearly pure Brönsted acidity, which promoted the formation of acrolein, and large mesopores which significantly reduced pore blocking by coke deposition. Therefore, the use of mesoporous materials favors the dispersion of the active phase and hinders the deactivation processes. Moreover, the incorporation of heteroatoms, such as Al, Zr or Ti, in the synthesis step of mesoporous silica can generate a higher number of acid centers [47]. Katryniok et al. also corroborated that the doping with zirconium enhances the acidity of the support and the catalyst stability [48].

In a previous study, it was found that niobium incorporation to a zirconium doped mesoporous silica had a noticeable influence on the nature of superficial niobium species, and consequently on the catalytic performance in glycerol dehydration [49]. Those results encourage us to improve the catalytic performance of the best catalyst assayed. Thus, a niobium catalyst supported on a Zr-doped SBA-15 silica with a loading of 8 wt% Nb_2O_5 was undergone to a treatment with phosphoric acid, synthesizing a family of catalysts with different Nb/P molar ratio. The main goal of this work was to evaluate the influence of such treatment on both textural and acid properties, and how the variation of these properties affects the catalytic activity and special attention was paid to the reusability and deactivation of catalysts.

2. Experimental

2.1. Preparation of catalysts

The preparation details of the support (labeled as *Zr*) and the catalyst with a 8 wt% of Nb_2O_5 (*ZrNb*) have been previously reported [49]. Thus, ZrNb was prepared by means of incipient wetness impregnation with a niobium oxalate solution to achieve 8 wt% Nb_2O_5 and subsequent calcination at 400° C for 4 h. The *ZrNb* catalyst was treated with aqueous solutions of H_3PO_4 to attain different Nb/P molar ratio by using also the incipient wetness impregnation method. Next, these materials (denoted as *ZrNbPx*, where *x* indicated the Nb/P molar ratio employed; x = 0.1-1) were dried at 60 °C, calcined at 400 °C for 4 h. Another catalyst with a Nb/P molar ratio of 0.2 was prepared by impregnation of the *Zr* support with a niobium oxalate − oxalic acid solution (8 wt% Nb_2O_5), and after drying at 60 °C overnight, it was impregnated with a phosphoric acid aqueous solution (Nb/P molar ratio of 0.2), dried at 60 °C and calcined at 400 °C. This latter catalyst was subjected to just one calcination procedure; therefore, to distinguish it from the ZrNbP*x* catalyst, it was named as *ZrNbP0.2-1c*, where *1c* emphasizes that one calcination step was carried out.

For comparison reasons, a catalyst without niobium (*ZrP0.*2) was prepared following the same recipe as the *ZrNbP0.2* catalyst, excepting the addition of the niobium precursor. Likewise, a SBA-15 silica without zirconium was synthesized and used as support to prepare a catalyst (*NbP0.2-1c*) following the same procedure as for *ZrNbP0.2-1c*.

A list of the synthesized catalyst can be found in the Supplementary Information.

2.2. Characterization of catalysts

Powder X-ray diffraction patterns were collected on an ŔPert Pro MPD automated diffractometer (PANanalytical) equipped with a Ge (1 1 1) primary monochromator (strictly monochromatic Cu-Kα radiation) and a X'Celerator detector.

The textural parameters were determined from the nitrogen adsorption–desorption isotherms at −196 °C, obtained by using an automatic ASAP 2020 model of gas adsorption analyser from Micromeritics. Prior to N_2 adsorption, the samples were outgassed at 200 °C and 10^{-4} mbar for 10 h. Surface areas were determined by using the Brunauer–Emmett–Teller (BET) equation and a nitrogen molecule cross section of 16.2 $Å^2$. The Density Functional Theory method (DFT) was employed to determine the pore size distribution.

X-ray photoelectron spectra were obtained with a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300 W, 15 kV, and 1253.6 eV) with a multi-channel detector. Spectra were recorded in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine the binding energies of the different element core levels more accurately.

FTIR spectra were collected on a Varian 3100 FT-IR spectrophotometer, and the samples were diluted in KBr.

The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out to evaluate the total surface acidity. The catalyst (80 mg) was treated by increasing the temperature from room temperature up to 400 °C with a heating rate of 10 °C min^{-1}, and maintained at 400 °C for 15 min under a helium flow. Right after, the catalyst was cooled at 100 °C, it was put in contact with an ammonia flow. The NH_3-TPD was performed by raising the temperature from 100 to 550 °C, under a helium flow of 40 mL min^{-1}, with a heating rate of 10 °C min^{-1}, and maintained at 550 °C for 15 min. The evolved ammonia was analyzed by using a TCD detector of a gas chromatograph (Shimadzu GC-14A).

FTIR spectra after pyridine adsorption were recorded on a Shimadzu Fourier Transform Infrared Instrument (FTIR8300). Self supported wafers of samples with a weight/surface ratio of about 15 mg cm^{-2} were placed in a vacuum cell greaseless stopcocks and CaF_2 windows. Samples were thermally treated at 300 °C and 10^{-4} mbar overnight, exposed to pyridine vapors at room temperature (pressure of 200 mbar) for 10 min, and then outgassed at 200 °C. The amount of both Brönsted and Lewis acid sites have been calculated from integrated areas of the bands located about 1450 (19b vibration mode) and 1550 cm^{-1} (19b vibration mode) using the extinction coefficients E_L = 1.11 cm μmol^{-1} and E_B = 0.73 cm μmol^{-1}, respectively [50].

Thermogravimetric analysis (TGA) of spent catalysts was carried out