Influence of the niobium supported species on the catalytic dehydration of glycerol to acrolein

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ABSTRACT

The present work deals with the catalytic performance of a series of supported niobium oxide (1–12 wt% Nb_2O_5) catalysts in the gas phase dehydration of glycerol. The niobium species were supported on a mesoporous zirconium doped silica (Si/Zr molar ratio of 5) by incipient wetness impregnation. The catalysts were characterized by means of XRD, N_2 adsorption, NH_3–TPD, Raman spectroscopy, adsorption of pyridine coupled to FTIR spectroscopy and XPS. The catalytic reaction was carried out in gas phase at 325 °C. The support exhibits the highest glycerol conversion (91 mol%) after 2 h, but it is less selective to acrolein (25 mol%). The supported niobium species do not ameliorate the glycerol conversion, but the acrolein selectivity is markedly improved, attaining a value of 45 mol% after 2 h for the catalyst with 8 wt% of Nb_2O_5. This catalyst can be regenerated by thermal treatment under an air flow for 4 h, although the regeneration causes a lowering of the Brönsted/Lewis acid sites ratio, thus decreasing the selectivity toward acrolein.

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1. Introduction

Nowadays, society is experiencing a growing concern about the impact of human activity on the environment. Many of the problems associated with deterioration of air quality are related to the excessive use of fossil fuels, which has led to a notable increase of emissions of greenhouse gases and pollutants. In this sense, currently, much attention is being paid to the development of renewable sources for production of energy and chemicals, aiming to fossil fuels replacing.

Concerning transportation liquid fuels, it is feasible to substitute and mix gasoline and diesel with bioethanol and biodiesel, respectively. However, most of the current feedstocks for the production of these two biofuels compete with the food industry, consequently affecting to the world market price of such raw materials. In this scenario, for instance, second-generation biodiesel production involves the use of triglycerides derived from *Jatropha curcas* [1–3], microalgae [4], or waste cooking oils [5].

The worldwide production of biodiesel has also generated an important surplus of glycerol, as byproduct of this oleochemical industry [6]. To date, glycerol finds applications in cosmetics, pharmaceuticals, tobacco industry, among others, up to reach more than 1500 direct applications [7]. However, it has not been used as raw material for the synthesis of other chemicals due to the high price of refined glycerol. Nevertheless, as a consequence of the outbreak of biodiesel production, the glycerol price has experienced a drastic decline, thus, opening the possibility to use it for the synthesis of a large spectrum of chemicals.

In this context, acrolein has attracted considerable attention of many research groups because of its many industrial applications, among which are the synthesis of acrylic acid (precursor of acrylic polymers), *L*-methionine (essential aminoacid used in animal feeding), among others. Currently, acrolein is obtained in the petrochemical industry from the partial oxidation of propene. Therefore, there is a great deal of interest in the production of acrolein from a renewable source (glycerol), developing a greener and environmentally friendly process along with an economic improvement in the oleochemical platform.

Initially, the synthesis of acrolein from glycerol was studied in aqueous phase, under sub-supercritical and supercritical conditions, using homogeneous catalysts [8,9]. This process presents several technical and environmental problems, which have led to be discarded and replaced by the gas phase reaction, under heterogeneous catalysis. Gas phase dehydration of glycerol to acrolein

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has been carried out in the presence of different solid acid catalysts, such as zeolites [10–14], heteropolyacids [15–19], tungsten oxide [20–26], mesoporous silica with anchored sulphonic groups [27] or doped with heteroatoms [28,29], phosphate impregnated metal oxides [30], sulfated zirconia [31] and mixed oxides [32–37]. Moreover, the interest of the industry in the dehydration of glycerol is demonstrated by the numerous patents devoted to this reaction [38–42]. On the other hand, the main drawback of many catalysts evaluated in the gas-phase dehydration of glycerol is their deactivation with time on stream [43–45]. However, lately, some promising catalytic systems have been developed showing a suitable stability [26,32,46].

Among solid acid catalysts, niobium based catalysts are water-tolerant, and they have been used in aqueous media to obtain valuable chemicals from biomass. Thus, they have been also tested in the dehydration of glycerol to acrolein [36,45,47–49]. Chai et al. [45] employed amorphous niobium oxide, evaluating the impact of calcination temperature of $Nb_2O_5 \cdot nH_2O$ on the catalytic activity. The calcination treatment affected to the acid strength distribution and hence to the glycerol conversion and acrolein selectivity. An amorphous catalyst, prepared after calcination at 400 °C, showed the highest glycerol conversion (88 mol%) and acrolein selectivity (51 mol%). The effect of calcination temperature was also studied by Shiju et al. [47] for niobia supported on silica catalysts, and they found that glycerol conversion and acrolein selectivity increased with the niobia loading, reaching the highest values (70 and 65 mol%, respectively) for a catalyst with 20 wt% Nb_2O_5, calcined at 400 °C. However, higher calcination temperatures led to lower glycerol conversion and acrolein selectivity values. This behavior was attributed to the higher acid strength of catalysts calcined at lower temperatures. In these two aforementioned works, the niobia catalysts showed initial glycerol conversion close to 100%, but it decreased rapidly with time-on-stream. Nevertheless, catalysts fully recovered the initial catalytic activity after an oxidation treatment under an oxygen flow.

Massa et al. [48] have evaluated the catalytic behavior of niobia supported on alumina, silica and titania, at a reaction temperature of 305 °C, studying the influence of niobia dispersion on the catalytic performance. Thus, niobia supported on SiO_2 was the least selective to acrolein because of the existence of crystalline Nb_2O_5 particles. The authors attributed the acrolein formation to the presence of Brönsted acid sites, whereas hydroxyacetone was correlated to the Lewis acid sites. Moreover, they demonstrated that oxygen co-feeding reduced the deactivation process, since the formation of coke precursors was inhibited.

On the other hand, niobium supported on ZrO_2 [20] attained an acrolein yield of 75%, with full glycerol conversion at 305 °C. Raman and FTIR spectroscopies have allowed concluding that superficial polymeric structures with Nb–OH Brönsted acid sites were the most selective to acrolein. It was not observed any synergistic effect when niobia was co-supported with tungsten.

Niobium was also studied as mixed oxides with zirconium [32,36] and tungsten [21]. Lauriol-Garbay et al. [32,36] found that mixed oxides were very stable with time-on-stream, attaining glycerol conversion of 82% and acrolein selectivity of 72%, after 177 h at 300 °C. The selectivity to acrolein was attributed to the presence of weak or moderate Brönsted acid sites, associated to polymeric niobium oxide species. Moreover, the stability of catalysts was due to the neutralization of Lewis acid sites of zirconia, which were unselective coke initiator sites.

Omata et al. [21] also synthesized W–Nb mixed oxides with a layered structure in the c-direction, prepared under hydrothermal conditions and calcined between 400 to 1000 °C. The W–Nb–O catalysts calcined at lower temperature resulted in a high acrolein yield (>70%). The temperature of calcination influenced on the structure of the a–b plane, affecting to the product distribution.

However, W–Nb–O catalysts calcined at 1000 °C, with an ordered arrangement based on the $Nb_8W_9O_{47}$, gave a higher yield of hydroxyacetone and lower of acrolein, whereas the calcination at 700 °C gives rise to a disordered arrangement, and the acrolein yield increased.

In the present study, zirconium doped mesoporous silica has been used as support for the preparation of a new family of niobium based catalysts. The support was prepared following a synthetic route similar to that of SBA-15 materials in order to gain in hydrothermal stability; moreover, the Si/Zr molar ratio was fixed at 5 since, in a previous work [28], it was demonstrated the good catalytic performance of a MCM-41 catalyst with such molar ratio. The niobium loading was varied in a wide range in order to obtain different superficial niobium species and correlate the nature of these species with acid properties and product selectivity in the gas phase dehydration of glycerol.

2. Experimental

2.1. Catalyst preparation

A zirconium doped mesoporous silica was synthesized by using P123 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol, Aldrich)) as structure directing agent. Firstly, P123 was dissolved in a 1.7 M HCl aqueous solution, under magnetic stirring at 40 °C. Then, silicon and zirconium precursors (tetraethyl orthosilicate (Aldrich) and zirconium n-propoxide (Aldrich), respectively) were added dropwise, with a Si/Zr molar ratio of 5. The final molar composition of the synthesis gel was $P123/SiO_2/ZrO_2/HCl/H_2O = 1/55/11/350/11100$. The resulting suspension was stirred at 40 °C for 72 h. The solid product was recovered by filtration, washed with deionized water and dried at 60 °C. Finally, it was calcined in air at 550 °C for 6 h with a heating rate of 1 °C min^{-1}. This support was labeled as SiZr5.

The niobium was supported by incipient wetness impregnation, using niobium oxalate/oxalic acid solutions [50], with nominal values of Nb_2O_5 ranging between 1 and 12 wt%. Solids were dried in an oven at 60 °C, and then calcined at 400 °C during 4 h (heating rate of 2 °C min^{-1}). Niobium catalysts were labeled as xNb where x stands for wt% of Nb_2O_5.

2.2. Catalyst characterization

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

X-ray photoelectron spectroscopy (XPS) studies were performed with a Physical Electronics PHI 5700 spectrometer equipped with a hemispherical electron analyzer (model 80-365B) and a Mg Kα (1253.6 eV) X-ray source. High-resolution spectra were recorded at 45° take-off-angle by a concentric hemispherical analyzer, operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was done against adventitious carbon (C 1s at 284.8 eV). The pressure in the analysis chamber was kept lower than 5×10^{-6} Pa. PHI ACCESS ESCA-V6.0 F software package was used for data acquisition and analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves in order to determine more accurately the binding energy of the different element core levels.

N_2 adsorption–desorption isotherms at −196 °C were obtained using a gas adsorption analyzer from Micromeritics, Inc. (ASAP 2020 model). Prior to N_2 adsorption, samples were evacuated at 200 °C (heating rate 10 °C min^{-1}) for 18 h. Pore size distributions