Catalysis Today xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Pd-Nb binfunctional catalysts supported on silica and zirconium phosphate heterostructures for O-removal of dibenzofurane

A. Infantes-Molina[a,**], E. Moretti[b], E. Segovia[a], A. Lenarda[a], E. Rodríguez-Castellón[a,*]

[a] Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain
[b] Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155/B, 30172 Mestre Venezia, Italy

ARTICLE INFO

Article history:
Received 28 July 2015
Received in revised form 28 October 2015
Accepted 7 December 2015
Available online xxx

Keywords:
HDO
DBF
Noble metals
Palladium
Niobium
SiO_2
Phosphate heterostructures

ABSTRACT

Bifunctional PdNb catalysts were studied in the hydrodesoxygenation (HDO) reaction of dibenzofuran (DBF) at 275 °C and 15 bar of H_2 pressure. The influence of both the support employed (silica and zirconium phosphate heterostructure (PPH)) and the catalyst preparation procedure were evaluated in the catalytic response in the HDO reaction. The catalysts were prepared by incipient wetness impregnation by using two synthetic routes. The catalysts were characterized by means of X-ray diffraction (XRD), N_2 adsorption-desorption, thermoprogrammed desorption of NH_3 (TPD-NH_3), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and elemental analysis. The results show that silica supported catalysts are much more active than those supported on PPH. While the characterization results point to a higher dispersion of the supported catalysts on PPH and better textural and acidic properties, the $PdCl_2$ precursor salt remains on these catalysts even after calcination and catalytic tests, explaining the lower catalytic performance presented by these systems: fewer active centers and more residues of carbon. With respect to the preparation method, regardless the support employed, the catalysts synthesized by incorporating Pd after Nb incorporation and calcination, are more active, most probably due to a better phase dispersion and therefore to a higher amount of active centers.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Biomass has been described as the renewable energy source with the greatest potential to contribute to the energy needs of modern society. Biomass can be defined as any organic material of plant or animal origin, including materials from natural or artificial transformation [1]. The use of biomass as an energy source instead of fossil fuels involves a number of environmental benefits: reduction of sulfur emissions; reduced particulate emissions; reduction of pollutants such as CO, HC and NOx; CO_2 neutral cycle; no contribution to greenhouse effect; and use of agricultural waste. These advantages make the biomass one of the potential sources of energy to be employed in the future, being a very important element of territorial balance, especially in rural areas.

Lignocellulosic biomass from the plant cell walls is mainly composed of three biopolymers: cellulose (40–50%), hemicellulose (25–35%) and lignin (16–33%). Their structures contain a high percentage of oxygen, which results in the presence of 30–60% by weight of oxygen in the fast pyrolysis bio-oil. Therefore, it is necessary to reduce the levels of oxygenates to use it as a starting point in the synthesis of biofuels. That is why there is a considerable interest in investigating deoxygenation processes to reach such a goal [2]. Hydrodeoxygenation (HDO) is considered one of the most promising methods for this purpose. As a result of the HDO, a hydrocarbon mixture comparable to those derived from petroleum fractions can be obtained. The main purpose of this reaction is to partially remove oxygen, under moderate temperatures (250–600 °C) with high pressure of hydrogen in the presence of a heterogeneous bifunctional catalyst. The ideal catalyst for the "upgrading" of this bio-oil, should possess the following characteristics: (1) high deoxygenation activity to minimize the size of the reactor and to obtain the desired performance; (2) ability to withstand large amounts of coke and/or minimize its formation, as the bio-oil tends to form more coke than the typical petroleum fractions; (3) ability to regenerate through a simple process to minimize capital expenditures; (4) high tolerance to poisons from the viewpoint of increasing the life of the overall catalyst charged; and (5) high tolerance to water since the catalysts are expected to be exposed to large amounts of water. Previous studies indicated that the presence of water can have a detrimental effect on the performance of the catalyst [3].

---

* Corresponding author. Fax: +34 952131870.
** Corresponding author.
E-mail addresses: ainfantes@uma.es (A. Infantes-Molina), castellon@uma.es, ainfantes@uma.es (E. Rodríguez-Castellón).

http://dx.doi.org/10.1016/j.cattod.2015.12.006
0920-5861/© 2015 Elsevier B.V. All rights reserved.

Please cite this article in press as: A. Infantes-Molina, et al., Pd-Nb binfunctional catalysts supported on silica and zirconium phosphate heterostructures for O-removal of dibenzofurane, Catal. Today (2015), http://dx.doi.org/10.1016/j.cattod.2015.12.006

Both hydrogenation (HYD) and acid sites are needed for the HDO pathway, and this bifunctionality is a critical step in the catalyst design process when developing HDO catalysts [4]. To this end, great strides have been made in finding catalysts that are sufficiently active and/or selective. Carbides, nitrides and phosphides of transition metals were investigated due to their good properties for hydrotreating reactions and because they are catalytically active for many reactions involving hydrogen transfer, since they behave as metals from groups 8, 9 and 10 of the periodic Table for most reactions. They possess hydrogenating properties similar to those of noble metals and exhibit high tolerance to streams with high sulfur content. These materials have been proven to be more efficient in hydrotreating reactions than conventional catalysts [5]. In particular, transition metal phosphides presented very promising properties for HDO reactions [6].

Other investigations are focused on the study of active phases based on noble metals such as Ru, Rh, Pd and Pt for HDO processes [7–13]. Wildschut et al. [14] reported the promising activity of supported Ru, Pd, and Pt catalysts for the hydrotreating of whole bio-oils compared to traditional transition metal sulfides catalysts. Supported noble metals are an attractive alternative because they can activate molecular hydrogen, no sulfur feed is required as in the case of traditional sulfide phases; they are not disabled so easily in the presence of water and show good yields with long lifetimes of the catalyst. With mild operation conditions, these catalysts have much better performance than conventional catalysts, since they are very efficient in the activation of molecular hydrogen. Unfortunately, the main drawback of theses catalysts is their high cost [4]. Another approach is the preparation of bimetallic catalysts coupling a noble metal with a non noble metal, that not only increases the activity in hydrotreating processes, but it is also an opportunity to reduce the cost of the catalyst. Moreover an acidic function is incorporated into the resultant catalyst. With this catalyst formulation, hydrogen is activated and is easily split over the interface or surface to react with other reagents, and oxygenates can be adsorbed and activated at different sites, mainly acid sites, or metal-support interface [7,13,15,16].

Niobium species show a promoting effect when added in small amounts to known catalysts, improving the catalytic activity and selectivity and prolonging the catalyst life. Niobium oxides show a great variety of functions in catalysis, such as promoter, support, redox and acid properties, and they have been proposed as effective catalysts or catalyst promoters for many reactions [17,18]. Moreover, niobium oxide is highly acidic, especially in amorphous form. The hydrated niobium oxide, known as niobic acid ($Nb_2O_5{\cdot}nH_2O$) shows high acidity. It also presents a high catalytic activity, selectivity and stability for acid catalyzed reactions where water molecules are released [19].

The main goal of this paper is the preparation of bifunctional catalysts, where a noble metal and a transition metal oxide presenting acidic properties, such is the case of niobium oxide, are combined. PdNb based catalysts, supported on two different porous supports, SiO_2 and PPH, presenting different textural and acidic properties, were prepared and studied in the O-removal of a model molecule present in biomass derived bio-oil.

2. Experimental

2.1. Preparation of catalysts

PdNb supported catalysts on silica and porous zirconium phosphate heterostructure (PPH) materials were prepared by following the incipient wetness impregnation method. Commercial silica (fumed silica from Sigma–Aldrich) was used as received, on the contrary the PPH support was synthesized according to the procedure described by Jiménez-Jimenez et al. [20]. Thus Pd and Nb were added by a two step impregnation process following two synthetic routes.

2.1.1. Route 1

The desired concentration of niobium(V) oxalate was added to the incipient volume of deionized water and the impregnated support. After drying at 60 °C overnight, the palladium aqueous solution with the desired concentration of palladium(II) chloride was incorporated into the Nb containing solid, dried at 60 °C overnight and finally calcined at 450 °C for 2 h.

2.1.2. Route 2

The incorporation of Pd took place after the calcination of the Nb-containing solid at 450 °C for 2 h. All other steps of the preparation procedure remained the same.

Thus, four catalysts containing a total metal loading of 2 wt% (1.07 wt% Pd and 0.93 wt% Nb) and a Pd/Nb atomic ratio of 1 were prepared and denoted as PdNbc/SiO_2, PdNb/SiO_2, PdNbc/PPH y PdNb/PPH, where *c* indicates that Pd was incorporated after calcination of Nb containing solid.

2.2. Characterization of catalysts

BET specific surface areas were determined from N_2 adsorption-desorption isotherms at −196 °C by using a Micrometric ASAP 2020 apparatus. Prior to analysis, all the samples were outgassed at 200 °C (10 h). Pore size distributions were analyzed by the BJH method applied to the desorption branch of the isotherm. X-ray diffraction patterns were obtained with a Philips X'pert PRO MPD diffractrometer, using $CuK_{\alpha1}$ ($\lambda = 1.5406$ Å) radiation and X'Celerator RTMS (Real Time Multiple Strip) detector. The acidity of pure supports and prepared catalysts was determined by temperature-programmed desorption (TPD) of ammonia measurements, carried out in a Shimadzu GC-14A chromatograph as described elsewhere [21]. HRTEM micrographs were measured using a Philips CCCM 200 Supertwin-DX4 microscope. X-ray photoelectrom spectra were recorded with a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300 W, 15 kV, and 1486.6 eV) provided 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 1*s* 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. The amount of coke in the used catalysts was determined be elemental analysis with a PerkinElmet 240C equipment.

2.3. Catalytic activity

The prepared catalysts were evaluated in the HDO of dibenzofuran (DBF) (2 wt% in decaline) as a model molecule. The catalytic test was carried out in a high-pressure fixed-bed catalytic reactor operating in the down flow mode. The organic feed was supplied by means of a Gilson 307SC piston pump (model 10SC). For the activity tests, 0.25 g of catalyst were used (particle size 0.85–1.00 mm) and were diluted with quartz sand to 3 cm^3. Catalytic activities were measured at 275 °C under 1.5 MPa of H_2, at a flow rate of 30 mL min^{-1} and feed flow of 0.18 mL min^{-1} (WHSV 0.8 h^{-1} and τ 6 s^{-1})

Please cite this article in press as: A. Infantes-Molina, et al., Pd-Nb binfunctional catalysts supported on silica and zirconium phosphate heterostructures for O-removal of dibenzofurane, Catal. Today (2015), http://dx.doi.org/10.1016/j.cattod.2015.12.006

Download English Version:

https://daneshyari.com/en/article/4757359

Download Persian Version:

https://daneshyari.com/article/4757359

Daneshyari.com