Applied Catalysis B: Environmental 136–137 (2013) 140–149

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

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

Oxygen-removal of dibenzofuran as a model compound in biomass derived bio-oil on nickel phosphide catalysts: Role of phosphorus

J.A. Cecilia[a], A. Infantes-Molina[b], E. Rodríguez-Castellón[a], A. Jiménez-López[a,*], S.T. Oyama[c,d]

[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] Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain
[c] Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, United States
[d] Department of Chemical Systems Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ky, Tokyo 113-8656, Japan

ARTICLE INFO

Article history:
Received 7 November 2012
Received in revised form 23 January 2013
Accepted 28 January 2013
Available online 6 February 2013

Keywords:
Nickel phosphide (Ni_2P)
Dibenzofuran
Hydrodeoxygenation
Hydrotreatment

ABSTRACT

The hydrodeoxygenation (HDO) of dibenzofuran (DBF) was investigated over silica-supported nickel phosphide catalysts with low metallic loadings (2.5–10 wt.%) and with different initial P/Ni atomic ratios. The formation of the nickel phosphide phase as well as the textural, structural and acidic properties of the catalysts were evaluated by X-ray fluorescence (XRFS), H_2-temperature programmed reduction (H_2-TPR), X-ray diffraction (XRD), CO chemisorption at 35 °C, N_2 adsorption–desorption isotherms at −196 °C, NH_3-temperature programmed desorption (NH_3-TPD) and elemental analysis (CNHS). The effect of metallic loading, the initial P/Ni molar ratio as well as the feed O-concentration on the catalytic activity were studied. Characterization results reveal that smaller particle sizes are formed at lower metallic loadings and high P/Ni atomic ratios, and that the acidity increases linearly with the metallic loading pointing to nickel and phosphorous species as the acidic centers in reduced catalysts. Nickel phosphide catalysts display good activity and stability in the HDO of DBF, reaching high DBF conversion values at moderate temperatures (300 °C) and with high selectivity to bicyclohexane (BCH), the main deoxygenated product which was obtained by hydrogenation of both aromatic rings (HYD pathway). Catalyst deactivation due to coke was minimal due to the low strength of the acid sites, while the formation of water did not present an inhibiting effect even under high O-concentration. This behavior might occur because water interacts preferentially with the excess phosphorous present on the catalyst surface and thus nickel phosphide particles do not undergo oxidation.

1. Introduction

Depletion of petroleum reserves, new stringent environmental regulations and rapid growth of global energy consumption have led to an increasing interest and necessity to find alternatives to fossil fuels. As a kind of renewable energy resource, biomass has recently drawn considerable attention for the production of liquid fuels and chemicals [1]. A promising method for obtaining liquid fuels is biomass fast pyrolysis, but unfortunately the liquid products obtained contain high contents of oxygen containing compounds, about 15–40 wt.% in which water takes up to 30 wt.% [2,3]. The average composition of pyrolysis oils includes organic acids, aldehydes, ketones, furans, phenolic compounds, guaiacols, syringols and sugar based compounds [3]. The presence of these molecules with high oxygen content contributes to some deleterious properties of the biofuels, such as high viscosity, corrosiveness, poor heating value, immiscibility with hydrocarbon fuels, low chemical and thermal stability, as well as to undesirable formation of carbon deposits in parts of automotive engines upon combustion [4,5]. In order to improve the physical and chemical stability of these liquid precursors, the oxygen must be removed by a hydrodeoxygenation process (HDO) through cleavage of C–O bonds, producing water and/or carbon oxides as by-products. Oxygen elimination can be performed by decarboxylation (CDO) or fluid catalytic cracking (FCC) [6]. Oxygen removal can also be carried out with conventional hydrotreating processes which generally operate under high pressure (3–10 MPa) of hydrogen at moderate temperatures (300–500 °C) [7]. This is applied to petroleum fractions, as conventional crudes may contain up to 2 wt.% oxygen [7]. Hydrodeoxygenation (HDO), hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and the saturation of olefins/aromatics at high hydrogen pressure occur

---

* Corresponding author. Tel.: +34 595 213 18 76; fax: +34 595 213 20 00.
E-mail address: ajimenezl@uma.es (A. Jiménez-López).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.01.047

during the hydrotreating process [8]. Common probe molecules to evaluate the catalyst performances in HDO reactions are derivative furan compounds [9–11] among which dibenzofuran is a very low reactivity compound [7] and therefore a good choice as a model molecule to test HDO capability.

The catalysts most frequently studied for HDO have been sulfided Mo/Al_2O_3 catalysts, promoted by elements of group 9–10 (Co, Ni) [12–14]. However these catalysts suffer a progressive deactivation during the HDO reaction due to the oxidation of the active phase [15], so this makes desirable the development of new efficient catalysts. For this reason, new compositions showing a good hydrogen transfer properties have been assayed in hydrotreating processes. Among these, noble metals [16–18], metal carbides [19,20], metal nitrides [21,22], metal borides [23] and transition metal phosphides [24–27] have been tested in HDO.

In the last decade, transition metal phosphides have attracted great attention as new hydroprocessing catalysts. A plethora of research articles has reported that transition metal phosphides show excellent properties in hydrotreating reactions due to the presence of phosphorous that provides an ensemble effect and high stability [28,29]. In this way, the effect of phosphorous content in the hydroprocessing performance of phosphides is becoming a key factor to consider. Oyama et al. have reported [29] that the HDS conversion goes through a maximum when a P/Ni molar ratio of 3 was employed. In recent years, several studies have revealed that supported transition metal phosphides such as Ni_2P/SiO_2 [25,29], MoP/SiO_2 [25] and Ru_2P/SiO_2 [27] have shown high conversion in the HDO of phenol, furan, benzofuran, guaiacol and anisole.

In this work the formation, activity and catalytic stability of nickel phosphide catalysts in the HDO of dibenzofuran (DBF) is investigated. These catalysts have been synthesized according to a method previously described [30] that uses a precursor salt containing an excess of phosphorous. In the present study the P/Ni initial ratio, the metallic loading as well as the O-concentration in the feed are studied focusing on the role of phosphorous on the catalytic performance of these systems.

2. Experimental

2.1. Materials

The support used in this study was a commercial silica (Cab-o-Sil M-5, Riedel-de Haen, Sigma–Aldrich). The reagents used to prepare the catalyst precursors were phosphorous acid (H_2PO_3H, Aldrich 99%), and nickel(II) hydroxide ($Ni(OH)_2$, Aldrich 99%). The chemical products utilized in the reactivity study were dibenzofuran (Aldrich 98%) dissolved in cis-, trans-decahydronaphthalene (Sigma–Aldrich 98%). The gases employed were He (Air Liquide 99.99%), H_2 (Air Liquide 99.999%), N_2 (Air Liquide 99.9999%), NH_3 (Air Liquide 99.9%) and CO (Air Liquide 99.9%).

2.2. Preparation of catalysts

Phosphorus and nickel were introduced by the incipient wetness impregnation method using a solution of nickel(II) dihydrogenophosphite ($Ni(HPO_3H)_2$) as precursor, prepared from stoichiometric amounts of nickel(II) hydroxide ($Ni(OH)_2$) and phosphorous acid (H_2PO_3H). The support employed was a commercial silica Cab-o-Sil due to its purity and inherent inertness as a support [31,32]. After the nickel aqueous salt solution was added to the pelletized support (0.85–1.00 mm), it was air dried, and then treated by temperature programmed reduction (H_2-TPR) to convert the precursor phosphite into phosphide. For this purpose, 80 mg of sample were placed in a tubular reactor with a heating rate of 3 °C min^{-1} and a hydrogen flow rate of 100 mL min^{-1}. These reduction conditions have been optimized in previous works [30,32]. The concentration of the precursor solutions were adjusted to the desired metal loading. Four catalysts were prepared with a nickel loading ranging from 2.5 to 10 wt.% of Ni. The prepared catalysts will be referred to as Ni_2P-*x*, where *x* represents the percentage in weight of nickel present in the sample.

Furthermore another series of nickel phosphide catalysts were also prepared by H_2-TPR, keeping constant the nickel content (5 wt.% Ni) and varying the initial phosphorous content. The samples prepared had initial P/Ni molar ratios of 1, 2 and 3, respectively. Thus,Ni_2P-5-P/Ni = 2 is prepared by adding stoichiometric amounts of $Ni(OH)_2$ and H_2PO_3H to the incipient volume to form the precursor salt $Ni(HPO_3H)_2$ containing 5 wt.% of Ni. Similarly, Ni_2P-5-P/Ni = 1 is synthesized by mixing $Ni(HPO_3H)_2 + Ni(OH)_2$ (5 wt.% Ni and P/Ni atomic ratio = 1). Finally, Ni_2P-5-P/Ni = 3 is prepared by mixing $Ni(HPO_3H)_2 + H_2PO_3H$ (5 wt.% Ni and P/Ni atomic ratio = 3).These catalysts will be denoted as Ni_2P-5-P/Ni = *y*, *y* being the initial P/Ni ratio present on each sample.

2.3. Characterization of catalysts

Elemental bulk composition of the catalysts in terms of Ni and P loading was determined by X-ray fluorescence spectrometry (XRFS) using a Horiba XGT-500 spectrometer with a probe diameter of 1.2 mm. The X-ray tube was set at 50 kV with an acquisition time of 500 s and a current intensity between: 0.26 and 0.32 mA.

The temperature programmed reduction of the precursor phosphite to nickel phosphide was carried out by placing 80 mg of precursor in a tubular reactor, with heating at a linear temperature ramp (3 °C min^{-1}) in flowing hydrogen (100 mL min^{-1}) from 100 to 800 °C. The evolved gases were sampled in a quadrupole mass spectrometer Balzer GSB 300 02 equipped with a Faraday detector (0–200 uma), and the masses 2 (H_2), 18 (H_2O), 31 (P), 34 (PH_3) and 124 (P_4) were monitored during the experiment. The signals and temperature were recorded in real time by an online computer.

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

CO chemisorption analyses were performed under static volumetric conditions in a Micromeritics ASAP 2020 apparatus. Samples were reduced ex situ and transferred in an inert atmosphere. Prior to measurement, samples were re-reduced in situ in H_2 at 300 °C and evacuated at 25 °C for 10 h. The chemisorption isotherm was obtained by measuring the amount of CO adsorbed between 10 and 600 mmHg at 35 °C. After completing the initial analysis, the reversibly adsorbed gas was evacuated and the analysis repeated to determine only the chemisorbed amounts.

The textural parameters (S_{BET}, V_P and d_P) were evaluated from nitrogen adsorption–desorption isotherms at −196 °C as determined by an automatic ASAP 2020 system from Micromeritics. Prior to the measurements, samples were outgassed at 200 °C and 10^{-4} mbar overnight. Surface areas were determined by using the Brunauer–Emmett–Teller (BET) equation and a nitrogen molecule cross section of 16.2 $Å^2$. The pore size distribution was calculated by applying the Barret–Joyner–Halenda (BJH) method to the desorption branch of the N_2 isotherm. The total pore volume was calculated from the adsorption isotherm at $P/P_0 = 0.996$.

The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out to evaluate the total surface acidity of the catalysts. A quantity of 80 mg of catalyst precursor was reduced at atmospheric pressure by flowing hydrogen (100 mL min^{-1}) with a heating rate of 3 °C min^{-1} from room temperature to the reduction temperature established in the H_2-TPR. After flushing with helium and adsorption of ammonia at 100 °C, NH_3-TPD using a helium flow was performed by raising the temperature from 100 to 550 °C at a