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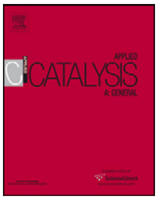

Ni_2P and CoP catalysts prepared from phosphite-type precursors for HDS–HDN competitive reactions

A. Infantes-Molina[a], J.A. Cecilia[b], B. Pawelec[a], J.L.G. Fierro[a],
E. Rodríguez-Castellón[b], A. Jiménez-López[b,*]

[a] Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain
[b] Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga,
Campus de Teatinos, 29071 Málaga, Spain

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ABSTRACT

Silica-supported nickel and cobalt phosphide catalysts were synthesized with low metal-loading (5 wt%). The formation of Ni_2P and CoP phases was achieved by temperature-programmed reduction of phosphite-based precursors, $Ni(HPO_3H)_2$ and $Co(HPO_3H)_2$, respectively. The catalysts were characterized by X-ray fluorescence (XRFS), N_2 adsorption–desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and elemental analysis (CNHS). These catalysts were tested in the individual reactions of hydrodesulfurization (HDS) of dibenzothiophene (DBT) and hydrodenitrogenation (HDN) of quinoline (Q), and also in the simultaneous HDS and HDN reactions. These tests were conducted by feeding 3000 ppm of DBT or 3000 ppm of Q. Additional tests were performed with the aim to evaluate S-removal capability by keeping constant Q concentration in the feed (3000 ppm) and varying DBT concentration (200 and 2000 ppm). The catalytic results show that these phosphide catalysts achieve high DBT and Q conversion values at high temperatures though the rate of HDS reaction is higher than that of HDN. In all cases Ni_2P is more active than CoP. Moreover, the presence of N-containing molecules in the feed does not affect the S-removal as sulfur is almost completely removed after 48 h on-stream.

1. Introduction

Demands for a cleaner environment have led to a global tightening in the allowed sulfur content in fuels and increasing restrictions in the release of nitrogen oxides are also being imposed. The environmental protection agency (EPA) has legislated a reduction of sulfur content from 500 to 10 parts per million by weight (wppm) at the beginning of 2011 [1]. The restrictive regulations in the European union are also similar, and a maximum sulfur content of 10 wppm is imposed [2]. Moreover, feedstocks of lower quality (typical crude contains 1.5 wt% S) are being treated due to the reduction in petroleum reserves. Accordingly, considerable efforts are being devoted to develop new technologies for the production of clean fuels such as biodesulfurization (BDS) [3,4], oxidative desulfurization (ODS) [5], ultrasound-assisted oxidative desulfurization (UAOD) [6]. However, hydroprocessing appears to be the technologically preferred solution. Hydroprocessing refers to a variety of catalytic hydrogenation processes that saturate heteroatomatic rings and remove S, N, O, and metals from different petroleum streams in a refinery.

The environmental legislation demands in terms of fuel sulfur content have been attained with HDS commercial catalysts such sulfides based on Mo or W and doped with Ni or Co [3] that have been modified using several promoters or changing the material support [7–9]; and non-traditional catalytic materials such carbides and nitrides [10,11]. Recently, transition metal phosphides, MoP [12,13], WP [14,15], CoP [16,17] and Ni_2P [18–20] have been reported as very active phases in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions. Among these phosphides, the Ni_2P phase has been reported the most active one for HDS reactions, even presenting a higher HDS activity than that found for traditional sulfides [21,22]. Several researches have also pointed out a high activity and stability of the CoP phase in HDS reactions [17,23]. It has been shown that during the HDS reaction there is a transformation on the phosphide surface due to sulfur incorporation and formation of a phosphosulfide phase, considered as the real active phase in HDS reactions catalysed by phosphides [24,25]. Moreover, it should be kept in mind that sulfur and nitrogen are always present in crude oil. Accordingly, and in order to fulfil the environmental laws, the strong suppression of sulfur removal by nitrogen compounds [26] is a fundamental problem which is

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* Corresponding author. Tel.: +34 952131876; fax: +34 952137534.
E-mail address: ajimenezl@uma.es (A. Jiménez-López).

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exacerbated by the decline in the overall quality of crudes. Thus, nitrogen removal is a key problem in HDS, in particular deep HDS to levels of 50 ppm S or less. It is well recognized that HDN is more difficult than HDS, requiring more severe conditions of pressure and temperature. With this premises, it turns out interesting to find a catalytic system capable of eliminating both N- and S-containing molecules. Ni_2P has been considered one of the most active phases for both HDS and HDN reactions [16]. The effect of phosphorus content in the hydroprocessing performance of phosphides is considered a key factor. Oyama et al. [27] reported that the HDS reaction hardly changes with the initial Ni/P ratio while the HDN conversion goes through a maximum when a Ni/P molar ratio of 0.5 was employed, as in the case of this study. On contrary, Bussell and co-workers [25] have reported the opposite effect, i.e., they found a strong variation of the HDS activity with the initial Ni/P ratio, as long as when high Ni/P ratios are used, $Ni_{12}P_5$ impurities are present that deleteriously affected the HDS properties of the catalysts.

On the other hand, the role of the support has shown to be complex due to the interaction active phase precursor-support. In the case of acid supports such as MCM-Zr or γ-Al_2O_3, a strong interaction with the active phase precursors and support is developed [17,20] thus requiring a higher reduction temperature. Other supports based on hexagonal mesoporous silica such as MCM-41 [28] or SBA-15 [29] have been widely used but the phosphorus excess necessary to allow the formation of phosphide causes a blockage of the mesoporous structure. Silica has been often tested as a support for phosphide catalysts [16] because the support–precursor interaction is weak due to the low acidity of the silica.

In this paper, the formation, activity and catalytic stability of nickel and cobalt phosphide catalysts in HDS, HDN and HDS–HDN competitive reactions are described. These catalysts have been synthesized by impregnation of the support with nickel(II) dihydrogenphosphite, $Ni(HPO_3H)_2$, or cobalt(II) dihydrogenphosphite, $Co(HPO_3H)_2$. Subsequently, the precursor was reduced in H_2 flow (TPR) leading to the Ni_2P [30] or CoP [17] phase, respectively. As regard to the support, commercial silica has been chosen due to its low cost and the interesting results found previously in hydrotreating reactions [17,20]. The catalysts prepared here only possess a 5 wt% of metal and they will be studied in the DBT HDS, Q HDN reactions and in HDS–HDN competitive reactions by varying the ratio of N- and S-compounds, i.e., studying the possible suppression of sulfur removal by the presence of nitrogen compounds.

2. Experimental

2.1. Materials

The support used in this study was commercial silica (Cab-osil® M-5, Riedel-de Haën, Sigma–Aldrich). The reactants used to prepare the catalyst precursors were phosphorus acid (H_2PO_3H, Aldrich 99%), cobalt(II) hydroxide ($Co(OH)_2$, Aldrich 95%) and nickel(II) hydroxide ($Ni(OH)_2$, Aldrich). The chemical products utilized in the reactivity study were dibenzothiophene (Aldrich 98%) and quinoline (Aldrich 98%) in cis-, trans-decahydronaphthalene (Sigma–Aldrich 98%). The gases employed were He (Air Liquide 99.99%), H_2 (Air Liquide 99.999%) and N_2 (Air Liquide 99.9999%).

2.2. Preparation of catalysts

Nickel phosphide and cobalt phosphide catalysts with 5 wt% of nickel and cobalt, respectively, were prepared. The support used was a commercial silica Cab-osil ($S_{BET} = 257\ m^2\ g^{-1}$ and $V_p = 0.72\ cm^3\ g^{-1}$). The catalysts were prepared following the incipient wetness impregnation method. Solutions of nickel(II) dihydrogenphosphite ($Ni(HPO_3H)_2$) and cobalt(II) dihydrogenphosphite ($Co(HPO_3H)_2$) were prepared by mixing the stoichiometric amounts of phosphorus acid (H_2PO_3H) and nickel(II) hydroxide ($Ni(OH)_2$) or cobalt(II) hydroxide ($Co(OH)_2$) [30], as accordingly, to the incipient volume. Subsequently, each solution was added to the pelletized silica (0.85–1.00 mm), and air dried at 40 °C. Finally, a temperature programmed reduction was used to convert the phosphite into the desired phosphide according to the method previously described [30], i.e., the sample was placed in a tubular reactor, heating at linear temperature ramp ($3\ ^\circ C\ min^{-1}$) in flowing H_2 ($100\ mL\ min^{-1}$) from 100 °C to 500 °C as it was optimised in previous works [17,20].

2.3. Characterization of catalysts

Elemental bulk composition of the catalysts in terms of Ni, Co and P loading was achieved by X-ray fluorescence spectrometry (XRFS) of dispersive energy using a XGT-500 equipment 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 textural parameters were evaluated from the nitrogen adsorption–desorption isotherms at −196 °C as determined by an automatic ASAP 2020 system from Micromeritics.

X ray diffraction patterns (XRD) of the precursor, reduced and spent catalysts were obtained with a X'Pert PRO MPD Philips diffractometer (PANanalytical), using monochromatic CuKα radiation ($\lambda = 1.5406$ Å). The Kα radiation was selected with a Ge (1 1 1) primary monochromator. The X-ray tube was set at 45 kV and 40 mA.

Transmission electron micrographs of the precursor and reduced catalysts were obtained by using a Philips CM 100 Supertwin-DX4 microscope. Samples were dispersed in ethanol and a drop of the suspension was put on a Cu grid (300 mesh).

Elemental chemical analysis was performed for spent catalysts with a LECO CHNS 932 analyser to determine the sulfur and the nitrogen content present after the catalytic test through the combustion of the samples at 1100 °C in pure oxygen to form NO and SO_2.

X-ray photoelectron spectra were collected using a physical electronics PHI 5700 spectrometer with non monochromatic AlKα radiation (300 W, 15 kV, and 1486.6 eV) with a multi-channel detector. Spectra of pelletized samples 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. Reduced and spent catalysts were stored in sealed vials with an inert solvent. The sample preparation was done in a dry box under a N_2 flow, where the solvent was evaporated prior to its introduction into the analysis chamber, and directly analyzed without previous treatment.

2.4. Catalytic test

For the catalytic tests, the HDS of DBT and the HDN of quinoline were chosen, which were performed in a high-pressure fixed-bed continuous-flow stainless steel catalytic reactor (9.1 mm in diameter, and 230 mm in length), operated in the down-flow mode. The reaction temperature was measured with an interior placed thermocouple in direct contact with the catalyst bed. The organic feed was adjusted to solutions in cis- trans-decaline of: DBT (3000 ppm) for the study of HDS reaction, quinoline (Q) (3000 ppm) for the