



# Dibenzothiophene hydrodesulfurization over cobalt phosphide catalysts prepared through a new synthetic approach: Effect of the support

J.A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López \*

Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain

## ARTICLE INFO

### Article history:

Received 12 May 2009

Received in revised form 13 July 2009

Accepted 20 July 2009

Available online 25 July 2009

### Keywords:

Mesoporous MCM-41

Silica

Alumina

MCM-Zr

Cobalt phosphide

Dibenzothiophene

HDS

## ABSTRACT

Several cobalt phosphide catalysts, with a cobalt loading of 10 wt%, were prepared by means of temperature-programmed reduction (TPR) of cobalt(II) hydrogenphosphite ( $\text{Co}(\text{HPO}_3\text{H})_2$ ) supported on different carriers: two mesoporous supports, MCM-41 and zirconium doped MCM-41 (MCM-Zr), as well as two commercial supports,  $\text{SiO}_2$  (Cab-osil) and  $\gamma\text{-Al}_2\text{O}_3$ . The purpose of this work is to study the role of the support on the formation of CoP or  $\text{Co}_2\text{P}$  and the analysis of the catalytic activity in the hydrodesulfurization (HDS) of dibenzothiophene (DBT). It is the CoP phase which is favoured on these catalysts under the given experimental conditions, except for that supported on  $\gamma\text{-Al}_2\text{O}_3$  (CoP-10 (Al)), which only displays the diffraction lines of the  $\text{Co}_2\text{P}$  phase after the reduction process. The interaction support-precursor salt seems to determine which of the phases is formed. The catalytic results showed that this family of catalysts obtained high DBT conversion values at high temperatures, mainly via the direct desulfurization (DDS) route, i.e., yielding biphenyl (BP) as majority product and attaining turnover frequency (TOF) values of  $0.87 \times 10^{-3} \text{ s}^{-1}$ . The stability with time on stream showed that the silica (Cab-osil) supported catalyst, CoP-10 (Cab), was highly stable with time on stream (48 h) with conversion values close to 100% and with a performance similar to that of  $\text{Ni}_2\text{P}$  catalysts and better than other cobalt phosphide catalysts reported in the literature. In contrast, the CoP-10 (Zr) and CoP-10 (Si) samples decrease in activity after 16 h on stream, although their conversions are between 65% and 70% after 48 h on stream. Finally, the CoP-10 (Al) catalyst provided lower conversion values and underwent deactivation with time on stream due to the low activity of the  $\text{Co}_2\text{P}$  compound formed on this sample. Furthermore, the analysis of the spent catalyst showed the presence of sulfur on the surface, assigned to the formation of phosphosulfide species.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

A cleaner environment requirement has led to government regulations to produce and use fuels with lower sulfur, nitrogen and aromatic content. The Environment Protection Agency (EPA) has legislated a reduction of sulfur content from 500 to 15 parts per million by weight (wppm) during the period 2007–2010, and the laws will be more restrictive at the beginning of 2011 when the sulfur content must be reduced to less than 10 wppm [1]. The restrictive regulations in the European Union are also similar, and a maximum sulfur content of 10 wppm is forecast. Moreover, the reduction in petroleum reserves has provoked the use of feedstocks of lower quality (typical crude contains 1.5% sulfur). Hence a renewed interest has arisen to develop highly active catalysts for sulfur removal in hydrotreating reactions. The sulfur compounds

present in feedstock are mostly refractory molecules from the thiophene or dibenzothiophene family that can also possess alkyl groups, which hinder the removal of sulfur [2]. Therefore, a worldwide search for improved catalysts has been undertaken.

One of the research areas is to improve the traditional sulfide catalysts, which are mainly based on alumina supported molybdenum or tungsten sulfides, where cobalt or nickel is present in the form of a so-called “Co-Mo-S” or “Ni-No-S” promoter phase at the edges of the molybdenum or tungsten sulfided crystals. These promoters modify the particle morphologies and increase the catalyst acidity [3,4]. Phosphorus has also been added as a secondary promoter to modify the properties of the support, as well as indirectly acting on the active phase [5], thus increasing the heteroatom removal activity, and improving the mechanical and thermal stability [6].

New approaches have also been taken by using transition metal carbides [7,8], nitrides [8,9], borides [10] and above all phosphides [11,12]. All of them show high activity in both hydrodesulfurization (HDS) and hydrodenitritication (HDN) reactions. The main

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

drawback of carbides and nitrides is their instability in the presence of H<sub>2</sub>S (the product obtained during the HDS reaction), whereby they undergo deactivation [13]. Unlike the latter, transition metal phosphides are found to be active and stable under HDS conditions. The initial studies of phosphides were carried out in hydrogenation reactions [14] and subsequently their applications in HDS and HDN reactions were realised [15]. Following this, a great number of studies were devoted to the synthesis and hydrotreating activity of phosphide based catalysts. Hence, a number of transition metal phosphides have been prepared: Ni<sub>2</sub>P [11,12,16], CoP [17,18], Co<sub>2</sub>P [19], MoP [20], WP [19] as well as mixed phosphides such as CoMoP [21], NiMoP [22], Co<sub>x</sub>Ni<sub>2-x</sub>P [23]. Regarding the phosphide family, the Ni<sub>2</sub>P phase has been fully documented as being the most active [18] and has consequently been the subject of the most detailed studies. Authors in this area of research have demonstrated, by different experimental techniques that during the catalytic run a superficial incorporation of sulfur takes place, coating the phosphide particles with the formation of a superficial phosphosulfide phase. This intermediate phase is the active component of the transition metal phosphides in HDS reactions [24,25].

There has been very little research on the HDS properties of cobalt phosphide catalysts, as the activity of this phase is reported to be lower than that of Ni<sub>2</sub>P, although better than other phosphides [18]. Also, as is the case with nickel phosphides, cobalt phosphides exist with different stoichiometries: CoP, Co<sub>2</sub>P and CoP<sub>2</sub>. The CoP structure exhibits most activity and stability [17] in the HDS reaction. The formation of the desired cobalt phosphide depends on two factors, the P/Co ratio and the interaction phosphorous–support. Bussell and co-workers [17] have recently reported that high P/Co ratios (>2) lead to the formation of CoP, whereas low P/Co ratios (<0.5) favour the formation of Co<sub>2</sub>P. The precursor–support interaction is directly correlated to the support acidity. Thus, it has been reported that the phosphine (PH<sub>3</sub>) formed during reduction reacts with metallic particles, which are first reduced to form the corresponding phosphide [26]. Therefore, the phosphorous–support interaction determines the PH<sub>3</sub> liberation and/or the formation of the corresponding phosphide. With respect to this, Oyama et al. [11] found greater phosphine and water loss when less acidic supports were used and the support–precursor interaction is lesser. Also of consequence are the geometric and electronic properties of the active phase obtained.

The role of the support has been studied in both traditional sulfide [27] and nickel phosphide catalysts [28]. However, its effect on cobalt phosphide systems has hardly been considered. In general, silica has been the most frequently used support for phosphide catalysts [18] because the support–precursor interaction is weak due to the low acidity of the silica. Besides silica, various other supports have been tested, such as the mesoporous silica MCM-41 [29] and SBA-15 [30].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has also been considered as the best carrier for traditional sulfided catalysts. However, when it was used as support of transition phosphides, it strongly interacted with the precursors to form AlPO<sub>4</sub> [26,28], requiring a higher reduction temperature.

In this paper, we describe the formation and catalytic properties of cobalt phosphide catalysts in the DBT HDS reaction. Traditionally, this phosphide has been synthesized by impregnation of the support with (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> or NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and Co(NO<sub>3</sub>)<sub>2</sub>, and the cobalt phosphide particles being formed after calcination and H<sub>2</sub> thermoprogrammed reduction [18]. In this work, a new method [31] that combines cobalt hydroxide, Co(OH)<sub>2</sub>, and phosphorous acid, H<sub>2</sub>PO<sub>3</sub>H, that reacts to form Co(HPO<sub>3</sub>H)<sub>2</sub>, is proposed. This method has several advantages: there is no need of the calcination step of the precursors and also lower reduction temperature and hydrogen flows are required to obtain the desired active phase

than those used in the literature. The catalytic results reported here are much better than those found in the literature for cobalt phosphide catalysts in the HDS reaction [18], which indicates the importance of the preparation method exposed here.

## 2. Experimental

### 2.1. Materials

The supports used in this study were traditional mesoporous silica MCM-41 [32], mesoporous silica doped with zirconium with a Si/Zr molar ratio = 5 [33], a commercial silica (Cab-osil<sup>®</sup> M-5) and a commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supplied by REPSOL. Cobalt(II) hydroxide (Co(OH)<sub>2</sub> Aldrich 95%) and phosphorous acid (H<sub>2</sub>PO<sub>3</sub>H Aldrich 99%) were employed to obtain the precursor Co(HPO<sub>3</sub>H)<sub>2</sub>. The chemical products utilized in the reactivity study were dibenzothiophene (Aldrich 98%) in cis-, trans-decahydronaphthalene (Sigma–Aldrich 98%). The gases employed were He (Air Liquide 99.99%), H<sub>2</sub> (Air Liquide 99.999%), N<sub>2</sub> (Air Liquide 99.9999%), NH<sub>3</sub> (Air Liquide 99.9%) and CO (Air Liquide 99.9%).

### 2.2. Preparation of catalysts

Four cobalt phosphide catalysts with a 10 wt% of cobalt supported on different supports were prepared. The supports used were the traditional mesoporous silica (MCM-41) [32]; that doped with zirconium with a Si/Zr molar ratio = 5 [33]; a commercial silica such as Cab-osil; and a commercial alumina such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Phosphorus and cobalt were introduced by the incipient wetness impregnation method but using a solution of cobalt(II) dihydrogenophosphate (Co(HPO<sub>3</sub>H)<sub>2</sub>), prepared by adding the stoichiometric amounts of cobalt(II) hydroxide (Co(OH)<sub>2</sub>) and phosphorous acid (H<sub>2</sub>PO<sub>3</sub>H) to the incipient volume. Once the cobalt(II) aqueous salt solution was added to the pelletized support (0.85–1.00 mm), it was air dried. A XRD measurement of the supports impregnated with this salt was carried out previously in order to discard the presence of undesired phases. The diffractogram did not show any peaks since this compound is totally amorphous. Finally, a temperature-programmed reduction was used to convert the phosphite into phosphide according to the method previously described [31], i.e., it was carried out in a tubular reactor, heating at linear temperature ramp (3 °C min<sup>-1</sup>) in flowing hydrogen (100 ml min<sup>-1</sup>) from 100 °C to the corresponding reduction temperature.

The concentration of the precursor solutions was adjusted to 10 wt% of cobalt, and they will be referred to as CoP-10 (Si), CoP-10 (Zr), CoP-10 (Cab) and CoP-10 (Al), when the supports used are MCM-41, MCM-Zr, Cab-osil and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively.

### 2.3. Characterization of catalysts

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-K<sub>α</sub> radiation) and an X'Celerator detector.

The evolved gases in the H<sub>2</sub>-temperature-programmed reduction (TPR) experiments were sampled into a quadrupole mass spectrometer Balzer GSB 300 02 equipped with a Faraday detector, and masses 2 (H<sub>2</sub>), 18 (H<sub>2</sub>O), 31 (P) and 34 (PH<sub>3</sub>) were monitored during the experiment. These signals in real time versus temperature were recorded by on-line computer.

CO chemisorption was analyzed in a Micromeritics ASAP 2010 apparatus under static volumetric conditions. Samples were reduced ex situ and transferred in inert atmosphere. Prior to measurement, samples were re-reduced in situ in H<sub>2</sub> at 300 °C and evacuated at 35 °C for 10 h. The chemisorption isotherm

Download English Version:

<https://daneshyari.com/en/article/47519>

Download Persian Version:

<https://daneshyari.com/article/47519>

[Daneshyari.com](https://daneshyari.com)