



Simultaneous hydrodesulfurization and hydrodenitrogenation on MoP/SiO₂ catalysts: Effect of catalyst preparation method

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ABSTRACT

Silica-supported MoP catalysts were prepared by temperature-programmed reduction (H₂-TPR) at 550, 600 and 700 °C of the corresponding dried or calcined substrates. Two catalysts were prepared by using two different synthetic approaches. A MoP catalyst was prepared using the method described in the literature that uses ammonium phosphate (NH₄H₂PO₄) and ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) precursors, calcination and subsequent H₂-TPR at high temperature. A new synthetic approach was carried out to prepare another MoP catalyst using ammonium molybdate ((NH₄)₂MoO₄) and phosphorous acid (H₂PO₃H) as precursors and subsequent H₂-TPR. The catalytic activity was evaluated in the individual and simultaneous hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions performed in a flow reactor under a hydrogen pressure of 3.0 MPa. The fresh reduced and spent catalysts were characterized by ICP, N₂ adsorption–desorption isotherms at –196 °C, XRD, HRTEM, NH₃-TPD, XPS and elemental chemical CNHS analysis. The silica-supported MoP catalysts prepared by the new synthetic method were more active in the HDS of DBT than the catalyst prepared by reduction of calcined substrate. The catalyst characterization results showed that the lower reduction temperature required to form the MoP species is responsible for the enhancement in catalytic performance. The key factors influencing on the catalytic activity are: a large specific surface area, high acidity and good dispersion of MoP phase on the support substrate. Activity measurements in simultaneous HDN–HDS showed that quinoline conversion is enhanced in the presence of a small amount of DBT whereas the HDS of DBT reaction does not appear to be inhibited by a small amount of quinoline added to the feed.

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1. Introduction

In order to achieve a large reduction of S- and N-content in fuels due to more stringent environmental restrictions and lower quality of the remnant petroleum reserves, improved methods for removal of organosulfur and organonitrogen compounds from fuel will become of greater importance. Therefore, new catalytic phases highly active for hydrotreating reactions are being claimed. Actually more efficient catalytic systems are being searched combining Ni, Mo, W and Co transition metals with carbon [1,2], nitrogen [1,3] and recently phosphorus [4,5], becoming a promising alternative to the traditional sulfides. Nitrides and carbides are unstable under

the presence of H₂S as long as they are transformed into sulfide under the typical operating conditions [6]. Nonetheless, transition metal phosphides belong to a group of catalysts which display excellent activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions [4,5], being the real alternative to sulfides in hydrotreating conditions. Several reviews have been devoted to the synthesis methods, nature, structure and activity of transition metal phosphides [5,6]. Thus, the metal-rich MP or M₂P (M = transition metal) compounds have metallic properties. They combine the properties of metals and ceramics, and thus are good conductors of heat and electricity, are hard and strong, and have high thermal and chemical stability [7].

Several research groups have investigated the synthesis and performance of transition metal phosphide catalysts. Using several metallic phosphides, Oyama [4] concluded that the activity for HDS of DBT and HDN of Q follows the order: Fe₂P < CoP < MoP < WP < Ni₂P. The Ni₂P/SiO₂ catalyst exhibits better hydrotreating activity than the traditional NiMoS/Al₂O₃ and

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CoMoS/Al₂O₃ systems and it is also efficient in the presence of aromatics and N-containing compounds, which are common inhibitors in the HDS reaction catalysed by sulfides. Stinner et al. [8] prepared six transition metal phosphide catalysts (Co₂P, Ni₂P, MoP, WP, CoMoP, NiMoP) that were tested in the HDN reaction of *o*-propylaniline. They concluded that the cobalt phosphides, Co₂P and CoMoP, were the least active; Ni₂P and NiMoP displayed an intermediate behaviour, meanwhile MoP and WP were the most active, being the MoP catalyst the most active one. Moreover, Li et al. [9] reported that MoP is less active than the traditional Ni-Mo/Al₂O₃ sulfide catalyst but still more active in the HDN of Q.

The activity trend found in the literature is that MoP-based catalysts present a lower HDS capability than other phosphides but higher than traditional sulfides, while presenting a higher activity in HDN reactions [10–12]. In this regard, Phillips et al. [10] found that a molybdenum phosphide catalyst supported on silica (MoP/SiO₂) was four times more active than a MoS₂/SiO₂ catalyst in the HDS of thiophene after 150 h on-stream. Similarly, Montesinos-Castellanos et al. [11] observed that MoP/Al₂O₃ catalyst turned out to be twice more active in the HDS reaction of DBT than a traditional MoS₂/Al₂O₃ catalyst with the same Mo-loading. Interestingly, it was found that the activity of a MoP catalyst increases progressively with the time on-stream as a consequence of the formation of a phosphosulfide phase, which is reported to be the active phase in phosphide based catalysts [13].

Concerning the preparation, a first study revealed that MoP can be easily obtained by temperature-programmed reduction (TPR) of a metal phosphate precursor [9]. However, novel synthesis methods have been reported to prepare unsupported and supported transition metal phosphides [14–20]. Metal thiophosphates [16] and amorphous alloys [17] precursors, citric acid modified precursors [18], solvothermal synthesis methods [19], novel reducing agents [20] among others have been used. In general, most of these methods yield a high dispersion of supported phosphides. Despite recent advances in the synthesis methods [14,15 and references within] of phosphides, a number of unanswered questions remain. For instance, understanding of factors that govern HDS activity of transition metal phosphides, and the role played by nanoparticles are a few points in the search of metal phosphides for hydrotreating reactions. Accordingly, this work was undertaken with the aim to provide some explanations to the above questions by preparing silica-supported MoP catalysts having nanoparticles of varying size.

In general, the TPR method has been the preferred option to prepare transition metal phosphides. In this method, supported metal phosphides are prepared by impregnating the support with the corresponding metallic precursor salt and ammonium monohydrogenphosphate (NH₄)₂HPO₄, followed by calcination step to develop the oxidic precursor, and finally reduction under hydrogen at high temperature to form the desired phosphide [4]. However, the TPR method itself is poorly suited for alumina-supported phosphide catalysts, because of the high reactivity of alumina toward phosphate, generating aluminium phosphate [15]. In this sense, the use of silica as a support instead of alumina has been explored [21–23]. Moreover, hydrogen reduction of transition metal phosphates typically requires high temperature, upwards of 580 °C to reduce phosphate species due to the P–O bond strength. Recently, with the goal to enhance the traditional catalyst preparation method, a new synthetic approach for nickel and cobalt phosphide-based catalysts was developed in our laboratory [21–23]. In this new synthesis method, the phosphate based precursors are substituted by nickel(II) or cobalt(II) hydrogenphosphite (Ni(HPO₃H)₂ or Co(HPO₃H)₂) as precursor salts to form the corresponding phosphide. Moreover the catalysts prepared by this new method were found to be active and stable in the HDS of DBT and also in simultaneous reactions of HDS and HDN. Recently, the effect of the use of

different phosphorous sources (H₃PO₄, (NH₄)₃PO₄, and NH₄H₂PO₄) in the preparation of bulk MoP catalysts was studied by also Gong et al. [24].

To determine how the effect of precursor affects HDS and HDN activities of MoP/SiO₂ catalysts, we have prepared different molybdenum phosphide catalysts employing ammonium molybdate ((NH₄)₂MoO₄) and phosphorous acid (H₂PO₃H) as precursors of molybdenum and phosphorous, respectively, instead of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) and ammonium dihydrogenphosphate ((NH₄)H₂PO₄) employed in the traditional synthetic route. The main goal is the preparation of MoP based catalysts under softer conditions, i.e., at lower reduction temperature. To this end, a phosphorus precursor with lower oxidation state; the usage of molybdate instead of heptamolybdate as molybdenum precursor; as well as the absence of the calcination step were employed. Moreover the activity of these catalysts has been compared with one prepared by the conventional method presented in the literature.

2. Experimental

2.1. Substrate and reagents

The support used in this study was Cab-o-sil type commercial silica. Ammonium heptamolybdate tetrahydrate, (NH₄)₆Mo₇O₂₄·4H₂O (Merck 99%), ammonium dihydrogenphosphate, (NH₄)H₂PO₄ (Merck 99%), ammonium molybdate, (NH₄)₂MoO₄ (Aldrich 99.98%), and phosphorous acid, H₂PO₃H (Aldrich 99%) were employed as molybdenum and phosphorous precursor salts. The chemical products utilized in the reactivity study were dibenzothiophene (Aldrich 98%) and quinoline (Sigma–Aldrich 98%) in *cis*-, *trans*-decahydronaphthalene (Sigma–Aldrich 98%). The gases employed were He (Air Liquide 99.99%), H₂ (Air Liquide 99.999%) and N₂ (Air Liquide 99.9999%).

2.2. Preparation of catalysts

2.2.1. Conventional method

A Cab-o-sil type commercial silica was used as a support of MoP-based catalyst (15 wt% of Mo) prepared by the conventional method. The preparation of the catalyst was carried out following the incipient wetness impregnation method by adding the desired amounts of ammonium heptamolybdate tetrahydrate, (NH₄)₆Mo₇O₂₄·4H₂O, and ammonium dihydrogenphosphate, (NH₄)H₂PO₄, to the incipient volume. The impregnated solid was dried at 60 °C, and then calcined in air at 550 °C (1 °C min⁻¹) for 6 h, obtaining so the corresponding catalyst precursor. Finally, the precursor was reduced from 100 °C to 700 °C (2 °C min⁻¹) under a H₂ flow of 100 mL min⁻¹. The precursor and reduced catalyst prepared by this method will be referred to as MoP-c and MoP-c/r700, respectively; c/r refers to calcinated/reduced. Prior to the reduction, all the samples were treated with a He flow of 60 mL min⁻¹ for 1 h at 100 °C.

2.2.2. Novel method

A novel MoP/SiO₂ catalyst was also prepared using Cab-o-sil type commercial silica as a support. The preparation of the catalyst was carried out following the incipient wetness impregnation method by adding the desired amounts of ammonium molybdate, (NH₄)₂MoO₄, and phosphorous acid, (H₂PO₃H), to the incipient volume. Equimolar amounts of molybdenum and phosphorous salts were used to obtain 15 wt% of MoP. Once the aqueous salt precursor solution was added to the pelletized support (0.85–1.00 mm), the impregnated solid was air dried. Finally, temperature programmed reduction with hydrogen was used to develop the MoP phase. In

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