



NiMoS HDS catalysts – The effect of the Ti and Zr incorporation into the silica support and of the catalyst preparation methodology on the orientation and activity of the formed MoS₂ slabs

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ABSTRACT

HDS NiMo catalyst precursors supported on SiO₂, SiO₂-TiO₂ or SiO₂-ZrO₂, having high specific surface areas and highly dispersed Mo species were prepared using a one-pot sol-gel methodology or by wet impregnation. After the catalyst precursor sulfidation, HRTEM and Raman analyses evidenced the effective formation of MoS₂ slabs on the support. For the NiMoS-Si catalyst (precursor one-pot synthesized), there was a high formation of edge-bonded oriented MoS₂ slabs, whereas for the NiMoS/Si prepared by impregnation, basal-bonded MoS₂ slabs were more abundant. Coherent with the formation of MoS₂ slabs and the promoting effect of Ni, all of the prepared NiMoS catalysts were active in the HDS of thiophene, with those one-pot supported on SiO₂ or SiO₂-ZrO₂ being the most active. Due to the strong interaction between Mo and Ti, the NiMoS-SiTi catalyst did not show consistent formation of MoS₂ slabs and consequently it presented the lowest activity. No observable effect in the HDS activity of the Zr incorporation into the SiO₂ framework was noticed. The considerable specific activity (SA) of the catalysts NiMoS-Si and NiMoS/Si, was respectively related to the formation of the most active edge-bonded MoS₂ slabs and to the well-active Type II HDS catalysts on multilayer basal-bonded MoS₂ slabs. The studied NiMoS-Si and NiMo-SiZr with high SA values evidences that the one-pot sol-gel synthesis methodology used to prepare the catalyst precursor leads to highly active HDS catalysts with the important advantages of reducing the preparation time, energy consumption, and consequently diminishing the catalyst production cost.

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1. Introduction

The growing demand for high performance fuels associated with highly restrictive environmental laws have imposed rigorous constraints and led to the optimization of the hydrotreatment processes in petroleum refineries to produce fuels with extremely low levels of precursor pollutants such as sulfur organic compounds [1,2]. The conventional removal of sulfur from petroleum fuels is carried out by the well-known hydrodesulfurization process (HDS), in which the oil fractions react with hydrogen under severe

operational conditions and in the presence of a catalyst producing sulfidic acid and sulfur free compounds [1,2].

The commercial HDS catalysts usually consist of Mo sulfides promoted with Co or Ni sulfides supported on γ -alumina [1]. There is a constant search for more active catalysts which may involve the use of new active phases, additives, new carriers or combination of them [3–5]. Regarding new supports, a challenge is to obtain solids with high specific surface area allowing high dispersion of the active phase in adequate interaction with the carrier surface. Thus, aiming to improve the mentioned properties, new supports such as SiO₂ [6], MgO [7], ZrO₂ [8], TiO₂ [9], zeolites [10], mesoporous materials [11,12] and carbon nanotubes [12] have been studied. ZrO₂ [13] and TiO₂ [14] have been used as HDT catalyst carriers, and sulfided catalysts with higher intrinsic activity have been obtained by some research groups [13–15]. However, ZrO₂ and TiO₂ have

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low specific surface area and pore volume and limited thermal stability that have restricted their application. Mixed oxides such as $\text{Al}_2\text{O}_3\text{-ZrO}_2$ [16,17], $\text{TiO}_2\text{-Al}_2\text{O}_3$ [18], $\text{ZrO}_2\text{-SiO}_2$ [19] and $\text{TiO}_2\text{-SiO}_2$ [20,21], or ordered mesoporous silicas as MCM-41 [22], HMS [23] or SBA-15 [24], with isomorphically substituted Ti [25] or Zr [11], have been proposed as support for HDT catalysts in order to overcome those limitations.

As pointed out, besides of the physicochemical properties of the support which determine the interaction with metal precursors and the dispersion of the active phase, the textural properties, as porosity and pore volume, have an important role in the activity of the HDS catalysts. Several methods have been used to synthesize supports with improved textural properties. The sol-gel methodology with its well-known advantages as purity, homogeneity, and tunable porosity of the obtained materials, as well as the possibility of preparing materials with high specific surface areas at low temperatures [26], has been highly used. High specific surface area Al_2O_3 [27], SiO_2 [28], TiO_2 [29], ZrO_2 [30], $\text{TiO}_2\text{-Al}_2\text{O}_3$ [31], $\text{SiO}_2\text{-Al}_2\text{O}_3$ [32] or $\text{ZrO}_2\text{-TiO}_2$ [33] supports have been synthesized by sol-gel and have shown better performance and thermal stability than when prepared by precipitation or co-precipitation.

The sol-gel method is a process in which a solution or sol undergoes to a transition state and becomes a rigid mass (gel). This is a multistep procedure involving chemical and physical steps associated with the hydrolysis and polycondensation of organometallic or inorganic precursors, drying, and densification. Basically, it is used in a homogeneous three-component system: a precursor of the metallic oxide, a solvent, and an acid or basic catalyst. The most commonly used precursors are metal alkoxides $\text{M}(\text{OR})_n$, such as alkoxysilanes ($\text{Si}(\text{OR})_4$): tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) [34,35] or aluminum isopropoxide, zirconium propoxide or titanium tetraisopropoxide [36,37].

In order to tune the porosity and the pore volume of the final desired support, an organic template may be also added into the sol-gel mixture. In this sense, citric acid has been satisfactorily used, with the size and volume of the generated mesopores, linearly increasing with the amount of citric acid added and, consequently, also increasing the specific surface area of the formed solid [38]. Therefore, oxides or mixed oxides prepared by sol-gel, such as SiO_2 , $\text{SiO}_2\text{-TiO}_2$ or $\text{SiO}_2\text{-ZrO}_2$ could be versatile materials to be used as catalyst support, as their textural properties could be tailored [37–39]. It is also claimed by several authors [38,40–43] that during the sol-gel preparation, the presence of citric acid in the sol mixture promotes the dispersion of the metallic species due to their ability to chelate metal ions. On the other hand, it has also been reported that the addition of chelating ligands such as citric acid to the impregnating solution has a beneficial effect on the activity of the HDS catalysts [41,44,45]. The improved activity has been ascribed to a better dispersion of nickel (or cobalt) and molybdenum on the support and to a higher sulfidation temperature of those promoters (Ni or Co) when compared with catalysts prepared without a chelating agent [46]. Both factors would enhance the formation of the so-called Ni–Mo–S type II active sites [47], which are considered the best active phase in hydrotreatment catalysts [7].

On the other hand, as an alternative to the conventional catalyst preparation by impregnation, it has recently been quite applied the addition of the metallic precursor salts into the sol mixture used in the sol-gel preparation of the support [17,30,43]. This one-pot methodology reduces the synthesis steps and it has been claimed that the obtained catalyst precursors present the active metallic species better dispersed [48].

Taking into consideration the above discussion, the purpose of the present work was to prepare silica, silica-titania and silica-zirconia supported NiMo oxides, the precursors of HDS NiMoS catalysts, by a one-pot sol-gel methodology and to compare their properties with similar catalysts prepared by wet impreg-

nation with a chelating agent on the corresponding carriers. HDS of thiophene was used as a model reaction for evaluating the catalytic activity of the sulfided catalysts. Atomic absorption spectroscopy (AAS), Energy-dispersive X-ray spectroscopy (EDS), nitrogen physisorption, X-ray diffraction (XRD), temperature programmed reduction by hydrogen ($\text{H}_2\text{-TPR}$), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), High resolution transmission electronic microscopy (HRTEM) and Raman spectroscopy were used to sample characterization.

2. Experimental

2.1. Synthesis by a sol-gel methodology of silica, silica-titania and silica-zirconia pure supports and of supported NiMo oxides

The silica, silica-titania and silica-zirconia pure supports were obtained by a sol-gel synthesis methodology using a Si/Me ratio of 10 (Me = Ti or Zr), tetraethylorthosilicate, zirconium propoxide, titanium isopropoxide, ethanol and citric (CA) and nitric acids. The composition of the resultant sol mixture was: Si: 0.1Ti(Zr): 4H₂O: 6EtOH: yCA, with y = 1 or 3 for the synthesis of pure silica or the mixed oxides, respectively. The sol mixture was dried at 70 °C for 72 h and the obtained gel calcined in static air at 550 °C during 2.5 h.

The supported NiMo oxides, the precursors of the supported silica, silica-titania and silica-zirconia NiMoS catalysts, were prepared adding the necessary amount of Ni and Mo salts in the sol mixture of the respective support to generate solids with 3 wt% of NiO and 12 wt% of MoO₃ (one-pot synthesis methodology). For comparison purposes, precursors of the catalysts with the same composition were prepared by wet impregnation using a mixture containing citric acid (chelating agent), ammonium heptamolybdate and nickel nitrate (CA/Mo mole ratio = 1), being subsequently dried and calcined in the same conditions defined above. The corresponding supported NiMo oxides were denominated as NiMo(ox)-Si; NiMo(ox)-SiTi; NiMo(ox)-SiZr when the one-pot procedure was used or as NiMo(ox)/Si; NiMo(ox)/SiTi; NiMo(ox)/SiZr when prepared by wet impregnation.

2.2. Pure supports, catalyst precursors and NiMoS catalysts characterization

The chemical composition of the catalyst precursors was obtained by atomic absorption spectroscopy (AAS) analyses that were carried out in a Perkin Elmer 5000 series spectrometer. Chemical analyses of the supports for the determination of the composition of Ti and Zr were also performed by EDS using an electron microscope FEI Magellan L 400, operating at 15 V of acceleration voltage. Supports and the catalyst precursors were characterized by powder X-ray diffraction (XRD) in a Shimadzu DRX-600 spectrometer using a CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The textural properties of the supports and the catalyst precursors were determined from N₂ adsorption/desorption isotherms obtained at –196 °C on an ASAP 2020 Micromeritics equipment. Prior to sorption experiments, the samples were degassed under vacuum at 190 °C during 2 h. The UV–vis diffuse reflectance spectra (UV–vis DRS) of supports and catalyst precursors were recorded at room temperature using a Varian Cary 5G spectrometer and barium oxide as a reference material. The $\text{H}_2\text{-TPR}$ experiments were carried out in a Micromeritics Pulse Chemisorb 2920 analyzer with the samples being previously treated under nitrogen flow at 200 °C during 30 min. The measurements were performed from room temperature to 1000 °C using a heating rate of 10 °C min^{–1} and a H₂ flow (10% V/V in N₂). HRTEM images of the sulfided catalysts were obtained using a FEI TECNAI F20 microscope operating at 200 kV. Raman spectra of the sulfided catalysts were obtained in a Horiba Jobin-Yvon Raman micro-

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