



# Behavior of NiMo/SBA-15 catalysts prepared with citric acid in simultaneous hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene

Tatiana E. Klimova\*, Diego Valencia, Juan Arturo Mendoza-Nieto, Patricia Hernández-Hipólito

Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Coyoacán, México D. F. 04510, Mexico

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## ABSTRACT

In the present work, NiMo catalysts supported on SBA-15 were prepared using citric acid (CA) during the synthesis. The objective of this work was to realize a comparative study of NiMoCA/SBA-15 catalysts prepared under different conditions in order to get a deeper insight into the effect of the thermal treatment and pH of the impregnation solution used on the catalytic behavior in deep hydrodesulfurization (HDS). Catalysts were prepared by simultaneous impregnation of Ni and Mo species and CA, using impregnation solutions of acidic or basic pH values (pH = 1 or 9, respectively). The speciation diagrams of Ni(II) and Mo(VI) species in aqueous solution as a function of pH were established.  $\text{NiCit}_2^{4-}$  complex was formed in aqueous solution at pH = 9. After the impregnation, NiMoCA/SBA-15 catalysts were dried at 100 °C and some of them were calcined at 500 °C in air atmosphere. Prepared catalysts were characterized by thermogravimetric analysis (TGA/DTG), nitrogen physisorption, powder X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), temperature-programmed reduction (TPR), and high-resolution transmission electron microscopy (HRTEM) and tested in simultaneous HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in a batch reactor at 300 °C for 8 h. XRD characterization showed that Ni and Mo oxide species were well dispersed in all catalysts prepared with CA. In contrast, reference NiMo/SBA-15 catalysts prepared by co-impregnation of Ni and Mo species, without the addition of CA, showed signals of crystalline phases:  $(\text{NH}_4)_4[\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 4\text{H}_2\text{O}$  after drying at 100 °C and  $\text{NiMoO}_4$  after calcination at 500 °C. HDS of DBT showed differences in activity and selectivity of the catalysts depending on the pH of the impregnation solutions and the temperature at which the catalysts were treated: NiMoCA/SBA-15 catalysts prepared from acidic impregnation solutions were more active for HDS of DBT than those prepared using basic ones. Both dried and calcined catalysts prepared at pH = 1 were selective toward the hydrogenation (HYD) route of hydrodesulfurization. However, the selectivity of the catalysts prepared from basic solutions (pH = 9) was strongly affected by the thermal treatment: dried catalyst was highly selective for the direct desulfurization (DDS) of DBT, whereas the calcined one for the HYD route. NiMoCA/SBA-15 catalysts with high hydrogenation ability showed high activity in hydrodesulfurization of 4,6-DMDBT.

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## 1. Introduction

Nowadays, the demand of high-quality, low-sulfur transportation fuels is growing because of the necessity to solve environmental problems induced by  $\text{SO}_x$  emissions and improving air quality [1,2]. Sulfur removal is also strongly desirable in order to increase the durability of refinery equipment and to minimize the poisoning of the  $\text{DeNO}_x$  and combustor catalysts that use noble metals [2]. The main industrial process to accomplish this purpose is hydrodesulfurization (HDS), in which S-containing molecules react with hydrogen in the presence of a heterogeneous catalyst at high temperatures and pressures. The main components of the traditional

HDS catalysts are the active phase (transition metal sulfide, generally  $\text{MoS}_2$  or  $\text{WS}_2$ ), promoter (NiS or CoS), and support ( $\gamma\text{-Al}_2\text{O}_3$ ) [3,4]. In order to attend the demand of production of low-sulfur-containing fuels, many efforts are aimed to design novel hydro-treating catalysts, highly active and selective especially for HDS of the refractory polyaromatic sulfur compounds.

In general, there are different possibilities that allow to modify the characteristics of HDS catalysts and as a consequence, their behavior. For instance, using new supports (MCM-41, SBA-15, KIT-6, etc.) with appropriate physicochemical properties such as large surface area, good thermal and mechanical resistance, and the ability to disperse well NiMo and CoMo HDS active phases leads to attractive HDS catalysts [5–7]. Some mesostructured silica supports have been modified with different heteroatoms (P, Al, Ti, Zr, W, etc.) to increase the activity and selectivity of NiMo and CoMo HDS

\* Corresponding author. Fax: +52 55 5622 5371.

E-mail address: [klimova@unam.mx](mailto:klimova@unam.mx) (T.E. Klimova).

catalysts [8–17]. Another route to enhance the catalytic activity relies on correctly selecting metal precursors and solvents; the use of Keggin-type heteropolyacids ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) for example, as distinct precursors for NiMo and NiW catalysts supported on SBA-15 has also led to good results [18]. A third option consists in using chelating agents and organic ligands (L) in the preparation of HDS catalysts [19]. It is well known that, under the appropriate experimental conditions (solution pH, metal and ligand concentrations, etc. [20]), chelating agents are able to coordinate metals and thus increase solubility and stability of the metal precursors used for the preparation of supported catalysts. CoMo and NiW catalysts supported on  $\gamma\text{-Al}_2\text{O}_3$  prepared with nitriloacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and cyclohexanediaminetetraacetic acid (CyDTA) showed higher HDS and HYD activities than those prepared without the chelating agents [21]. In the same work, however, the activity of NiMo/ $\gamma\text{-Al}_2\text{O}_3$  catalysts almost did not change when ligands were used. In work [22], high activity in thiophene HDS was obtained for NiWS catalysts supported on silica prepared with the same ligands (EDTA, NTA, and CyDTA). It was found that the addition of chelating agents results in a decrease in the temperature of reduction of the active phase and an increase in the temperature of sulfidation of Ni species. When Ni–L complexes were used, both Ni and W were converted into sulfides at similar temperatures, leading to the formation of an active NiWS phase [22]. CoMo catalysts supported on alumina and silica–alumina prepared with chelating agents (EDTA, NTA) had better catalytic performance when they were sulfided without previous calcination [23] which was attributed to a better promotion of the CoMoS phase [24,25]. Most of the above studies used HDS of thiophene or hydrogenation reactions of alkenes as catalytic tests. However, when CoMo–NTA catalyst supported on  $\gamma\text{-Al}_2\text{O}_3$  was tested in HDS of dibenzothiophene (DBT), one of the refractory model molecules of gasoline and diesel fuels, no changes in activity or selectivity were detected [26].

Citric acid (CA) was employed to synthesize  $\text{Co}_2[\text{Mo}_4(\text{C}_6\text{H}_5\text{O}_7)_2\text{O}_{11}]$  complex in aqueous solution at acidic pH to be used as a precursor of the CoMoS phase [27]. CoMo/ $\gamma\text{-Al}_2\text{O}_3$  catalysts prepared from this complex showed improved activity for deep HDS. Some changes in the behavior of these materials were observed when they were treated at different temperatures (in the range of 100–500 °C) [28]. This was ascribed to the calcination of the complex and formation of different Co–Mo–CA species adsorbed on  $\gamma\text{-Al}_2\text{O}_3$  surface before sulfidation [29]. Catalysts supported on metal oxides other than  $\text{Al}_2\text{O}_3$  or alumina modified with zeolites were found to be active in hydrodesulfurization of refractory compounds such as DBT and 4,6-dimethyldibenzothiophene (4,6-DMDBT). For example, attractive results were obtained with CoMoP/HY- $\text{Al}_2\text{O}_3$  catalyst prepared with CA [30]. This catalyst diminished the sulfur content below 16 ppm of S and had some advantages in resistance to the presence of N-containing compounds reaching elimination of N below 5 ppm at 350 °C. Addition of CA to this catalyst resulted in a considerable increase in activity when commercial diesel was used. This was ascribed to a better dispersion of the active phase and the prevention of the sulfidation of Co at low temperatures [31]. The optimal temperature for the thermal treatment of this catalyst before sulfidation stage was 100 °C. At higher temperatures (between 300 and 500 °C), the rate constants decreased [32]. Citric acid was also used in the preparation of CoMo/ $\gamma\text{-Al}_2\text{O}_3$  catalysts modified with boron. Addition of CA increased the dispersion of Co and Mo species, resulting in a larger amount of Co–Mo–S phase after sulfidation without active-site blocking by cobalt sulfide clusters [33]. NiMo catalysts supported on  $\text{ZrO}_2\text{-TiO}_2$  were prepared at acidic pH with the addition of EDTA or CA, and they were sulfided without previous calcination [34]. For both chelating agents, rate constants of DBT HDS increased. Better activity results were obtained when the Ni/CA molar ratio was 1:2,

although no selectivity modifications were observed for any molar ratio.

In summary, the results described above are sometimes contradictory. This means that the behavior of HDS catalysts prepared with ligands strongly varies with a number of factors: preparation conditions and thermal treatment, nature of the support as well as active phase and promoter used, model molecule used for catalytic tests, etc.

In our group, a series of NiMo catalysts supported on SBA-15 were prepared with citric acid and tested in hydrodesulfurization of DBT [35,36]. We selected this mesoporous molecular material as a support because of its high hydrothermal stability, attractive textural properties (high surface area and pore volume), and pore size appropriate for the transformation of large organic molecules such as dibenzothiophene-type compounds [18]. In work [35], NiMo/SBA-15 catalysts were prepared varying the pH of the impregnation solution and conditions of the thermal treatment after the impregnation step. We observed that these two factors modified activity and selectivity of the catalysts in HDS of DBT. A detailed kinetic study undertaken in this work confirmed this result. However, no clear explanation could be drawn for the changes observed in catalytic behavior. In the following work [36], NiMo/SBA-15 catalysts were prepared using basic impregnation solutions containing different amounts of citric acid. These catalysts were sulfided without previous calcination and showed very high selectivity for the direct desulfurization of DBT. In both works, we found that all catalysts prepared with citric acid contained a small amount of carbon, which increased along with the amount of citric acid used in the catalyst preparation. In the present work, we tried to achieve a greater insight into the effect of citric acid on the characteristics and behavior of NiMo/SBA-15 catalysts in deep HDS. For this, NiMo(CA)/SBA-15 catalysts were prepared from impregnation solutions of two pH values (pH = 1 or 9) and subjected to different thermal treatments. We were interested in following the evolution in the characteristics of Ni and Mo species upon the addition of citric acid to the solutions used for catalyst preparation, impregnation of these solutions to the SBA-15 support and drying or calcination treatment, up to the sulfidation of the catalysts. Our interest was to look for the relationship between the characteristics of Ni and Mo species at different steps of the catalyst preparation and their activity and selectivity in simultaneous HDS of two model compounds, dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

## 2. Experimental

### 2.1. Catalyst preparation

SBA-15 silica with hexagonal  $p6mm$  structure was prepared according to a reported procedure [37,38] using the triblock copolymer Pluronic P123 ( $M_{av} = 5800$ ,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , Aldrich) as the structure-directing agent and tetraethyl orthosilicate (TEOS, Aldrich, 99.999%) as the silica source. P123 copolymer (4 g) was dissolved in water (30 g) and 2 M HCl (120 g) solution at 35 °C. Then, TEOS (8.5 g) was added into the solution. The mixture was stirred at 35 °C for 20 h and then aged at 80 °C for 48 h without stirring. The solid product was recovered by filtration, washed with deionized water, and air-dried at room temperature. Calcination was carried out in static air at 550 °C for 6 h.

NiMo catalysts supported on SBA-15 were prepared by a standard incipient wetness co-impregnation technique reported elsewhere [39]. The calcined support was co-impregnated using aqueous solutions of ammonium heptamolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (Merck, 99%), nickel nitrate,  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (Baker), and citric acid,  $\text{C}_6\text{H}_8\text{O}_7\cdot \text{H}_2\text{O}$  (Merck, 99.5%) at pH = 1 and 9. Acidic pH

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