

Study of the impregnation of NiMo assisted by polymeric chelating agent for HDS supported catalyst over mesoporous silica.

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1. Introduction

The increase in the atmospheric pollution has induced lower permissible sulfur content in the environmental laws. Industrially to fulfill these standards, it is employed catalysts and high-pressure processes. However, this is a task complicated because the high refractories sulfur composition of some crude oils. Nowadays, commercial unsupported catalysts meet these regulations, but with high costs. In consequence, many of the new scientific research is focused in the development of cheaper supported catalyst with low and well-dispersed metal loadings. In this context, despite the difficulties in obtaining highly dispersed catalyst, the most common and simple method is the incipient impregnation [1]. Additionally to the well dispersion of the active phase, it is necessary to attain a special configuration of the metals loaded on the catalyst. In the hydrodesulfuration (HDS) field, it is accepted that the MoS₂ forms a hexagonal microstructure surrounded by Ni atoms located on the rim and edges. Sulfidation of Ni promoter begins at room temperature while the molybdenum precursor begins at 75 °C; this leads the formation of bulk NiS_x crystals instead of the NiMoS highly active phase. One way to overcome this problem is to employ chelating agents to increase the viscosity and modify the activation temperature of the precursor. This yields that the sulfidation process occurs in the opposite direction i.e. Mo is first sulfided over the Ni, which produce a high proportion of NiMoS crystals. Commonly, the chelating agents contain carboxylic acid and amine functional groups, which produce a Lewis acid-base reaction with metals. Among these agents, citric acid and ethylenediaminetetraacetic acid (EDTA) are the most employed [2,3]. Therefore, in the present work, three chelating agents were employed in the synthesis of surface-modified NiMo catalysts supported on KIT-6 and their performance was compared in the HDS of a model molecule such as dibenzothiophene (DBT).

2. Experimental/methodology

KIT-6 was prepared following the Soni and collaborators methodology modified [4, 5]. The surface of the support was modified employing a solution of aluminium tri-sec-butoxide and 2-propanol. This solution was added via incipient impregnation ultrasonic assisted, followed by drying at 60°C, and calcination at 550°C. Citric acid (Ch.1) and EDTA (Ch.2) chelating agents were used as reference. Two polymeric chelating agents based on polyacrylic acid were synthesized in order to obtain molecular weights of 1000 g/mole (Ch.3), and 9000 g/mole (Ch.4). A Ni-chelating agent complex was formed with a stoichiometric proportion of ammonium hydroxide. After the drying and calcination steps, ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was also impregnated in the proportion to obtain a 16 %wt of metals with a ratio of $\frac{Ni}{Ni + Mo} = 0.3$. Then the materials were activated and the catalyst powders were characterized by the BET method, high-resolution transmission electron microscopy (HRTEM) and thermal analysis (TGA). The catalytic performance was carried out in a batch reactor at 350 °C, 3.4 MPa and 600 RPM. The initial concentration of the DBT/decaline solution was

5000 ppm of sulfur. Samples were taken each 30 minutes by 5 h. Collected samples were analyzed by gas chromatography (GC) and sulfur concentration was determined with a FID detector.

3. Results and discussion

BET surface areas for KIT-6 was 700 m²/g, while for NiMoS catalysts with Ch.1, Ch.2, Ch.3 and Ch.4 were 260, 290, 360, 110 m²/g, respectively. The decreasing in the surface areas could be caused by the metal loaded and organic species (chelating agent). The HRTEM images of the catalysts prepared by three activation steps, showed crystal size of 5-7 nm and crystal stacking of 4-5 sulfur slabs, while for the catalysts prepared by one activation step and without calcinations, the crystals size was 3-4 nm and the average stacking of crystals was 2-3 sulfur slabs. The performance in the HDS activity for DBT was determined for the catalysts with calcinations and three activation steps, showing rate constants of 9.4, 12.5, 7 and 6 (10⁻⁷ mole/s*g) for Ch.1, 2, 3 and 4 respectively. Based on these results, the catalyst with the best performance was Ch.2, which contains EDTA as chelating agent. This behavior could be explained in terms of the viscosity of the system, where a high viscosity value provides a slower evaporation of the solvent and as consequence a better dispersion of the metals. Additionally, the EDTA contains Na, which after calcination may act as active sites for interacting with the metals. Conversely, NiMoS-Ch.1 synthesized without calcinations showed a rate constant of 18x10⁻⁷ mol/s*g, suggesting that the chelating agent retained the Ni during the activation step. This was observed in the TGA analysis as the thermal degradation in the temperature range of 230-350 °C. Therefore, a gradual temperature raised exerted during the activation step, slowly degraded the organic molecule releasing the Ni at a higher temperature, and allowing the formation of NiMoS crystals.

4. Conclusions

Three chelating agents were employed in the preparation of NiMo catalyst supported on KIT-6 and their performance was tested in the HDS of DBT. The sequence of drying, calcination and the activation methodology were also studied. The catalyst prepared with citric acid without calcination and activated with a slow temperature ramp, presented small and few stacked crystals, and subsequently showed the highest catalytic activity. The catalytic performance was even higher than a commercial catalyst with a higher metal load supported on alumina. Conversely, the catalysts prepared with a fast activation temperature ramp showed low catalytic activity because carbon was deposited on the Ni, hindering the sulfidation.

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