

Hydrotreating catalysts prepared by salts of heteropolyacids. Hydrodesulfurization of 4,6-DMDBT in presence of nitrogen compounds

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Introduction

The environmental care is one of the worldwide increasing worries. This fact encourages scientists to make efforts in finding more efficient hydrodesulfurization (HDS) catalysts to fulfill the increasing demand for low sulfur fuels. It is known according to works published by Gates et. al (1) that in promoted Mo(W) by Co(Ni) catalysts, the increasing in HDS activity is directly related to the number of sites of Co(Ni)MoS phase, which is formed during catalyst sulfidation. To accomplish this requirement, special attention must be paid when selecting the precursor oxides and method for HDS catalysts preparation. Under this context, some studies have been reported using salts of heteropoly acid (HPA) compounds for the preparation of HDS catalysts. The use of the 12-phosphomolybdic acid having the Keggin type structure is reported (2,3). These structures are able to incorporate high loads of Co(Ni). This means that can be prepared precursors in which all the elements are together. To the date, there are few reports on the application of HPA compounds in HDS. In these studies, catalysts based on HPA of molybdenum and tungsten were only tested with model molecules as thiophene and dibenzothiophene (3-5) obtaining promising results.

In the present work, salts of heteropoly acids of Mo and P like precursors of HDS catalysts, is proposed. It is expected that the NiMoP supported catalysts prepared with this method, will take the advantage of associate all elements to be deposited in the same compound. In addition, due to the absence of counterions (NH_4^+ , NO_3^- , (present in ammonium heptamolybdate and nickel nitrate precursors) a strong interaction between promoter (Ni) and heteropoly acid in the impregnating solution must exist, giving rise during the catalyst activation step to a higher number of structures of mixed phase NiMoS (active phase). Moreover, the presence of phosphorus will provide acidity to the catalytic system. These catalysts will be evaluated in the HDS reaction of 4,6 DMDBT with presence of nitrogen compounds.

Materials and Methods

The supports ($\text{SiO}_2/\text{Al}_2\text{O}_3$) were prepared by impregnation of a commercial alumina with tetraethylortosilicate (TEOS) in a non aqueous solvent (isopropyl alcohol). Then were dried (100 °C) during 24 h and calcined (550 °C) for 4 h.

Catalysts were prepared by incipient wetness impregnation of supports using solutions with proper amount of salts of HPA with 12.5 % Mo as MoO_3 , P/Mo = 1:12 and Ni/Mo=0.4. After that the solids were dried (100 °C) for 24 h and calcined (450°C) for 4 h. The salt of HPA was prepared according to (6).

For comparison purposes, a sample of NiMoP supported catalyst with the same Mo loading was prepared using conventional method (ammonium heptamolybdate, nickel nitrate and phosphoric acid). Here in after, NiMoP will be labeled to the catalyst prepared by conventional method and NiHPA to the one prepared by the salt of heteropolyacid.

Supports and catalysts were characterized by nitrogen physisorption, XRD and FTIR.

Prior to catalytic evaluation, samples were activated at 400 °C, during 4 h in flow of $\text{H}_2\text{S}/\text{H}_2$. HDS of 4,6 DMDBT (1000 ppm S in n-decane) was conducted in batch reactor at 325 °C during 6 h and 1000 psia. Carbazole as nitrogen compound (80 ppm N)

Results and Discussion

The results of nitrogen physisorption indicate that after Mo, Ni and P impregnation important changes in the support textural properties did not occurred. XRD and FTIR characterization showed that the structure of the salt of the heteropolyacid was preserved.

The conversion of 4,6 DMDBT was of 50% for NiHPA catalysts whereas for NiMoP was about 20%. This result could be attributed to the close contact of Mo and Ni atoms during catalysts sulfidation increasing in this way the number of NiMoS phase structures (active sites). In addition, the presence of phosphorus confers the acidic property which is responsible of dissociation and spill over of hydrogen necessary in HDS and HDN processes for the hydrogenation of aromatic rings. The improvement in the hydrogenation (HYD) route was corroborated by calculating the HYD/DDS ratio, which was 4 and 5 for NiMoP and NiHPA respectively.

Significance

The use of salts of HPA of Mo and P during catalyst preparation, improve the activity of hydrodesulfurization and hydrodenitrogenation, essential to fulfill the present environmental regulations.

References

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