Mo/TiO₂ catalyst doped with niobium sulfide for HDS process.

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Introduction
Among the new catalytic phases proposed to obtain more active hydrodesulfurization (HDS) catalysts, the use of niobium sulfide has attracted attention. Previous reports indicate that in the unsupported state, niobium sulfide exhibits unique acidic properties [1], and when supported on carbon or alumina it is possible to obtain catalytic activities in HDS higher than those of a MoS₂/Al₂O₃ catalyst with equivalent metal loading [2-3]. It has been demonstrated that the nature of the niobium precursor salt and the support also influence the HDS activity and the difficulty of sulfidation of the catalyst. Moreover, the addition of niobia as promoter to the typical hydroprocessing catalysts resulted in an increase of the HDS and HDN activities [4].

In the present work, we analyze the effect that the incorporation of small amounts of Nb to MoS₂/TiO₂ catalysts by different methods causes on their HDS activity. Two different routes were used to incorporate niobium to the catalyst support in order to produce a Ti-Nb mixed oxide, or a TiO₂ covered with niobium oxide.

Experimental
Nb-TiO₂ mixed oxides were prepared by the simultaneous hydrolysis of Ti isopropoxide and Nb ethoxide, followed by drying (373K, 24 h) and calcination (773K, 4 h). The niobium-covered samples, Nb/TiO₂, were prepared by pore volume impregnation of TiO₂ (Degussa P-25, 74 m²/g) with niobium ethoxide followed by hydrolysis in wet air. The Nb-TiO₂ and Nb/TiO₂ samples were prepared with Nb contents of: 2, 4 and 6 wt %. The deposition of Mo on the calcined supports was also achieved by pore volume impregnation using an aqueous solution of ammonium heptamolybdate. The catalysts were dried at 100°C during 24 h and calcined at 500°C (4 h). As reference, two additional samples were prepared by similar methods, molybdenum supported on alumina (Gilder, 180 m²/g), Mo/Al₂O₃, and molybdenum supported on alumina covered with niobium oxide (4 wt % as Nb), Mo/Nb/Al₂O₃.

The supports were characterized by x-ray diffraction (XRD), N₂ adsorption-desorption isotherms (surface areas and pore diameter distribution) and FT-Raman. The acid properties of the supports and catalysts were obtained from the analysis of the IR spectra of adsorbed pyridine.

A conventional TPR apparatus with TCD and UV detectors was used for the study of the reducibility of calcined and sulfided (TPR-S) catalysts. The sulfided catalysts were analyzed by TPR-S before and after the reaction test, as described previously [5]. The catalytic activity tests for thiophene HDS, at 623 and 673K, were carried out at atmospheric pressure in a typical continuous-differential micro-reactor apparatus.
Results and discussion

The results from the textural characterization, for the Nb(wt %)-TiO₂ mixed oxides and titania covered with niobium oxide (Nb(wt %)/TiO₂), show all the samples exhibit textural properties similar to those of the reference commercial and synthesized titania. This indicates that the incorporation of small amounts of niobium do not alter significantly the textural properties of the original corresponding titania support. Moreover, the structural characterization by XRD and FT-Raman show only the presence of anatase phase, indicating a reasonably good dispersion of the Nb phases in all cases. Because of these minor differences only the samples with 4 wt % Nb prepared by the two methods were evaluated in the activity tests and characterized further to explain the observed differences in HDS catalytic activity.

The method of Nb incorporation affects the acid sites distribution in the catalyst support. Two important results were obtained; i) the incorporation of Mo promoted the formation of Brönsted acid sites without altering in the same proportion the total number of acid sites. This indicates that part of the original Lewis sites present in the support are suppressed by the deposition of Mo while the Mo species provides additional Brönsted sites. This is clearly evidenced in the case of Mo supported on Nb/TiO₂ since in this sample the Brönsted acid sites were created only after the incorporation of Mo. ii) When Nb is incorporated to titania, the acidity changes depend of the preparation method. For titania covered with Nb, no Brönsted sites are detected while in the Nb-TiO₂ mixed oxide the presence of Brönsted sites is clearly evident.

Comparison of the activities of the Mo/Nb/TiO₂ and Mo/Nb-Ti catalysts indicate clearly that the effect of adding Nb to the titania support depends on the method of Nb incorporation. The sample Mo/Nb-TiO₂ in which the Nb was incorporated trough a sol-gel method leading to a Ti-Nb mixed oxide, and where Nb is present as isolated species forming Ti-O-Nb-O-Ti bonds, exhibited an activity three times smaller than the Mo/Nb/TiO₂ sample, in which the Nb was deposited on the surface of TiO₂, leading to the formation of more polymerized Nb oxide species. These results are perfectly consistent with the quantification of the H₂S evolution in the 300-673 K temperature region of the TPR of sulfided samples (TPR-S). This H₂S evolution is directly related to the concentration of anionic sulfur vacancies in the active MoS₂ phase.

References