Hydrodesulfurization of 4,6 DMDBT on Boron-modified CoMo/Al_2O_3 and NiMo/ Al_2O_3 catalysts.

Jorge Ramírez, Pablo Torres, Rogelio Cuevas and Aída Gutiérrez-Alejandre
Departamento de Ingeniería Química, Facultad de Química, UNAM, Cd. Universitaria, Mexico D.F. (04510), Mexico. Email: lptorres@infosel.com

Introduction

Modification of the acid-base properties of alumina by boron is well known and Alumina-Boria itself has been used as an acid catalyst[1]. The effect of adding boron to conventional Co-Mo/γ-Al_2O_3 catalysts on their catalytic properties has been studied in the past[2,3]. Nevertheless the experiments were focused on the hydrodesulfurization (HDS) of compounds like thiophene or dibenzothiophenes. Due to its acid properties and enhanced hydrodesulfurization activities it would be interesting to test the performance of boria-modified CoMo/Al_2O_3 and NiMo/ Al_2O_3 catalysts in the hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT), a sterically hindered compound which can be used to study the deep desulfurization process. The 4,6-DMDBT can be desulfurized over commercial CoMoS and NiMoS/Alumina catalysts via two parallel reactions[4-6]; direct desulfurization (DDS), which yields dimethylbiphenyl (DMBP) and desulfurization with primary hydrogenation of one aromatic ring, which gives tetrahydrodimethyldibenzotiophene (4,6-THDMDBT), and then methylcyclohexiltoluene (MCHT). The introduction of an acid function in the catalyst renders more complex the reaction scheme. In this case reactions such as isomerization, trans-alkylation and cracking can take place. However, the adequate use of an acid function could lead to the elimination of the steric hindrance caused by the sustituents in the 4 and 6 positions, leading to higher HDS rates. The work studies the changes in catalytic activity during the HDS of 4,6 DMDBT caused by the incorporation of boron to CoMo and NiMo supported on Alumina. The activity of the borated-alumina support in the acid-promoted reactions of 4,6 DMDBT is also examined.

Results and Discussion

The activity of the borated-alumina support was tested in a tubular continuous reactor at 800 psia and temperatures between 300 and 375 °C, using 4,6 DMDBT (500 ppm S) in hexadecane. The supports were prepared with 1 wt %B and the catalysts contain 12 wt % MoO_3 and a 0.33 Co(or Ni)/(Co(or Ni)+Mo) atomic ratio. The reaction, performed at several temperatures (300, 325 , 350 y 375°C) showed that at 375 °C the 4,6 DMDBT transforms partially to 4-MDBT and trimethylDBT. This indicates that the support alone is capable of promoting the trans-alkylation of 4,6DMDBT. As it is well known, these compounds desulfurize easier than 4,6 DMDBT . Some cracking of the hexadecane used as solvent was also evidenced.

The CoMo /Al_2O_3 -B(1.0) catalyst was tested in the HDS of 4,6 DMDBT at 300 and 350 °C in a tubular reactor using 0.3 g of catalyst sulfided previously with a CS_2/Ciclohexane mixture. The results, shown in Table 1, indicate that the 4,6 DMDBT is converted by the catalyst but that also some cracking of hexadecane, which becomes more important at high temperatures, takes place. A careful analysis of the chromatogram of the sulfur compounds indicates that some sulfur compound other than 4,6 DMDBT appear indicating s transformation possibly related to isomerization, transalkylation or craking without eliminating the sulfur heteroatom. These results were corroborated in a batch test, carried out at 300 °C and 600 psia, where it was observed at low residence times an increase in the concentration of sulfur compounds other than 4,6 DMDBT, indicating the existence of an acid route in the case of the CoMo catalyst. The results with the NiMo catalyst however do not show the same behavior indicating a possible effect of a Co-B phase in the reaction.

Table 1. Activity of the CoMo/Al_2O_3-B(1.0) catalyst.

	Cracking of hexadecane (% conversion)	HDS of 4,6 DMDBT (% Conversión)	Product sulfur content (ppm S)
Feed	-	-	500
300°C	6.7	66.5	167.5
350°C	50.8	84.1	79.5

Characterization of the catalysts was performed by TPD-NH_3, FT-IR of adsorbed pivalonitrile, UV-vis diffuse reflectance spectroscopy and X-ray diffraction.

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