HDS of 4,6-DMDBT in the presence of carbazole over NiMoP(x)/SiO_2-Al_2O_3 catalysts

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Introduction

Hydrodesulfurization (HDS) is one of the most important processes in petroleum refineries. The problem of deep HDS is due to the presence of molecules that present steric hindrance to HDS process, like 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT). However there is an additional problem, the hydrogenation of 4,6-DMDBT is inhibited by the presence of nitrogen compounds that adsorb competitively by the same sites.

To overcome this problem, hydrogenation and isomerization routes must be enhanced. It has been reported that silica-supported catalysts display increased hydrogenation properties and that the modification of HDS catalysts with relatively mild acidic represent one of the methods for improving their activity.

In the present work, a series of NiMoP(x) catalysts prepared with different phosphorous amounts supported on alumina modified by silica were evaluated in the hydrodesulfurization of 4,6-DMDBT with and without the presence of carbazole.

Materials and Methods

Al_2O_3-SiO_2 support was obtained by grafting of SiO_2 (10 wt%) on commercial Al_2O_3 (Sasol, 207 m^2/g) support.

The catalysts were synthesized by co-impregnation (pore volume method) of: MoO_3 (12.5wt%), NiO (3wt%) and P_2O_5 (0.0, 0.5, 1.5 and 2.5wt%) at pH=5. After that, the samples were dried and calcined in air at 373 (24 h) and 673 K (4h) respectively.

Previous to catalytic evaluation, the catalysts were activated at 673 K for 4 h using a H_2S(15%)/H_2 mixture. The HDS of 4,6-DMDBT (1000 ppm of S) with and without carbazole (100 ppm of N) was performed in batch reactor at 593 K and 1200 psi during 6 h. Analysis of the reaction products was performed with an HP 6890 chromatograph.

Results and Discussion

Figure 1 shows a comparison of the 4,6-DMDBT conversion with and without carbazole as a function of the reaction time. For HDS reaction, phosphorus addition does not have an important effect, but when carbazole is present, it is evident that there is an improvement of 35% in the HDS activity after 6 hours of reaction.

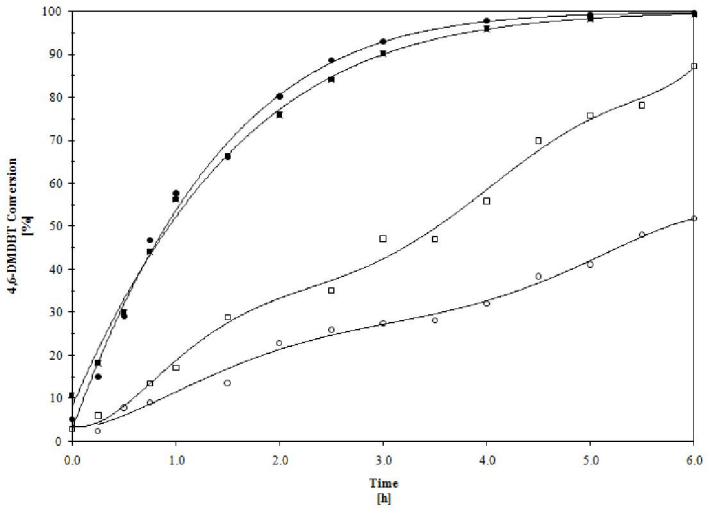

Figure 1. 4,6-DMDBT conversión for (●) HDS: 0.0wt% P_2O_5 (■) HDS: 2.5wt% P_2O_5 (○) HDS-HDN: 0.0wt% P_2O_5 (□) HDS-HDN: 2.5wt% P_2O_5. 793 K and 1200 psi

The catalyst with 2.5wt% P_2O_5 shows the best selectivity in HDS of 4,6-DMDBT in absence and presence of carbazole.

Significance

Phosphorus addition (2.5wt% P_2O_5) to NiMo/SiO_2-Al_2O_3 catalysts improves the HDS catalytic activity of refractory molecules such as 4,6-DMDBT when nitrogen compounds are present.