

NiMoP heteropolycompounds supported on Ti/SBA-15 as catalysts for desulfurization of 4,6-dimethyl dibenzothiophene

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Introduction

The need to comply with the strict regulations on the sulfur content in transport fuels has encouraged the search of more active and selective hydrodesulfurization catalysts. At the same time, there is a requirement to process heavier petroleum feeds with high content of contaminants like sulfur and nitrogen molecules as well as heavy metals Ni and V). To achieve sulfur levels close to zero ppm it is necessary to hydrodesulfurize compounds such as 4,6-dimethyldibenzothiophene, which are highly refractory to HDS.

Two ways to improve the performance of the catalyst are the use of a support with high specific surface area and the use of active phase precursor that improve either the acidity or the level of promotion of the catalyst. In this case, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and nickel citrate were used as precursors of the active phase.

In this work, a series of NiMoP HDS catalysts prepared from $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and nickel citrate supported on SBA-15 covered with different amounts of Ti (15 and 30 wt %) were prepared, characterized by different techniques and tested in the hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT). The activity of the catalysts was compared with a NiMoP catalyst prepared by the conventional pore volume impregnation of a dissolution containing ammonium heptamolybdate, nickel nitrate and phosphoric acid.

Materials and Methods

The Ti-SBA-15 support was prepared by pore volume impregnation of SBA-15 with a solution containing the required amounts of titanium isopropoxide and propanol to achieve 15 and 30 wt % Ti. The NiMo/Ti(x)-SBA-15 catalysts were prepared impregnating the Ti-SBA-15 support with a solution containing the required amounts of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and nickel citrate to achieve 13 wt % Mo (as MoO_3), 3.5 wt % Ni (as NiO) and 0.5 wt % P (as P_2O_5). The dried catalysts were directly sulfided in $\text{H}_2/\text{H}_2\text{S}$ (15 vol. %). The catalysts were characterized by nitrogen physisorption, XRD, FT-Raman, pyridine adsorption analyzed by FTIR, SEM, UV-vis-DRS, and were tested in the hydrodesulfurization of 4,6-dimethyldibenzothiophene.

Results and Discussion

The results presented in Table 1 showed that there is a maximum in the HDS activity of the catalysts at Ti content of 15 wt % and that the catalyst prepared by the conventional method (NiMoP(C)/SBA-15) has an activity more than five times lower than the NiMoP/Ti(15)-SBA-15 catalyst. The use of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and nickel citrate as precursors of the active phase has an important effect increasing the HDS activity in 4.5 times while the incorporation of 15 wt %

Ti to the SBA-15 support produces a catalyst with 1.3 times the activity of the NiMoP/SBA-15 catalyst.

Table 1. Pseudo first order rate constants for the HDS of 4,6-DMDBT

Catalyst	Pseudo first order Rate constant, k_{HDS} (h^{-1})
NiMoP(C)/SBA-15	0.10
NiMoP/SBA-15	0.45
NiMoP/ Ti(15)-SBA-15	0.57
NiMoP/ Ti(30)-SBA-15	0.49

The characterization of the catalyst showed that the Lewis acidity decreases and Brønsted acidity increases with the Ti content in the catalyst. At high Ti contents (30 wt %) the structure of SBA-15 deteriorates; because of this, the activity of the sample with 30 wt % Ti decreased.

Significance

The work highlights the use of Mo-P heteropolyacids in the preparation of HDS catalysts. The use of the Ti-modified SBA-15 ordered mesoporous material as catalyst support is also highlighted.