

Mo and Ni loading Influence on catalytic activity of NiO-MoO₃/MgO-TiO₂ catalysts: HDS of DBT.

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Introduction

In many countries legislative limits of sulfur concentration in fuels used in transportation are currently in the order of 50 ppm of S. The European Community, Japan and the US propose to reach the use of fuels with less than 10 ppm of sulfur by 2009. [1] Consequently in Mexico too, gasoline and diesel nearly sulfur-free are considered. The most common industrial process for sulfur removal is hidrodesulfurization. Considerably efforts have been made in the last few years to develop better catalysts for this process. CoMo/Al₂O₃ is the most industrially used catalyst and its active phase consists of well-dispersed MoS₂ nanocrystallites decorated with Co or Ni atoms as promoters, according to Topsoe's model [2]. These phases are obtained by sulfidation of an oxide precursor that is generally prepared by incipient wetness impregnation of an alumina support with ammonium heptamolybdate and cobalt or nickel nitrate solutions [3]. HDS and hydrogenation activities of MoS₂ are several times higher on TiO₂ and MgO than over alumina. However, it has been found that Ni synergy is lower on TiO₂ and MgO than on alumina supported homologues [4, 5]. That effect could be explained by different precursor-support interactions. The aim of this work is to get a better understanding of precursor-support interactions by a careful analysis of Ni and Mo species present on a MgO-TiO₂ support at different steps of preparation.

Materials and Methods

MgO-TiO₂ mixed oxides with 95 % mol of MgO were synthesized by the sol-gel method. NiO-MoO₃/MgO-TiO₂ catalysts, containing 12, 15 and 20 % of MoO₃ and a Ni(Ni+Mo)=0.3 mol ratio, were prepared by co-impregnation of the support with (NH₄)₆Mo₇O₂₁ and Ni(NO₃)₂ aqueous solution. The pH of impregnation was adjusted to pH 9. Characterization of the support was performed by N₂ physisorption and ζ-potential method. Ni and Mo superficial species were analyzed by UV-Vis diffuse reflectance (UV-vis-DRS) and Raman spectroscopy. Catalysts evaluation was carried out in a micro reactor with continuous flow and the flow leaving the reactor was analyzed by gas chromatography.

Results and Discussion

The specific area of the MgO-TiO₂ mixed oxide obtained was 266 m²g⁻¹. Results obtained by the ζ-potential method showed that our support presents a net surface pH of 5.5. The main results obtained by UV-Vis-DRS and Raman spectroscopy are resume in the table 1:

Table 1. Species present on the NiO-MoO₃ catalysts.

Catalyst	%Mo	Mo	Local geometry	Ni	Local Geometry
NiO-MoO ₃ dried at 120 °C	12	MoO ₄ ²⁻ MoO ₃	Td	[Ni ²⁺ 4O ²⁻]	Td
	15	MoO ₄ ²⁻ MoO ₃	Td	[Ni ²⁺ 4O ²⁻]	Td
	20	MoO ₄ ²⁻ MoO ₃	Td	[Ni ²⁺ 4O ²⁻]	Td
NiO-MoO ₃ calcinated at 400 °C	12	---	---	[Ni ²⁺ 4O ²⁻] NiMoO ₄	Td
	15	---	---	[Ni ²⁺ 4O ²⁻] NiMoO ₄	Td
	20	---	---	[Ni ²⁺ 4O ²⁻] NiMoO ₄	Td

The high interaction between MoO₄²⁻/[Ni²⁺ 4O²⁻]-support allows a higher loading of Mo and Ni. Net surface pH of support does not modify Ni and Mo species of impregnation solution. Thus, these species are conserved after impregnation.

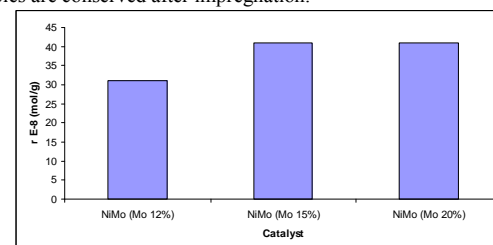


Figure 1. Dibenzothiophene Hidrodesulfurization on NiO-MoO₃/MgO-TiO₂ catalysts. T= 300°C, P= 30 bars. After 8 hours of reaction. Feed: 0.12 cm³/min of a 500 ppm S/n-heptane solution + 35 cm³/min of H₂.

On the other hand, catalysts evaluation showed that activity is improved with Mo loading. The results indicate the importance of the Mo loading in formation of oxide precursors and its effect on catalytic activity. Thus, the NiMo/MgO-TiO₂ catalyst could be considered as a hidrodesulfurization catalyst.

References

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