

# Effect of titania loading and method of support preparation on the development of NiMo/TiO<sub>2</sub>-SBA-15 catalysts in 4,6-DMDBT hydrodesulfurization

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## Introduction

Mo-based hydrotreating catalysts supported on  $\gamma$ -alumina have been traditionally used for hydrodesulfurization (HDS) of oil feedstocks [1]. Recently, in a search for new supports for HDS catalysts, titania has attracted attention due to the higher intrinsic activity demonstrated by Mo catalysts supported on this oxide [2]. However, pure TiO<sub>2</sub> supports present one important disadvantage: they generally have low surface area and porosity. Because of this problem, some attempts to obtain titania-based supports with high surface area have been made in recent years. Thus, in our group mesoporous molecular sieves of SBA-16 type have been synthesized, modified with titania and tested as supports for NiMo catalysts [3]. The activity of this series of catalysts in 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS was about 20% higher than that of the conventional NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Further increase in HDS activity was observed when SBA-16 material used as matrix for TiO<sub>2</sub> incorporation was replaced with SBA-15, support with hexagonal arrangement of cylindrical mesopores of larger size than in SBA-16. In the present work, with the aim of obtaining new improved supports that provide good Mo dispersion and therefore high HDS activity, we prepared and characterized a series of TiO<sub>2</sub>-modified SBA-15 supports and the respective NiMo catalysts and studied the effect of the preparation method of TiO<sub>2</sub>-SBA-15 supports and TiO<sub>2</sub> loading on the dispersion of titania, characteristics of the Ni and Mo supported species, and the performance of the obtained catalysts in the 4,6-dimethyldibenzothiophene HDS.

## Materials and Methods

The pure siliceous SBA-15 was synthesized according to the literature [4]. TiO<sub>2</sub>-containing SBA-15 supports were prepared by three post-synthetic methods: incipient wetness impregnation (method A); internal hydrolysis (method B) and grafting-precipitation (method C). In all cases, Ti (IV) isopropoxide was used as TiO<sub>2</sub> source and n-propanol as solvent. Prepared supports were designated as TiSBA-15(X/Y) samples, where X represents the method of preparation used and Y is the wt. % of TiO<sub>2</sub> in the support (Y = 18, 30, 42 and 54). NiMo catalysts (12 wt % of MoO<sub>3</sub>, 3 wt % of NiO) were prepared by successive impregnation of aqueous solutions of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O on the supports. Supports and catalysts were characterized by N<sub>2</sub> physisorption, XRD, UV-Vis DRS, TPR, SEM-EDX and HRTEM. The HDS activity tests were performed in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h using a hexadecane solution of 4,6-DMDBT (1000 ppm of S). Prior to the activity tests, the catalysts were sulfided *ex-situ* at 400°C for 4 h in a stream of H<sub>2</sub>S-H<sub>2</sub>.

## Results and Discussion

Ti-containing SBA-15 materials prepared by post-synthetic methods did not show considerable degradation of the initial SBA-15 structure (N<sub>2</sub> physisorption, small-angle XRD).

The appearance of anatase signals in the XRD patterns was observed for samples prepared by all methods used (A, B and C) when TiO<sub>2</sub> loading was higher than 30 wt. %. However, the size of anatase crystals and the amount of titania present in the crystalline form outside SBA-15 mesopores changed depending on the preparation method used. Thus, method C resulted in supports with larger TiO<sub>2</sub> crystals and method B with smaller ones (Table 1). TiO<sub>2</sub> incorporation in the SBA-15 support resulted in stronger interaction of Ni and Mo oxidic species with the support (TPR) providing better dispersion to the sulfided metal species (HRTEM).

Table 1. Catalytic activity and selectivity in 4,6-DMDBT HDS

Catalyst	TiO <sub>2</sub> crystal-line size, nm	Initial reaction rate, mol/(L·s·g catalyst)	4,6-DMDBT conv., %		HYD* DDS
			4 h	8 h	
NiMo/SBA-15	-	3.6 x 10 <sup>-6</sup>	35	70	9.9
NiMo/TiSBA-15(A/42)	15.0	4.4 x 10 <sup>-6</sup>	58	87	15.2
NiMo/TiSBA-15(B/42)	6.5	4.3 x 10 <sup>-6</sup>	54	84	14.2
NiMo/TiSBA-15(C/42)	18.5	4.8 x 10 <sup>-6</sup>	58	95	17.5
NiMo/TiSBA-15(C/18)	-	4.6 x 10 <sup>-6</sup>	56	90	14.5
NiMo/TiSBA-15(C/30)	7.8	4.8 x 10 <sup>-6</sup>	65	95	18.0
NiMo/TiSBA-15(C/54)	19.4	4.5 x 10 <sup>-6</sup>	55	89	11.3
NiMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	-	3.1 x 10 <sup>-6</sup>	33	61	n. a.

\*at 50% 4,6-DMDBT conversion

All NiMo catalysts supported on TiSBA-15(X/Y) materials showed high activity in HDS of 4,6-DMDBT (Table 1). Their activities were about 50 % higher than that of conventional NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The most active NiMo catalysts were prepared using method C for TiO<sub>2</sub> incorporation. The optimum TiO<sub>2</sub> loading in the support was between 30 and 42 wt %.

## Significance

Nowadays, much effort is aimed at improvement of HDS catalysts in view of the greater concern over environmental pollution and more stringent limitations to S contents in gasoline and diesel fractions. Ti-SBA-15 materials prepared via post-synthetic methods show promising features as supports for NiMo catalysts highly active in 4,6-DMDBT HDS.

## Acknowledgments

Financial support by CONACYT-Mexico (grant 46354) is gratefully acknowledged. The authors wish to thank M. Aguilar Franco, I. Puente and C. Salcedo for technical assistance.

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