

Highly Active, Low NiW Content Catalysts for HDT Prepared from H₃PW₁₂O₄₀ Supported on Al, Ti and Zr-modified SBA-15

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Introduction

Novel approaches for improving hydrotreating (HDT) catalysts are driven by the pressing requirement of ultra-clean transport fossil fuels with a view to reducing exhaust emissions. Further requirements not only for diesel sulfur content, but also for diesel cetane index, density and polyaromatics content have been introduced in many countries since 2005. Many efforts are aimed to improve hydrodesulfurization (HDS) catalysts by using new materials as catalytic supports. Mesoporous molecular sieves such as SBA, have attracted attention because of their high stability and better textural properties, compared to the traditional γ -alumina support. Another way to modify catalytic activity is to change the nature of the precursor of the active phase. In our previous works [1, 2] we showed that the use of SBA-15-supported, Ni-promoted Keggin-type Mo and W heteropolyacids (HPAs), instead of conventional precursor salts, yield highly active catalysts for HDS of hindered dibenzothiophenes as a result of an enhancement in the hydrogenation (HYD) route. In the seek to improve the catalyst performance by having a better control on the dispersion of the active NiW phase, the present work is aimed at the synthesis of homogeneous oxide and sulfide species by means of the incorporation of anchoring sites (Al, Ti or Zr) on the SBA-15 support surface together with the use of Keggin-type H₃PW₁₂O₄₀ as precursor.

Materials and Methods

SBA-15 was prepared according to [3], using Pluronic P123 as structure-directing agent and TEOS as the silica source. Modified SBA-15 supports (M-SBA, M= Al, Ti or Zr) were prepared by chemical grafting using dry ethanol as solvent in all cases and AlCl₃, Ti(i-PrO)₄ and Zr(n-PrO)₄ as M sources. W was incorporated to the supports by impregnation of methanol solutions of Keggin-type H₃PW₁₂O₄₀. Nickel nitrate was used as promoter source. After each impregnation, the samples were calcined for 2 h at 350°C in air. The composition of all the catalysts was 9.5 wt % of W and 2.4 wt % of Ni. A reference catalyst, NiW/Al₂O₃ (16 wt % of W and 4 wt % of Ni), was prepared and tested for comparison. The supports and catalysts were characterized by N₂ physisorption, SEM-EDX, small- and wide-angle XRD, UV-Vis DRS, ³¹P MAS-NMR, FT-IR and TPR. Catalysts' activation was carried out *ex situ* in a tubular reactor at 400 °C for 4 h in a stream of H₂S/H₂ (15 vol %). Sulfided catalysts were evaluated in HDS of dibenzothiophene, 4,6-dimethyldibenzothiophene and hydrodearomatization (HDA) of naphthalene. The catalytic activity tests were performed in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h.

Results and Discussion

It was found that modified supports and catalysts can be obtained without substantial loss of SBA-15 characteristics (small-angle XRD, N₂ physisorption). Wide-angle

XRD of the catalysts demonstrated that deposited metal oxidic species are well-dispersed in all samples, as no crystalline phases were detected. DRS spectra show a decrease in particle size of the W oxide precursors when they are supported on modified SBA compared to the pure siliceous analog. TPR characterization of promoted catalysts (Fig. 1) shows that the reduction temperature of W species decreases when supported on modified SBA, especially in the case of NiW/Zr-SBA sample, where a more homogeneous distribution of easily reducible species is evidenced by a well defined reduction profile. HRTEM studies of sulfided catalysts show that the most uniform distribution of small crystals (2 layers, 3 nm long) was obtained on NiW/Zr-SBA catalyst, confirming that a good dispersion of metal species in the oxide state of the catalyst leads to better dispersed active phases. Catalytic activity results presented below show that modifying the surface of SBA-15 with Al, Ti and Zr improves the catalysts' performance, especially in the case of NiW/Zr-SBA sample, which is in close agreement with the characterization data.

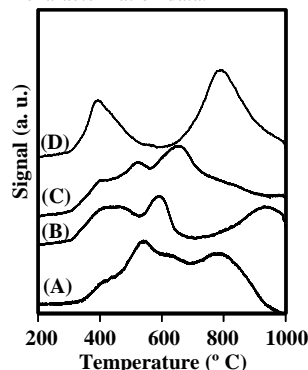


Figure 1. TPR profiles of NiW catalysts supported on A) SBA-15, B) Al-SBA, C) Ti-SBA, D) Zr-SBA.

Table 1. Catalytic activity in HDS of DBT and HDA of naphthalene

Catalyst	k ₁ (L/(s mol W))	
	DBT	Naphthalene
NiW/SBA	4.5x10 ⁻²	1.0x10 ⁻¹
NiW/Al-SBA	7.3x10 ⁻²	1.2x10 ⁻¹
NiW/Ti-SBA	8.1x10 ⁻²	1.3x10 ⁻¹
NiW/Zr-SBA	8.2x10 ⁻²	1.4x10 ⁻¹

Table 2. Catalytic activity in HDS of 4,6-DMDBT

Catalyst	k ₁ (L/(s mol W))	4,6-DMDBT conversion % at 8 h
NiW/SBA	3.6x10 ⁻²	88
NiW/Al-SBA	6.2x10 ⁻²	97
NiW/Ti-SBA	6.1x10 ⁻²	97
NiW/Zr-SBA	7.1x10 ⁻²	98
NiW/Al ₂ O ₃	1.2x10 ⁻²	67

Significance

Even though NiW-based catalysts are known for their high hydrogenation ability, a desirable feature for HDS of hindered DBTs, their use is not as widely spread within industry as NiMo or CoMo formulations because of cost factors and activation difficulties. In this work we synthesized NiW catalysts with very low W content (9.5 wt % of W), which are easy to sulfide at low temperatures, yielding highly active catalysts in HDS of 4,6-DMDBT, one of the key molecules to desulfurize for the production of ultra-clean diesel fuels.

References

- Lizama, L., Amezcua J.C., Reséndiz R., Guzmán S., Fuentes G.A. and Klimova, T. *Stud. Surf. Sci. Catal.* 165, 799 (2007).
- Lizama, L. and Klimova, T. *Appl. Catal. B: Environmental* 82, 139 (2008).
- Zhao, D., Huo, Q., Feng, J., Chmelka, B.F., and Stucky, G.D. *J. Am. Chem. Soc.* 120, 6024 (1998).