

DBT HDS Over Mo-P on Wide-pore Al₂O₃. Ni Addition Method Effect.

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Introduction

Hydroprocessing of oil-derived residual streams comprises operations aimed to obtain valuable products from heavy feedstocks with high content of S, N, aromatics and metals (mainly Ni and V). Wide-pore carriers are highly desirable because they contribute to mitigate diffusional limitations that could appear due to the very large molecular size of the hydrocarbon molecules present in those residual oils [1]. Sulfided Mo-based supported catalysts are commonly employed in those schemes [2]. Thus, the efficient integration of promoters (Ni or Mo) results a major issue in the development of improved formulations. Chelating ligands have been used [3] to enhance the promoting degree in sulfided materials. In the present work, a study on the effect of various methods of nickel integration on the hydrodesulfurization (HDS) activity of NiMo-based sulfided catalysts prepared with and without chelating agent was addressed. Wide-pore (~10-60 nm) Al₂O₃ prepared by hydrothermal method was used as carrier.

Materials and Methods

The wide-pore Al₂O₃ support (calcined at 550 °C) was synthesized under hydrothermal conditions (140 °C) utilizing Al(NO₃)₃•9H₂O, CTAB as surfactant (CTAB/Al³⁺=0.02) and NH₄OH (pH=8). The Ni-Mo-P impregnated precursors (2.8 Mo atoms/nm², Ni/(Ni+Mo)=0.3 and P₂O₅/(NiO+MoO₃)=0.2) were obtained by successive impregnation (Mo and P first) at incipient wetness. After depositing Mo+P, ((NH₄)₆Mo₇O₂₄•4H₂O+H₃PO₄) the samples (M) were calcined at 400 °C. In a highly-basic solution (Ni(NO₃)₂•6H₂O+NH₄OH), EDTA (equimolar to Ni²⁺) was added as complexing agent (E-NM). Impregnated dried materials were sulfided at 400 °C through contacting with an H₂S/H₂ mixture (1 h). Catalysts were tested in the dibenzothiophene (DBT) HDS (at 320 °C, 1028 psi, *n*-hexadecane as solvent) in a slurry batch reactor. A NiMo material prepared without EDTA (NM) was used as reference during characterization and catalytic test. Materials were studied by N₂ physisorption, XRD, thermal analysis, ²⁷Al NMR, FTIR, UV-vis and Raman. Sulfided catalysts were studied by Raman and X-ray photoelectronic spectroscopies.

Results and Discussion

The calcined γ -Al₂O₃ support (S_g=189 m²/g, V_p=0.77cm³/g) showed a wide distribution of large pores (Fig. 1). This characteristic, mainly dictated by the hydrothermal treatment practiced [1], contributed to their suitability as carrier of catalyst to be applied in hydroprocessing bulky hetero-molecules [1]. By Raman spectroscopy, octahedral polyoxomolybdates (bands at 940-960cm⁻¹ corresponding to Mo=O stretching vibrations of dioxo groups) were identified on both dried and air-calcined impregnated precursors. On the other hand, for impregnated samples annealed under inert atmosphere also bands characteristics of deposited carbon (1350 and 1580 cm⁻¹) and MoO₃ were registered. In the DBT HDS, the best catalysts were those where the complexing effect of EDTA was absent (Fig. 2), either because

the organic was not present during Ni impregnation (NM) or due to the air-annealing of the impregnated precursor with organic chelator (E-NMc). The promotion observed (expressed as k_{NM}/k_M) in those cases was very high (~30) suggesting that nickel was well-integrated to form the “NiMoS” phase after sulfiding. In the opposite to that commonly claimed [3], Ni complexation by EDTA (sample E-NM) did not result in improved HDS catalyst. This could be due to the successive impregnation used. In our case, Mo was deposited from heptamolybdate solution at acidic pH (by addition of H₃PO₄ as phosphorous source) whereas in other reported works one-pot (MoO₃+EDTA-Ni) impregnation under strongly basic media (conc. NH₄OH) was practiced [4]. It appeared that simultaneous impregnation is required to obtain improved promotion by EDTA addition. In fact, other authors [4] that carried out successive CoMo impregnation (Mo first) over alumina found just a modest enhancement on the HDS activity (in heavy gas oil desulfurization) of the corresponding catalysts, by Co-complexation with EDTA.

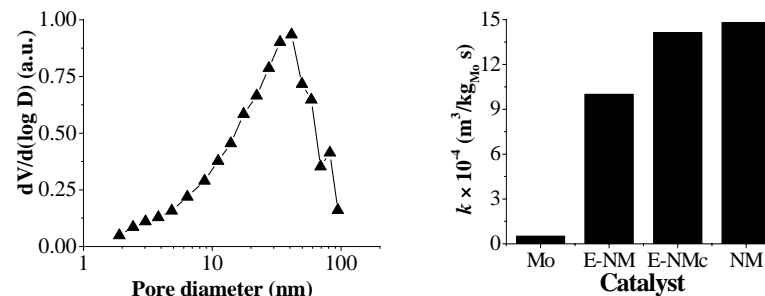


Figure 1. Pores size distribution of the Al₂O₃ support used (T_c= 550 °C).

Figure 2. Pseudo first order kinetic constant (DBT HDS) of various NiMo/Al₂O₃ catalysts prepared with or without EDTA.

Detailed physicochemical characterization by the aforementioned techniques was tried to explain the activity trends observed. Those results will be further presented and discussed.

Significance

Improved catalyst for hydroprocessing heavy oil-derived residua are necessary considering that the proportion of heavy crudes to be refined will progressively increase. Valuable streams will have to be obtained by upgrading that kind of low-ranked raw materials.

References

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