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ALUMINA MODIFIED WITH Co, Ni AND B AS A SUPPORT OF
HYDRODESULFURIZATION CATALYSTS PREPARED FROM ANDERSON
HETEROPOLYMOXYBDATES

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Fulfilling of the environmental restriction imposed on sulfur content in liquid fuels requires highly active catalysts for hydrodesulfurization (HDS) processes. Recent catalysts of the HDS consist of CoMo and NiMo phase supported on γ -Al₂O₃ support. The aim of this work was to modify the support with Co, Ni, and B and to deposit high loadings of Anderson type heteropolyoxomolybdates such as (NH₄)₃[Co(OH)₆Mo₆O₁₈]·7H₂O and (NH₄)₃[Ni(OH)₆Mo₆O₁₈]·7H₂O. The γ -Al₂O₃ (specific surface area 200 m² g⁻¹ [1]) was impregnated with aqueous solution of Co(NO₃)₂, Ni(NO₃)₂, or H₃BO₃ prior to deposition of the heteropolyoxomolybdates. After each impregnation step, the samples were dried at 105 °C for 4 h and calcined at 350 °C for 2 h. Surface area (S_{ext}), pore size distribution, and sulfide phase dispersion of the catalysts were determined by N₂ physisorption and O₂ chemisorption, respectively. Samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, infrared and UV-Vis spectrometry, and temperature programmed reduction. The activity in HDS of 1-benzothiophene was measured in tubular continuous flow micro-reactor with fixed bed of catalyst at 360 °C and 1.6 MPa after in-situ sulfidation at 400 °C with H₂S/H₂ mixture. It was acquired that preliminary incorporation of 1.3 wt % Co into the support increased sharply the HDS activity of the CoMo catalysts exhibiting the optimal molar Co/Mo ratio equal to 0.27. IR and UV-Vis DR data revealed the partial decomposition of the initial Anderson type CoMo complex with a formation of new surface compounds, including heteropolyoxomolybdates, separated polymeric oxomolybdenum compounds and Co-oxide particles. Preliminary introduction of cobalt stabilized the heteropolyanion on the surface and promoted formation of a higher concentration of the active CoMo complex. Nickel-modified alumina increased the HDS activity and dispersion of the NiMo phase almost two times in comparison to cobalt-, boron- and unmodified-alumina. IR results confirmed stability of the heteropolyoxomolybdate structure in the calcined catalysts. Mixture of initial and aluminum heteropolyoxomolybdates were present in the catalysts. The authors highly acknowledge the Bulgarian and Czech Academies for Support of Scientific Cooperation. The financial support of Czech Science Foundation (grant no. P106/11/0902) is greatly appreciated and acknowledged.

References:

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