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2014

Dostupný z <http://www.nusl.cz/ntk/nusl-175001>

Dílo je chráněno podle autorského zákona č. 121/2000 Sb.

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Datum stažení: 29.09.2024

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Preparation of sulfide hydrorefining CoMo catalysts by equilibrium adsorption of MoO₃ onto SiO₂-Al₂O₃ supports

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Catalysts with various MoO₃ contents were prepared by reaction of acidic SiO₂-Al₂O₃ supports containing 12–52 wt.% of Al₂O₃ with aqueous slurry of MoO₃. An amorphous silica-alumina with Al₂O₃ content equal to 52 wt. % (Al52) was synthesized by cogelification from aqueous solutions of sodium metasilicate and aluminium nitrate. The Al52 was then modified with nitric acid to decrease the Al₂O₃ content to 12-33 wt. % (samples Al33, Al24, Al22, Al19, Al12). The prepared supports Al52, Al33, Al19 and the pure SiO₂ were allowed to react with aqueous slurry of MoO₃ at 95 °C for 8 h. The unreacted MoO₃ slurry was removed from the support by decantation. The samples were dried and analyzed for actual MoO₃ content. A good linear correlation was found between the saturated adsorption loading of MoO₃ and Al₂O₃ content in the SiO₂-Al₂O₃ supports. The supports Al24, Al22, Al12 were then allowed to react with the MoO₃ amount deducted from the correlation. In this series, all MoO₃ was adsorbed and the samples were dried. The catalysts were sulfided in the mixture of hydrogen and hydrogen sulfide at 400 °C. The sulfided catalysts were impregnated from methanolic solution of cobalt acetylacetonate to achieve molar ratio Co/(Co+Mo) = 0.3 and resulfided. The selected supports and catalysts were characterized by ICP/AAS, XRD, N₂ physisorption and O₂ chemisorption. In fixed-bed flow microreactors, the acidity of the support and the CoMo catalysts were determined by cyclohexene isomerization (240 °C, 0.5 MPa of H₂) and cumene cracking (400 °C, 0.5 MPa of H₂) and the activity of Mo and CoMo catalysts were determined by 1-benzothiophene (BT) HDS at 360 °C and 1.6 MPa of H₂.

It has been concluded that equilibrium adsorption of MoO₃ is a suitable method for the deposition of the compound onto the acidic SiO₂-Al₂O₃ supports. X-ray diffraction and Raman measurements did not show MoO₃ crystalline phase in the catalysts. Only low intensity and quite broad signal at about 960 cm⁻¹ was found in the Raman spectra. This band is mostly ascribed to the interaction species of polymolybdates with the support. This proves that the deposited species were well dispersed over the support surface as monolayers. The promotion effect of Co on the HDS activity of Mo catalysts was expressed as a ratio of the activity of CoMo catalyst and the activity of Mo catalyst and it possessed values 3.3-7.4 with a pronounced maximum at Al₂O₃ content in SiO₂-Al₂O₃ of about 17 wt.%. The SiO₂-Al₂O₃ modified by acid leaching is a promising support for the sulfidic CoMo phase to achieve high HDS activities. The acidic properties of the modified SiO₂-Al₂O₃ supports in terms of cyclohexene isomerization and cumene cracking were preserved after deposition of the sulfidic CoMo phase. The main factor influencing these properties was found to be the Al₂O₃ content.

The authors gratefully acknowledge the financial support of the Czech Science Foundation (grant no. P106/11/0902).

Literature

L. Kaluža, D. Gulková, Z. Vít, M. Zdražil, Fuel 112, 272-276 (2013).

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