Preparation of Sulfide Hydrorefining CoMo Catalysts by Equilibrium Adsorption of MoO3 onto SiO2-Al2O3 Supports

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Preparation of sulfide hydrorefining CoMo catalysts by equilibrium adsorption of MoO_3 onto SiO_2-Al_2O_3 supports

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Catalysts with various MoO_3 contents were prepared by reaction of acidic SiO_2–Al_2O_3 supports containing 12–52 wt.% of Al_2O_3 with aqueous slurry of MoO_3. An amorphous silica-alumina with Al_2O_3 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 Al_2O_3 content to 12-33 wt. % (samples Al33, Al24, Al22, Al19, Al12). The prepared supports Al52, Al33, Al19 and the pure SiO_2 were allowed to react with aqueous slurry of MoO_3 at 95 °C for 8 h. The unreacted MoO_3 slurry was removed from the support by decantation. The samples were dried and analyzed for actual MoO_3 content. A good linear correlation was found between the saturated adsorption loading of MoO_3 and Al_2O_3 content in the SiO_2–Al_2O_3 supports. The supports Al24, Al22, Al12 were then allowed to react with the MoO_3 amount deducted from the correlation. In this series, all MoO_3 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, N_2 physisorption and O_2 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 H_2) and cumene cracking (400 °C, 0.5 MPa of H_2) and the activity of Mo and CoMo catalysts were determined by 1-benzothiophene (BT) HDS at 360 °C and 1.6 MPa of H_2.

It has been concluded that equilibrium adsorption of MoO_3 is a suitable method for the deposition of the compound onto the acidic SiO_2–Al_2O_3 supports. X-ray diffraction and Raman measurements did not show MoO_3 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 Al_2O_3 content in SiO_2–Al_2O_3 of about 17 wt.%. The SiO_2–Al_2O_3 modified by acid leaching is a promising support for the sulfidic CoMo phase to achieve high HDS activities. The acidic properties of the modified SiO_2–Al_2O_3 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 Al_2O_3 content.

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Literature

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