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DEPOSITION OF Mo AND Co SULFIDES ON UNCONVENTIONAL SILICA-ALUMINA SUPPORTS FOR MODEL HYDROTREATING REACTIONS.

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More stringent environmental regulations contributes to maintain a high interest in the development of more effective hydrotreating catalysts. New supports are therefore investigated as an alternative to conventionally used gamma-Al_2O_3 to achieve more efficient catalysts or catalysts with new function. Among them, the silica-alumina possesses interesting features due to its acidity.

We have investigated amorphous silica-alumina with Al_2O_3 content equal to 52 wt.% (SA52), which was synthesized by cogelification from aqueous solutions of sodium metasilicate and aluminium nitrate[1]. The SA52 was then modified with nitric acid to decrease the Al_2O_3 content to 30 and 19 wt.% (MSA30, MSA19). The prepared supports and the pure SiO_2 were allowed to react with aqueous slurry of MoO_3 at 95°C for 8 h. The unreacted slurry was removed from the support and the sample was sulfided in the mixture of hydrogen and hydrogen sulfide at 400°C. Parts of 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 was found that MoO_3 does not adsorb onto pure SiO_2 despite its relatively high surface area (400 m^2/g). In contrast, SA52, MSA30, and MSA19 with surface areas 430, 580 and 600 m^2/g adsorbed about 14, 7 and 3 wt.% of MoO_3, respectively. The content of Al_2O_3 in the SA based materials thus well correlated with the adsorption loadings of MoO_3 achieved by the saturation experiments. Moreover, it was acquired that the highest dispersion and HDS activities were achieved over catalysts containing dealuminated MSA supports despite of relatively low loadings of Mo.

After Co deposition, the weight normalized activities in BT HDS increased 2.2 and 4.3 times (the samples CoMo/MSA30 and CoMo/MSA19) reflecting on effective MoS_2 promotion by Co on more acidic supports. Furthermore, those catalysts keep the high acidities of the original supports, as it was determined by cyclohexene isomerization and cumene cracking, while industrial reference CoMo catalysts supported onto gamma-Al_2O_3 was found to exhibit low acidity.

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References:

[1] Vít, Z., Šolcová, O. Micropor. Mesopor. Mater. **2006**, 96, 197-204.