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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-Al₂O₃ 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 Al₂O₃ content equal to 52 wt.% (SA52), which was synthesized by cogelification from aqueous solutions of sodium metasilicate and aluminium nitrate¹. The SA52 was then modified with nitric acid to decrease the Al₂O₃ content to 30 and 19 wt.% (MSA30, MSA19). The prepared supports and the pure SiO₂ were allowed to react with aqueous slurry of MoO₃ 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, 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 was found that MoO₃ does not adsorb onto pure SiO₂ despite its relatively high surface area (400 m²/g). In contrast, SA52, MSA30, and MSA19 with surface areas 430, 580 and 600 m²/g adsorbed about 14, 7 and 3 wt.% of MoO₃, respectively. The content of Al₂O₃ in the SA based materials thus well correlated with the adsorption loadings of MoO₃ 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 MoS₂ 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-Al₂O₃ was found to exhibit low acidity.

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References:

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

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