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# Hydrodesulfurization NiMo catalysts supported on Co, Ni and B modified Al<sub>2</sub>O<sub>3</sub> from Anderson heteropolymolybdates

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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 gamma-Al<sub>2</sub>O<sub>3</sub> support. The aim of this work was to modify the support with Co, Ni, and B and to deposit high loadings of Anderson type heteropolyoxomolybdate (NH<sub>4</sub>)<sub>3</sub>[Ni(OH)<sub>6</sub>Mo<sub>6</sub>O<sub>18</sub>].7H<sub>2</sub>O. The gamma-Al<sub>2</sub>O<sub>3</sub> (specific surface area 200 m<sup>2</sup>/g)<sup>1</sup> was impregnated with aqueous solution of Cobalt nitrate, nickel nitrate, or boric acid prior to deposition of the heteropolymolybdate. 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<sub>BET</sub>), pore size distribution, and sulfide phase dispersion of the catalysts were determined by N<sub>2</sub> physisorption and O<sub>2</sub> chemisorption<sup>2</sup>, 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 H<sub>2</sub>S/H<sub>2</sub> mixture. It was acquired that preliminary incorporation of Co, Ni and B into the support increased the HDS activity of the deposited NiMo phase. IR and UV-Vis DR data revealed the partial decomposition of the initial Anderson type NiMo complex with a formation of new surface compounds, including heteropolymolybdates and separated polymeric oxomolybdenum compounds. X-ray photoelectron spectroscopy showed that the degree of Mo sulfidation expressed by the ratio of Mo<sup>4+</sup>/(Mo<sup>4+</sup> + Mo<sup>6+</sup>) is the smallest for the catalysts prepared over unmodified alumina and boron-modified alumina. On the other hand, the highest degree of sulfidation was found for the catalysts supported over Co- and Ni-modified alumina. The nickel-modified alumina increased the HDS activity and dispersion of the NiMo phase the most (almost two times in comparison to cobalt-, boron- and unmodified-alumina), which was associated with the formation of the largest number of active sites. IR results confirmed stability of the heteropolymolybdate structure in the calcined catalysts. Mixture of initial and aluminum heteropolymolybdates were present in the catalysts. The authors highly acknowledge the Bulgarian and Czech Academies for Support of Scientific Cooperation. The financial support of the Czech Science Foundation (grant no. P106/11/0902) is greatly appreciated and acknowledged.

## Literature:

- [1] R. Palcheva; A. Spojakina; K. Jirátová; L. Kaluža, *Catal. Lett.* 137, 216-223 (2010).
- [2] V. Schwartz, V.T. da Silva, S.T. Oyama, *J. Mol. Catal. A* 163, 251-268 (2000).