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Kaluža, Luděk
2018

THE NOVEL PREPARATION OF HYDROTREATING CATALYSTS USING MECHANOCHEMICAL ACTIVATION OF ALUMINUM NITRATE AND NIMO COMPLEXES

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The hydrodesulfurization (HDS) process continuously faces strict regulations on sulfur content in liquid fuels on one hand and diminution of available low sulfur feedstock on the other hand. Apart from more severe process condition or major investments into plants, more efficient catalysts represent convenient way how to solve this challenge. The conventional hydrodesulfurization catalysts either γ-Al_2O_3-supported CoMo, NiMo, NiW or unsupported NiMoW sulfides are therefore comprehensively studied in the recent literature. The support is widely modified or replaced by other oxides or non-oxide materials and deposition of the active phase is thoroughly investigated. We have recently reported on novel preparation of γ-Al_2O_3 support by mechanochemical activation of aluminum nitrate hydrate and ammonium carbonate mixture in an agate mill with pestle followed by calcination.

The aim of the present work is to explore optimum preparation route of NiMo catalysts for the novel mechanochemically prepared Al_2O_3 to achieve high HDS activity. Specifically, the novelty of this report lays in comparison of deposition of two type of NiMo complexes: i) the NTA NiMo complex formed by dissolution of $(NH_4)_6Mo_7O_{24}$, $Ni(NO_3)_2$ and NTA and ii) the Anderson-type heteropolyoxymolybdate $(NH_4)_4Ni(OH)_6Mo_6O_{18}$ (HPO) complex. The conventional sequential impregnation using $(NH_4)_6Mo_7O_{24}$ (first) and $Ni(NO_3)_2$ (second) is studied as the reference method. The prepared catalysts in their sulfided forms are evaluated by temperature programed reduction (TPR), nitrogen physisorption, oxygen chemisorption, x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and their activities are determined in reaction of 1-benzothiophene HDS at 360 °C and 1.6 MPa.

The complexes of NiMo with NTA or $(NH_4)_4Ni(OH)_6Mo_6O_{18}$ were found to be feasible precursors for preparation of catalysts highly active in hydrodesulfurization reaction of 1-benzothiophene. The NTA assisted deposition resulted in the catalyst with low metal-support interaction and 1.5 higher activity than the conventionally prepared NiMo counterpart. The most promising method of NiMo catalyst preparation for the studied γ-Al_2O_3 was the deposition of $(NH_4)_4Ni(OH)_6Mo_6O_{18}$. An optimal interaction between this complex and the new alumina, manifested by the presence of MoO_4^{2-} or MoO_xS_y species, was found to be beneficial and determining factor of about 1.9 and 1.4 higher HDS activity in comparison to the conventionally prepared NiMo and reference commercial NiMo counterparts, respectively.

Acknowledgements. L.K. and D.G. appreciate and acknowledge the Czech Science Foundation (project no. 17-22490S) for financial support. Scientific Cooperation Funds of Bulgarian and Czech Academies are acknowledged. Albemarle (The Netherlands) and BASF (Germany) companies are acknowledged for providing of the reference NiMo and Mo catalysts, respectively.

Reference. Kaluža, L., Jirátová, K., Tyuliev, G. et al. Reac Kinet Mech Cat (2018). https://doi.org/10.1007/s11144-018-1436-7