Effect of Promotion Metals on Activity of Zirconia Supported Molybdenum Sulfide Catalyst in Parallel Hydrodesulfurization of 1-Benzotiophene and Hydrogenation of 1-Methyl-Cyklohex-1-ene.

Kaluža, Luděk
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EFFECT OF PROMOTION METALS ON ACTIVITY OF ZIRCONIA SUPPORTED MOLYBDENUM SULFIDE CATALYST IN PARALLEL HYDRODESULFURIZATION OF 1-BENZOTHIOPHENE AND HYDROGENATION OF 1-METHYL-CYCLOHEX-1-ENE

Luděk Kaluža and Daniela Gulková

Institute of Chemical Process Fundamentals of CAS, v. v. i.; Rozvojová 135; 165 02 Prague 6–Suchdol; Czech Republic

Promotion of hydrodesulfurization and hydrogenation activity of MoS_2 supported on unconventional support ZrO_2 (baddeleyite, S_{BET} = 108 m^2g^{-1}) by Co, Ni, Ru, Rh, Pd, Ir, and Pt was studied. The model reactions were hydrodesulfurization of 1-benzothiophene (HDS) and in selected cases also parallel hydrodesulfurization of 1-benzothiophene and hydrogenation of 1-methyl-cyclohex-1-ene (HYDO) [1]. Methods of deposition of Mo and the promoters were compared using aqueous and toluene impregnation methods. Despite the fact that the transition metal governed the ranking of the HDS activity (CoMo ≈ NiMo > PtMo ≈ RhMo > PdMo > IrMo > RuMo), the preferred way of preparation was found to be the deposition of the promoter form the solution of the metal acetylacetonate in toluene onto sulfided Mo species previously deposited onto the ZrO_2 from aqueous solution of ammonium heptamolybdate. The catalysts prepared by this preferred way were compared in 1-methyl-cyclohex-1ene hydrogenation (HYDO) that proceeded together with 1-benzothiophene HDS. It was found that HYDO reaction decreased the catalysts activity in HDS reaction by the factor 0.64-0.85 but did not change the HDS activity ranking. The ZrO_2 support eased up the temperature-programmed reduction (TPR) of sulfide Co(Ni)Mo phase but led to practically the same amount of chemisorbed O_2 as it was observed for the reference industrial Al_2O_3-supported counterparts. The Mo/ZrO_2 promoted with Ru, Rh, Pd, Ir, and Pt did not consumed so pronounced amount of H_2 during TPR in the region 100-280 °C as it is typical for Co(Ni)Mo phase. The promotional effect of the novel metal on HDS activity was lower than it is typical for Co and Ni. The activities in HYDO over all ZrO_2-supported catalysts were desirably low and about the same as those over the reference Al_2O_3-suppored catalysts. The weight normalized HDS activities of Co(Ni)Mo/ZrO_2 catalysts remained lower than that of the high surface area (S_{BET} 325 (253) m^2g^{-1}) reference Al_2O_3-supported (S_{BET} 325 (253) m^2g^{-1}) counterparts.

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Reference:

[1] Kaluža, L.; Gulková, D. Reac. Kinet. Mech. Cat. **2016**, 118, 313-324.