Activity of Transition Metal Sulfides Supported on Alumina, Titania and Zirconia in Parallel Hydrodesulfurization of 1-Benzothiophene and Hydrogenation of 1-Methyl-cyclohex

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ACTIVITY OF TRANSITION METAL SULFIDES SUPPORTED ON ALUMINA, TITANIA AND ZIRCONIA IN PARALLEL HYDRODESULFURIZATION OF 1-BENZOTHIOPHENE AND HYDROGENATION OF 1-METHYL-CYCLOHEX-1-ENE

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Sulfided conventional transition metals Co, Ni, Mo, and W and noble metals Rh, Pd, Ir, Pt, and Re deposited over conventional support gamma-Al_2O_3 ($S_{BET} = 262$ m^2g^{-1}), and unconventional supports TiO_2 (anatase, $S_{BET} = 140$ m^2g^{-1}) and ZrO_2 (baddeleyite, $S_{BET} = 108$ m^2g^{-1}) were studied in parallel hydrodesulfurization of 1-benzothiophene (HDS) and hydrogenation of 1-methyl-cyclohex-1-ene (o-HYD) at 360 °C and 1.6 MPa. 1-Methyl-cyclohex-1-ene transformation was found to lead cyclic olefins containing also ethylcyclopentene and dimethylcyclopentene isomers. All volatile isomerization products were isolated directly from diluted reaction mixture via combination of chromatographic techniques including preparative gas chromatography, and were undoubtedly assigned by NMR spectroscopy [1]. Nevertheless, during each catalytic experiment, the model compound 1-methyl-1-cyclohex-1-ene yielded from more than 90% the mixture of the following four compounds: 1-,3- and 4-methyl-cylohex-1-enes and methylcyclohexane, which were quantified. It was ascertained that the 1-methyl-cyclohex-1ene hydrogenation (o-HYD) that proceeded together with 1-benzothiophene hydrodesulfurization (HDS) did not significantly affected the HDS activity ranking of the studied transition metal sulfides supported on Al_2O_3, TiO_2 and ZrO_2 which was found before for the HDS reaction of 1-benzothiophene without 1-methyl-cyclohex-ene [2]. Mo, W, Co, and Ni sulfided catalysts exhibited relatively low activity in both HDS and o-HYD. For these sulfides, the TiO_2 and ZrO_2 support effect varied by the factor 0.4-9.3 and the o-HYD decreased the HDS activity by the factor 0.4-0.8. In contract, the supported sulfides of Rh, Re, Pd, Pt, and Ir were highly active in HDS with low TiO_2 and ZrO_2 support effect (Rh/ZrO_2 being an exception) and o-HYD influenced the HDS activity by the factor 0.6-1.6. Nevertheless, Rh, Re, and Pd sulfided species exhibited relatively low activities in o-HYD reaction while Ir and Pt species exhibited high activities in o-HYD. The reference bimetallic CoMo and NiMo Al_2O_3 supported catalysts exhibited desirable high HDS but low o-HYD activities [3].

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Al DISTRIBUTION IN TNU-9 ZEOLITE

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Zeolites are crystalline microporous aluminosilicate molecular sieves defined, ordered framework formed by corner-sharing AlO_4 and SiO_4 tetra isomorphous substitution of Al atoms in the silicon framework results in the of negatively charged AlO_4^- in the zeolite framework. This charge is balance framework cationic species which represent active sites in a number of acid redox catalytic reactions. The combination of a variety of tunable active si selectivity of the zeolite channel system and other zeolite properties results that zeolites represent the widest group of industrial heterogeneous catalysts.

Distribution of Al atoms in the zeolite framework determines its abili active sites both for reactants and guest ions. This phenomenon was demons described for FER, MOR, BEA and ZSM-5 type zeolites [1-3]. Current work the question of Al distribution within the framework of recently synthesize zeolite [4]. Methods used to solve presented problem encompasses Vis-NIR, NMR spectroscopy as well as introduction of probe molecules into the zeolite The composition of materials was analyzed using XRF. Samples of TN prepared according to earlier described methods [4]. Post synthesis mater calcined in air and converted into sodium, ammonium or cobalt balanced form

Analysis of prepared samples resulted in ruling out the presence of Al Al sequences reflected in the ^{29}Si MAS NMR signal. Two main Al arrangeme framework thus represents: (i) single Al atoms not able to stabilize Co^{2+} complexes and (ii) Al pairs of Al-O-$(SiO)_2$-Al-O sequences located in one 6 ring, able to accommodate bare Co^{2+} ions. Three types of Al pairs were ident TNU-9 and their position in the channel system was discussed.

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