

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-Al₂O₃ (S_{HT} = 262 m²g⁻¹), and unconventional supports TiO₂ (anatase, S_{HT} = 140 m²g⁻¹) and ZrO₂ (baddeleyite, S_{HT} = 108 m²g⁻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-cyclohex-1-enes and methylcyclohexane, which were quantified. It was ascertained that the 1-methyl-cyclohex-1-ene 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 Al₂O₃, TiO₂ and ZrO₂ which was found before for the HDS reaction of 1-benzothiophene without 1-methyl-cyclohex-1-ene [2]. Mo, W, Co, and Ni sulfided catalysts exhibited relatively low activity in both HDS and o-HYD. For these sulfides, the TiO₂ and ZrO₂ 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 contrast, the supported sulfides of Rh, Re, Pd, Pt, and Ir were highly active in HDS with low TiO₂ and ZrO₂ support effect (Rh/ZrO₂ 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 Al₂O₃ supported catalysts exhibited desirable high HDS but low o-HYD activities [3].

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References

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AI DISTRIBUTION IN TNU-9 ZEOLITE

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Zeolites are crystalline microporous aluminosilicate molecular sieves defined, ordered framework formed by corner-sharing AlO₄ and SiO₄ tetrahedra of negatively charged AlO₄⁻ in the zeolite framework. This charge is balanced by redox catalytic species which represent active sites in a number of acid catalytic reactions. The combination of a variety of tunable active sites that zeolites represent the widest group of industrial heterogeneous catalysts.

Distribution of Al atoms in the zeolite framework determines its abundant active sites both for reactants and guest ions. This phenomenon was demonstrated for FER, MOR, BEA and ZSM-5 type zeolites [1-3]. Current work addresses the question of Al distribution within the framework of recently synthesized zeolite [4]. Methods used to solve presented problem encompasses Vis-NIR, ²⁹Si NMR spectroscopy as well as introduction of probe molecules into the zeolite framework. The composition of materials was analyzed using XRF. Samples of TNU prepared according to earlier described methods [4]. Post synthesis milled catalysts in air and converted into sodium, ammonium or cobalt balanced forms.

Analysis of prepared samples resulted in ruling out the presence of Al sequences reflected in the ²⁹Si MAS NMR signal. Two main Al arrangements in the framework thus represents: (i) single Al atoms not able to stabilize Co²⁺ ions in the ring, able to accommodate bare Co²⁺ ions. Three types of Al pairs were identified in TNU-9 and their position in the channel system was discussed.

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