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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**

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2014

Dostupný z <http://www.nusl.cz/ntk/nusl-177569>

Dílo je chráněno podle autorského zákona č. 121/2000 Sb.

Tento dokument byl stažen z Národního úložiště šedé literatury (NUŠL).

Datum stažení: 29.09.2024

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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<sub>2</sub>O<sub>3</sub> (S<sub>HT</sub> = 262 m<sup>2</sup>g<sup>-1</sup>), and unconventional supports TiO<sub>2</sub> (anatase, S<sub>HT</sub> = 140 m<sup>2</sup>g<sup>-1</sup>) and ZrO<sub>2</sub> (baddeleyite, S<sub>HT</sub> = 108 m<sup>2</sup>g<sup>-1</sup>) 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 Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> 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 TiO<sub>2</sub> and ZrO<sub>2</sub> 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 TiO<sub>2</sub> and ZrO<sub>2</sub> support effect (Rh/ZrO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub> supported catalysts exhibited desirable high HDS but low o-HYD activities [3].

Acknowledgement. The author gratefully appreciates and acknowledges the financial support of the Czech Science Foundation (grant No. P106/11/0902).

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 AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra of negatively charged AlO<sub>4</sub><sup>-</sup> in the zeolite framework. This charge is balanced by redox catalytic reactions. The combination of a variety of tunable active sites and selectivity of the zeolite channel system and other zeolite properties result 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, 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 muller calcined 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 <sup>29</sup>Si MAS NMR signal. Two main Al arrangements in the framework thus represents: (i) single Al atoms not able to stabilize Co<sup>2+</sup> ions in the ring, able to accommodate bare Co<sup>2+</sup> ions. Three types of Al pairs were identified in TNU-9 and their position in the channel system was discussed.

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