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## **Preparation of Hydrodesulfurization Magnesia Supported Cobalt-Molybdenum Catalysts**

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2014

Dostupný z <http://www.nusl.cz/ntk/nusl-177571>

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

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

Datum stažení: 19.07.2024

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PREPARATION OF HYDRODESULFURIZATION MAGNESIA SUPPORTED  
COBALT-MOLYBDENUM CATALYSTS

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Hydrodesulfurization (HDS) reactions are conventionally proceeded over gamma-Al<sub>2</sub>O<sub>3</sub> supported CoMo, NiMo or NiW sulfides. Alternative supports are intensively studied to increase activity in HDS to meet increasingly stringent regulation on sulfur level in fuels. Particularly, MgO support exhibits higher basicity in comparison to gamma-Al<sub>2</sub>O<sub>3</sub>, which results in high dispersion and activity of deposited MoS<sub>2</sub>, high synergy in CoMo phase and high resistance to coking. These advantages are still insufficiently utilized mainly because of the difficulties with the deposition of CoMo active phase onto hydrothermally little stable surface of MgO. However, we have reported on reaction of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>7</sub> or MoO<sub>3</sub> with the high surface area MgO in methanol slurry which resulted in well-defined saturated Mo monolayer and high activity in HDS of 1-benzothiophene. In the second step, Co was deposited over MoO<sub>3</sub>/MgO catalyst from the solution of Co(NO<sub>3</sub>)<sub>2</sub> in methanol by impregnation, which resulted in high synergic effect of Co and about 2-fold increase in activity in benzothiophene HDS than it was observed for conventional gamma-Al<sub>2</sub>O<sub>3</sub> support. The aim of the present work was to elucidate the possibility of deposition of molybdenyl- and cobalt-acetylacetonates on the high surface area MgO by impregnation from solutions of these compounds in methanol. Furthermore, non-aqueous solutions of MoO<sub>3</sub> and CoCO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>MoO<sub>7</sub> and Co(NO<sub>3</sub>)<sub>2</sub>, MoO<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> and Co(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> with chelating agent, nitriooracetic acid (NTA) were studied for CoMo deposition in one impregnation step. It was found that the highly dispersed and x-ray amorphous loadings of Mo linearly corresponded to specific surface area of the MgOs studied (about 330 m<sup>2</sup> g<sup>-1</sup> and 500 m<sup>2</sup> g<sup>-1</sup>) and HDS activities. TPR measurement revealed that high Mo content in the Mo/MgO catalyst led to a decrease in the temperature of sulfides reduction and decrease in hydrogen consumption. The decrease of the reduction temperature is well related to the increase in the catalytic activity. In contrast, the decrease in hydrogen consumption indicated a decrease of sulfur edge sites, which may be in agreement with the high loadings of Mo but it is contradicted to the high HDS activities observed. Neither the hydrogen consumption nor the O<sub>2</sub> uptake, as a measure of the sulfide dispersion, explained the HDS activity trends. Furthermore, the depositions of Co resulted in 13-46 fold promotion of the activity of Mo/MgO catalysts. This promotion, however, was highly sensitive to the method of Co deposition and the MgO type. The most active catalysts were prepared by i) deposition of Co onto oxidic Mo catalyst prepared from MoO<sub>3</sub>/methanol slurry or ii) deposition of Co onto presulfided Mo catalyst prepared from MoO<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>/methanol solution and iii) by co-impregnation from MoO<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>, Co(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> and NTA solution of freshly calcined and dechlorinated MgO support with surface area of about 330 m<sup>2</sup> g<sup>-1</sup>. The authors gratefully acknowledge the financial support of the Czech Science Foundation (grant no. P106/11/0902).

Reference

L. Kaluža, D. Gulková, Z. Vít, M. Zdražil, Appl. Catal. B: Environ. 162 (2015) 430-436

CONDENSATION REACTION CATALYZED BY FUNCTIONALIZED  
MCM-41

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Condensation reactions play an important role in the synthesis of fine chemicals *f. ex.* containing double bond in conjugation with carbonyl group. These reactions are usually catalyzed by homogeneous basic catalysts or by homogeneous catalyst containing metals. With increasing interest in environment this catalysts are replaced by heterogeneous catalysts - offering easy separation from reaction mixture and reuse.

Within this work, several types of functionalized MCM-41 were prepared using post-grafting method - MCM-41 was grafted by 3-propylcarboxy-, 3-propylsulfoxy-, 3-aminopropyl-, 3-(2-aminoethyl)-3-aminopropyl-, 3-glycidoxypropyl and 3-propylisocyanate groups.

Prepared functionalized MCM-41s were used as catalysts in following reactions:

1. Aldol condensation of benzaldehyde and heptanal, which gives desired product *jasminaldehyde*.
2. Acylation of syringaldehyde using acetic anhydride - desired product *syringaldehyde diacetate*.
3. Acylation reaction of ethylvanillin using acetic anhydride - desired product *ethylvanillin diacetate*.
4. Acylation of 4-dimethylaminobenzaldehyde using acetic anhydride - desired product *4-dimethylaminobenzaldehyde diacetate*.

Influence of the reactants amount, temperature, type of catalyst or solvent on the reaction course was monitored. Optimal reaction conditions were suggested.

**Acknowledgement**

Financial support from specific university research (MSMT No 20/2014).