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HDS OF 4,6-DIMETHYLDIBENZOTHIOPHENE ON SILICA-ALUMINA SUPPORTED NOBLE METAL CATALYSTS

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Removal of sulfur from petroleum fractions approaching to ppm S levels (deep HDS) is difficult due to the presence of refractory S molecules with sterically blocked S atom. 4,6-dimethyldibenzothiophene (4,6-DMDBT) is a typical example. On conventional CoMo/alumina sulfide catalysts, reaction of 4,6-DMDBT proceeds partly by direct desulfurization (DDS) and "hydrogenation route" (HYD). The latter pathway, which facilitates the transformation of 4,6-DMDBT, becomes overwhelming on the catalysts with good hydrogenation activity, such as noble metals. Combinations Pd-Pt on acidic supports are used for hydrogenation of aromatics and recently have been also studied as possible candidates for deep HDS.

Bimetallic Pd-Pt catalysts prepared from mesoporous silica-alumina with modified acidity showed recently high activities in HDS of simple molecules such as thiophene and benzothiophene [1]. The aim of the present work is to evaluate their efficiency in transformation of model feed containing 4,6-DMDBT at 300°C and 5 MPa of pressure.

The supports were silica-aluminas (9 % Al₂O₃, BET = 643 m²/g and 13 % Al₂O₃, BET = 611 m²/g). The catalysts containing around 0.5-1.0 wt. % of metals (Pt, Pd and Pd-Pt) were prepared by impregnation and co-impregnation of the supports, followed by H₂ reduction. The reaction was carried out in the gas phase in an integral flow reactor with fixed bed of catalyst. The feed contained 500 wppm of S in n-decane.

Preliminary results are discussed with relation to the composition of the active phase and support acidity. The bimetallic Pd-Pt catalysts showed higher rate of 4,6-DMDBT transformation than the monometallic ones. The contribution of DDS pathway, which is generally difficult and typical for conventional CoMo catalysts, was below 2 %. Instead of this, reactions facilitating 4,6-DMDBT transformation (isomerization, dealkylation) and hydrogenation followed by cracking were prevailing on noble metal catalysts.

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References:

[1] Vít, Z.; Kmentová, H.; Kaluža, L.; Gulková, D.; Boaro, M. *Appl. Catal. B: Environmental* **2011**, *108*, 152-160.