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SUPPORTS MICROSTRUCTURAL EFFECT IN DEPOSITION OF COBALT-MOLYBDENUM PHASE FOR HYDRODESULFURIZATION CATALYSTS

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The conventional Al_2O_3 support and unconventional carbon, ZrO_2 and TiO_2 supports of CoMo hydrodesulfurization (HDS) catalysts in the form of cylindrical extrudates were studied using inverse gas chromatography with single pellet-string column (SPSC) configuration, high pressure mercury porosimetry and nitrogen adsorption methods to assess both the transport and textural characteristics. The emphasis was focused on investigation of changes in microstructural properties of the supports after deposition of CoMo phase. The supports were impregnated by saturation from the aqueous slurry of MoO_3. In the second step, MoO_3 supported catalysts were impregnated by saturation by the aqueous slurry of $CoCO_3.Co(OH)_2$. The transport and textural parameters of all CoMo catalysts both in their dried oxide and sulfide form were compared with that of the parent supports. It was concluded that the support effect, represented in the present work by surface area *S(BET)*, saturated adsorption loading *L* and mainly the mean transport-pore radius $\langle r \rangle$, governed resultant activity of CoMo catalysts. The increasing mean transport-pore radii either of the support or of the sulfide catalyst qualitatively well correlated with the increasing activity in HDS of 1-benzothiophene in the order: $ZrO_2 \sim TiO_2 < Al_2O_3 < C$. Nevertheless, according to the both microstructural analysis and HDS activity study, the supports and catalysts could be ranked into two main groups. The first group, ZrO_2- and TiO_2-based systems, exhibited low microstructural changes in terms of textural and transport characteristics after deposition of CoMo (both in oxide and sulfide stage) onto the supports, relatively narrow mean transport-pore radii between 19-33 nm, and low HDS activities of CoMo catalysts (this holds both for weight and volume normalized activities). In contrast, the second group, Al_2O_3- and C-based systems, revealed significant changes in microstructure after deposition of the CoMo phases onto the supports, but exhibited wider mean transport-pore radii ranging from 40 to 221 nm, and more than 1.8 times higher HDS activities of CoMo catalysts than the first group. The activated carbon supported CoMo catalyst exhibited the highest HDS activity and the mean transport-pore radius despite the highest volume of micropores, which emphasized relevancy of further research.

It was concluded that the inverse gas chromatography represents valuable method of investigation into supported HDS catalysts. Up to our best knowledge, it has been firstly applied for monitoring of deposition of CoMo phase by observing distinctive stages of preparation procedure i.e. support microstructure, the microstructure of supported oxide, and the microstructure of resultant sulfide CoMo catalyst.

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Reference:

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