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Comparison by ³⁵S Radiotracer Methods of Hydrodesulfurization Behavior for Molybdenum, Cobalt-Molybdenum and Nickel-Molybdenum Catalysts Supported on γ-Alumina and High Specific Surface Area Titania

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The differences between MoS₂, CoMoS and NiMoS HDS catalysts supported on γ-

alumina and high SSA titania are investigated based on the results of [35 S]DBT HDS experiments. Previous studies of MoS₂ and CoMoS are reviewed, discussed and compared with new results for NiMoS. Introduction of Ni or Co to MoS₂/Al₂O₃ catalysts classically yields a significant increase in HDS performance. Irrespective of the promoter, an increase in S_0 , the number of labile sulfur atoms, is observed. In contrast, k_{RE} , the H₂S liberation rate constant, plotted as a function of the Ni/Mo ratio, presents a volcano profile on Ni-promoted catalysts, but k_{RE} reaches a plateau from low Co/Mo ratios on Co-promoted catalysts. The 'TiMoS' phase, which is formed *in-situ* during HDS on Mo/TiO₂ catalysts, promotes sulfur mobility and makes Mo/TiO₂ catalysts more active than

Mo/Al₂O₃ catalysts. Nevertheless, CoMo/TiO₂ catalysts are less active than CoMo/Al₂O₃ catalysts because further promotion of 'TiMoS' phase with Co might yield excessive weakening of the metal-sulfur bonds, and/or some Co atoms might be 'lost' in the TiO₂ matrix without interacting with MoS₂. In contrast, introduction of Ni to Mo/TiO₂ catalysts yields significant increases in both $k_{\rm RE}$ and S_0 . The NiMo/TiO₂ catalysts exhibit HDS performances close to those of Al₂O₃-supported catalysts. Clearly catalytic behavior over Co- and Ni-promoted catalysts is different.

Keywords: Hydrodesulfurization, Dibenzothiophene, γ -Alumina, High surface area titania, Nickel molybdenum catalyst, Radiotracer method

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