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Preparation and Characterization of Co-Mo Model Sulfide Catalysts for Hydrodesulfurization

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Development of highly active hydrodesulfurization (HDS) catalysts is one of the most urgent problems in the petroleum industry. Better characterization and understanding of the nature of HDS catalysts on the molecular scale are of great importance for the rational design of highly active HDS catalysts. Our approaches for this purpose involve the fabrication of model catalysts using metal carbonyls to overcome the difficulties caused by the heterogeneity of practical catalysts. One of our new approaches uses the synthesis of intrazeolite homogeneous Mo, Co and Co-Mo sulfide clusters with well defined structures. The local structure of intrazeolite Mo sulfide dimer clusters, Mo_2S_4, depends on the composition of the host zeolite. Thermally stabilized $Co_2Mo_2S_6$ binary sulfide clusters, which show catalytic synergies between Co and Mo for thiophene HDS, with a thiocubane type structure are formed in zeolite. The intrinsic HDS activity of Co sulfide clusters depends on the host zeolite. The hydrode-selenium reaction of selenophene, combined with an extended X-ray absorption fine structure (EXAFS) study, over Mo_2S_4 and MoS_2 clusters suggests a microscopic HDS reaction mechanism. More practical modeling of Co-Mo sulfide catalysts using a selective preparation method of CoMoS phases supported on refractory oxides is established to understand the nature of practical HDS catalysts. No effects of the support are found with the CoMoS phase supported on Al_2O_3, TiO_2 and ZrO_2, whereas the CoMoS phase supported on SiO_2 shows a higher intrinsic activity. The fraction of the CoMoS phase accessible to NO adsorption is elucidated, based on the number of the CoMoS phase in the model catalyst, suggesting a new model of the CoMoS

structure. The maximum potential HDS activity of Co(Ni)-Mo(W) catalysts is evaluated by using $Co(CO)_3NO$ as a probe molecule. Such model catalysts provide important information about the effects of the catalyst preparation and additives, the catalyst structure and the fundamental aspects of HDS catalysts such as microscopic reaction mechanisms and structure-reactivity relationship.

Keywords: Hydrodesulfurization, Model catalyst, Zeolite, Support effect, Cobalt molybdenum catalyst, Characterization

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