

Sono-Synthesis and Characterization of Nanophase Hydrodesulfurization Catalysts

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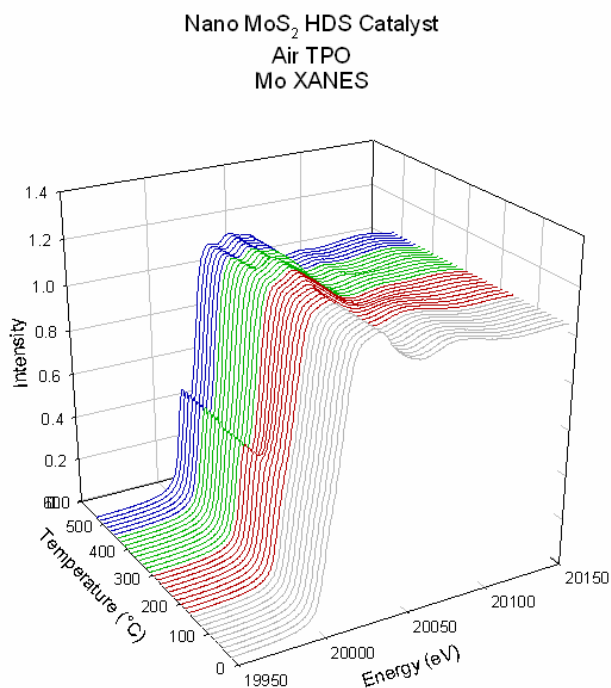
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Introduction

The generation of microporous and small-particle chalcogenides for catalytic hydrodesulfurization (HDS) of transportation fuels and heavy crude is of interest. However, currently employed commercial wet chemical synthesis techniques result in large sheets of MoS₂. A few recent reports include preparation of supported MoS₂ on alumina catalyst with a Co promoter, sonolysis of Mo(CO)₆/Co(CO)₃NO/wide-pore Al-MCM-41 in decalin to produce nano particles of Mo and Co oxides on an alumina support that was further treated to form the HDS catalyst, and sonochemical preparation of supported nano HDS catalysts, Co-Mo-S/ Al₂O₃, Ni-Mo-S/ Al₂O₃, and Co-Ni-Mo-S/ Al₂O₃. These catalysts were shown to exhibit several-fold higher HDS activity than comparable micrometer-sized commercial catalysts.

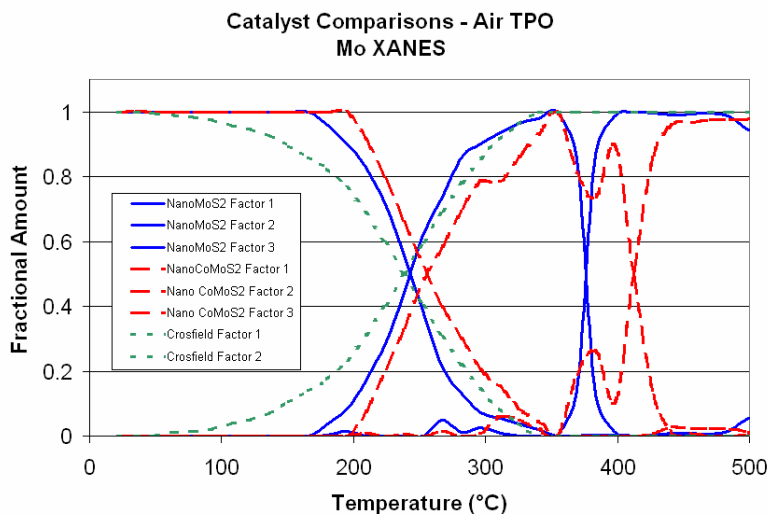
Results and Discussion

A convenient synthesis of nano-size HDS catalytic materials in several-gram quantities is the main focus of the present activity at Brookhaven National Laboratory (BNL) and Argonne National Laboratory (ANL). Several hydrocarbon solvents have been evaluated to optimize “cavitation” that is critical to produce nano Mo metal particles by decomposition of molybdenum hexacarbonyl. Further *in situ* complexation of nano Mo with elemental sulfur yields nano MoS₂. With a known ratio of Co₂(CO)₈/Mo(CO)₆, the method produces nano Co/MoS₂. Sonolysis of Mo(CO)₆ in the presence of γ -Al₂O₃ produced supported nano Mo, i.e., nano MoS₂/ γ -Al₂O₃. The yields of all three nano-sized materials are >90% based on the starting Mo(CO)₆.



The prepared samples are being characterized at the National Synchrotron Light Source (NSLS) at BNL and the Advanced Photon Source (APS) at ANL. The measurement of these materials is a challenge. Preliminary x-ray diffraction (XRD) data show that the prepared materials indeed are nano-size. Transmission electron microscopy (TEM) (with a resolution of 0.16 nm) is being used to measure the morphology and particle size of the samples.

The nano-scale materials exhibit temperature-programmed reduction (TPR) profiles that are about 75°C higher than the commercially available catalyst. Adding cobalt to the molybdenum has no effect on the temperature of the reduction but does lower the overall amount of hydrogen adsorption. The MoS₂ nanophase materials are highly reactive and susceptible to oxidation in air. Running x-ray adsorption near edge spectroscopy (XANES) at the APS in temperature-programmed oxidation (TPO) mode shows that the native material oxidizes at the relatively low temperature of 365°C. The addition of Co to the nanophase MoS₂ material (necessary for HDS catalytic activity) removes some of this oxidation instability. Principle component analysis (PCA) provides us with an estimate of the amount of a specific component at any given temperature.



Preliminary HDS runs in the presence of an olefin show that the nano-phase CoMoS₂ material does less olefin hydrogenation and hence less loss in octane than a standard commercial catalyst.

These data will be presented in this presentation.

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