

# COMPARISON OF NICKEL MOLYBDENUM HYDROUS METAL OXIDES WITH COMMERCIAL CATALYSTS FOR HDS/HDN OF COAL LIQUIDS

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## INTRODUCTION

Improved efficiency in direct coal liquefaction processes can be obtained by developing catalysts with better activity, selectivity, and life. In previous exploratory research at Sandia National Laboratories, catalysts prepared via hydrous metal oxide (HMO) ion exchangers have been shown to have potential for application to a number of reactions associated with the conversion of coal to liquid fuels.<sup>1</sup> In the present effort, one member of this class of catalysts, hydrous titanium oxide (HTO), has been used to develop catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of coal liquids.

## EXPERIMENTAL

### Synthesis

The HTO catalysts have been prepared in both a bulk form and a thin-film variation. Specifics on preparation of the HTOs are found elsewhere.<sup>2</sup> Briefly, tetra-ethyl orthosilicate and tetra-isopropyl titanate were combined in a 1:5 molar ratio with NaOH and excess methanol. The soluble intermediate resulting from this reaction was either coated onto a support or precipitated from solution with an acetone/water wash. The catalyst was acidified followed by ion-exchanging with ammonium molybdate. Nickel in a nitrate form was applied by incipient wetness.

### Batch Testing

For batch model compound screening studies, the bulk (unsupported) catalysts were pelletized, crushed to 30/40 mesh, calcined at 500°C for 1 hour, sulfided at 420°C for 2 hours in 10% H<sub>2</sub>S/H<sub>2</sub>, ground to -200 mesh, and evaluated. The supported catalysts were calcined and sulfided in the extrudate form, ground to -200 mesh, and evaluated. Batch model compound hydrogenation studies were conducted with pyrene. Pyrene (100 mg), hexadecane (1 g), and catalyst (10 mg) were loaded into a microautoclave reactor that was pressurized to 500 psig with hydrogen. Reaction conditions were 300°C for 10 minutes.

### Continuous Testing

For studies involving continuous testing, a subbituminous coal derived liquid feed was obtained from HRI's catalytic two-stage PDU. The reactor was loaded with 10 grams of catalyst mixed with 10 grams of  $\alpha$ -alumina diluent, which was placed in the center of either a 7/16" or 3/4" I.D. stainless steel tube. Approximately 2" of  $\alpha$ -alumina was placed above, and below the 30/40 mesh catalyst bed as pre-heat and post-heat zones. All catalysts were sulfided *in situ* with a 10% H<sub>2</sub>S/90% H<sub>2</sub> gas mixture at 100 scfm for 4 hours at 400°C. The coal derived liquid, fed at 0.45 cc/min, had a composition of ca. 500 ppm sulfur and 1400 ppm nitrogen. Typical experiments lasted 4 to 5 days and were run at 400°C and at either 500, 1000, or 1500 psig hydrogen. Coal liquid samples were pulled 4 to 5 times a day and analyzed for sulfur and nitrogen content using an Antek 7000 S/N analyzer. Activities are reported as percent sulfur/nitrogen removed from the feed. A few coal liquid samples were characterized by proton NMR using a technique developed by CONSOL<sup>3</sup> to evaluate hydrogen distribution. In addition, the feed was further characterized by separating the material into paraffins and aromatics over acidic alumina.

## RESULTS AND DISCUSSION

### Feed and Product Characterization

<sup>1</sup> Sandia Technical Report, SAND89-2400, Sandia National Laboratories, Albuquerque, NM (1990)

<sup>2</sup> Sandia Technical Report, SAND89-2399, Sandia National Laboratories, Albuquerque, NM (1990)

<sup>3</sup> R. A. Winschel, G.A. Robbins, F.P. Burke, *Fuel*, **65**, pp 526-532 (1986)

Proton NMR spectra for the feed were compared to proton NMR spectra for product samples from two different catalyst runs: 500 psig and 1000 psig with nickel molybdenum hydrous metal oxide (NiMoHTO) on an Amocat 1C blank. These spectra indicated that little change in hydrogen character occurred at either condition. To further quantify the feed, the non-paraffinic portion of the feed was extracted over a column of acidic alumina. The effluent oil from the alumina column was compared to the feed oil by gas chromatography and results indicated that the feed was of a highly paraffinic nature. Due to the high paraffin content of the feed, it was reasonable that minimal boiling point upgrading occurred. These experiments indicated that the coal derived oil selected was an appropriate feed material, in that the HDS/HDN reactions would not be in competition for feed hydrogen with bond saturation reactions.

#### Batch Testing - Hydrogenation (HYD) of Pyrene.

The results for the pyrene HYD experiments are shown in Figure 1. The first order HYD activities are calculated on both a catalyst weight basis and on a weight of total active metals basis, *i.e.* molybdenum and nickel. The activity of the bulk (unsupported) NiMoHTO (8.5%Mo/2.9%Ni) was higher than either Shell 324 (13%Mo/2.7%Ni) or Amocat (10.7%Mo/2.4%Ni) on either basis. When comparing the activities for the supported NiMoHTO catalysts with their commercial counterparts, the NiMoHTO catalysts had higher activities. For the NiMoHTO on the Shell support (8.8%Mo/2.9%Ni), the NiMoHTO was 12% more active on a catalyst weight basis and 81% more active on an active metals basis. The results for the NiMoHTO on the Amocat support (9.2%Mo/3.0%Ni) compared to the Amocat 1C catalyst were similar: 25% more active on a catalyst weight basis and 52% more active on a metals basis. The higher activities of the NiMoHTO catalysts as compared to the commercial catalysts, especially on an active metals basis, is due in part to the high dispersion of the MoS<sub>2</sub> on the HTO. TEM studies have indicated that the MoS<sub>2</sub> dispersion is higher on a NiMoHTO catalyst as compared to a commercial catalyst. A second explanation for the higher activity is the higher acidity of the NiMoHTO as compared to commercial catalysts supported on alumina. The catalyst acidity was measured by ammonia adsorption. In terms of moles of ammonia per gram of catalyst, the bulk NiMoHTO adsorbed 43% more ammonia than Shell 324. The higher acidity of the NiMoHTO may lead to a higher HYD activity for the HTO catalysts.

#### Flow Reactor Testing - HDS and HDN of Coal Liquids.

The HDS/HDN activity in terms of total removed sulfur and nitrogen was measured at 500, 1000, and 1500 psig for unsupported (bulk) NiMoHTO, Shell 324, Amocat 1C, and NiMoHTO catalysts supported on Shell and Amocat blanks. The bulk and supported NiMoHTO catalysts had a lower total active metals concentration than either Shell 324 or Amocat 1C. The following results are presented as a percentage sulfur or nitrogen removed at a constant reactor space velocity (SV). The SV was based on total catalyst weight and not on active metals. If the results were based on total active metals, the activity of the NiMoHTO catalysts would be higher. In general, the estimated error in the HDS and HDN activities was estimated to be  $\pm 1-2\%$ . In the interest of publication space, only the HDS results are shown in Figures 2-7.

(i) 500 psig The HDS activities of the evaluated catalysts are shown in Figures 2 and 3. At 500 psig, the bulk NiMoHTO activity (9.7%Mo/3.2%Ni) was higher than either Shell 324 or Amocat 1C. The bulk NiMoHTO catalyst had a higher activity than Amocat 1C with a lower loading of active metals. Since the NiMoHTO catalysts have a higher dispersion of MoS<sub>2</sub> than standard commercial catalysts<sup>1</sup>, it is not unexpected that HDS activities can be maintained with a lower NiMo composition. At 500 psig, the bulk NiMoHTO was significantly more active for HDS than Shell 324 (Figure 3).

The trends for the HDN activities were similar to the HDS activities. After 80 hours on-line, the HDN activity for the bulk NiMoHTO was about 21%. This was significantly higher than the 80 hour HDN activities of Shell 324, Amocat 1C, and NiMoHTO on an Amocat blank: 13%, 9%, and 15% respectively. In general at 500 psig, the bulk NiMoHTO outperformed, and the supported NiMoHTO catalysts achieved near equal performance to the commercial catalysts for HDS and HDN activities while containing less active metals.

(ii) 1000 psig The HDS activities for the bulk NiMoHTO (9.6%Mo/3.2%Ni), Amocat supported NiMoHTO (8.1%Mo/2.7%Ni) and Amocat 1C catalysts are shown in Figure 4. Line-out HDS activities were between 86% and 90% for all three catalysts with the

Amocat 1C activity being slightly higher than either of the NiMoHTO catalysts. Figure 5 shows the data for the bulk NiMoHTO, Shell 324, and Shell supported NiMoHTO (8.9%Mo/2.9%Ni) catalysts. The HDS activity of the Shell 324 was higher than either the Shell supported NiMoHTO or the bulk NiMoHTO catalysts by about 3%.

The 80 hour HDN performance for the five catalysts in Figures 4 and 5 were ranked as follows; Shell 324 (45%), bulk NiMoHTO (43%), Amocat 1C (42%), Amocat supported NiMoHTO (42%), and Shell supported NiMoHTO (39%). Given an estimated error of  $\pm 2\%$ , minimal differences were found in performance on a total catalyst weight basis, although the supported NiMoHTO catalysts contained 18% and 25% less active metals as compared to Amocat 1C and Shell 324 respectively.

(iii) 1500 psig The HDS activity for the bulk NiMoHTO (9.6%Mo/3.2%Ni), Amocat supported NiMoHTO (7.8%Mo/2.6%Ni) and Amocat 1C catalysts are shown in Figure 6. The bulk NiMoHTO and Amocat 1C catalysts performed slightly better than the Amocat supported NiMoHTO. The Shell 324, Shell supported NiMoHTO, and the bulk NiMoHTO performed similarly (Figure 7). The HDN activities for the Bulk NiMoHTO, Shell 324 and Shell supported NiMoHTO all performed similarly; about  $64 \pm 2\%$ . The results for the Amocat 1C and Amocat supported NiMoHTO were significantly less: about 55%.

### CONCLUSIONS

For HYD of pyrene, unsupported NiMoHTO catalysts performed better than commercial benchmark catalysts on either a catalyst weight or active metals basis. In a side-by-side comparison of supported NiMoHTO catalysts with commercial counterparts, the supported NiMoHTO catalysts outperformed the Shell 324 and Amocat 1C catalysts for HYD of pyrene. For HDS/HDN of coal liquids, the supported and bulk forms of the NiMoHTO catalysts equaled the performance of the commercial catalysts at 500, 1000, and 1500 psig while containing less active metals. Possible reasons for the high activity of the NiMoHTO catalysts are a high dispersion of the active  $\text{MoS}_2$  phase and a high acidity of the bulk NiMoHTO.

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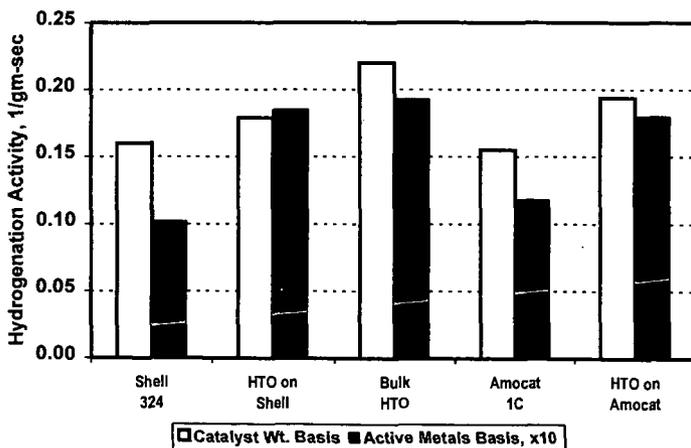


Figure 1. HYD Pyrene Activity of Commercial and Hydrous Metal Oxide Catalysts

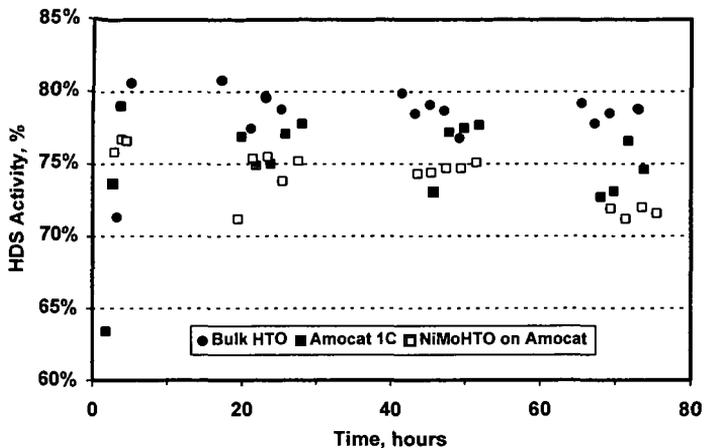


Figure 2. 500 psig HDS Activity of Benchmark and HTO Catalysts  
(note change in scale)

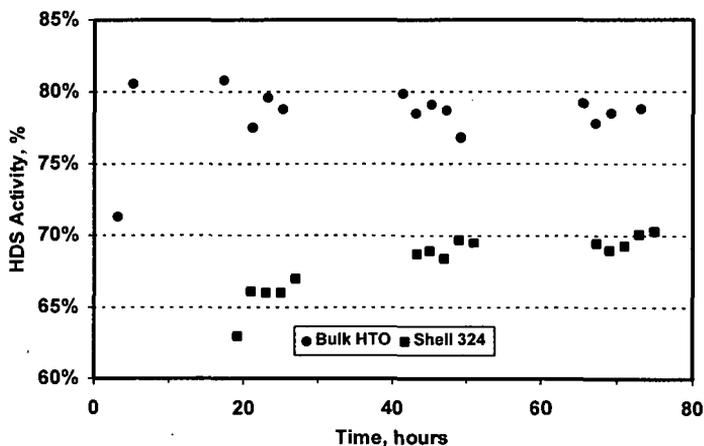


Figure 3. 500 psig HDS Activity of Benchmark and HTO Catalysts  
(note change in scale)

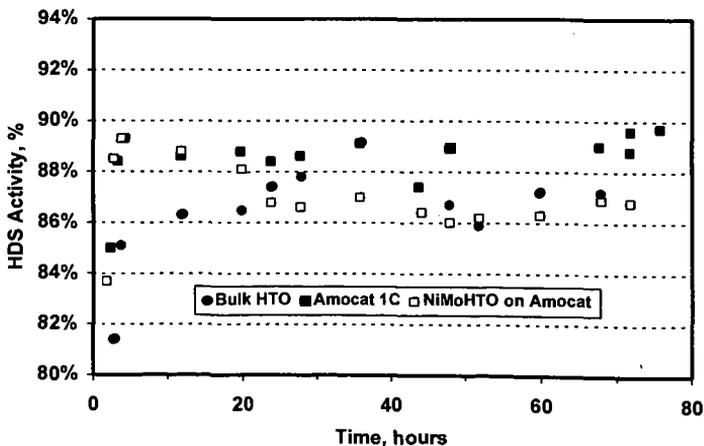


Figure 4. 1000 psig HDS Activity of Benchmark and HTO Catalysts  
(note change in scale)

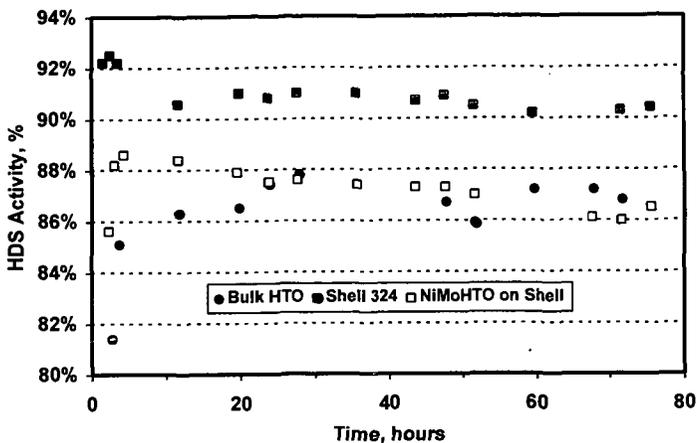


Figure 5. 1000 psig HDS Activity of Benchmark and HTO Catalysts  
(note change in scale)

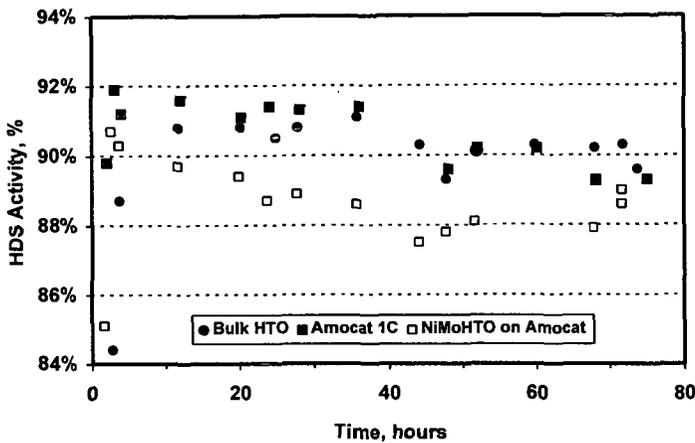


Figure 6. 1500 psig HDS Activity of Benchmark and HTO Catalysts  
(note change in scale)

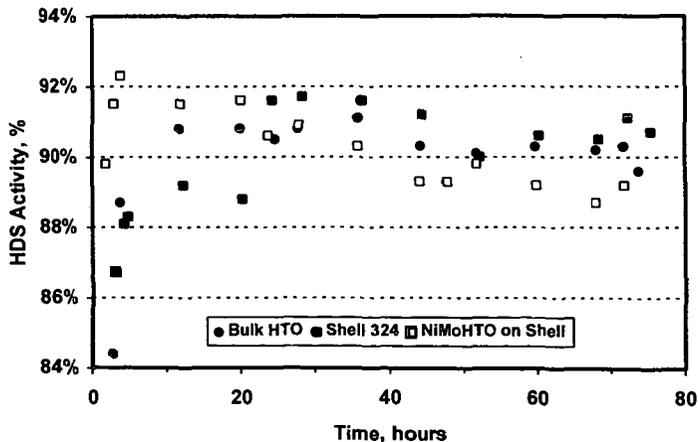


Figure 7. 1500 psig HDS Activity of Benchmark and HTO Catalysts  
(note change in scale)