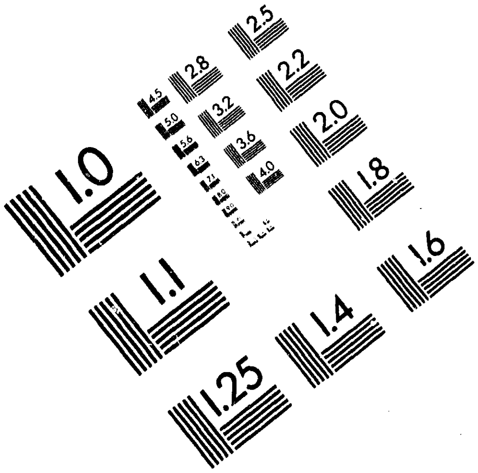

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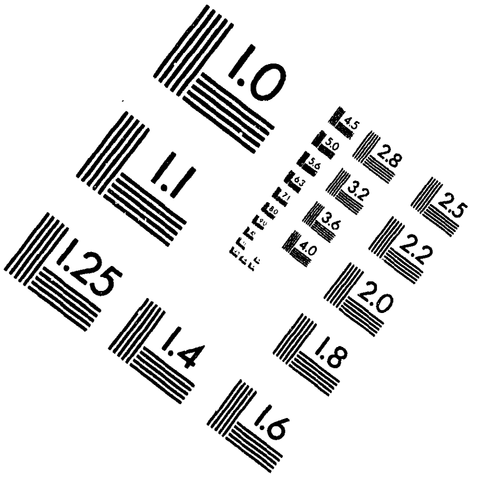

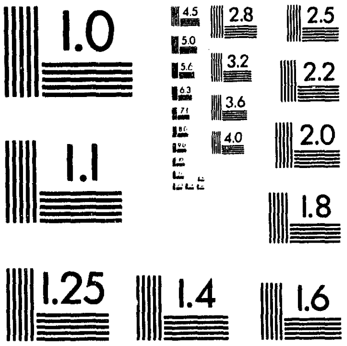

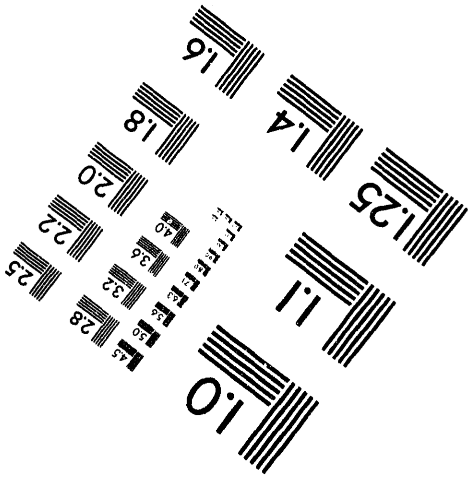

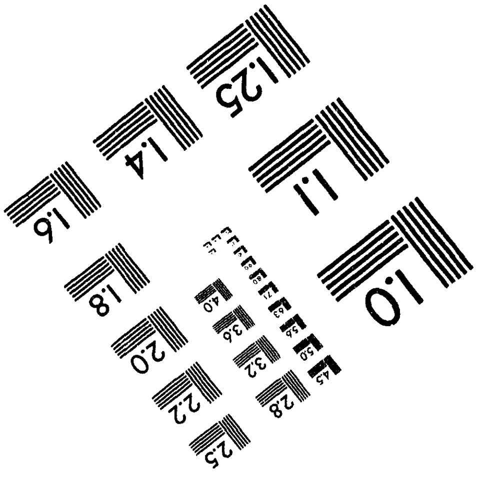

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UPGRADING OF COAL LIQUIDS BY HYDROUS METAL OXIDE CATALYSTS

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INTRODUCTION

Hydrous Metal Oxides (HMOs) are chemically synthesized materials which contain a homogeneous distribution of ion exchangeable alkali cations that provide charge compensation to the metal-oxygen framework. Both the presence of these alkali cations and the resulting high cation exchange capacities (4-5 meq/g) clearly set these HMO materials apart from conventional precipitated hydrous oxides.[1,2] For catalyst applications, the HMO material serves as an ion exchangeable support which facilitates the uniform incorporation of catalyst precursor species. Following catalyst precursor incorporation, an activation step is required to convert the catalyst precursor to the desired active phase.

Considerable process development activities at Sandia National Laboratories related to HMO materials have resulted in bulk silica-doped hydrous titanium oxide (HTO:Si)-supported NiMo catalysts that are more active in model compound reactions than commercial NiMo catalysts. These reactions, e.g. pyrene hydrogenation, simulate direct coal liquefaction. However, extension of this process to produce NiMo/HTO:Si catalyst coatings on commercial supports is of interest for liquefaction applications since overall catalyst cost can be reduced and bulk HTO:Si mechanical limitations can be circumvented. In the present effort, NiMo/HTO:Si has been evaluated for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of coal derived liquids. NiMo/HTO:Si catalysts have been evaluated in both bulk (unsupported) form and a supported form on commercial alumina extrudates.

EXPERIMENTAL

Synthesis

The NiMo/HTO:Si catalysts were prepared in both a bulk form and a thin-film variation. HMO-supported catalyst preparation involves a multiple step chemical procedure that begins with the synthesis of a bulk HMO powder or HMO coating. This chemistry, which can be utilized to produce alkali titanates, alkali zirconates, alkali niobates, or alkali tantalates, has been described in detail elsewhere.[3] 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

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[1] A. Ruvarac, Inorganic Ion Exchange Materials, A. Clearfield , ed., CRC press, Boca Raton, 1982, pp. 141-160

[2] M. Abe, Inorganic Ion Exchange Materials, A. Clearfield, ed., CRC press, Boca Raton, 1982, pp.161-273

[3] Sandia Technical Report, SAND89-2399, Sandia National Laboratories, Albuquerque, NM (1990)

catalyst was acidified followed by ion-exchanging with ammonium molybdate. Nickel in a nitrate form was applied by incipient wetness. Previous work has demonstrated that SiO_2 additions (Ti:Si molar ratio = 5:1) to HMO materials act to stabilize HMO support surface area at high temperature ($\geq$ 500°C) without significantly altering ion exchange properties.[4]

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_2S/H_2, 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 α-alumina diluent, which was placed in the center of either a 7/16" or 3/4" I.D. stainless steel tube. Approximately 2" of α-alumina was placed above, and below the 30/40 mesh catalyst bed as pre-heat and post-heat zones. All catalysts were sulfided *insitu* with a 10% H_2S/90% H_2 gas mixture at 100 sccm 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[5] 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

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 NiMo/HTO:Si 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

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[4] Sandia Technical Report, SAND89-2400, Sandia National Laboratories, Albuquerque, NM (1990)

[5] R. A. Winschel, G.A. Robbins, F.P. Burke, *Fuel*, **65**, pp 526-532 (1986)

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) NiMo/HTO:Si (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 NiMo/HTO:Si catalysts with their commercial counterparts, the NiMo/HTO:Si catalysts had higher activities. For the NiMo/HTO:Si on the Shell support (8.8%Mo/2.9%Ni), the NiMo/HTO:Si was 12% more active on a catalyst weight basis and 81% more active on an active metals basis. The results for the NiMo/HTO:Si 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 NiMo/HTO:Si catalysts as compared to the commercial catalysts, especially on an active metals basis, is due in part to the high dispersion of the MoS_2 on the HTO:Si. TEM studies have indicated that the MoS_2 dispersion is higher on a NiMo/HTO:Si catalyst as compared to a commercial catalyst. A second explanation for the higher activity is the higher acidity of the NiMo/HTO:Si 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 NiMo/HTO:Si adsorbed 43% more ammonia than Shell 324. The higher acidity of the NiMo/HTO:Si may lead to a higher HYD activity for the HTO:Si 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) NiMo/HTO:Si, Shell 324, Amocat 1C, and NiMo/HTO:Si catalysts supported on Shell and Amocat blanks. The bulk and supported NiMo/HTO:Si 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 NiMo/HTO:Si catalysts would be higher. In general, the estimated error in the HDS and HDN activities was estimated to be ±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 NiMo/HTO:Si activity (9.7%Mo/3.2%Ni) was higher than either Shell 324 or Amocat 1C. The bulk NiMo/HTO:Si catalyst had a higher activity than Amocat 1C with a lower loading of active metals. Since the NiMo/HTO:Si catalysts have a higher dispersion of MoS_2 than standard commercial catalysts[1], it is not unexpected that HDS activities can be maintained with a lower NiMo composition. At 500 psig, the bulk NiMo/HTO:Si 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 NiMo/HTO:Si was about 21%. This was significantly higher than the 80 hour HDN activities of Shell 324, Amocat 1C, and NiMo/HTO:Si on an Amocat blank: 13%, 9%, and 15% respectively. In general at 500 psig, the bulk NiMo/HTO:Si outperformed, and the supported NiMo/HTO:Si 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 NiMo/HTO:Si (9.6%Mo/3.2%Ni), Amocat supported NiMo/HTO:Si (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 NiMo/HTO:Si catalysts. Figure 5 shows the data for the bulk NiMo/HTO:Si, Shell 324, and Shell supported NiMo/HTO:Si (8.9%Mo/2.9%Ni) catalysts. The HDS activity of the Shell 324 was higher than either the Shell supported NiMo/HTO:Si or the bulk NiMo/HTO:Si 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 NiMo/HTO:Si (43%), Amocat 1C (42%), Amocat supported NiMo/HTO:Si (42%), and Shell supported NiMo/HTO:Si (39%). Given an estimated error of ±2%, minimal differences were found in performance on a total catalyst weight basis, although the supported NiMo/HTO:Si 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 NiMo/HTO:Si (9.6%Mo/3.2%Ni), Amocat supported NiMo/HTO:Si (7.8%Mo/2.6%Ni) and Amocat 1C catalysts are shown in Figure 6. The bulk NiMo/HTO:Si and Amocat 1C catalysts performed slightly better than the Amocat supported NiMo/HTO:Si. The Shell 324, Shell supported NiMo/HTO:Si, and the bulk NiMo/HTO:Si performed similarly (Figure 7). The HDN activities for the bulk NiMo/HTO:Si, Shell 324 and Shell supported NiMo/HTO:Si all performed similarly; about 64±2%. The results for the Amocat 1C and Amocat supported NiMo/HTO:Si were significantly less: about 55%.

(iv) Summary The HDS or HDN effectiveness of the five catalysts evaluated was calculated by comparing the sulfur or nitrogen removed from the feed per hour per total active metal weight loadings. Total active metals loading was defined as the total weight of molybdenum and nickel. The results of these calculations are shown in Figures 8 and 9. The relative HDS effectiveness of the NiMo/HTO:Si catalysts was higher than their commercial counterparts since the NiMo/HTO:Si catalysts maintained a similar HDS activity while incorporating lower active metal loadings. In terms of a relative HDN effectiveness, the Shell 324, NiMo/HTO:Si on Shell, and bulk NiMo/HTO:Si catalysts all had near equal activities. The Amocat 1C and the NiMo/HTO:Si supported on Amocat blank displayed lower relative activities, especially at 1500 psig. It is possible that the Amocat support is somewhat less effective for HDN, based on these data.

CONCLUSIONS

For HYD of pyrene, unsupported NiMo/HTO:Si catalysts performed better than commercial benchmark catalysts on either a catalyst weight or active metals basis. In a side-by-side comparison of supported NiMo/HTO:Si catalysts with commercial counterparts, the supported NiMo/HTO:Si catalysts outperformed the Shell 324 and Amocat 1C catalysts for HYD of pyrene. For HDS of coal liquids, the supported and bulk forms of the NiMo/HTO:Si catalysts on an active metals weight basis equaled or exceeded the performance of the commercial catalysts at 500, 1000, and 1500 psig while containing less active metals. For HDN of coal liquids, the supported and bulk forms of the NiMo/HTO:Si catalysts on an active metals basis mostly equaled the performance of the commercial catalysts at 500, 1000, and 1500 psig. Possible reasons for the high activity of the NiMo/HTO:Si catalysts are a high dispersion of the active MoS_2 phase and a high acidity of the bulk NiMo/HTO:Si.

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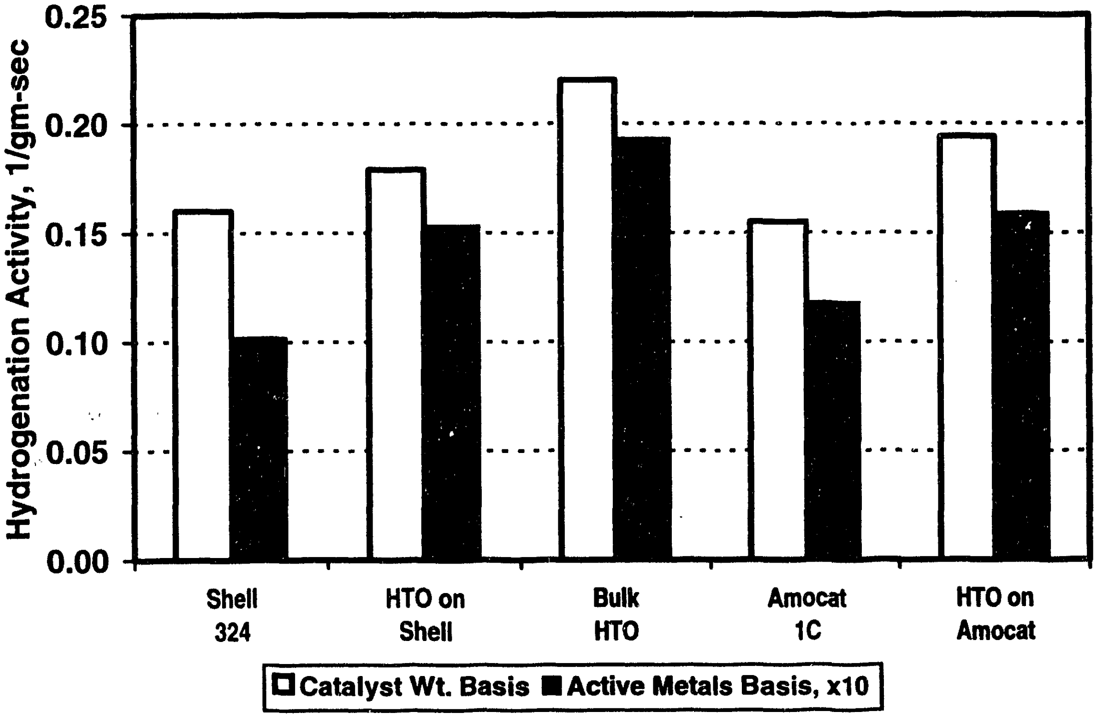

Figure 1. HYD Pyrene Activity of Commercial and NiMo/HTO:Si Catalysts

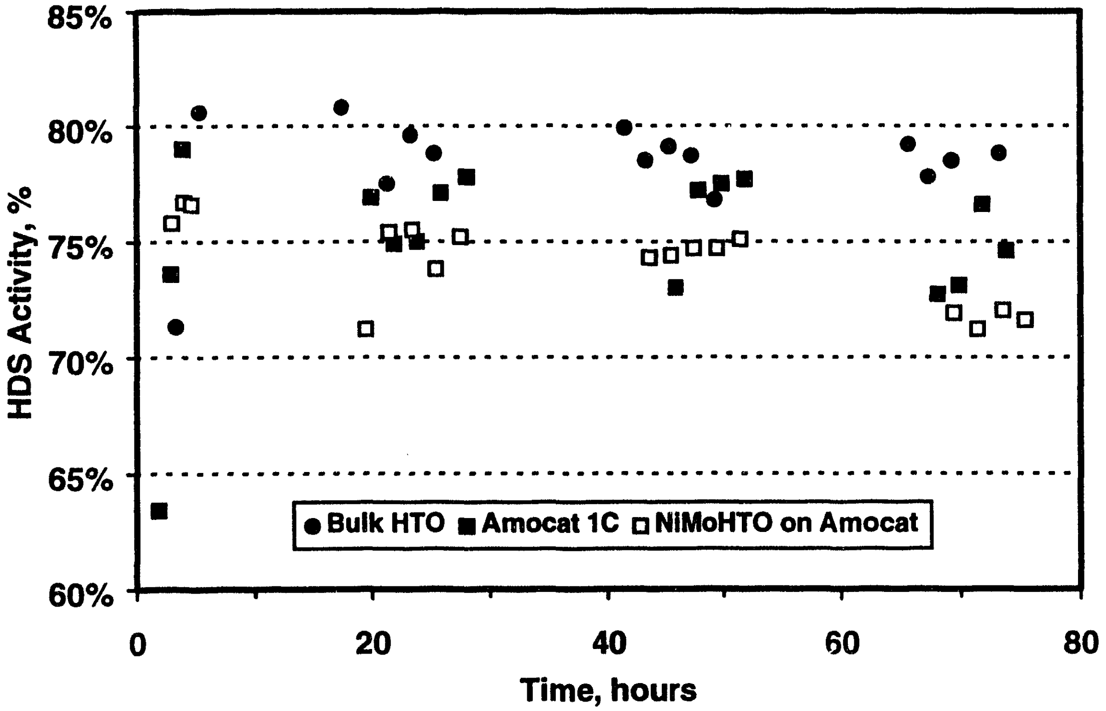

Figure 2. 500 psig HDS Activity of Benchmark and NiMo/HTO:Si Catalysts

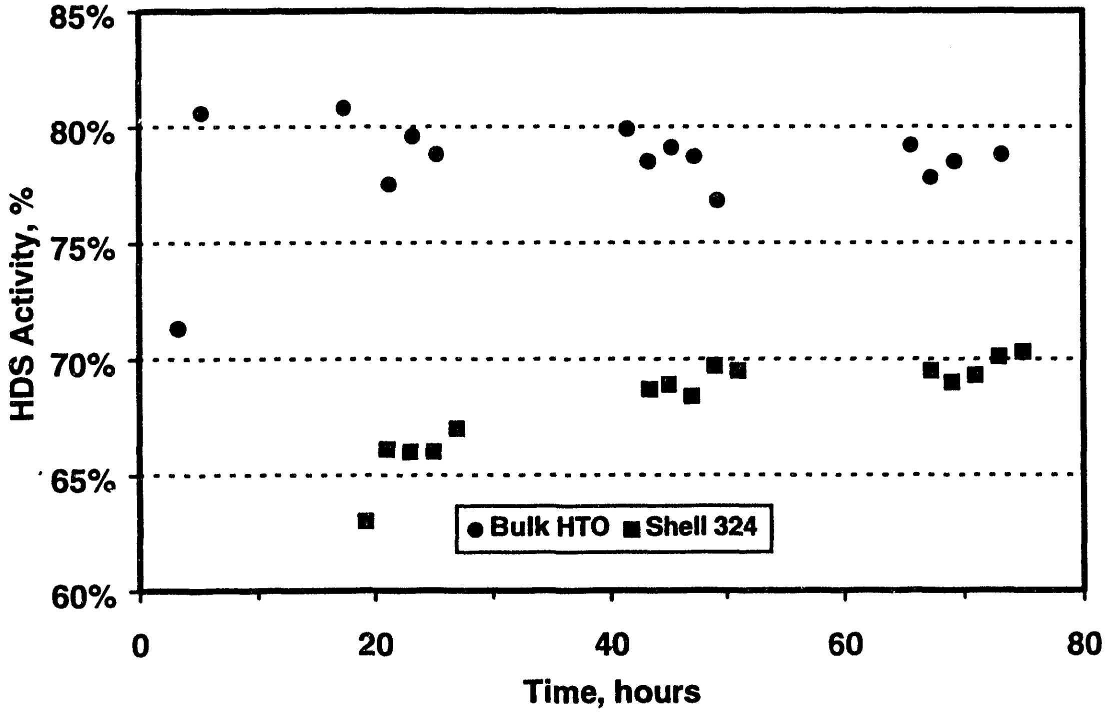

Figure 3. 500 psig HDS Activity of Benchmark and NiMo/HTO:Si Catalysts

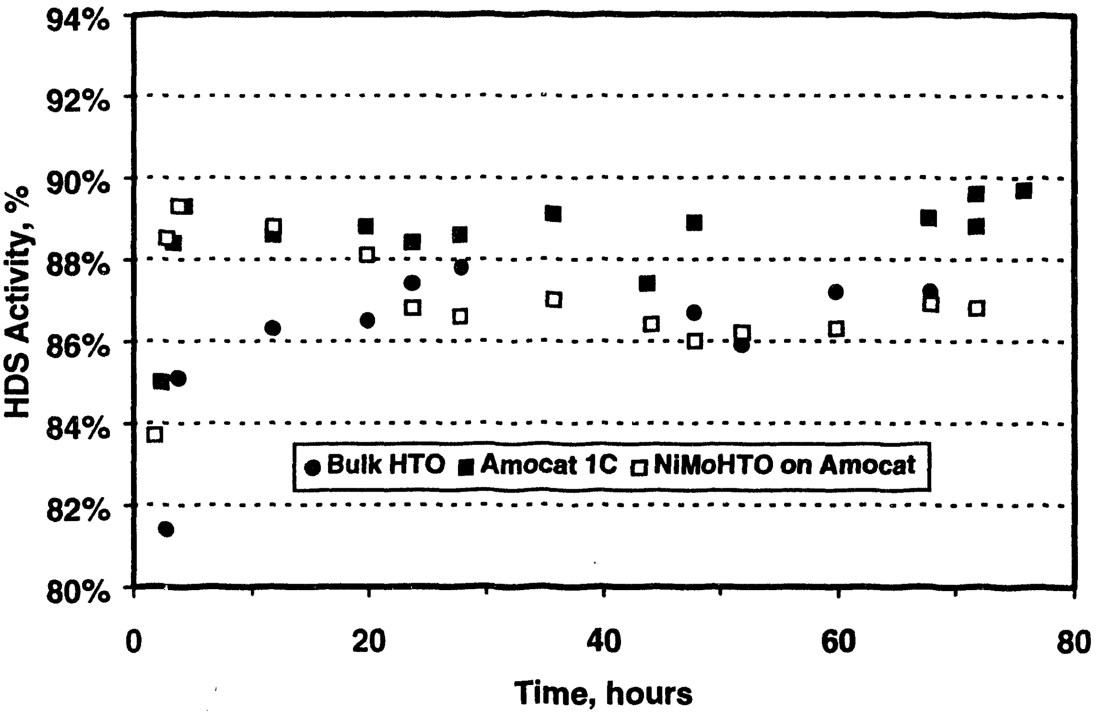

Figure 4. 1000 psig HDS Activity of Benchmark and NiMo/HTO:Si Catalysts

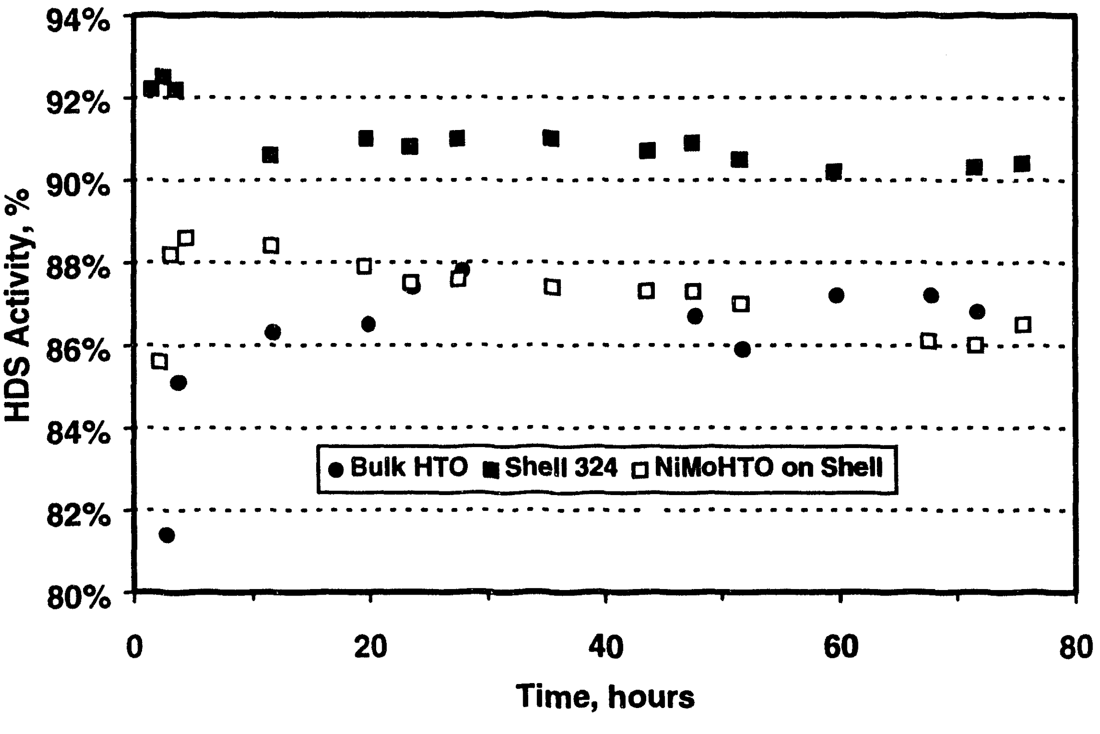

Figure 5. 1000 psig HDS Activity of Benchmark and NiMo/HTO:Si Catalysts

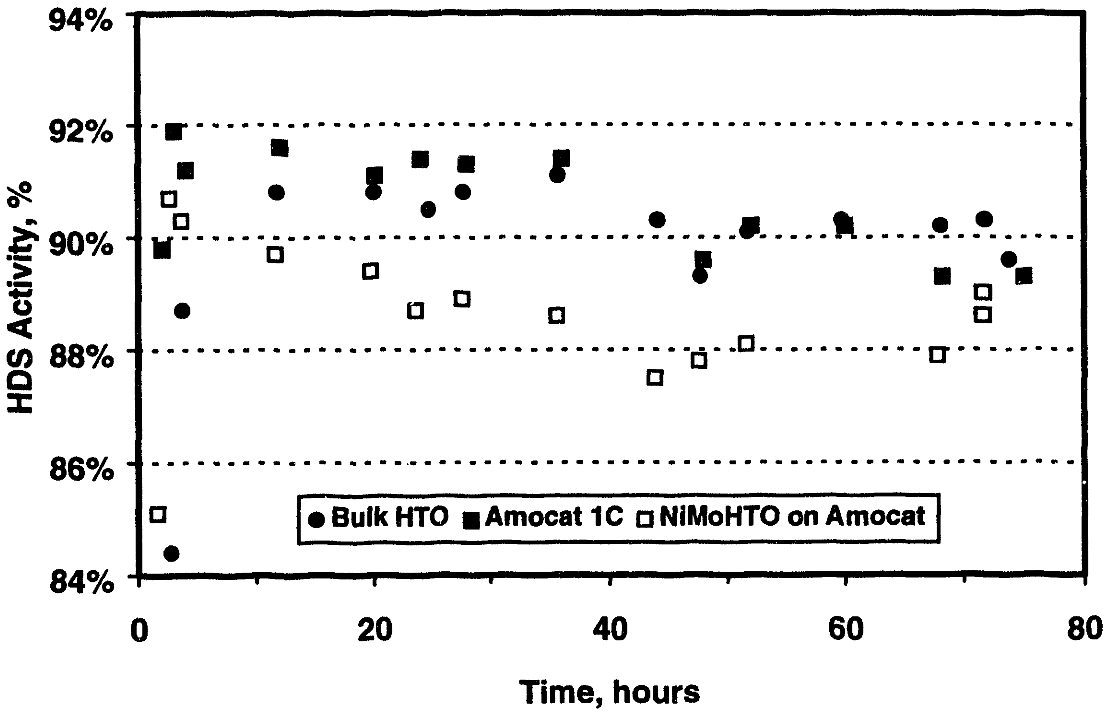

Figure 6. 1500 psig HDS Activity of Benchmark and NiMo/HTO:Si Catalysts

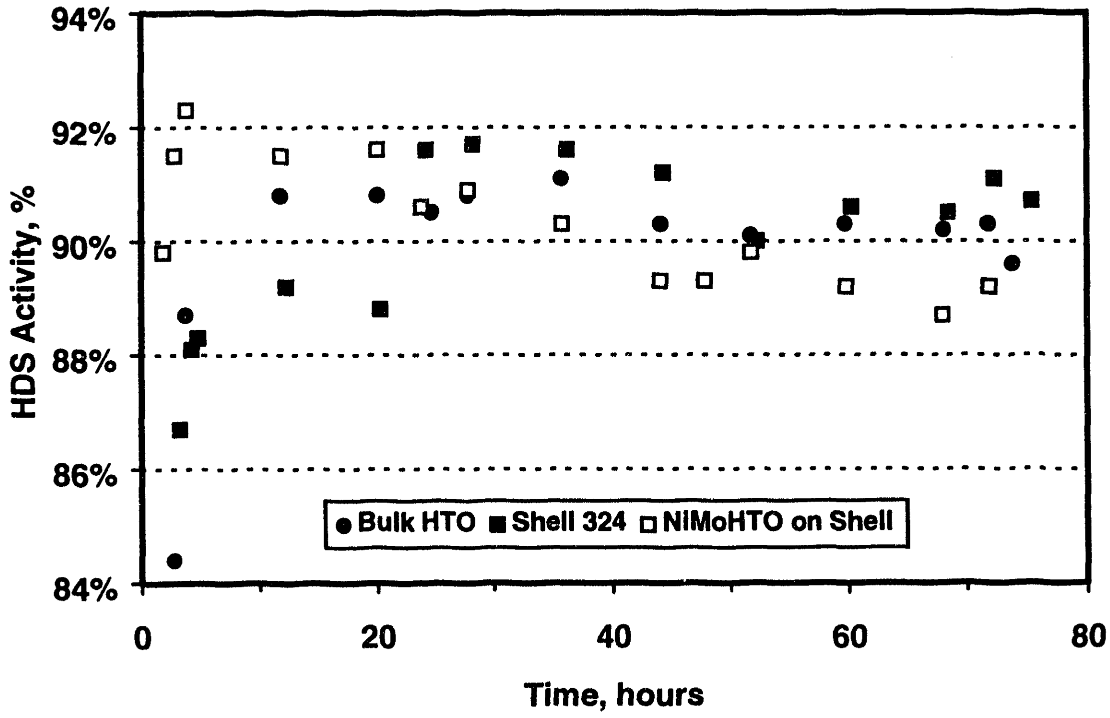

Figure 7. 1500 psig HDS Activity of Benchmark and NiMo/HTO:Si Catalysts

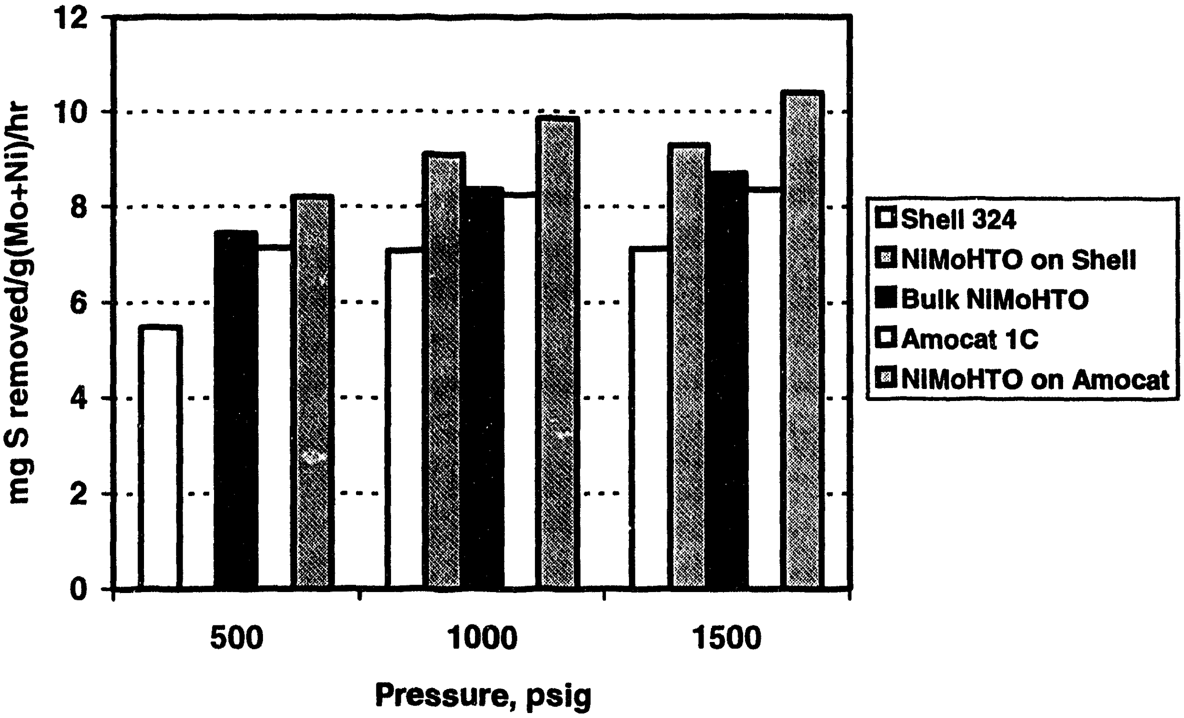

Figure 8. HDS Effectiveness of Benchmark and NiMo/HTO:Si Catalysts

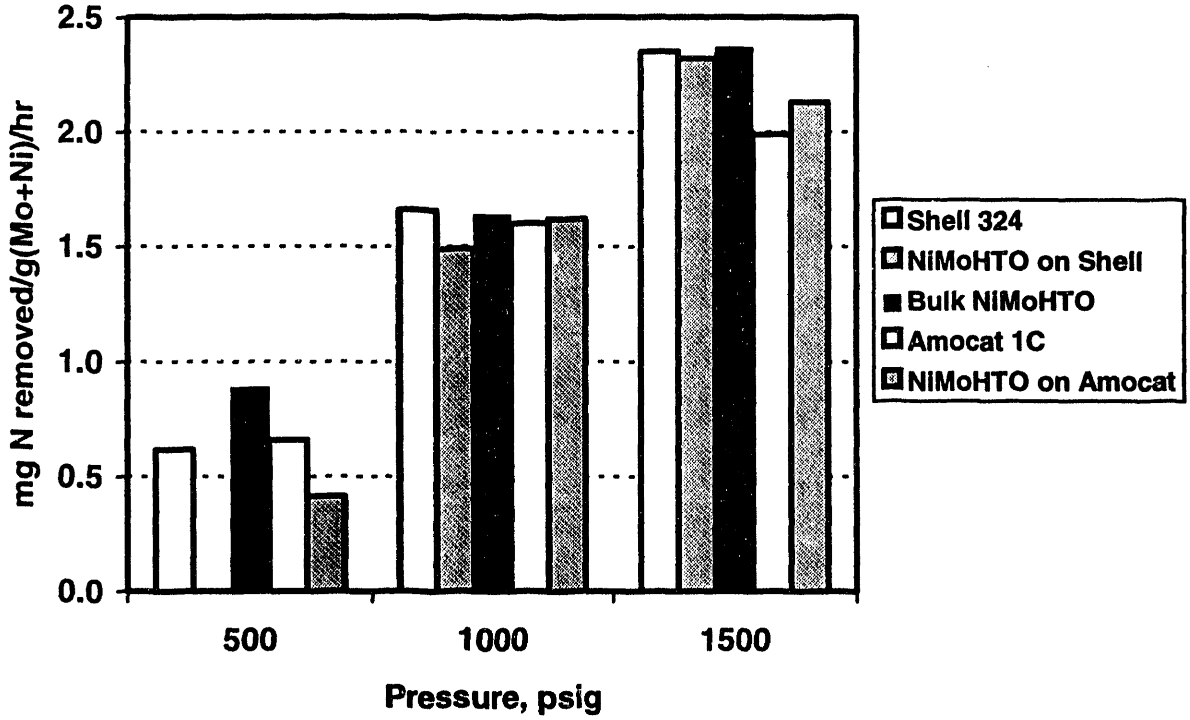

Figure 9. HDN Effectiveness of Benchmark and NiMo/HTO:Si Catalysts

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