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HYDROTREATING STUDIES INVOLVING NiMo/SILICA-DOPED HYDROUS TITANIUM OXIDE (HTO:Si)-COATED ALUMINA 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. In terms of the major types of inorganic ion exchangers defined by Clearfield,[1] these amorphous HMO materials are similar to both hydrous oxides and layered oxide ion exchangers (e.g., alkali metal titanates). 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.[2] 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.[3,4,5] Recently, both bulk and coated HTO:Si-based catalysts have been evaluated for hydrotreating coal-derived liquids in a trickle-bed reactor unit.[6,7] This work determined that the bulk and coated HTO:Si-based catalysts were more active for heteroatom (S and N) removal on a total active metals basis than commercial alumina-supported catalysts. The current work builds on this previous study by evaluating similar materials for the hydrotreatment of a petroleum-derived medium gas-oil feed. This feed material differed from the previous coal-derived liquid in that hydrogenation was a possible competing reaction with heteroatom (S and N) removal during hydrotreatment.

EXPERIMENTAL

Although NiMo/HTO:Si catalysts can be prepared in both bulk and coated forms, this study involved only NiMo/HTO:Si-coated catalysts. HMO-coated catalyst preparation involves a multiple step procedure that begins with the synthesis of an HMO coating on an appropriate engineered support. This chemistry, which can be utilized to produce

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alkali titanates, alkali zirconates, alkali niobates, or alkali tantalates, has been described in detail elsewhere.[8,9] Previous work has demonstrated that SiO_2 additions (Ti:Si molar ratio = 5:1) to hydrous titanium oxide (HTO) materials act to stabilize support surface area at high temperature ($\geq$ 500°C) without significantly altering ion exchange properties.[4,9,10] Briefly, titanium isopropoxide and tetraethyl orthosilicate were combined in a 5:1 Ti:Si molar ratio with NaOH and excess methanol to give a Ti:Na molar ratio of 2:1. The soluble intermediate resulting from this reaction was coated onto γ-Al_2O_3 extrudate supports (Amocat 1C blank extrudates) to form an ion exchangeable coating. Ion exchange and/or adsorption was accomplished by first acidifying the coated material (pH < 4), followed by contacting the acidified material with ammonium heptamolybdate (target Mo loading was 10 wt.% on a calcined basis). Following Mo precursor addition and room temperature vacuum drying, nickel in a nitrate form was added by incipient wetness to give a ratio of moles Ni/(moles Ni + moles Mo) = 0.35. After overnight drying in ambient air at room temperature and oven drying in air at 100°C for 2 h, the dried NiMo/HTO:Si-coated catalyst precursor material was calcined in extrudate form at 500°C for 1 h in air.

In a previous study,[11] TEM results showed that the final MoS_2 phase present in the NiMo/HTO:Si coated Amocat catalyst is indeed partitioned between the HTO:Si coating phase and the γ-Al_2O_3 extrudate surface. However, it was also shown that the overall pyrene hydrogenation activity of the NiMo/HTO:Si-coated Amocat catalyst was dominated by the MoS_2 phase dispersed on the HTO:Si coating.[11] Additional TEM examination showed that the incorporation of the HTO:Si coating was uniform throughout the interior and exterior of the γ-Al_2O_3 extrudate geometry.[11]

For studies involving continuous testing, a petroleum-derived liquid feed, produced by catalytic cracking of a heavy gas oil fraction (Shell Westhollow Research and Development Center (Houston, TX)), was used. Hydrotreating studies involving similar liquid feeds have been reported in the literature.[12,13] This feed was a medium gas-oil blend (boiling point range from 300 to 950°F) with an average molecular weight of 230, an average H:C ratio of 1.22, containing ~2.5 wt.% S and ~700 ppm N. The 11 mm I.D. stainless steel reactor was loaded with 10 grams of -30/+40 mesh catalyst. Approximately 5 cm of -30/+40 mesh α-alumina was placed above and below the catalyst bed as pre-heat and post-heat zones. Following *insitu* He purging (100 sccm) at 150°C for 30 min, the catalysts were sulfided with a 10% H_2S/90% H_2 gas mixture at 150 sccm using a staged temperature ramping procedure with 1 h hold times at set points of 175, 260, 350, and 405°C. Typical hydrotreating experiments lasted 14 days and were run at 400°C. After an initial phase that involved lining out the catalyst at 1500 psig (5 days), the hydrogen pressure was lowered to 500 psig, and after achieving steady state operation, the hydrogen pressure was returned to 1500 psig for a comparison to the original data. The feed rate of the petroleum-derived liquid was adjusted to give a constant liquid hourly space velocity (LHSV) of 2.5 $g/g_{cat}/h$. A hydrogen feed rate of 300 cc/min (4000 scf/bbl) was used for all conditions. These process parameters effectively duplicated those of previous experiments using a coal-derived liquid feed.[6,7] Product liquid samples were pulled 4 times a day and analyzed for sulfur and nitrogen content using an Antek 7000 S/N analyzer (Antek Industrial Instruments, Inc., Houston, TX). Selected product liquid samples were analyzed for H:C ratio (Huffman Laboratories, Inc., Golden, CO) and by simulated distillation using ASTM D-2887 (AC Analytical Controls, Inc., Bensalem, PA). Catalyst activities are reported as percent sulfur/nitrogen removed from the feed.

RESULTS AND DISCUSSION

This petroleum-derived liquid feed allowed the evaluation of catalyst activity for both heteroatom (S and N) removal reactions and hydrogenation reactions. All experiments were run at a constant temperature (400°C) and liquid hourly space velocity (2.5 $g/g_{cat}/h$), with the hydrogen pressure cycled between 1500 and 500 psig. The liquid product was analyzed in terms of the total removed sulfur and nitrogen, the change in H:C ratio, and the change in boiling point distribution. All of the reported results represent "lined out" values for the various catalysts at the different pressure conditions. The hydrotreated product results are shown below in Table 1, including those of a control sample (Amocat blank) which was tested to evaluate the non-catalytic or thermal contribution to the overall activity. Also included in Table 1 are the Mo and Ni contents of the catalysts examined in this study.

The data in Table 1 for the Amocat blank support shows that there is a suprisingly large non-catalytic or thermal contribution to S removal from the feed. Although the non-catalytic or thermal contribution for N removal is also significant at higher pressure, it drops off considerably at lower pressure. As expected, there is very little increase in the H:C ratio due to thermal effects or hydrogenation functionality of the blank alumina support.

For the Amocat 1C catalyst, S and N removal were nearly complete at 1500 psig hydrogen pressure. S removal slightly decreased at lower hydrogen pressure (500 psig); N removal decreased significantly under these conditions. The significant increase in H:C ratio for the liquid product shows that significant hydrogenation is occurring in conjunction with the hydrodesulfurization (HDS)/hydrodenitrogenation (HDN) reactions. The results for the Sandia NiMo/HTO:Si-coated Amocat catalyst show a possible beneficial effect of the HTO:Si-based catalyst coating. Even though this material contains significantly less Ni and Mo than the Amocat 1C material, its S and N removal are generally comparable. Although the NiMo/HTO:Si-coated Amocat catalyst has a slightly lower S removal at 500 psig than the Amocat 1C catalyst, it shows a significantly improved N removal under similar conditions and slightly higher H:C ratios in product liquids at all conditions. Also of note is the fact that the final catalyst activity of the NiMo/HTO:Si-coated Amocat catalyst is significantly higher than that of Amocat 1C after cycling from 1500 to 500 to 1500 psig hydrogen pressure.

Figure 1 shows the boiling point distribution for the initial petroleum-derived liquid feed and for various hydrotreated products obtained with different supports/catalysts. The thermal or non-catalytic effect of the alumina support produces a small shift toward lower boiling point materials which can possibly be attributed to thermal cracking.

Hydrotreating with a supported NiMo catalyst produced a much more significant shift in the simulated distillation curve toward lower boiling point materials, as indicated by the curves for the Amocat 1C and the NiMo/HTO:Si-coated Amocat catalysts. A possible beneficial effect of the NiMo/HTO:Si-coated Amocat catalyst versus the Amocat 1C catalyst was noted in that it produced a slight increase in lower boiling point material. This result is similar to the beneficial effect observed with a NiMo/HTO:Si-coated Amocat catalyst relative to Amocat 1C in direct coal liquefaction tests at Amoco Oil Company.[14] More detailed experiments are required to verify these observations.

Table 1. Petroleum-Derived Feed Hydrotreatment
Results at 400°C and LHSV = 2.5 $g/g_{cat}/h$.

Catalyst	Wt.% Mo (Calcined Basis)	Wt.% Ni (Calcined Basis)	H_2 Pressure (psig)	% S Removal	% N Removal	H:C Ratio (Feed = 1.22)
Amocat Blank	0	0	1500	40.2	36.3	1.29*
			500	29.8	6.2	1.24*
			1500	NA[+]	NA[+]	1.28*
Amocat 1C	10.7	2.4	1500	98.2	96.1	1.47
			500	88.0	17.0	1.31
			1500	96.3	86.7	1.43
NiMo/HTO:Si-Coated Amocat	7.84	2.58	1500	98.0	98.6	1.51
			500	82.1	26.6	1.34
			1500	96.3	95.8	1.46

[*] Actual H:C data were unavailable; this data was predicted using a linear correlation between H:C and index of refraction data for various alumina-supported NiMo catalysts and NiMo/HTO:Si-coated catalysts.

[+] NA denotes that data were unavailable.

Due to the relatively severe operating conditions selected for these studies (T = 400°C), S and N removal were very high (95-100%) for all catalysts at the high hydrogen pressure condition (1500 psig), making a fair evaluation of catalysts at this condition difficult. These test conditions were selected in order to reproduce those previously used with similar catalysts to hydrotreat a highly paraffinic coal-derived liquid containing ~500 ppm S and ~1400 ppm N.[6,7] The high hydrogen pressure (1500 psig) test condition with the coal-derived feed resulted in high S removal (~90%) but only intermediate N removal (~60%). However, the main benefit observed for the bulk or coated HTO:Si-based catalysts in this previous study with the coal-derived liquid feed was that similar activities were observed at lower active metals loadings compared to the commercial alumina-supported NiMo catalysts.[6,7] The results of this current study indicate that these catalysts may offer additional advantages for petroleum-derived feeds. These potential advantages are increased N removal at lower hydrogen pressure and increased hydrogenation activity, which may be manifested in increased H:C ratios as well as increased yields of lower boiling point distillate fractions in the product liquid. Further investigations of these catalysts at less aggressive operating conditions (lower temperature) might also be warranted.[15]

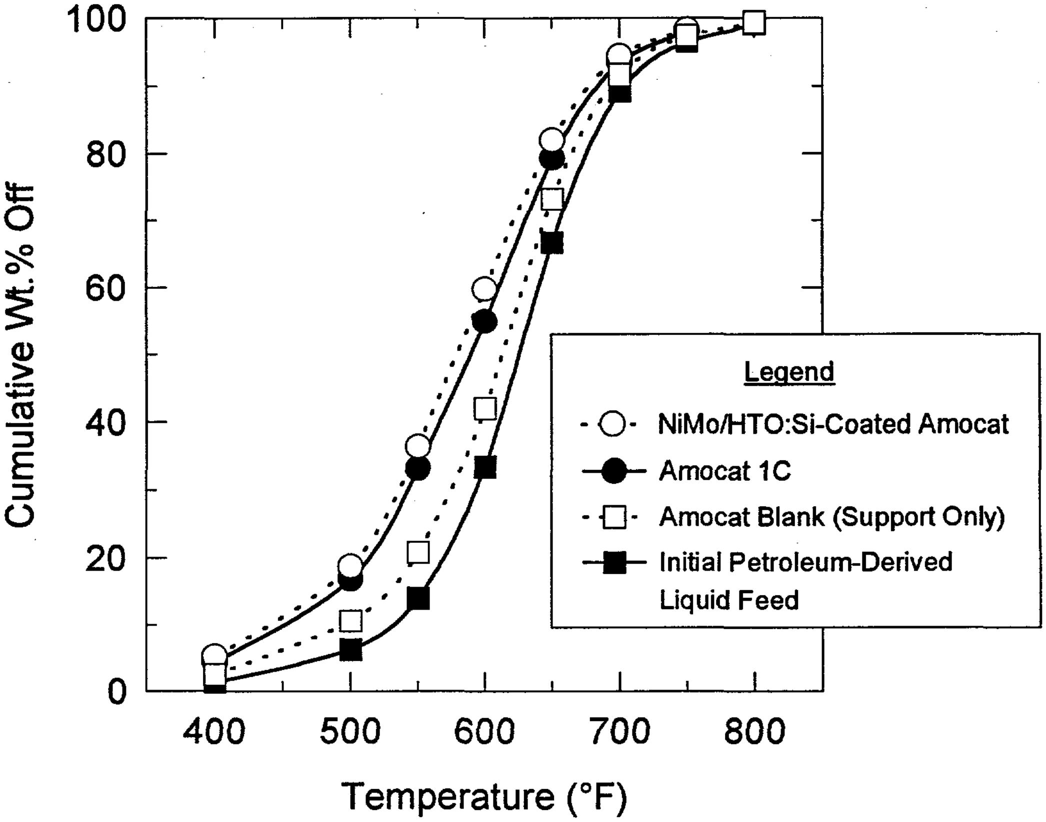

Figure 1. Simulated distillation curves for the petroleum-derived liquid feed and products obtained *via* hydrotreating using various catalyst/support materials. The product data shown represent those of catalysts/supports after maximum possible deactivation (i.e., after cycling between 1500, 500, and 1500 psig hydrogen pressure.

We are in the process of evaluating a bulk NiMo/HTO:Si catalyst in an effort to better understand the differences observed between the NiMo/HTO:Si-coated Amocat catalyst and the Amocat 1C catalyst. These tests will be important in determining whether a possible synergistic effect exists in the case of the NiMo/HTO:Si-coated Amocat catalyst and whether bulk or coated HTO:Si-based catalysts offer benefits for hydrotreating coal-derived or petroleum-derived liquids containing significant aromatic contents. If these benefits are realized, we plan to investigate the potential use of these novel catalysts in hydrotreating co-processing derived liquids, particularly those involving mixtures of petroleum resid and coal.

SUMMARY

For hydrotreating a petroleum-derived liquid feed at 400°C, LHSV = 2.5 $g/g_{cat}/h$, and 1500 psig hydrogen pressure, both HDS and HDN activities were roughly equivalent for a NiMo/HTO:Si-coated Amocat catalyst and a commercial alumina-supported NiMo catalyst (Amocat 1C). Superior HDN performance was exhibited by the NiMo/HTO:Si-coated Amocat catalyst at low hydrogen pressure (500 psig) and after hydrogen pressure cycling (1500-500-1500 psig) relative to the Amocat 1C catalyst. Consistent with previous results obtained on a coal-derived liquid feed, the HDS/HDN results with the petroleum-derived liquid showed that the performance of the NiMo/HTO:Si-coated Amocat catalyst on an active metals weight basis exceeded the performance of the Amocat 1C at all test conditions. The NiMo/HTO:Si-coated Amocat catalyst also showed potentially increased hydrogenation activity, increased resistance to deactivation, and increased yields of lower boiling point distillate fractions, although further work is necessary to verify these initial trends.

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