

# CHARACTERIZATION OF SILICA-DOPED HYDROUS TITANIUM OXIDE (HTO:Si)-SUPPORTED NICKEL MOLYBDENUM (NiMo) CATALYST COATINGS

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Keywords: hydrous titanium oxide, ion exchange, Mo

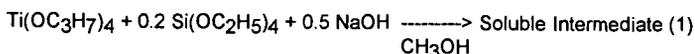
## INTRODUCTION

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.<sup>1,2</sup> 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 reactions which simulate direct coal liquefaction (e.g., pyrene hydrogenation) than commercial NiMo catalysts. 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. This paper will describe how the bulk NiMo/HTO:Si catalyst preparation process was extended to fabricate catalyst coatings on engineered supports. Initial efforts related to the catalyst coating procedures and the characterization of the Mo ion exchange/adsorption procedure will be discussed. The Mo ion exchange/adsorption process is complicated in the case of the catalyst coatings due to the presence of two potential Mo adsorption sites (i.e., HTO:Si film vs. commercial support). These results will be correlated with pyrene hydrogenation reactivity and catalyst coating microstructure.

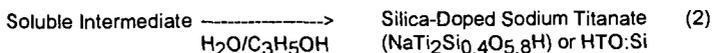
## EXPERIMENTAL PROCEDURE

HMO-supported catalyst preparation involves a multiple step chemical procedure which 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.<sup>3-5</sup> Previous work has demonstrated that SiO<sub>2</sub> additions (Ti:Si molar ratio = 5:1) to HMO materials act to stabilize HMO support surface area at high temperature ( $\geq 500^{\circ}\text{C}$ ) without significantly altering ion exchange properties.<sup>4,5</sup> A brief review of the synthesis of silica-doped sodium titanate (HTO:Si) with a maximum ion exchange capacity (Na:Ti mole ratio = 0.5) will be given here as an example. The first step of the reaction scheme involves the addition of a mixture of tetraethoxysilane and titanium isopropoxide to a dilute (~10 wt.%) solution of sodium hydroxide in methanol, resulting in the production of a soluble intermediate species as follows:



The exact chemistry involved in the formation and subsequent reaction of the soluble intermediate species is extremely complex. Possible competing reactions include exchange of methoxide groups for isopropoxide groups coordinated to Ti, precipitation and redissolution of titanium methoxide, partial hydrolysis or condensation of the various Si, Ti, or mixed alkoxide species, and sodium methoxide formation. Structural studies are in progress to better characterize the nature of the soluble intermediate species.

To prepare bulk HTO:Si powders, the soluble intermediate is subsequently hydrolyzed in a mixed water/acetone solution to produce the silica-doped sodium titanate as follows:



The chemical formula in equation (2) assumes uniform incorporation of all reactants; this has been confirmed by various chemical analyses. The amorphous HTO:Si precipitate is filtered, washed, and vacuum dried at room temperature to produce the material for subsequent ion exchange (IE) processing.

As an alternative to bulk HTO:Si preparation, HTO:Si coatings can be prepared by exposing the soluble intermediate from equation (1) to other materials with a pre-engineered shape (e.g., monoliths, spheres, extrudates, etc.). Depending on the porosity and surface chemistry of the pre-engineered shape, dilution of the soluble intermediate, the coating technique, and the drying conditions, thin or thick film HTO:Si coatings can be fabricated.<sup>4,5</sup> This paper will focus on thick film catalyst coatings on  $\gamma\text{-Al}_2\text{O}_3$  extrudate (Amocat 1C alumina blanks, 1/12 in. dia, 8879-85-C), and the resulting NiMo catalysts, although many other pre-engineered materials, shapes, and catalysts have been evaluated. These coatings were prepared by soaking the as-received  $\gamma\text{-Al}_2\text{O}_3$  extrudate in an undiluted soluble intermediate solution for 24 h, followed by vacuum filtration, and room temperature vacuum drying.

With the exception of the Amocat 1C catalyst, which was commercially prepared by an incipient wetness technique, similar Ni and Mo loading techniques were used for all other catalysts. Following the fabrication of the bulk HTO:Si powder or HTO:Si coated  $\gamma\text{-Al}_2\text{O}_3$  extrudate, these materials were initially acidified with HCl to pH 2.5 or 4.0 (for coated vs. bulk catalysts, respectively) to remove Na, washed with deionized  $\text{H}_2\text{O}$ , and vacuum dried. Following this procedure, Mo anion exchange/adsorption was performed over a 30 min or 24 h period (for bulk vs. coated catalysts, respectively) in an aqueous solution (0.02-0.07 M) of ammonium heptamolybdate (AHM),  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , at an initial pH of 3.5-3.9. Nominal targeted Mo loading for both the bulk HTO:Si powder and the HTO:Si coated  $\gamma\text{-Al}_2\text{O}_3$  catalysts was ~10 wt.%. The Mo precursor loaded materials were vacuum filtered, rinsed with deionized  $\text{H}_2\text{O}$  and acetone, and subsequently dried under vacuum at room temperature. After chemical analysis for Mo by atomic absorption spectrophotometry, Ni was added to the Mo precursor loaded materials via incipient wetness using  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , followed by overnight drying in ambient air at room temperature and oven drying in air at 100°C for 2 h. Regardless of the Mo loading level in the catalyst, a constant ratio of moles Ni/(moles Ni + moles Mo) = 0.35 was used to determine the Ni loading for each batch. The final catalyst precursor was activated by first calcining in air at 500°C for 1 h and then sulfiding in 10%  $\text{H}_2\text{S}$  in  $\text{H}_2$  at 420°C for 2 h. Bulk catalysts were pelletized and granulated to -10/+20 mesh prior to activation, while coated catalysts were activated in extrudate form. Following activation, all catalysts were granulated to -200 mesh and evaluated for reactivity using pyrene hydrogenation as a model reaction. Pyrene (0.1 g), hexadecane (1 g), and catalyst (0.010 g) were loaded into a batch microautoclave reactor and tested at 300°C under 500 psig  $\text{H}_2$  for 10 min.

In addition to fabricating standard bulk NiMo/HTO:Si catalysts, which contain nominally 8-10 wt.% Mo and 2.5-3.5 wt.% Ni, several other catalysts were made in an attempt to simulate the potential extremes involved in the Mo loading of NiMo/HTO:Si coated  $\gamma\text{-Al}_2\text{O}_3$  extrudate. Because of the presence of at least two competing Mo anion adsorption sites, one for the HTO:Si film surface and one for the  $\gamma\text{-Al}_2\text{O}_3$  extrudate surface, it is important to determine the partitioning of Mo between these potential sites and the effect of this partitioning on catalyst reactivity. These two extremes were simulated by performing similar acidification and Mo exchange procedures on the  $\gamma\text{-Al}_2\text{O}_3$  extrudate only and on bulk HTO:Si powder. The quantities of  $\gamma\text{-Al}_2\text{O}_3$  extrudate and bulk HTO:Si powder exposed to the AHM solution were determined by estimating the weight fractions of the HTO:Si coating and the  $\gamma\text{-Al}_2\text{O}_3$  extrudate in the actual HTO:Si coated  $\gamma\text{-Al}_2\text{O}_3$  extrudate. These values, estimated from weight change measurements and separate chemical

analyses, were 20 wt.% HTO:Si coating, and 80 wt.%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate. In both the case of the bulk HTO:Si powder and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate, these IE conditions represented approximately a two fold excess of Mo relative to their respective individual Mo adsorption capacities.

## RESULTS AND DISCUSSION

The experimental conditions used to prepare these various sulfided NiMo catalysts resulted in a range of Ni and Mo loadings, which are summarized below in Table 1.

Table 1  
Catalyst Compositions Resulting from Various Preparation Techniques

Catalyst Description	Wt. % Mo*	Wt. % Ni*
Amocat 1C	10.7	2.4
Bulk NiMo/HTO:Si	9.7	3.2
Blank IE on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	4.2	1.4
High Mo Bulk NiMo/HTO:Si	14.7	4.8
NiMo/HTO:Si Coated $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	8.5	2.8

\* Catalyst weight loadings are expressed on a calcined basis.

For the bulk NiMo/HTO:Si materials, high Mo loadings (> 20 wt.%) are possible due to the high affinity of acidified HTO:Si for anionic Mo species.<sup>3</sup> For our IE conditions, the predominant Mo species in solution should be either (Mo<sub>7</sub>O<sub>23</sub>OH)<sup>-5</sup> or (Mo<sub>7</sub>O<sub>24</sub>)<sup>-6,6</sup> Standard bulk NiMo/HTO:Si batches, which contain 8-10 wt.% Mo incorporated via ion exchange/adsorption, are well within the Mo adsorption capacity for these materials. The high affinity of these HTO:Si materials for anionic Mo species is in contrast to oxide supports such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, which have reported equilibrium Mo adsorption capacities of < 10 wt.%.<sup>7-9</sup> Consistent with this literature, use of the same IE procedure with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate only (referred to in Table 1 and Figure 1 as Blank IE) results in a lower Mo loading (< 5 wt.%) via ion exchange/adsorption. The fact that the Mo loading is significant, although smaller, on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate, indicates that in the case of the NiMo/HTO:Si coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, a competition may exist between ion exchange/adsorption sites on the HTO:Si coating vs. the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate surface.

The different Mo loading experiments also revealed potential problems with these IE procedures. In the case of the extrudate samples, exposure to the Mo loading solution over a 24 h period resulted in a fine white precipitate which could clearly be differentiated from the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate. Several previous authors have reported similar results, with the precipitate being possibly attributed to a polymerized (NH<sub>4</sub>)<sub>3</sub>Mo<sub>8</sub>O<sub>27</sub>·4H<sub>2</sub>O surface phase.<sup>7</sup> Similar to aqueous Mo speciation, this precipitation is strongly influenced by the AHM concentration, solution chemistry and pH, and ageing.<sup>7,10</sup> The significant difference in morphology between the extrudate and the precipitate allows easy visual identification of the precipitation problem; subsequent separation of the precipitate from the extrudate was achieved by repeated deionized H<sub>2</sub>O washing and filtering, and/or sieving. In agreement with previous work, blank IE treatments with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudates using a lower concentration (0.007 M) AHM solution, resulted in similar Mo loadings with no obvious precipitation.<sup>7</sup>

Use of a bulk, granular powder (such as bulk HTO:Si or Al<sub>2</sub>O<sub>3</sub> powder) precludes any visual identification of precipitation problems.<sup>7</sup> It is therefore possible that the high Mo adsorption capacity of the HTO:Si material might be at least partly attributed to surface precipitation. Further experiments will be performed in the future to confirm whether ion exchange/adsorption or precipitation of Mo species dominates in the case of the HTO:Si material.

Results of the pyrene hydrogenation experiments are shown in Figure 1. The first order hydrogenation 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 both the bulk NiMo/HTO:Si and the Amocat 1C catalysts are based on large historical databases. As shown in a previous paper, the activity of the bulk NiMo/HTO:Si was

higher than the Amocat 1C catalyst on either basis.<sup>11</sup> A significant development effort resulted in the optimization of bulk NiMo/HTO:Si catalyst activity; key steps in optimizing catalyst performance included the addition of silica to the HTO support, controlled drying procedures, optimizing acidification and Mo and Ni precursor loading conditions, and understanding the catalyst activation process.<sup>4,5,12</sup> The combination of these improvements resulted in an increase in pyrene hydrogenation activity of 2-3X. Transmission electron microscopy (TEM) analysis of these catalysts showed that the NiMo/HTO:Si catalyst possesses a higher dispersion of MoS<sub>2</sub> than typical commercial catalysts. A second possible explanation for the higher activity is the higher acidity of the NiMo/HTO:Si as compared to commercial Amocat 1C supported on alumina.<sup>11</sup>

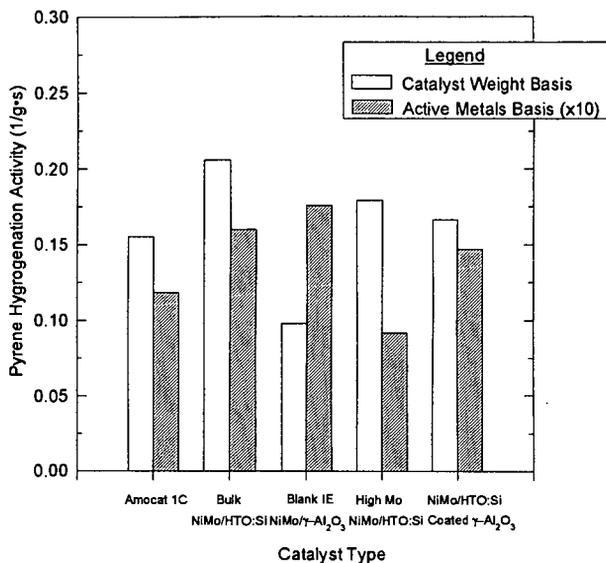


Figure 1. Pyrene Hydrogenation Activity of Commercial and Hydrous Metal Oxide Catalysts

For the other catalyst types, duplicate batches were prepared and tested to ensure representative data; with average values represented in Figure 1. Interesting results were observed for the two extreme cases which simulate NiMo/HTO:Si coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> IE conditions. For the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, a low pyrene hydrogenation activity was observed on a catalyst weight basis, but when normalized on a metals basis this proved to be a very active catalyst. This is consistent with the fact that higher MoS<sub>2</sub> dispersions would be expected at lower weight loadings. The high Mo bulk (~15 wt.%) NiMo/HTO:Si catalyst had a slightly lower pyrene hydrogenation activity on a catalyst weight basis than the standard bulk NiMo/HTO:Si catalysts. This is in agreement with previous data suggesting that pyrene hydrogenation activity does not continue to improve with Mo loadings in excess of 10 wt.%.<sup>5</sup> The significant decrease in catalyst activity of this catalyst on a metals basis probably indicates that the MoS<sub>2</sub> dispersion is significantly lower for this sample relative to the standard (8-10 wt.% Mo) bulk NiMo/HTO:Si catalysts. Significant microstructural evaluation is necessary to confirm our speculation regarding changes in MoS<sub>2</sub> dispersion for these samples.

The results for the NiMo/HTO:Si coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst proved to be interesting with respect to the two extreme cases described above. Since a significant amount of Mo was used in the Mo IE procedure, it is plausible that both the HTO:Si coating and the

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate surfaces were at least partially loaded with Mo by ion exchange/adsorption. Preliminary TEM examination shows the existence of MoS<sub>2</sub> on both HTO:Si and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces. Given the results shown for the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and bulk NiMo/HTO:Si catalysts, it is probable that the MoS<sub>2</sub> associated with the HTO:Si coating is responsible for most of the activity of the NiMo/HTO:Si coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Finally, although the NiMo/HTO:Si coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was less active than the standard bulk NiMo/HTO:Si catalyst, it was slightly better (~10%) on a catalyst weight basis and 25% more active on a metals basis compared to the commercial Amocat 1C catalyst. These results are significant since this activity was achieved with a lower catalyst cost with respect to bulk NiMo/HTO:Si catalysts. Cost savings would be realized due to a decreased use of metal alkoxides and Mo in the case of the NiMo/HTO:Si coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

Future work will be focused in three areas: quantifying HTO:Si coating coverage and optimizing coating techniques, identifying the nature of ion exchanged/adsorbed Mo species on both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HTO:Si surfaces, and careful TEM examination of extrudate surfaces to determine the distribution of HTO:Si coating and MoS<sub>2</sub> partitioning between the extrudate and HTO:Si coating surfaces.

## CONCLUSIONS

For hydrogenation of pyrene, bulk NiMo/HTO:Si catalysts have been developed that perform better than a commercial benchmark catalyst (Amocat 1C) on either a catalyst weight or active metals basis. This preparation process has been extended to produce NiMo/HTO:Si-coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate with intermediate catalytic activity with respect to Amocat 1C and bulk NiMo/HTO:Si catalysts. Controlled experiments which simulated the Mo ion exchange conditions for the NiMo/HTO:Si-coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with either bulk HTO:Si or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate showed that ion exchange/adsorption of Mo is possible on both. Higher Mo loadings with higher catalyst activity (catalyst weight basis) were obtained on the HTO:Si than the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> extrudate, indicating that the catalyst activity of the NiMo/HTO:Si-coated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is dominated by the MoS<sub>2</sub> present on the HTO:Si coating. Future experiments are in progress to provide additional chemical and microstructural evidence to support these findings.

This work was performed at Sandia National Laboratories and was supported by the U.S. Department of Energy under contract DE-AC04-94AL85000.

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