

ACTIVATION OF HYDROUS TITANIUM OXIDE-SUPPORTED
CATALYSTS FOR HYD, HDS, and HDO REACTIONS*

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INTRODUCTION

The objective of our current work is to develop catalysts, based on hydrous titanium oxide (HTO) ion exchangers [1], for use in direct coal liquefaction processing. The ultimate goal of the program is an improved coal liquefaction catalyst produced in quantities that allow testing in a large-scale process development unit such as the Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama. This paper will give an overview of Sandia's catalyst development program and present results of studies of HTO catalyst preparation and pretreatment procedures.

Catalysts currently employed in process development units for coal liquefaction are hydroprocessing catalysts developed for petroleum refining [2]. They are composed of combinations of the metals Mo or W along with Co, Ni and other promoters dispersed on alumina or silica-alumina supports. When used in liquefaction, these catalysts deactivate rapidly [3], causing decreases in product yield and quality and problems with process operability. Thus the existing generation of supported catalysts cannot adequately meet the demanding requirements for use in coal liquefaction processes.

Past efforts for development of coal liquefaction catalysts have focused on alumina-supported systems and, except for exploratory studies, little attention has been given to systematic development of novel formulations. A particularly promising approach to the development of new catalysts specifically designed for coal liquefaction processes lies in the formulation of multicomponent systems that, in comparison to work on single or bimetallic systems, are essentially unexplored. Use of multimetallic systems offers the possibility of multifunctional catalysts that are needed to perform the many different reactions encountered in coal processing. Because of its versatility for the preparation of multimetallic catalysts, the HTO system is an excellent candidate for further development.

Hydrous titanium oxide ion exchange compounds exhibit a number of properties that make them desirable as substrates for active

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metals: (1) ions of any active metal or mixture of metals can be atomically dispersed over a wide range of concentrations by an easily controlled process; (2) the ion exchange capacity of the materials is large, permitting high loadings of active metals; (3) solution chemistry can be used to provide control of the oxidation state of the active metal; (4) catalyst acidity can be modified by ion exchange; (5) the materials have high surface areas; (6) the ion exchanger substrates are stable in oxidizing and reducing atmospheres, and over a wide pH range in aqueous solution; and 7) the ion exchangers can be prepared as thin films on a wide variety of supports. The latter property offers the potential for tailor-made catalysts for chosen chemical, physical, and mechanical characteristics.

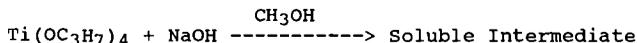
HTO catalysts have been evaluated in several fossil fuel applications including direct coal liquefaction and hydrolysis. Initial batch microreactor tests [4] using equal weights of Shell 324M (a NiMo/Al₂O₃ catalyst that is commonly used in direct coal liquefaction), Ni HTO, Mo HTO, and Pd HTO catalysts with Illinois #6 coal and SRC-II heavy distillate showed that the HTO catalysts, even at low active metals loadings of 1 wt%, are equally effective for conversion of coal to low molecular weight products as Shell 324M, which contains 15 wt% active metals. In addition, for the same oil yield, the HTO catalysts used less hydrogen than the commercial catalyst. HTO catalysts have also been evaluated at the Pittsburgh Energy Technology Center in bench-scale tests with a 1:1 distillate solvent/residuum feed from the Wilsonville Advanced Coal Liquefaction R & D Facility. Results [5] showed that a CoNiMo HTO catalyst gave conversions to cyclohexane solubles, H/C product ratios, and hydrodesulfurization activities that were similar to those obtained with Shell 324M. The CoNiMo HTO catalyst had not been optimized for hydrotreating coal-derived liquids. Studies [6] of hydrolysis using a coal coated with a Pd HTO catalyst (0.7 wt% Pd on daf coal basis) showed a 50% increase in tar yield compared to a reaction performed with the addition of ground NiMo/Al₂O₃ catalyst (3.6 wt% active metals on daf coal basis). These results all indicate that HTO catalysts have potential in coal liquefaction processes.

EXPERIMENTAL

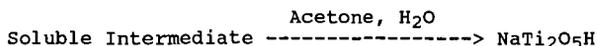
HTO Catalyst Preparation

Hydrous titanium oxide ion exchangers are amorphous inorganic compounds synthesized in the form of salts of weak acids represented by the empirical formula C(Ti_xO_yH_z)_n, where C is an exchangeable cation. HTO catalysts can be prepared by a technique that consists of synthesis of sodium hydrous titanate ion exchange material followed by exchanging active metal ions for the sodium. The synthesis involves three steps:

(1) Reaction of tetraisopropyl titanate with an alkali or alkaline earth metal hydroxide in alcohol solution to form a soluble intermediate:



(2) Hydrolysis of the soluble intermediate in acetone/water mixtures to form the HTO exchange material:



(3) Ion exchange of the alkali or alkaline earth metal for active metal ions in aqueous solution to form the catalyst:



Co, Mo, Pd, and NiMo HTO catalysts are prepared by similar procedures. HTO-Si support materials were made by adding tetraethyl orthosilicate to the tetraisopropyl titanate prior to addition of NaOH.

Activity Testing

All catalysts were tested as powders and were sulfided in an atmospheric pressure flow reactor prior to activity testing. Sulfiding was carried out at 425°C for 2 h using a 10 mol% H₂S/H₂ mixture. Some of the catalysts were calcined in air by heating at 5°C/min to 450°C followed by a 10°C/min increase to 500°C with 2 h at this temperature. All activity results are reported on a weight of active metals basis and results are compared to those of Shell 324M.

Hydrogenation (HYD) activities were determined by measuring the rate of hydrogenation of pyrene to dihydropyrene. Experiments were performed at 300°C in 26 cm³ batch microreactors that were loaded with 100 mg pyrene, 1 g of hexadecane as the solvent, and 500 psig H₂ cold charge pressure. Reaction times were 20 min and catalyst loadings, which were varied depending on the activity of the catalyst, ranged from 10 to 25 mg. The concentrations of pyrene and dihydropyrene in the products were determined using gas chromatography (GC).

Hydrodeoxygenation (HDO) activities were evaluated using the rate of disappearance of dibenzofuran (DBF). Experiments were performed at 300°C in 26 cm³ batch microreactors that were loaded with 100 mg DBF, 25 mg catalyst, 1 g hexadecane, and 1200 psig H₂ cold charge pressure. Reaction times were 15 min and products were analyzed by GC.

Hydrodesulfurization (HDS) activities were measured in a flow reactor system using thiophene as the model compound. Reaction rates for the HDS of thiophene to butene were determined at 325°C and atmospheric pressure.

RESULTS and DISCUSSION

Because the HTOs are new catalytic materials with properties that are significantly different from well-known catalysts such as those supported on alumina, a thorough and systematic approach to their development must be taken. The elements included in this approach are (1) process definition and catalyst requirements; (2) catalyst preparation, pretreatment and characterization; (3) catalyst testing; and (4) catalyst scaleup and processing evaluation. The relationship among the program elements is shown in

Figure 1. The aspects of this program that will be discussed in this paper involve studies of the catalyst preparation and pretreatment procedures that are aimed at enhancing catalyst activity for coal liquefaction.

Seven NiMo HTO catalysts were prepared at an acidification pH of 4. They were evaluated for HYD and HDO activities and the results compared to Shell 324M (Table 1). This series of catalysts was analyzed to determine the effects on catalyst activity of the 500°C calcination procedure, Si addition to the HTO support, and removal of Na from the catalyst. The results show that there is a direct correlation (correlation coefficient = 0.98) between HYD and HDO activities for all the catalysts (HTOs and Shell 324M).

Analysis of the activities of the first three pairs of catalysts (runs 1-6) shows that the calcined catalyst in each pair has significantly greater activity than the noncalcined. The NiMo HTO catalysts without Si gave the lowest activities and the sulfided, calcined catalyst with a Ti:Si ratio of 5 (run 6) gave the highest HYD and HDO activities. These results show that Si addition is beneficial, but that too much Si (Ti:Si=3) causes a decrease in activity. The first six catalysts in Table 1 contained small amounts of Na (0.6 to 1.1 wt %), whereas the catalyst used in run 7 had <0.1 wt%. Comparison of activity results from runs 6 and 7 shows that removal of the Na gives a catalyst with the highest HYD activity; this catalyst has 90% of the HYD activity of Shell 324M. These results are in agreement with studies that show Na can poison catalyst sites. Parameters that are currently being studied to improve the performance of NiMo HTO catalysts include optimizing the Si content, evaluating the effects of the pH used in the acidification step, determining the impacts of different calcining conditions, and analyzing the effects of varying the active metal loadings.

Studies have been performed to determine why Si addition in the support increases catalyst activity. This work was performed with Pd HTO catalysts, which also show an increase in activity with Si addition to the support. Figure 2a shows the effects of the Ti:Si ratio in the support and the acidification pH on the surface areas of Pd HTO catalysts that have been calcined at 300°C in air. The presence of a 6:1 Ti:Si mole ratio results in a 2- to 3-fold increase in surface area with respect to Pd HTO. When the Ti:Si ratio is increased to 2, any discernible enhancement in surface area is limited to materials with the lower pHs. The effect of pH on the surface areas of catalysts prepared on the same supports is more difficult to discern. There appears to be a general trend whereby the surface areas of samples acidified at pH 4 and 5 are slightly enhanced with respect to materials that were not acidified (pH>6) or were treated at pH 2. Increasing the calcination temperature to 500°C (Figure 2b) shows similar trends to those observed at 300°C. As would be expected, the higher temperature resulted in an overall decrease in surface area for all materials. The results of this study on Pd HTO catalysts suggest that it may be possible to increase the activity of the NiMo HTO catalysts by decreasing the calcination temperature, decreasing the Ti:Si ratio to lower values than those shown in Table 1, and using a somewhat higher pH during acidification.

Optimization of the calcination process for these materials is

aimed at maintaining the dispersion of the active metals in the as prepared material while giving a catalyst that is stable under reaction conditions. The usual procedure for preparing alumina supported catalysts involves calcining after the metals have been impregnated onto the support. This procedure has been used in all previous studies of HTO catalysts. However, a different method, calcination of the support prior to ion exchange, may be possible with these materials. The potential benefit of this procedure, which will subsequently be referred to as precalcining, is that the metal is not present during calcination so that it will not sinter, while the possible disadvantage is that the ion exchange capacity of the calcined material may be too low to enable preparation of a good catalyst. The impact of precalcining temperature on the ion exchange capacities of HTOs are shown in Figure 3. The results obtained on two sets of catalysts, one exchanged with Co and the other with Mo, show that the exchange capacity decreases with increasing precalcination temperature. For Co, about 2/3 of the HTO's noncalcined exchange capacity is maintained between 400°C and 700°C. In contrast, Mo exchange shows a sharp decrease due to precalcining at 200°C and a more gradual decrease with increasing precalcination temperature. After a 500°C precalcination, only about 1/4 of the initial Mo exchange occurs. These results suggest that formation of a CoMo HTO catalyst may require two separate exchange steps: the Mo could be exchanged at room temperature followed by calcination and subsequent exchange with Co. Studies are currently underway to compare activities of catalysts prepared using precalcination and calcination after ion exchange.

Studies of HTO calcination after ion exchange are also being performed. Recent work (Figure 4) has shown the effect of calcination temperature on the thiophene HDS activities of two NiMo HTO catalysts. With calcination above 400°C, both catalysts show a significant increase in HDS activity. Differential thermal analyses of these catalysts showed that a thermal event occurred at this temperature. The NiMo HTO catalyst with the lower total metals loading maintains this higher activity up to a calcination temperature of at least 600°C. The NiMo HTO with the higher metals loading shows additional activity enhancement up to a calcination temperature of 500°C and then an activity decrease. The reasons for these phenomena are not yet known. Differential scanning calorimetry and thermal gravimetric analysis techniques are currently being performed in conjunction with activity testing to learn more about calcination and activation procedures for these materials.

CONCLUSIONS

Hydrous titanium metal oxide catalysts are extremely versatile materials that have promise as coal liquefaction catalysts. Previous studies have shown that they perform well in both batch and bench-scale coal liquefaction tests. Efforts to improve preparation and activation procedures for these catalysts have identified several promising research areas that either have or may lead to enhancements in catalyst activity. For, example, addition of Si to the support of NiMo HTO catalysts has yielded 2- to 3-fold increases in surface areas and has resulted in a 33% increase in HYD activity

and a doubling of HDO activity compared to an HTO catalyst without Si. In addition, it may be possible to maintain the high atomic dispersion of the metals at reaction conditions by calcining prior to ion exchange of the metal onto the support or reducing the calcination temperature. Current research is addressing these areas.

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Table 1. HYD and HDO testing of NiMo HTO catalysts.

Run	Ti:Si ^b	Pretreatment	Wt % Metals		Activity Testing ^a	
			Ni	Mo	HYD	HDO
1	No Si	Sulfide	3.23	12.40	0.134	0.004
2	No Si	Sulfide+calcine	3.23	12.40	0.480	0.037
3	3	Sulfide	3.03	9.69	0.236	0.017
4	3	Sulfide+calcine	3.03	9.69	0.613	0.069
5	5	Sulfide	2.69	9.62	0.227	NA ^c
6	5	Sulfide+calcine	2.69	9.62	0.812	0.080
7	5(No Na)	Sulfide+calcine	4.08	9.75	0.904	NA
	Shell 324M	Sulfide	2.80	12.40	1.026	0.112

a $k(g^{-1}(\text{active metal}) \text{sec}^{-1})$

b Mole ratio

c Not analyzed.

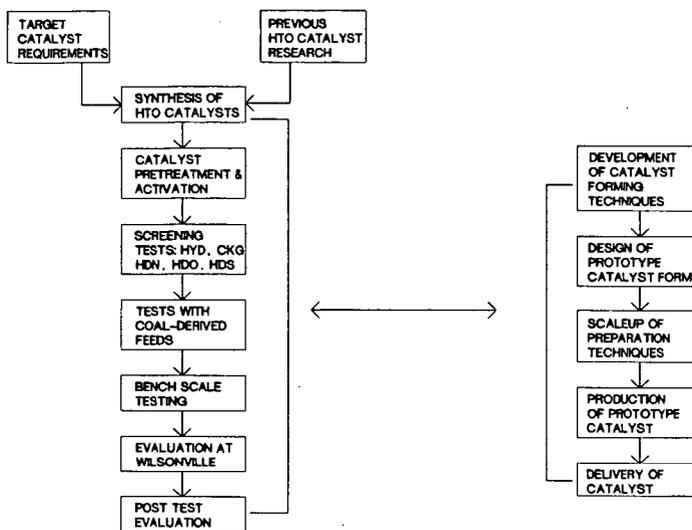


Figure 1. Overview of Sandia's catalyst development program.

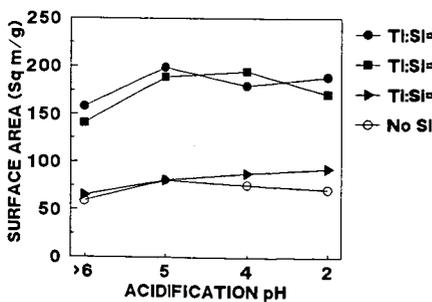


Figure 2a. Calcination at 300 C

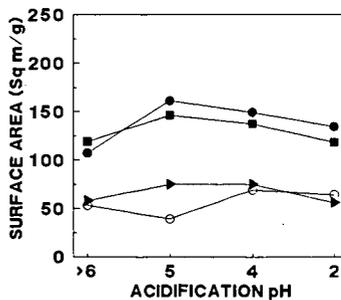


Figure 2b. Calcination at 500 C.

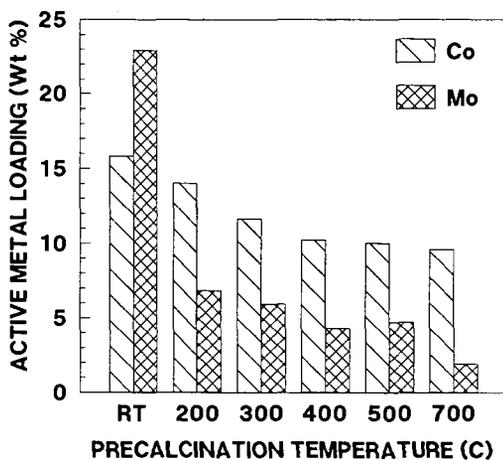


Figure 3. Effects of HTO precalcination temperature on ion exchange capacity.

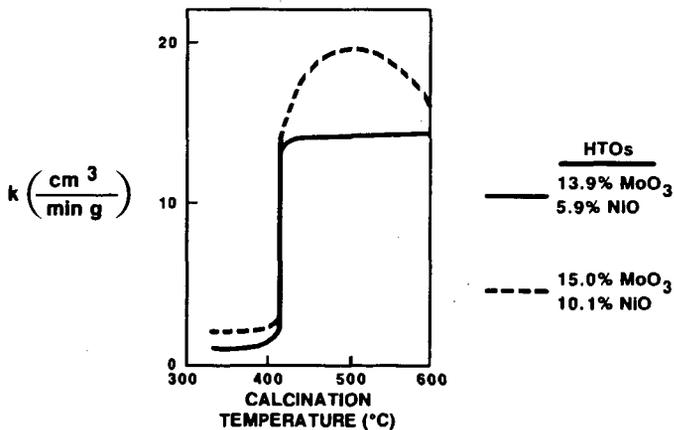


Figure 4. Effects of calcination temperature on thiophene HDS activity for two NiMo HTO catalysts.