

PERFORMANCE OF HYDROUS TITANIUM OXIDE-SUPPORTED CATALYSTS
IN COAL-LIQUIDS UPGRADING

by

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ABSTRACT

Experimental tests were performed in a continuous-flow hydrotreating unit at Pittsburgh Energy Technology Center to evaluate the performance of hydrous titanium oxide-supported (HTO) catalysts as hydrotreating catalysts for use in two-stage coal liquefaction. Catalysts containing either a combination of Co, Ni, and Mo as the active metal components or Pd as the active metal component were tested with representative hydrotreater feed stocks from the Wilsonville Advanced Coal Liquefaction Research and Development Facility. Catalyst performance evaluation was based on desulfurization and denitrogenation activity, the conversion of cyclohexane-insoluble material, and hydrogenation activity during 100-hour reactor runs. Results indicated that the HTO catalysts were comparable to a commercial Ni/Mo-alumina supported catalyst in the areas evaluated.

INTRODUCTION

Personnel from the Pittsburgh Energy Technology Center (PETC) have been collaborating with researchers at Sandia National Laboratories (SNL) to further development of the novel hydrous titanium oxide-supported (HTO) catalysts for use in the hydrotreatment of coal-derived liquids. The HTO materials were originally developed at SNL for use as precursors for ceramic materials¹ and as ion-exchange materials for the decontamination of aqueous nuclear waste streams.² The properties of these materials, including high surface areas and ion exchange capacities, chemical stability, variable Bronsted acidities, and the ability to apply them in thin films, have led to investigations related to their performance as catalysts in a variety of chemical systems.³⁻⁵ They have also been applied to coal-oil coprocessing,⁶ coal hydropyrolysis tars.⁷

The HTO catalysts containing either Co, Ni, and Mo (CoNiMo-HTO) as the active metal components or Pd (HTO-Pd) as the active metal component were tested in a continuous-flow hydrotreater at PETC for possible use as hydrotreating catalysts in the second stage of the integrated Two-Stage Liquefaction process. The PETC has been testing catalysts used in the hydrotreater of the Wilsonville Advanced Coal Liquefaction Research and Development Facility (ACL RDF). Such areas as the effect of catalyst pore size distribution,⁸ the effect of active metals loading,⁹ and the determination of the thermal component of residuum hydrogenation¹⁰ have been studied. The objective of this study was to ascertain if the HTO catalysts could be used to hydrotreat a typical two-stage liquefaction feedstock material containing coal-derived residuum. Catalyst performance

was based on comparison of the desulfurization, denitrogenation, hydrogenation, and cyclohexane-insoluble conversion activities of the HTO catalysts with those of a commercial alumina-supported Ni/Mo-alumina catalyst (Shell 324M) that has been used widely in these types of applications.

Experimental

A typical Two-Stage Liquefaction process¹¹ consists of a thermal liquefaction first stage, followed by a solvent-deashing step, and a subsequent catalytic-hydrotreating stage (Figure 1). The feedstock for the work described herein came from the Wilsonville ACLRD Facility and consisted of a distillate vehicle from the thermal first stage (designated V-178) and the deashed residuum (WSRC) from the solvent-deashing step. These were supplied to PETC from the Wilsonville ACLRD Facility and have been documented elsewhere.^{10,11} Typical analyses of these materials are presented in Table 1. The feedstock used in these experiments consisted of a 1:1 mixture of V-178 and WSRC. The hydrous titanium oxide-supported catalysts were prepared from an HTO-Na material by ion exchange of the Na with Co, Mo, Ni, and Pd from aqueous solutions of their salts. The HTO-Na was prepared by hydrolyzing the product of a reaction between tetraisopropyl titanate and a methanol solution of NaOH. Detailed preparation procedures have been described elsewhere.³⁻⁵

The HTO catalysts remain in the form of a low-tap-density powder (0.3 g/cm³) through the ion exchange step used to load the active metals. For this application, the ion-exchanged powders were pressed into discs, which were subsequently crushed and screened to -10/+20 mesh to minimize diffusion effects in comparing the HTO catalysts with the Ni/Mo-alumina catalysts. The latter were obtained as 1/32-inch extrudates. The as-prepared HTO catalysts are calcined prior to use to remove the volatiles (15 to 25 wt %), which consist primarily of water along with small amounts of alcohols. This calcination can be done either in the reactor or in an external furnace before the catalysts are loaded into the reactor. A density change accompanies calcination of the hydrous titanium oxide-supported catalyst, so that bed shrinkage during calcination in a system that utilizes constant catalyst volumes must be compensated for in loading the catalyst bed. In either case the material was calcined in a nitrogen atmosphere using a temperature of 100°C to remove the bulk of the volatiles and a final one-hour soak at 375°C for the CoNiMo-HTO catalysts and at 300°C for the HTO-Pd catalysts.

Sulfiding of the CoNiMo-HTO catalyst was done in the reactor with a hydrogen gas stream containing 10 vol% hydrogen sulfide for five hours at 390°C. The Ni/Mo-alumina catalyst was activated by heating in the same manner. The HTO-Pd catalyst did not require sulfiding prior to use.

Compositions and some physical properties of the catalysts used in this work are presented in Table 2. Two HTO-Pd catalysts are listed because there was a significant difference in the way the materials were prepared. The difference involved the acidification step used to increase the Bronsted acidity of the support; phosphoric acid was used in the preparation of HTO-Pd1, but sulfuric acid was used in the preparation of HTO-Pd2. The use of different acids resulted in variations in surface area, as well as the expected compositional changes.

Two experiments of 100-hour duration using the CoNiMo-HTO catalyst and two experiments of 100- and 700-hour duration using the Ni/Mo-alumina

catalyst were completed. The reaction conditions (temperature, pressure, and volume hourly space velocity) were kept the same for both catalyst systems and are presented in Table 3. The reaction conditions used with the HTO-Pd catalysts were the same as those given in Table 3 with the following exceptions. The run using the HTO-Pd1 catalyst was intended to be a 100-hour run but was terminated at 42 hours owing to a power failure. The duration of the run with the HTO-Pd2 was 100 hours; however, the run temperature was held at 320°C for at least 24 hours, and the temperature was then raised to 370°C and finally to 390°C during the course of the run.

RESULTS AND DISCUSSION

The average run results of tests using the CoNiMo-HTO and Ni/Mo-alumina catalysts are presented in Table 4. There were sufficient variations in the slurry feed rate of the continuous-flow unit to cause the volume hourly space velocity to vary, thus precluding a detailed comparison of the catalyst activities. In examining the data in Table 4, it is apparent that there are significant differences in the results of the two CoNiMo-HTO 100-hour runs. This may be because two different batches of catalyst were used, but it is more likely due to variations in the space velocity during the runs. Differences of the same magnitude are observed when comparing the 100-hour Ni/Mo-alumina run with the first 100 hours of the 700-hour Ni/Mo-alumina run. Since these runs did not use different batches of catalyst, the variations in the results are probably due to a variable space velocity. The differences between the average results of the first 100 hours of the 700-hour Ni/Mo-alumina run and those of the final 500 hours of the 700-hour run are due to catalyst deactivation. These differences are not as great as those seen when comparing the initial 100 hours of both Ni/Mo-alumina runs. However, there appear to be trends in the data that allow for a qualitative comparison of the HTO and Ni/Mo-alumina catalyst systems using the average activities calculated over the duration of the runs specified in Table 4.

The CoNiMo-HTO catalyst appears to be similar in overall activity to the Ni/Mo-alumina system (Shell 324M). Hydrogenation activity, as measured by the change in the hydrogen-to-carbon atomic ratio (H/C) of the product as compared to the feed, was on the order of 10% for each catalyst. The range of conversions of cyclohexane-insoluble material to cyclohexane-soluble material and the desulfurization activity of the two catalytic materials also appear to be comparable. The denitrogenation activity of the CoNiMo-HTO catalyst was somewhat lower than that of the Ni/Mo-alumina catalyst based on the 100-hour tests. However, when the level of denitrogenation of the CoNiMo-HTO is compared to the "lined-out" activity of the Ni/Mo-alumina catalyst at 700 hours, both catalysts seem to have similar activities. The activity of the Shell 324 Ni/Mo-alumina catalyst is known to "line out" after approximately 200 hours under the conditions used in these runs. Long-term runs, i.e., 700 hours, with the CoNiMo-HTO catalyst are needed before a more definitive comparison can be made.

One would expect that a noble metal such as palladium would be an ineffective catalyst under the conditions described herein owing to sulfur and nitrogen poisoning. However, batch tests indicated that the HTO support seems to provide some protection to the Pd against sulfur poisoning and that the degree of protection increased with increasing temperature. The Pd catalyst, HTO-Pd1, used in the initial test, which was done under

conditions in Table 3, deactivated early in the run. Table 5 shows that the most sensitive indicator of this was the change in H/C atomic ratio of the product with respect to the feed. Conversions of cyclohexane- and pentane-insoluble materials also decreased somewhat while the desulfurization activity appeared to remain relatively constant. The run was prematurely ended at 42 hr owing to a power failure.

The second test of a HTO-Pd catalysts used a material that was considerably different both in composition and in surface area (Table 2). Batch testing indicated that the palladium hydrous titanium oxide-supported catalyst was active at lower temperatures, and consequently, the operation of the continuous-flow unit was altered with respect to reaction temperature as described previously where the temperature was increased stepwise from 320°C to 390°C throughout the course of the 100-hour run. All other experimental conditions were the same as those given in Table 3. At the time this paper was written, the only analytical results available for this run were the H/C ratios given in Table 6. As can be seen, the HTO-Pd₂ experienced a decrease in hydrogenation activity during the first 19 hours at 320°C. Increasing the run temperature restored the activity to that observed during the initial 7 hours of the run, and the hydrogenation activity appeared to be increasing during the final 24 hours of the run at 390°C.

CONCLUSIONS AND RECOMMENDATIONS

The experimental results indicate that HTO-supported catalysts such as CoNiMo-HTO are capable of achieving catalytic activities similar to those of a Ni/Mo-alumina catalyst (Shell 324M), which is considered to be as good as any commercial catalyst for this particular application. A HTO-Pd catalyst also showed considerable promise for this application. Both HTO-supported materials must be subjected to further research before definitive comparisons can be made with other catalyst systems.

Previous testing of the Ni/Mo-alumina system has shown that only moderate increases in catalytic activities can be achieved by manipulating the average pore size distribution and pore structure of the alumina support. Since no attempt has been made as yet to modify or optimize the physical properties of HTO supports, there may be potential for significant improvements in these materials.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Representative Analysis of Feed Materials

	RESIDUUM (WSRC)	VEHICLE (V-178)
Elemental Analysis, wt%		
Carbon	88.6	88.3
Hydrogen	6.8	9.8
Nitrogen	1.3	0.4
Sulfur	0.6	0.3
Moisture, wt%	0.1	0.1
Ash, wt%	0.3	< 0.01
Specific Gravity, 60°F/60°F	1.19	1.01
Solvent Analysis, wt%		
Toluene insolubles	12.1	< 0.02
Asphaltenes*	47.8	4.9
Oils** (by difference)	40.1	94.9

* Toluene soluble, pentane insoluble

** Toluene soluble, pentane soluble

Table 2. Physical Properties and Composition of Catalysts After Calcining

	Shell 324M	CoNiMo- HTO	HTO-Pd1	HTO-Pd2
BET surface area, m ² /g	161	245	116	320
Pore Volume, cm ³ /g	0.427	0.310	*	*
Average Pore Diameter, Å	106	39	*	*
Cobalt, wt%	-	0.9	-	-
Nickel, wt%	2.5	1.1	-	-
Molybdenum, wt%	13.0	10.6	-	-
Palladium, wt%	-	-	5.4	7.5
Phosphate, wt%	-	-	17.5	-
Sulfate, wt%	-	-	-	4.5

* Not determined

Table 3. Reaction Conditions for Shell 324M NiMo and CoNiMo-HTO Runs

Pressure	2000 psig
Temperature	390°C
Catalyst charge	80 cm ³
Target hourly space velocity	0.6 cm ³ resid /cm ³ cat
Hydrogen gas feed rate	8 scfh
Slurry feed rate	114 g/hr
Feedstock	WSRC/V178 weight ratio = 1/1

Table 4. Results of Reactor Runs using CoNiMo-HTO and Shell 324M Catalysts

CATALYST	CoNiMo-HTO	CoNiMo-HTO	Ni/Mo-alumina		
			Shell 324M	Shell 324M (100)**	Shell 324M
Test duration, hr	100*	100	100	(100)**	200-700
Variation of space velocity	0.49-0.65	0.59-0.74	0.46-0.84	0.57-0.60	0.56-0.63
Percent change in H/C atomic ratio	10	7	9	10	9
Conversions, wt%					
cyclohexane	73	57	71	58	54
Desulfurization, wt%	85	76	85	71	52
Denitrogenation, wt%	22	20	40	23	16

* The catalyst was contacted with kerosene at room temperature prior to this test, and a carbon residue was left on a portion of the catalyst. This was not planned and did not seem to affect catalyst performance.

** First 100 hours of the 700-hour test

Table 5. Hydrotreating Results Using HTO-PdI Catalyst

Time, hr	10	22	35
Percent change in H/C atomic ratio	12	11	3
Conversions, wt%			
cyclohexane	77	78	68
pentane	60	58	56
Desulfurization, wt%	75	75	75

Table 6. Hydrogenation Activity of HTO-Pd2

Operating Conditions		Change in Atomic H/C ratio, percent
temp., °C	time, hr	
320	7	7
320	10	4
320	19	2
320	23	3
	27 temp. change	
370	35	4
370	36	3
370	45	5
	50 temp. change	
390	63	8
390	67	7
390	73	8
390	85	8
390	91	9
390	98	8

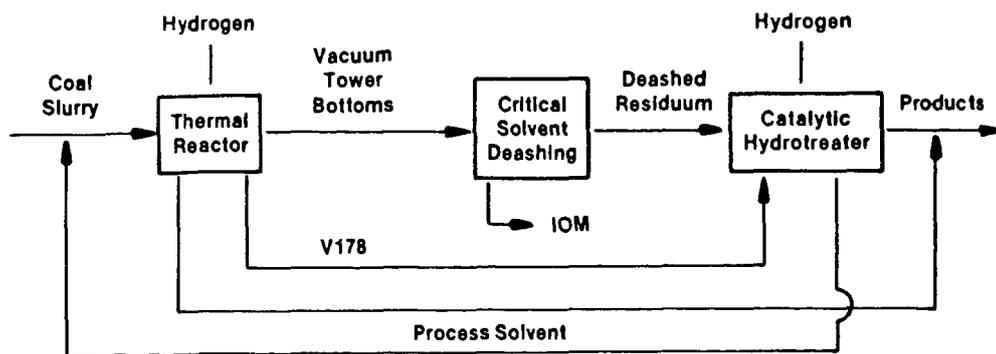


Figure 1. Typical Two-Stage Liquefaction Process