SECTION 3
SIMULTANEOUS NH_3 AND H_2S REMOVAL TESTS

Several catalysts containing Ni, Co, Mo, and W (with Al_2O_3, TiO_2, and other oxides as supports) were prepared and tested by themselves or in combination with a zinc titanate sorbent. To rank the activities of the new materials prepared, a number of baseline materials were designated. These included HTSR-1 and molybdenum sulfide catalysts (CRC-653 and CRC-530) tested by SRI (Krishnan et al., 1988), L-3787M, molybdenum-doped zinc titanate developed for the GE moving-bed desulfurization system (Ayala, 1993), and ZT-4, a granulated zinc titanate sorbent prepared by RTI for fluidized beds (Gupta and Gangwal, 1992). The tests were conducted using fixed-bed microreactors at SRI and GE and a 2.0-in. high-temperature, high pressure (HTHP) bench-scale fluidized-bed reactor system at RTI. The catalyst preparation was conducted primarily at SRI and GE. Details of these preparations are given in Appendix A (pages 20–23) and Appendix B (pages 5–6). A detailed description of experimental apparatus and results of testing at SRI and GE are provided in Appendix A (pages 16–48) and Appendix B (pages 1–22), respectively.

3.1   SUMMARY OF RESULTS

Numerous catalysts were prepared and tested for the simultaneous NH_3 and H_2S removal approach. These catalysts are summarized in Table 2.

Unfortunately, none of the catalysts and sorbent catalysts prepared exhibited significant NH_3 decomposition activity at temperatures up to 725 °C in Texaco coal gas containing up to 7,500 ppmv H_2S. In contrast, the baseline catalyst, HTSR-1, exhibited significant ammonia decomposition activity at 800 °C or higher in the presence of H_2S. Thus the simultaneous NH_3 and H_2S removal approach was de-emphasized in favor of the high-temperature catalytic decomposition approach. Selected highlights of results for the simultaneous NH_3 and H_2S removal approach are presented below:

- HTSR-1 exhibited excellent activity for NH_3 decomposition in simulated Texaco gas without H_2S, at 725 °C. With H_2S the catalyst was poisoned, but the activity could be restored at 800 °C even in the presence of H_2S.

Table 2. Catalysts Tested for Simultaneous NH_3 and H_2S Removal

HTSR-1 + ZT-4 (zinc titanate)	Co/TiO_2
MoS_2 (CRC-653)	Mo/TiO_2
MoS_2 (CRC-530)	$Co\text{-}Mo/TiO_2$ + ZT-4
ZT-4	W/TiO_2
Ni/TiO_2 - ZrO_2	$W\text{-}Mo/TiO_2$
$Ni\text{-}Mo/TiO_2$ - ZrO_2	ZnO - WO_3
Co-Mo-L-3787M (zinc titanate)	$Co\text{-}ZnO\text{-}WO_3\text{-}ZrO_2$

- MoS_2-based catalysts show low activity for NH_3 decomposition. Surface area stabilization with ZrO_2 was necessary for these catalysts to have any activity at all.

- The catalysts containing Ni, Co, Mo, and W on a high surface area TiO_2 support showed moderate activity (typically 10 to 20 percent decomposition) for NH_3 decomposition at 725 °C. The TiO_2 support sintered extensively at 725 °C and required stabilization with ZrO_2.

- Mixing the Ni, Co, Mo, and W catalysts with zinc titanate sorbent allowed the catalysts to function longer. As the sorbent got loaded with H_2S, the exit H_2S level increased, thereby decreasing the activity for NH_3 decomposition.

3.2   HIGH-PRESSURE TESTS AT RTI

3.2.1   HTHP Test Facility

The HTHP facility used at RTI to test simultaneous NH_3 and H_2S removal was a modified version of a facility used in the fluidized-bed zinc titanate test program (Figure 2). This bench-scale test facility is described in detail by Gupta and Gangwal (1992).

The reactor is constructed using a 4-in., schedule-160, 316 stainless steel (SS) pipe. Most of the other system components are constructed with either 316 or 304 SS. All hot H_2S-wetted parts are Alon-processed (a high-temperature aluminum vapor treatment) to prevent corrosion of SS by sulfur gases in the presence of steam. The main components of the reactor facility are (1) gas delivery system, (2) reactor assembly, (3) data acquisition and process control, (4) gas analysis system, and (5) reactor offgas venting system. Each is briefly described below.

A battery of seven mass flow controllers (MFCs) capable of operation at pressures up to 100 atm controls the flow rate and composition of simulated coal gas using bottled gases for CO, H_2, CO_2, N_2, H_2S, O_2, and air. A positive displacement pump feeds deionized water to a boiler and superheater to generate steam. The delivery system can generate simulated coal gasifier gases representative of all types of gasifiers.

The fluidized-bed desulfurization reactor is also shown in Figure 2. The unique feature of this reactor is a removable cage for easy loading and unloading of the sorbent. The reactor can accommodate both 7.62-cm (3-in.) and 5.1-cm (2-in.) dia sorbent cages. A removable α-alumina distributor plate is positioned at the bottom of each cage to introduce hot coal gas into the reactor. The reactor is housed inside a three-zone furnace equipped with separate temperature controllers for each zone and the furnace can heat the reactor up to 850 °C. Ceramic thimble filters downstream of the reactor capture particles from the sulfidation and regeneration exit lines upstream of the condensers. The reactor exit gas, after passing through the thimble filters, is cooled using heat exchangers.

The reactor temperature is monitored at the bed inlet below the distributor, halfway in the bed, and at the bed outlet in the freeboard using Type-K thermocouples. The thermocouples, equipped with a digital display, are connected to a data acquisition system described later. Pressure is
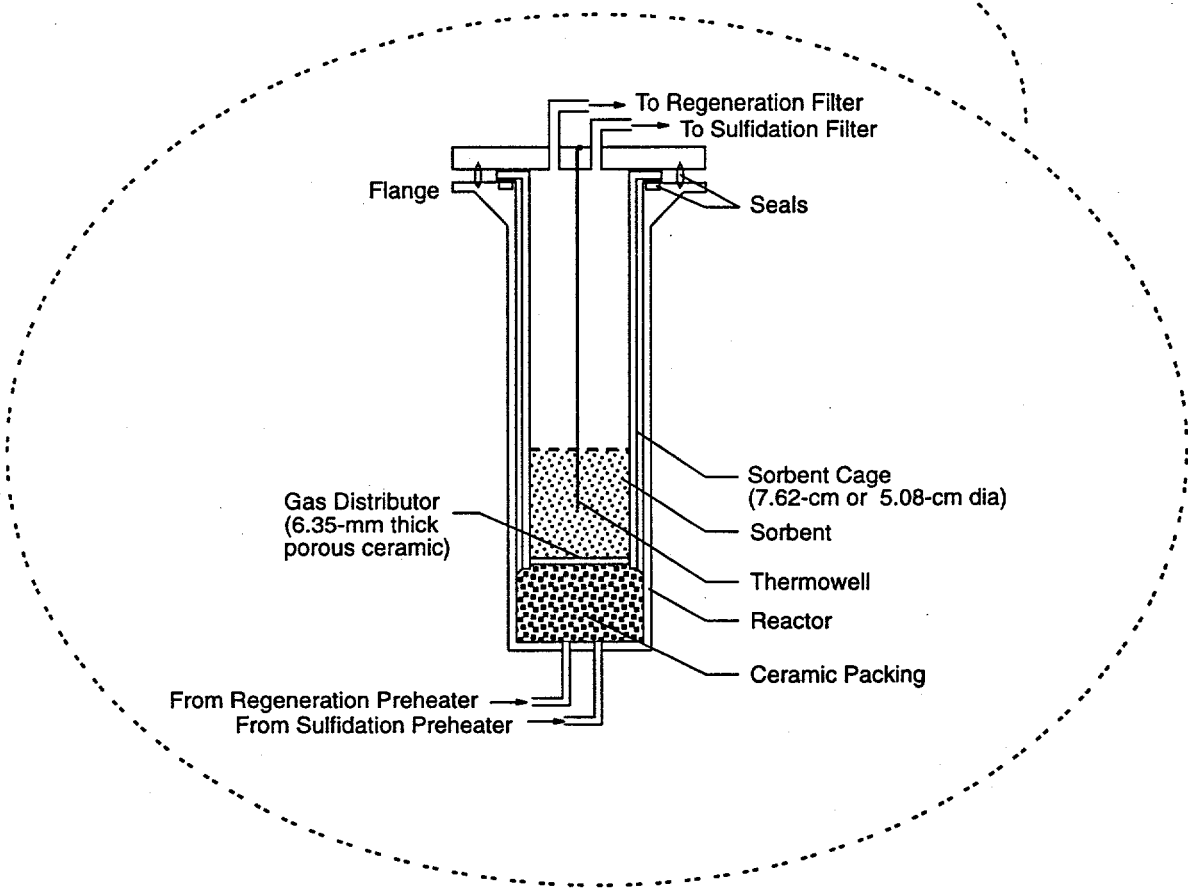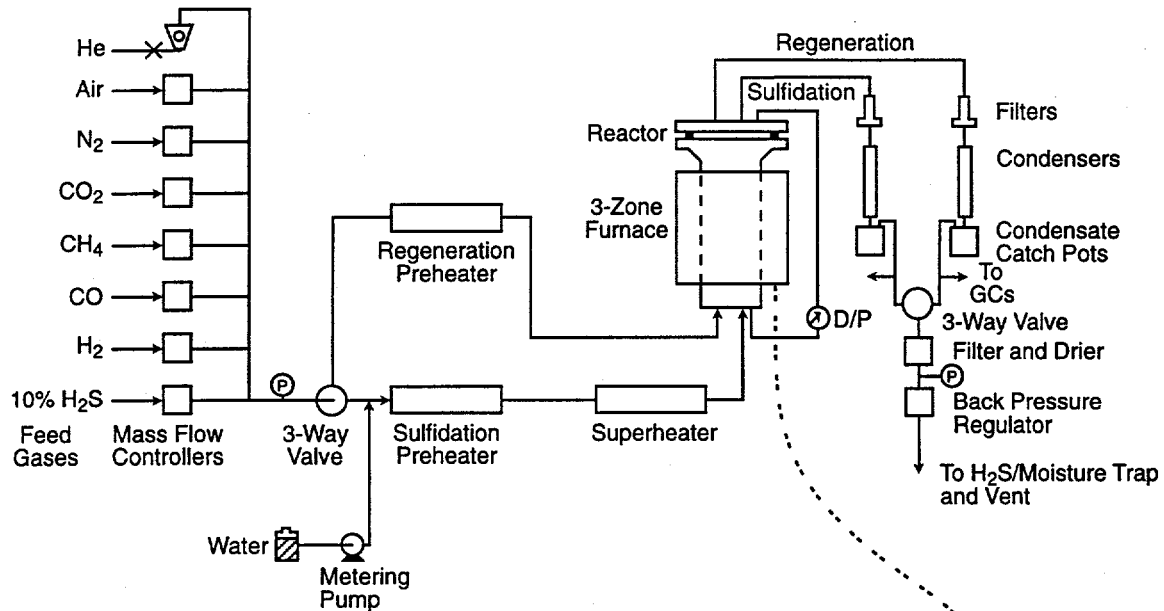
Figure 2. Bench-scale fluidized-bed sorbent test facility.

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controlled precisely by two back pressure regulators (BPRs) in series. A differential pressure indicator across the reactor provides an indication of fluidization behavior of the hot sorbent in the reactor.

A small slipstream of steam-free gas from the reactor is diverted to an online gas analysis system that consists of two gas chromatographs (GCs)—a Carle series 400 AGC with a thermal conductivity detector (TCD) and a Varian 3300 with a flame photometric detector (FPD). Both FPD and TCD are connected to Spectra Physics SP4270 integrators to measure the gas composition intermittently. Multiple GC sampling valves and dual loops in the Varian FPD measure H_2S and COS from 1,500 ppmv to <0.1 ppmv every 6 min. High concentrations of H_2S, SO_2, and other bulk gases (H_2, CO_2, N_2, O_2, CH_4, and CO_4) are measured every 25 min with the Carle TCD to evaluate mass balance. An online continuous SO_2 analyzer, Model 721 AT2 from Western Research, is used to measure the SO_2 evolution during sorbent regeneration.

A digital OM-480 Modular Data Logging Systems from Omega Instruments (Model No. 163568-96A) is used to automatically transfer process flow, concentration, pressure, and temperature data to personal computer via an RS232 serial cable. The computer is equipped with LabTech Note-Book software for real-time data acquisition and control of inflow and outflow of information from various channels of the data logger. Using this software, collected data are processed in real time through an extensive list of mathematical functions, displayed to the screen, and logged to a disk in a format that is directly compatable with a spreadsheet program such as Excel.

The facility, as shown in Figure 2, was modified for the NH_3 tests. These modifications included:

- Installing a heated sampling line for NH_3 analysis including a heated copper-bed to remove H_2S

- Installing a GC with a photoionization detector (PID) for analyzing NH_3 in coal gas (with most H_2S removed to prevent interference)

- Installing a feed MFC for a NH_3/N_2 or NH_3/H_2 mixture.

These modifications made the RTI HTHP unit's NH_3 sampling and analysis procedure equivalent to the system at SRI described in detail in Appendix A (pages 16–17). The NH_3 sampling/ analysis was carried out as described below.

A slipstream of hot coal gas (at about 250 °C) was withdrawn just downstream of the thimble filter and upstream of the water condenser. By using two hot metering valves in series and a pressure gauge, a flow rate of 500 to 600 cm^3/min was maintained. From this stream, about 35 cm^3/min was split to provide a sample for the GC. The entire slipstream flow path was heated to a temperature exceeding 150 °C to prevent water condensation and also to prevent ammonium carbonate formation.

The GC sample stream was passed through a bed of copper turnings which was heated to 180 °C for removal of hydrogen sulfide. It was believed that hydrogen sulfide in the GC sample could

cause problems with ammonia analysis because of reaction between ammonia and H_2S on-column or co-elution of ammonia and H_2S.

A six-port valve fitted with a 0.25 cm^3 SS loop and heated to 120 °C was used to inject a sample onto the column. The column consisted of a 6 ft by 1/8 in. OD Teflon tube packed with 80/100 mesh Chromosorb 103, operated at 120 °C. A helium carrier gas flow of 30 cm^3/min was maintained.

Ammonia was detected by a PID (OI Corporation Model 4430) which contains a 10.2 EV ultraviolet lamp. The detector operating temperature was 180 °C and it was mounted on a Hewlett-Packard Model 5890 GC. A detector sweep gas consisting of 30 cm^3/min helium was used to prevent contact of the column effluent with the detector lamp window (which could cause fouling).

Instrument control and chromatographic peak processing was performed with a Hewlett-Packard Model 3396 integrator. Analysis for ammonia was performed in a 2-min chromatographic run. Calibration of the detector response was performed daily with a 1,050-ppm ammonia in dry nitrogen compressed gas standard. Detector response linearity across the range of expected concentrations was verified.

3.2.2 Shakedown Test in a Blank Reactor

For checking the data quality of the HTHP facility a shakedown test was first conducted with no sorbent or catalyst in the Alon-processed SS reactor to ascertain complete NH_3 recovery and any decomposition of NH_3 due to catalytic activity of the reactor. Conditions for this test are outlined in Table 3.

Before carrying out the test, GC was calibrated using a primary standard containing 1,050 ppm NH_3 in N_2. Table 4 shows the results of GC-PID analysis. As can be seen, nearly complete ammonia recovery is obtained. The feedstock ammonia concentration determined by controlling the flow rate using an electronic MFC was 1,800 ppmv. The average outlet concentration of NH_3, as shown in

Table 3. Test Conditions for Shakedown Tests

Reactor temperature	727 °C
Reactor pressure	15 atm
Reactor total gas flow rate	35 slpm
Slipstream vent flow	$\approx$500 cm^3/min
GC sample flow (through the copper bed)	$\approx$35 cm^3/min

Feed Composition:

Gas	mol %
NH_3	0.18 (1,800 ppm)
H_2S	0.0857 (857 ppm)
CO_2	12%
H_2	30%
H_2O	18%
CO	40%

Sample Flowpath Temperatures:

Pressure reducing needle valve	169 °C
Copper bed	179 °C
Transfer tubing	194 °C
GC inlet tubing	147 °C

Table 4, was 1,827 ppmv with a standard deviation of 25 ppmv. These data clearly indicate complete NH_3 recovery with no apparent decomposition due to any catalytic activity of Alon-processed SS reactor.

3.2.3 Testing with Plain Zinc Titanate

Following the empty reactor test, the next series of tests were performed using the baseline ZT-4 zinc titanate sorbent in the reactor using a simulated Texaco coal gas shown in Table 5 with other conditions the same as shown in Table 3.

During the first cycle with ZT-4, it appeared that zinc titanate did decompose ammonia. However, it was later discovered that NH_3 sampling line going to the gas chromatograph had developed a leak. Therefore, validity of the data for this run was questionable.

The above run was repeated with the same batch of zinc titanate. Figure 3 shows the H_2S and NH_3 concentration profiles as a function of time. The feedstock level of NH_3 was about 1,800 ppm and the outlet ammonia concentration was also in the vicinity of 1,800 ppm, indicating no ammonia decomposition by the sorbent. This was expected and it confirmed the results obtained at SRI and GE.

To confirm that H_2S breakthrough behavior is not affected by the presence of ammonia in the coal gas, the next run was made without any NH_3 in coal gas. This run confirmed that the presence of NH_3 does not affect the H_2S capture efficiency of the sorbent.

Table 4. GC-PID Analysis Results

Time in the run (min)	NH_3 outlet concentration (ppm)
5	1,797
22	1,799
32	1,836
42	1,795
53	1,825
62	1,822
72	1,838
83	1,853
93	1,884
103	1,829
114	1,830
124	1,816
Mean:	1,827 ppm
Standard deviation:	25 ppm

Table 5. Nominal Texaco Coal-Gas Composition Used at RTI

Component	Vol%
CO	38.00
CO_2	12.85
H_2	28.50
H_2O	18.10
N_2	1.62
NH_3	0.18
H_2S	0.75
Total	100.0

3.2.4 Testing with Co-Mo Catalyst Mixed with Zinc Titanate

Having established no ammonia decomposition by zinc titanate, a Co-Mo catalyst was tested for its NH_3 decomposition activity. SRI prepared this catalyst by impregnating cobalt and molybdenum salts into a high surface titania. This catalyst contained approximately 10 percent Mo and 2 percent Co on titania.

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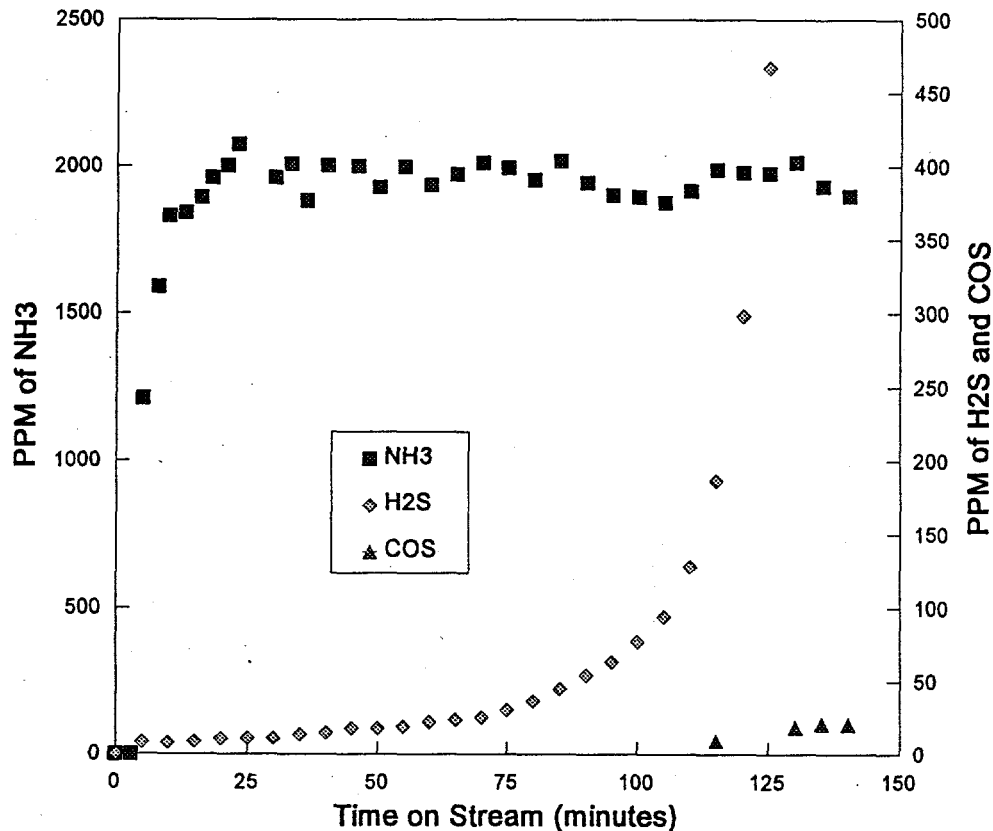**1000 K; Texaco Gas containing 1800 ppm NH3**

Figure 3. Ammonia decomposition by ZT-4.

Fifty grams of this catalyst were thoroughly mixed with 300 g of ZT-4 sorbent. This sorbent-catalyst mixture was loaded in the 2-in. ID sorbent cage, then the reactor was assembled and pressure-tested. A multicycle run comprised of 10 sulfidation-regeneration cycles was initiated to determine the long-term H_2S removal efficiency of the sorbent and the NH_3 decomposition activity of the catalyst.

The test conditions for this 10-cycle test are shown in Table 6.

Figure 4 shows the NH_3 and H_2S concentrations in the reactor exit gas as a function of time on stream. As expected, sorbent removed >99.9 percent H_2S before breakthrough. The NH_3 ppm profile indicates that the ammonia level is about 1,200 ppm (average) in the reactor exit gas, indicating about 33 percent NH_3 decomposition.

In order to keep Mo in the sulfided state, the sulfided sorbent-catalyst mixture was only partially regenerated. Regeneration was stopped approximately half-way in the steady-state SO_2

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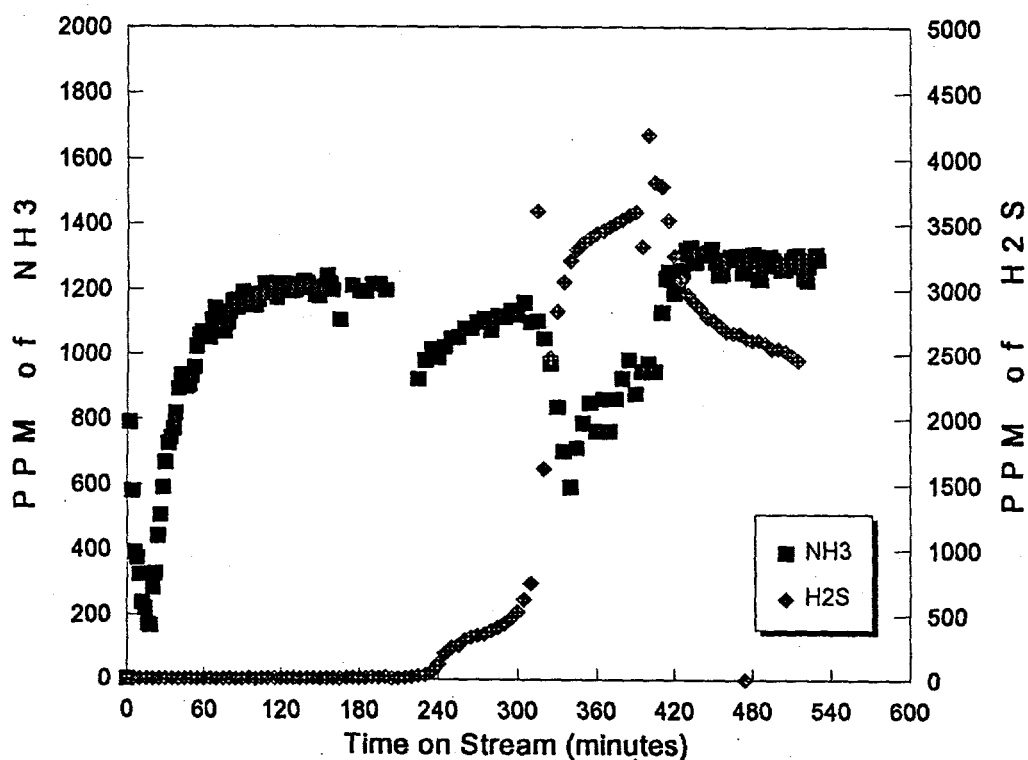## 300 g ZT-4 + 50 g Catalyst; 1000 K; Texaco Gas

Figure 4. Ammonia decomposition with Co-Mo catalyst.

concentration region as determined by the amount of sulfur captured during the sulfidation and SO_2 evolution rate during the regeneration.

The above sulfidation-regeneration sequence was continued for 10½ cycles. During Cycles 1 to 11, the NH_3 and H_2S evolution behavior was very similar to that of Cycle 1 shown in Figure 4 indicating about 33 percent NH_3 decomposition during all 11 cycles.

To confirm that this NH_3 decomposition was real and was free from analytical or sampling errors, a 2-cycle test was made with ZT-4 with no catalyst. During this test NH_3 evolution profile indicated a very similar trend (except that the calculated NH_3 decomposition was about 20 to 25 percent compared to 30 to 35 percent with sorbent-catalyst mixture) that was observed with 10½ cycle sorbent-catalyst testing described above. As shown previously in Figure 3, ammonia decomposition by zinc titanate was negligible, indicating that there was an error somewhere. To investigate this problem, a detailed check was performed to ensure that no NH_3 was lost in the sampling system. This was established by passing a 1,000-ppm calibration standard sample stream through the sampling system and measuring it downstream by GC/PID. This check indicated nearly complete NH_3 recovery. The second check was on the flow rate of NH_3 stream

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Table 6. Test Conditions for Multicycle Test

Sorbent charge	300 g of ZT-4
Catalyst charge	50 g of Co-Mo catalyst
Total gas flow	17.5 slpm
Space velocity	~3,800/h[a]
Total pressure	15 atm
Sulfidation	
Temperature	~727 °C (1,000 K)
Sulfidation gas	Simulated Texaco-Gas[b]
Inlet NH_3 concentration	1,800 ppm
Regeneration	
Temperature	720 to 760 °C
Regeneration gas	2 to 2.5% O_2 in N_2

[a] Calculated assuming 80 lb/ft^3 bulk density of sorbent-catalyst mixture. It is based on the total combined volume of sorbent and catalyst and calculated at 0 °C at 1 atm (STP).

[b] Nominal gas composition: CO = 38%; CO_2 = 12.85%; H_2 = 28.5%; N_2O = 18.1%; N_2 = 1.62%; H_2S = 0.75% (7,500 ppm) and NH_3 = 0.18% (1,800 ppm).

by a 4 slpm MFC; measurement of flow rate found this to be functioning properly. Finally, the last thing that could have been responsible for this error was the composition of NH_3 in the gas mixture bottle. It was a certified mixture of 10.7 percent NH_3 in N_2 purchased from Matheson Gas. This gas cylinder was checked against our previous gold standard that was used earlier during the shakedown tests. This gold standard was used when tests were performed with ZT-4 to establish no NH_3 decomposition by the sorbent (Figure 3).

Testing of this 10.7 percent NH_3 in N_2 mixture in the GC/PID indicated that the actual NH_3 concentration was only 7.7 percent as opposed to 10.7 percent certified by the vendor. This led to a feedstock NH_3 composition of about 1,300 ppm (as opposed to the intended 1,800 ppm). This error in the gas composition resulted in a maximum of 10 percent NH_3 decomposition by the sorbent catalyst as compared to 33 percent as suspected earlier.

Based on the its NH_3 decomposition potential, the simultaneous NH_3 and H_2S removal approach was de-emphasized in favor of the high-temperature catalytic decomposition approach described in Section 4.