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Simultaneous Removal of H_2S and HN_3 From Coal Gas

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ABSTRACT

Hydrogen sulfide (H_2S) and ammonia (NH_3) are the primary sulfur and nitrogen contaminants released when coal is gasified. Before coal gas can be utilized in an integrated gasification combined cycle (IGCC) plant to produce electricity, these contaminants need to be removed. The objective of this research was to develop sorbent-catalysts with the ability to simultaneously remove H_2S and NH_3 from coal gas. Microreactor tests with HART-49, a zinc-based sorbent-catalyst with Ni, Co, and Mo as catalyst additives, showed that this material had the potential to remove 90 percent NH_3 and reduce H_2S to <20 ppmv at 1 atm and 550 to 700 °C. HART-49 was prepared in attrition-resistant fluidizable form (HART-56) using up to 75 wt% binder. Bench-scale fluidized-bed multicycle tests were conducted with the attrition-resistant sorbent-catalyst, HART-56, at 20 atm and 550 °C. The H_2S and NH_3 removal performance over the first two cycles was good in the presence of 5 percent steam but deteriorated thereafter when steam level was increased to 15 percent. The results point to a complex mechanism for simultaneous H_2S and NH_3 removal, potentially involving both chemisorption and catalytic decomposition of NH_3. Further research and development is needed to develop a sorbent-catalyst for simultaneous H_2S and NH_3 removal at IGCC hot-gas cleanup conditions.

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EXECUTIVE SUMMARY

Advanced integrated gasification combined cycle (IGCC) power plants under development employ hot particulate removal and hot-gas desulfurization (HGD) to achieve higher thermal efficiency than conventional IGCC plants employing cold gas cleanup. HGD involves the removal of hydrogen sulfide (H_2S) using metal regenerable metal oxide sorbents. These sorbents, typically zinc-based, remove the H_2S by sulfidation and are regenerated by air-oxidation of the metal sulfide in a cyclic manner.

Coal gas also contains ammonia (NH_3) that needs to be removed to reduce NO_x formation in the gas turbine. Catalytic decomposition of NH_3 to nitrogen (N_2) and hydrogen (H_2) is an attractive method for NH_3 removal. By combining the NH_3 decomposition catalyst with the H_2S metal oxide sorbent to produce a simultaneous H_2S and NH_3 removal sorbent-catalyst, cost savings can be potentially achieved.

The objective of this study is to develop and demonstrate catalytic approaches for decomposing a significant percentage (up to 90 percent) of the NH_3 present in coal gas to N_2 and H_2 at elevated temperatures (550 to 900 °C).

Both high-temperature catalytic decomposition upstream of HGD and simultaneous H_2S and NH_3 removal approaches were investigated. A Topical Report on high-temperature catalytic decomposition submitted earlier details the work until the end of FY97 and is attached as Appendix 1. In this work, catalytic decomposition of up to 90 percent NH_3 in the presence of H_2S at temperatures >850 °C was demonstrated in both bench-scale and coal gasifier slipstream tests. Preliminary attempts at developing a combined sorbent-catalyst were only moderately successful. Hampton University and Research Triangle Institute (RTI) in a parallel study (DOE Contract No. DE-FG22-93MT93005) developed a promising zinc-based HART-49 sorbent-catalyst in laboratory research. Based on this research, the present work was undertaken at RTI with Hampton University as a subcontractor.

The HART-49 sorbent-catalyst powder showed >90 percent NH_3 removal and H_2S removal down to <20 ppmv in microreactor tests at 1 atm and 500 to 700 °C. Using the HART-49 sorbent composition, a series of attrition-resistant fluidizable sorbent-catalysts (HART-50 to HART-55) were prepared with up to 75 percent binder. HART-55 gave the best combination of attrition resistance and performance in microreactor testing. HART-55 was scaled up to produce a 200-g batch (designated HART-56) which was selected for fluidized-bed bench-scale testing. A 20-cycle bench-scale test was conducted on this material at 20 atm and 550 °C.

Microreactor tests with HART-55 showed that pressure promoted the removal of NH_3, contrary to thermodynamic predictions. Some NH_3 release occurred from the sorbent-catalyst during regeneration, which indicated chemisorption during sulfidation as a potential explanation of the pressure effect. At 10 atm, >90 percent NH_3 removal was maintained up to 6 wt% sulfur loading on the sorbent-catalyst, consistently over seven cycles.

The 20-cycle bench-scale test showed a high degree of NH_3 removal with 5 percent steam in coal gas over the initial cycles. This result agreed with the microreactor results. However, when the steam was increased to 15 percent in subsequent cycles, the NH_3 removal performance deteriorated significantly. The results indicate that HART-56 was not successful in achieving significant NH_3 removal at 550 °C and 20 atm except when low steam (around 5 percent) was present in the coal gas. Also, reversible adsorption of NH_3 appeared to occur on the sorbent, which could be removed by purging.

The NH_3 removal mechanism on the HART-49 based sorbent-catalysts is complex with reversible adsorption as well as decomposition occurring at higher pressure. Further work is needed to optimize the sorbent-catalyst preparation to get a balanced material with acceptable attrition resistance, NH_3 removal performance, and cost. With high levels of binder used here, an attrition resistance better than needed was achieved but at the expense of reactivity. The NH_3 removal mechanism needs to be evaluated with fundamental studies, particularly with respect to adsorption behavior on the sorbent catalyst at higher pressure and the dramatic effect of steam. The attrition-resistant HART-56 sorbent appears to have potential for removing 90 percent NH_3 and reduce H_2S to <20 ppmv, when 5 percent steam is present in the coal gas. However, further development of the material is needed for coal gas with higher steam.

1.0 INTRODUCTION AND OBJECTIVES

Integrated coal gasification combined cycle (IGCC) electric power plants are being developed worldwide because of their potential for higher thermal efficiency and superior environmental performance compared to conventional pulverized-coal combustion-based plants (1-4). Coal gasification results in a number of contaminants that are released into the coal gas. These include particulates, sulfur gases (principally hydrogen sulfide [H_2S]), nitrogen compounds (principally ammonia [NH_3]), and trace contaminants such as alkali, chloride, and heavy metals. These contaminants need to be removed or significantly reduced before the coal gas can be burned in an IGCC gas turbine to make electricity. The coal gas is typically quenched using a water spray down to low temperatures (below 50 °C), and conventional contaminant removal operations are conducted. The cooling, however, results in a significant thermal efficiency penalty and a waste-water stream that must be disposed of. These plants also end up being capital intensive.

1.1 Hot-Gas Desulfurization

To reduce the cost of IGCC and to increase its overall thermal efficiency, advanced IGCC plants employing hot-gas cleanup methods, rather than quench/low-temperature cleanup, are being developed (3,5-7). The sponsorship and leadership in this development have been provided by the U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC). Hot-gas cleanup methods employ hot particulate removal (using ceramic filters) and hot-gas desulfurization (HGD) subsystems operating at high-temperature, high-pressure (HTHP) conditions downstream of the coal gasifier and upstream of the gas turbine.

Research on HGD methods for coal gas in IGCC systems has concentrated on the use of regenerable metal oxide sorbents (8-16). Oxides of copper, cerium, manganese, cobalt, tin, iron, and zinc, both individually and in combinations, have been evaluated as regenerable sorbents. These metal oxide or mixed-metal oxide sorbents have been investigated without, as well as combined with, a secondary oxide, typically silica, alumina, titania, and chromium oxide. The roles of these secondary oxides include support for strengthening mechanical structure and stabilizer against reduction of the metal.

Zinc titanate, formed by combining zinc oxide and titanium oxide at high temperature, is currently one of the sorbent candidates for HGD (8,9). It can remove H_2S down to low parts-per-million levels over a wide temperature range and it can be regenerated for multicycle operation. Depending on the Zn to Ti ratio in zinc titanate, a number of phases such as $ZnTiO_3$, $Zn_2Ti_3O_8$, and Zn_2TiO_4 can form.

At demonstration-scale, the HGD process is carried out in a two-reactor system, consisting of a sulfider and an air-regenerator (8,11). An example of such a system is the M.W. Kellogg transport-reactor HGD unit (Figure 1) at the Sierra-Pacific Clean Coal Demonstration Plant (11). Using $ZnTiO_3$ as an example, the HGD reactions are shown below:

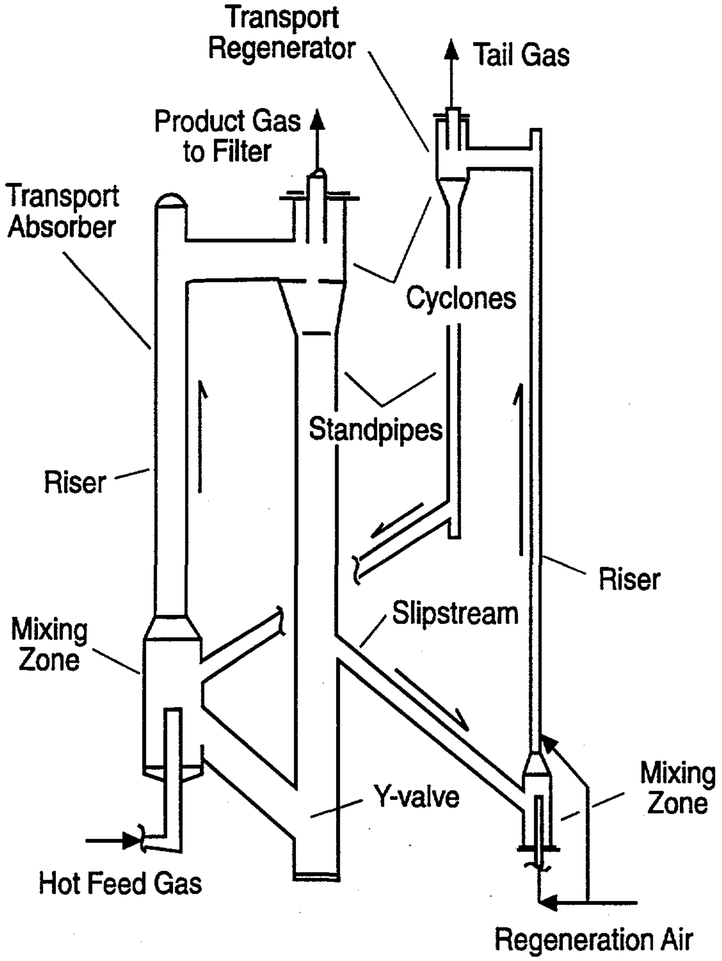

Figure 1. Schematic of Sierra-Pacific transport reactor system.

$$ZnTiO_3 + H_2S \rightarrow ZnS + TiO_2 + H_2O \qquad \text{(sulfider)}$$

$$ZnS + TiO_2 + \frac{3}{2} O_2 \rightarrow ZnTiO_3 + SO_2 \qquad \text{(regenerator).}$$

The zinc titanate sorbent continuously circulates between the two reactors. The SO_2 containing tail gas from the regenerator can be converted to salable products such as sulfuric acid or elemental sulfur or disposed of as calcium sulfate in downstream operations (17).

1.2 Ammonia Removal

The principal nitrogen contaminant released during coal gasification is NH_3. When coal gas is combusted in a gas turbine, NH_3 has the propensity to form oxides of nitrogen (NO_x) which are difficult-to-remove pollutants and precursors to acid rain and ozone. There are three potential methods of controlling NO_x emissions in an advanced IGCC plant (18,19). These include postcombustion selective catalytic reduction (SCR), two-stage combustion in the turbine and catalytic NH_3 decomposition ($NH_3 \rightleftharpoons [1/2]\ N_2 + [3/2]\ H_2$) upstream of the gas turbine. SCR, while a proven technology, would be very expensive downstream of the turbine due to a large volume, dilute tail gas. Scaleup will be difficult for the two-stage combustion approach. A somewhat analogous approach of selective catalytic oxidation of NH_3 using NO has also been investigated (20,21). The most attractive option is believed to be catalytic decomposition of the NH_3 in the HTHP coal gas since the high temperature is already available.

Studies of catalytic NH_3 decomposition under hot coal gas conditions are relatively few. A ZnO catalyst, a bulk iron catalyst, a Pt-Al_2O_3 catalyst, and an Ag-Al_2O_3 catalyst were tested under simulated coal gas conditions at 425 to 750 °C (21). Although these catalysts moderately reduced the NH_3 concentration, they were quickly poisoned in the presence of H_2S. A nickel-based catalyst from Haldor-Topsoe was shown to be effective for NH_3 decomposition under simulated coal gas conditions above 800 °C (18,19) in the presence of moderate levels of H_2S and at 550 to 725 °C in the presence of low parts-per-million levels of H_2S. However, moderate levels of H_2S quickly poisoned the catalyst in the 550 to 725 °C range. Molybdenum in its sulfided form (MoS_2) has been shown to have moderate activity for NH_3 decomposition (18). The addition of molybdenum to zinc titanate has also been shown to be somewhat effective for NH_3 decomposition (22). The use of very high temperatures (>800 °C) is one option for catalytic NH_3 decomposition. However, this temperature is available only upstream of the high-temperature particulate filter in an IGCC system. Thus, the catalyst would have to be active in the presence of particulates. The high temperature would also tend to sinter the catalyst (23,24).

1.3 Simultaneous H_2S and NH_3 Removal

An attractive approach appears to be to add a NH_3 decomposition catalyst to the zinc titanate sorbent and use the resulting sorbent-catalyst to simultaneously remove the H_2S and the NH_3 from hot coal gas. If successful, this approach would result in reducing the cost of the IGCC plant (22,25). However, the catalyst must be stable in both reducing and oxidizing atmosphere and in the presence of H_2S over multiple cycles.

1.4 Objective

The objective of this study is to develop and demonstrate catalytic approaches for decomposing a significant percentage (up to 90 percent) of the NH_3 present in coal gas to N_2 and H_2 at elevated temperatures (550 to 900 °C).

2.0 PREVIOUS WORK

Previous work until the end of FY97 under this contract was submitted as a Topical Report to DOE and is attached as Appendix 1. In this work, catalytic decomposition of up to 90 percent NH_3 in the presence of H_2S at temperatures >850 °C was demonstrated in both bench-scale and coal gasifier slipstream tests. Preliminary attempts at developing a combined sorbent-catalyst using zinc titanate for simultaneous H_2S and NH_3 removal were only moderately successful. Hampton University and the Research Triangle Institute (RTI) in a parallel study (DOE Contract No. DE-FG22-93MT93005) developed a zinc-based HART-49 sorbent-catalyst in laboratory research. The HART-49 sorbent-catalyst was a zinc-based sorbent-catalyst containing 5 wt% each of Ni, Co, and Mo (the preparation procedure is proprietary). The BET surface area of this material was 4.7 m^2/g. In a 1-g fixed-bed microreactor, at 1 MPa and 500 to 700 °C, this material showed decomposition of >90 percent NH_3 and removal of H_2S to <20 ppmv over a substantial portion of the desulfurization cycle. Also, the material, tested over 30 cycles, showed excellent regenerability. Thus the HART-49 sorbent-catalyst was chosen in this study for further development and scaleup in attrition-resistant form. Based on the research at Hampton University, the present work was undertaken at RTI with Hampton University as a subcontractor.

3.0 HART-49 SORBENT-CATALYST DEVELOPMENT

Using the HART-49 sorbent composition, a series of attrition-resistant fluidizable sorbent-catalysts (HART 50-55) were prepared with up to 75 percent binder. HART-55 gave the best combination of attrition resistance and performance in microreactor testing. HART-55 was scaled up to produced a 200-g batch (designated HART-56) which was selected for fluidized-bed bench-scale testing.

3.1 Experimental Apparatus and Conditions

The fixed-bed microreactor and bench-scale fluidized-bed reactor systems are shown in Figures 2 and 3, respectively.

The microreactor system consisted of a simulated coal gas delivery subsystem, a reactor with 1 g of sorbent-catalyst surrounded by a furnace, and a downstream sample collection, vent and gas analysis setup. The simulated coal gas and conditions used for the tests are shown in Table 1. This gas simulated a typical gas from an air-blown KRW coal gasifier. Steam was added using a high-pressure syringe pump feeding deionized water into a vaporizer. NH_3 and H_2S were added downstream of the vaporizer to prevent undesirable low-temperature reactions in the tubing.

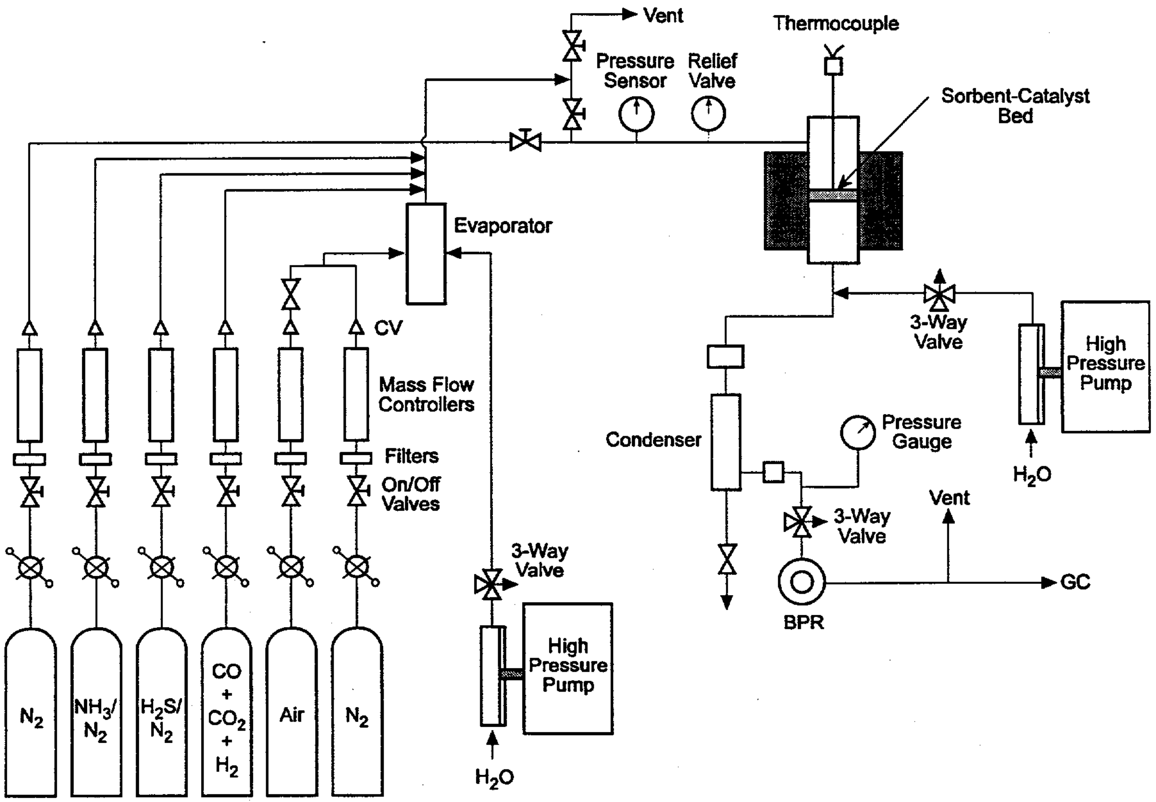

Figure 2. Fixed-bed microreactor sorbent-catalyst test unit.

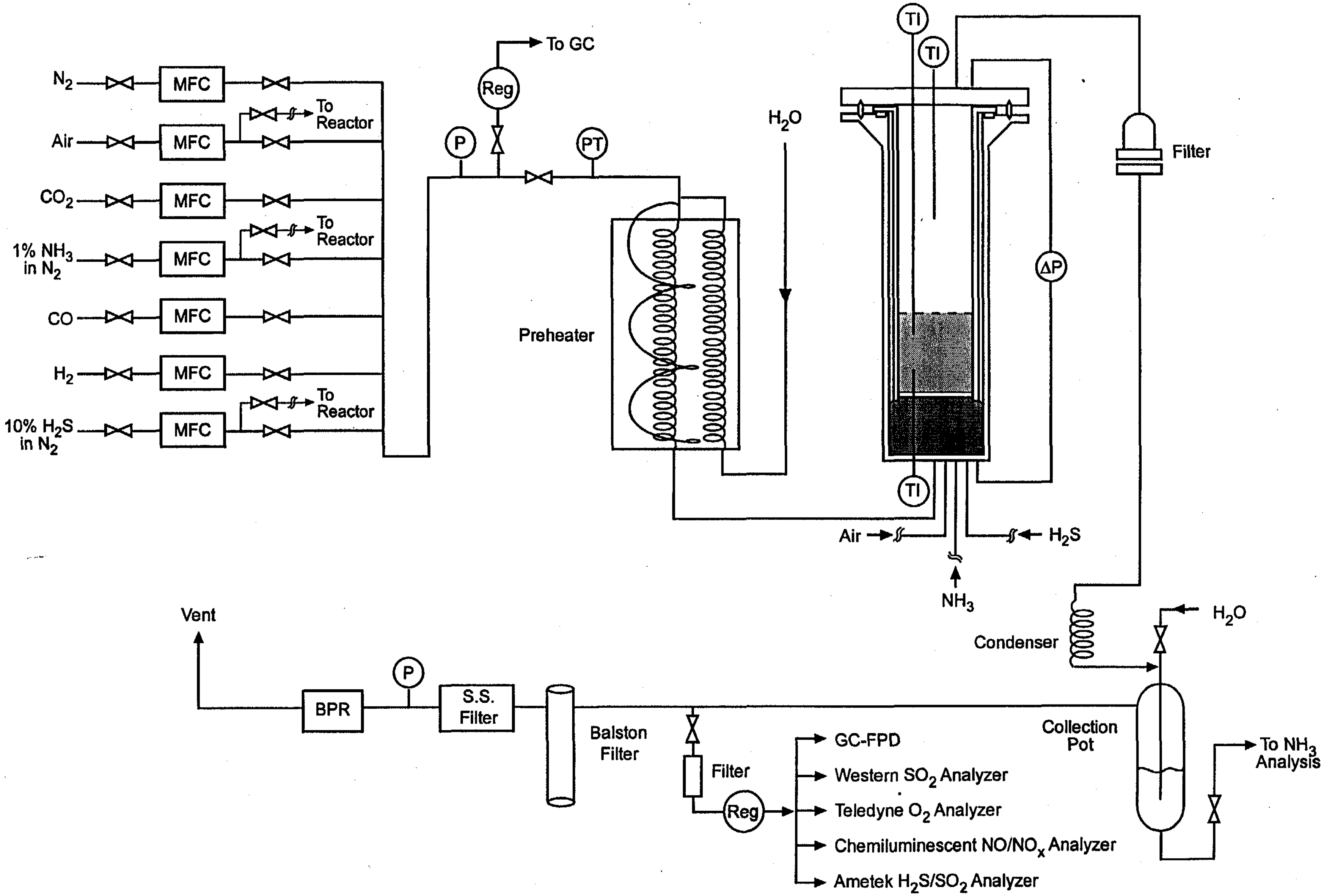

Figure 3. Bench-scale fluidized sorbent-catalyst test unit.

The reactor was constructed using a ½-in. 316 stainless steel (SS) tube, aluminized on the inside (by Alon Processing, Tarentum, Pennsylvania) to prevent corrosion due to H_2S. A porous alumina frit in the middle of the tube was used to support 1 g of the material. A thermocouple was positioned to measure the sorbent-catalyst bed temperature.

The gas leaving the reactor was mixed with deionized water supplied by a pump at 0.5 cm^3/min to scrub out the NH_3. The liquid sample was collected in a catchpot-condenser and analyzed every 15 min for NH_3 breakthrough and to measure percent NH_3 conversion (removal). Thus, the NH_3 conversion was based only on the disappearance of NH_3 and products associated with NH_3 removal or decomposition were not analyzed. The NH_3 measurement in the liquid sample was conducted using an Orion Model 95-12 ammonia ion selective electrode (ISA). Independent measurements of the liquid samples for ammonium ion using a Dionex ion chromatograph gave about 10 to 15 percent higher values of NH_3 in the sample than the ISA.

The gas leaving the condenser was verified to be free of NH_3 by bubbling it through an impinger containing water over a long period of time and analyzing the water using the ISA. The gas was vented through a back-pressure regulator and sent to a gas chromatograph (GC) with flame-photometric detector (FPD) for measurement of H_2S during sulfidation and SO_2 during regeneration.

A typical cycle in a run consisted of flowing coal gas at desired temperature through the sorbent-catalyst bed. H_2S and NH_3 were periodically measured in the effluent. When H_2S broke through to a level of 100 to 500 ppm, the sulfidation was stopped, and regeneration was begun at 550 to 700 °C using 2 vol% O_2 in N_2. SO_2 was measured in the effluent gas and when SO_2 dropped below 50 ppm, the regeneration was stopped. Multicycle tests were conducted by repeating cycles in this manner.

The bench-scale fluidized-bed reactor system (Figure 3) was essentially a scaled-up version of the microreactor system, with minor differences. The reactor housed a 2.0 in. Alon-processed 316 SS sorbent-catalyst cage capable of testing up to 300 g of material. The NH_3 was collected in the water effluent and analyzed using ion chromatography. The effluent gas was analyzed for H_2S during sulfidation and SO_2, O_2, and NO/NO_x during regeneration. The simulated coal gas composition and sulfidation test conditions used for the microreactor and bench-scale reactor are shown in Tables 1 and 2.

3.2 Results and Discussion

The results of microreactor testing of HART-49 sorbent-catalyst powder are shown in Figures 4-6. The performance of HART-49 at 1 atm and 700 °C is shown in Figure 4. The H_2S removal below 20 ppm was maintained for 400 min prior to breakthrough in both the presence and absence of steam. NH_3 removal of >90 percent was maintained throughout the cycle in the absence of steam. Even with 15 percent steam, >90 percent NH_3 removal was maintained for 190 min. Results of the 10th, 20th, and 30th cycle for HART-49 at 700 °C and 1 atm (Figure 5) show consistent NH_3 and H_2S removal over 30 cycles by this sorbent-catalyst. The effect of tem-

Table 1. Simulated KRW Gas Composition (vol%)

	Bench-scale fluidized bed	Fixed-bed microreactor
H_2	10.6	10.0
CO	17.0	15.0
CO_2	9.0	5.0
H_2O	5.0 to 15.0	0 to 15.0
H_2S	0.3 to 0.6	1.0
NH_3	0.16	0.18
N_2	Balance	Balance

Table 2. Reaction Conditions

	Bench-scale fluidized bed	Fixed-bed microreactor
Pressure (atm)	20	1 to 10
Temperature (°C)	550	550 to 700
Space velocity $\left(\frac{\text{std cm}^3}{\text{cm}^3 \cdot \text{h}}\right)$	7,500	2,500

perature on performance of the HART-49 sorbent is shown in Figure 6. Even at a temperature as low as 500 °C, NH_3 removal remained high for 70 min, up to 6 wt% sulfur loading on the sorbent.

At this point, modifications were made to the HART-49 powder to develop it in attrition resistant fluidizable form. The preparation is proprietary. After a number of trials, HART-55 sorbent was prepared. Its attrition resistance was better than commercial fluidized catalytic cracking (FCC) catalysts used extensively in refineries. A high level of binder was incorporated in the sorbent to impart it a high degree of attrition resistance.

The effect of pressure on the window of high NH_3 removal by HART-55 is shown in Figure 7. As seen, pressure promotes the removal of NH_3. This is contradictory to thermodynamic predictions and indicates the possibility of NH_3 chemisorption on the sorbent, in addition to decomposition. Some NH_3 release from the sorbent was observed during regeneration, which lends credence to the possibility of NH_3 chemisorption during sulfidation. Figure 8 shows the

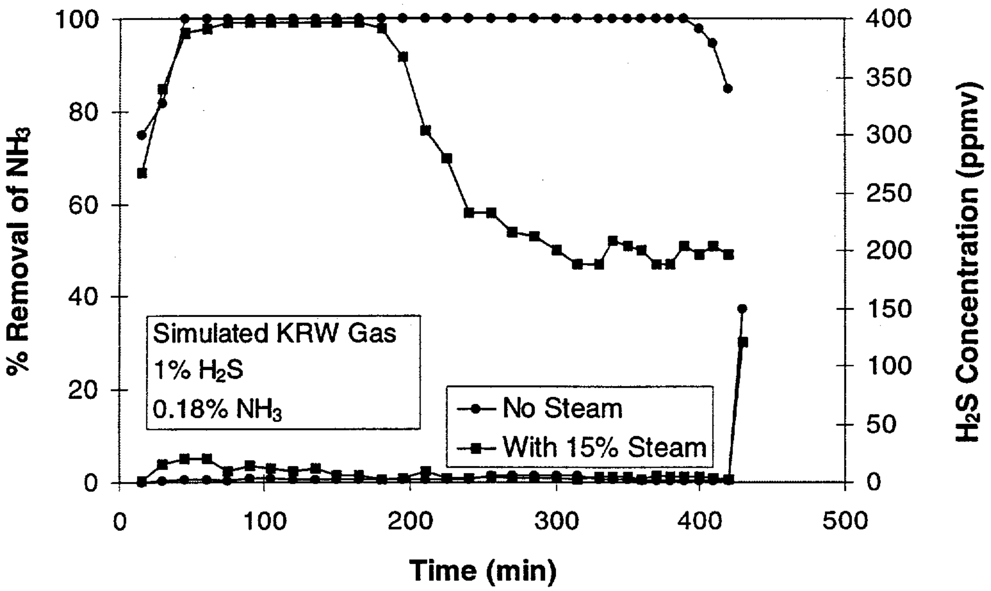

Figure 4. Simultaneous H_2S and NH_3 removal using HART-49 at 700 °C and 1.0 atm.

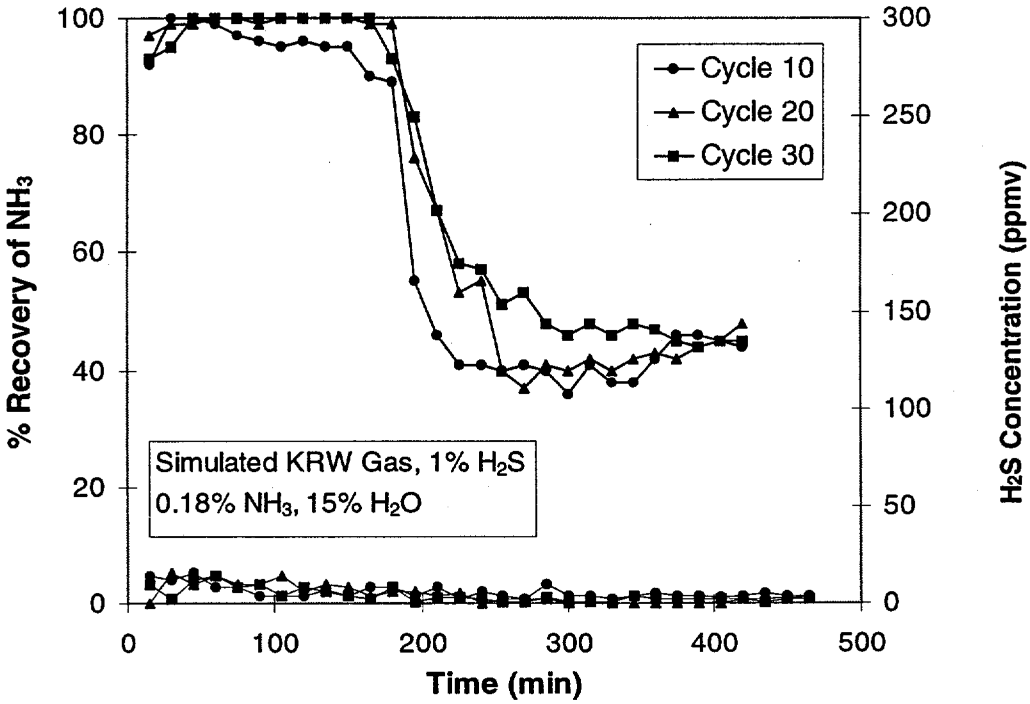

Figure 5. Multicycle NH_3 removal performance of HART-49 at 700 °C and 1.0 atm.

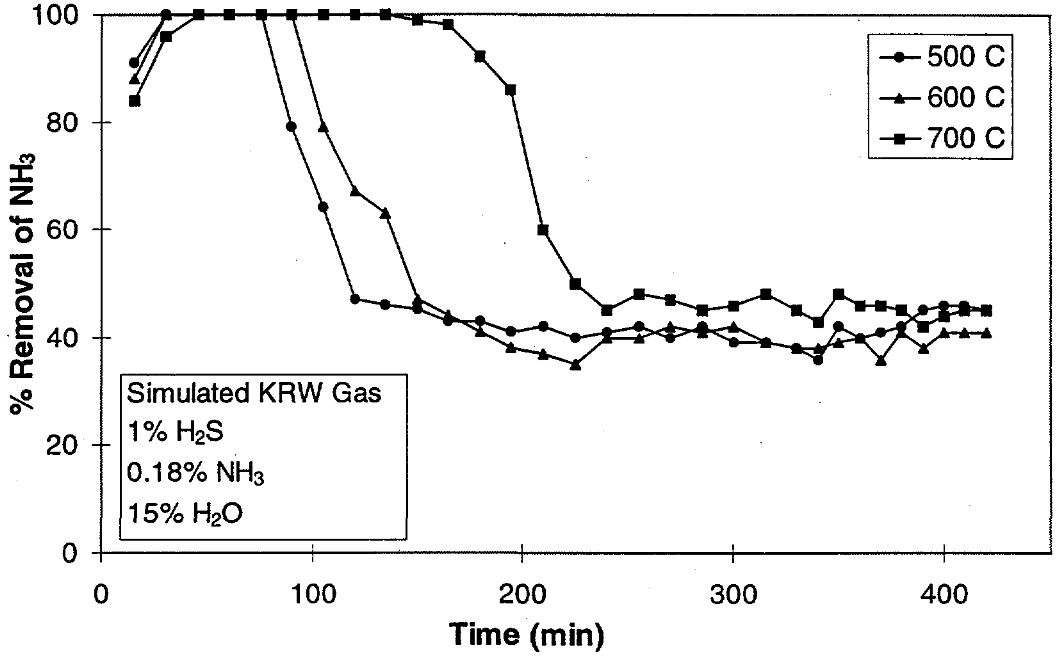

Figure 6. Effect of temperature on NH_3 removal by HART-49 at 1.0 atm.

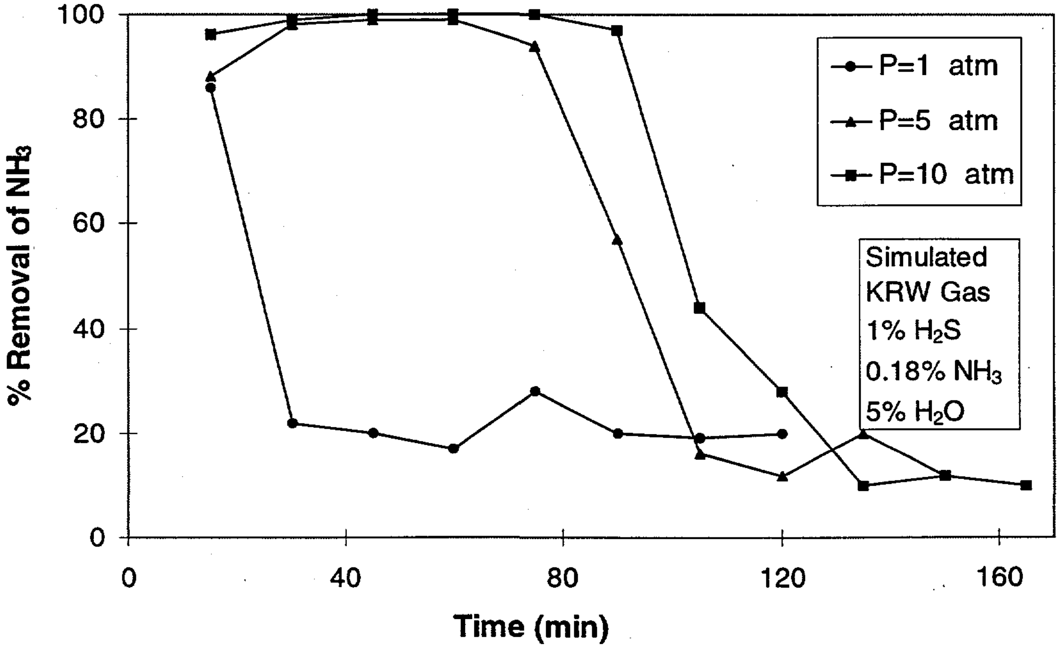

Figure 7. Effect of pressure on NH_3 removal by HART-55 at 550 °C.

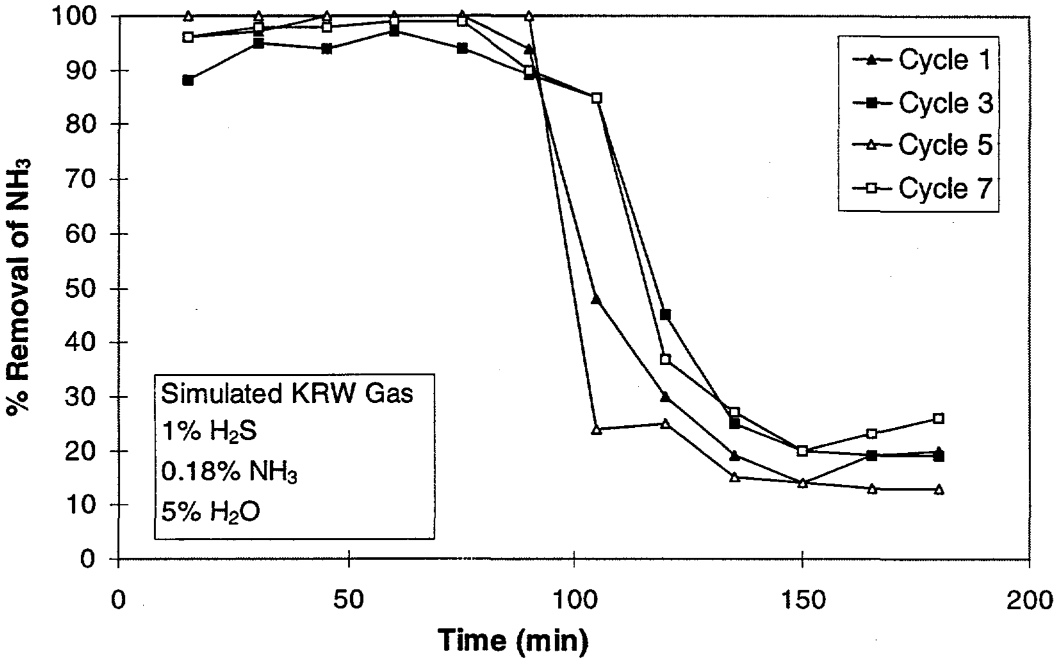

Figure 8. Removal of NH_3 on HART-55 at 550 °C and 10 atm.

results of a seven-cycle test at 10 atm on HART-55. The consistent results over seven cycles show that the sorbent is behaving reproducibly after regeneration.

At this point the HART-55 sorbent-catalyst preparation was scaled up to prepare 200 g for the 20 atm fluidized-bed tests. The scaled-up material, designated HART-56, was tested over 20 cycles in the 2.0-in. bench-scale fluidized-bed reactor system. The average NH_3 and H_2S removal results for the first two cycles (with 5 percent steam in the KRW gas) are shown in Figure 9. A high degree of NH_3 and H_2S removal was achieved over the first two cycles, confirming the micro-reactor results of Figure 8. However, NH_3 was seen to elute from the material during purges and regeneration, again indicating chemisorption during sulfidation. Performance after the first two cycles, when steam in the coal gas was increased to 15 percent, deteriorated. The NH_3 balance over the 20 cycles is shown in Figure 10.

The reactor was purged with N_2 after both sulfidation (purge #1) and regeneration (purge #2) during the 20-cycle test. During regeneration, no NO or NO_2 was found in the regeneration tail gas. As seen, the average NH_3 accounted for during cycles 1 and 2 was about 59 percent, indicating only about 41 percent average removal during sulfidation. The average removal deteriorated significantly during cycles 3 to 20, carried out with 15 percent steam. The results indicate that HART-56 was not successful in achieving significant NH_3 removal at 550 °C and 20 atm except when 5 percent steam was present in the simulated coal gas. Also, reversible adsorption of NH_3 appeared to occur on the sorbent, which could be removed by purging.

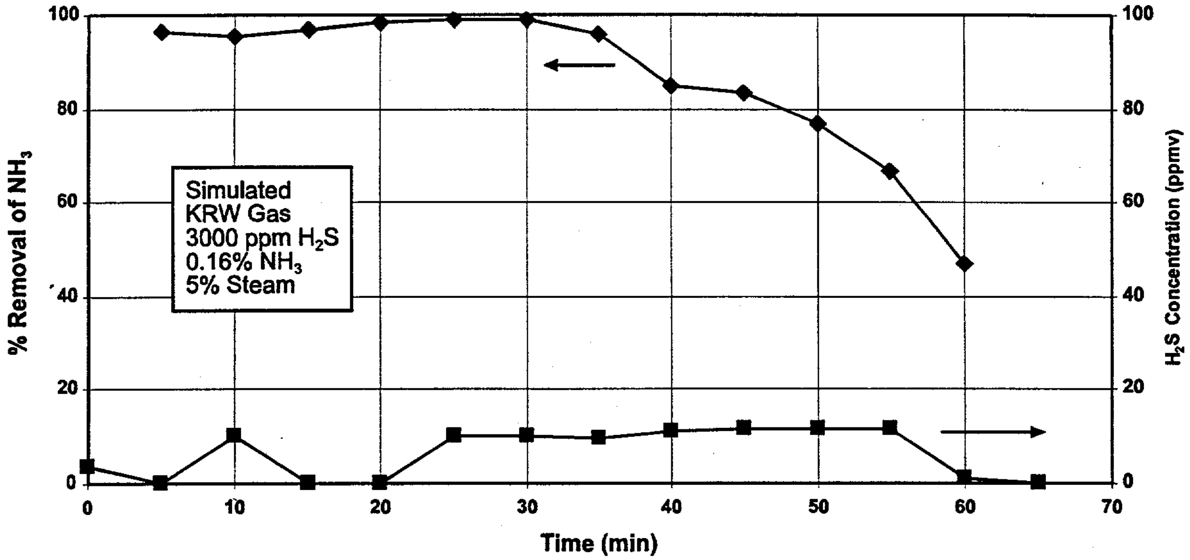

Figure 9. NH_3 and H_2S removal by HART-56 at 20 atm and 550 °C, bench-scale cycles 1 and 2.

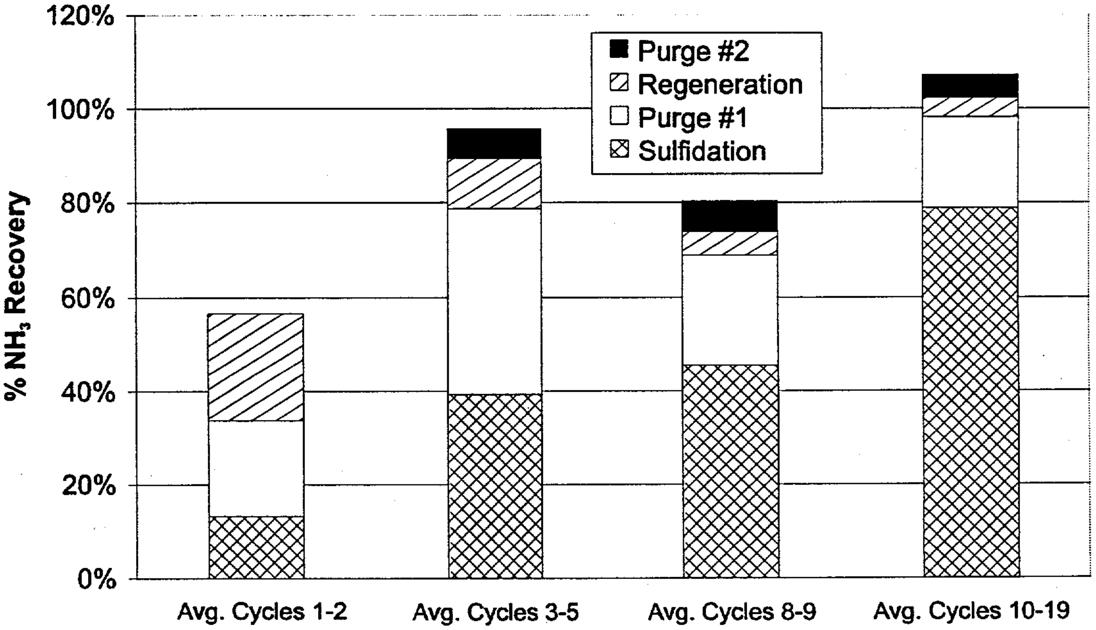

Figure 10. Summary of NH_3 removal and recovery in bench-scale tests.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Successful development of a sorbent-catalyst for simultaneous removal of H_2S and NH_3 will result in reducing the overall cost of IGCC systems. HART-49, a lab-scale powder preparation (with high levels of active materials and no binder), showed promising results for simultaneous H_2S and NH_3 removal at 1 atm and 500 to 700 °C. The removal efficiency decreased as temperature decreased but increased significantly as steam concentration in simulated coal gas decreased. Addition of significant level of binder (up to 75 wt%), with corresponding reduction in the amount of active ingredients, resulted in a hard attrition-resistant sorbent-catalyst with better attrition resistance than FCC catalyst. However, its H_2S and NH_3 removal performance deteriorated. The NH_3 removal mechanism on the HART-49-based sorbent-catalysts is complex with reversible adsorption as well as decomposition occurring at higher pressure.

Further work is needed to optimize the sorbent-catalyst preparation to get a balanced material with acceptable attrition resistance, NH_3 removal performance, and cost. With high levels of binder used here, an attrition resistance better than needed was achieved but at the expense of reactivity. The NH_3 removal mechanism needs to be evaluated with fundamental studies, particularly with respect to adsorption behavior on the sorbent-catalyst at higher pressure and the dramatic effect of steam. The attrition-resistant HART-56 sorbent appears to have potential for removing 90 percent NH_3 and reduce H_2S to <20 ppmv, when 5 percent steam is present in the coal gas. However, further development of the material is needed for coal gas with higher steam.

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Appendix 1

Catalytic Ammonia Decomposition for Coal-Derived Fuel Gases

Topical Report

July 1997

Catalytic Ammonia Decomposition for Coal-Derived Fuel Gases

Topical Report

Work performed under
Contract No. DE-AC21-92MC29011

for
U.S. Department of Energy
Federal Energy Technology Center
3610 Collins Ferry Road
Morgantown, WV 26505

by
S.K. Gangwal
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July 1997

ABSTRACT

When coal is gasified, fuel bound nitrogen compounds are principally released as ammonia (NH_3) which would readily oxidize to NO_x during combustion of the fuel gas in the turbine. The objective of this project, a joint effort between Research Triangle Institute, SRI International, and General Electric, is to develop catalytic approaches for decomposing a significant percentage (up to 90 percent) of the NH_3 present in fuel gas to N_2 and H_2 at elevated temperatures (550 to 900 °C) and pressures.

Two catalytic approaches for decomposing NH_3 have been experimentally evaluated. The first approach, evaluated during the early phases of this project, involved the screening of catalysts that could be combined with hot-gas desulfurization sorbents (e.g., zinc titanate) for simultaneous NH_3 and hydrogen sulfide (H_2S) removal. In a commercial system, this approach would reduce capital costs by eliminating a process step. Numerous catalysts and catalyst-sorbent combinations were prepared and tested for their NH_3 decomposition activity. These included catalysts based on Ni, Co, Mo, and W in various proportions combined with zinc titanate, titania, or refractory supports. Although some of the catalysts tested had high initial decomposition activity, they quickly deactivated in the presence of 2,000 ppmv H_2S and achieved only 10 to 40 percent NH_3 decomposition at 700 to 750 °C and 1 to 15 atm. Thus, this approach was deemphasized in favor of a stand-alone high-temperature (800 to 900 °C) catalytic decomposition approach.

Four nickel-based catalysts were selected for evaluation as high-temperature NH_3 decomposition catalysts. These included HTSR-1, G-47 (3 percent Fe_2O_3 on silica) from United Catalysts, Inc. (UCI), C11-9 (12 percent Ni on a ceramic support) from UCI, and C100N (proprietary Ni on stabilized alumina) from Contract Materials Processing, Inc. (CMP). Screening tests were conducted with these catalysts at 850 °C, 10,000 std $cm^3/(cm^3 \cdot h)$ in the presence of Texaco coal gas containing 1,800 ppmv NH_3 and 7,500 ppmv H_2S. The HTSR-1 demonstrated a steady 90 percent ammonia decomposition while the other catalysts showed <50 percent decomposition at equivalent test conditions. Based on these screening tests, HTSR-1 was selected for long-term (100-h) durability testing.

Two 100-h tests were conducted using HTSR-1. The first test was conducted using a mobile reactor facility at U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC) with a hot slipstream of actual coal gas from the FETC 10-in. diameter fluidized-bed coal gasifier. The 3-in. diameter NH_3 decomposition reactor in the mobile reactor facility was operated at 11 atm, 780 °C, and 5,000 std $cm^3/(cm^3 \cdot h)$. The FETC coal gas had average NH_3 and H_2S concentrations of 3,000 ppmv and 1,300, respectively. Over the 100-h test duration, NH_3 decomposition averaged 90 percent with no catalyst deactivation apparent due to trace contaminants in coal gas. The second test was conducted using a simulated Texaco coal gas nominally containing 7,500 ppmv H_2S and 1,800 ppmv NH_3 at 8.5 atm, 900 °C, and 5,000 to 10,000 std $cm^3/(cm^3 \cdot h)$. The catalyst showed a small amount of deactivation over the first 40 h of operation and then a stable catalytic activity level was achieved. The average NH_3 decomposition was 80 percent at 10,000 std $cm^3/(cm^3 \cdot h)$ and 88 percent at 5,000 std $cm^3/(cm^3 \cdot h)$.

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EXECUTIVE SUMMARY

BACKGROUND

Advanced coal gasification-based electric power plants such as integrated gasification combined cycle (IGCC) and molten carbonate fuel cell (MCFC) systems call for hot-gas cleanup downstream of coal gasification in order to achieve high thermal efficiency. The Federal Energy Technology Center (FETC) hot-gas cleanup research program has focused on the development of high-temperature removal methods for particulates and chemical contaminants. Chemical contaminants that have received the most attention are sulfur gases, particularly hydrogen sulfide (H_2S). However, other chemical contaminants, such as nitrogen compounds, must also be considered in the design of the hot-gas cleanup train.

During gasification, fuel-bound nitrogen in coal is principally released into the coal gas as ammonia (NH_3). NH_3 concentration in coal gas can vary from 200 to 5,000 ppmv depending on the nitrogen content of the coal and the configuration and operation of the gasifier. When this coal gas is combusted in a gas turbine, NH_3 has the propensity to form oxides of nitrogen (NO_x) that are difficult to remove pollutants and are precursors to "acid rain."

One potential approach for enhancing NH_3 decomposition would be to use a heterogenous catalyst in the hot-gas cleanup train to increase the decomposition rate. To be effective, the catalyst must be active in the harsh coal gas environment and resistant to poisoning by H_2S, steam, and other gases. Past studies at SRI International and General Electric have indicated that nickel- and/or molybdenum-based catalysts have the potential to decompose NH_3 at 550 to 800 °C in a coal gas environment.

OBJECTIVES

The objective of this study is to develop and demonstrate catalytic approaches for decomposing a significant percentage (up to 90 percent) of the NH_3 present in fuel gas to N_2 and H_2 at elevated temperatures (550 to 900 °C).

APPROACH

The NH_3 concentration considered in this study was ~1,800 to 2,000 ppmv, which is typical of oxygen-blown, entrained-flow gasifiers such as the Texaco coal gasifier being employed at the TECO Clean Coal Technology Demonstration plant. Catalysts containing Ni, Co, Mo, and W were candidates for the study. Before undertaking any experiments, a detailed thermodynamic evaluation was conducted to determine the concentration of NH_3 in equilibrium with the Texaco gasifier coal gas. Thermodynamic evaluations were also performed to evaluate the stability of the catalytic phases (for the various catalysts under consideration) under NH_3 decomposition conditions to be used in this study. Two catalytic approaches for decomposing NH_3 were experimentally evaluated. The first approach evaluated during the early phases of this project involved the screening of catalysts that could be combined with the hot-gas desulfurization sorbents (e.g., zinc titanate) for simultaneous NH_3 and H_2S removal. In a commercial system, this approach would reduce captial costs by eliminating a process step. The second approach evaluated was high-temperature catalytic decomposition at 800 to 900 °C. In a commercial hot-gas cleanup system this could be carried out after radiative cooling of the gas to 800 to 900 °C but upstream of the convective cooler, the hot particulate filter, and the hot-gas desulfurization reactor. Both approaches were tested in the presence of up to 7,500 ppmv H_2S in simulated fuel gas or actual fuel gas from a coal gasifier. Reactor systems ranged from high-pressure micro-reactor (approximately a few grams of catalyst) up to 3.0 in. diameter high-temperature, high-pressure (HTHP) skid-mounted units containing up to 2 pounds of catalyst.

ACCOMPLISHMENTS/RESULTS

- A detailed thermodynamic evaluation was conducted to evaluate the level of NH_3 decomposition as a function of temperature and pressure and the stability of the various catalytic materials in reducing, sulfiding, and oxidizing atmospheres.

- The thermodynamic evaluation indicated that, from an inlet value of 1,800 ppmv, NH_3 could be decomposed down to about 160 ppmv at 20 atm, 550 °C, and down to about 100 ppmv at 20 atm, 900 °C, in Texaco gas.

- All of the catalytic phases (metal, sulfide, and oxide) for the catalytic species considered were found to be thermodynamically stable at conditions of interest except for molybdenum oxide. However, molybdenum oxide had the potential to stabilize via formation of molybdate-type mixed metal compounds.

- Several catalysts containing Ni, Co, Mo, and W (with Al_2O_3, TiO_2, and other oxides as supports) were prepared and tested individually or in combination with a zinc titanate sorbent. These catalysts exhibited low-to-moderate activity for NH_3 decomposition.

- Among a number of catalysts tested, a commercially available nickel-based catalyst, HTSR-1, was found to be the best catalyst for use at temperatures >800 °C. However, it rapidly deactivated in the presence of H_2S at lower temperatures.

- Based on a number of screening and bench-scale tests, HTSR-1 was selected for extended testing. Two HTHP 100-h tests were conducted at 800 to 900 °C.

- The first 100-h test was conducted at 780 to 850 °C in an actual coal gas (~1,300 ppm H_2S) environment using a slipstream from the FETC's coal gasifier to a 3.0-in. HTHP skid-mounted reactor system housed in a mobile laboratory close to the gasifier. The second 100-h test was conducted at 900 °C in simulated Texaco gas containing 7,500 ppmv H_2S.

- Both extended tests demonstrated the excellent potential of the HTSR-1 catalyst for the high-temperature catalytic decomposition approach. At a space velocity of 5,000 std $cm^3/(cm^3 \cdot h)$, 90 percent NH_3 decomposition was achieved and no deleterious effect of coal gas contaminants or high temperature was observed.

CONCLUSIONS AND RECOMMENDATIONS

The efforts to develop a successful combination of an NH_3 decomposition catalyst with an H_2S sorbent were not successful. Numerous combinations containing catalysts based on Ni, Co, Mo, and W with zinc titanate exhibited low-to-moderate activity for NH_3 decomposition.

For the high-temperature catalytic decomposition approach, the HTSR-1 catalyst, a nickel-based catalyst on a refractory support, gave excellent results. The two 100-h tests with HTSR-1 demonstrated that it is capable of decomposing up to 90 percent of the NH_3 present in typical coal gasifier gases.

Further work is needed to reduce the cost of the catalyst and develop it in a form, such as monolith, that could operate in the presence of particles. Also continued research is needed for development of catalysts that would work at relatively lower temperatures down to 500 °C. Fundamental studies of what catalyst forms are active for NH_3 decomposition, what causes catalyst poisoning, and how it can be minimized could lead to the development of a successful combined sorbent-catalyst.

SECTION 1
INTRODUCTION

Advanced coal gasification-based electric power plants such as integrated gasification combined cycle (IGCC) and molten carbonate fuel cell (MCFC) systems call for hot-gas cleanup downstream of coal gasification in order to achieve high thermal efficiency. The U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC) hot-gas cleanup research program has focused on the development of high-temperature removal methods for particulates and chemical contaminants. Chemical contaminants that have received the most attention are sulfur gases, particularly hydrogen sulfide (H_2S). However, other chemical contaminants, such as nitrogen compounds, must also be considered in the design of the hot-gas cleanup train.

During gasification, fuel-bound nitrogen in coal is principally released into the coal gas as ammonia (NH_3). When this coal gas is combusted in a gas turbine, NH_3 has the propensity to form oxides of nitrogen (NO_x) that are difficult to remove pollutants and are precursors to "acid rain."

According to published data, the NH_3 concentration in coal gas can vary from 200 to 5,000 ppmv depending on the nitrogen content of coal and the configuration and operation of the gasifier. For example, the coal gas from a Texaco entrained-bed coal gasifier gasifying Illinois coal typically contains 1,800 to 2,000 ppmv NH_3. In contrast, a fixed-bed coal gasifier (e.g., Lurgi) typically produces about 5,000 ppmv NH_3 whereas a fluidized-bed coal gasifier (e.g., U-Gas, Kellogg) produces about 1,000 ppmv or less NH_3.

The NH_3 concentration in the exit coal gas appears to depend on the time-temperature history of the gas in the gasifier, with longer residence time at high temperature (~1,000 °C or higher) favoring removal of NH_3 by thermal decomposition [$NH_3 \rightarrow (½)\ N_2 + (3/2)\ H_2$]. However, the NH_3 concentration does not reduce further via thermal decomposition once the fuel gas exits the gasifier because of the low temperature and short residence time in downstream process piping.

One potential approach for enhancing NH_3 decomposition would be to use a heterogenous catalyst in the hot-gas cleanup train to increase the decomposition rate. To be effective, the catalyst must be active in the harsh coal gas environment and resistant to poisoning by H_2S, steam, and other gases.

1.1 BACKGROUND

Studies of ammonia decomposition under coal gas conditions are relatively few. The Institute of Gas Technology (1983) tested four catalysts under simulated coal gas conditions at temperatures from 425 to 750 °C—ZnO, a bulk iron catalyst, Pt-supported on alumina, and Ag-supported on alumina. All the catalysts reduced ammonia concentration at 550 °C; zinc- and iron-based catalysts were more effective than others. However, these catalysts exhibited a four- to six-fold decrease in catalytic activity on exposure to a feed gas containing H_2S. Limestone-based materials have been shown to possess low-to-moderate activity for NH_3 decomposition in coal gas at around 900 °C, as discussed in Appendix A (page 4).

SRI International (SRI) (Krishnan et al., 1988) clearly showed that, in the absence of H_2S, decomposition of ammonia can be carried out readily in the temperature range of 550 to 800 °C using Ni-based catalysts. The SRI study demonstrated that HTSR-1, a proprietary Ni-based catalyst exhibited excellent activity and high-temperature stability. However, its tolerance of H_2S was found to be a function of temperature. At 800 °C and above, no catalyst deactivation was observed even in the gas streams containing 2,000 ppmv of H_2S. At lower temperatures, HTSR-1 deactivated rapidly when significant levels of H_2S were present in the coal gas.

Both Krishnan et al. (1988) at SRI and Ayala (1993) at General Electric (GE) have reported on the catalytic role of molybdenum sulfide (MoS_2) in ammonia decomposition. An MoS_2 catalyst reduced NH_3 levels from 5,000 to 1,500 ppm at 790 °C (Krishnan et al., 1988). Ayala (1993) disclosed an invention related to additives to mixed-metal oxides that act simultaneously as sorbents and catalysts in cleanup systems for hot coal gases. Such additives generally act as a sorbent to remove sulfur from the coal gases while they catalytically decompose appreciable amounts of ammonia from the coal gases simultaneously. According to this invention, sorbents for high-temperature desulfurization of coal gases are usually mixed-metal oxides fabricated from zinc oxide, iron oxide, and titanium dioxide, or a combination of these three with other binders and metal oxides. The innovative aspect of the preparation of the sorbents is the addition of molybdenum to the ferrite and titanate sorbents. Molybdenum trioxide (MoO_3) or any other form of molybdenum was added from 0 to 5 percent by weight to the mixed-metal oxide sorbent to create a base mixture. The pelletized calcinated base mixture was activated, preferably by subjecting the pelletized base mixture to a calcination process where a gas is passed over the base mixture by a conventional gas passing technique such that the gas contains 1 percent or less by volume of H_2S at approximately 1,000 °F for approximately 1 h. The activation process was repeated several times, if necessary, with interim contact of the catalyst with a gaseous mixture of 1 percent O_2 in nitrogen at approximately 1,000 °F for at least 1 h. The activated base mixture was then placed in a flow of hot coal gas where the amount of sulfur and NH_3 in the hot-coal gases was substantially reduced. During absorption of H_2S from coal gases, the Zn and Fe atoms form sulfides according to well-known reactions found in the literature. Mo was also known to form sulfides, for instance, $MoO_3 + 2H_2S \rightarrow MoS_2 + 3H_2O$. Based on literature data on catalytic activity of MoO_3 and MoO_2 for hydrocracking and methanation reactions, Mo may have activity toward breaking hydrogen bonds with other atoms and, hence, be able to break down the hydrogen-nitrogen bond with ammonia, according to $NH_3 \leftrightharpoons N_2 + H_2$.

1.2 OBJECTIVES

The objective of this study is to develop and demonstrate catalytic approaches for decomposing a significant percentage (up to 90 percent) of the NH_3 present in fuel gas to N_2 and H_2 at elevated temperatures (550 to 900 °C).

1.3 SCOPE/APPROACH FOR CURRENT WORK

This report is the result of a combined effort by Research Triangle Institute (RTI), prime contractor, and SRI and GE, subcontractors. The detailed final reports by SRI and GE are attached as Appendices A and B, respectively. The main body of the report prepared by RTI primarily details the RTI portion of the effort, with highlights of the SRI and GE work, to provide a logical flow to the report.

The NH_3 concentration considered in this study was ~1,800 to 2,000 ppmv, which is typical of oxygen-blown, entrained-flow gasifiers such as the Texaco coal gasifier being employed at the TECO Clean Coal Technology Demonstration plant. Catalysts containing Ni, Co, Mo, and W were candidates for the study.

Before undertaking any experiments, a detailed thermodynamic evaluation was conducted to determine the concentration of NH_3 in equilibrium with the Texaco gasifier coal gas. Thermodynamic evaluations were also performed to evaluate the stability of the catalytic phases (for the various catalysts under consideration) under NH_3 decomposition conditions to be used in this study.

Two catalytic approaches for decomposing NH_3 have been experimentally evaluated. The first approach evaluated during the early phases of this project involved the screening of catalysts that could be combined with the hot-gas desulfurization sorbents (e.g., zinc titanate) for simultaneous NH_3 and H_2S removal. Zinc titanate reaction chemistry and testing have been described in detail elsewhere (Gupta and Gangwal, 1992). The sulfidation-regeneration cycle involved in H_2S removal from hot coal gas using one of the zinc titanate phases ($ZnTiO_3$) is shown below:

$$ZnTiO_3 + H_2S \rightarrow ZnS + TiO_2 + H_2O \qquad \text{(sulfidation)}$$
$$ZnS + TiO_2 + (3/2)O_2 \rightarrow ZnTiO_3 + SO_2 \qquad \text{(regeneration)}$$

In a commercial system, this approach would be carried out downstream of the hot particulate filter at the operating temperatures (550 to 725 °C) of the hot-gas desulfurization reactor. It could reduce capital and operating costs by eliminating a process step and the need for a secondary catalytic material. However, in order to be effective, the combined sorbent-catalyst would have to be active in the harsh coal gas environment (containing H_2S, H_2O, and other potential poisons). In addition, the sorbent-catalyst metallic species would have to be stable at the operating temperatures in reducing, sulfiding, and oxidizing atmospheres.

The second approach evaluated was high-temperature catalytic decomposition at 800 to 900 °C. In a commercial hot-gas cleanup system this could be carried out after radiative cooling of the gas to 800 to 900 °C but upstream of the convective cooler, the hot particulate filter, and the hot-gas desulfurization reactor. For this approach, the catalyst would not only have to be active and stable at these elevated temperatures, but would also have to function in an environment containing particulate. Thus, the catalyst would have to be in a physical form not to retain significant particulates, e.g., metal coating on monolithic support containing channels for gas flow. In this work, we have not attempted to develop a monolithic catalyst that could be the subject of a follow-on investigation. Rather, the emphasis has been on testing catalyst pellets in a particulate-free environment to first find effective catalytic species.

Both the simultaneous NH_3 and H_2S removal and the high-temperature catalytic decomposition approaches have been tested in the presence of up to 7,500 ppmv H_2S in simulated fuel gas or actual fuel gas from a coal gasifier.

SECTION 2
THERMODYNAMIC EVALAUTION

Thermodynamic calculations were performed by SRI to determine the concentration of NH_3 in equilibrium with a coal gas stream typical of the Texaco entrained-bed coal gasifier. The range of Texaco gas compositions selected for thermodynamic evaluation and experimental study is shown in Table 1. Further details of the thermodynamic evaluation are provided in the SRI final report, Appendix A (pages 7–15).

The equilibrium concentration of NH_3 in a Texaco coal gas as a function of temperature (500 to 900 °C) and pressure (1 to 20 atm) is shown in Figure 1. Since the ammonia decomposition reaction is endothermic, the concentration of NH_3 decreases with increasing temperature. However, at elevated pressures, the equilibrium levels of NH_3 may be at a maximum at about 600 °C. This characteristic is attributed to a greater level of CH_4 formation at lower temperatures that reduce H_2 concentration. For example, at 500 °C and 20 atm, the calculated equilibrium compositions of CH_4 and H_2 are 28.1 and 2.6 vol%, respectively. In contrast, at 900 °C, the equilibrium compositions of CH_4 and H_2 are 2.31 and 28.7 vol%, respectively. Hence, at temperatures below 600 °C, NH_3 decomposition is favored by the removal of H_2 due to CH_4 formation, and at higher temperatures the equilibrium of the NH_3 decomposition reaction ($NH_3 \rightarrow (\frac{1}{2}) N_2 + (3/2) H_2$) begins to determine the equilibrium NH_3 levels. Equilibrium values in Figure 1 indicate that the extent of NH_3 decomposition is thermodynamically limited, but NH_3 decomposition >90 percent is possible in the temperature range of 500 to 900 °C in Texaco gas.

Thermodynamic calculations were also performed to evaluate the stability of the catalysts and their desirable phases under NH_3 decomposition conditions of interest in this study. For the simultaneous NH_3 and H_2S removal approach, state of the catalyst in reducing, sulfiding, and oxidizing environment was considered. For the high-temperature catalytic decomposition approach, state of the catalyst in reducing and sulfiding environment at high temperature was considered.

The activity of the sulfide-based catalysts (MoS_2, WS_2) for NH_3 decomposition could depend on whether the catalyst can be kept in the sulfided state. Thermodynamic calculations show that MoS_2 will be stable at 723 °C (1,000 K) at an H_2S to H_2 mole ratio of 0.0005 or higher. At the same temperature WS_2 will be stable at ratios higher than 0.001. The product gas stream from the Texaco gasifier contains sufficient H_2S to keep these sulfides stable for the high-temperature catalytic decomposition approach. However, in the simultaneous NH_3 and H_2S removal approach, the zinc titanate sorbent could reduce the H_2S concentration in the bed dramatically. In this environment, the sulfides may reduce to metal as the stable phase that may resulfide once the H_2S

Table 1. Texaco Gasifier Simulated Gas Composition (vol%)

H_2	28.5-31.1
CO	38.0-45.7
CO_2	10.0-12.9
H_2O	12.5-18.1
H_2S	0.5-0.75
NH_3	0.18-0.20
N_2	0.0-1.62

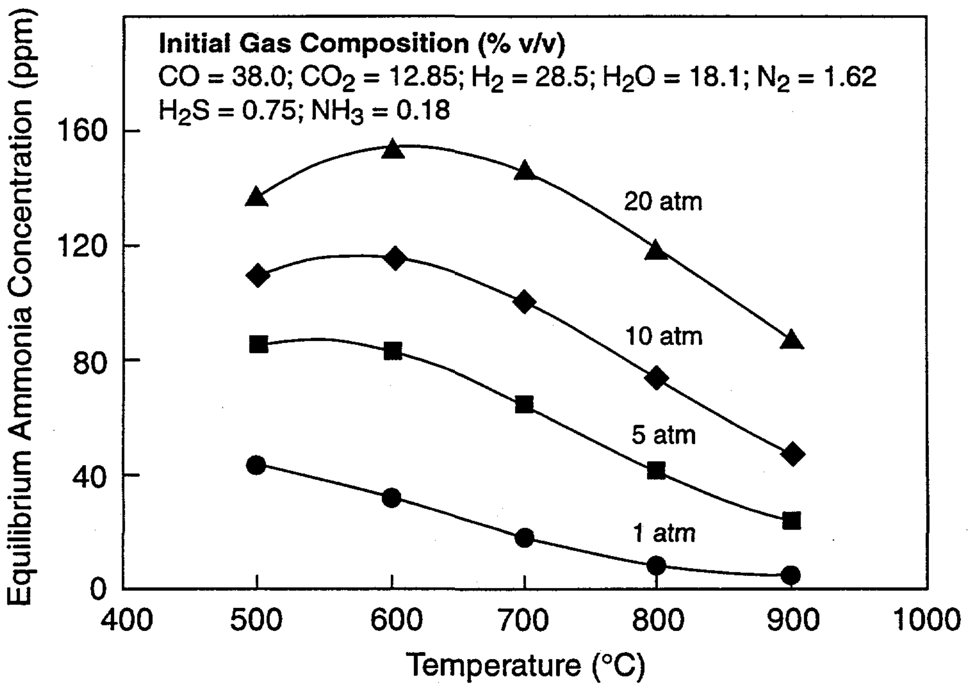

Figure 1. Equilibrium concentration of ammonia as a function of temperature and pressure in a Texaco coal gasifier gas stream.

concentration increases. Thermodynamic calculations indicate that vapor pressures of the sulfided and metallic states of the catalytic species of interest are insignificant in reducing environment.

In the simultaneous NH_3 and H_2S removal approach, a combined desulfurization sorbent and NH_3 decomposition catalyst need to survive oxidative regeneration. This implies that whatever state they exist in during regeneration, they should not disappear by vaporization. During regeneration, all the catalytic and active sorbent species are likely to be converted to oxide or sulfate.

Based on thermodynamic calculations, the only species among all of the catalytic species with considerable volatility during regeneration was found to be molybdenum oxide. Thermodynamic calculations indicate that Mo_3O_9, Mo_4O_{12}, and Mo_5O_{15} are the dominant vapor species in equilibrium with solid MoO_3 in the temperature range 525 to 825 °C. Equilibrium partial pressures at 625 °C, for example, of Mo_3O_9 and Mo_4O_{12} vapor in the presence of 2 vol% O_2 are 4.4×10^{-6} and 4.1×10^{-6} atm, respectively, that may lead to significant loss of Mo during regeneration. One possible mechanism by which Mo vaporization could be reduced or rendered insignificant is by formation of a bimetallic species involving Mo such as molybdates. Among the five metals (Cu, Co, Fe, Ni, and Zn) considered as possibly capable of forming molybdates, thermodynamic calculations indicated that Cu was the only metal that formed a molybdate above 527 °C (800 K). It effectively reduced the total vapor pressure of Mo-containing species by four orders of magnitude.

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-Mo/TiO_2 + ZT-4
ZT-4	W/TiO_2
Ni/TiO_2 - ZrO_2	W-Mo/TiO_2
Ni-Mo/TiO_2 - ZrO_2	ZnO - WO_3
Co-Mo-L-3787M (zinc titanate)	Co-ZnO-WO_3-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

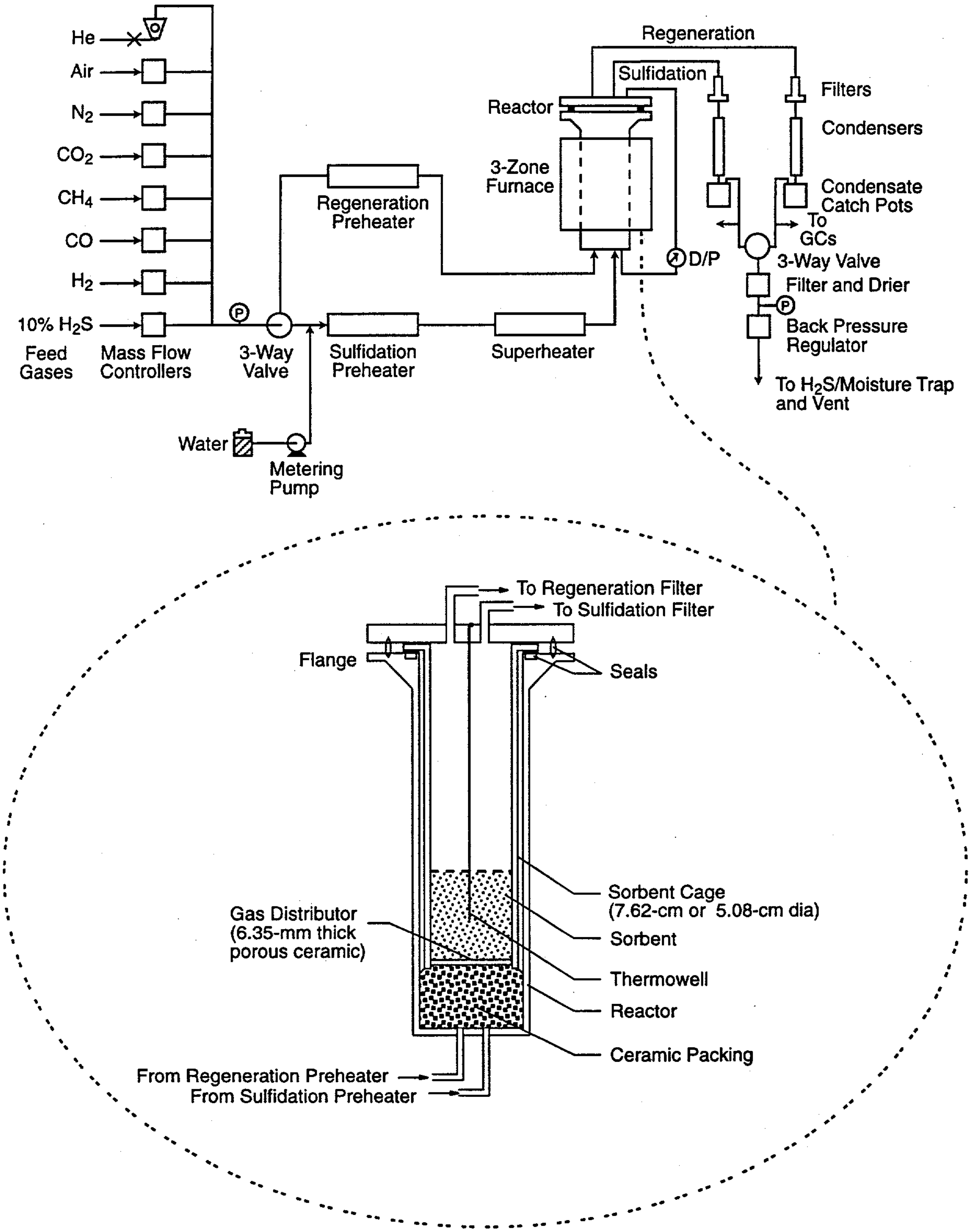

Figure 2. Bench-scale fluidized-bed sorbent test facility.

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 NoteBook 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.

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	≈500 cm^3/min
GC sample flow (through the copper bed)	≈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

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 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.

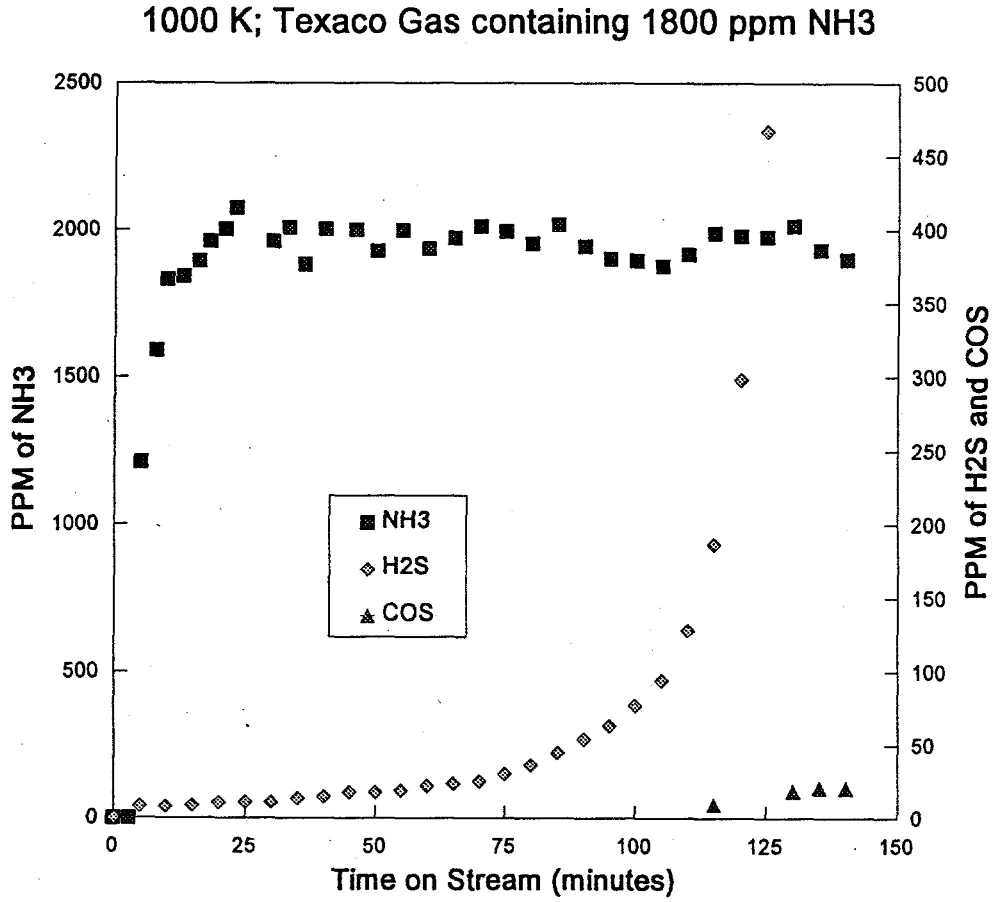

Figure 3. Ammonia decomposition by ZT-4.

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

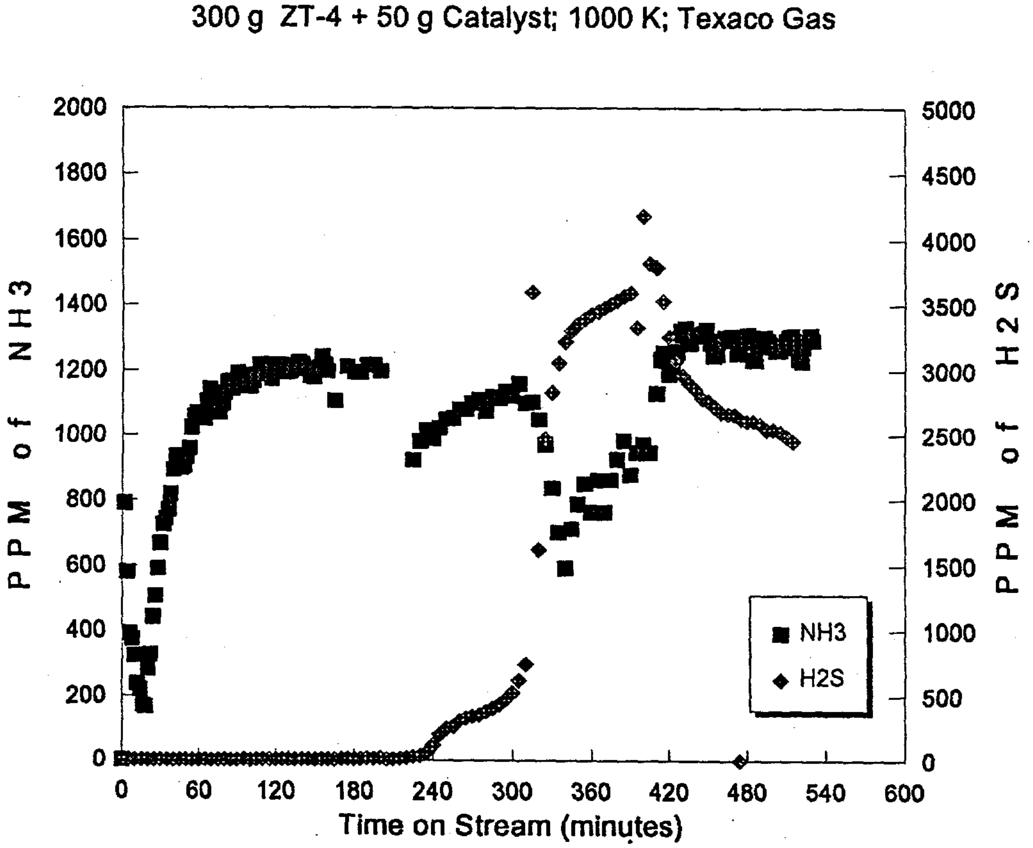

Figure 4. Ammonia decomposition with Co-Mo catalyst.

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 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).

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).

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.

SECTION 4
HIGH-TEMPERATURE CATALYTIC DECOMPOSITION

The high-temperature catalytic decomposition approach, as described in Section 1.3, requires a catalyst that can operate between 800 and 900 °C in a coal-gas environment. A number of catalysts were selected and tested at low and high pressure with simulated and actual coal gases for up to 100 h.

4.1 CATALYSTS SELECTED FOR TESTING

Based on discussion with several catalyst vendors, a number of catalysts were selected. Nonproprietary information about these catalysts is presented in Table 7.

These catalysts are commercially available candidates for steam reforming of natural gas at elevated temperature. Note that HTSR-1 is also the base material previously tested. The surface area of HTSR-1 after an 8-h exposure to Texaco coal gas with 1,800 ppm NH_3 was 14 m^2/g.

4.2 SCREENING TESTS

4.2.1 Atmospheric-Pressure Tests

A number of different reactor test units ranging from low to high pressures and 50 to 600 g catalysts were used in the testing. The low-pressure screening tests were conducted using a 1-in. quartz reactor system (Figure 5).

The reactor is a quartz column (26-mm ID and 76-cm long) separated midway into two sections by a quartz frit. The catalyst bed is supported on the quartz frit. The section below the frit is filled

Table 7. Catalysts Tested for High-Temperature Catalytic Decomposition Approach

Catalyst	Vendor	Composition	Surface area (g/cm^3)	Bulk density ($g/\mu m^3$)	Morphology
HTSR-1	Haldor Topsoe (Denmark)	A proprietary Ni-based catalyst on a refractory support	32	1.6	Cylindrical pellets (1/8" dia., 1/8" long)
G-47	UCI	3% Fe_2O_3 on a SiO_2-Al_2O_3 support	—	1.1	Spherical pellets (1/4" dia.)
C11-9-02	UCI	12% Ni on a ceramic support	—	1.1	Rings (5/16" by 5/16" by 1/8")
C100N	CMP	10% Ni on a stabilized Al_2O_3 support	133	0.5	Powder between 90 and 150 μm

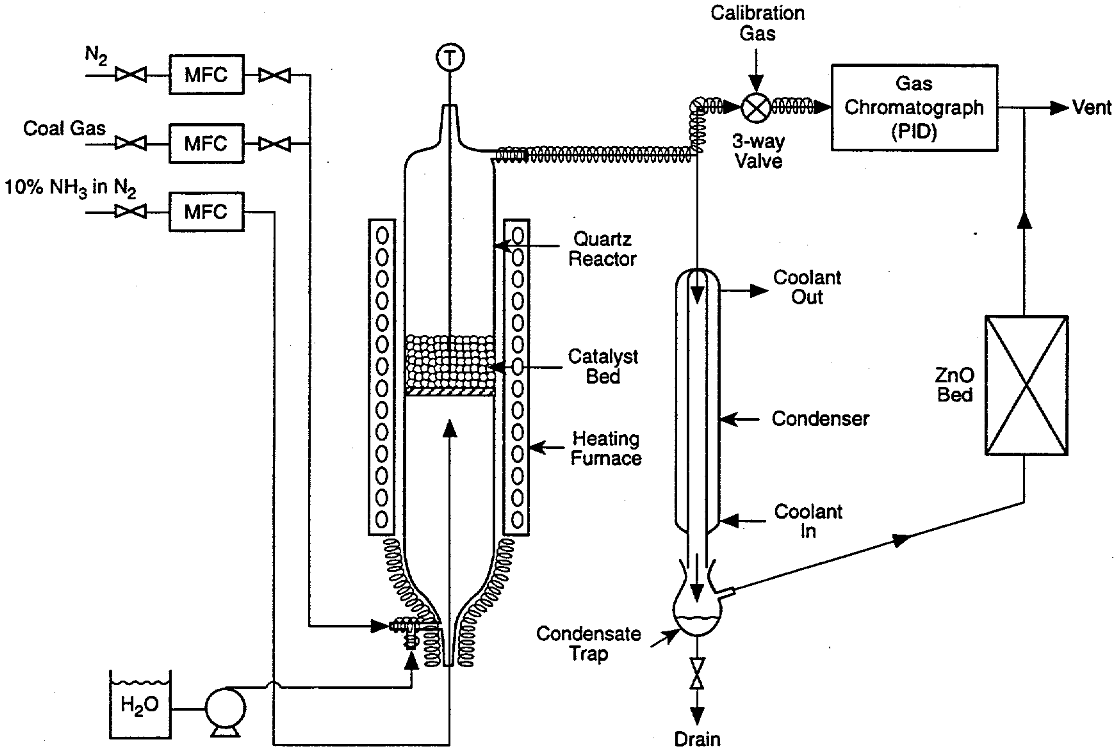

Figure 5. Schematic of the atmospheric bench-scale unit to study catalytic decomposition of ammonia.

with quartz rings (approximately 5-mm dia and 7-mm long) for gas heating and distribution. The reactor is heated by a single zone electric furnace.

The coal gas and water are fed to the bottom of the reactor. Ammonia is fed to the reactor via a quartz capillary that extends from the reactor bottom to about 5 cm below the frit. With this design, ammonia comes in contact with the coal gas at only high temperatures (>150 °C), thus preventing formation of ammonium carbonate (at temperatures lower than 150 °C, the ammonia will react with the CO_2 in the coal gas to form ammonium carbonate) and ammonium sulfide. The reactor temperature is monitored continuously using a K-type thermocouple.

The ammonia in the effluent gas is analyzed using a GC equipped with a PID. A slipstream (30 to 35 cm^3/min) of reactor effluent gas is injected hot (120 to 160 °C) in the GC. The remaining flow of the effluent gas is then passed through a condenser to condense steam and ammonia. The noncondensable gas is then passed through a ZnO bed to remove H_2S and to a vent.

The first series of screening tests consisted of evaluating HTSR-1, G-47, and C11-9-02 catalysts for NH_3 decomposition at 850 °C and 10,000 h^{-1} space velocity in Texaco coal gas with 1,800 ppmv NH_3. The total gas flow at 10,000 h^{-1} space velocity for catalyst loading at L/D equal to 3 was 6.9 slpm. The Texaco coal-gas composition was as shown in Table 5. A typical experiment consisted of loading the catalyst, heating to 850 °C in nitrogen purge, and then passing the desired flow of coal gas.

Figure 6 shows the extent of NH_3 decomposition with time for the three catalysts studied. The HTSR-1 catalyst decomposes over 95 percent of the feed NH_3 compared to about 40 and 20 percent NH_3 decomposition observed with UCI's C11-9-02 and G-47 catalysts, respectively. Thus, HTSR-1 appears to have better catalytic activity for NH_3 decomposition than the other two catalysts.

With the C11-9-02 catalyst, coal gas was initially passed for 215 min. The coal gas was then replaced with nitrogen for 3 hours followed by flow of coal gas again. As shown in Figure 7, the decomposition was 95 percent compared to about 40 percent observed in coal-gas environment. This greater decomposition in nitrogen than in the coal gas may be due to either reversible H_2S poisoning of the catalyst or due to the presence of coal gas. Steam in coal gas can partially oxidize the catalyst and thereby reduce its activity.

Following the screening of the three catalyst samples at a space velocity of 10,000/h (@ STP) a 50-h test was carried out on HTSR-1 at a space velocity of 20,000 h^{-1} at 850 °C and 1 atm. We loaded 33.8 g of catalyst in our 1 in.-ID quartz reactor and passed 6.9 slpm of coal gas simulating Texaco coal-gas composition (CO: 38%; CO_2: 12.85%: H_2: 28.5%; H_2S: 0.75%; NH_3: 0.18%;

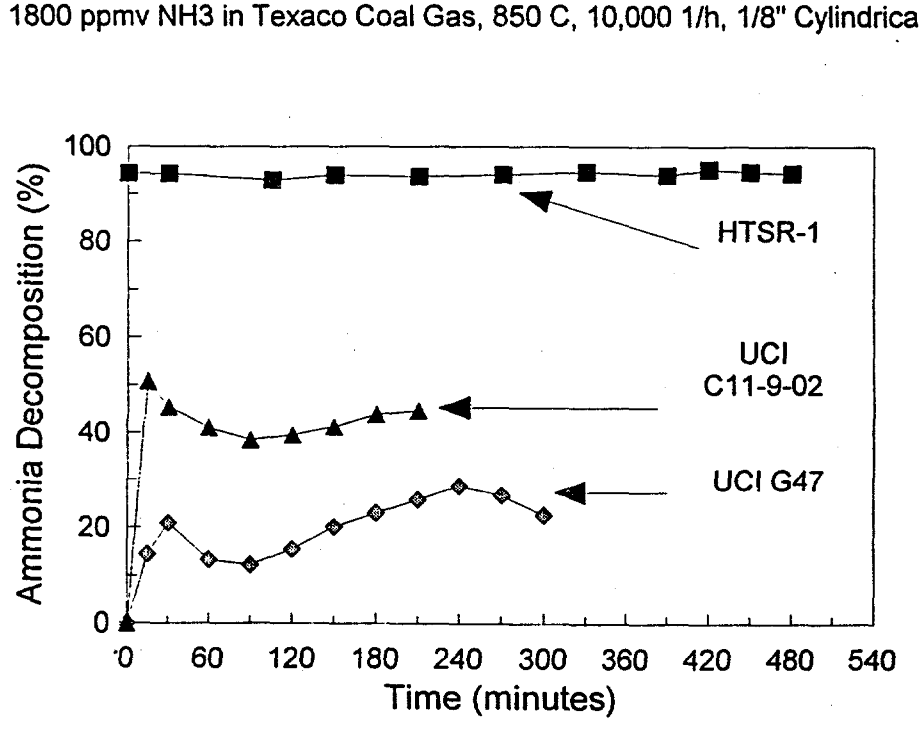

Figure 6. Catalytic decomposition of ammonia.

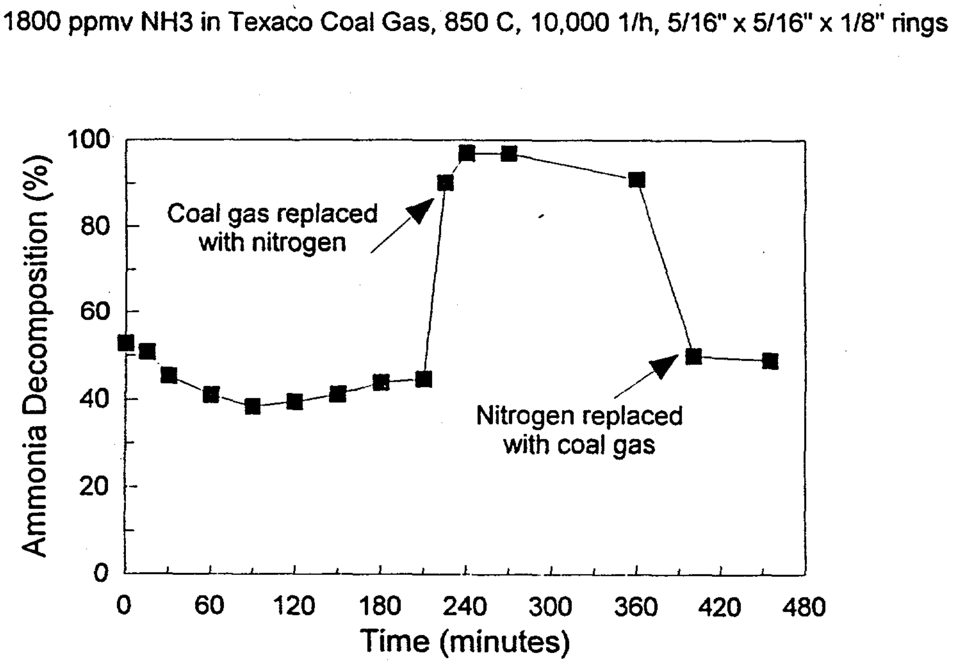
1800 ppmv NH3 in Texaco Coal Gas, 850 C, 10,000 1/h, 5/16" x 5/16" x 1/8" rings

Figure 7. Decomposition of ammonia using UCI C11-9-02 catalyst.

N_2: 1.62%; and H_2O: 18.1%). We experienced some problems in analyzing ammonia in the reactor exit gas because of the formation of ammonium sulfides in the gas sampling system. As a result, the GC analysis data indicated 5 to 9 ppm of NH_3 in the outlet gas. We, however, collected the condensate samples at regular intervals to confirm the GC results. These condensate samples were analyzed for NH_4^+ ions using an ion chromatograph. According to these results, the ammonia decomposition ranged from 54 to 70 percent of the feedstock (i.e., 1,800 ppmv); the ammonia in the outlet gas ranged from 550 to 850 ppmv. Considering a high space velocity of 20,000 h^{-1}, these decomposition values are reasonably good with coal gas containing 7,500 ppmv of H_2S at 850 °C (1,562 °F) and 1 atm. Increase in pressure is expected to bring down the extent of ammonia decomposition.

4.2.2 High Pressure Tests

The HTSR-1 and C100N catalysts were evaluated for their ammonia decomposition activity at high pressure using the HTHP bench-scale reactor system shown earlier in Figure 2.

Both of these catalysts were tested at 10,000 h^{-1} space velocity (@ STP), 850 °C, and 150 psig (11.2 atm abs) pressure in a simulated Texaco coal-gas composition (Table 5). The HTSR-1 catalyst pellets were tested in the fixed-bed mode. To obtain a space velocity of 10,000 h^{-1} with 293 g of the catalyst in the 2 in.-ID reactor (L/D = 3.5), the total gas flow rate was 30 slpm. Because of its particle size, the C100N catalyst was tested in the fluidized-bed mode. Fifty grams of catalyst were loaded in the reactor and a gas flow rate of 15.5 slpm was used to get a superficial gas velocity of 4.7 cm/s that corresponded to a space velocity of 10,000 h^{-1}. A typical experiment consisted of loading the catalyst in the reactor, heating to 850 °C in nitrogen purge, pressurizing the reactor to 150 psig, and then passing the desired flow of coal gas. In addition to measuring the NH_3 in the exit gas using the GC, we also collected the condensate samples at regular intervals for NH_4^+ ion analysis by an ion chromatograph in order to confirm the GC results as discussed above.

4.2.2.1 Test Results for HTSR-1 Catalyst

Figure 8 shows the percent ammonia decomposition as a function of time for HTSR-1 catalyst under HTHP conditions specified above. This test was carried out for a duration of about 8 h to determine any short-term deactivation of the catalyst. As stated above, the ammonia concentration values measured by GC were corrected based on the analysis of the condensate samples collected during the run at regular intervals. Initially, when we started the run, the ammonia decomposition was in the vicinity of 70 to 80 percent, but it went down with time stabilizing around 50 percent after ~4 h. We had some problems in getting a good sample for GC between 90- to 240-min run duration; that is why no data points are shown in Figure 8 for this duration.

Based on the chemical equilibrium calculations, the upper limit on ammonia decomposition under these conditions is 96 percent, i.e., about 70 ppmv ammonia in the outlet gas. However, the values obtained in this test were close to 900 ppmv so we were well within the kinetic regime. Calculation for a first-order rate constant based on the gas residence time and conversion under steady-state conditions gave rise to a value of "k" of 0.7632/s. This value was obtained using the following equation:

$$x - 1 - \exp(-k\tau)$$

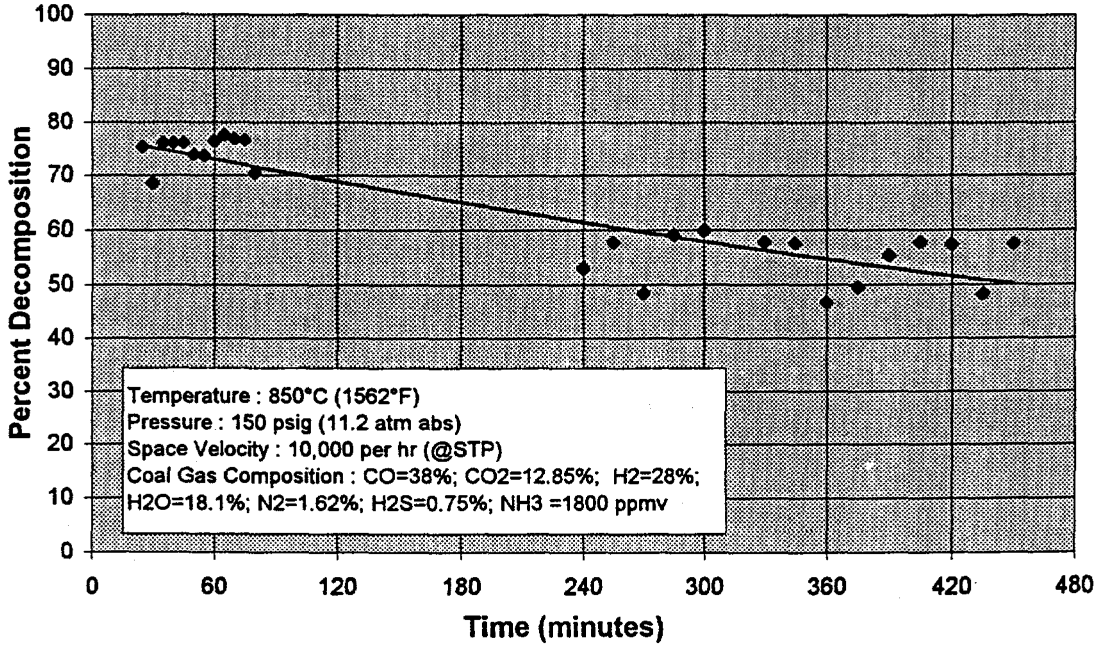

Figure 8. Ammonia decomposition by HTSR-1 catalyst.

where "x" is the fractional ammonia decomposition (in this case, it is 0.5267), k is the first order rate constant and τ is the residence time determined from the space velocity ($\tau = 0.98$ s in this case).

4.2.2.2 Effect of H_2S on the Performance of HTSR-1 Catalyst

It is well known that H_2S is a strong poison for the Ni-based ammonia decomposition catalysts. Because poisoning by H_2S is quite severe at lower temperatures and leads to almost complete deactivation of the catalyst within the first few hours depending on the H_2S concentration in the coal gas, the recommended operating temperature for the HTSR-1 catalyst is above 800 °C.

Figure 9 shows the effect of H_2S addition in the coal gas. Initially, with 7,500 ppmv of H_2S present in coal gas, the ammonia decomposition was in the vicinity of about 50 percent. After about 3 h, the H_2S flow was stopped and, as a result, the performance of catalyst improved immediately and an ammonia decomposition of about 85 percent was achieved. After running the system for about 4 h without any H_2S, the H_2S flow was restored and, as can be seen from Figure 9, the ammonia decomposition went down immediately to its original value of about 50 percent. Clearly, H_2S has some reversible poisoning of catalyst even at 850 °C. We believe that increasing the temperature to 900 °C or even higher will reduce the extent of H_2S poisoning of the HTSR-1 catalyst.

4.2.2.3 Test Results for C100N Catalyst

Figure 10 shows the ammonia decomposition as a function of time for the C100N catalyst. As indicated previously, this catalyst was tested under identical conditions as that of HTSR-1 to get

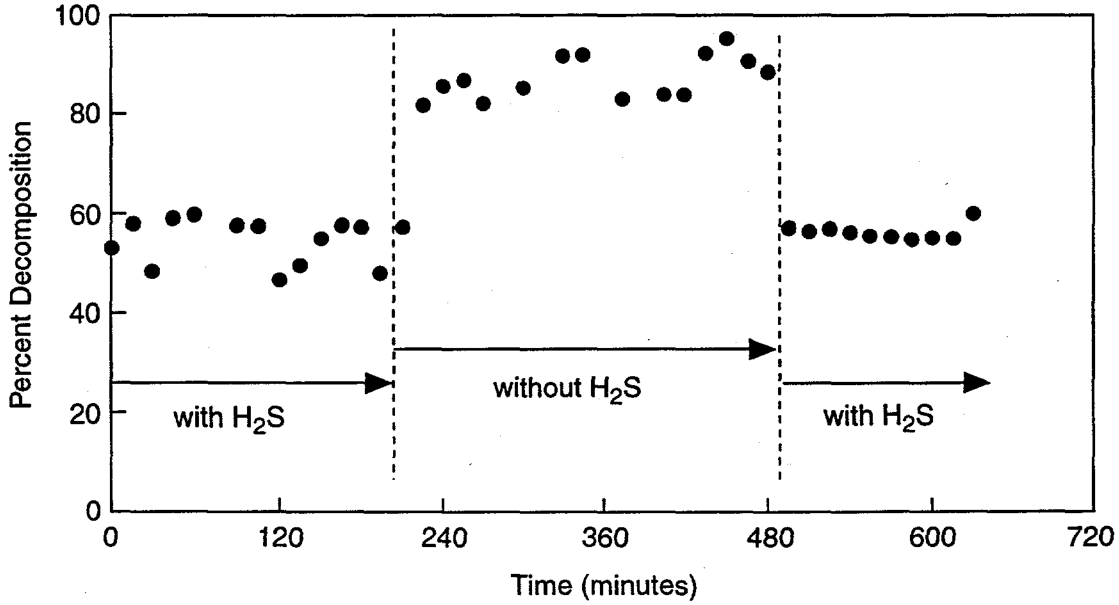

Figure 9. Effect of H_2S on ammonia decomposition by HTSR-1 catalyst.

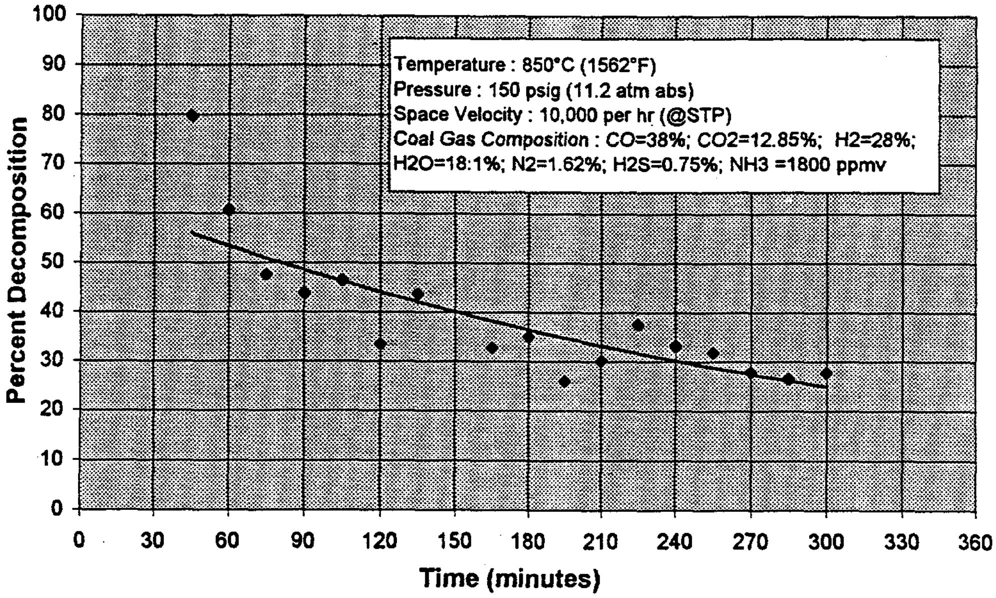

Figure 10. Ammonia decomposition by C100N catalyst.

a direct comparison of performance. As can be seem, the initial ammonia decomposition with this catalyst was about 50 percent which decreased with time to a value of about 25 percent within 5 h. It appears that this catalyst was deactivating exponentially under these conditions. Therefore, this catalyst, in its present form, may not be suitable in commercial applications.

Based on the screening tests, HTSR-1 was selected for extended testing with simulated gas and actual coal gas.

4.3 EXTENDED TESTING WITH SIMULATED GAS

GE successfully conducted a 100-h test with HTSR-1. This test and its results are described in detail in Appendix B (pages 22–33).

4.4 FIELD TEST WITH ACTUAL COAL GASIFIER GAS

4.4.1 Summary

As part of the 1995 slipstream test program conducted in conjunction with operation of the 10-in. fluidized-bed coal gasifier located at DOE's FETC, ammonia decomposition catalyst HSTR-1 was exposed to coal gas for 100 h. Ammonia in the coal gas was reduced by an average of 91.8 percent based on acid impinger sampling and 87.4 percent based on condensate sampling. Reactor operating conditions were 780 °C and 146 psig at a gas hourly space velocity of 4,975 h^{-1}.

4.4.2 Equipment Description

The reactor system used to test the ammonia decomposition catalyst is part of a skid-mounted pilot plant in RTI's mobile laboratory. Operation of this pilot plant depends on an external source of coal gas. The 10-in. fluidized-bed coal gasifier located at DOE/FETC's Morgantown facility currently provides the gas source.

The corrosive nature of sulfur gases particularly in the presence of steam requires the use of either 316 or 304 SS components. Corrosion resistance of critical parts is enhanced by Alon processing (a high-temperature aluminum vapor treatment). Figure 11 is a simplified schematic of the reactor system. This reactor system contains the following features: (1) gas conditioning, (2) a fixed-bed reaction chamber, (3) process control, (4) data acquisition, (5) gas and condensate sampling, and (6) reactor off-gas venting. Each of these features is discussed briefly below.

Temperature of the coal gas feed is maintained with Temptrace® metal-sheathed mineral-insulated heat tracing and Omega temperature controllers. In addition to heating the coal gas, coal or ash fines being conveyed with the coal gas are removed with a Mott GasShield™ filter. Specifications for this filter claim it removes >99.9999999 percent of all particles down to 0.01 μm.

The reactor is constructed of 4-in. schedule 160 316 SS pipe and is identical to the bench-scale reactor at RTI (Figure 2). A unique feature of this reactor is the removable cage allowing easy loading and unloading of the catalyst. The reactor can accommodate either a 7.62 cm (3 in.) or a 5.1 cm (2 in.) dia cage. A removable α-aluminia 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 a separate temperature controller for each zone.

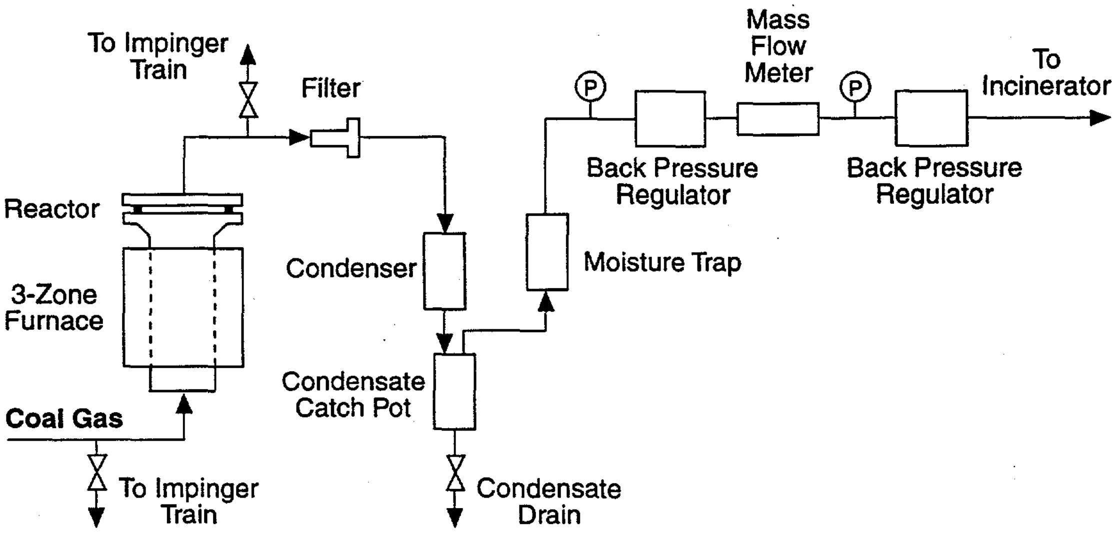

Figure 11. Schematic of skid-mounted reactor system.

Reactor pressure is controlled by two BPRs connected in series. One is upstream of an electronic mass flow meter (MFM), and the other is downstream. This configuration maintains reactor pressure at 150 psig and limits the pressure drop across the MFM to within the specified operating range. The signal from the MFM serves as an input for a PID controller used to maintain the coal gas flow rate at 68 slpm with a Badger valve

An Omega OM480 data logger and LabTech Notebook software record temperature, flow rates, and pressures for the entire mobile laboratory. For this reactor system, stored data include flow rates, reactor temperatures, and stream or skin temperatures needed to monitor or evaluate system performance.

Small slipstreams of coal gas are periodically removed before and after the reactor. The ammonia contained in these streams is captured in an acid impinger train. Each impinger train consisted of three impingers and a dry gas test meter. The first two impingers are filled with 15 mL of 0.1 N hydrochloric acid. The third impinger is filled with 75 to 80 mL of silica gel. The dry gas meter measures the volume of coal gas tested. Slipstreams pass through the acid impinger trains for approximately 1 h at 1 slpm at 6-h intervals.

A ceramic filter is used to capture particles elutriated from the reactor. After filtration, the coal gas is cooled in a double-pipe heat exchanger with cold process water in the outer shell. Condensate formed during this cooling stage is periodically drained from a catch pot into a measuring flask. The cold reactor effluent is dried in a moisture trap containing Drierite®. After passing through the BPRs and MFM, the cold effluent is vented to an incinerator.

4.4.3 Test Conditions and Sampling Procedures

- Reactor Loading

  For the 100-h test of the ammonia decomposition catalyst, HSTR-1, a 7.62 cm (3 in.) cage was used. The reactor cage was initially loaded with beryl saddles to a depth of 25.4 cm (10 in.). Approximately 820 cm^3 or 1,539 g of HSTR-1 catalyst was loaded on top of the beryl saddle bed. The beryl saddle bed ensured the coal gas was at temperature before reaching the catalyst. The height-to-diameter ratio for the catalyst bed was 2.3. The gas hourly space velocity for the catalyst bed, assuming a coal gas flow rate of 68 slpm, is about 5,000 h^{-1}. The temperature in the catalyst bed was measured by a thermocouple with its tip 10.16 cm (4 in.) below the catalyst surface, roughly the middle of the catalyst bed.

- Ammonia Sampling

  After the acid impinger train had been exposed to a slipstream for the required period, the content of each acid impinger was emptied into its own sample bottle. Any residual acid solution containing ammonia in the impinger or connecting tubing was rinsed out and into the appropriate sample bottle with distilled water. The content of the sample bottle was diluted to form 30 mL of solution with distilled water. Each sample bottle was carefully labeled to identify data, time, and impinger from which the sample was removed. These were the standard procedures for preparing samples for ammonia testing. If the silica gel had been

Table 8. Average Wet Coal Gas Compositions During 100-h Test

	Wet coal gas composition	
	Wt%	Vol%
CH_4	1.86	2.87
H_2S	0.18	0.13
H_2	1.14	14.14
Ar	0.78	0.48
CO_2	19.92	11.21
CO	13.42	11.87
N_2	54.86	48.50
H_2O	7.61	10.47
NH_3	0.23	0.33
Total	100	100

exhausted or would be exhausted during the next sampling period, the silica gel was replaced.

In addition to impinger samples, samples of the condensate were collected twice a day for ammonia analysis. A condensate sample was also collected for the raw coal gas by FETC personnel on a daily basis. Condensate sampling began after ~40 h of operation to check and confirm ammonia concentrations being obtained by impinger sampling.

Ammonia analysis was performed by FETC personnel using a Dionex Series 4000 ion chromatograph with an IonPac® CS14 column. The eluent was 10 milimolar methane sulfonic acid at a flow rate of 2 mL/min. Detection was by conductivity.

4.4.4 Results

The average composition of the coal gas during this 100-h test is provided in Table 8. During the first 40 h of operation the results obtained from ammonia in the acid impinger trains were extremely low. This initiated the collection of condensate samples to provide an alternative measurement of ammonia concentration in the gas stream. Removal of the filters used to condition the slipstreams generated acid samples in which ammonia concentrations were in the anticipated range and reasonably close to values determined from condensate samples. Ammonia concentrations for both impinger and condensate sampling are provided in Table 9. Some of the difference observed between the two methods results because only one condensate sample for the raw coal gas was collected each day by FETC personnel. Other potential sources of discrepancy between the two methods are not as easily identified.

Ammonia conversion was calculated from the changes in ammonia concentration in the gas stream entering and leaving the reactor. Ammonia conversion and reactor operating conditions are presented in Table 10. A visual picture of ammonia conversion as a function of operating time is shown in Figure 12. Average ammonia decomposition for HSTR-1 based on impinger sampling was 91.7 and 87.4 percent based on condensate sampling. During the 60 h of operation for which reliable data were available, no deactivation of the catalyst was observed.

Table 9. Ammonia Concentration in Coal Gas as Determined by Impinger and Condensate Sampling

Cumulative time of operation (h)	Ammonia concentration (ppmv)			
	Impinger sampling		Condensate sampling	
	Before reactor	After reactor	Before reactor	After reactor
40.83	2,128	315		
42.30	3,311	167		
46.58			3,009	442
50.83	3,641	131		
52.25			3,009	238
53.67	2,712	170		
62.00			3,009	487
63.73	3,564	199		
71.70	3,391	173		
74.00			3,273	310
80.22	4,016	478		
86.00			3,273	549
88.50	3,627	629		
94.77	3,425	149		
98.00			2,251	239

Table 10. Ammonia Conversion and Reactor Operating Conditions

Cumulative time of operation (h)	Ammonia conversion (%)		Reactor temperature (°C)	Reactor pressure (psig)	Gas hourly space velocity (h^{-1})
	Impinger	Condensate			
40.83	85.18		794	143	4,975
42.30	94.94		777	146	4,975
46.58		85.31	784	148	4,975
50.83	96.40		795	134	4,975
52.25		92.09	784	138	4,975
53.67	93.70		769	153	4,975
62.00		83.81	777	150	4,975
63.73	94.42		777	149	4,975
71.70	94.90		790	149	4,975
74.00		90.53	786	148	4,975
80.22	88.11		785	146	4,975
86.00		83.25	771	148	4,975
88.50	82.65		778	146	4,975
94.77	95.66		795	145	4,975
98.00		89.36	787	147	4,975

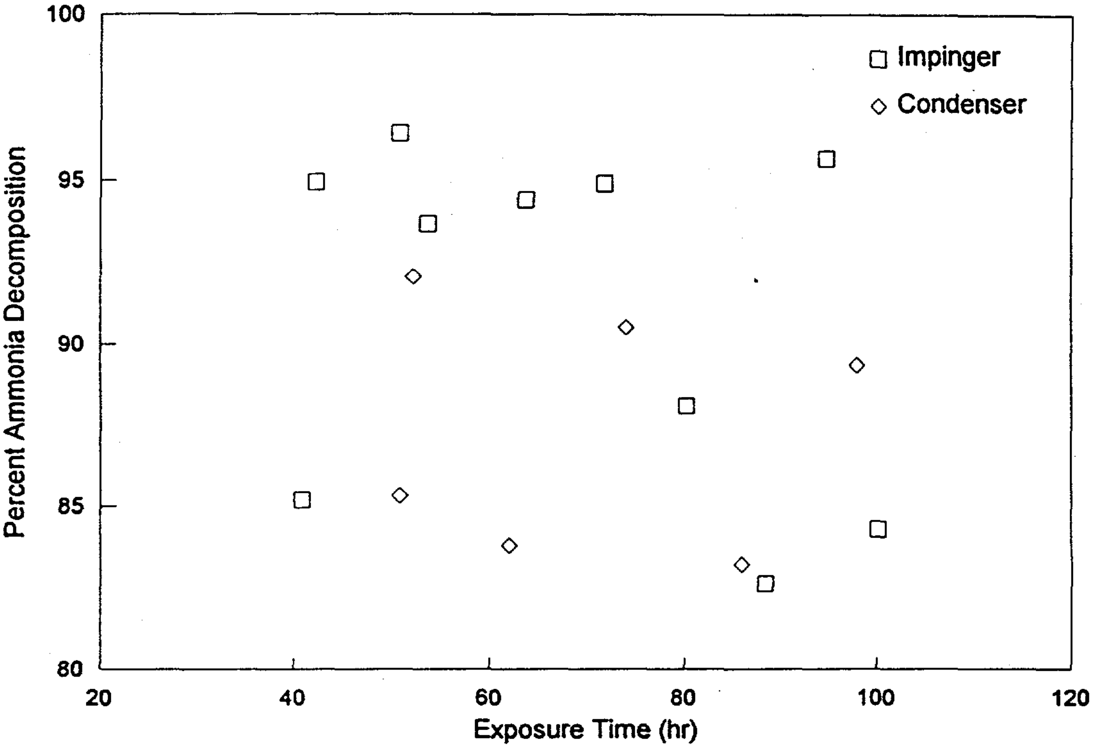

Figure 12. Performance of ammonia decomposition catalyst as function of exposure time.

4.4.5 Conclusions

Ammonia decomposition catalyst, HSTR-1, was exposed to real coal gas for 100 h at an average temperature of 780 °C, pressure and 146 psig, and gas hourly space velocity of 4,975 h^{-1}. During this test period, ammonia decomposition averaged 91.7 percent based on impinger sampling and 87.4 percent based on condensate sampling. Over the last 60 h for which reliable data were available, no catalyst deactivation could be detected.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The efforts to develop a successful combination of an NH_3 decomposition catalyst with an H_2S sorbent were not successful. Numerous combinations containing catalysts based on Ni, Co, Mo, and W with zinc titanate exhibited low-to-moderate activity for NH_3 decomposition.

For the high-temperature catalytic decomposition approach, the HTSR-1 catalyst, a nickel-based catalyst on a refractory support, gave excellent results. The two 100-h tests with HTSR-1 demonstrated that it is capable of decomposing up to 90 percent of the NH_3 present in typical coal gasifier gases.

Further work is needed to reduce the cost of the catalyst and develop it in a form, such as monolith, that could operate in the presence of particles. Also continued research is needed for development of catalysts that would work at relatively lower temperatures down to 500 °C. Fundamental studies of what catalyst forms are active for NH_3 decomposition, what causes catalyst poisoning, and how it can be minimized could lead to the development of a successful combined sorbent-catalyst.

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APPENDIX A

Final Report by SRI International

Final Report • March 1996

SIMULTANEOUS REMOVAL OF HYDROGEN SULFIDE AND AMMONIA USING MIXED-METAL OXIDE SORBENTS

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SRI Project PYD-4151

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DRAFT

SUMMARY

During coal gasification, nitrogen compounds in the coal are primarily converted to NH_3 and when the coal gas is burnt in a gas turbine to produce electricity NH_3 is converted to nitrogen oxides. To minimize the formation of these toxic pollutants, removal of NH_3 from coal gas stream is desirable. Development of sorbents for the removal of H_2S at high temperatures is being actively pursued. Combining removal of both H_2S and NH_3 in one process unit will reduce the capital and operating costs of coal gas generation.

Catalytic decomposition of NH_3 into its elements N_2 and H_2 is desirable and thermodynamic calculations indicate that decomposition can reduce the level of NH_3 at temperatures above 900 K. Conventional ammonia decomposition catalysts cannot be used under hot coal gas conditions because H_2S and steam present in the hot coal gas stream act as poisons for these catalysts. Hence, novel catalysts must be developed that can function in steam concentrations greater than 10% and H_2S levels greater than 0.5%. Combining both desulfurization sorbent and NH_3 decomposition catalyst in the same unit requires that the catalyst not only function in the presence of H_2S but also should survive the oxidative regeneration of the desulfurization sorbent.

In this program, SRI tested several metal-supported catalysts in combination with a zinc titanate sorbent for removing both NH_3 and H_2S from simulated coal gas streams. Thermodynamic equilibrium calculations were made to determine the stability of the active metal phases in hot coal gas environments and under oxidative regeneration conditions. These calculations indicated that metals like Mo and W will be converted to their corresponding sulfides when exposed to typical coal gas streams. The calculations also showed that only molybdenum oxides have significantly high vapor pressures ($>1 \times 10^{-4}$ atm) at temperatures above 725°C to be of a concern. Other oxides such as CoO, CuO, ZnO, NiO, and W_2O_6 have very low vapor pressures ($<1 \times 10^{-12}$ atm). Loss of active components by vaporization will not be a problem except in the case of molybdenum.

Alumina, a commonly used catalyst support, could be converted to aluminum sulfate when exposed to SO_2 and O_2 present during oxidative regeneration of the spent sorbent. Aluminum sulfate is easily more sinterable than alumina. Thus, it could be expected that the surface area of an

alumina-based catalyst could decrease during cyclic sulfidation-regeneration steps. Oxides such as titania and zirconia are less prone to sulfation than alumina.

Experiments showed that a high surface area (>250 m^2/g) TiO_2 powder obtained from Rhone-Poulenc sintered when exposed to a gas stream containing 20% steam at 725°C. The surface area decreased from about 280 m^2/g to about 15 m^2/g in 24 h. When the titania was intimately mixed with zirconia, the reduction in surface area was much less severe; after 24 h in 20% steam, the surface area was about 30 m^2/g.

SRI identified in a previous program that HTSR-1, a supported Ni catalyst proprietary to Haldor-Topsøe A/S, Copenhagen, Denmark, exhibited excellent activity for NH_3 decomposition at a temperature of 800°C even in the presence of 2,000 ppm of H_2S. It also had a superior high temperature stability. Experiments conducted in this program confirmed these observations. At temperatures lower than 800°C, the steady-state NH_3 decomposition activity was a function of H_2S concentration. At 725°C, the catalyst was severely poisoned when exposed to 0.5% H_2S. Mixing the catalyst with a zinc titanate sorbent allowed the catalysts to function for an extended period of time. As the sorbent gets loaded with H_2S, the residual H_2S level increases thereby decreasing the activity of the catalyst for NH_3 decomposition. The HTSR-1 catalyst could be regenerated by oxidizing in a gas stream containing 2% O_2. However, the activity of the regenerated catalyst was less than the original catalyst.

About ten catalytic formulations were synthesized using either Ni, Co, Mo, and W as active components and titania or titania stabilized with zirconia as supports. Both single and dual active component mixtures were prepared. These catalysts were tested at 725°C in a simulated coal gas mixture representative of a Texaco oxygen-blown gasifier. Although the initial activity of some of these catalysts was high, it declined with time. Under steady-state conditions, less than 20% the feed NH_3 (~1800 ppm) decomposed at 725°C.

The following recommendations are made for further investigation into the removal of fuel-bound nitrogen from hot coal gas streams.

- The HTSR-1 should be tested using hot coal gas streams from an operating coal gasifier. The effects of trace components of the hot coal gas stream that could not be simulated in the laboratory must be determined.
- Alternative catalysts that have a high NH_3 decomposition activity at a temperature of about 550°C in the presence of H_2S must be developed.

- The regeneration of sulfur-poisoned HTSR-1 must be investigated. Although this catalyst can tolerate significant levels of H_2S at 800°C, it is slowly poisoned at low temperatures. Regeneration of the catalyst will allow continued use of this catalyst in a hot coal gas cleanup process.

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INTRODUCTION

FUEL-BOUND NITROGEN COMPOUNDS IN COAL GAS STREAMS

Fuel-bound nitrogen compounds such as ammonia and hydrogen cyanide are formed during gasification of coal and these compounds are readily converted to oxides of nitrogen (NO_x) during combustion of coal gas. U.S. coals contain from 0.5 to 2 wt% nitrogen on a dry basis [Chen et al., 1982]. The nitrogen in coal is chemically combined with the carbon in polycyclic aromatic rings [Axworthy, 1975]. Such chemical structures possess strong C-N bonds. At gasification temperatures, C-C bonds are readily broken, but the C-N bonds survive. Thus, HCN is the initial nitrogen-bearing gaseous product of pyrolysis [Solomon et al., 1982]. In a gasifier, the oxygen potential and the temperature near the inlet are sufficiently high to convert the HCN, through an NH_x intermediate, to NO and N_2. As the gases travel through the bed, oxygen is depleted and the NO is converted back to HCN and to NH_3. This general mechanistic pathway has been suggested by a number of investigators [Haynes, 1977; Smith et al., 1982] and has been confirmed by Highsmith et al. [Highsmith et al., 1985] in experimental measurements in a pilot-scale gasifier.

Fuel-bound nitrogen compounds become an undesirable contaminant in coal gas destined for high-temperature applications such as the generation of electricity in gas-fired turbines. In this use, during combustion the NH_3 is readily oxidized to NO_x (fuel-NO_x), a highly undesirable and difficult-to-remove atmospheric pollutant. Unlike the formation of NO_x from atmospheric nitrogen (thermal NO_x), the oxidation of fuel-bound nitrogen occurs at temperatures as low as 800°C; thus small decreases in flame temperature do not prevent the formation of fuel-bound NO_x. In molten carbonate fuel cell applications (MCFC), when the anode exhaust gas is burned with air to supply CO_2 for the regeneration of the carbonate electrolyte, the fuel NO_x formed can react with the electrolyte to form relatively volatile nitrates that lead to loss of electrolyte by evaporation [TRW, 1981]. Thus, removal of NH_3 from coal gas is highly desirable before the coal gas is used in these applications.

The concentration of fuel-bound nitrogen compounds in coal gas depends on factors such as temperature, pressure, residence time, and coal rank. Chen et al., [1982] who studied the combustion of a variety of coals in an oxygen-deficient atmosphere, found that low rank coals favored the formation of ammonia. An extensive examination of nitrogen compounds in the product gas of coal gasifiers was reported by Kilpatrick [1986]. In this study, conducted from 1977 to 1981, gas samples taken from working gasifiers producing low- and medium-Btu gas were analyzed for a number of chemical components, including NH_3 and HCN. The results revealed levels of NH_3 in the range 180 to 3100 ppm, depending on the type of gasification process, and they confirmed that NH_3 is a major nitrogen-bearing contaminant in coal gas. The concentration of HCN is typically an order of magnitude less than that of NH_3.

Haldipur et al. [1989] reported the concentration of NH_3 found in the KRW air-blown fluidized-bed pilot plant gasifier. The gasifier was operated at about 1100°C and limestone was used for in-bed desulfurization. The ammonia concentration was measured by scrubbing an aliquot of coal gas with an acid solution and analyzing the extract with a gas chromatograph. The NH_3 concentration varied from 20 to 340 ppm, corresponding to a coal nitrogen conversion ranging from 0.6% to 8.8%. The fate of the remainder of the nitrogen present in the coal was not reported.

Kurkela and Ståhlberg [1992] measured the concentration of NH_3 and HCN in fluidized-bed gasifiers operating with peat, brown coal, and wood sawdust. The concentration of NH_3 varied from about 500 to 9000 ppm depending on the type of fuel and the operating pressure. Similarly, the HCN level in the gas stream varied from about 10 to 200 ppm. Generally, the NH_3 levels were found to be highest with peat, moderate with brown coal, and low with wood sawdust feeds.

PREVIOUS STUDIES

Thermal decomposition of NH_3 to its elements, N_2 and H_2, is highly desirable as a method of removal, because such a reaction would not introduce any additional contaminants into the coal gas stream. Because of this reaction's high activation energy (92 kcal• mol^{-1}) (Yamura and Asabe, 1981) it is ineffective for reducing NH_3 levels at temperatures typical of hot coal gas streams. A catalyst is required, and hence, research efforts must focus on catalytic decomposition of ammonia.

Because of great interest in ammonia synthesis, the reverse reaction, catalytic decomposition of ammonia, has been examined by many investigators over the last 50 years. Most of these studies are related to the development of highly active catalysts such as bulk iron and promoted bulk iron formulations used in ammonia synthesis and they were devoted mainly to understanding reaction mechanisms and optimizing reaction conditions for high yields of ammonia. Such studies are of little importance to the hot coal gas cleanup conditions because steam, carbon monoxide, and hydrogen sulfide present in the coal gas are highly detrimental to the activity of the iron catalyst.

Nearly all kinetic studies of the decomposition of ammonia suggest that the decomposition occurs through successive dehydrogenation of adsorbed NH_x species to form surface adstates of nitrogen atoms and hydrogen atoms. The adstates then combine and desorb to form gaseous nitrogen and hydrogen. At low concentrations of NH_3 and high temperatures, the rate is limited by the rate of dissociative adsorption of NH_3 on the catalyst surface. At high concentrations of NH_3 and low temperatures, the desorption of product nitrogen molecules determines the overall rate.

The activity of the catalyst is related to the bond between the nitrogen adstate and the catalyst surface (Tamaru, 1961). If this bond is too weak, there is little driving force for dissociative adsorption of NH_3. At the opposite extreme, where the binding energy of the nitrogen adstate is strong, solid-state interactions such as dissolution and nitride formation are favored over associative desorption of nitrogen atoms. Indeed, the observed ammonia decomposition rate was found to be proportional to the heat of formation of the highest oxide of a metal (assumed to be proportional to the heat of formation of nitrides); the metals that form oxides with moderate heats of formation exhibit the highest activities. Such metals include ruthenium, cobalt, iron, and nickel. Strong nitride-forming metals such as tungsten were found to have very low activities.

Krishnan, et al. (1988) studied the removal of fuel-bound nitrogen compounds in simulated coal gas streams using a laboratory scale reactor. This study investigated several catalysts including supported nickel catalysts, zinc ferrite sorbents containing NiO or CuO additives, and a MoS_2 catalyst at 550° and 800°C under simulated coal gas compositions representative of fixed-, fluidized-, and entrained-bed gasifiers. HTSR-1, a catalyst proprietary to Haldor-Topsøe A/S, Copenhagen, Denmark, exhibited excellent activity, even in the presence of 2,000 ppm of H_2S, and high temperature stability. G-65*, an SRI catalyst, demonstrated superior activity in the temperature range 550° to 650°C at H_2S levels below 10 ppm. The presence of impurities such as HCl and HCN did not affect the catalyst performance in the temperature range studied. Tar contaminants can lead to carbon deposits that are easily removed at 800°C.

Other oxide and sulfide catalysts also have shown some activity for NH_3 decomposition (Krishnan et al., 1988) . An MoS_2 catalyst reduced NH_3 levels from about 5000 ppm to 1500 ppm at 790°C. Ni- and Cu-doped zinc ferrite sorbents exhibited initial activity for NH_3 decomposition at 550°C, but the activity could not be sustained as the sulfide is absorbed by the sorbent.

A few other studies have also been performed on the catalytic decomposition of ammonia under simulated coal gas conditions. The Institute of Gas Technology (1983) reports that, although zinc- and iron-based catalysts were more effective in decomposing NH_3, the catalysts exhibited a four- to six-fold decrease in catalytic activity on exposure to a feedgas containing H_2S. Similarly, a study by Engelhard Corporation (Farruto, 1986) found that a catalyst containing nominally NiO and MnO_2 supported on a proprietary alumina exhibited very high activity for ammonia decomposition but deactivated in the presence of steam and H_2S. A marked decrease in catalytic activity was noted when the steam and H_2S concentrations exceeded 10% and 10 ppm, respectively; steam was more deleterious than H_2S.

Cooper and Lungström (Cooper et al., 1989; Cooper and Ljungström, 1988) studied the decomposition of NH_3 over silica and calcined and sulfated limestone materials. In the temperature range 840° to 960°C, the activities of these materials were found to be moderate in a fluidized-bed reactor and a stream of NH_3 and Ar. The presence of H_2 reduced the rate of decomposition, as expected. The rate constants for NH_3 decomposition on these materials are significantly lower than the value (220 s^{-1}) found for the HTSR-1 catalyst.

The effect of water vapor and hydrocarbons on the rate of decomposition of NH_3 by CaO, MgO, and dolomite was investigated by Björkman and Sjöström (1991). Steam and hydrocarbons that can form carbonaceous material on the catalysts inhibited the decomposition. At 900°C, in a mixture of 0.1% NH_3, 8% steam and 91.9% He, the extent of conversion of NH_3 was less than 10% in comparison to a >90% conversion in a mixture of 0.1% NH_3 and 99.9% He.

Leppälahti et al. [1991] also investigated the conversion of nitrogen compounds from a peat gasifier over several inexpensive materials such as dolomite, limestone, iron sinter, and ferrous dolomite. The gas stream used in these tests contained only about 100 ppm of H_2S. Limestone, dolomite, and silicon carbide had very little catalytic effect. But, ferrous materials such as iron sinter and ferrous dolomite decomposed NH_3 and organic nitrogen compounds at temperatures 900°C. About 80% of the feed NH_3 (2250 ppm) dissociated on these materials. But they were not as effective as nickel catalysts which decomposed nearly 100% of feed NH_3 under the same conditions.

Krishnan et al. (1990) performed a preliminary cost estimate for the process of catalytic removal of fuel-bound nitrogen from hot coal gas streams. The gas stream was assumed to be from a KRW gasifier operating in air-blown mode with 2000 ppm NH_3 present. Removal of 90% of the fuel-bound nitrogen was the design objective. The catalytic unit is of a fixed-bed type and placed downstream of the particle removal equipment but upstream of the desulfurization units.

The operating pressure, temperature, and space velocity are 225 psia, 750°C and 2500 h^{-1}, respectively. For a plant capacity of 100 MW_e, the catalytic unit consists of two refractory-lined fixed-bed reactors with an internal diameter of 4 m and a height of 8.3 m. The capital cost is estimated to be $1,237,000. The operating cost including catalyst replacement every four years, labor, maintenance, and cost of capital is estimated to be about 0.1¢/kWh, a very modest burden on the cost of electricity. A change in the capital recovery factor from 25% to 15% will decrease the cost of catalytic removal of fuel-bound nitrogen by about 20%. A 25% change in the catalyst cost will change the annual operating cost by about 9%.

SIMULTANEOUS REMOVAL OF AMMONIA AND HYDROGEN SULFIDE

Coal gas streams contain several impurities that need to be removed. Providing a separate reactor and process stage for each impurity would be economically impractical. Combined removal of H_2S and NH_3 in one process step would minimize capital and operating costs. Ayala [1993] claimed that addition of metal oxides such as MoO_3 to zinc oxide-based sorbents would decompose NH_3 while removing H_2S at about 530°C. Recently, Jothimugerasan et al. (1995) reported that zinc titanate sorbents containing additives such as Ni, Mo, and W compounds were able to remove H_2S and NH_3 simultaneously. At a temperature of 700°C, the H_2S level was reduced from 1% to 75 ppm while about 50% conversion of feed NH_3 (0.18%) was observed.

Zinc titanate sorbents have proven to be durable for hot coal gas desulfurization applications. Hence, they are ideal candidates to be used as supports for the active NH_3 decomposition formulations. The integration of the catalyst and the sorbent may be accomplished in several ways: physical mixing of catalyst and sorbent particles, precipitation of the catalyst formulation on to the sorbent, or wet impregnation of the sorbent with the catalytic material.

The catalyst-sorbent mixture must be able to survive the oxidative regeneration conditions. Under these conditions, many of the candidate NH_3 decomposition catalyst surfaces are likely to be converted to the oxides or sulfates. For example, the equilibrium partial pressure of oxygen for conversion of Ni to NiO at 800°C is 1×10^{-14} atm which is well below the partial pressure of oxygen in the regeneration atmosphere. Similarly, we expect that Mo, Co, Ni, and W and their respective sulfides will be converted to oxides during the sorbent regeneration process step.

For the catalyst-sorbent mixture to be useful in long-term applications, the volatility of the catalyst under oxidizing conditions must be negligibly small. Thermodynamic calculations indicate that Mo_3O_9 and Mo_4O_{12} species have appreciable vapor pressures (~6×10^{-4} atm) at 1000 K, and thus they would likely disappear from the bed at an unacceptably high rate. However, formation of molybdates may lower the vapor pressure of the molybdenum oxides significantly. Also, oxides of Ni, Co, and W have significantly lower vapor pressures, less than 1×10^{-10} atm, at 1000 K.

The densities of MoS_2, WS_2, NiS and CoS are lower than their corresponding oxides. Hence, cyclic sulfidation-oxidation steps may lead to volume changes that are detrimental to the physical integrity of the catalyst-sorbent mixture. However, if the fractional quantity of the catalyst is small in comparison to the sorbent, then changes in the catalyst particle volume may not have a significant effect on the strength of the catalyst.

SCOPE OF THE REPORT

The objective of the proposed program is to identify and test, at a laboratory-scale, various catalysts that will both decompose NH_3 and remove H_2S in the hot coal gas desulfurization environment. The program consists of three tasks:

A. Submission of NEPA information and development of a test plan

B. Catalyst selection, synthesis, and testing

C. Data analysis.

In Task A, the information necessary for the preparation of the NEPA document was submitted. A test plan was also submitted previously to select and evaluate various catalysts in a laboratory scale reactor. This report provides the results of Tasks B and C. The next chapter describes the thermodynamic calculations made to determine (a) the equilibrium decomposition of NH_3 and (b) the stability of the catalysts and sorbents under various conditions. The experimental procedures used for testing the activity catalysts and sorbents are described next. The observed results and their interpretation are presented next followed by a summary of conclusions and recommendations.

THERMODYNAMIC CALCULATIONS

Thermodynamic calculations were performed to determine the concentrations of NH_3 in equilibrium with coal gas streams typical of two gasifiers: Texaco's entrained-bed unit (Texaco) and METC's Gasifier Product Improvement Facility (GPIF). The Texaco gasifier is operated in an oxygen-blown mode whereas the GPIF gasifier performs in an air-blown mode. The concentrations of NH_3 and other components are substantially different in the respective product streams of these gasifiers (Table 1).

TABLE 1

PRODUCT GAS COMPOSITION (VOL %) IN TEXACO AND GPIF GASIFIERS

Component	Texaco Gasifier	GPIF Gasifier
H_2	31.1	12.5
CO	45.7	21.6
H_2O	12.5	25.0
CO_2	10.0	2.39
H_2S	0.5	0.13
NH_3	0.18	0.34

The equilibrium partial pressure of NH_3 as a function of temperature in the product gas of these respective gasifiers at total pressures of 1 and 20 atm are illustrated in Figures 1 and 2. As expected, the partial pressure of NH_3 decreases with increasing temperature at a total pressure of 1 atm. However, at 20 atm, the equilibrium partial pressure of NH_3 is low at 500°C, but increases at higher temperatures. A maximum level in NH_3 partial pressure is attained in the temperature range 600° to 800°C depending on the gas composition. At very high temperatures, the equilibrium partial pressure is decreased even at 20 atm total pressure.

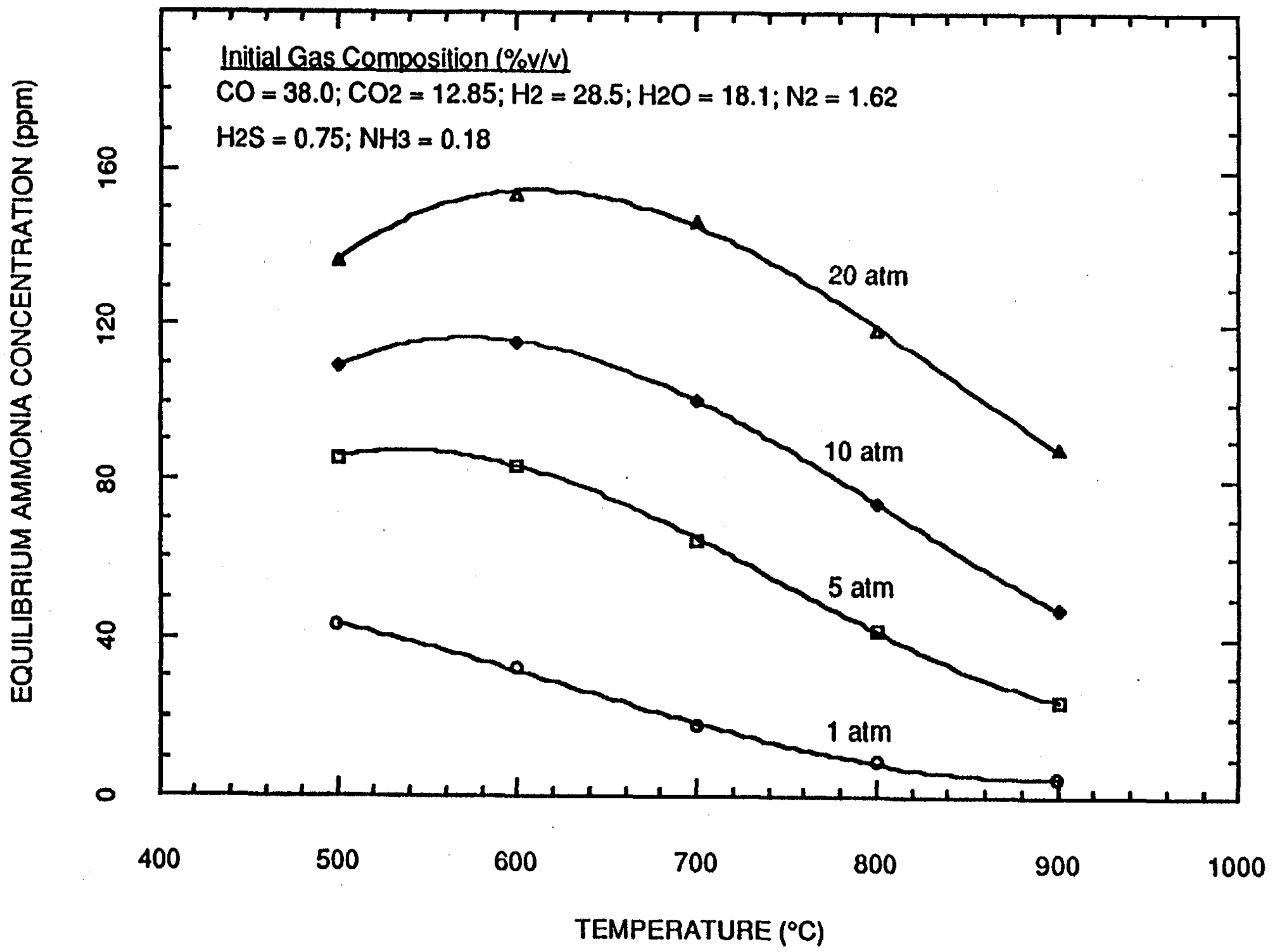

Figure 1. Equilibrium concentration of ammonia as a function of temperature and pressure in a Texaco coal gasifier gas stream.

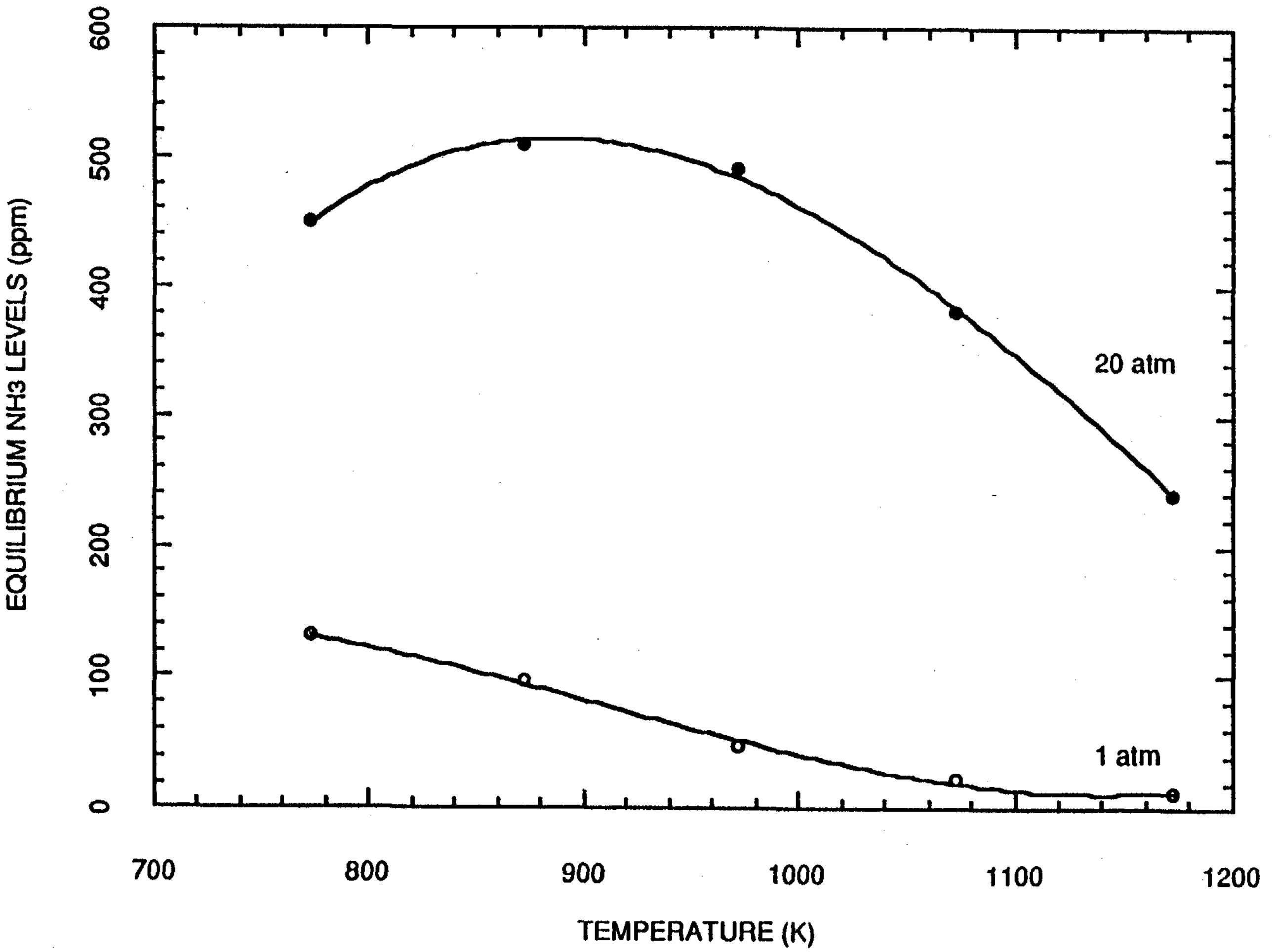

Figure 2. Equilibrium levels of ammonia as a function of temperature and pressure in GPIF's air-blown gasifier stream.

The low NH_3 partial pressure calculated for the Texaco gasifier stream at 500°C appears to be due to the formation of CH_4, a process that reduces the partial pressure of H_2. Thermochemically, the extent of decomposition of NH_3 is inversely proportional to the partial pressure of H_2. Because the formation of CH_4 is thermodynamically favored at lower temperatures and higher pressures, the process is beneficial to the decomposition of NH_3 under such conditions. Table 2 shows the equilibrium partial pressures of CH_4 and H_2 as functions of temperature at a total pressure of 20 atm..

TABLE 2

CALCULATED EQUILIBRIUM PARTIAL PRESSURES OF CH_4, AND H_2 AT A TOTAL PRESSURE OF 20 ATM IN A TEXACO GASIFIER STREAM

Temperature (°C)	% CH_4	% H_2
500	28.1	2.6
600	23.4	6.45
700	15.7	13.4
800	7.63	22.2
900	2.31	28.7
1000	0.47	30.6

Nickel and MoS_2 based catalysts have been shown to be effective in decomposing NH_3 in the presence of H_2S in simulated coal gas streams. The activity of the sulfide based catalysts for NH_3 decomposition may depend on whether the catalyst can be kept in the sulfided state. Our thermodynamic calculations indicate that MoS_2 will be stable at 723°C at a $p(H_2S)/p(H_2)$ ratio higher than 0.5×10^{-3} (Figure 3). At the same temperature, WS_2 will be stable at ratios higher than 1×10^{-3} (Figure 4). The product gas streams from both Texaco and GPIF gasifiers contain more than enough H_2S to keep these sulfides in stable conditions. However, after passage through a zinc titanate sorbent the concentration of H_2S will decrease substantially. Under equilibrium conditions in this environment, the sulfides may be reduced to metals as the stable phases.

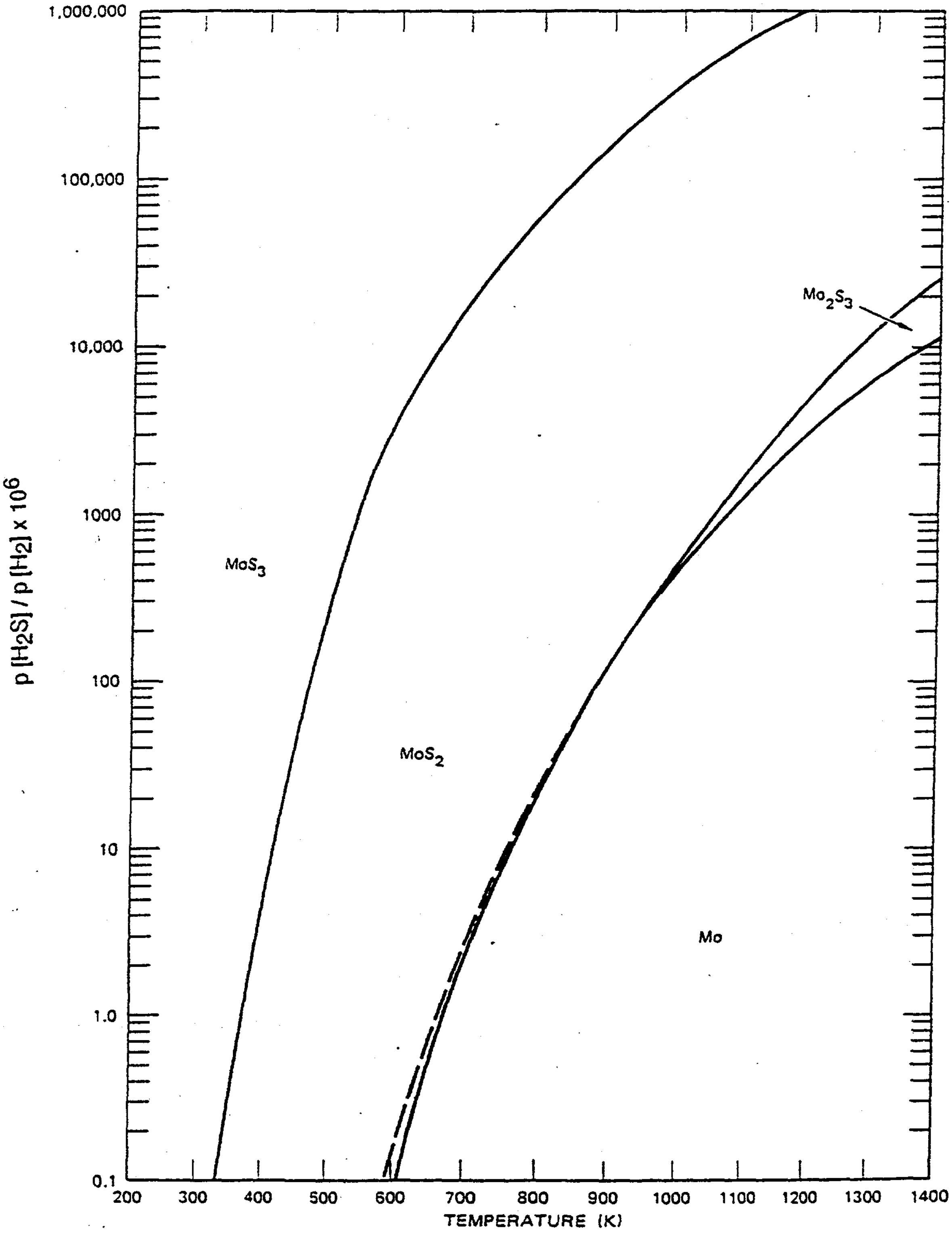

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Figure 3. Stability of molybdenum sulfides in hydrogen.

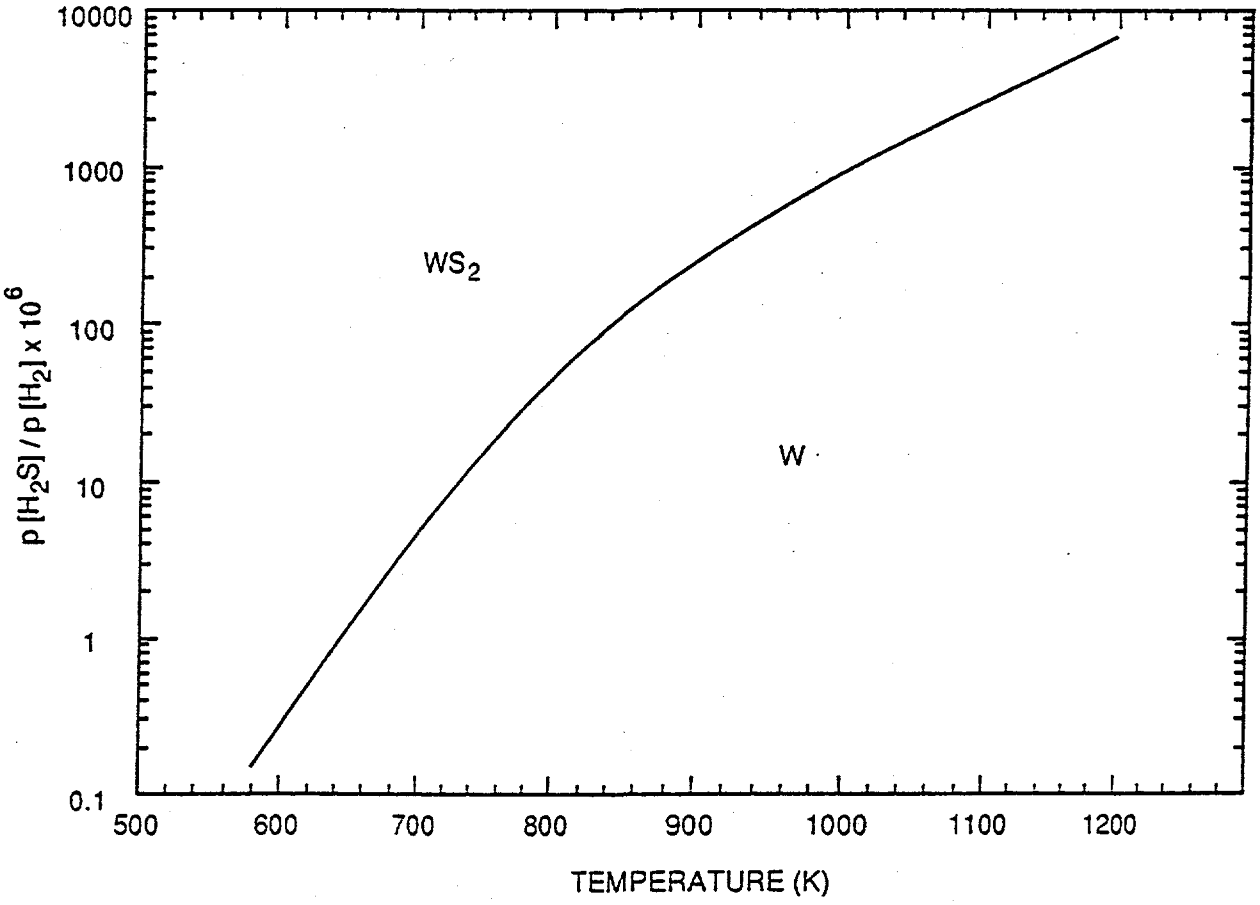

Figure 4. Stability of tungsten disulfide in hydrogen

Combining both the desulfurization sorbent and NH_3 decomposition catalyst in the same unit requires that the catalyst not only function in the presence of H_2S but also must survive the oxidative regeneration of the sulfided sorbent. During this process step, the loss of active components by volatilization must be minimized. To predict the possible extent of loss by vaporization, we calculated the equilibrium vapor pressures of several metal oxides as a function of temperature (Table 3). Of the oxides considered, only the molybdenum oxides have significant vapor pressure at temperatures above 600°C. Detailed calculations (Table 4) indicated that Mo_3O_9, Mo_4O_{12}, and Mo_5O_{15} are the dominant vapor species in the temperatures range 525–825°C in equilibrium with solid MoO_3.

TABLE 3

EQUILIBRIUM PARTIAL PRESSURES OF METAL OXIDE VAPORS IN THE PRESENCE OF 2% O_2 AT 625° AND 725°C

Oxide Vapor	p(MO) at 625°C (atm)	p(MO) at 725°C (atm)
CoO	2.7×10^{-23}	6.9×10^{-20}
CuO	8.7×10^{-18}	3.7×10^{-15}
FeO_2	1.4×10^{-20}	5.8×10^{-18}
ZnO	3.8×10^{-17}	1.2×10^{-14}
NiO	2.3×10^{-22}	3.2×10^{-19}
W_2O_6	1.6×10^{-21}	7.0×10^{-12}
Mo_3O_9	4.4×10^{-6}	2.9×10^{-4}
Mo_4O_{12}	4.1×10^{-6}	3.5×10^{-4}

TABLE 4

CALCULATED PARTIAL PRESSURES OF SPECIES OVER MoO_3(c) IN PRESENCE OF PURE O_2 AT 0.02 ATM TOTAL PRESSURE

	Partial Pressure (atm)				
Species	700 K	800 K	900 K	1000 K	1100 K
Vapor Species			MoO_3(c)		
Mo	1.21×10^{-81}	1.23×10^{-68}	1.53×10^{-58}	1.84×10^{-50}	6.11×10^{-44}
MoO	4.76×10^{-62}	7.35×10^{-52}	5.89×10^{-44}	1.21×10^{-37}	1.34×10^{-32}
MoO_2	5.48×10^{-39}	2.76×10^{-32}	4.30×10^{-27}	5.97×10^{-23}	9.86×10^{-20}
MoO_3	5.93×10^{-19}	1.76×10^{-15}	8.52×10^{-13}	1.16×10^{-10}	3.98×10^{-9}
Mo_2O_6	3.01×10^{-14}	3.63×10^{-11}	8.59×10^{-9}	6.52×10^{-7}	8.76×10^{-6}
Mo_3O_9	2.20×10^{-11}	2.19×10^{-8}	4.42×10^{-6}	2.92×10^{-4}	2.20×10^{-3}
Mo_4O_{12}	9.37×10^{-12}	1.45×10^{-8}	4.07×10^{-6}	3.46×10^{-4}	2.02×10^{-3}
Mo_5O_{15}	1.10×10^{-13}	4.04×10^{-10}	2.20×10^{-7}	3.13×10^{-5}	1.76×10^{-4}
O	5.02×10^{-17}	1.12×10^{-14}	7.54×10^{-13}	2.17×10^{-11}	3.09×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	1.93×10^{-2}	1.56×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.44×10^{-15}	2.34×10^{-14}	7.81×10^{-14}
Σ p(Mo) (atm)	**3.15×10^{-11}**	**3.68×10^{-8}**	**8.72×10^{-6}**	**6.70×10^{-4}**	**4.41×10^{-3}**
Solid Phases					
Mo(c)	No	No	No	No	No
MoO_2(c)	No	No	No	No	No
MoO_3(c)	Yes	Yes	Yes	Yes	No
Mo_4O_{11}(c)	No	No	No	No	No
Mo_8O_{23}(c)	No	No	No	No	No
Mo_9O_{26}(c)	No	No	No	No	No

Addition of another metal oxide can suppress the vaporization of molybdenum oxide, just as the presence of titanium oxide in zinc titanate sorbents decreases the vaporization of zinc. We calculated the equilibrium partial pressures of molybdenum oxide vapors in the presence of copper, cobalt, iron, nickel, and zinc oxides (Table 5). Appendix A describes the results of thermodynamic calculations with several molybdates and tungstates. Copper oxides were effective in decreasing the vaporization of molybdenum oxides by about four orders-of-magnitude. Other oxides do not promote the formation of the corresponding molybdates, and hence, no reduction in the equilibrium vapor pressures of molybdenum oxides is achieved.

TABLE 5

TOTAL PRESSURE OF Mo-CONTAINING SPECIES OVER MoO_3(c) + $MMoO_4$(c)
IN THE PRESENCE OF PURE O_2 AT 0.02 ATM TOTAL PRESSURE

	Total Pressure of Mo-Containing Species (atm)				
Oxide	700 K	800 K	900 K	1000 K	1100 K
MoO_3(c)	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}
$CuMoO_4$(c)	1.17×10^{-15}	2.34×10^{-12}	8.04×10^{-10}	8.10×10^{-8}	3.30×10^{-6}
Fe_2O_3 + MoO_3(c)	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	5.45×10^{-3}
NiO + MoO_3(c)[1]	4.94×10^{-15}	1.11×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}
Co_3O_4+ MoO_3 (c)	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	5.05×10^{-3}
ZnO + MoO_3(c)	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}

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[1] At temperatures below 800K, $NiMoO_4$ was the equilibrium solid phase.

EXPERIMENTAL PROCEDURE

THE FIXED-BED REACTOR SYSTEM

A laboratory-scale reactor system was assembled to determine the activity of selected catalyst–sorbent systems for their NH_3 decomposition activity and H_2S removal ability. This system includes a feed gas supply section in which the simulated coal gas components, supplied from standard high pressure cylinders equipped with pressure regulators, are mixed and metered by a bank of electronic mass flow controllers (Figure 5). Steam is added to the feedstock using an in-line stainless steel evaporator to which water is added by a precision liquid-metering pump. All lines downstream from the steam generator are heated to prevent condensation of water. NH_3 is added to the gas mixture downstream of the steam generator where the temperature is high enough to avoid the formation of $(NH_4)_2CO_3$. A second reactor was used for pretreating the catalysts.

The product gases from the reactor are analyzed by gas chromatography (GC). For the NH_3 analysis, the product gas, prior to the condensation of steam, first passes through an H_2S trap (copper sponge or zinc oxide kept at a temperature of about 200°C) and is then sampled by a high-temperature injection valve into a GC with a chromosorb 103 column. This column separates NH_3 from the other components of the sample stream. The effluent from the column first passes through a photoionization detector (PID) for analysis of NH_3 and then through a flame ionization detector for analysis of CH_4. Of all the components of the sampled gas stream, only NH_3 (and H_2S, if it is not removed) are detected by the photoionization detector. The calibration of the PID for NH_3 is shown in Figure 6. As expected, a linear correlation between the signal intensity and concentration of NH_3 was observed.

The concentration of H_2S in the gas stream is determined on a second sample from which steam is removed by condensation in a trap. This sample flows into a flame photometric detector (FPD) that is sensitive exclusively to sulfur compounds. A thermal conductivity detector used in series with the FPD is used to determine the concentration of the major components of the gas stream. Because NH_3 in this sample is effectively removed during steam condensation, the separation of NH_3 and H_2S is unnecessary. Hence, a Haysep Q column was used to separate the H_2S from the rest of the gases. During sorbent regeneration, the concentration of liberated SO_2 will be measured using this technique. The calibration of the FPD for H_2S is shown in Figure 7.

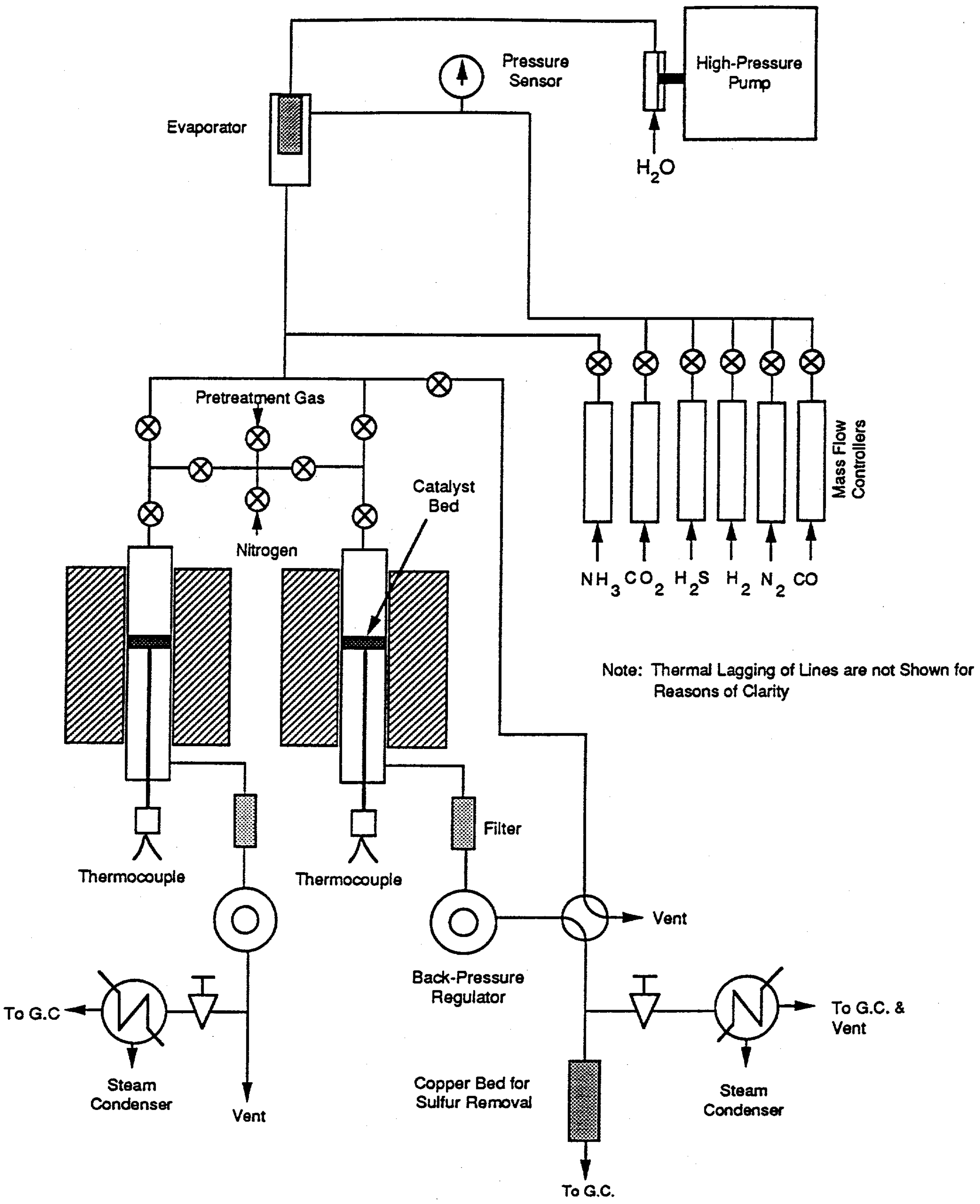

Figure 5. Schematic diagram of the fixed-bed reactor system.

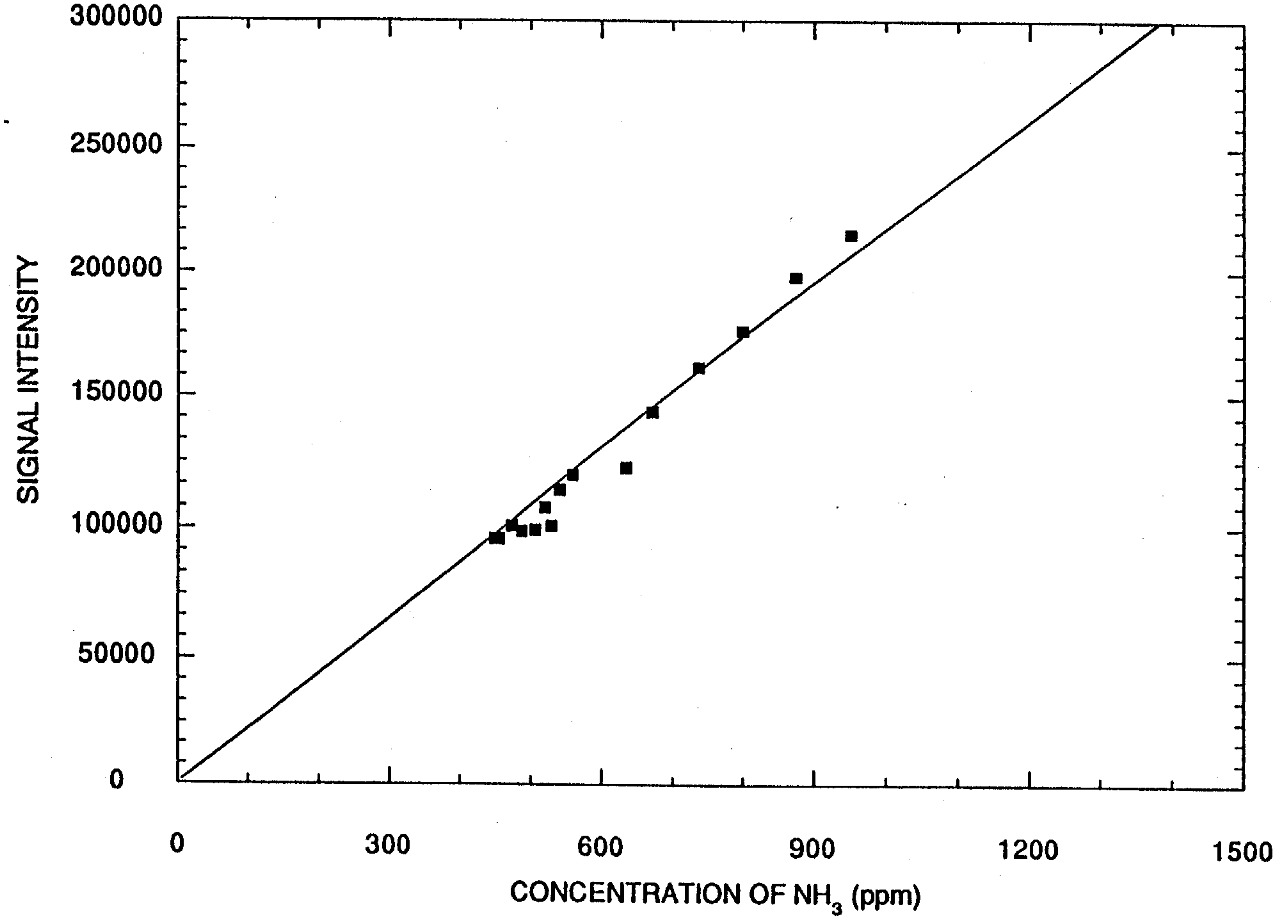

Figure 6. Calibration of photoionization detector for NH_3 gas.

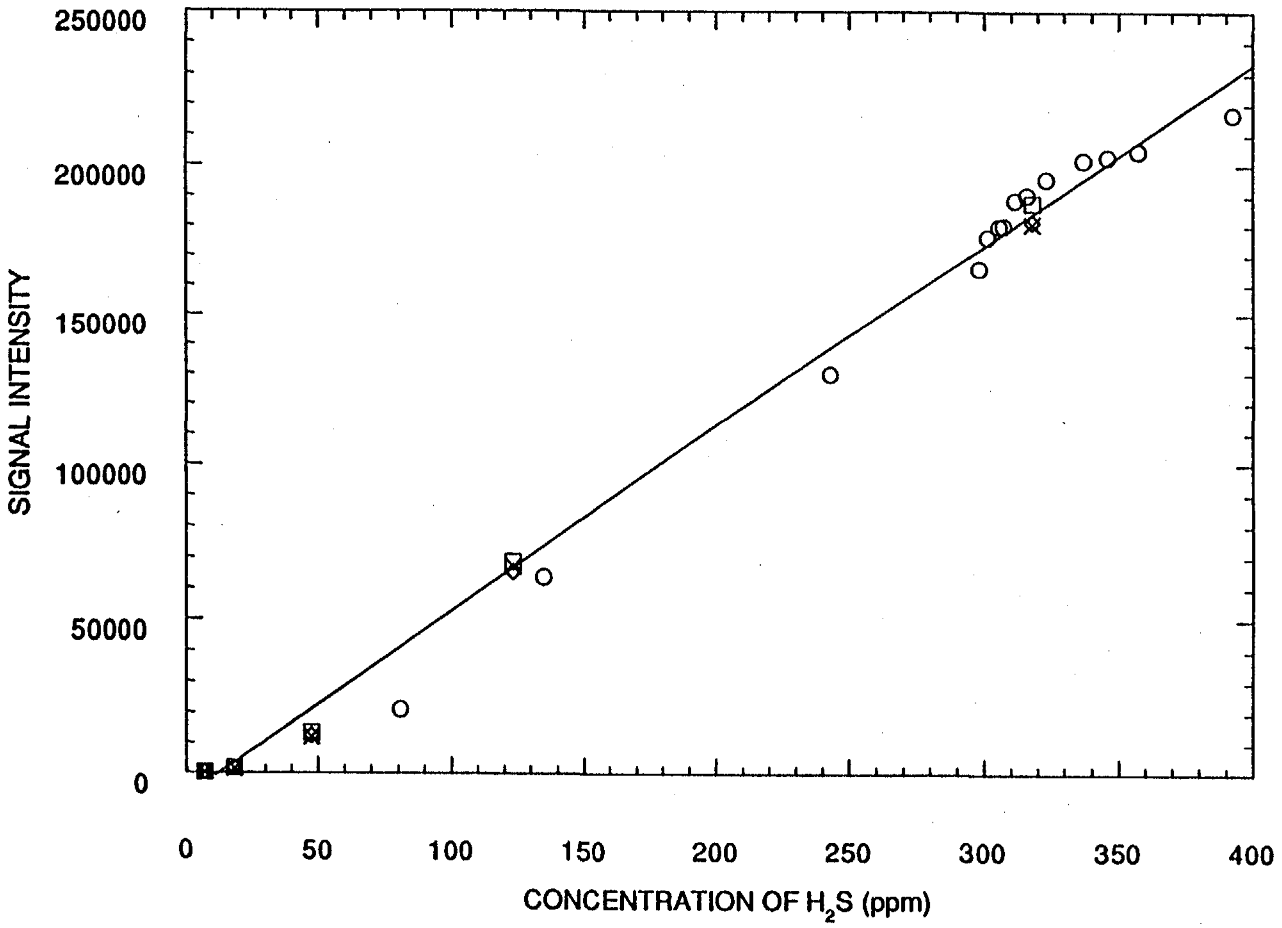

Figure 7. Calibration of flame photometric detector for H_2S gas

A bypass line from the feed gas manifold and a selector valve permits injection of feed gas samples into the chromatographs. Thus the fractional reduction of NH_3 and changes in other components of the simulated coal gas during passage through the reactor can be measured directly. The rate of the ammonia decomposition reaction is calculated from the measured fractional conversion and the space velocity of the gas in the reactor.

PREPARATION OF CATALYSTS

A Ni-supported on a ceramic support (HTSR-1) and a MoS_2 stabilized with zirconia were designated as the baseline catalysts. These two catalysts were tested extensively by SRI in a previous program for NH_3 decomposition. HTSR-1, manufactured by Haldor-Topsoe AG, Copenhagen, Denmark, was found to be an excellent catalyst for decomposing NH_3. The MoS_2 catalysts (CRC-653 and CRC-530) were prepared by Catalyst Research Corporation, Palisades Park, NJ. CRC-653, which had ZrO_2 as a stabilizing agent, showed a significant catalytic activity for the decomposition of NH_3 in the presence of 0.3% H_2S. CRC-530 did not contain any stabilizing agent.

The HTSR-1 catalyst contains alumina and other oxides that could be converted to sulfates readily when exposed to SO_2-containing gas streams such as the one expected during oxidative regeneration of the spent catalyst. Titania and zirconia are less prone to sulfate formation than alumina. Hence, several formulations using titania or zirconia as support materials and nickel, cobalt, or molybdenum, and tungsten as active components were prepared.

Catalysts containing Ni as the active component were prepared using a high surface area (>250 m^2/g) titania obtained from Rhone-Poulenc. To a slurry of this titania in isoproponal, a solution of zirconyl propoxide (in isoproponal) was added. Zirconium oxide was precipitated by adding water to this mixture resulting in an intimate contact between titania and zirconia. Nickel was incorporated in this substrate by adding a solution of nickel nitrate and precipitating it with ammonium hydroxide. The resulting solid mixture was dried and calcined. The estimated composition of the catalyst (Ni/TiO_2) is 20 wt% NiO, 20 wt% ZrO_2, and 60 wt% TiO_2.

The dried catalyst had a surface area of 193 m^2/g. After calcination in air at 550°C, the surface area was reduced to 115 m^2/g. Reduction in hydrogen at this temperature did not change the surface area (118 m^2/g) significantly. However, calcination in air at 725°C for 2.5 h resulted in a further reduction in surface area to 22 m^2/g. The measured surface area is less than the manufacturer-specified value of 48 m^2/g after calcination in air at 750°C for 2 h.

Catalysts containing either cobalt or cobalt and molybdenum on high surface area titania were prepared. Cobalt (~20 wt%) was deposited on the TiO_2 support by slow precipitation by adding ammonium carbonate to a dilute solution of cobalt nitrate containing the support. The final pH was kept below the isoelectric point for cobalt hydroxide (~11.5) so that the cobalt compound is adsorbed on the TiO_2 support. The catalyst (Co/TiO_2) was then dried and calcined in hydrogen at 500°C for 4 h. The surface area of the calcined catalyst was 63 m^2/g.

A batch of Co-Mo supported on TiO_2 was prepared by impregnating the Co-TiO_2 catalyst (prepared as described above) with a solution of ammonium molybdate under incipient wet conditions. The impregnation was performed three times to bring the total amount of Mo to 6.4 wt%. The catalyst ($Co\text{-}Mo/TiO_2$) was calcined in hydrogen at 550°C until all the molybdate was decomposed.

Two Mo-supported on TiO_2 catalysts (Mo-TiO_2) were made by impregnating high surface area TiO_2 powders with an ammonium molybdate solutions. Two W-supported on TiO_2 (W-TiO_2) catalysts were synthesized by impregnating TiO_2 powders with an ammonium tungstate solutions. The impregnated powders were dried overnight at 100°C, reduced in H_2 at 550°C.

Another catalyst containing 5 wt% Co and 15 wt% W on TiO_2 was prepared by impregnating the TiO_2 powder with ammonium tungstate solution three times. The catalyst was dried at 110°C between impregnation. After heating in H_2 at 550°C, cobalt was incorporated into the catalyst with wet impregnation with a cobalt nitrate solution. Finally, the catalyst ($W\text{-}Co/TiO_2$) was treated in H_2 at 550°C until all the nitrate was removed.

At the elevated temperature of 725°C, the TiO_2 support may sinter. The decrease in the surface area of the support due to sintering may contribute to the decline in the catalytic activity with time. To determine the sintering rate of the support, the TiO_2 powder was exposed to a mixture of 80% air-20% steam at 725°C for periods up to 72 h and the change in surface area was measured (Figure 8). These measurements indicated that the surface area of TiO_2 powder decreased from an initial value of about 280 m^2/g to about 15 m^2/g after 72 h.

To stabilize the surface area of TiO_2, 25 mole% ZrO_2 was added by precipitating the ZrO_2 from a zirconium propoxide solution. This procedure allows intimate contact between the TiO_2 and ZrO_2. The mixture of TiO_2-ZrO_2 was calcined at 350°C for 2h and then exposed to air-steam (25%) mixture at 725°C for periods up to 24 h. Surface area determination of the exposed samples indicated that ZrO_2 addition is beneficial in stabilizing the surface area. The samples containing ZrO_2 have nearly twice the surface area as those which do not contain ZrO_2 (Table 6).

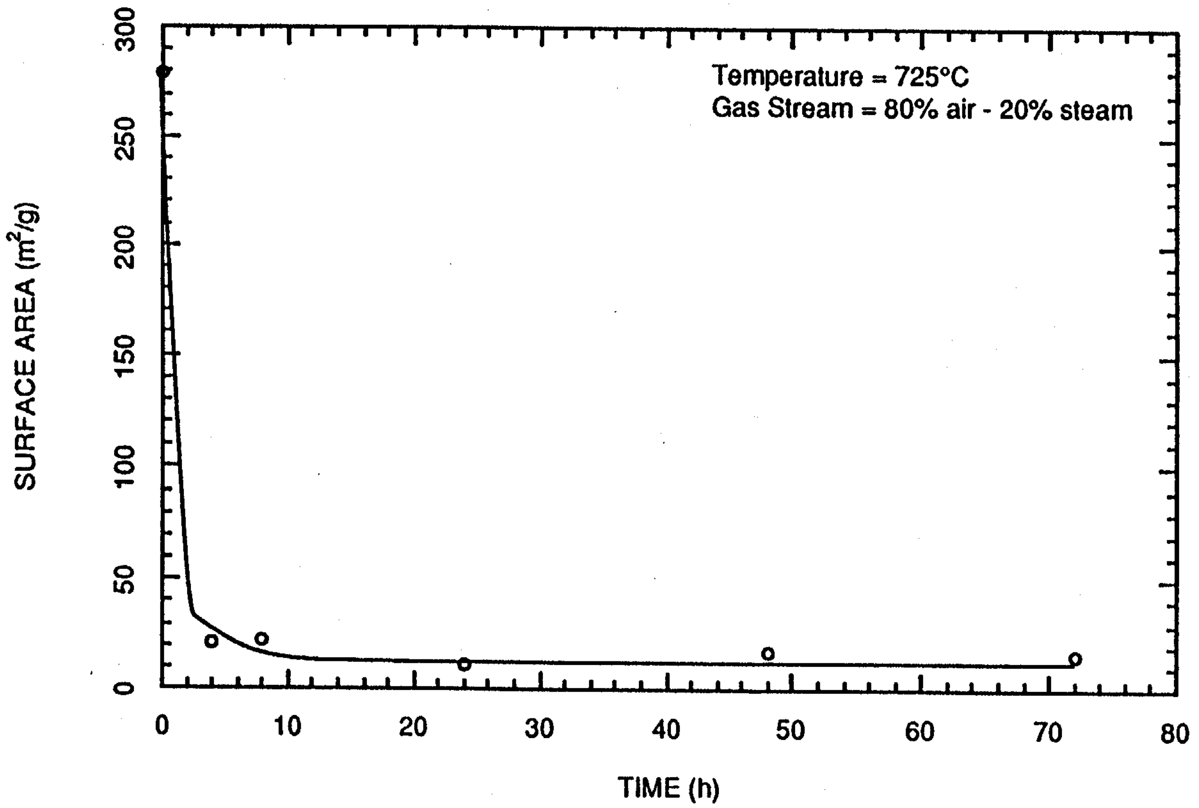

Figure 8. Change in surface area of a titania support as a function of time at 725°C.

TABLE 6

SURFACE AREA CHANGES IN TIO_2 and TiO_2-ZrO_2 POWDERS DURING EXPOSURE TO STEAM AT 725°C[1]

Time (h)	Area of TiO_2 Powder (m^2/g)	Area of TiO_2-ZrO_2 Powder[2] (m^2/g)
0	279	157
4	21	37
8	22	33
24	11	29
48	17	-
72	16	-

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[1] The powders were exposed to a gas stream containing 80% air and 20% steam.

[2] The initial ZrO_2-TiO_2 sample was calcined at 350°C for 2 h.

RESULTS AND DISCUSSION

BASELINE CATALYSTS

The HTSR-1 catalyst decomposed about 80% of the feedgas NH_3 at 725°C under steady state conditions in the absence of H_2S (Figure 9). Although CH_4 was not added to the feedgas, the reactor effluent contained about 3.5% of CH_4 due to methane formation from CO and H_2 in the feedgas. However, when 0.5% H_2S was added to the feedgas, both the decomposition of NH_3 and the formation of CH_4 were inhibited. The concentration of H_2S in the reactor effluent was initially low, but a breakthrough was observed after about 100 minutes. The concentration of H_2S reached the feedgas value after about 200 minutes of exposure. After this period, the formation of CH_4 and decomposition of NH_3 were negligibly small.

The activity of the poisoned catalyst was not restored even when the catalyst was kept overnight at 725°C in pure H_2, indicating that the H_2S is irreversibly adsorbed at this temperature. However, when the temperature of the poisoned catalyst was increased to 800°C, the NH_3 decomposition activity was restored (Figure 10). Initially, the concentration of H_2S in the reactor effluent was higher than feedgas level indicating a desorption of adsorbed sulfur on the catalyst. As the catalyst became free of adsorbed sulfur, its activity for the decomposition of NH_3 also increased. At this high temperature and low pressure, the concentration of CH_4 in the reactor effluent was negligibly small.

The effectiveness of HTSR-1 to catalyze the decomposition of NH_3 at low levels of H_2S was also determined by placing the catalyst downstream of a zinc titanate bed and exposing them to a simulated Texaco coal gas containing 0.5% H_2S and 0.18% NH_3. Under these conditions, when H_2S level was about 10 ppm, nearly 90% of the feed NH_3 was decomposed (Figure 11). These set of experiments demonstrated that HTSR-1 is an effective catalyst for the decomposition of NH_3 at about 725°C when H_2S level is not very high.

An experiment was also performed by mixing both the zinc titanate sorbent and HTSR-1 catalyst in equal proportions and exposing them to the simulated Texaco coal gas at 725°C. When the concentration of H_2S in the reactor effluent was below 10 ppm, nearly 80% conversion of the feed NH_3 was observed. As the quantity of H_2S removed by the sorbent-catalyst bed decreased

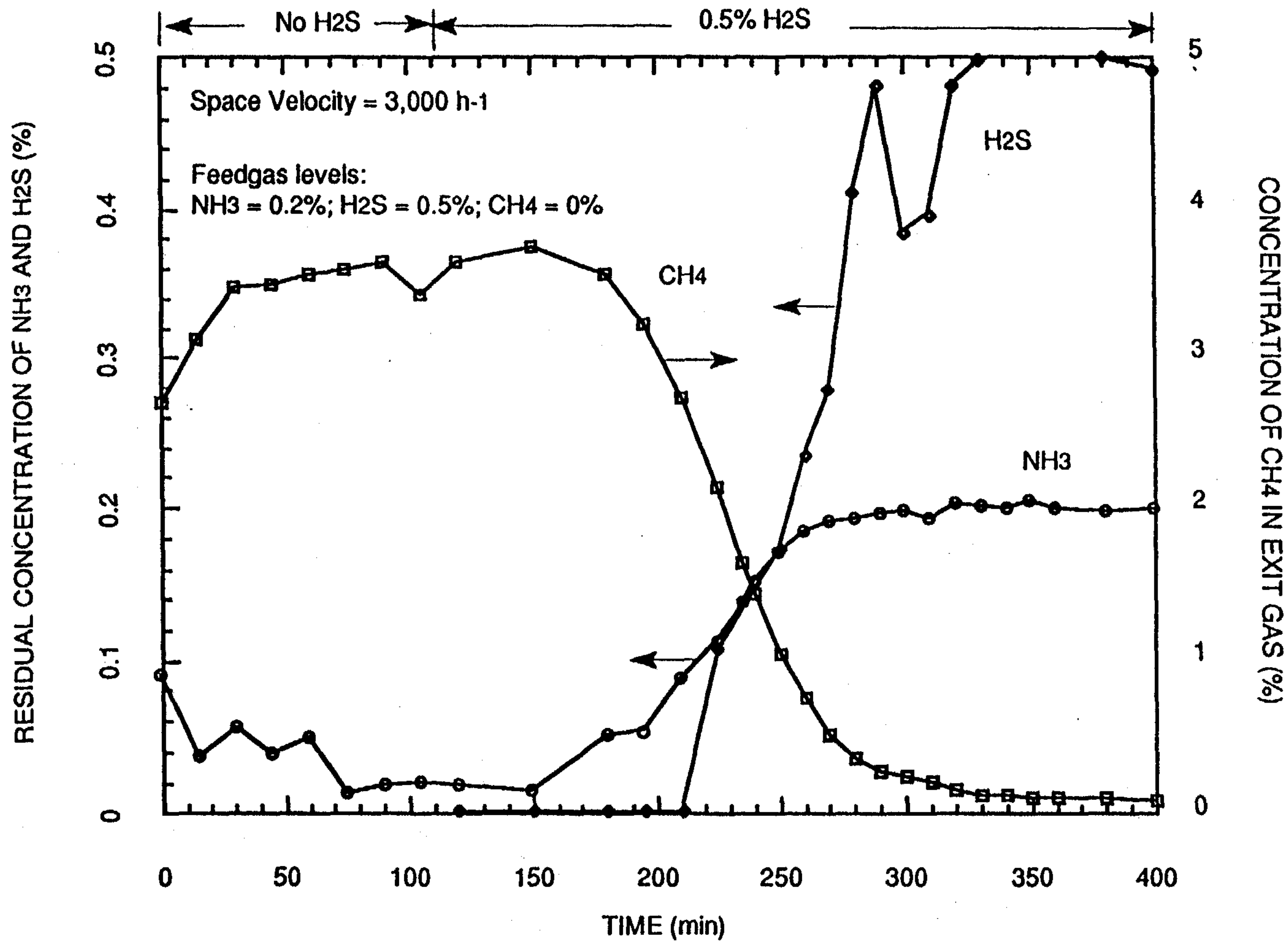

Figure 9. The conversion of NH_3 on HTSR-1 catalyst at 725°C in simulated Texaco gasifier stream.

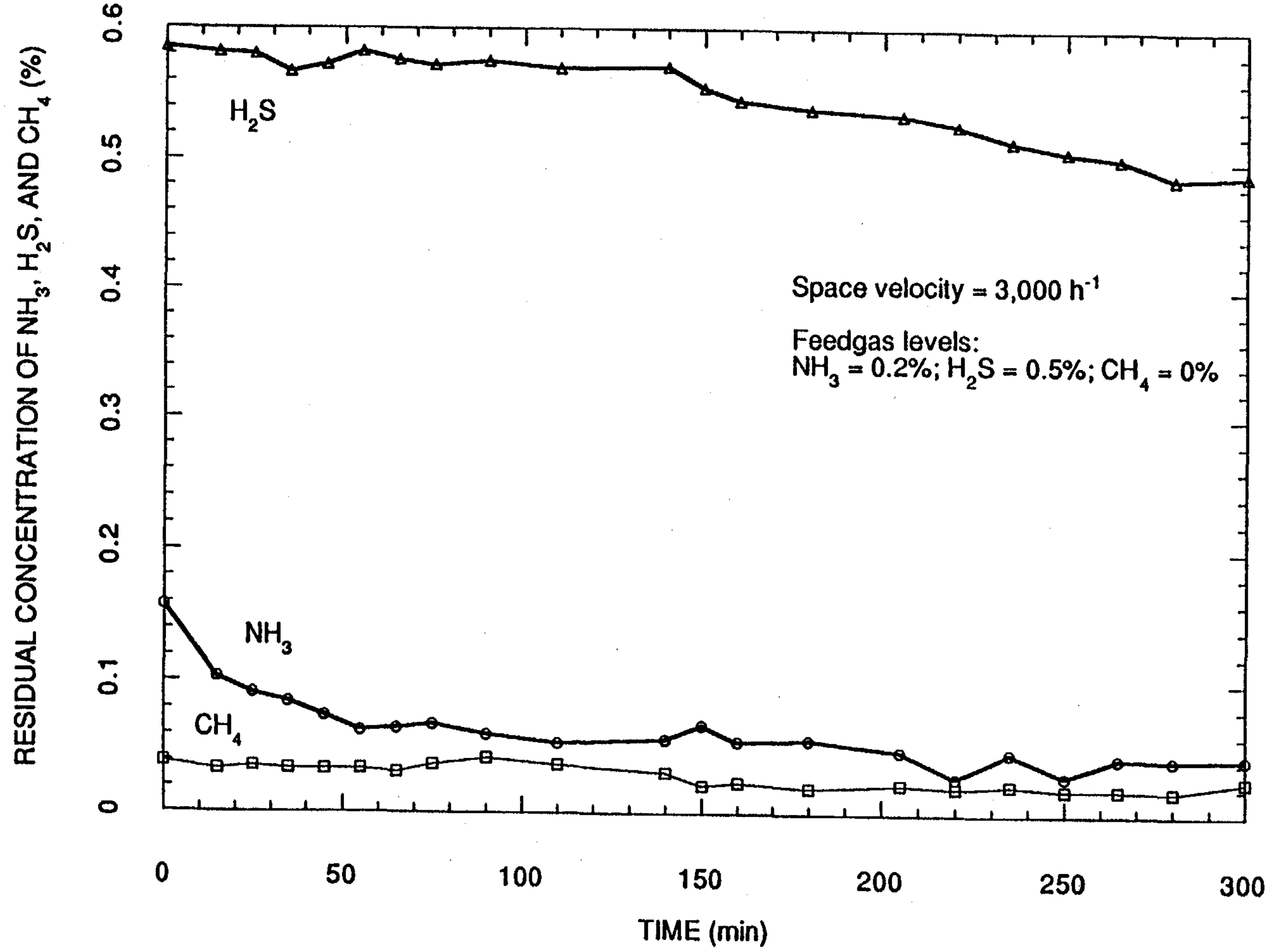

Figure 10. Conversion of NH_3 on HTSR-1 catalyst at 800°C in simulated Texaco gasifier stream.

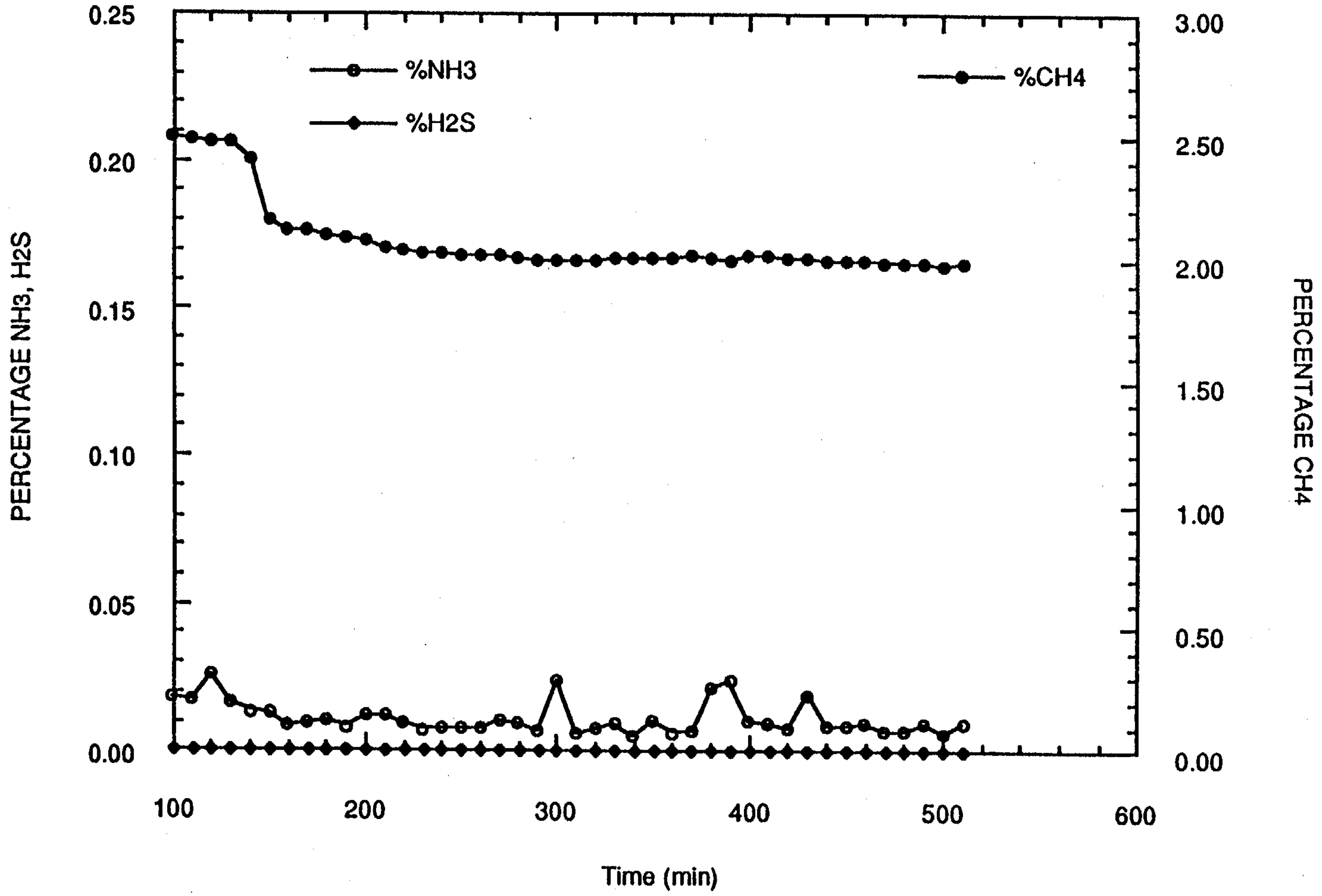

Figure 11. The Conversion of NH3 on HTSR-1 placed downstream of a zinc titanate bed.

(or the residual H_2S level is increased), the extent of NH_3 decomposition also decreased (Figure 12).

The effect of regeneration on the performance of HTSR-1 catalyst was also determined by exposing the sulfided zinc titanate and HTSR-1 bed to a gas stream of 2% O_2 and balance N_2 at 725°C. The regeneration was terminated when O_2 breakthrough was observed in the effluent gas stream. The regenerated bed was then exposed to the simulated Texaco coal gas stream at the same temperature. During the initial 50 minutes, about 50% of the feed NH_3 decomposed (Figure 13). Subsequently, the conversion of NH_3 decreased with time.

The HTSR-1 catalyst was also tested at a pressure of 200 psig and a temperature of 725°C in the absence of H_2S in the feedgas stream. As shown in Figure 14, the catalyst had decomposed more than 95% of NH_3 in the feedgas. The concentration of CH_4 in the effluent gas was high, about 6.5% (v/v). Thus, the HTSR catalyst promotes both NH_3 decomposition and methanation reactions effectively in the absence of H_2S at 725°C.

MoS_2-based catalysts were also shown to exhibit activity for decomposition of NH_3 in hot coal gas streams. One of this formulations (CRC-653) in which MoS_2 was stabilized with ZrO_2 decomposed nearly 80% of the feedgas NH_3 initially. However, its activity declined with time (Figure 15). However, a second formulation (CRC-530) that did not contain any ZrO_2 did not decompose any measurable quantity of NH_3. These results indicate that although MoS_2 is capable of decomposing NH_3, it could sinter at 725°C unless effective stabilizing agents area added.

Surface area measurements indicated that the initial MoS_2 catalyst had a surface area of about 74.2 m^2/g. After exposure to the simulated coal gas stream for about 8 h, the surface area decreased to about 11.7 m^2/g. Oxidation of the MoS_2 with 2% O_2 also decreased the surface area, even further, to 6.8 m^2/g. But exposure of the oxidized catalyst to a simulated coal gas stream containing H_2S increased the surface area to 19.5 m^2/g.

The following conclusions can be derived from the tests with the baseline catalysts :

- HTSR-1, a Ni-based catalyst has a high activity for NH_3 decomposition at 725°C in simulated coal gas streams under low H_2S levels. The tolerance of the catalysts for H_2S increases as the temperature is increased.
- HTSR-1 when mixed with a desulfurization sorbent such as zinc titanate could decompose NH_3 effectively until the removal of H_2S by zinc titanate decreases.
- HTSR-1 continues to exhibit an activity for NH_3 decomposition even after exposure to zinc titanate regeneration conditions.

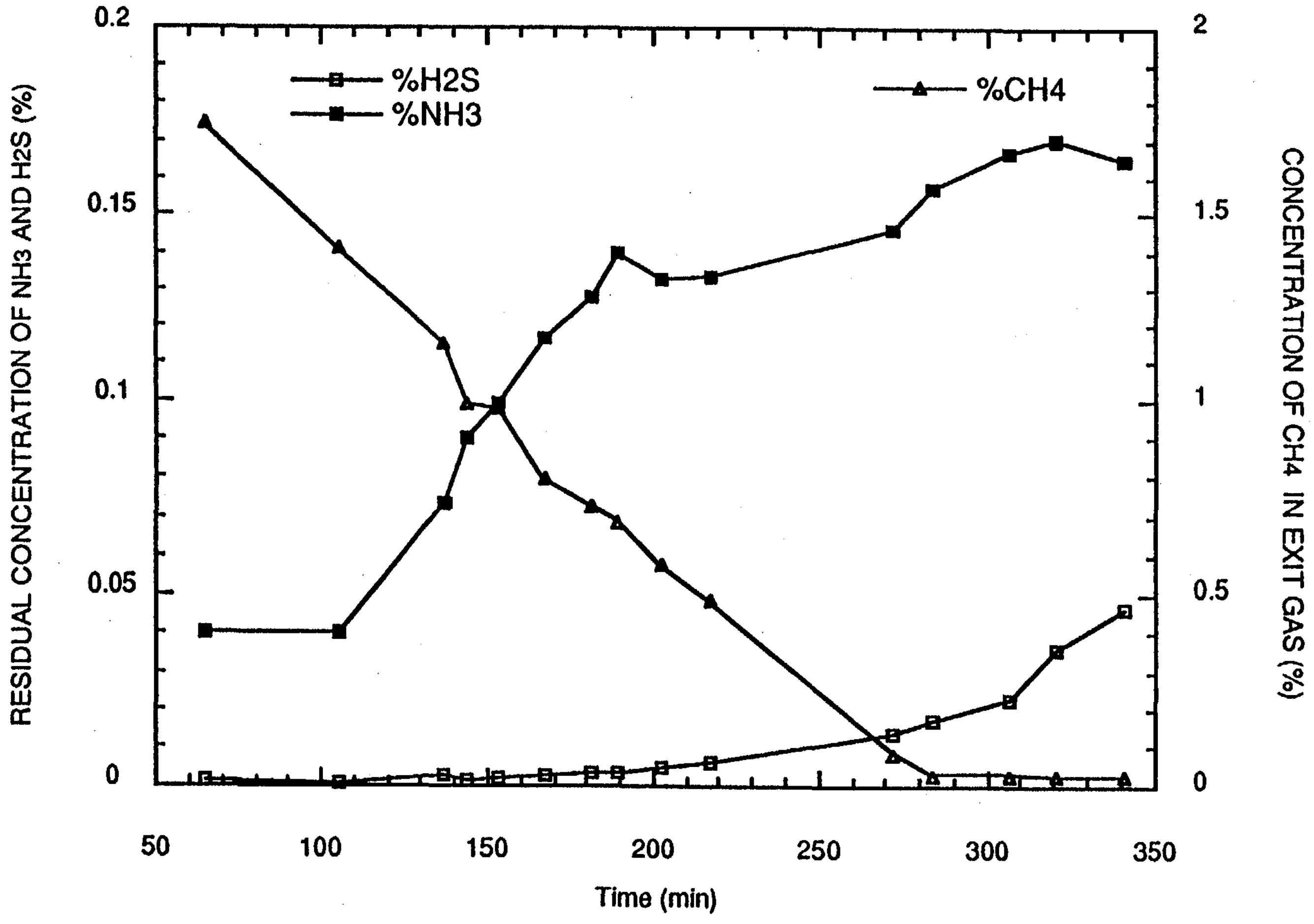

Figure 12. The conversion of ammonia on ZT-4T sorbent and HTSR-1 catalyst mixed together.

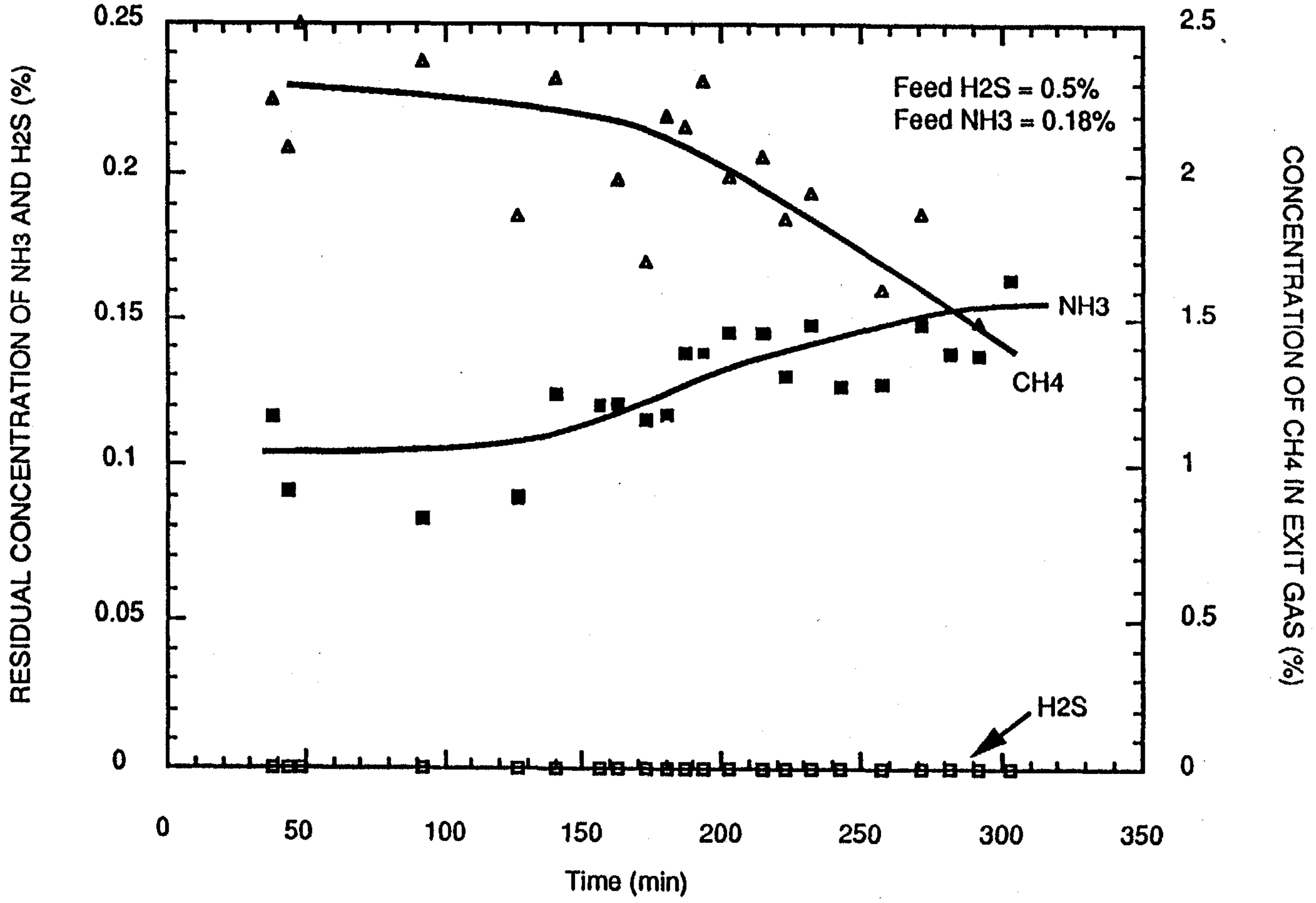

Figure 13. The conversion of NH3 on a regenerated HTSR-1 catalyst mixed with ZT-4 sorbent in a simulated Texaco gasifier stream.

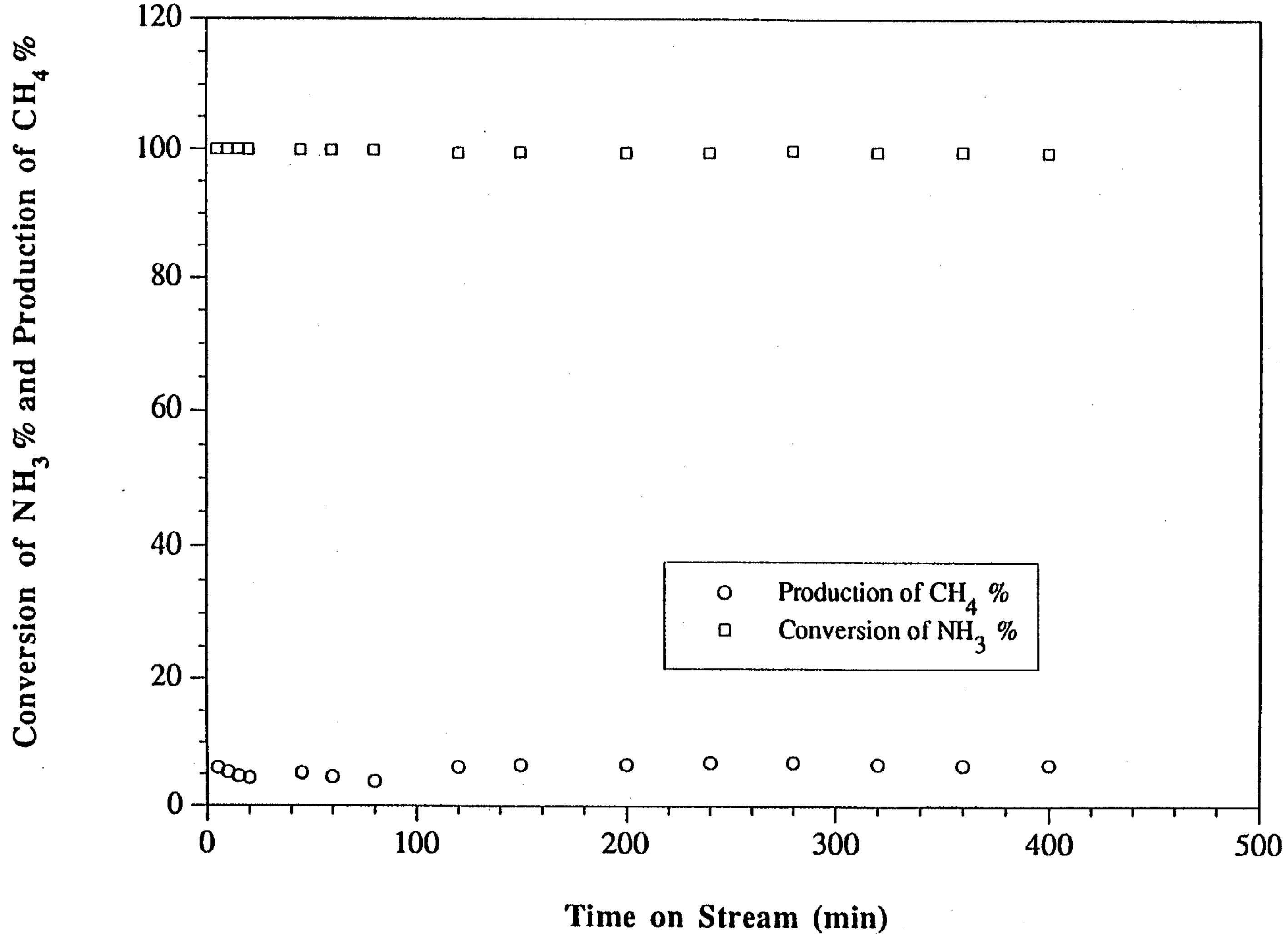

Figure 14. Decomposition of NH_3 over HTSR-1 catalyst at 725°C and 200 psig pressure in a simulated coal gas stream.

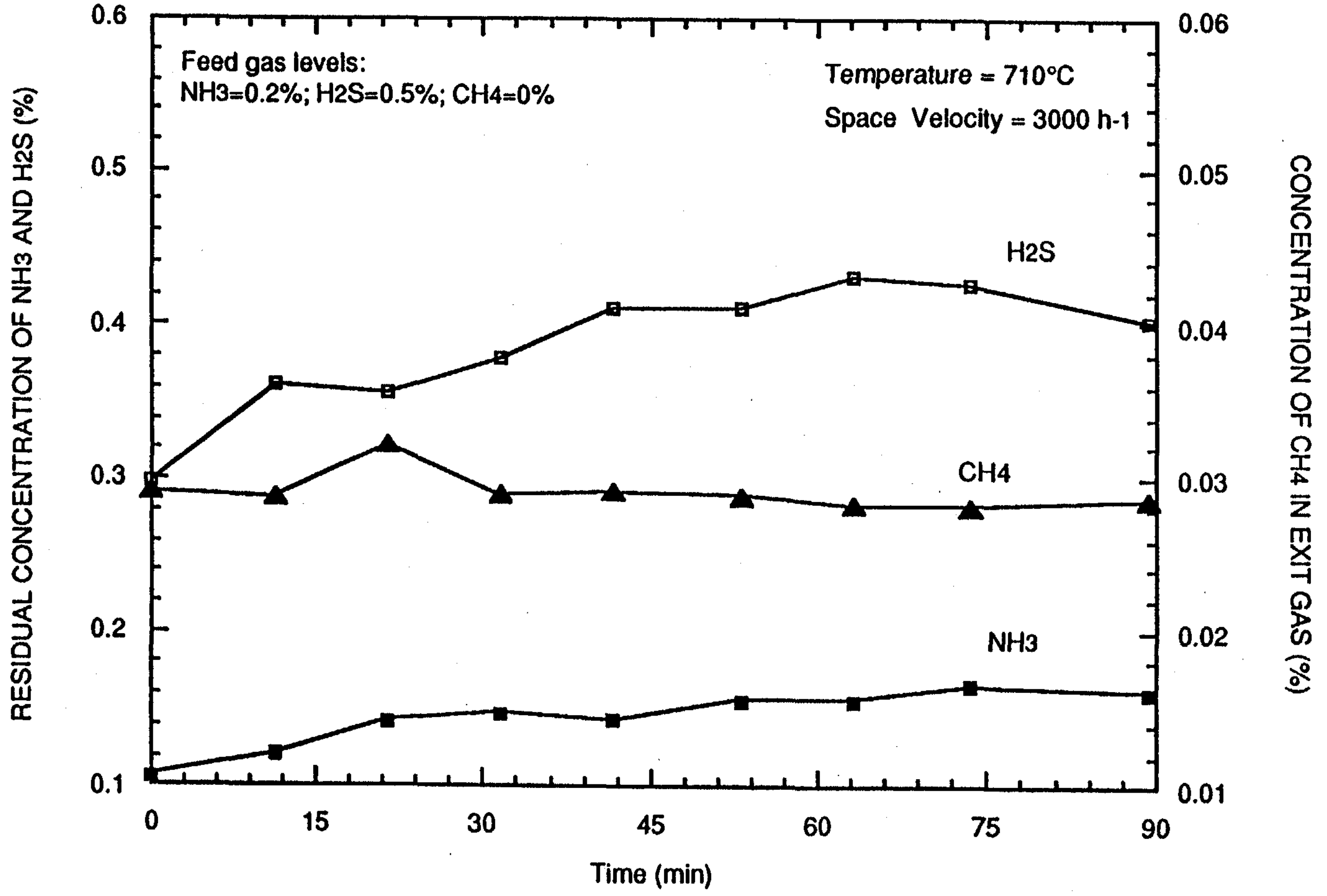

Figure 15. The conversion of NH3 and H2S on CRC-653 catalyst in simulated Texaco gasfier stream.

- MoS_2 is also a catalyst for the decomposition of NH_3. However, its surface area needs to be maintained by addition of suitable stabilizing agents for sustained activity.

Zinc titanate is one of the best sorbent for removing H_2S in hot coal gas streams. A sorbent formulation (ZT-4) obtained from RTI was tested for its NH_3 decomposition activity. At a temperature of 725°C, its catalytic activity either in the presence or absence of H_2S was low; only less than 10% of the feedgas NH_3 decomposed (Figure 16).

NICKEL ON TITANIA CATALYSTS

The Ni/TiO_2 catalyst (stabilized with ZrO_2) after treatment in hydrogen at 550°C was tested for its NH_3 decomposition activity at 725°C using a simulated coal gas (38% CO, 28.5% H_2, 12.8% CO_2, 18.1% H_2O, 0.75% H_2S, 0.18% NH_3, and 1.6% N_2). Equal quantities of zinc titanate (ZT-4) sorbent and the catalyst were mixed together and exposed to the simulated coal gas at a space velocity of 3000 h^{-1}. The results of this test, shown Figure 17, indicate that the activity of the catalyst for ammonia decomposition and methane synthesis is high initially, but declines with time. This could be attributed to the poisoning of the catalyst by H_2S. When sulfur breakthrough occurred, the extent of ammonia decomposition was observed to be small. Sintering of the catalyst could be also a factor in the decreased activity as the exposed catalyst had a surface area of only 18 m^2/g.

The Ni/TiO_2 was further modified by incorporating molybdenum. A solution of ammonium molybdate was added to the catalyst by incipient wetness technique. This procedure repeated again to increase the total Mo content to 12 wt%. The catalyst ($Ni\text{-}Mo/TiO_2$) was then treated in H_2 at 550°C for 3 h until no NH_3 evolution was observed. Then the temperature was increased to 725°C and the gas mixture was changed to the Texaco gas composition with 600 ppm of H_2S and 0.18% NH_3. The behavior of the catalyst was not different from that of the catalyst containing only nickel. The activity of the $Ni\text{-}Mo/TiO_2$ catalyst for ammonia decomposition at 725°C under steady state conditions was negligibly small.

COBALT ON TITANIA CATALYSTS

The Co/TiO_2 catalyst was tested for NH_3 decomposition activity at 725°C using a simulated Texaco coal gasifier gas stream. Even in the absence of H_2S in the gas stream, the activity was negligibly small. The presence of 5,000 ppm H_2S did not improve the catalytic activity.

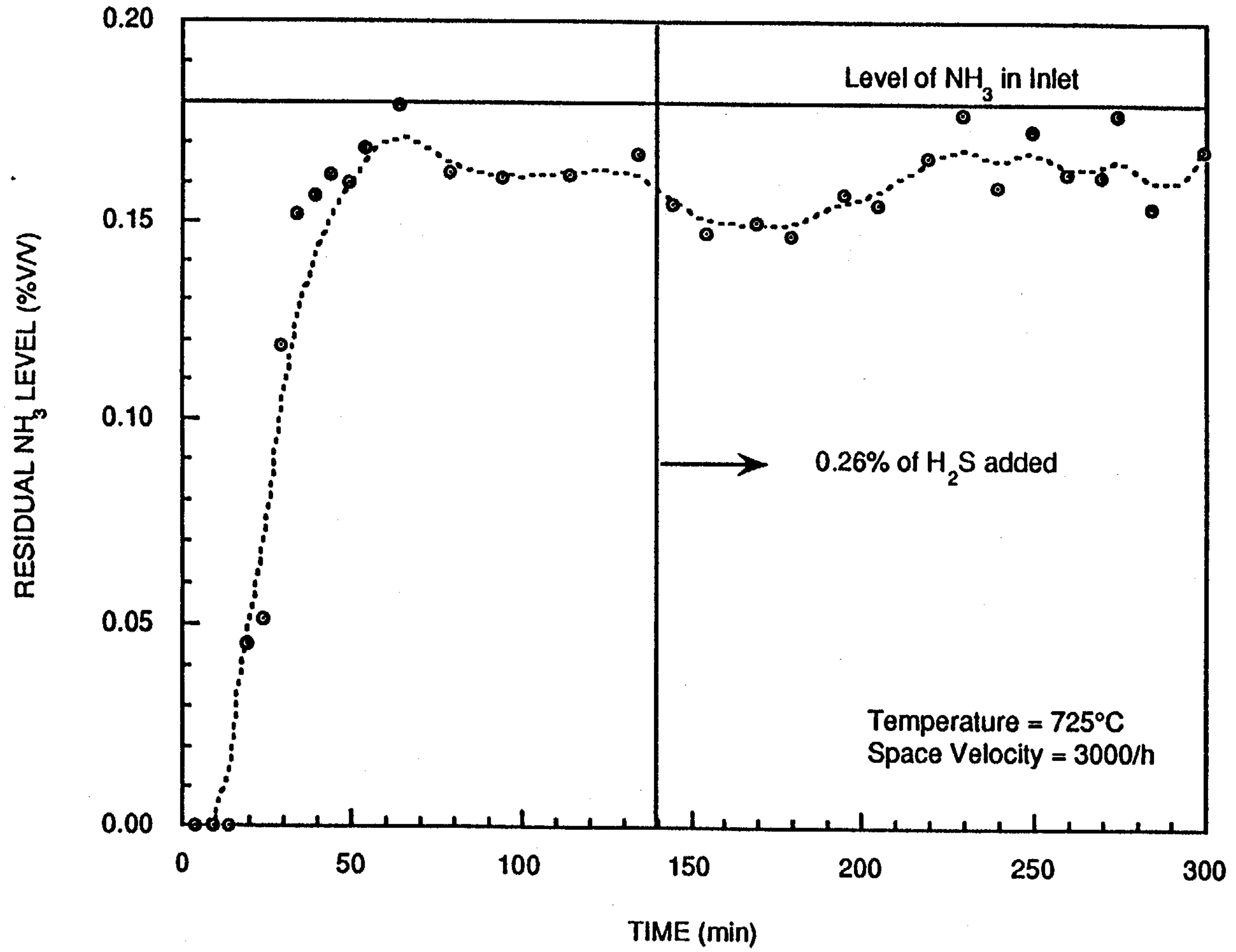

Figure 16. Decomposition of ammonia on a zinc titanate (ZT-4) sorbent at 725°C.

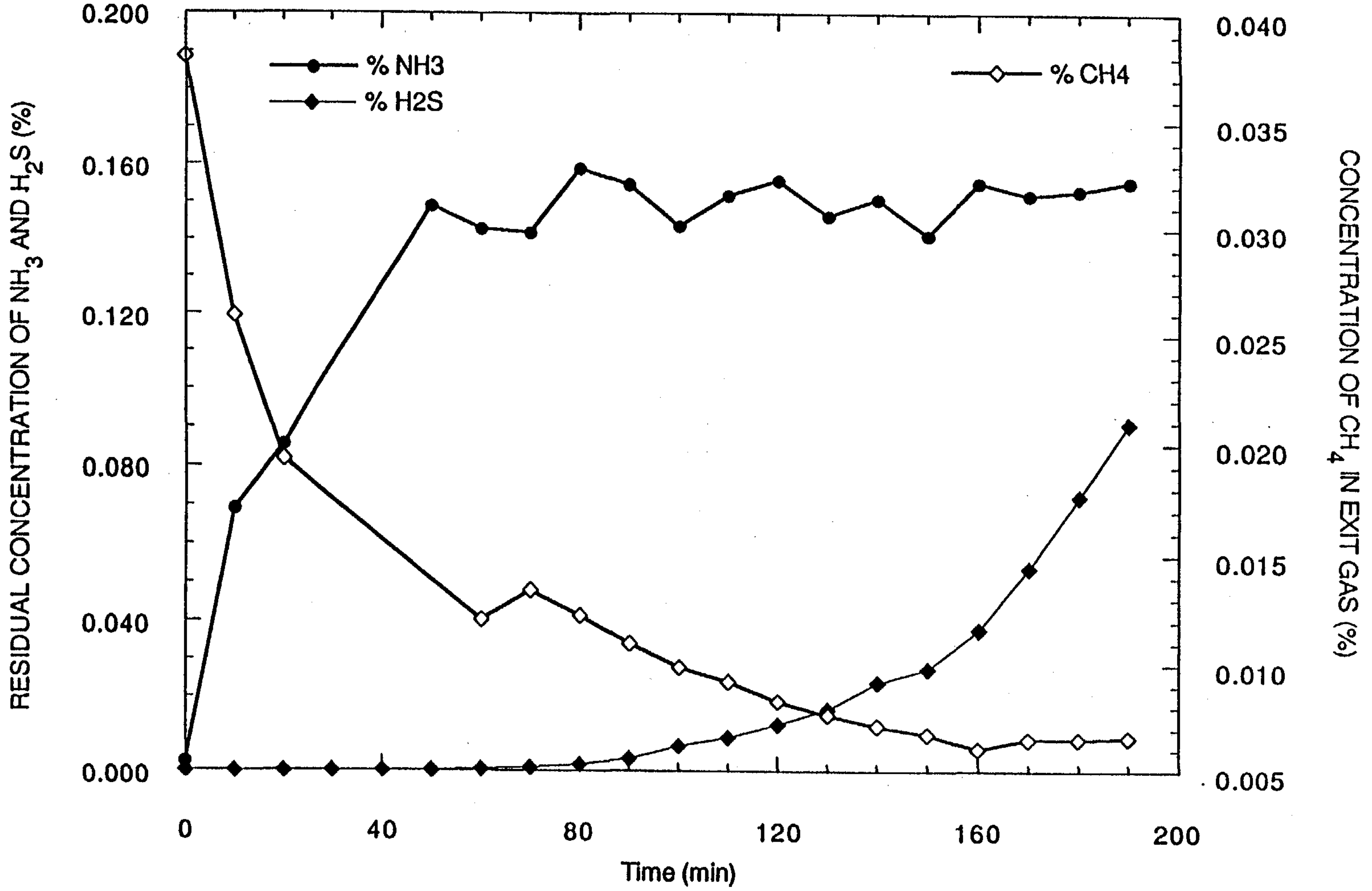

Figure 17. The conversion of NH_3 on a Ni-TiO_2 catalyst mixed with ZT-4 sorbent in a simulated coal gas stream at 725°C.

A batch of Co-Mo supported on TiO_2 was prepared by impregnating the Co-TiO_2 catalyst with a solution of ammonium molybdate under incipient wet conditions. The impregnation was performed three times to bring the total amount of Mo to 6.4 wt%. The catalyst (Co-Mo/TiO_2) was calcined in hydrogen at 550°C until all the molybdate was decomposed.

The Co-Mo/TiO_2 catalyst showed an initial activity for decomposition of NH_3 at 725°C; about 20% of the feed NH_3 was decomposed. However, the activity declined with time even in the absence of H_2S and became negligibly small after only 4 h.

The Co-Mo catalyst was also sulfided at 550°C using 1% H_2S-H_2 for 7 hours to convert the metals to their sulfide form. The purpose of this experiment to test the assumption that the sulfides could be more active for NH_3 decomposition than the metals. But the catalytic activity of the catalyst at 725°C did not improve with sulfidation; the fraction of the NH_3 decomposed was less than 5%.

MOLYBDENUM ON TITANIA CATALYSTS

A Mo/TiO_2 catalyst was also tested for its NH_3 decomposition activity at 725°C in a simulated Texaco oxygen-blown gasifier gas stream. With a 7.7 wt% Mo on titania, the NH_3 in the reactor exit gas increased steadily reaching the feedstock level in about 400 minutes (Figure 18). In this test, no H_2S was added to the feedgas. However, because the system has been exposed to high levels of H_2S in previous runs, a residual level of about 1 to 10 ppm was detected in the reactor exit gas during the run. This catalyst did not promote the formation of CH_4. The amount of CH_4 formed was less than 0.01% v/v.

A run was also made with a Mo/TiO_2 catalyst containing 10.8 wt% Mo. Initially, the residual level of NH_3 increased rapidly during the initial 50 minutes (Figure 19). After this period, the rate of decrease in ammonia conversion was slow. After about 250 minutes, a near steady state conversion of about 20% was observed. The conditions of this test was similar to the test described above.

The experimental results suggest that Mo-containing catalysts may decompose H_2S at 725°C. However, the surface area of these catalyst appear to decrease with time at that temperature.

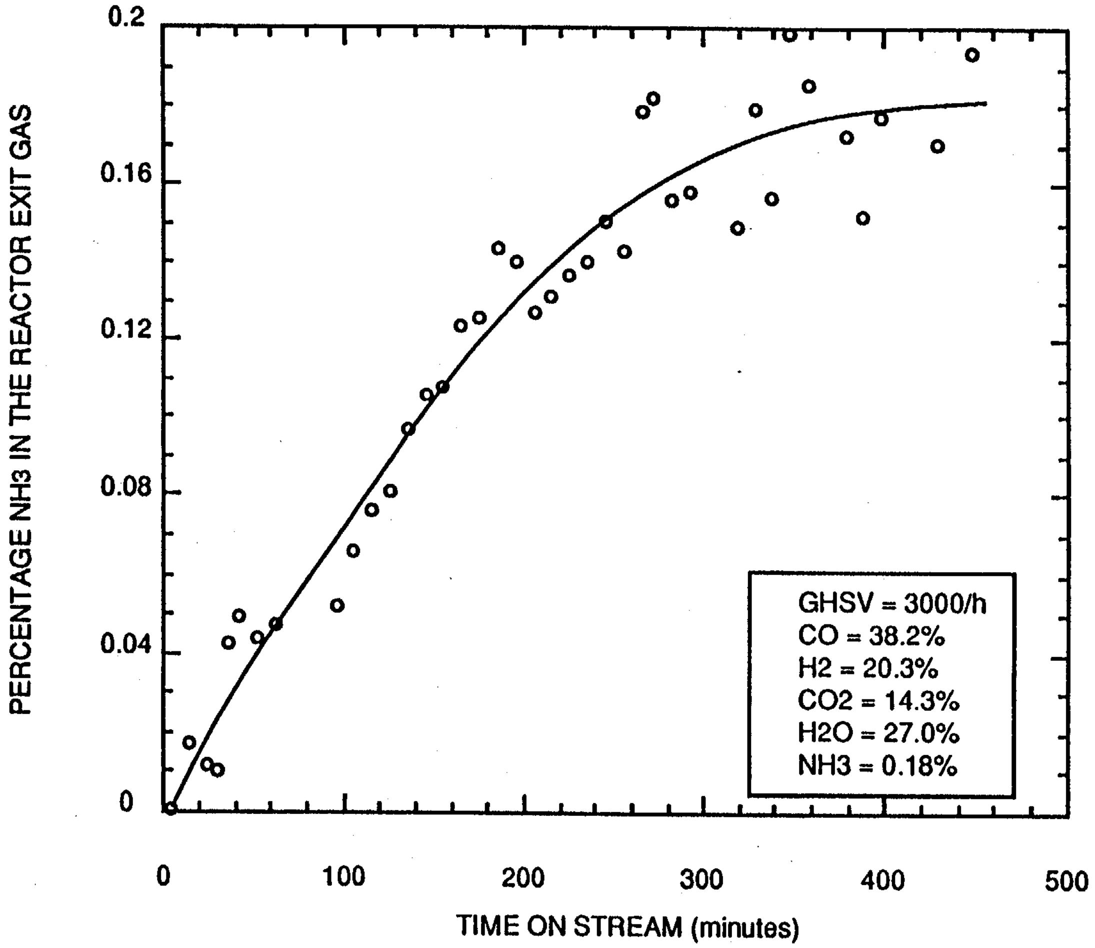

Figure 18. Decomposition of ammonia on a 7.7 wt% Mo on Titania catalyst at 725°C.

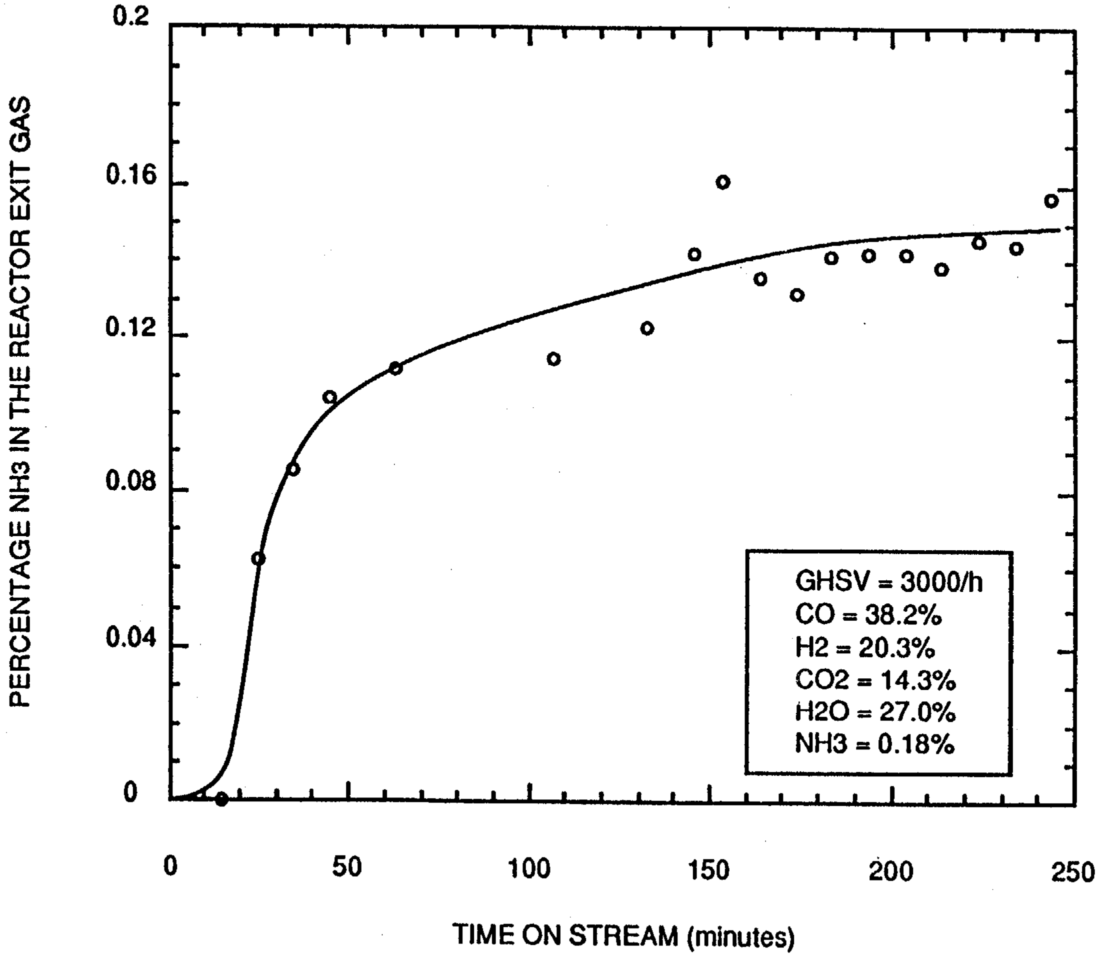

Figure 19. Decomposition of ammonia on 10.8 wt% Mo on titania catalyst at 725°C.

COBALT AND MOLYBDENUM ON TITANIA CATALYSTS

A 100 g batch of 2% Co-10% Mo on titania catalyst was prepared for bench-scale testing at Research Triangle Institute. A sample of this catalyst mixed with additional zinc titanate powder was tested at SRI's laboratory-scale reactor at 1-atm pressure. The results indicated that at a space velocity of 3000 h^{-1} and 725°C, the catalyst reduced the level of NH_3 from about 1700 ppm to about 1500 ppm (Figure 20). Another sample of this catalyst was sulfided overnight and then tested for NH_3 decomposition activity. The activity of the sufided catalyst was similar to the unsulfided catalyst indicating that Co-Mo/TiO_2 catalyst has a moderate activity for NH_3 decomposition even after sulfidation (Figure 21).

The catalyst was analyzed using X-ray diffraction (XRD) and Auger electron spectroscopy (AES). The X-ray diffraction pattern of the catalyst under as-prepared conditions indicated peaks corresponding only to titania (Figure 22). This observation suggests that both cobalt and molybdenum are in an amorphous state and presumably finely-dispersed on the titania substrate. Analysis by AES, a technique which is sensitive only to the surface layers (~2 nm depth) of a solid material, indicated that both Mo and Co are present on the surface of the titania (Figure 23).

XRD analysis was also performed with catalysts exposed to the simulated hot coal gas streams. The XRD pattern of a Co-Mo/TiO_2 catalyst mixed with zinc titanate and after a 8-h exposure at 725°C showed the presence of ZnS, MoS_2, Co_9S_8, and TiO_2 (Figure 24). This observation indicates that all the active components were sulfided during hot coal gas exposure. The XRD pattern of a tungsten impregnated on titania after reaction to the simulated Texaco coal gas stream at 725°C showed the presence of WS_2 (Figure 25).

TUNGSTEN ON TITANIA CATALYSTS

The W/TiO_2 catalyst was tested in a simulated Texaco oxygen-blown gasifier gas stream. The residual NH_3 level in the reactor exit gas was low during the initial 50 minutes. After this period it increased to about 1600 ppm and remained at that level for the next two hours. The percentage of decomposition under these conditions correspond to about 10% of the feedstock NH_3 (Figure 26).

The behavior of W-Mo/TiO_2 catalyst was similar to that W/TiO_2 catalyst (Figure 27). The steady-state decomposition activity did not differ significantly whether H_2S is present or absent. The conversion of feedstock NH_3 was less than 10% with the W-Mo/TiO_2 catalyst.

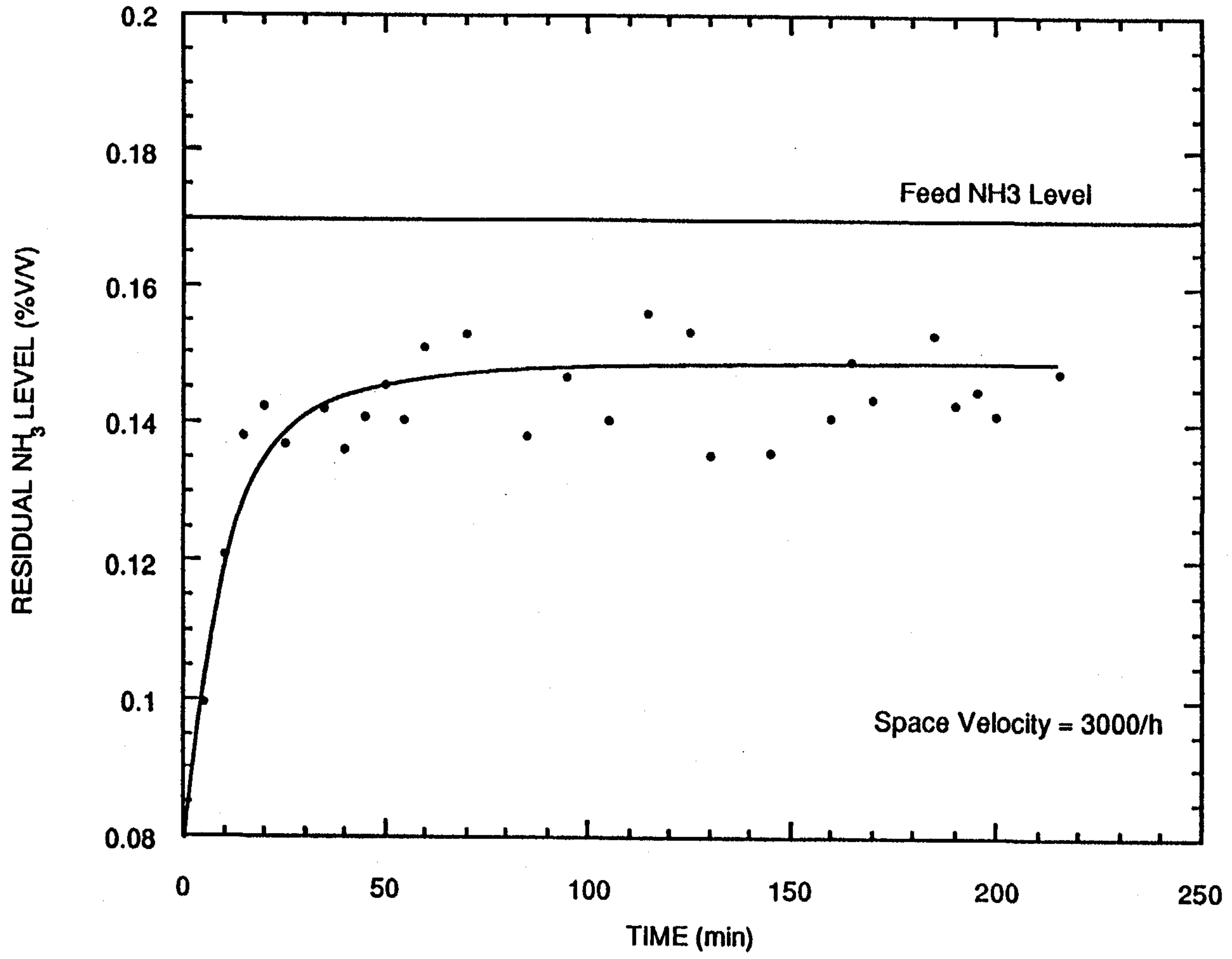

Figure 20. The catalytic activity of a Co-Mo/titania catalyst at 725°C.

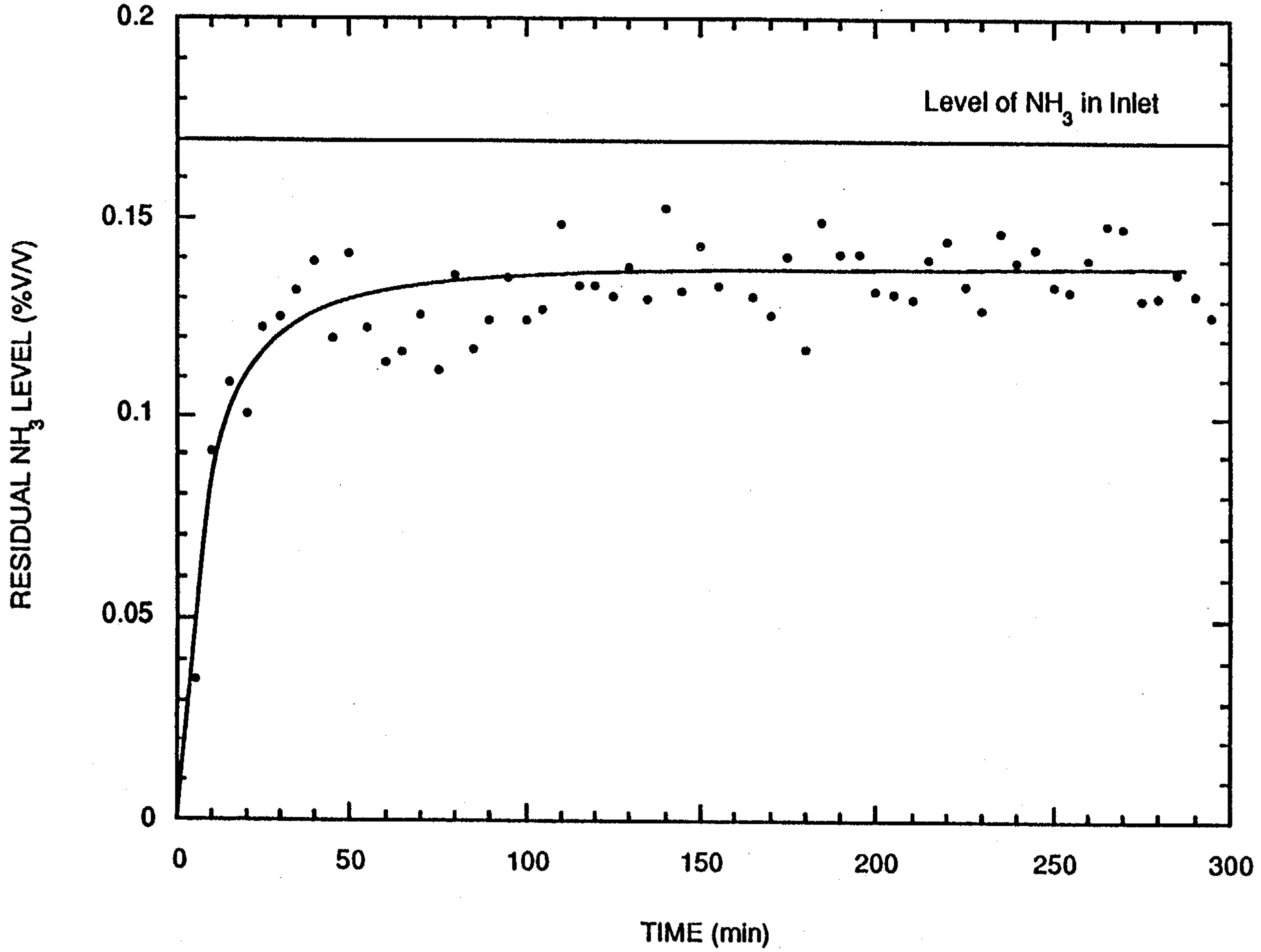

Figure 21. The catalytic activity of a Co-Mo/titania catalyst at 725°C after sulfidation.

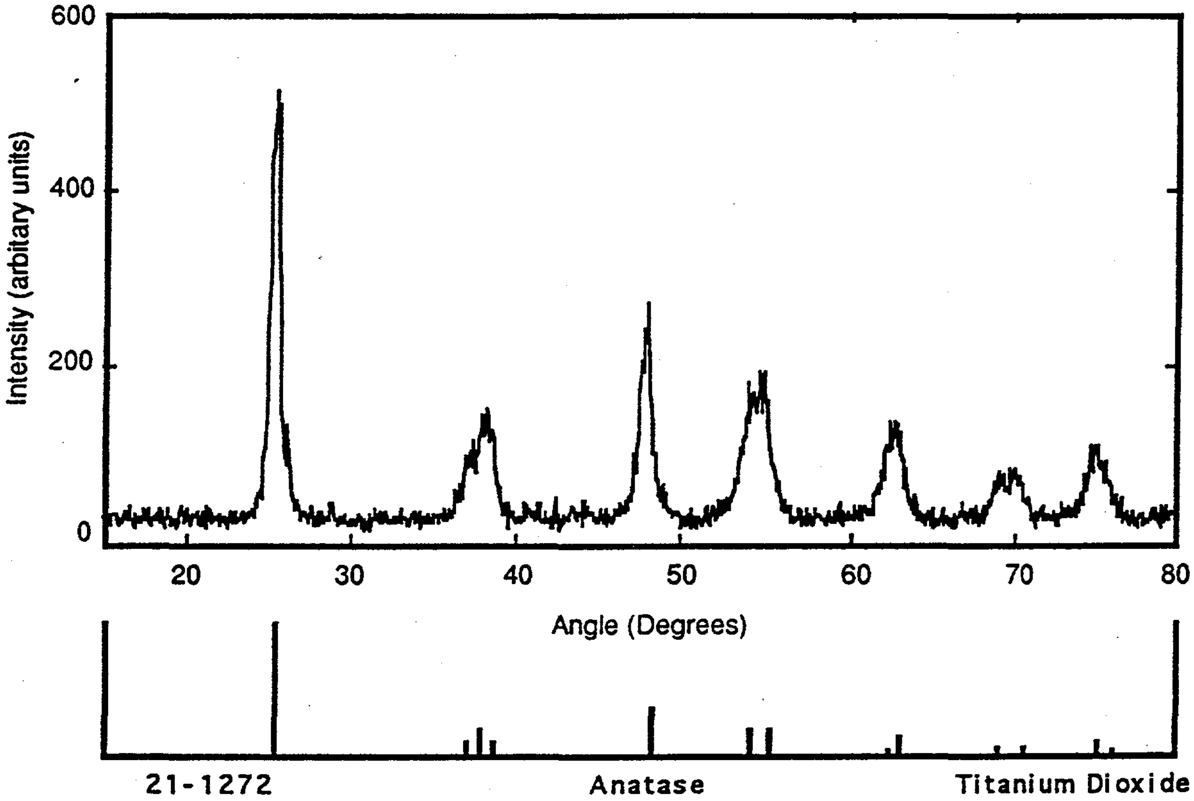

Figure 22. X-ray diffraction pattern of a Co-Mo-Titania catalyst.

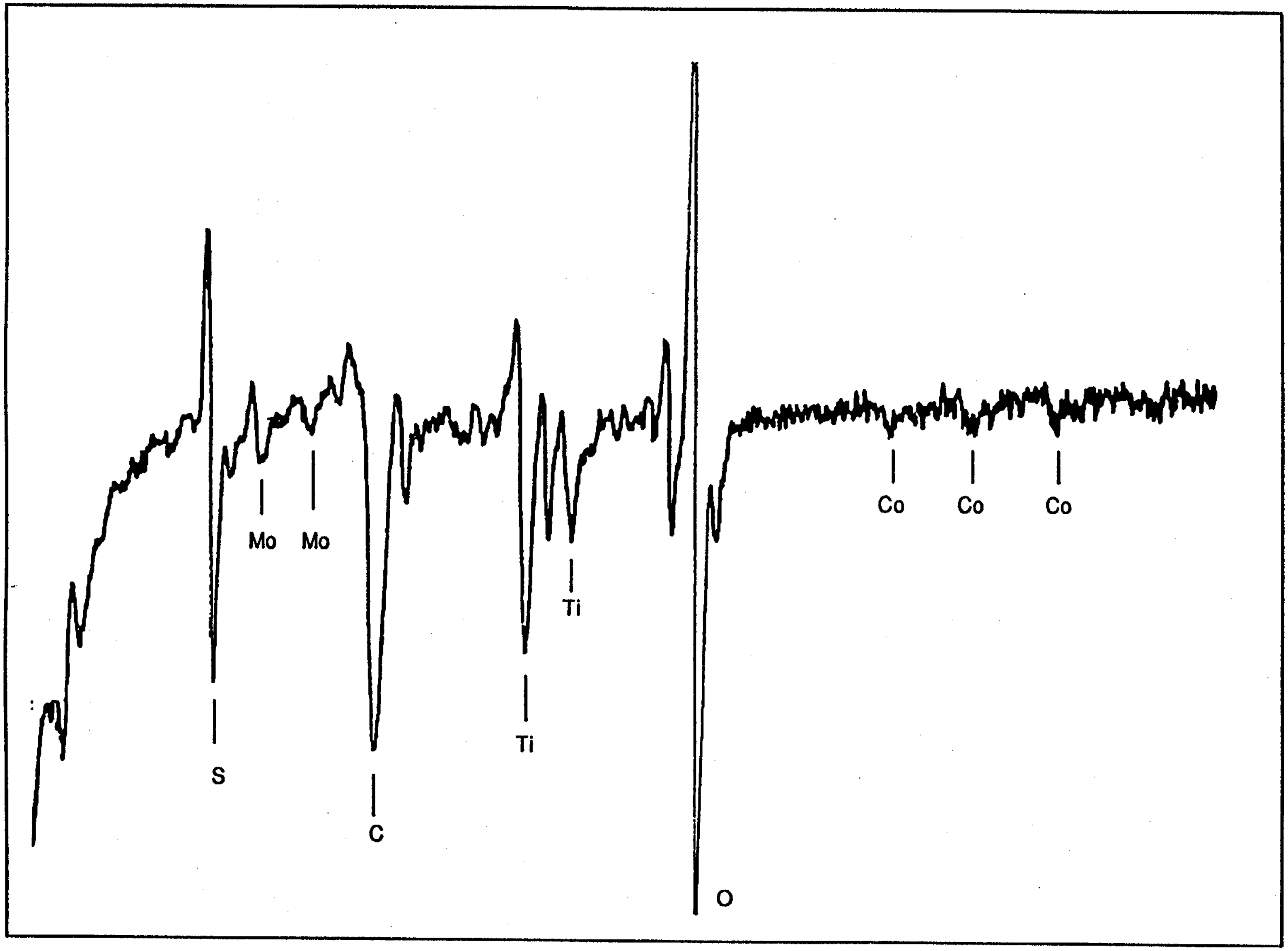

Figure 23. AES spectrum of Co-Mo on titania catalyst.

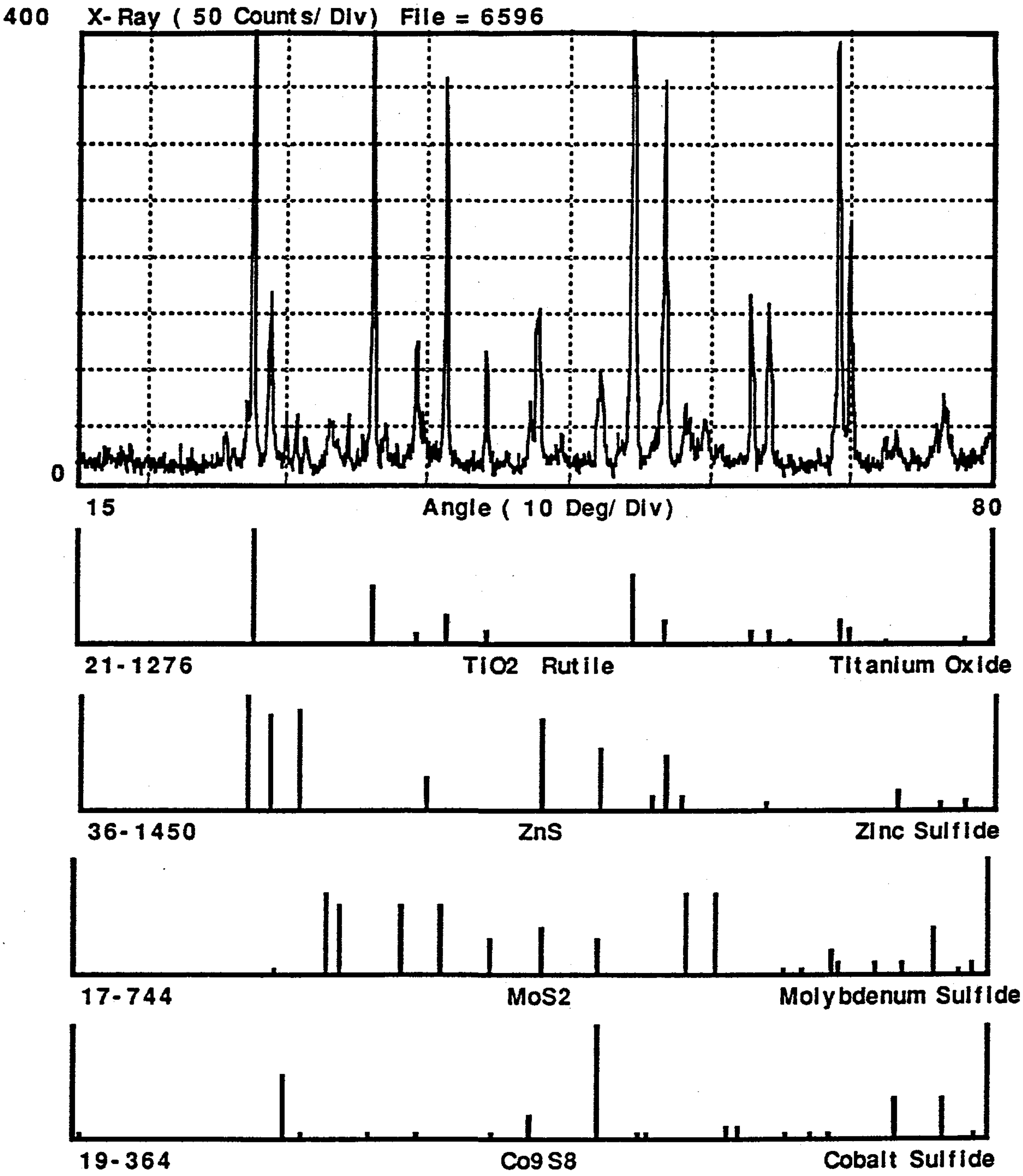

Figure 24. X-ray diffraction pattern of a reacted Co-Mo catalyst mixed with zinc titanate.

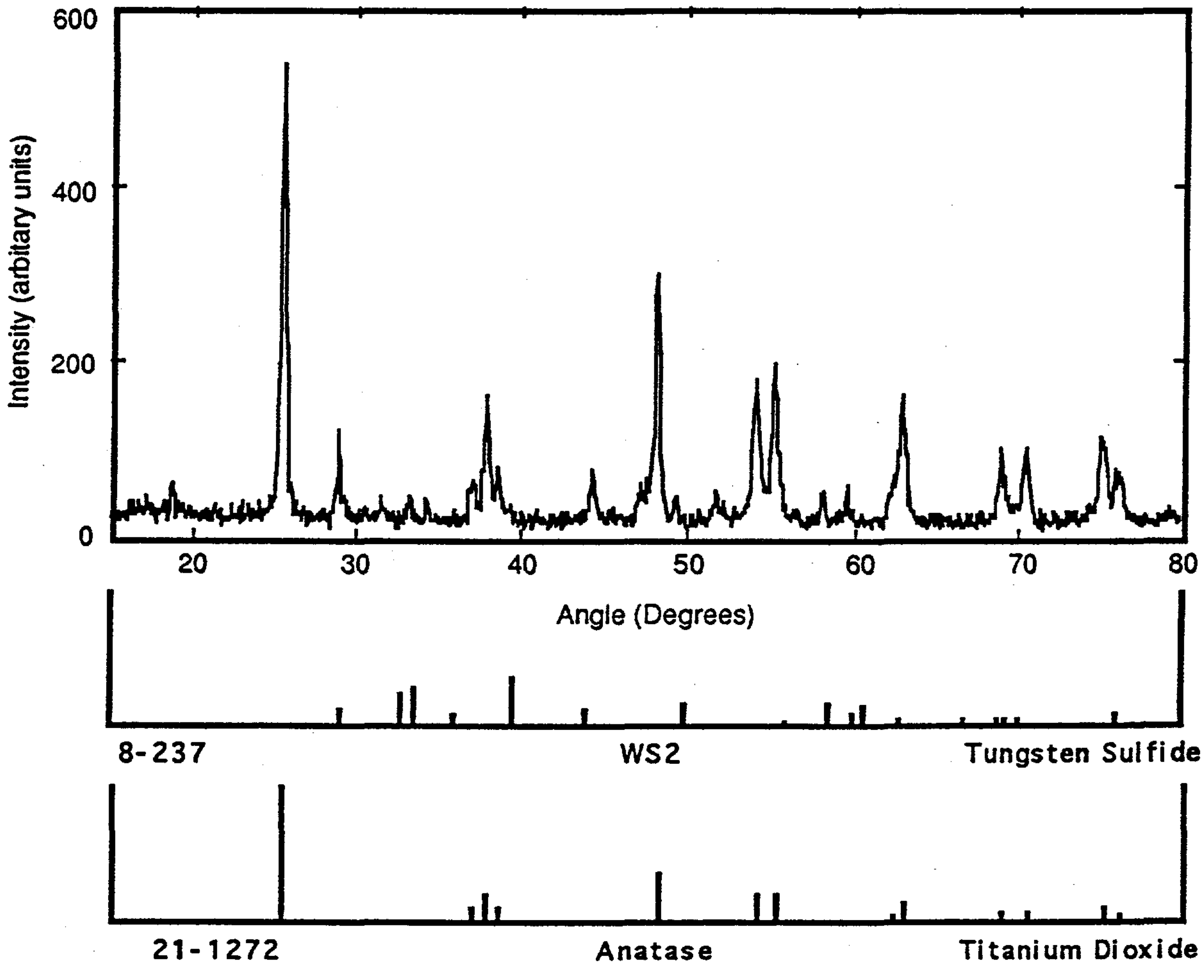

Figure 25. X-ray diffraction pattern of a Co-W-Titania catalyst after reaction.

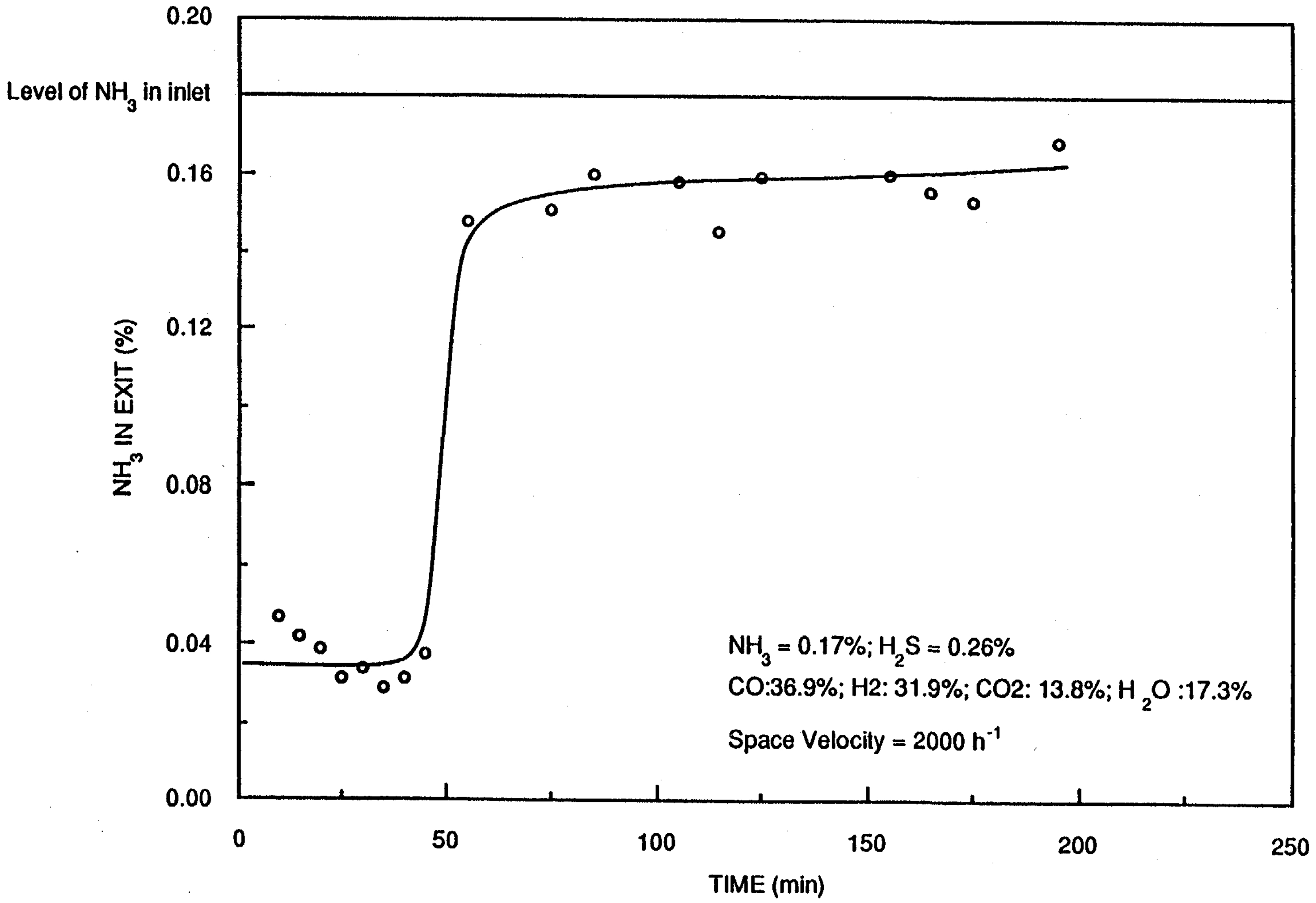

Figure 26. Decomposition of NH_3 over W/TiO_2 at 725°C.

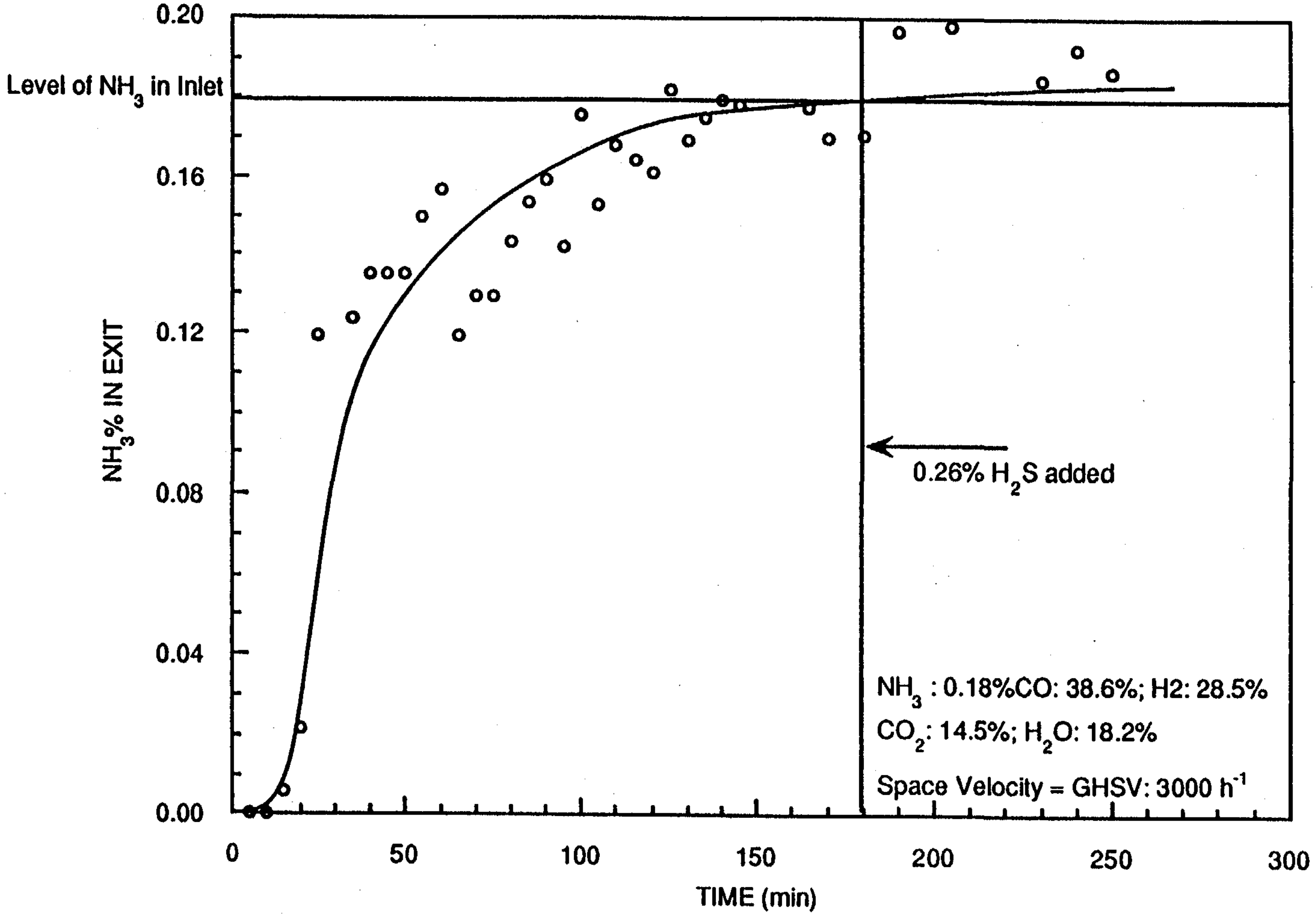

Figure 27. Decomposition of NH_3 over Co-W/TiO_2 at 725°C

The experimental results suggest that W-containing catalysts are not very active for decomposing NH_3 in simulated coal gas stream at 725°C. It is feasible that the surface area of the TiO_2 support decreased with time at the reaction temperature contributing to the decline in catalytic activity.

TUNGSTEN OXIDE-ZINC TITANATE CATALYSTS

RTI supplied two catalysts (#82 and #83) to be tested for their ammonia decomposition activity at a pressure of 200 psig and a space velocity of 3000 h^{-1}. The catalyst #82 contained ZnO and WO_3 in a molar ratio of 1:1. The catalyst #83 was made of ZnO and WO_3 in an equimolar ratio with additions of 5% CoO and 2% ZrO_2. Although these catalysts decomposed NH_3 initially, the catalytic activities decreased with time at 725°C (Figure 28). No significant activity was observed with the catalyst #82 after 150 minutes. The amount of CH_4 formed with this catalyst was also negligibly small. The #83 catalyst appears to have a higher activity than the #82 for both methanation and NH_3 decomposition reactions (Figure 29). Even with this catalyst, the steady-state rate constant for the decomposition reaction is only 0.02 s^{-1}.

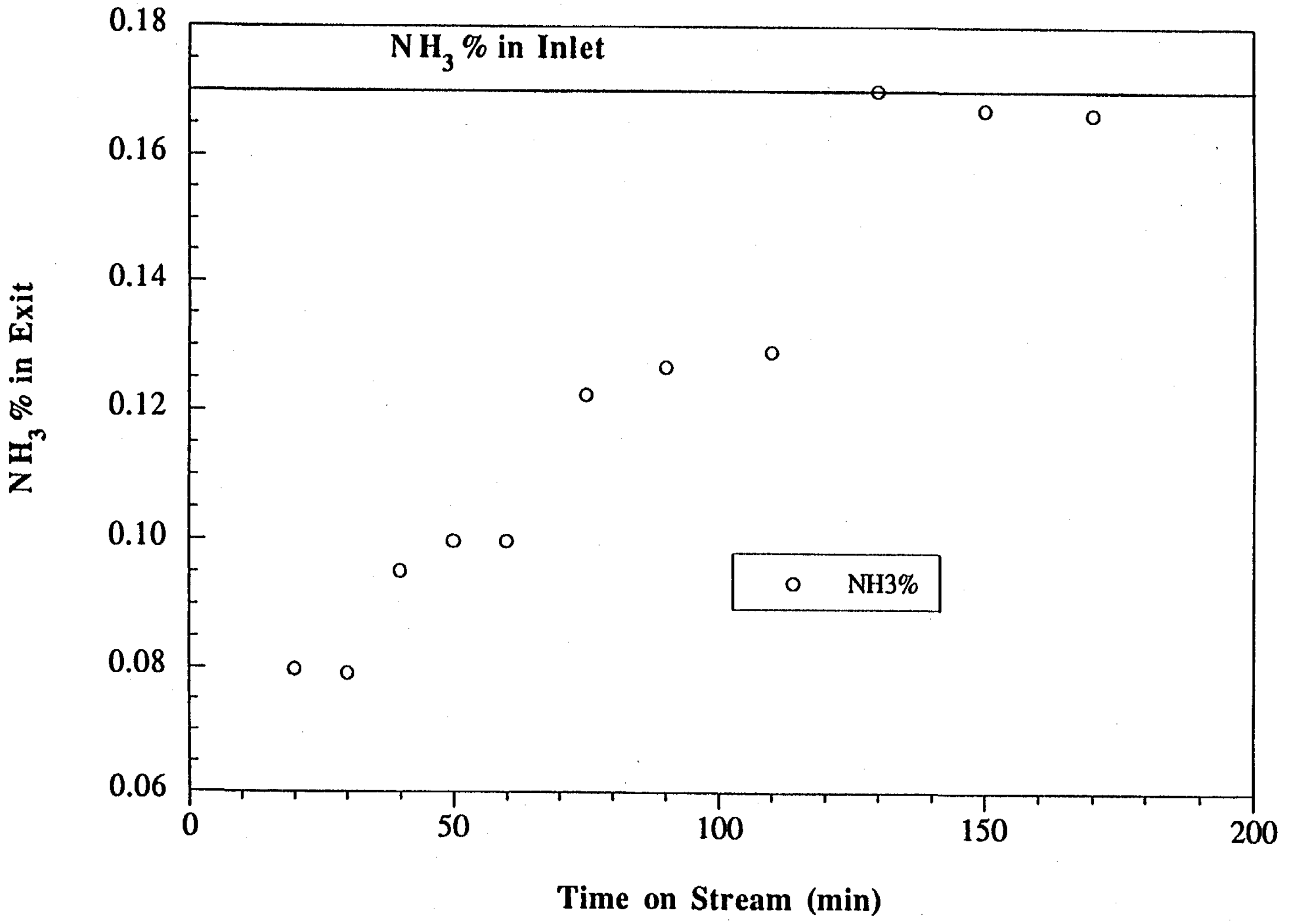

Figure 28. The conversion of NH_3 on RTI #82 catalyst in a simulated coal gas stream at 725°C and 200 psig.

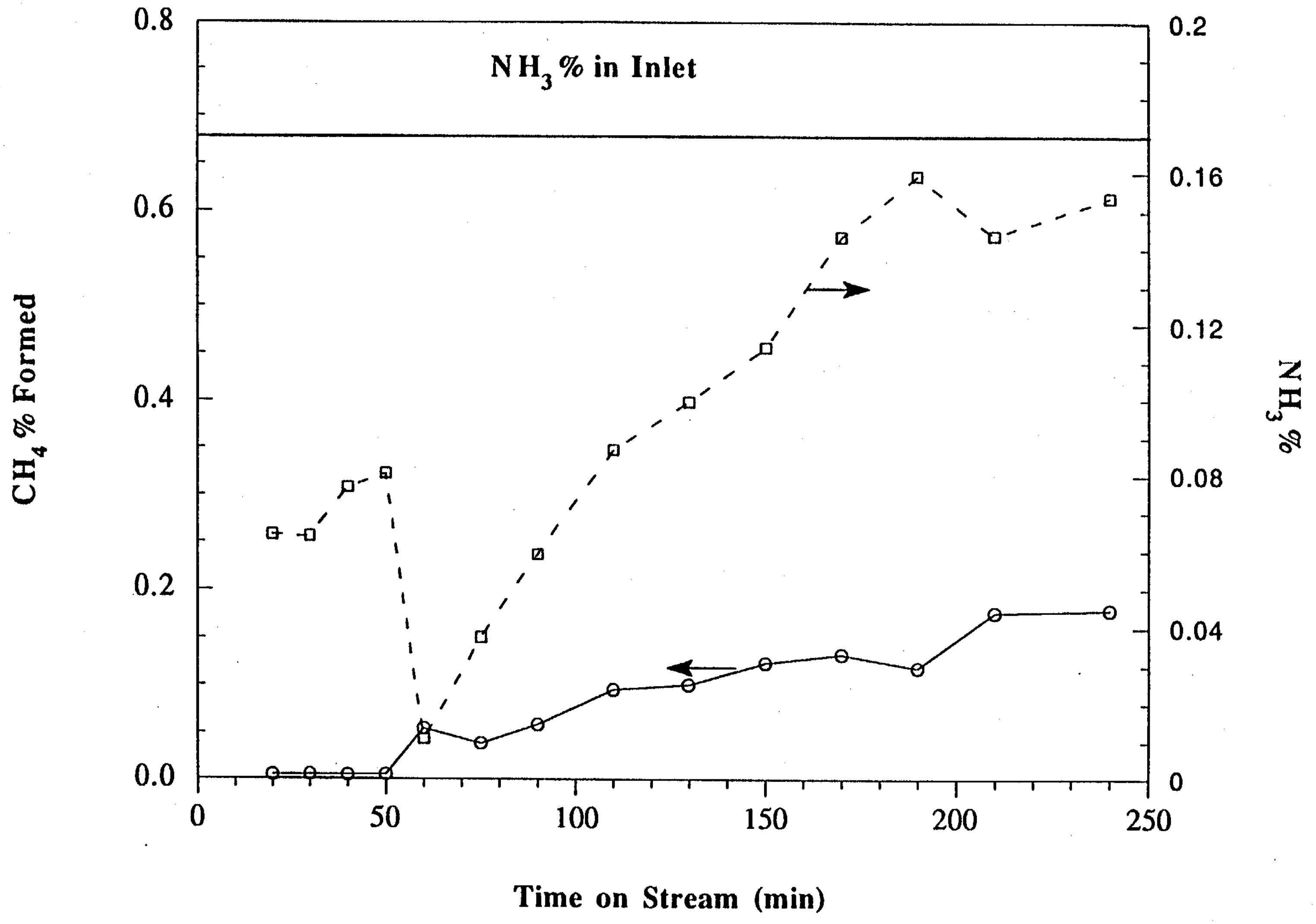

Figure 29. The conversion of NH_3 on RTI #83 catalyst in a simulated coal gas stream at 725°C and 200 psig.

CONCLUSIONS AND RECOMMENDATIONS

Based on the experimental results and theoretical analysis, the following conclusions are derived:

- HTSR-1, a catalyst proprietary to Haldor-Topsøe A/S, Copenhagen, Denmark, exhibited excellent activity for the decomposition of NH_3 in hot coal gas streams. The tolerance of this catalyst to H_2S increased with increasing temperatures.

- MoS_2-based catalysts showed only a moderate activity for NH_3 decomposition. These catalysts required surface area stabilization.

- Many catalysts containing Ni, Co, Mo, and W on a high surface TiO_2 support showed only a moderate activity for NH_3 decomposition.

- Mixing the catalysts with a zinc titanate sorbent allowed the catalysts to function for an extended period of time. As the sorbent gets loaded with H_2S, the residual H_2S level increases thereby decreasing the activity of the catalyst for NH_3 decomposition.

- The titania support sinters excessively at a temperature of 725°C in the presence of steam. Adding ZrO_2 to the titania decrease the rate of sintering.

The following recommendations are made for further investigation into the removal of fuel-bound nitrogen from hot coal gas streams.

- The HTSR-1 should be tested using hot coal gas streams from an operating coal gasifier. The effects of trace components of the hot coal gas stream that could not be simulated in the laboratory must be determined.

- Alternative catalysts that have a high NH_3 decomposition activity at a temperature of about 550°C in the presence of H_2S must be developed.

- The regeneration of sulfur-poisoned HTSR-1 must be investigated. Although this catalyst can tolerate significant levels of H_2S at 800°C, it is slowly poisoned at low temperatures. Regeneration of the catalyst will allow continued use of this catalyst in a hot coal gas cleanup process.

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APPENDIX A

THERMODYNAMIC CALCULATIONS OF THE VAPORIZATION OF METAL OXIDES

TABLE 1.

CALCULATED PARTIAL PRESSURES OF SPECIES OVER MoO$_3$(c) AND SOME MMoO4(c) IN PRESENCE OF PURE O$_2$ AT 0.02 ATM TOTAL PRESSURE

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			MoO$_3$(c)		
Mo	1.21×10^{-81}	1.23×10^{-68}	1.53×10^{-58}	1.84×10^{-50}	6.11×10^{-44}
MoO	4.76×10^{-62}	7.35×10^{-52}	5.89×10^{-44}	1.21×10^{-37}	1.34×10^{-32}
MoO$_2$	5.48×10^{-39}	2.76×10^{-32}	4.30×10^{-27}	5.97×10^{-23}	9.86×10^{-20}
MoO$_3$	5.93×10^{-19}	1.76×10^{-15}	8.52×10^{-13}	1.16×10^{-10}	3.98×10^{-9}
Mo$_2$O$_6$	3.01×10^{-14}	3.63×10^{-11}	8.59×10^{-9}	6.52×10^{-7}	8.76×10^{-6}
Mo$_3$O$_9$	2.20×10^{-11}	2.19×10^{-8}	4.42×10^{-6}	2.92×10^{-4}	2.20×10^{-3}
Mo$_4$O$_{12}$	9.37×10^{-12}	1.45×10^{-8}	4.07×10^{-6}	3.46×10^{-4}	2.02×10^{-3}
Mo$_5$O$_{15}$	1.10×10^{-13}	4.04×10^{-10}	2.20×10^{-7}	3.13×10^{-5}	1.76×10^{-4}
O	5.02×10^{-17}	1.12×10^{-14}	7.54×10^{-13}	2.17×10^{-11}	3.09×10^{-10}
O$_2$	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	1.93×10^{-2}	1.56×10^{-2}
O$_3$	1.45×10^{-17}	3.14×10^{-16}	3.44×10^{-15}	2.34×10^{-14}	7.81×10^{-14}
Σ P(Mo) (atm)	**3.15×10^{-11}**	**3.68×10^{-8}**	**8.72×10^{-6}**	**6.70×10^{-4}**	**4.41×10^{-3}**
Mo(2896[a])	0	0	0	0	0
MoO$_2$(c)	0	0	0	0	0
MoO$_3$(1075)	1[b]	1	1	1	0
Mo$_4$O$_{11}$(c)	0	0	0	0	0
Mo$_8$O$_{23}$(c)	0	0	0	0	0
Mo$_9$O$_{26}$(c)	0	0	0	0	0

TABLE 1. (Continued)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$CuMoO_4(c)$		
Cu	5.02×10^{-25}	1.77×10^{-20}	5.96×10^{-17}	3.86×10^{-14}	7.68×10^{-12}
CuO	2.38×10^{-25}	4.33×10^{-21}	8.70×10^{-18}	3.73×10^{-15}	5.21×10^{-13}
Mo	4.49×10^{-83}	5.71×10^{-70}	8.44×10^{-60}	1.10×10^{-51}	4.61×10^{-45}
MoO	1.76×10^{-63}	3.41×10^{-53}	3.24×10^{-45}	7.38×10^{-39}	1.15×10^{-33}
MoO_2	2.03×10^{-40}	1.28×10^{-33}	2.37×10^{-28}	3.70×10^{-24}	9.55×10^{-21}
MoO_3	2.19×10^{-20}	8.18×10^{-17}	4.69×10^{-14}	7.29×10^{-12}	4.36×10^{-10}
Mo_2O_6	4.11×10^{-17}	7.82×10^{-14}	2.61×10^{-11}	2.59×10^{-9}	1.05×10^{-7}
Mo_3O_9	1.11×10^{-15}	2.19×10^{-12}	7.40×10^{-10}	7.30×10^{-8}	2.90×10^{-6}
Mo_4O_{12}	1.75×10^{-17}	6.72×10^{-14}	3.75×10^{-11}	5.44×10^{-9}	2.92×10^{-7}
Mo_5O_{15}	7.63×10^{-21}	8.72×10^{-17}	1.12×10^{-13}	3.11×10^{-11}	2.78×10^{-9}
O	5.02×10^{-17}	1.12×10^{-14}	7.54×10^{-13}	2.20×10^{-11}	3.50×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.45×10^{-15}	2.46×10^{-14}	1.14×10^{-13}
Σ P(Mo) (atm)	**1.17×10^{-15}**	**2.34×10^{-12}**	**8.04×10^{-10}**	**8.10×10^{-8}**	**3.30×10^{-6}**
Cu(1358)	0	0	0	0	0
CuO(c)	0	0	0	0	0
$Cu_2O(1517)$	0	0	0	0	0
$CuMoO_4(c)$	1	1	1	1	1
Mo(2896)	0	0	0	0	0
$MoO_2(c)$	0	0	0	0	0
$MoO_3(1075)$	0	0	0	0	0
$Mo_4O_{11}(c)$	0	0	0	0	0
$Mo_8O_{23}(c)$	0	0	0	0	0
$Mo_9O_{26}(c)$	0	0	0	0	0

TABLE 1. (Continued)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$FeMoO_4(c)$		
Fe	2.95×10^{-46}	1.32×10^{-38}	1.12×10^{-32}	6.04×10^{-28}	5.28×10^{-24}
FeO	7.94×10^{-38}	1.15×10^{-31}	6.74×10^{-27}	4.21×10^{-23}	5.51×10^{-20}
FeO_2	3.61×10^{-28}	6.86×10^{-24}	1.39×10^{-20}	5.83×10^{-18}	7.44×10^{-16}
Mo	1.21×10^{-81}	1.23×10^{-68}	1.53×10^{-58}	1.84×10^{-50}	7.20×10^{-44}
MoO	4.76×10^{-62}	7.35×10^{-52}	5.89×10^{-44}	1.21×10^{-37}	1.53×10^{-32}
MoO_2	5.48×10^{-39}	2.76×10^{-32}	4.30×10^{-27}	5.97×10^{-23}	1.08×10^{-19}
MoO_3	5.93×10^{-19}	1.76×10^{-15}	8.51×10^{-13}	1.16×10^{-10}	4.23×10^{-9}
Mo_2O_6	3.01×10^{-14}	3.63×10^{-11}	8.59×10^{-9}	6.52×10^{-7}	9.88×10^{-6}
Mo_3O_9	2.20×10^{-11}	2.19×10^{-8}	4.42×10^{-6}	2.92×10^{-4}	2.64×10^{-3}
Mo_4O_{12}	9.37×10^{-12}	1.45×10^{-8}	4.07×10^{-6}	3.46×10^{-4}	2.57×10^{-3}
Mo_5O_{15}	1.10×10^{-13}	4.04×10^{-10}	2.20×10^{-7}	3.13×10^{-5}	2.37×10^{-4}
O	5.02×10^{-17}	1.12×10^{-14}	7.54×10^{-13}	2.17×10^{-11}	2.98×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	1.93×10^{-2}	1.45×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.44×10^{-15}	2.34×10^{-14}	7.04×10^{-14}
Σ P(Mo) (atm)	**3.15×10^{-11}**	**3.68×10^{-8}**	**8.72×10^{-6}**	**6.70×10^{-4}**	**5.45×10^{-3}**
Fe(1809)	0	0	0	0	0
FeO(1650)	0	0	0	0	0
$Fe_2O_3(c)$	1	1	1	1	1
$Fe_3O_4(c)$	0	0	0	0	0
$FeMoO_4(c)$	0	0	0	0	0
Mo(2896)	0	0	0	0	0
$MoO_2(c)$	0	0	0	0	0
$MoO_3(1075)$	1	1	1	1	0
$Mo_4O_{11}(c)$	0	0	0	0	0
$Mo_8O_{23}(c)$	0	0	0	0	0
$Mo_9O_{26}(c)$	0	0	0	0	0

TABLE 1. (Continued)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$NiMoO_4(c)$		
Mo	7.26×10^{-83}	8.62×10^{-69}	1.53×10^{-58}	1.84×10^{-50}	6.11×10^{-44}
MoO	2.85×10^{-63}	5.15×10^{-52}	5.89×10^{-44}	1.21×10^{-37}	1.34×10^{-32}
MoO_2	3.28×10^{-40}	1.94×10^{-32}	4.30×10^{-27}	5.97×10^{-23}	9.86×10^{-20}
MoO_3	3.55×10^{-20}	1.23×10^{-15}	8.51×10^{-13}	1.16×10^{-10}	3.98×10^{-9}
Mo_2O_6	1.08×10^{-16}	1.78×10^{-11}	8.59×10^{-9}	6.52×10^{-7}	8.76×10^{-6}
Mo_3O_9	4.72×10^{-15}	7.53×10^{-9}	4.42×10^{-6}	2.92×10^{-4}	2.20×10^{-3}
Mo_4O_{12}	1.20×10^{-16}	3.49×10^{-9}	4.07×10^{-6}	3.46×10^{-4}	2.02×10^{-3}
Mo_5O_{15}	8.47×10^{-20}	6.82×10^{-11}	2.20×10^{-7}	3.13×10^{-5}	1.76×10^{-4}
Ni	3.61×10^{-37}	5.60×10^{-31}	3.55×10^{-26}	2.49×10^{-22}	3.79×10^{-19}
NiO	2.45×10^{-31}	2.80×10^{-26}	2.33×10^{-22}	3.18×10^{-19}	1.14×10^{-16}
O	5.02×10^{-17}	1.12×10^{-14}	7.54×10^{-13}	2.17×10^{-11}	3.09×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	1.93×10^{-2}	1.56×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.44×10^{-15}	2.34×10^{-14}	7.82×10^{-14}
Σ P(Mo) (atm)	**4.94×10^{-15}**	**1.11×10^{-8}**	**8.72×10^{-6}**	**6.70×10^{-4}**	**4.41×10^{-3}**
Ni(1728)	0	0	0	0	0
NiO(c)	0	0	1	1	1
$NiMoO_4(c)$	1	1	0	0	0
Mo(2896)	0	0	0	0	0
$MoO_2(c)$	0	0	0	0	0
$MoO_3(1075)$	0	0	1	1	0
$Mo_4O_{11}(c)$	0	0	0	0	0
$Mo_8O_{23}(c)$	0	0	0	0	0
$Mo_9O_{26}(c)$	0	0	0	0	0

TABLE 1. (Concluded)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$CoMoO_4(c)$		
Co	1.38×10^{-39}	8.43×10^{-33}	1.57×10^{-27}	2.57×10^{-23}	8.24×10^{-20}
CoO	4.47×10^{-33}	1.45×10^{-27}	2.71×10^{-23}	6.91×10^{-20}	4.27×10^{-17}
Mo	1.21×10^{-81}	1.23×10^{-68}	1.53×10^{-58}	1.84×10^{-50}	6.77×10^{-44}
MoO	4.76×10^{-62}	7.35×10^{-52}	5.89×10^{-44}	1.21×10^{-37}	1.45×10^{-32}
MoO_2	5.48×10^{-39}	2.76×10^{-32}	4.30×10^{-27}	5.97×10^{-23}	1.05×10^{-19}
MoO_3	5.93×10^{-19}	1.76×10^{-15}	8.51×10^{-13}	1.16×10^{-10}	4.14×10^{-9}
Mo_2O_6	3.01×10^{-14}	3.63×10^{-11}	8.59×10^{-9}	6.52×10^{-7}	9.46×10^{-6}
Mo_3O_9	2.20×10^{-11}	2.19×10^{-8}	4.42×10^{-6}	2.92×10^{-4}	2.47×10^{-3}
Mo_4O_{12}	9.37×10^{-12}	1.45×10^{-8}	4.07×10^{-6}	3.46×10^{-4}	2.36×10^{-3}
Mo_5O_{15}	1.10×10^{-13}	4.04×10^{-10}	2.20×10^{-7}	3.13×10^{-5}	2.13×10^{-4}
O	5.02×10^{-17}	1.12×10^{-14}	7.54×10^{-13}	2.17×10^{-11}	3.03×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	1.93×10^{-2}	1.49×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.44×10^{-15}	2.34×10^{-14}	7.34×10^{-14}
Σ P(Mo) (atm)	**3.15×10^{-11}**	**3.68×10^{-8}**	**8.72×10^{-6}**	**6.70×10^{-4}**	**5.05×10^{-3}**
Co(1768)	0	0	0	0	0
CoO(c)	0	0	0	0	0
$Co_3O_4(c)$	1	1	1	1	1
$CoMoO_4(c)$	0	0	0	0	0
Mo(2896)	0	0	0	0	0
$MoO_2(c)$	0	0	0	0	0
$MoO_3(1075)$	1	1	1	1	0
$Mo_4O_{11}(c)$	0	0	0	0	0
$Mo_8O_{23}(c)$	0	0	0	0	0
$Mo_9O_{26}(c)$	0	0	0	0	0

a: Melting point.

b: Mole fraction of condensed phase.

TABLE 2.

TOTAL MO-CONTAINING SPECIES PRESSURE OVER MoO_3(c) AND SOME $MMoO_4$(c) IN PRESENCE OF PURE O_2 AT 0.02 ATM TOTAL PRESSURE

Oxide	**Total Mo-containing Species Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
MoO_3(c)	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}
$CuMoO_4$(c)	1.17×10^{-15}	2.34×10^{-12}	8.04×10^{-10}	8.10×10^{-8}	3.30×10^{-6}
$FeMoO_4$(c)	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	5.45×10^{-3}
$NiMoO_4$(c)	4.94×10^{-15}	1.11×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}
$CoMoO_4$(c)	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	5.05×10^{-3}

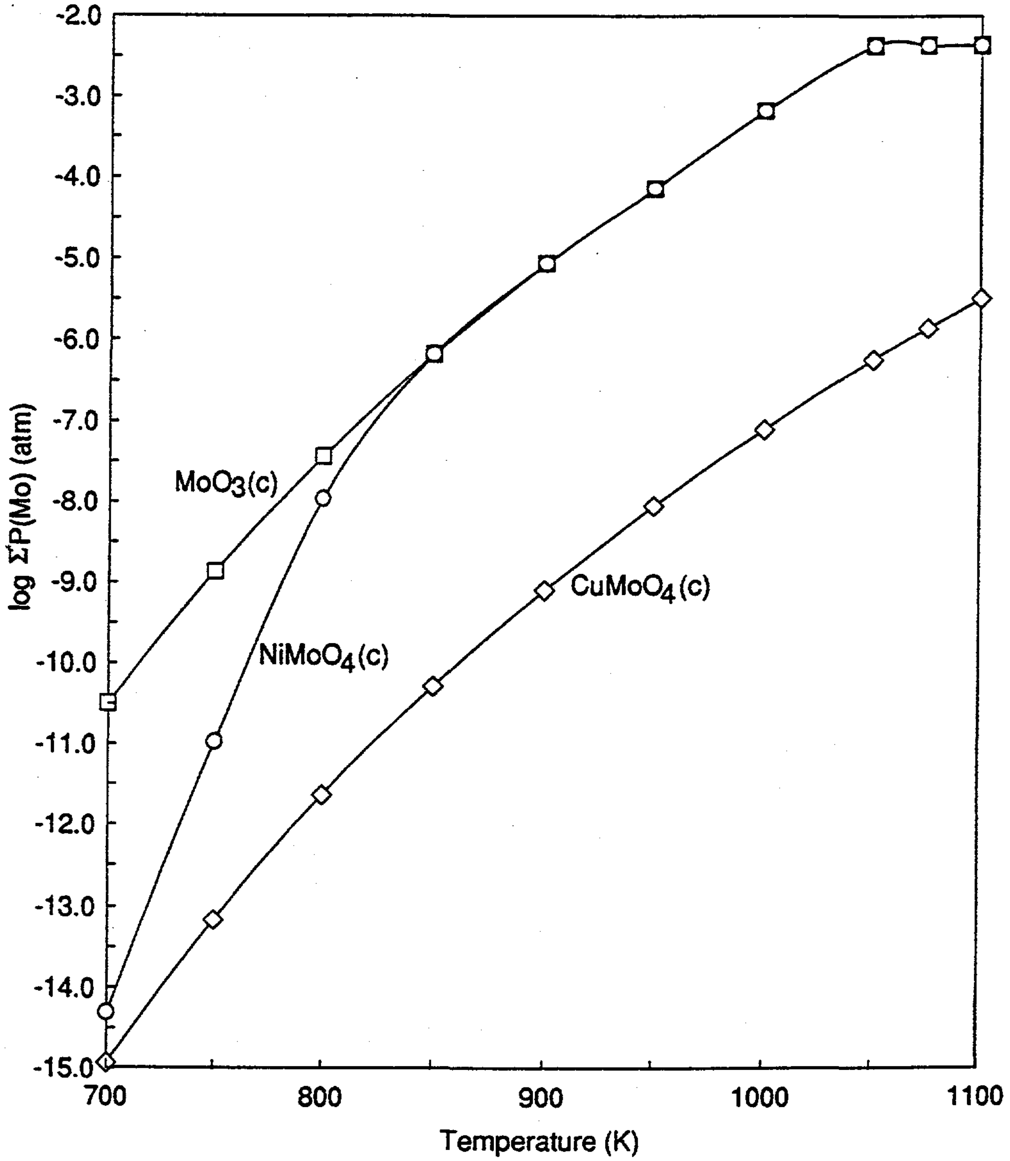

Figure 1. Plot of total Mo-containing species pressure vs temperature over MoO_3(c) and $MMoO_4$(c) in presence of pure O_2 at 0.02 atm total pressure.

TABLE 3.

CALCULATED PARTIAL PRESSURES OF SPECIES OVER WO_3(c) AND SOME MWO_4(c) IN PRESENCE OF PURE O_2 AT 0.02 ATM TOTAL PRESSURE

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			WO_3(c)		
W	8.79×10^{-104}	4.71×10^{-88}	7.95×10^{-76}	4.73×10^{-66}	4.61×10^{-58}
WO	6.85×10^{-73}	2.15×10^{-61}	1.79×10^{-52}	2.34×10^{-45}	1.49×10^{-39}
WO_2	7.07×10^{-50}	7.43×10^{-42}	1.23×10^{-35}	1.12×10^{-30}	1.22×10^{-26}
WO_3	1.98×10^{-29}	1.22×10^{-24}	6.28×10^{-21}	5.65×10^{-18}	1.42×10^{-15}
W_2O_6	3.55×10^{-24}	7.29×10^{-20}	1.57×10^{-16}	6.98×10^{-14}	9.72×10^{-12}
W_3O_8	2.01×10^{-42}	6.75×10^{-35}	4.56×10^{-29}	1.98×10^{-24}	1.15×10^{-20}
W_3O_9	6.80×10^{-25}	3.15×10^{-20}	1.26×10^{-16}	9.14×10^{-14}	1.86×10^{-11}
W_4O_{12}	9.90×10^{-27}	9.86×10^{-22}	7.12×10^{-18}	8.13×10^{-15}	2.37×10^{-12}
W_5O_{15}	7.26×10^{-34}	7.05×10^{-28}	2.97×10^{-23}	1.37×10^{-19}	1.23×10^{-16}
O	5.02×10^{-17}	1.12×10^{-14}	7.55×10^{-13}	2.20×10^{-11}	3.50×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.45×10^{-15}	2.46×10^{-14}	1.14×10^{-13}
Σ P(W) (atm)	**4.24×10^{-24}**	**1.05×10^{-19}**	**2.91×10^{-16}**	**1.69×10^{-13}**	**3.07×10^{-11}**
W(3695[a])	0	0	0	0	0
WO_2(c)	0	0	0	0	0
WO_3(1747)	1[b]	1	1	1	1
$W_{18}O_{49}$(c)	0	0	0	0	0
$W_{20}O_{58}$(c)	0	0	0	0	0
$W_{25}O_{74}$(c)	0	0	0	0	0

TABLE 3. (Continued)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$CoWO_4(c)$		
Co	1.37×10^{-39}	8.26×10^{-33}	1.47×10^{-27}	2.14×10^{-23}	4.73×10^{-20}
CoO	4.44×10^{-33}	1.42×10^{-27}	2.55×10^{-23}	5.84×10^{-20}	2.83×10^{-17}
W	3.75×10^{-106}	1.63×10^{-90}	2.40×10^{-78}	1.38×10^{-68}	1.46×10^{-60}
WO	2.92×10^{-75}	7.41×10^{-64}	5.41×10^{-55}	6.82×10^{-48}	4.71×10^{-42}
WO_2	3.02×10^{-52}	2.56×10^{-44}	3.72×10^{-38}	3.25×10^{-33}	3.85×10^{-29}
WO_3	8.46×10^{-32}	4.23×10^{-27}	1.90×10^{-23}	1.65×10^{-20}	4.50×10^{-18}
W_2O_6	6.46×10^{-29}	8.68×10^{-25}	1.44×10^{-21}	5.94×10^{-19}	9.73×10^{-17}
W_3O_8	1.56×10^{-49}	2.78×10^{-42}	1.26×10^{-36}	4.92×10^{-32}	3.65×10^{-28}
W_3O_9	5.28×10^{-32}	1.29×10^{-27}	3.50×10^{-24}	2.27×10^{-21}	5.90×10^{-19}
W_4O_{12}	3.28×10^{-36}	1.40×10^{-31}	5.96×10^{-28}	5.88×10^{-25}	2.37×10^{-22}
W_5O_{15}	1.02×10^{-45}	3.45×10^{-40}	7.51×10^{-36}	2.89×10^{-32}	3.90×10^{-29}
O	5.02×10^{-17}	1.12×10^{-14}	7.55×10^{-13}	2.20×10^{-11}	3.50×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.45×10^{-15}	2.46×10^{-14}	1.14×10^{-13}
Σ P(W) (atm)	**6.47×10^{-29}**	**8.74×10^{-25}**	**1.46×10^{-21}**	**6.13×10^{-19}**	**1.02×10^{-16}**
Co(1768)	0	0	0	0	0
CoO(c)	0	0	0	0	0
$Co_3O_4(c)$	0	0	0	0	0
$CoWO_4(c)$	1	1	1	1	1
W(3695)	0	0	0	0	0
$WO_2(c)$	0	0	0	0	0
$WO_3(1747)$	0	0	0	0	0
$W_{18}O_{49}(c)$	0	0	0	0	0
$W_{20}O_{58}(c)$	0	0	0	0	0
$W_{25}O_{74}(c)$	0	0	0	0	0

TABLE 3. (Continued)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$CuWO_4(c)$		
Cu	5.01×10^{-25}	1.77×10^{-20}	5.96×10^{-17}	3.86×10^{-14}	7.68×10^{-12}
CuO	2.38×10^{-25}	4.33×10^{-21}	8.70×10^{-18}	3.73×10^{-15}	5.21×10^{-13}
W	8.79×10^{-104}	4.71×10^{-88}	7.95×10^{-76}	4.73×10^{-66}	4.61×10^{-58}
WO	6.85×10^{-73}	2.15×10^{-61}	1.79×10^{-52}	2.34×10^{-45}	1.49×10^{-39}
WO_2	7.07×10^{-50}	7.43×10^{-42}	1.23×10^{-35}	1.12×10^{-30}	1.22×10^{-26}
WO_3	1.98×10^{-29}	1.22×10^{-24}	6.28×10^{-21}	5.65×10^{-18}	1.42×10^{-15}
W_2O_6	3.55×10^{-24}	7.29×10^{-20}	1.57×10^{-16}	6.98×10^{-14}	9.72×10^{-12}
W_3O_8	2.01×10^{-42}	6.75×10^{-35}	4.56×10^{-29}	1.98×10^{-24}	1.15×10^{-20}
W_3O_9	6.80×10^{-25}	3.15×10^{-20}	1.26×10^{-16}	9.14×10^{-14}	1.86×10^{-11}
W_4O_{12}	9.90×10^{-27}	9.86×10^{-22}	7.12×10^{-18}	8.13×10^{-15}	2.37×10^{-12}
W_5O_{15}	7.26×10^{-34}	7.05×10^{-28}	2.97×10^{-23}	1.37×10^{-19}	1.23×10^{-16}
O	5.02×10^{-17}	1.12×10^{-14}	7.55×10^{-13}	2.20×10^{-11}	3.50×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.45×10^{-15}	2.46×10^{-14}	1.14×10^{-13}
Σ P(W) (atm)	**4.24×10^{-24}**	**1.05×10^{-19}**	**2.91×10^{-16}**	**1.69×10^{-13}**	**3.07×10^{-11}**
Cu(1358)	0	0	0	0	0
CuO(c)	1	1	1	1	1
$Cu_2O(1517)$	0	0	0	0	0
$CuWO_4(c)$	0	0	0	0	0
W(3695)	0	0	0	0	0
$WO_2(c)$	0	0	0	0	0
$WO_3(1747)$	1	1	1	1	1
$W_{18}O_{49}(c)$	0	0	0	0	0
$W_{20}O_{58}(c)$	0	0	0	0	0
$W_{25}O_{74}(c)$	0	0	0	0	0

TABLE 3. (Continued)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$FeWO_4$(c)		
Fe	2.95×10^{-46}	1.32×10^{-38}	1.12×10^{-32}	5.89×10^{-28}	4.16×10^{-24}
FeO	7.94×10^{-38}	1.15×10^{-31}	6.74×10^{-27}	4.17×10^{-23}	5.09×10^{-20}
FeO_2	3.61×10^{-28}	6.86×10^{-24}	1.39×10^{-20}	5.88×10^{-18}	8.05×10^{-16}
W	8.79×10^{-104}	4.71×10^{-88}	7.95×10^{-76}	4.73×10^{-66}	4.61×10^{-58}
WO	6.85×10^{-73}	2.15×10^{-61}	1.79×10^{-52}	2.34×10^{-45}	1.49×10^{-39}
WO_2	7.07×10^{-50}	7.43×10^{-42}	1.23×10^{-35}	1.12×10^{-30}	1.22×10^{-26}
WO_3	1.98×10^{-29}	1.22×10^{-24}	6.28×10^{-21}	5.65×10^{-18}	1.42×10^{-15}
W_2O_6	3.55×10^{-24}	7.29×10^{-20}	1.57×10^{-16}	6.98×10^{-14}	9.72×10^{-12}
W_3O_8	2.01×10^{-42}	6.75×10^{-35}	4.56×10^{-29}	1.98×10^{-24}	1.15×10^{-20}
W_3O_9	6.80×10^{-25}	3.15×10^{-20}	1.26×10^{-16}	9.14×10^{-14}	1.86×10^{-11}
W_4O_{12}	9.90×10^{-27}	9.86×10^{-22}	7.12×10^{-18}	8.13×10^{-15}	2.37×10^{-12}
W_5O_{15}	7.26×10^{-34}	7.05×10^{-28}	2.97×10^{-23}	1.37×10^{-19}	1.23×10^{-16}
O	5.02×10^{-17}	1.12×10^{-14}	7.55×10^{-13}	2.20×10^{-11}	3.50×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.45×10^{-15}	2.46×10^{-14}	1.14×10^{-13}
$\Sigma P(W)$ (atm)	**4.24×10^{-24}**	**1.05×10^{-19}**	**2.91×10^{-16}**	**1.69×10^{-13}**	**3.07×10^{-11}**
Fe(1809)	0	0	0	0	0
FeO(1650)	0	0	0	0	0
Fe_2O_3(c)	1	1	1	1	1
Fe_3O_4(c)	0	0	0	0	0
$FeWO_4$(c)	0	0	0	0	0
W(3695)	0	0	0	0	0
WO_2(c)	0	0	0	0	0
WO_3(1747)	1	1	1	1	1
$W_{18}O_{49}$(c)	0	0	0	0	0
$W_{20}O_{58}$(c)	0	0	0	0	0
$W_{25}O_{74}$(c)	0	0	0	0	0

TABLE 3. (Continued)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
			$NiWO_4(c)$		
Ni	3.61×10^{-37}	5.59×10^{-31}	3.54×10^{-26}	2.44×10^{-22}	3.32×10^{-19}
NiO	2.45×10^{-31}	2.80×10^{-26}	2.32×10^{-22}	3.16×10^{-19}	1.13×10^{-16}
W	2.26×10^{-108}	3.73×10^{-91}	1.57×10^{-78}	1.97×10^{-68}	3.65×10^{-60}
WO	1.76×10^{-76}	1.70×10^{-64}	3.53×10^{-55}	9.77×10^{-48}	1.18×10^{-41}
WO_2	1.82×10^{-53}	5.88×10^{-45}	2.43×10^{-38}	4.66×10^{-33}	9.63×10^{-29}
WO_3	5.09×10^{-33}	9.69×10^{-28}	1.24×10^{-23}	2.36×10^{-20}	1.13×10^{-17}
W_2O_6	2.34×10^{-31}	4.57×10^{-26}	6.15×10^{-22}	1.22×10^{-18}	6.08×10^{-16}
W_3O_8	3.41×10^{-53}	3.35×10^{-44}	3.52×10^{-37}	1.44×10^{-31}	5.70×10^{-27}
W_3O_9	1.15×10^{-35}	1.56×10^{-29}	9.77×10^{-25}	6.64×10^{-21}	9.22×10^{-18}
W_4O_{12}	4.30×10^{-41}	3.87×10^{-34}	1.09×10^{-28}	2.47×10^{-24}	9.28×10^{-21}
W_5O_{15}	8.09×10^{-52}	2.19×10^{-43}	8.95×10^{-37}	1.73×10^{-31}	3.81×10^{-27}
O	5.02×10^{-17}	1.12×10^{-14}	7.55×10^{-13}	2.20×10^{-11}	3.50×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.45×10^{-15}	2.46×10^{-14}	1.14×10^{-13}
Σ P(W) (atm)	**2.45×10^{-31}**	**2.80×10^{-26}**	**2.32×10^{-22}**	**3.17×10^{-19}**	**1.13×10^{-16}**
Ni(1728)	0	0	0	0	0
NiO(c)	0	0	0	0	0
$NiWO_4$(c)	1	1	1	1	1
W(3695)	0	0	0	0	0
WO_2(c)	0	0	0	0	0
WO_3(1747)	0	0	0	0	0
$W_{18}O_{49}$(c)	0	0	0	0	0
$W_{20}O_{58}$(c)	0	0	0	0	0
$W_{25}O_{74}$(c)	0	0	0	0	0

TABLE 3. (Concluded)

Species	**Partial Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
$ZnWO_4$(c)					
Zn	2.22×10^{-26}	1.05×10^{-21}	4.31×10^{-18}	3.26×10^{-15}	7.30×10^{-13}
ZnO	2.43×10^{-26}	4.78×10^{-22}	9.87×10^{-19}	4.30×10^{-16}	6.11×10^{-14}
W	7.03×10^{-105}	4.68×10^{-89}	9.63×10^{-77}	6.78×10^{-67}	7.62×10^{-59}
WO	5.47×10^{-74}	2.13×10^{-62}	2.17×10^{-53}	3.36×10^{-46}	2.46×10^{-40}
WO_2	5.65×10^{-51}	7.37×10^{-43}	1.49×10^{-36}	1.60×10^{-31}	2.01×10^{-27}
WO_3	1.59×10^{-30}	1.22×10^{-25}	7.61×10^{-22}	8.10×10^{-19}	2.35×10^{-16}
W_2O_6	2.27×10^{-26}	7.18×10^{-22}	2.31×10^{-18}	1.44×10^{-15}	2.66×10^{-13}
W_3O_8	1.03×10^{-45}	6.60×10^{-38}	8.11×10^{-32}	5.84×10^{-27}	5.20×10^{-23}
W_3O_9	3.48×10^{-28}	3.08×10^{-23}	2.25×10^{-19}	2.69×10^{-16}	8.41×10^{-14}
W_4O_{12}	4.04×10^{-31}	9.57×10^{-26}	1.54×10^{-21}	3.43×10^{-18}	1.77×10^{-15}
W_5O_{15}	2.37×10^{-39}	6.79×10^{-33}	7.75×10^{-28}	8.29×10^{-24}	1.52×10^{-20}
O	5.02×10^{-17}	1.12×10^{-14}	7.55×10^{-13}	2.20×10^{-11}	3.50×10^{-10}
O_2	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}
O_3	1.45×10^{-17}	3.14×10^{-16}	3.45×10^{-15}	2.46×10^{-14}	1.14×10^{-13}
Σ P(W) (atm)	**2.30×10^{-26}**	**7.49×10^{-22}**	**2.54×10^{-18}**	**1.71×10^{-15}**	**3.52×10^{-13}**
Zn(693)	0	0	0	0	0
ZnO(2248)	0	0	0	0	0
$ZnWO_4$(c)	1	1	1	1	1
W(3695)	0	0	0	0	0
WO_2(c)	0	0	0	0	0
WO_3(1747)	0	0	0	0	0
$W_{18}O_{49}$(c)	0	0	0	0	0
$W_{20}O_{58}$(c)	0	0	0	0	0
$W_{25}O_{74}$(c)	0	0	0	0	0

a: Melting point.

b: Mole fraction of condensed phase.

TABLE 4.

TOTAL W-CONTAINING SPECIES PRESSURE OVER WO_3(c) AND SOME MWO_4(c) IN PRESENCE OF PURE O_2 AT 0.02 ATM TOTAL PRESSURE

Oxide	**Total W-containing Species Pressure (atm)**				
	700 K	800 K	900 K	1000 K	1100 K
WO_3(c)	4.24×10^{-24}	1.05×10^{-19}	2.91×10^{-16}	1.69×10^{-13}	3.07×10^{-11}
$CoWO_4$(c)	6.47×10^{-29}	8.74×10^{-25}	1.46×10^{-21}	6.13×10^{-19}	1.02×10^{-16}
$CuWO_4$(c)	4.24×10^{-24}	1.05×10^{-19}	2.91×10^{-16}	1.69×10^{-13}	3.07×10^{-11}
$FeWO_4$(c)	4.24×10^{-24}	1.05×10^{-19}	2.91×10^{-16}	1.69×10^{-13}	3.07×10^{-11}
$NiWO_4$(c)	2.45×10^{-31}	2.80×10^{-26}	2.32×10^{-22}	3.17×10^{-19}	1.13×10^{-16}
$ZnWO_4$(c)	2.30×10^{-26}	7.49×10^{-22}	2.54×10^{-18}	1.71×10^{-15}	3.52×10^{-13}

APPENDIX B

Final Report by General Electric

Simultaneous Removal of Hydrogen Sulfide and Ammonia Using Mixed-Metal Oxide Sorbents

TECHNICAL REPORT

By

S.L. Hung
R.E. Ayala

September 1996

Work performed under Research Triangle Institute's subcontract
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September 29 1992 to September 30 1996

For
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1. SUMMARY

The initial objective of this program was the development a material for use in hot gas cleanup of coal gas that will act both as a catalyst towards the decomposition of ammonia (NH_3) as well as a sorbent towards hydrogen sulfide (H_2S) removal. The focus of the work at General Electric's Corporate Research and Development (GE-CRD) was on the application of the sorbent-catalyst material to a moving-bed hot gas clean-up (HGCU) system. In the first phase of this program, powdered sorbent-catalyst samples were tested in a small scale microreactor to test their effectiveness towards NH_3 decomposition. The starting base material for all of GE-CRD's sorbent-catalyst formulations was zinc titanate, a material which was being studied as a potential commercial H_2S sorbent in a parallel DOE funded study at GE-CRD. MoS_2, which has been reported to be catalytically active towards the NH_3 decomposition reaction, was studied as the catalytic component. In addition to molybdenum, other species (Co, Ni, and Al) were used in the catalyst formulations in attempts to promote and stabilize the catalytic activity of MoS_2. A number of catalyst formulations were tested, and although some levels of NH_3 decomposition activity were observed, the catalytic activities were limited and incomplete NH_3 destruction levels were achieved at the operating conditions for desulfurization.

After the initial effort at studying simultaneous desulfurization and ammonia decomposition and showing the need for higher ammonia decomposition activity, GE-CRD focused on the development of a material only for decomposition of ammonia. As necessary, elevated temperatures were to be used to minimize potential catalyst inhibition or poisoning by H_2S. Previous tests at RTI produced encouraging results indicating that a commercially available steam reforming catalyst (HTSR-1 catalyst; Haldor Topsoe, Denmark) was sufficiently active towards the desired NH_3 decomposition reaction in fluidized-bed, bench-scale tests. In this second phase of work at GE-CRD, the HTSR-1 catalyst was tested and demonstrated to be effective towards the catalytic decomposition of NH_3 at elevated temperatures (900° C) and pressures (8.5 atm) in a 100-hr bench-scale test. Using an initial NH_3 concentration of ~1550 ppm (wet basis) and operating at a space velocity of 10,000 h^{-1}, NH_3 destruction levels of 80% were measured over extended periods of time. When the space velocity was reduced to 5000 h^{-1}, NH_3 destruction levels further increased to 88%, even in the presence of hydrogen sulfide.

2. MICROREACTOR SCREENING TESTS

2.1 CATALYST SELECTION

R. Ayala[1] and others[2] have shown molybdenum disulfide (MoS_2) to be active towards the catalytic decomposition of NH_3 in coal gas.

In the current study, the strategy for developing a stable NH_3 decomposition catalyst was to stabilize MoS_2 catalysts from commercial hydrodesulfurization processes to stabilize MoS_2 onto zinc titanate, a sorbent used for desulfurization of coal gases. Note that although hydrodesulfurization and the current application of the sorbent-catalyst (i.e., for application to HGCU system) are different, the operating conditions for the two processes are similar. In the petroleum refining industry, hydrodesulfurization involves the catalytic reaction of H_2 with sulfur containing hydrocarbons to form H_2S so that the sulfur may be removed as H_2S. The catalyst is typically a sulfided form of Co-Mo or Ni-Mo on an alumina support. One difference between the two catalysts is that Co-Mo-S will more easily catalyze the exothermic methanation reactions than Ni-Mo-S[3]. It has been cited that some hydrodesulfurization catalysts use tungsten (W) instead of molybdenum (Mo)[4]. The role of the alumina support (g-Al_2O_3) on the catalytic reaction(s) is unclear, but likely contributes to the stability and activity of the hydrodesulfurization catalyst. Note that while γ-Al_2O_3 may be stable for the temperatures found in hydrodesulfurization units (200-400 °C), α-Al_2O_3 may be the more stable form of alumina at the higher temperatures found in an HGCU gas stream (> 538 °C). The effect of the sorbent material (i.e., zinc and titanium oxides, sulfides, and sulfates) on the Molybdenum-based catalysts is unclear.

During the first phase of the test program, GE-CRD focused its efforts on Molybdenum-based catalysts and the use of additives which may promote and/or stabilize its catalyst activity.

2.2 EXPERIMENTAL SETUP FOR MICROREACTOR TESTS

A schematic diagram of GE's microreactor system is shown in Figure 2.2-1. As shown in this figure, mixtures of NH_3/H_2, H_2S/Ar, CO_2/CO were combined with pure gases (H_2, CO_2, Ar, and N_2) to give the desired coal gas compositions. The flow rates of these gases were metered using mass flow controllers. Water vapor, when needed, was produced by evaporating the water delivered via a syringe pump. To minimize the possible formation of ammonium carbonate (from NH_3 and CO) in the inlet gas manifold, the gases were heated to 120 °C prior to the introduction of NH_3. The gas composition used as the basis for this study corresponds to that typical from a Texaco oxygen-blown gasifier: 38.00% CO_2, 28.50% H_2, 12.85% CO_2, 18.10% H_2O, 1.62% N_2, 7500 ppm H_2S, and 1800 ppm NH_3. In some of the initial microreactor screening tests, H_2O and N_2 were not used in the gas mixture (Ar was used as the balance instead).

The microreactor was fabricated using a high temperature metallic alloy (800H) with a nominal composition of Ni-Fe-Cr. To minimize chemical interactions between the powdered sorbent-catalyst samples and the reactor, the tubes were coated with a 0.5-1.0 micron thick layer of SiO_2. The metallic reactor had an ID of 11 mm and was heated in a tube furnace. The packing arrangement of the powdered sorbent-catalyst samples within the microreactor assembly is shown in Figure 2.2-2.

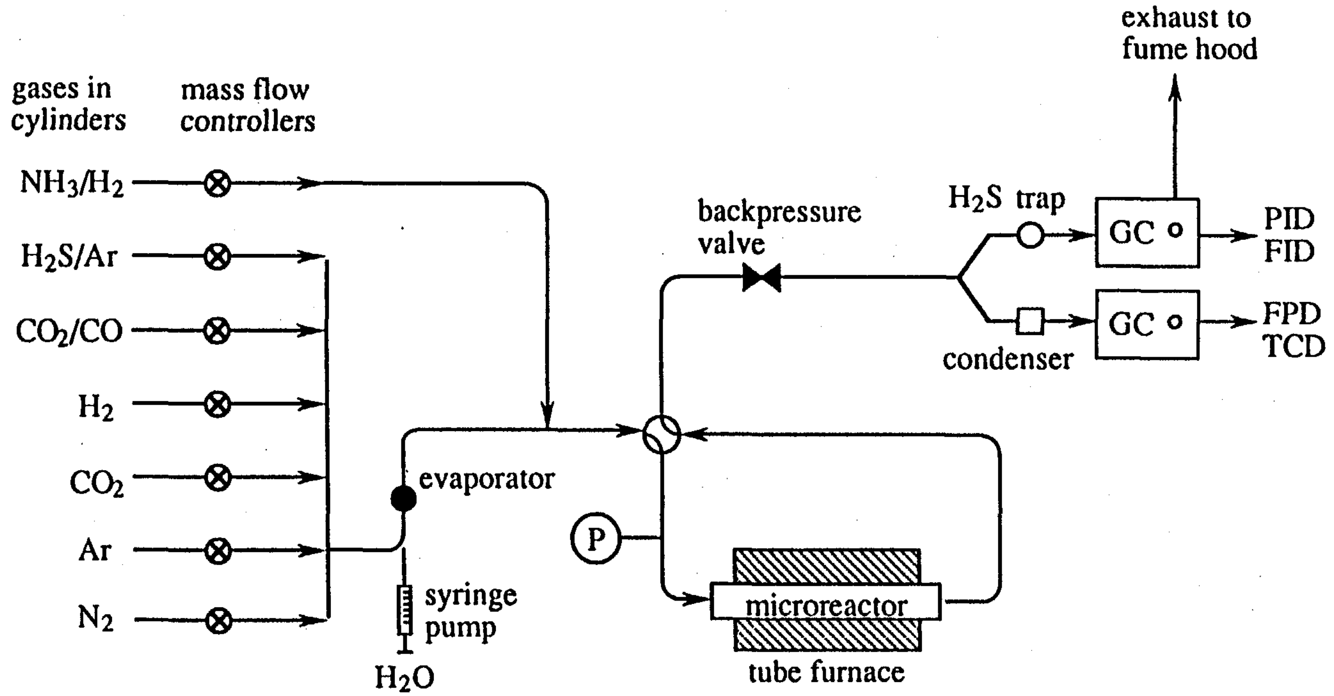

Figure 2.2-1 Microreactor System for Ammonia Decomposition Screening Tests

METC93-fig2

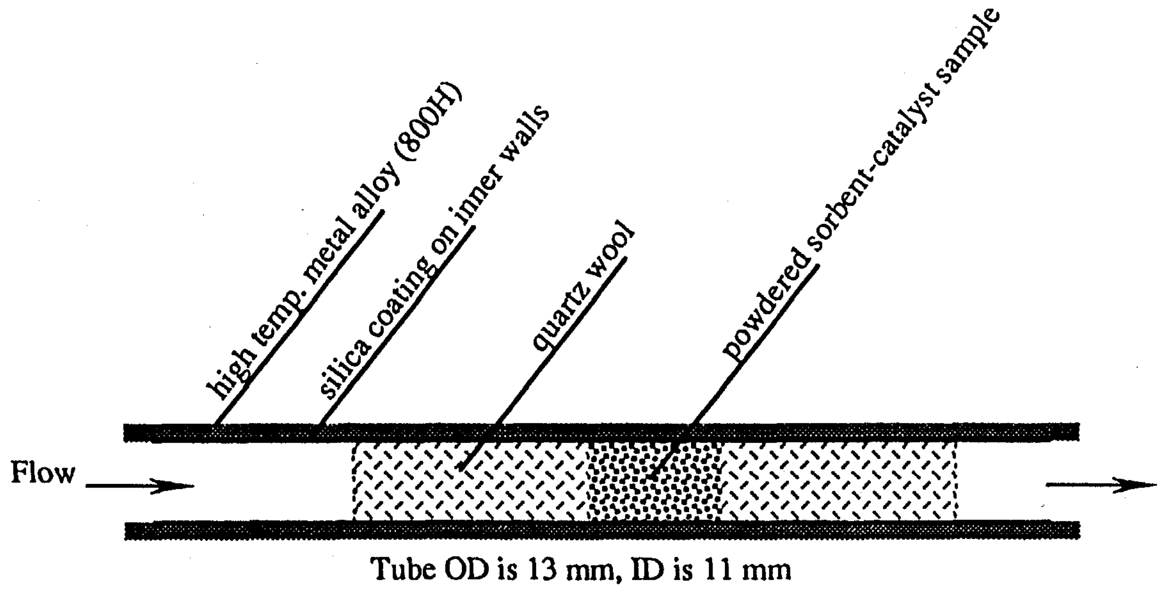

Figure 2.2-2 Schematic Diagram of GE-CRD's High Temperature, High Pressure Microreactor

The exhaust gases were analyzed for NH_3 using a gas chromatograph equipped with both a photo-ionization detector (PID) and flame ionization detector (FID). The PID was used for NH_3 analysis and the FID for CH_4 analysis. When needed, a second gas chromatograph equipped with an flame photometric detector (FPD) was used for H_2S analysis. With the GC/PID (with a Chromosorb 103 packed column), the lower detectable limit of NH_3 was 50-75 ppm. The present study did not focus on the mechanisms of H_2S adsorption onto the sorbent because the zinc titanate base material has been studied extensively as a desulfurization sorbent in other parallel studies.

2.3 RESULTS OF MICROREACTOR SCREENING TESTS

The objective of the initial microreactor tests was to screen various catalyst formulations based solely on their measured catalytic activities towards NH_3 decomposition. It was intended that other methods for better characterization of sorbent-catalyst materials (i.e., determine dispersion of Mo in the zinc titanate, surface area determination, etc.) would be made only if the materials displayed sufficient activity towards NH_3 decomposition to justify such extended work.

2.3.1 Co-Mo-zinc titanate

Co and Ni are commonly used to promote the activity of MoS_2 desulfurization and denitrification catalysts. Sorbent-catalyst samples of zinc titanate doped with cobalt-molybdenum were prepared by first crushing and sieving pellets of zinc titanate sorbents (United Catalyst, Inc., formulation L-3774M). The zinc titanate powders were then placed in an aqueous solution having the desired total amount of molybdenum (in the form of molybdic acid). The water was then dried and the powder heated and calcined. To add cobalt to the Mo-coated powder, the powder was then placed into a solution of cobalt nitrate containing the appropriate amount of the cobalt precursor followed by drying and calcination. The samples were then activated (presulfided) by introducing H_2S in a controlled reducing environment (typically 1% H_2S, 5% H_2, balance Ar, at 300 °C). The final catalyst, which consisted of cobalt and molybdenum impregnated onto the zinc titanate material, was labeled Co-Mo-zinc titanate.

Using a gas mixture of 1800 ppm NH_3 and a space velocity of 4000 h^{-1}, the catalytic decomposition of NH_3 was measured over Co-Mo-zinc titanate. The gas mixture contained 38.6% CO, 29.5% H2, 13.1% CO2, and balance Ar. The test results are presented in Figure 2.3.1-1 and show that NH_3 decomposition occurred. As the reaction temperature was increased from 350 °C to 725 °C, outlet NH_3 levels decreased from ~1800 ppm to 1200-1300 ppm. The effect that H_2S would have on the catalytic reaction was examined by adding 0.75% H_2S to the gas mixture. The data in Figure 2.3.1-1 show that after exposing the catalyst to H_2S (at 725 °C), the measured effluent NH_3 concentration first increased and then decreased. Finally, the NH_3 concentration leveled off near 1100 ppm. The cause for the transient increase/decrease in NH_3 concentration following the addition of H_2S was not clear although it is believed to be related to the accidental introduction of some oxygen (air) in the H_2S supply line when H_2S was introduced. By taking care to purge air from the H_2S lines (and gas regulator) prior to use, the transient response in NH_3 levels was eliminated in subsequent tests. Although high NH_3 destruction levels were not measured with this catalyst, the results showed that at 725 °C, the catalytic activity of Co-Mo-zinc titanate towards NH_3 decomposition was not inhibited by the presence of 0.75% H_2S in the gas mixture.

2.3.2 Ni-Mo-zinc titanate

As stated previously, both Co and Ni are used to promote the activity of MoS_2 hydrodesulfurization and hydrodenitrification catalysts. The effect of Ni added to a Mo coated zinc titanate for NH_3 decomposition was studied next. Samples of nickel-molybdenum-zinc titanate were prepared in a similar manner as described above (Section 2.3.1) for the preparation of Co-Mo-zinc titanate but by using Ni nitrate instead of Co nitrate.

Data for the Ni-Mo-zinc titanate catalyst were taken under the same conditions as in the tests with Co-Mo-zinc titanate (at 725 °C; 1 atm; space velocity of 4000 h^{-1}; gas composition of 1800 ppm NH_3, 38.6% CO, 29.5% H_2, 13.1% CO_2, and balance Ar). The data is presented in Figure 2.3.2-1 and show that although there was considerable noise in this data, the data showed that Ni-Mo-zinc titanate exhibited little or no activity towards NH_3 decomposition.

2.3.3 Co-Mo-Al-zinc titanate

Data taken with the previous two sorbent-catalyst formulations (Co-Mo-zinc titanate and Ni-Mo-zinc titanate) showed Co-Mo-zinc titanate to be more effective towards the catalytic decomposition of NH_3 when compared to Ni-Mo-zinc titanate. To further study the cobalt-molybdenum zinc titanate system, alumina (Al) was added to the Co-Mo-zinc titanate sorbent-catalyst formulation because alumina is typically used as the catalyst support for MoS_2 hydrodesulfurization and hydrodenitrification catalysts and may provide beneficial catalyst-support interactions. The catalyst was prepared in a similar manner as described for Co-Mo-zinc titanate.

The data presented in Figure 2.3.3-1 show that NH_3 concentrations at the reactor outlet decreased from 1700-1800 ppm at 350° C to approximately 1500-1600 ppm over the Co-Mo-Al-zinc titanate when the temperature was increased to 725° C. Figure 2.3.3-1 also shows that the catalytic activity of the Co-Mo-Al-zinc titanate sorbent-catalyst toward the NH_3 decomposition reaction improved significantly when the temperature was further increased to 775 °C (NH_3 levels were reduced to 700 ppm to achieve a 61% conversion).

Figure 2.3.3-2 shows that the catalytic activity of the Co-Mo-Al-zinc titanate material diminished as 0.75% H_2S was introduced into the gas mixture at 725 °C. This was surprising as the Co-Mo-zinc titanate (with no alumina) did not show any measurable loss of catalyst activity when H_2S was added (in Figure 2.3.1-1). It was speculated that the presence of alumina in the current Co-Mo-Al-zinc titanate sorbent-catalyst formulation lead to the formation of aluminum sulfate(s) which may have reduced the availability of the catalytic sites by blocking the catalyst surface or the pore channels.

2.3.4 Fresh Mo-doped zinc titanate

Of the three sorbent-catalyst samples discussed thus far, the Co-Mo-zinc titanate was found to be the best catalyst towards NH_3 decomposition. Although the activity of the Co-Mo-zinc titanate was not as high as that of Co-Mo-Al-zinc titanate, its activity did not diminish in the presence of H_2S. Next, a sample of a Mo-doped zinc titanate sample was tested (without the cobalt additive) so that the effect of cobalt on the Mo-zinc titanate material could be determined. Although this sample was prepared in our own lab, the final sorbent-catalyst sample composition was nominally similar to that of L-3787M.

Data taken over the Mo-zinc titanate is presented in Figure 2.3.4-1 and show that at 725 °C, NH_3 levels were reduced from 1800 ppm to 1200-1300 ppm. The activity of this catalyst was comparable to that of Co-Mo-zinc titanate (Figure 2.3.4-1 and Figure 2.3.1-1). Interestingly, NH_3 decomposition may have increased slightly as 0.75% H_2S was added to the gas mixture at 725 °C (see Figure 2.3.4-1).

2.3.5 Cycled L-3787M2 Mo-doped zinc titanate

It has now been shown that Co-Mo-zinc titanate and Mo-zinc titanate were both active towards the catalytic decomposition of NH_3 at relatively high temperatures (>700 °C) and that their activities were not affected by the presence of 0.75% H_2S in the gas mixture. In addition, it was also known from other work[1] that molybdenum doped zinc titanate is active towards NH_3 decomposition and that the activity improved as the material was subjected to multiple cycles of H_2S absorption and subsequent regeneration. Although it was not understood why increasing cycles of absorption and regeneration improved the catalyst activity, the increased activity may be related to the migration of the molybdenum within the zinc titanate material incurred from the operational cycles of the sorbent or the formation of MoS_2.

Tests were conducted to determine whether exposure of the Mo-doped zinc titanate to the operation cycles of adsorption and regeneration produced a more active NH_3 decomposition catalyst. This sample, designated L-3787M2, contained ~2.5% molybdenum oxide and was cycled through ten adsorption/regeneration cycles in GE-

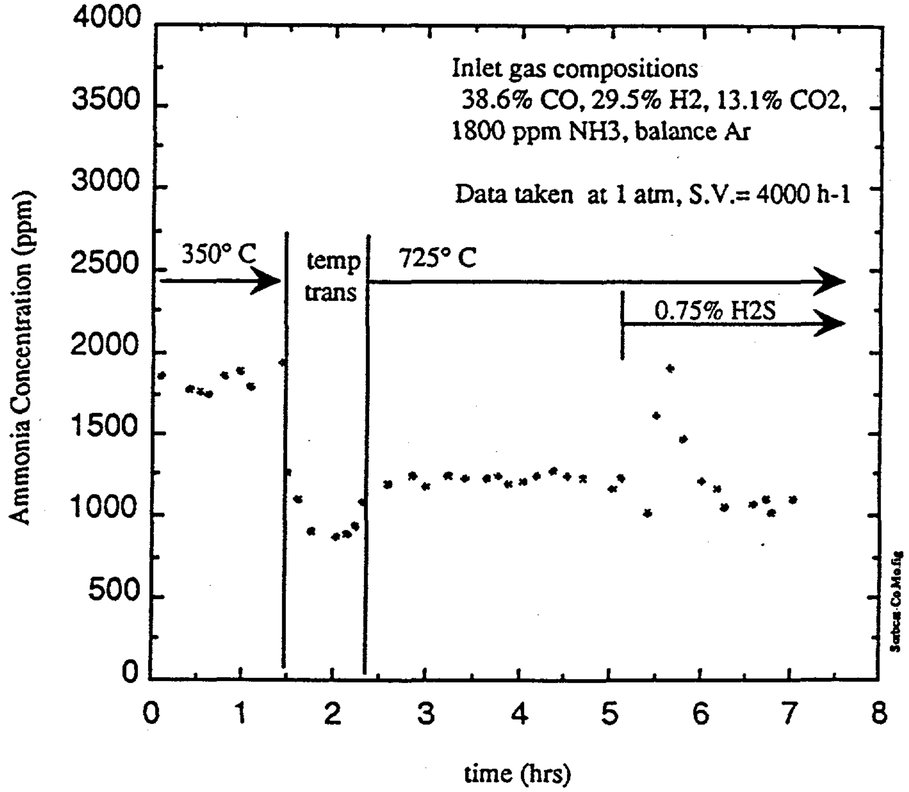

Figure 2.3.1-1 Preliminary Data of Ammonia Decomposition over Co-Mo-Zinc Titanate

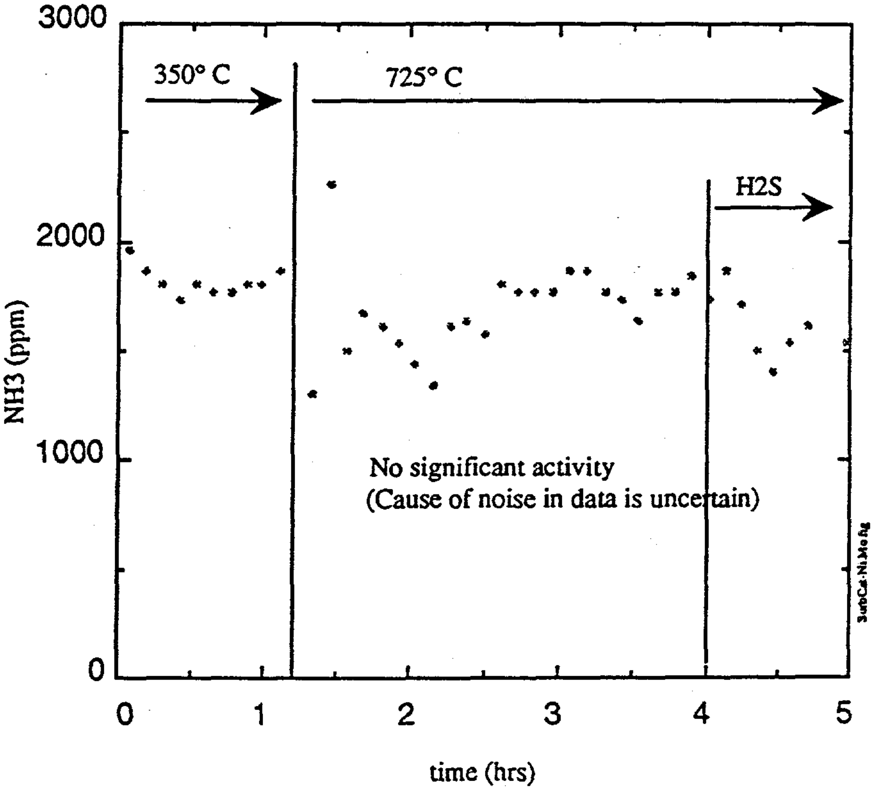

Figure 2.3.2-1 Ammonia Measurements for Ni-Mo-Zinc Titanate

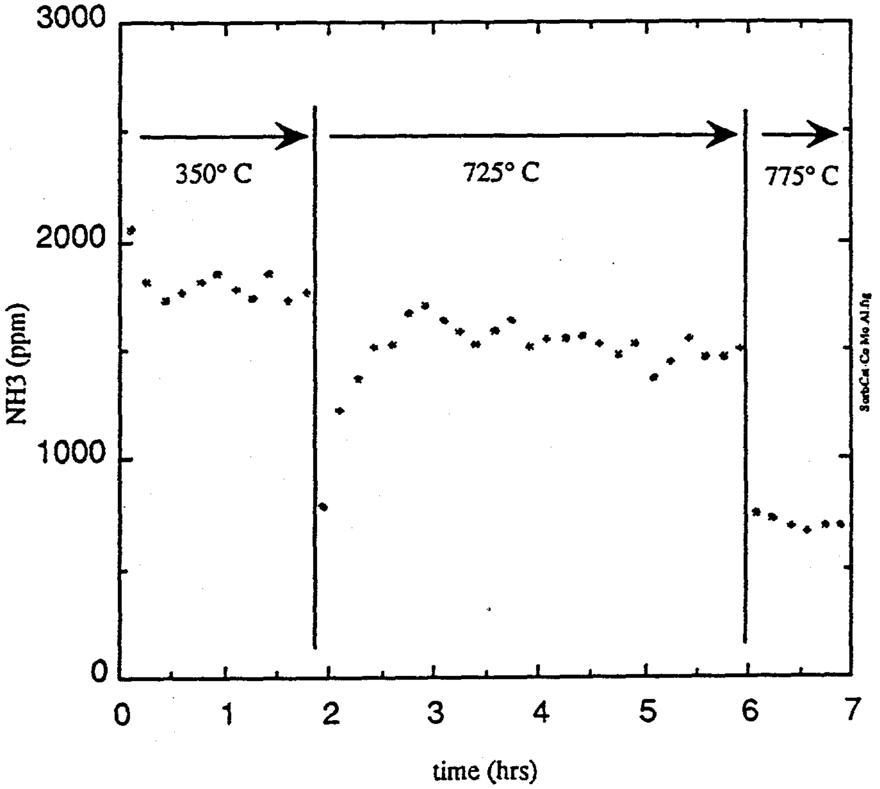

Figure 2.3.3-1 Ammonia Measurements for Co-Mo-Al-Zinc Titanate

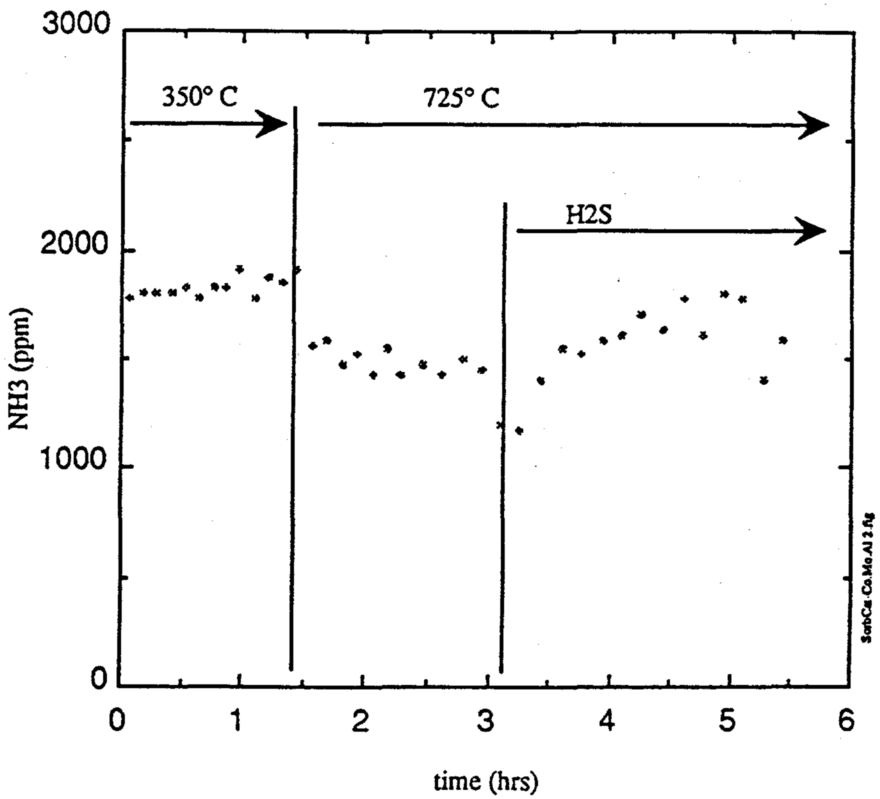

Figure 2.3.3-2 Ammonia Measurements for Co-Mo-Al-Zinc Titanate

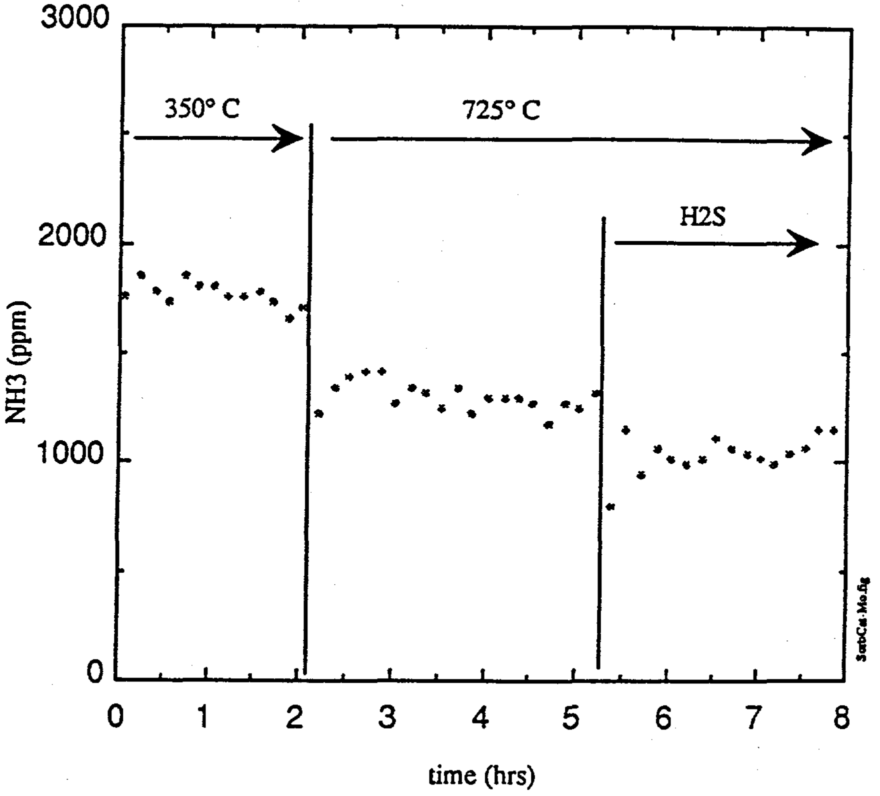

Figure 2.3.4-1 Ammonia Measurements for Mo-Zinc Titanate

CRD's bench apparatus (in pelletized form). Since these samples were previously exposed to H_2S, no presulfidation was used although the addition of H_2S to the feed gas was used to observe its effect on the catalyst activity.

For the microreactor studies, a gas composition of 28.6% H_2, 1750 ppm NH_3, and balance Ar was first used in this test. Using powdered L-3787M2 (in regenerated form) as sorbent-catalyst sample, Figure 2.3.5-1 shows that no measurable NH_3 decomposition was measured at 550 °C. Increasing the reaction temperature to 650 °C, 700 °C, and 725 °C (Figure 2.3.5-2) increased the catalyst activity, but NH_3 conversions remained low.

Next, NH_3 decomposition over the same catalyst was studied using a gas mixture containing 38.8% CO, 13.0% CO_2, 29.5% H_2, 1800 ppm NH_3, and balance Ar. This gas mixture approximates the nominal gas composition from a Texaco oxygen blown gasifier, but without any water vapor. Even at relatively high temperature of 725 °C and 750 °C, however, only limited NH_3 conversions were observed (Figure 2.3.5-3). For example, at 750 °C the NH_3 was reduced by only ~33% as NH_3 was reduced to ~1200 ppm (from 1800 ppm).

The effect of the presence of 0.75% H_2S in the gas mixture on the L-3787M2 catalytic activity was also investigated. Figure 2.3.5-4 shows the addition of 7500 ppm H_2S reduced the activity of the catalyst for NH_3 decomposition. The decrease in catalyst activity as H_2S was added was surprising as previous test data using zinc titanate doped with molybdenum showed the catalyst activity to be unaffected by H_2S over short duration (i.e., several hours; see Section 2.3.4).

2.3.6 Cycled L-3785M Mo-doped zinc titanate

Samples of a molybdenum doped zinc titanate with even higher levels of molybdenum than the L-3787M2 sample described in Section 2.3.5 were tested. This material, called L-3785M contained approximately 5% molybdenum oxide (by weight) and had a zinc to titanium molar ratio of 2 to 1. By contrast, the L-3787M2 material discussed in section 2.3.5 contained ~2.5% molybdenum oxide. The L-3785M samples were taken from a bench-scale packed bed test in which, like the L-3787M2 sample, the samples were previously subjected to ten absorption and regeneration cycles. Two separate L-3785M samples were tested. The first L-3785M sample was taken from the inlet end of the packed bed and the second L-3785M sample from near the outlet end of the packed bed. In the packed bed bench apparatus, the inlet end of the packed bed would be exposed to higher levels of H_2S and would achieve higher degrees of sulfidation then the sorbent near the outlet end. During regeneration, the inlet end of packed bed would be exposed to higher levels of oxygen and be more thoroughly regenerated than the sorbent near the outlet end. The outlet end of the packed bed, on the other hand, would also be exposed to higher concentrations of SO_2 during the regeneration stage. The significance of the differences between the inlet and outlet samples towards the catalytic activity of the L-

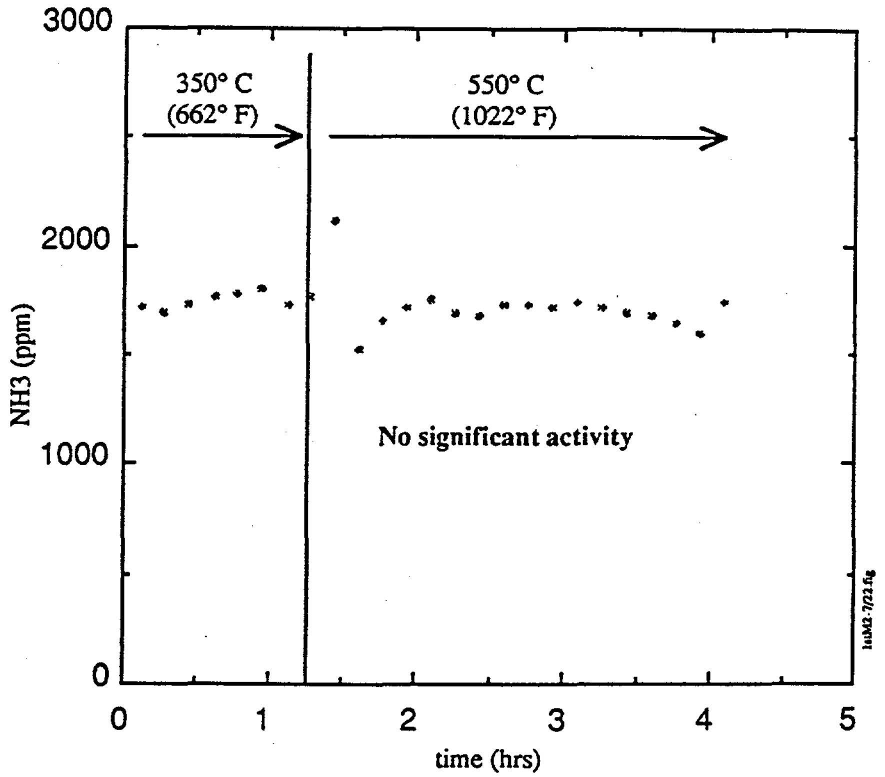

Figure 2.3.5-1 Ammonia Decomposition over L-3787M2 Previously Subjected to Ten Absorption/Regeneration Cycles

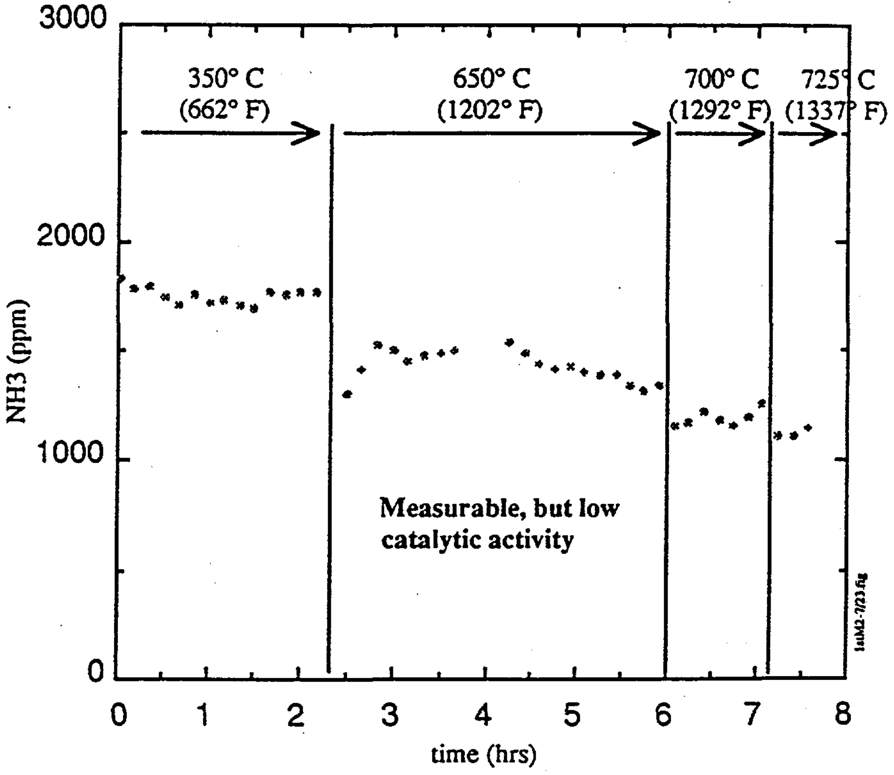

Figure 2.3.5-2 Ammonia Decomposition over L-3787M2 Previously Subjected to Ten Absorption/Regeneration Cycles

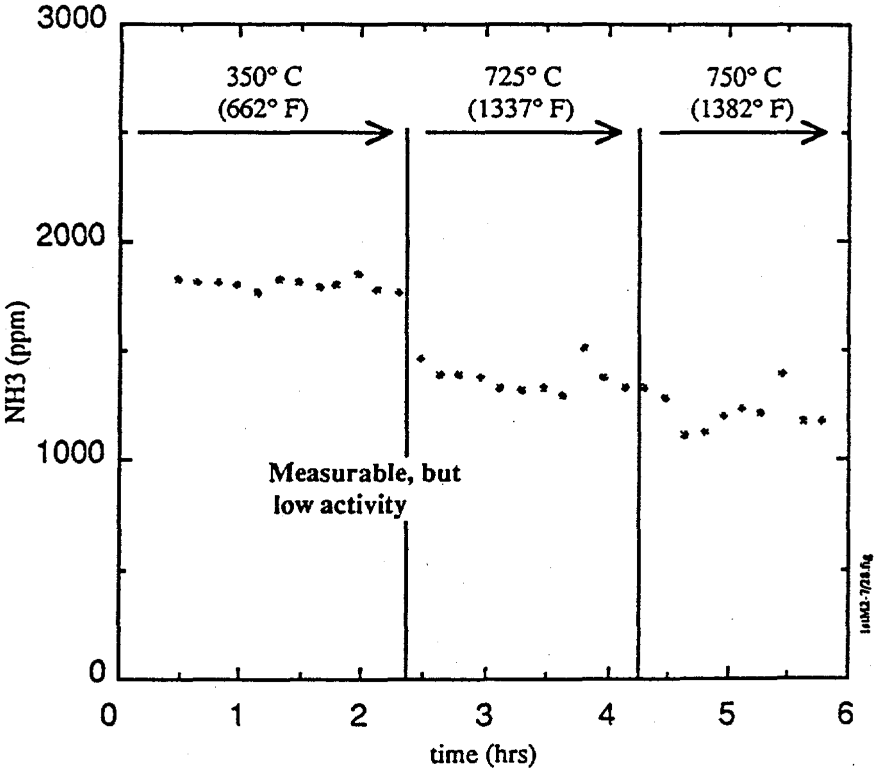

Figure 2.3.5-3 Ammonia Decomposition over L-3787M2 Previously Subjected to Ten Absorption/Regeneration Cycles

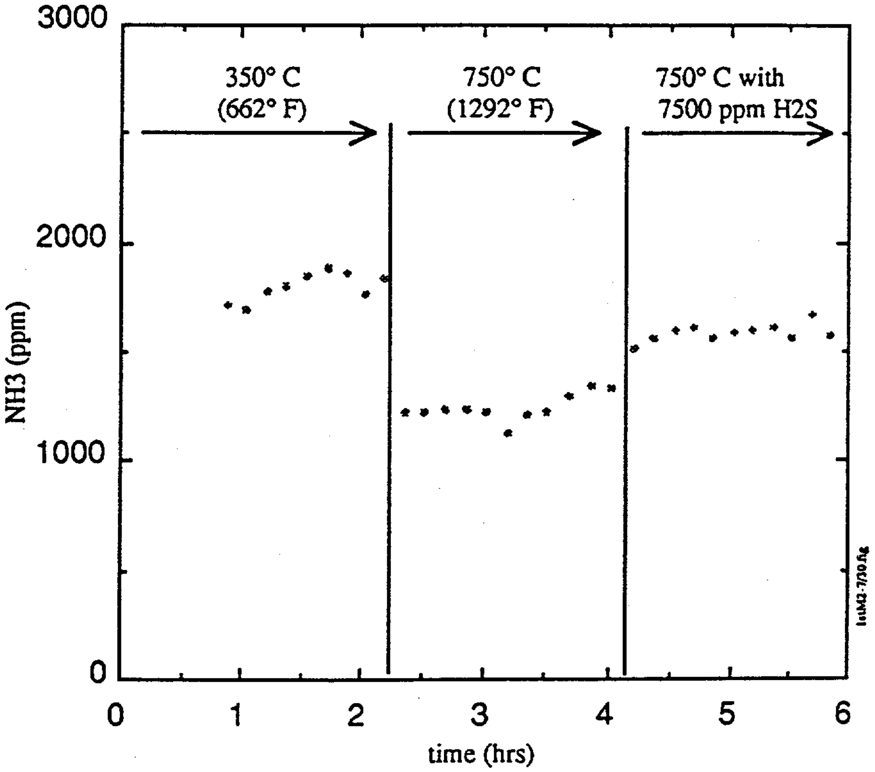

Figure 2.3.5-4 Ammonia Decomposition over L-3787M2 Previously Subjected to Ten Absorption/Regeneration Cycles

3785M was not clear, but it was known that at least part of the L-3785M packed bed was catalytic (from previous work by Ayala). The distinction was made here between the inlet and outlet sorbent samples to help better identify the part of the packed bed which was most catalytically active.

The L-3785M inlet and outlet pellet samples were taken from the same packed bed test following regeneration of the sorbent. The pellets were then crushed and sieved to obtain the desired size distribution for microreactor kinetic measurements.

The activity of the catalyst was first examined with a gas mixture containing 28.6% H_2, 1750 ppm NH_3, and balance Ar. The measured outlet NH_3 concentrations for the *L-3785M inlet sample* are presented in Figure 2.3.6-1 and show that although a decrease in the NH_3 concentration was measured at 750 °C, no measurable reduction in NH_3 was measured at 650 °C. By comparison, a ~20% reduction in the NH_3 level was measured under the same test conditions for the L-3785M *outlet sample* (Figure 2.3.6-2). The data confirmed that the degree of sulfidation and regeneration can have an influence on the catalytic properties of the molybdenum doped zinc titanate (L-3785M).

Next, the L-3785M *outlet sample* (the one that showed more activity in the previous run) was tested in a gas mixture containing CO and CO_2 in addition to H_2. The gas composition used is similar to that from a Texaco oxygen-blown gasifier, but without the water vapor: 38.8% CO, 13.0% CO_2, 29.5% H_2, 1800 ppm NH_3, and balance Ar. The measured NH_3 outlet concentrations at various temperatures are shown in Figure 2.3.6-3 which only show the NH_3 concentrations for the last 30-60 minutes at each temperature (at steady state). Other points were omitted from this plot because the integrator for the gas chromatograph was not working properly and it was necessary to integrate the peak areas by hand (a tedious task). A comparison of Figures 2.3.6-2 and 2.3.6-3 show that the presence of CO and CO_2 had little measurable influence on NH_3 conversions under the test conditions.

2.4 SUMMARY OF MICROREACTOR SCREENING TESTS

Seven (7) sorbent-catalyst formulations have been tested in GE-CRD's microreactor and characterized for their ability towards NH_3 decomposition. The base material for the H_2S sorbent was chosen to be zinc titanate, a material for which GE-CRD, RTI, and DOE-METC has considerable experience. GE-CRD focused its efforts on activating MoS_2 as the catalytic additive towards NH_3 decomposition (GE-CRD has previously demonstrated MoS_2 to be catalytically active). It was believed that although MoS_2 was catalytically active towards NH_3 decomposition, a method for stabilizing the molybdenum within the zinc titanate material was necessary to prevent the molybdenum from migration. Because Co and Ni are commonly used to promote the activity of MoS_2 and Al used as the catalyst support in hydrodesulfurization and hydrodenitrification catalysts, these metals were added to samples of molybdenum doped zinc titanate. Samples of: (1) Co-Mo-zinc titanate, (2) Ni-Mo-zinc titanate, (3) Co-Mo-Al-zinc titanate, and (4) Mo-zinc titanate

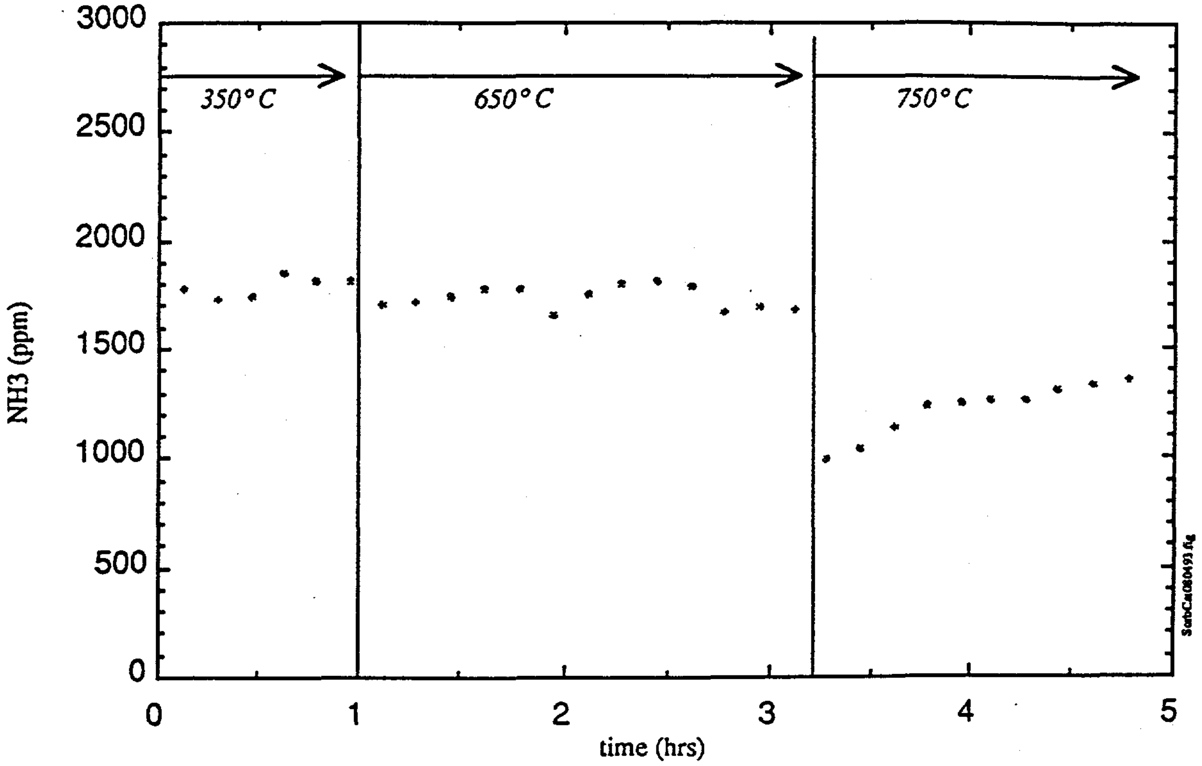

Figure 2.3.6-1 Ammonia Decomposition over L-3785M (Inlet Sample)

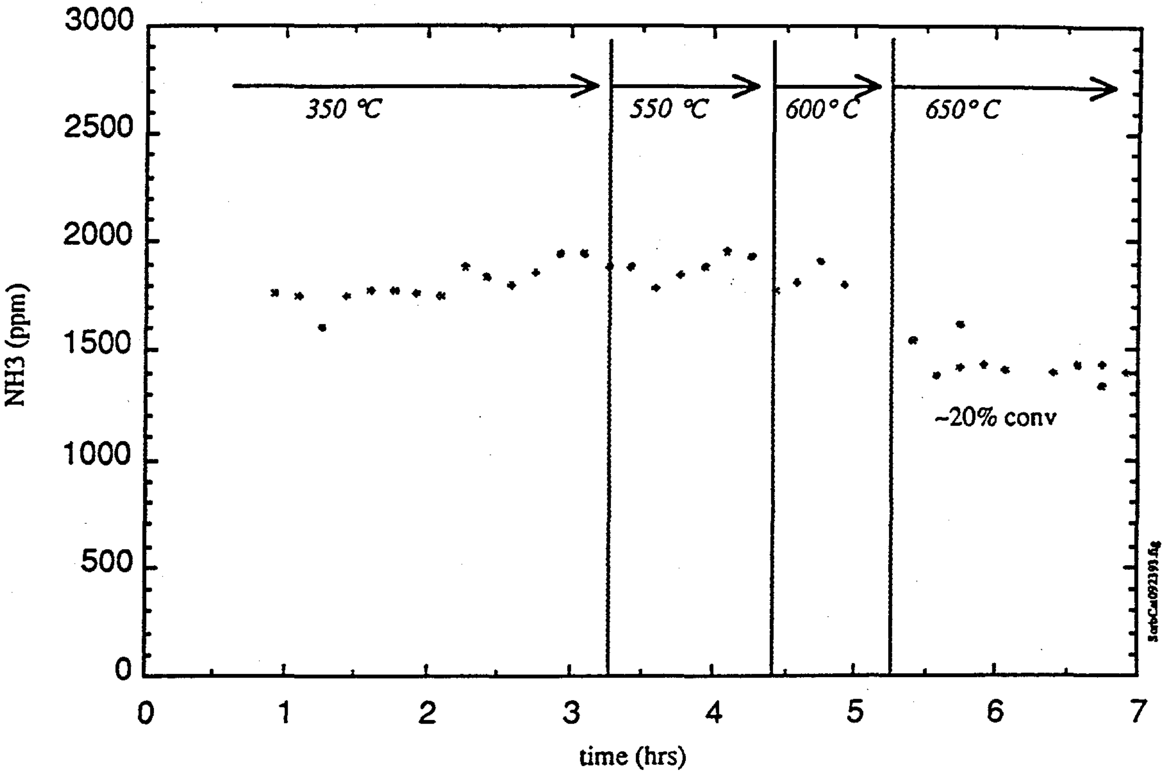

Figure 2.3.6-2 Ammonia Decomposition over L-3785M (Outlet Sample)

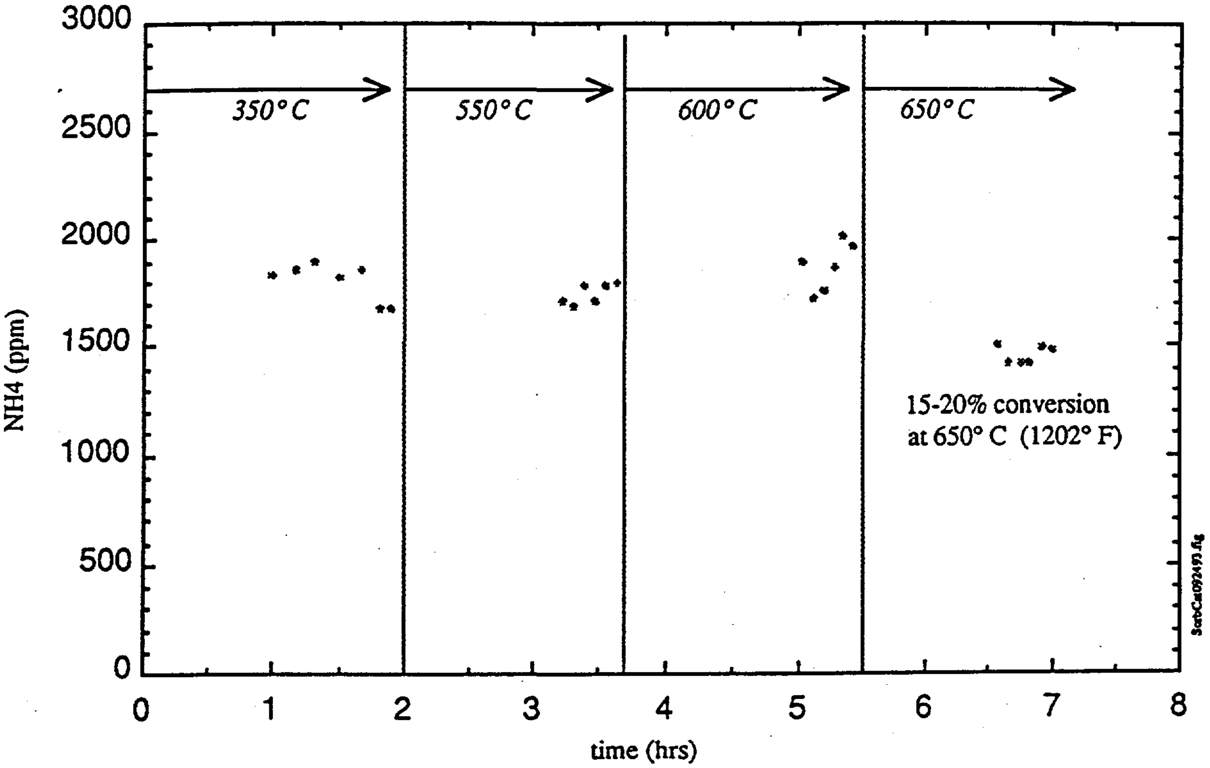

Figure 2.3.6-3 Ammonia Decomposition over L-3785M (Outlet Sample)

were characterized for their activity towards NH_3 decomposition. Ni-Mo-zinc titanate was immediately eliminated because no activity was measured. Although Co-Mo-Al-zinc titanate initially produced promising results when it showed the highest activity towards NH_3 decomposition, its activity was significantly inhibited by the presence of H_2S in the feed gas. The catalytic activities of Co-Mo-zinc titanate and Mo-zinc titanate were similar and both retained their activities towards NH_3 decomposition even in the presence of H_2S.

Although the ability of Co-Mo-zinc titanate and Mo-zinc titanate to decompose NH_3 even in the presence of H_2S was encouraging, we focused more on the Mo-zinc titanate composition to determine the role of molybdenum alone. A sample of Mo-doped zinc titanate, UCI formulation L-3787M2, was tested for its activity towards NH_3 decomposition. The L-3787M2 material used had a molybdenum content of 2.5% and had been previously subjected to ten absorption/regeneration cycles in a bench-scale test at GE-CRD. It was believed that perhaps cycling of the Mo-doped zinc titanate material would contribute to the activation of the material's catalytic activity towards NH_3 decomposition. Surprisingly, although the L-3787M2 was active towards NH_3 decomposition (at 750 °C) in the absence of H_2S, its activity was nearly completely inhibited by the presence of 0.75% H_2S in the feed gas. This contrasted sharply with data from the Co-Mo-zinc titanate and Mo-zinc titanate which showed that the H_2S had very little effect on the catalyst activity.

Tests were also conducted with samples of L-3785M which contained 5% molybdenum oxide. Two samples of L-3785M were tested. The first L-3785M sample was taken from the inlet and the second L-3785M sample was taken from the outlet of a bench-scale fixed bed in which the L-3785M material was subjected to ten absorption/regeneration cycles. Although both samples showed measurable levels of activity towards NH_3 decomposition, the NH_3 conversions were low (i.e., ~20% conversion) under the conditions tested.

3. PROVISION OF A BENCH UNIT AND 100-HR BENCH-SCALE TESTING

After reviewing the results of the microreactor sorbent-catalyst screening tests with DOE-METC, RTI, and SRI, the scope of the program was re-focused towards the development of a material only for the catalytic decomposition of NH_3 and elevated temperatures were to be used to minimize potential catalyst inhibition or poisoning by H_2S. In bench scale tests, RTI demonstrated that a commercial Haldor Topsoe steam reforming catalyst designated HTSR-1 was sufficiently active towards the desired NH_3 decomposition reaction in fluidized bed bench-scale tests. In the second phase of work at GE-CRD, the HTSR-1 catalyst was demonstrated to be effective towards the catalytic decomposition of NH_3 in a 100-hr test. Details of this extended duration bench-scale test are described in the following sections.

3.1 BENCH UNIT SETUP

A schematic diagram of the bench scale unit used at GE-CRD is presented in Figure 3.1-1. The desired gas composition which simulated gas from a Texaco oxygen-blown gasifier was made from individual gas cylinders of the constituent gases (i.e., CO, H_2, CO_2, N_2, H_2S) with NH_3 stored in H_2. Water vapor in the gas was produced by injection of liquid water into a heated line.

Prior to introduction of the reactant gases to the catalyst bed, the gases are first preheated in an external preheater to the reactor. This preheater is essentially a coiled stainless steel tube placed in a large diameter furnace. To extend the operational life of this stainless steel preheater coil, H_2S is added to the gas mixture *after* the preheater (and before the catalytic reactor). During the shakedown tests, however, it was found that the stainless steel preheater coils had catalyzed the methanation reaction in the simulated coal gas and had significantly altered the composition of the gas mixture approaching the catalyst bed. In fact, although no methane (CH_4) was initially used in the gas mixture, the gas exiting the preheater was measured to contain as much as 5-6% CH_4. This methanation reaction also caused significant shifts in the concentrations of the other gas species.

To prevent a shift in the gas composition due to methanation occuring in the preheater, the preheater coils were periodically poisoned by sulfiding them with a short pulse of 1% H_2S gas. A pulse lasting several minutes was usually sufficient. Gas composition measurements were used to confirm that the sulfur effectively poisoned the methanation reaction in the preheater coils. To avoid continuous injection of H_2S through the preheater and to preserve the operational life of the coils, H_2S was injected thereafter downstream of the preheater, keeping the periodic pulsing of the H_2S to suppress methanation. Further testing over several days have thus far shown that methanation of CO and CO_2 in the coal gas continues to be suppressed by the single pulse of H_2S passed through the preheater.

Following the shakedown tests in which NH_3 samples were taken and gas compositions were measure before and after the catalyst bed, the catalyst pellets were removed for inspection. Catalyst selection and description are presented in the next section. Visual inspection showed that the catalyst pellets were heavily coated with a black carbonaceous deposit. Although this carbonaceous deposit does not appear to have an immediate impact on the upcoming test, its long term effects and whether it will increase the mass transfer resistance of the reactant/product gases to/from the catalyst surface is unclear. Inspection of the reactor tube inner walls using a boroscope did not reveal any visual corrosion of the metal walls.

3.2 EXPERIMENTAL CONDITIONS

Following the shakedown tests, a fresh batch catalyst pellets was placed into the reactor for the 100-hr test. The HTSR-1 catalyst (Haldor-Topsoe, Denmark) was selected to

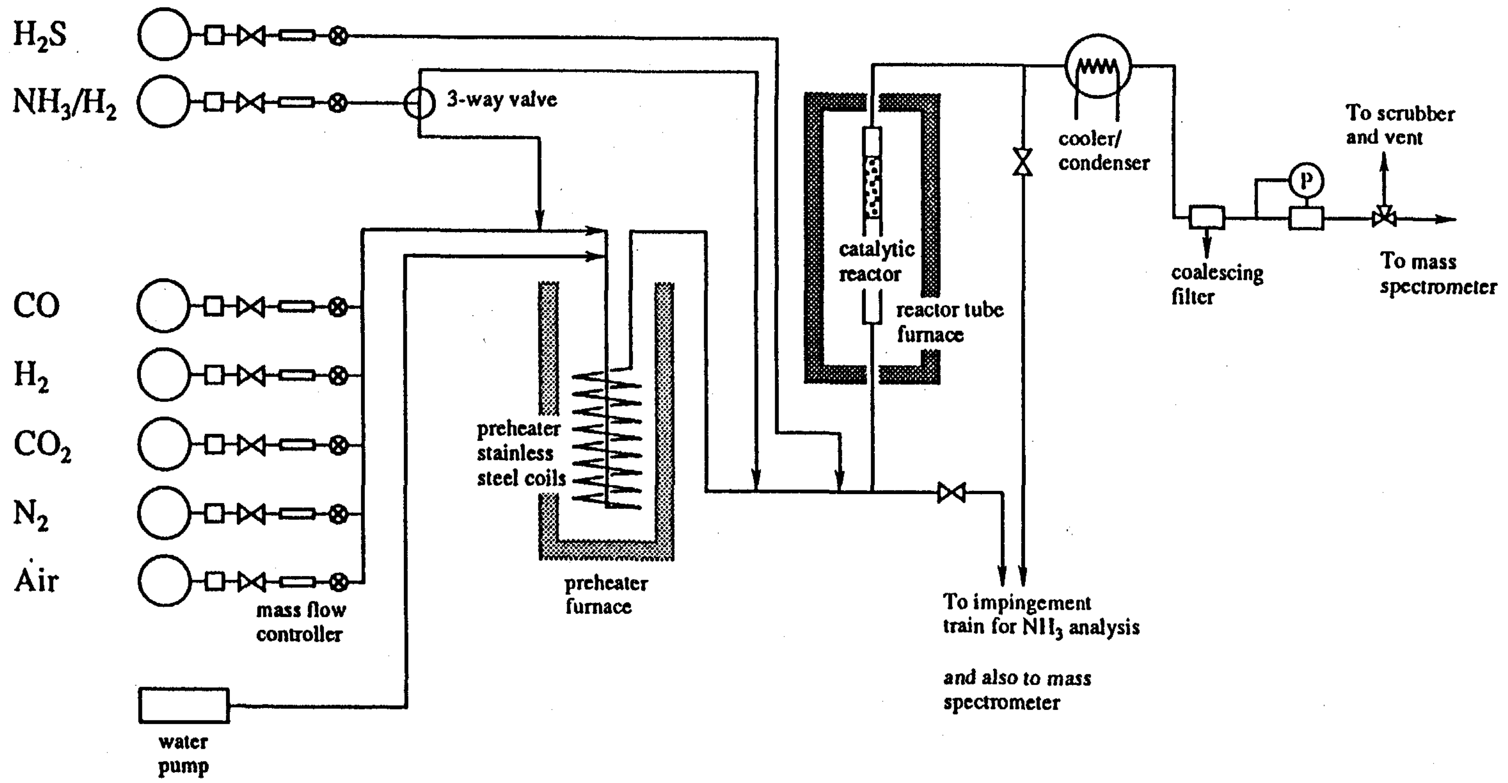

Figure 3.1-1 GE-CRD Bench-Scale Ammonia Decomposition Reactor System

conduct a 100-hr test in the bench reactor unit. The test objective called for characterization of the catalyst and measurement of its NH_3 decomposition effectiveness in the presence of high concentrations of H_2S in the simulated coal gas. The extended 100-hr nominal NH_3 decomposition test was conducted over the period from December 10 to December 14, 1995 for a total of 99 hrs of continuous operation at a reactor temperature of 900 °C (1652 °F). Because the reactor wall temperature had to be run at its maximum design limit of 927 °C (1700 °F) to maintain the desired reactor temperature and still meet safety regulations for operation at high pressure, a decision was made to reduce the reactor pressure from 10 atm to 8.5 atm to allow wider margin of safety should small temperature excursions were to occur. A nominal space velocity of 10,000 h^{-1} was selected throughout the run except for the last 6 hours during which the space velocity was reduced to 5,000 h^{-1} to measure the effect of space velocity on the catalyst performance.

As planned, very brief interruptions of gas flow were made during the run to replace empty gas cylinders. It is estimated that interruptions for gas cylinder changes were typically less than 5 minutes in duration.The catalyst bed was blanketed under nitrogen during such interruptions.

3.3 AMMONIA CONVERSION RESULTS

NH_3 decomposition concentrations were measured using an ion-selective electrode wet chemistry method (ASTM method 1426-79). The average inlet NH_3 concentration was 1950±240 ppm on a dry basis (or ~1550 ppm on a wet basis). During operation at a space velocity (S.V.) of 10,000 h^{-1}, the average outlet NH_3 concentration was 310 ± 100 ppm (wet) over the course of the run for an overall NH_3 decomposition efficiency of 80%. At the lower S.V. of 5,000 h^{-1}, outlet NH_3 concentrations (wet) were 200±40 ppm to give an NH_3 decomposition efficiency of 88%. Note that under the test conditions, equilibrium NH_3 concentrations were estimated to be 10-11 ppm.

NH_3 reactor inlet and outlet concentrations are plotted in Figure 3.3-1. It shows that the reactor outlet NH_3 concentration appeared to drift from about 200 ppm to 500-600 ppm (dry basis) over the first 40 hrs of operation. Potential causes for this apparent initial loss of catalyst effectiveness will be discussed later. Note, however, that after about 40 hours of operation, the reactor outlet NH_3 concentration remained nearly constant throughout the remainder of the run.

3.4 REACTOR INLET GAS COMPOSITION MEASUREMENTS

H_2S was by-passed around the preheater and was injected just upstream of the reactor tube during normal steady operation (Figure 3.1-1) to prevent excessive sulfur corrosion to the metal surfaces and extend the life of the stainless steel preheater coils. To prevent

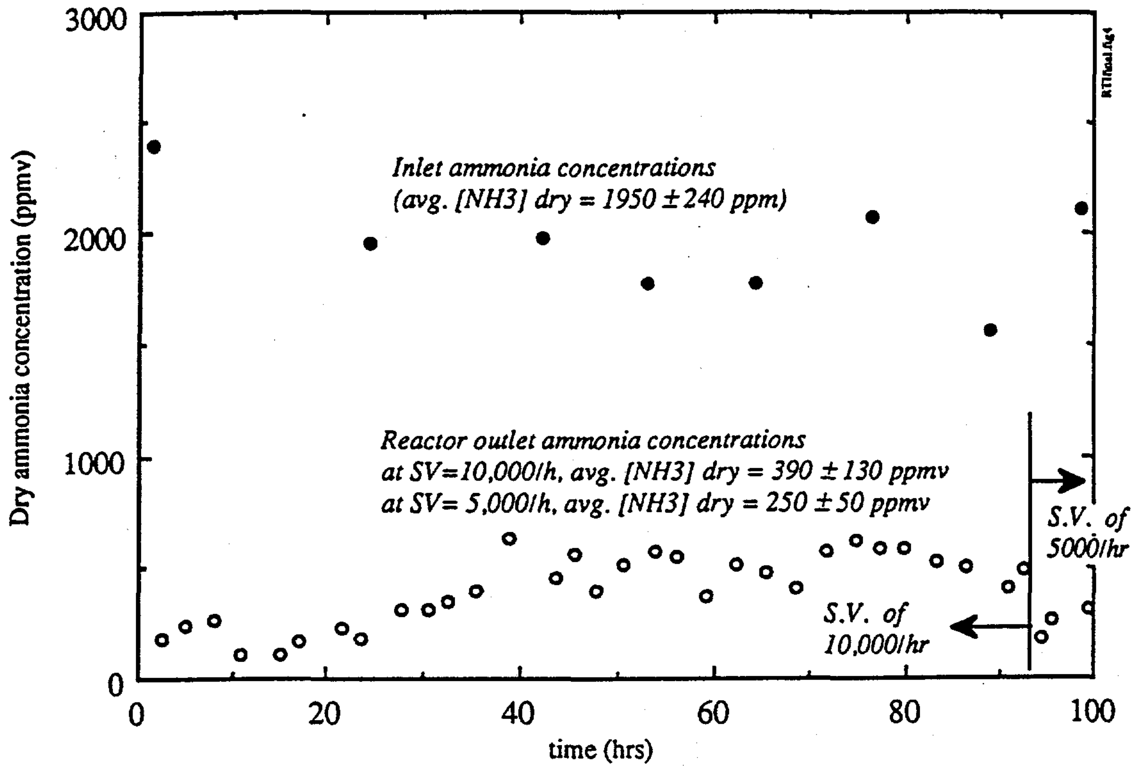

Figure 3.3-1 Ammonia (g) concentrations at reactor inlet and outlet

the methanation and water-gas shift reactions from altering the composition of the gases in the preheater coils, H_2S was periodically diverted into the preheater coils so that the sulfur could be used to temporarily inhibit these reactions on the preheater coil surface. Typically, the H_2S was diverted into the preheater coils for 10-30 minutes once every 12-hours.

The results of the reactor inlet gas measurements are presented in Figure 3.4-1. Although inlet gas concentrations were relatively constant throughout the run, there were brief periods when increasing amounts of methane were measured before H_2S was injected through the preheater coils. An example of where this can be seen in Figure 3.4-1 is the period between 10-20 hrs of operation. Note that besides the increase in CH_4 levels, other gas species concentrations were also varying at this same time. As methane levels slowly increased, CO concentrations were reduced by the methanation reaction:

$$CO + 3\,H_2 = CH_4 + H_2O \qquad \text{methanation reaction} \qquad (1)$$

CO_2 concentrations also increased significantly over this same period of time. The increased CO_2 is likely due to the onset of the water-gas shift reaction which would further reduce CO concentrations while increasing CO_2 concentrations:

$$CO + H_2O = CO_2 + H_2 \qquad \text{water-gas shift reaction} \qquad (2)$$

H_2S was diverted through the preheater coils during the 20th hr of the run. From Figure 3.4-1, it is apparent that both the progress of the methanation and water-gas shift reactions within the preheater coils were suppressed by the presence of H_2S. It is believed that H_2S inhibited the surface reactions on the stainless steel preheater coils which were likely responsible for these side reactions. By periodically flowing H_2S through the preheater coils, we were able to suppress the methanation and water-gas shift reactions (within the preheater) to minimal levels. As shown in Table 3.4-1, the measured reactor inlet gas composition was in close agreement with the nominal gas composition from an oxygen-blown Texaco gasifier.

Table 3.4-1 Comparison of Some Revelant Inlet Gas Compositions

Gas Species	Comparison of some reactor inlet gas compositions		
	Nominal oxygen-blown Texaco gas	Bench-scale data based on flow measurements	Bench-scale data based on M.S. measurements
H_2	28.50%	31.4%	32.3%
CO	38.00	39.6	36.9
CO_2	12.85	9.1	11.0
H_2S	0.75	0.78	0.72[1]
H_2O	18.10	18.8	18.8[2]
NH_3	0.18	0.19	0.16
N_2	1.62	—	0.0
CH_4	—	—	0.16

[1] Inlet H_2S measurements were unstable (likely because of insufficient mixing distance from H_2S injection location to the gas sampling location. Used exit H_2S measurements here.

[2] Water was not measured, the amount of water vapor in gas was calculated using flowrate measurements.

3.5 REACTOR OUTLET GAS COMPOSITION MEASUREMENTS

Reactor exit gas compositions are presented in Figure 3.5-1 and were extremely steady over the duration of the extended run. Average reactor exit gas compositions over the duration of the run are tabulated in Table 3.5-1. The water vapor content of the reactor exit gases was not measured directly, but was estimated by assuming that the H/C elemental ratio of the outlet gas mixture should be the equal to that of the inlet mixture. The resulting calculated water vapor content was in excellent agreement with the water vapor content estimated from a similar calculated made by balancing the inlet and outlet O/C ratios (i.e., water vapor content estimated from the H/C ratio and from the O/C ratio agreed to better than 0.1%).

Two thermodynamic calculations[5] of the gas mixture were made for comparison to the measured reactor exit gas composition. In the first thermodynamic calculation, the catalyst bed was assumed to be adiabatic (i.e., a constant enthalpy-pressure, HP, calculation). In this case, assuming that the inlet gases were at 899 °C (1650 ºF), the gases would react adiabatically to reach an equilibrium temperature of 921 °C (1690 ºF). In the second thermodynamic calculation, the catalytic reactor was assumed to be at constant temperature (i.e., a constant temperature-pressure, TP, calculation). As expected, the results from these two calculations are very similar because of the small temperature rise for the adiabatic gas mixture in the constant HP case. The results of both thermodynamic calculations are presented in Table 3.5-1 for comparison to the actual measured reactor exit gas composition.

Table 3.5-1 Comparison of Some Revelant Outlet Gas Compositions

Gas Species	Measured and equilibrium outlet compositions		
	Bench-scale measurementsat reactor exit	Equilibrium calc. based on constant HP[2]	Equilibrium calc. based on constant TP[3]
H_2	30.4%	34.1%	34.2%
CO	38.5	34.9	34.4
CO_2	9.3	12.9	13.4
H_2S	0.71	0.72	0.72
H_2O	20.7[1]	17.0	16.8
NH_3	309 ppm	10 ppm	11 ppm
N_2	-----	0.08	0.08
CH_4	0.40	0.28	0.44
		1690 °F, 921°C at 8.5 atm	1650 °F, 899 °C at 8.5 atm

[1] Amount of water vapor in exit gas was estimated by assuming that the H/C and O/C ratios of the inlet and exit gases will be constant.

[2] Inlet temperature of the constant HP (i.e., constant enthalpy and pressure) calculation was assumed to be 1650 °F (899 °C).

[3] Constant TP denotes constant temperature and pressure.

Interestingly, a close inspection of the reactor exit gas composition shows that more CO and H_2O were measured and less CO_2 and H_2 were measured than thermodynamic calculations predicted (see Table 3.5-1). Since these gas exit concentrations were further away from equilibrium levels than they were at the reactor inlet, an additional factor must have somehow favored the trend of these gas concentrations away from overall system equilibrium. Since lower temperatures favors lower CO and H_2O concentrations and higher CO_2 and H_2 concentrations (i.e., the reverse of what was observed), the possibility that continued progress of the water-gas shift reaction downstream of the catalyst bed at lower temperatures (perhaps in the gas sample lines) was ruled out. Perhaps one clue to the cause of the observed differences between the measured and thermodynamic predicted levels of CO, CO_2, H_2O, and H_2 is the observation of a black carbonaceous material found

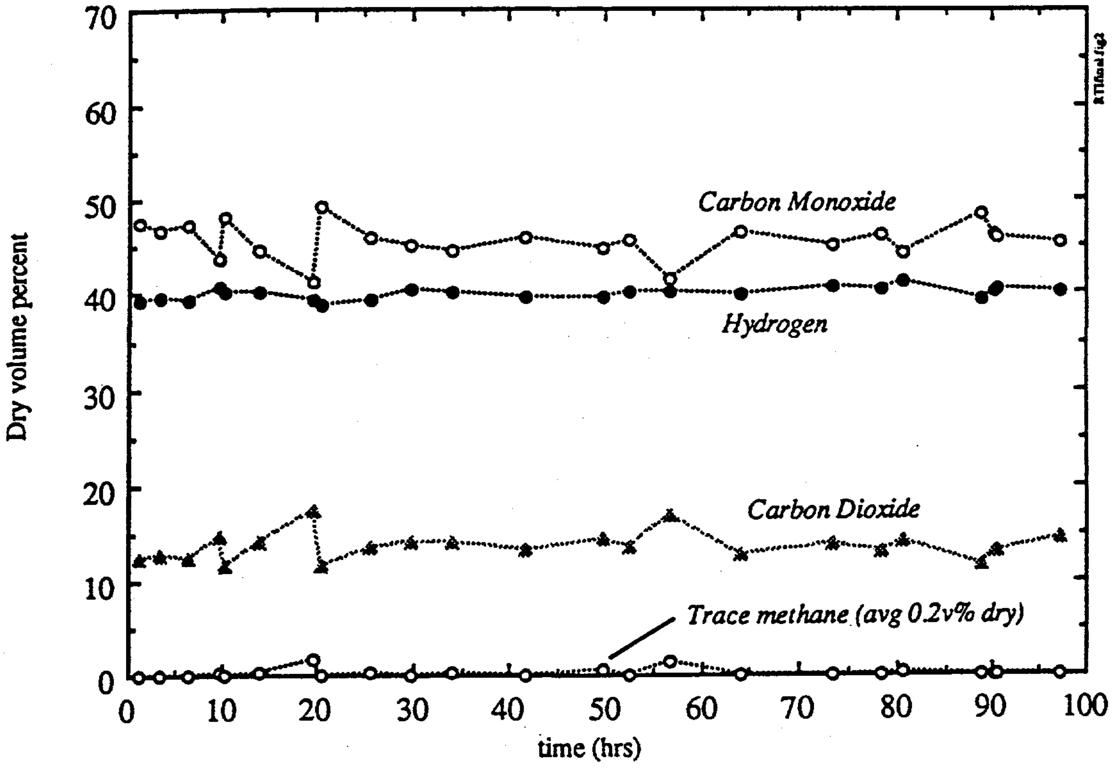

Figure 3.4-1 Reactor inlet dry gas concentrations for 100-hr run

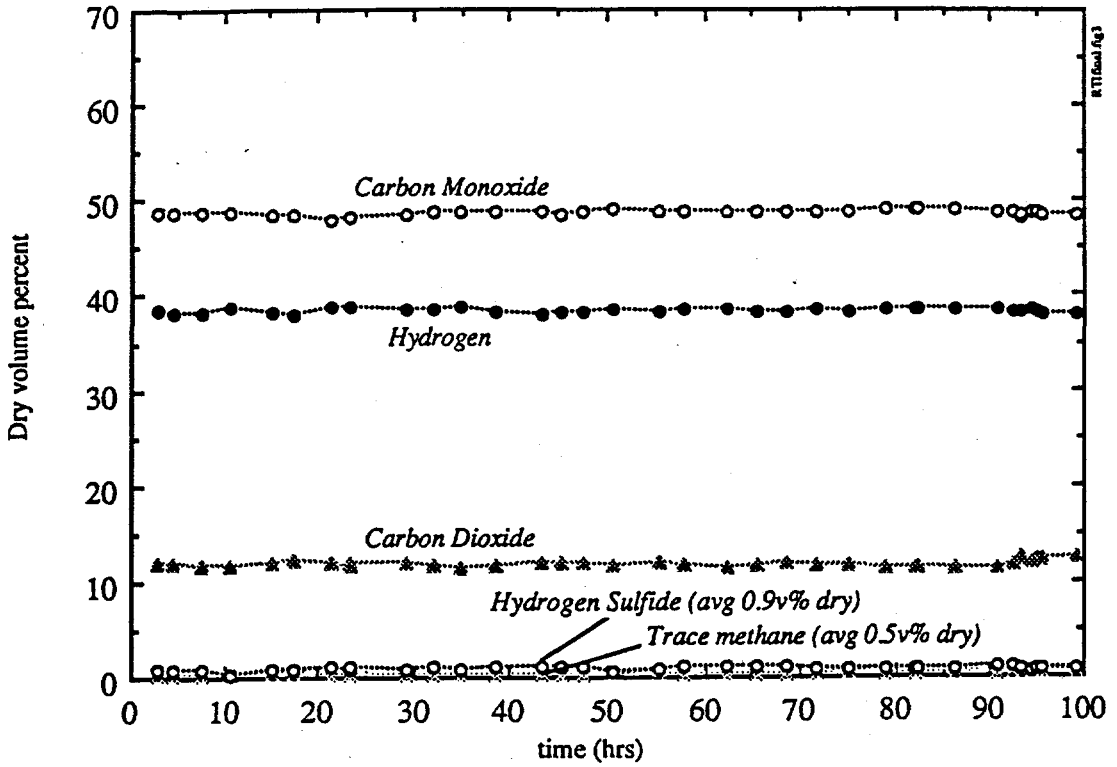

Figure 3.5-1 Reactor Exit dry gas concentration for 100-hr run

on all the interior surface of the catalytic reactor following the run. It appears that carbon first forms at the reactor inlet where the lower temperatures would be more favorable towards the formation of carbon from CO_2 and H_2:

$$CO_2 + 2\ H_2 = C(s) + 2\ H_2O \tag{3}$$

Assuming that the carbon hydrogenation reaction (which consumes carbon) is slow, carbon deposits can begin to accumulate (which was observed).

Further downstream in the reactor, the temperature increases and the partial equilibrium of carbon becomes less favorable. At higher temperatures, other reactions are likely to become significant. One reaction that can remove the carbon deposits is:

$$C(s) + CO_2 = 2\ CO \tag{4}$$

Note that the result of the combination of reactions (3) and (4) is a net reduction in CO_2 and H_2 concentrations and a net increase in CO and H_2O concentrations, a trend that is consistent with the experimental observations. We have insufficient information to substantiate these arguments in greater detail; however, the above explanation is offered only as one example of how CO, CO_2, H_2O, and H_2 concentrations could be shifted away from overall system equilibrium. Reactions involving carbon under such conditions can be highly complex and their study is beyond the scope of the current work.

3.6 GENERAL OBSERVATIONS

As mentioned in the previous section, a black carbonaceous deposit was found on the inner surfaces of the reactor tube. Visually, it was difficult to ascertain whether the carbonaceous material was also deposited onto the HTSR-1 material because this catalyst was initially black. Using a LECO analysis on fresh and spent catalyst samples, however, it was found that the spent catalyst contained negligible amounts of carbon following the run. The LECO analysis also indicated that whereas the fresh catalyst samples were found to contain very little sulfur (<0.1wt%), the spent catalysts were found to have 7-8wt% sulfur.

The reactor tube, which was made of an HR-160 material, was sawed apart at the reactor bed section following the run to inspect the condition of the metal wall surfaces. It was found that a single layer of catalyst pellets had fused against the reactor walls. This layer of pellets closed off of a fraction of the flow area in the tube and may have contributed to the initial decrease in catalyst performance observed during the first 40 hrs of operation (discussed earlier) by effectively increasing the space velocity through the catalyst bed. Although no further analysis were made, other factors, such as sintering and loss of catalyst surface area, may have also contributed to the initial loss of catalyst activity. To prevent the fusing of the catalyst pellets with the HR-160 reactor walls in future tests, it is recommended that a quartz liner to used in the reactor tubes to isolate the catalyst from the metallic walls.

3.7 SUMMARY BENCH-SCALE TESTING

In this second phase of work at GE-CRD, a sulfur-resistant nickel-based catalyst, HTSR-1, was tested in the bench-scale reactor at GE-CRD for 100 hours of continuous operation. The HTSR-1 catalyst demonstrated to be effective towards the catalytic decomposition of NH_3 at elevated temperatures (900° C) and pressures (8.5 atm) in the presence of approximately 0.8% H_2S. Using an initial NH_3 concentration of ~1550 ppm (wet basis) and operating at a space velocity of 10,000 h^{-1}, NH_3 destruction levels of 80% were measured over most of the run time. When the space velocity was reduced to 5000 h^{-1}, NH_3 destruction levels further increased to 88%, even in the presence of hydrogen sulfide.

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