

ACKNOWLEDGMENTS

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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 capital 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 H₂S 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 NH₃ 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, NH₃ 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 Al₂O₃, TiO₂, 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 NH₃ 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 H₂S 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 H₂S) 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 H₂S.
- 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 cm³/(cm³·h), 90 percent NH₃ 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 ($\sim 1,000$ °C or higher) favoring removal of NH_3 by thermal decomposition [$NH_3 \rightarrow (1/2) N_2 + (3/2) H_2$]. 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 H₂S, 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 H₂S 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 H₂S. At lower temperatures, HTSR-1 deactivated rapidly when significant levels of H₂S 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 (MoS₂) in ammonia decomposition. An MoS₂ catalyst reduced NH₃ 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 (MoO₃) 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 H₂S 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 O₂ 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 NH₃ in the hot-coal gases was substantially reduced. During absorption of H₂S 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, $\text{MoO}_3 + 2\text{H}_2\text{S} \rightarrow \text{MoS}_2 + 3\text{H}_2\text{O}$. Based on literature data on catalytic activity of MoO₃ and MoO₂ 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 $\text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2$.

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 NH₃ present in fuel gas to N₂ and H₂ at elevated temperatures (550 to 900 °C).

1.3 SCOPE/APPROACH FOR CURRENT WORK

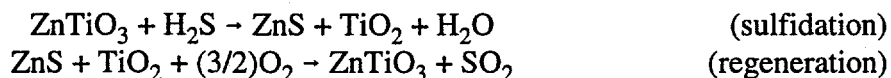
This report is the result of a combined effort by Research Triangle Institute (RTI), prime contractor, and SRI and GE, subcontractors. The detailed final reports by SRI and GE are attached as Appendices A and B, respectively. The main body of the report prepared by RTI

primarily details the RTI portion of the effort, with highlights of the SRI and GE work, to provide a logical flow to the report.

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Before undertaking any experiments, a detailed thermodynamic evaluation was conducted to determine the concentration of NH₃ 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 NH₃ decomposition conditions to be used in this study.

Two catalytic approaches for decomposing NH₃ 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 NH₃ and H₂S removal. Zinc titanate reaction chemistry and testing have been described in detail elsewhere (Gupta and Gangwal, 1992). The sulfidation-regeneration cycle involved in H₂S removal from hot coal gas using one of the zinc titanate phases (ZnTiO₃) is shown below:



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 H₂S, H₂O, 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 NH₃ and H₂S removal and the high-temperature catalytic decomposition approaches have been tested in the presence of up to 7,500 ppmv H₂S 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 ($\text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2$) 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

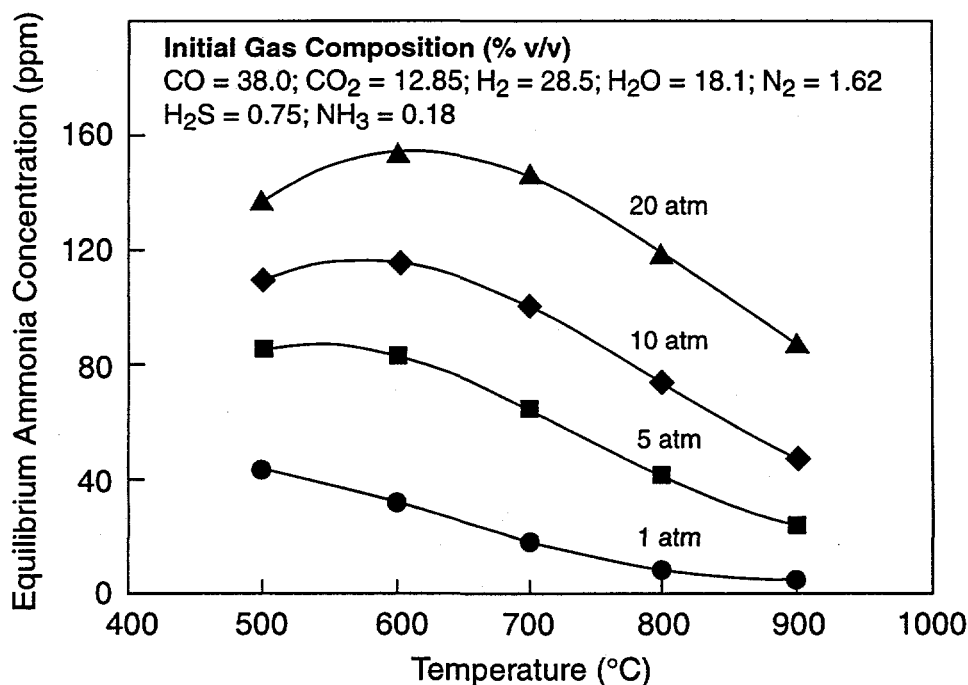


Figure 1. Equilibrium concentration of ammonia as a function of temperature and pressure in a Texaco coal gasifier gas stream.

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 NH₃ and H₂S removal approach, a combined desulfurization sorbent and NH₃ 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 Mo₃O₉, Mo₄O₁₂, and Mo₅O₁₅ are the dominant vapor species in equilibrium with solid MoO₃ in the temperature range 525 to 825 °C. Equilibrium partial pressures at 625 °C, for example, of Mo₃O₉ and Mo₄O₁₂ vapor in the presence of 2 vol% O₂ 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.