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Catalytic Ammonia Decomposition for Coal-Derived Fuel Gases

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Introduction

Advanced coal gasification-based electric power plants such as integrated gasification combined cycle (IGCC) and molten carbonate fuel cell (MCFC) call for hot-gas cleanup following gasification in order to achieve high thermal efficiency. The Morgantown Energy Technology Center (METC) 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 (H₂S). 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 (NH₃). When this coal gas is combusted in a gas turbine, NH₃ has the propensity to form oxides of nitrogen (NO_x) which are difficult to remove hazardous pollutants and precursors to "acid rain." In MCFC applications, when the anode exhaust gas is burned with air to supply CO_2 for the regeneration of the carbonate electrolyte, NO_x formed can react with the electrolyte to form relatively volatile nitrates that evaporate resulting in loss of electrolyte. Thus, it is desirable to remove NH₃ from the coal gas before use in IGCC or MCFC applications.

According to published data, the NH₃ 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 NH₃. In contrast, a fixed-bed coal gasifier (e.g., Lurgi) typically produces about 5,000 ppmv NH₃ whereas a fluidized-bed coal gasifier (e.g., U-Gas, Kellogg) produces about 1,000 ppmv or less NH₃.

The NH₃ 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 NH₃ by thermal decomposition [NH₃ \rightarrow ($\frac{1}{2}$) N₂ + ($\frac{3}{2}$) H₂]. However, the NH₃ 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 NH₃ 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 H₂S, steam, and other gases.

SRI International identified Ni- and MoS₂-based catalysts capable of decomposing NH₃ in hot coal-derived gas streams (Krishnan et al., 1988). The SRI study showed that, in the absence of H₂S, decomposition of NH₃ 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 on a refractory support from Haldor-Topsoe, exhibited excellent activity and high-temperature stability. However, its tolerance to H₂S was found to be a function of temperature. Above 800 °C, no catalyst deactivation was observed even in gas streams containing 2,000 ppmv of H₂S. At lower temperatures, HTSR-1 deactivated rapidly when significant levels of H₂S were present in the fuel gas. Molybdenum-based catalysts were also investigated as potential NH₃ decomposition catalysts. Both General Electric (Ayala, 1993) and SRI International (Krishnan et al., 1988) have reported on the catalytic role of molybdenum sulfide (MoS₂) in ammonia decomposition.

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 NH₃ 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 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. 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 up stream 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.

Project Description

Thermodynamic Evaluation

Thermodynamic calculations were performed 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.

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. As expected, 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 ($NH_3 \rightarrow (1/2) \ N_2 + (3/2) \ H_2$) 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.

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
$\rm H_2O$	12.5-18.1
H_2S	0.5-0.75
NH_3	0.18-0.20
N ₂	0.0-1.62

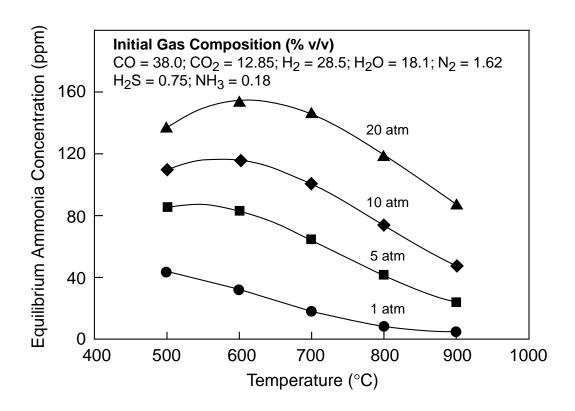


Figure 1. Equilibrium concentration of ammonia as a function of temperature and pressure in a Texaco coal gasifier gas stream.

Thermodynamic calculations were also performed to evaluate the stability of the catalysts and their desirable phases under NH₃ decomposition conditions of interest in this study. For the simultaneous NH₃ and H₂S 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 which may resulfide once the H_2S 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 ${\rm Mo_3O_9}$, ${\rm Mo_4O_{12}}$, and ${\rm Mo_5O_{15}}$ are the dominant vapor species in equilibrium with solid ${\rm MoO_3}$ in the temperature range 525 to 825 °C. Equilibrium partial pressures at 625 °C, for example, of ${\rm Mo_3O_9}$ and ${\rm Mo_4O_{12}}$ vapor in the presence of 2 vol% ${\rm O_2}$ are 4.4×10^{-6} and 4.1×10^{-6} atm, respectively, which 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.

Simultaneous NH₃ and H₂S Removal

Several catalysts containing Ni, Co, Mo, and W (with Al₂O₃, TiO₂, 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 International (Krishnan et al., 1988), L-3787M, molybdenum-doped zinc titanate developed for the General Electric (GE) moving-bed desulfurization system (Ayala, 1993), and ZT-4, a granulated zinc titanate sorbent prepared by the Research Triangle Institute (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. These systems have been described in detail in a previous paper (Gangwal et al., 1993) and a topical report (Gupta and Gangwal, 1992). Identical analytical systems including a photoionization detector for NH₃ measurement were installed with each reactor system for cross-checking of results.

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 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 deemphasized 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 in the Results section.

High-Temperature Catalytic Decomposition

A number of commercial catalysts, including HTSR-1, were tested for this approach. All tests were conducted using a simulated Texaco gas (Table 1) except for a 100-h test described below at METC using a mobile skid-mounted reactor system. Nonproprietary information about the catalysts tested is presented in Table 2.

Four separate reactor systems have been used for testing these catalysts. Initial screening of these catalysts at atmospheric pressure was conducted using a 1.0-in. quartz reactor system (Gupta and Gangwal, 1992) modified for operation with NH $_3$ up to 850 °C. Further screening of selected catalysts at high pressure was conducted using a HTHP 2.0-in. quartz reactor system (Krishnan et al., 1995) at RTI. This special reactor system consisted of a quartz insert within a HTHP 316-stainless steel reactor housing so that NH $_3$ and H $_2$ S came in contact only with the quartz at high temperature.

Finally, two 100-h tests of a selected catalyst were conducted by RTI and GE, respectively. The RTI test was conducted using a mobile skid-mounted reactor facility with a hot slip stream of actual coal gas from the METC 10-in. dia fluidized-bed coal gasifier. This facility is described in detail elsewhere (Gangwal et al., 1994). The schematic of the skid-mounted NH₃ decomposition reactor system used at METC is shown in Figure 2. As seen, the hot coal gas entered a 3.0-in. dia catalytic reactor surrounded by a 3-zone furnace. The nominal composition of the hot-coal gas is shown in Table 3. Reactor pressure was controlled using two back pressure regulators in series with an electronic mass flow meter (MFM) in between. This configuration maintained the reactor pressure at 150 psig and limited the pressure drop across the MFM to within specified limits. The MFM signal was sent to a proportional controller to control coal gas flow rate with a Badger high-temperature flow control valve. The system was designed to run at space velocities up to 5,000 scc/(cc·h) with one liter of catalyst. The inlet and outlet coal gas were sampled for NH₃

Table 2. Catalysts Tested for High-Temperature Catalytic Decomposition Approach

Catalyst Designation	Vendor	Composition/ Support	Bulk Density	Shape/Size
HTSR-1	Haldor-Topsoe	Ni on refractory support	1.6	Cylinder $(1/8" \times 1/8")$
G-47	UCI	3% Fe ₂ O ₃ on SiO ₂ /Al ₂ O ₃	1.1	Sphere (1/4")
C11-9-02	UCI	12% Ni on ceramic	1.1	Rings (5/16" × 5/16" × 1/8")
C-100 N	CMP	10% Ni on stabilized Al ₂ O ₃	0.5	Powder (90 to 150 μm)

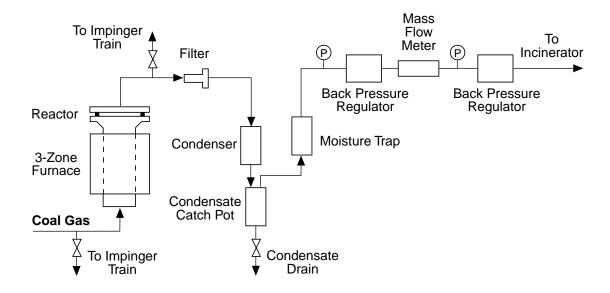


Figure 2. Schematic of skid-mounted reactor system.

measurement (by ion chromatography) using an acidic impinger. Also, condensate samples were periodically collected upstream and downstream to provide an integrated measure of NH₃ and its decomposition.

The GE 100-h test was conducted using a bench-scale reactor system shown in Figure 3, with simulated coal gas at 900 $^{\circ}$ C and 8.5 atm. Due to high operating temperature and high H_2S levels to be used (7,500 ppmv), the reactor was made from a 3/4-in. nominal pipe using a HR-160 material (a highly sulfur resistant material from Haynes International). The reactor had an inside diameter of 2.15 cm

and the system was designed to operate con-

Table 3. METC Gasifier Coal Gas Composition

Vol%
2.87
0.13
14.14
0.48
11.21
11.87
48.50
10.47
0.33

tinuously at 900 $^{\circ}$ C with space velocities of up to 10,000 scc/(cc·h). The analytical system was similar to that for the RTI system described above.

Results

Simultaneous NH₃ and H₂S Removal

Numerous catalysts were prepared and tested for this approach. These catalysts are summarized in Table 4. Nearly all the tests were performed at 725 $^{\circ}$ C, which was initially the target test temperature.

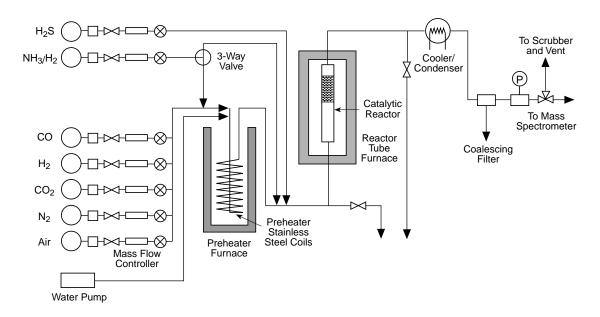


Figure 3. GE-CRD bench-scale ammonia decomposition reactor system.

Table 4. Catalysts Tested for Simultaneous NH₃ and H₂S Removal

HTSR-1 + ZT-4 (zinc titante)	Co/TiO ₂
MoS ₂ (CRC-653)	$\mathrm{Mo/TiO}_2$
MoS ₂ (CRC-530)	$Co-Mo/TiO_2 + ZT-4$
ZT-4	W/TiO ₂
$\mathrm{Ni/TiO_2}$ - $\mathrm{ZrO_2}$	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

Highlights of the results are as follows:

- HTSR-1 exhibited excellent activity for NH₃ decomposition in simulated Texaco gas without H₂S, at 725 °C. With H₂S the catalyst was poisoned but the activity could be restored at 800 °C even in the presence of H₂S.
- MoS₂-based catalysts show low activity for NH₃ decomposition. Surface area stabilization with ZrO₂ was necessary for these catalysts to have any activity at all.

- The catalysts containing Ni, Co, Mo, and W on a high surface area TiO₂ support showed moderate activity (typically 10 to 20 percent decomposition) for NH₃ decomposition at 725 °C. The TiO₂ support sintered extensively at 725 °C and required stabilization with ZrO₂.
- Mixing the Ni, Co, Mo, and W catalysts with zinc titanate sorbent allowed the catalysts to function longer. As the sorbent got loaded with H₂S, the exit H₂S level increased, thereby decreasing the activity for NH₃ decomposition.

High-Temperature Catalytic Decomposition

Screening Tests. Results are presented for catalyst screening and the two 100-h tests described earlier. Figure 4, which shows an activity comparison for the three fixed-bed catalysts in Table 2, clearly indicates the superiority of HTSR-1. In a separate experiment with C11-9-02 at 850 °C and atmospheric pressure, the inhibiting effect of H_2S -containing coal gas components was evaluated. It was found that replacing coal gas with N_2 increased the activity of C11-9-02 from about 40 percent decomposition to >90 percent decomposition. This phenomenon was reversible, i.e., when coal gas was restored, the activity fell back to around 40 percent decomposition. The number of catalysts to be tested further was narrowed at this point to HTSR-1 (for fixed beds) and C-100N (for fluidized beds).

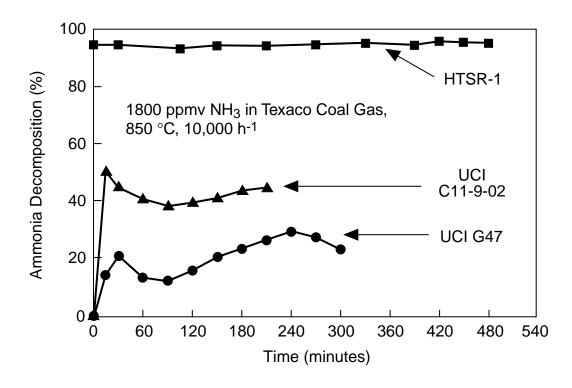


Figure 4. Activity comparison for HTSR-1, UCI C11-9-02, and UCI G47.

The ability of HTSR-1 to increase throughput was evaluated by testing it in Texaco gas at a space velocity of 20,000 scc/(cc·h), 1 atm, and 850 °C. Under these conditions, the conversion ranged between 54 and 70 percent over a 50-h test. Screening tests at high pressure were then initiated for HTSR-1 and C100-N.

The results of screening tests at 11.2 atm are shown in Figures 5 and 6. Figure 5 showed that under identical conditions, the HTSR-1 was better than C-100N. The decomposition over HTSR-1 was initially about 75 percent and stabilized at around 50 to 60 percent. But, the decomposition on C-100N decayed exponentially, indicating that under these conditions the catalyst was continuing to deactivate. Another interesting experiment to evaluate the effect of H_2S was conducted in the steady-state regime for HTSR-1 as shown in Figure 6. For a period of time, H_2S was removed from the coal gas. This increased the activity to around 90 percent decomposition. When H_2S was restored, the activity very quickly fell back to its earlier steady-state value. This result clearly indicates partial but reversible poisoning of NH_3 decomposition sites at $850\,^{\circ}C$ by H_2S .

100-h Tests

The results of the RTI 100-h test at METC with actual coal gas (Table 3) is shown in Figure 7. The conditions used for this test were 146 psig (10.8 atm), 780 °C, and 4,975 scc/(cc·h) space velocity. During the test period, ammonia decomposition averaged 91.7 percent based on impinger sampling and 87.4 percent based on condensate sampling. No catalyst deactivation was

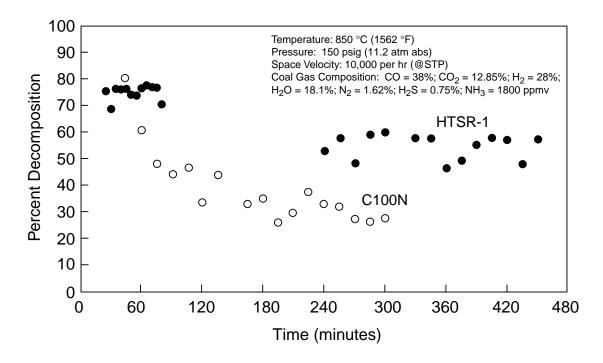


Figure 5. Comparison of high-temperature ammonia decomposition on HTSR-1 and C-100N catalysts.

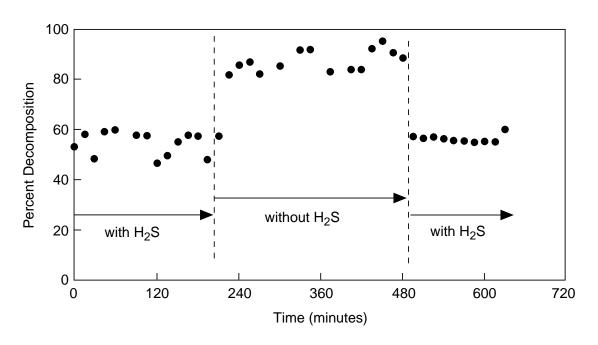


Figure 6. Effect of H₂S on ammonia decomposition by HTSR-1 catalyst.

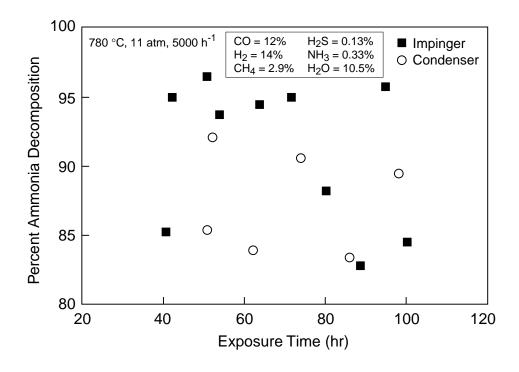


Figure 7. RTI 100-h test-ammonia decomposition on HTSR-1 catalyst.

observed over the test. One interesting observation was made during the test. The reactor inlet coal gas preheated to 850 $^{\circ}$ C dropped in temperature to 780 $^{\circ}$ C in the bed. N₂ under identical preheat and flow conditions remained at 850 $^{\circ}$ C in the bed. This suggests that an endothermic reaction may be occurring to absorb heat.

The results of the GE 100-h test carried out using a simulated Texaco gas (containing 7,500 ppmv H_2S) at 8.5 atm, and 900 °C are shown in Figure 8. The average inlet NH_3 on a dry basis was 1,950 ppmv (or ~1,550 ppmv on a wet basis). During operation at a space velocity of 10,000 h^{-1} , the average outlet NH_3 concentration was reduced to 310 ± 100 ppm (wet) over the course of the run to give an NH_3 conversion of 80 percent. At a reduced space velocity of 5,000 h^{-1} , outlet NH_3 concentration was further reduced to 200 ± 40 ppm to give an NH_3 conversion of 88 percent. Under the test conditions, equilibrium limitations were not present since the equilibrium NH_3 was estimated to be 10 to 11 ppm.

During the first 40 hours of the test, some catalyst deactivation was seen, but the activity stabilized thereafter. When the reactor was sawed apart at the end of the test, it was found that a single layer of catalyst pellets had fused against the reactor walls. This layer closed off a fraction of the flow area in the tube and may have contributed to the decrease in activity over the first 40 hours. Although no further analyses were made, other factors, such as catalyst sintering may have also contributed to the initial loss of activity.

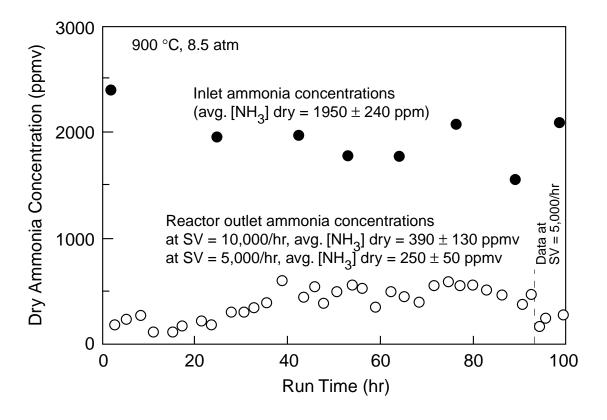


Figure 8. GE 100-h test-ammonia decomposition on HTSR-1 catalyst.

Applications

The two 100-h tests demonstrate that HTSR-1, a nickel-based catalyst on a refractory support, is capable of decomposing up to 90 percent of the NH $_3$ 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. Alternative technologies to catalytic decomposition include the use of conventional selective catalytic reduction (SCR) past the turbine at low pressure or using modified advanced turbines that could reduce NO $_x$ emissions. Because of the low pressure, high volumetric flow rates, and low NO $_x$ concentrations, the SCR approach is likely to be very expensive. While work is ongoing on the turbine modifications approach, it will be difficult to achieve a very high level, i.e., > 90 percent, NO $_x$ reduction in large-scale applications using this approach because of difficulties in scaleup.

Future Activities

Discussions are under way for development of an H₂S-resistant material that could be effective at temperatures as low as 500 °C for simultaneous H₂S removal and NH₃ decomposition. A topical report will be submitted to METC summarizing the work to date.

Acknowledgments

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