

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 NH₃ was 14 m²/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/μm 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 ₂ O ₃ on a SiO ₂ -Al ₂ O 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 ₂ O ₃ support	133	0.5	Powder between 90 and 150 μm

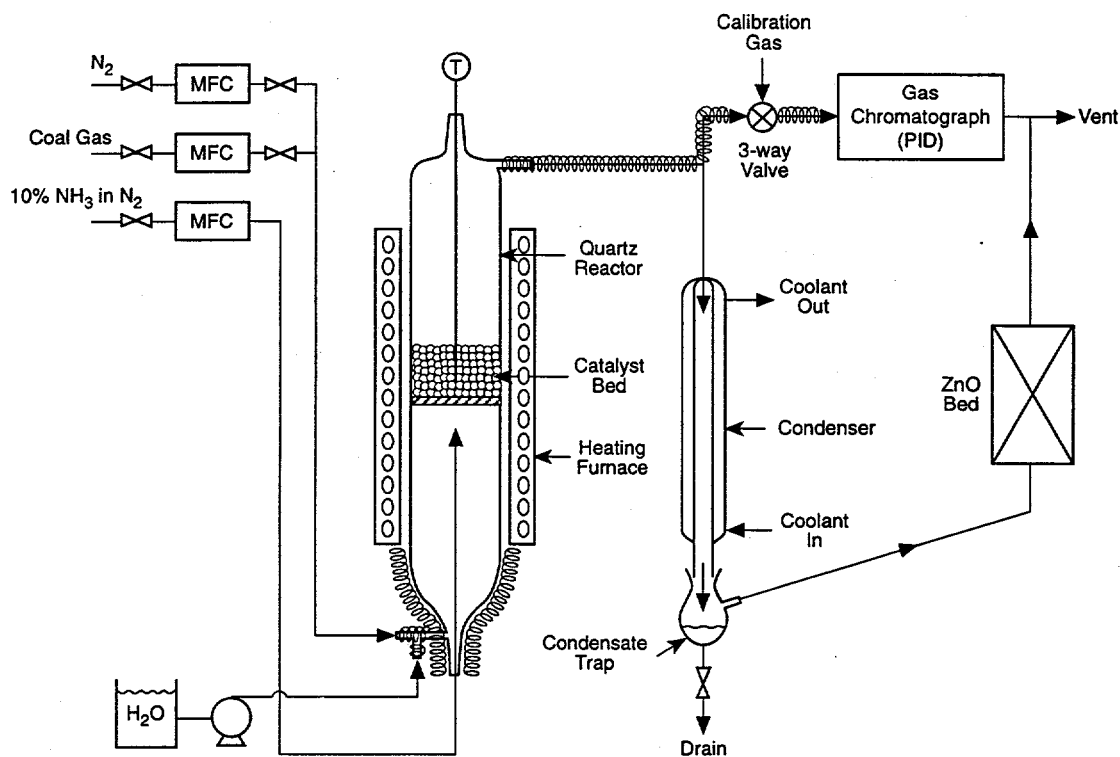


Figure 5. Schematic of the atmospheric bench-scale unit to study catalytic decomposition of ammonia.

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 ($>150\text{ }^{\circ}\text{C}$), thus preventing formation of ammonium carbonate (at temperatures lower than $150\text{ }^{\circ}\text{C}$, 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 $35\text{ cm}^3/\text{min}$) of reactor effluent gas is injected hot (120 to $160\text{ }^{\circ}\text{C}$) 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 $850\text{ }^{\circ}\text{C}$ and $10,000\text{ h}^{-1}$ space velocity in Texaco coal gas with $1,800\text{ ppmv NH}_3$. The total gas flow at $10,000\text{ h}^{-1}$ 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 NH₃ decomposition with time for the three catalysts studied. The HTSR-1 catalyst decomposes over 95 percent of the feed NH₃ compared to about 40 and 20 percent NH₃ decomposition observed with UCI's C11-9-02 and G-47 catalysts, respectively. Thus, HTSR-1 appears to have better catalytic activity for NH₃ 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 H₂S 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%; CO₂: 12.85%; H₂: 28.5%; H₂S: 0.75%; NH₃: 0.18%;

1800 ppmv NH₃ in Texaco Coal Gas, 850 C, 10,000 1/h, 1/8" Cylindrical Pellets

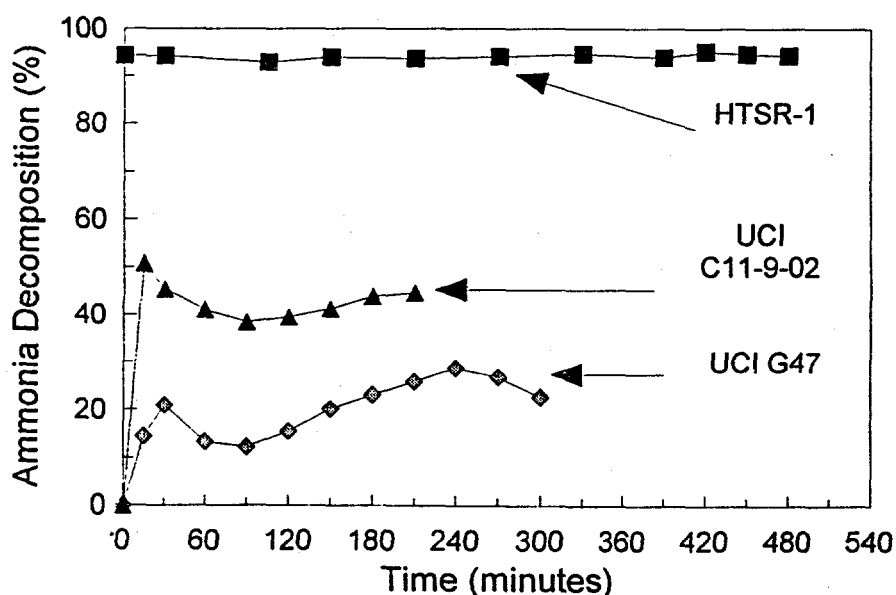


Figure 6. Catalytic decomposition of ammonia.

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

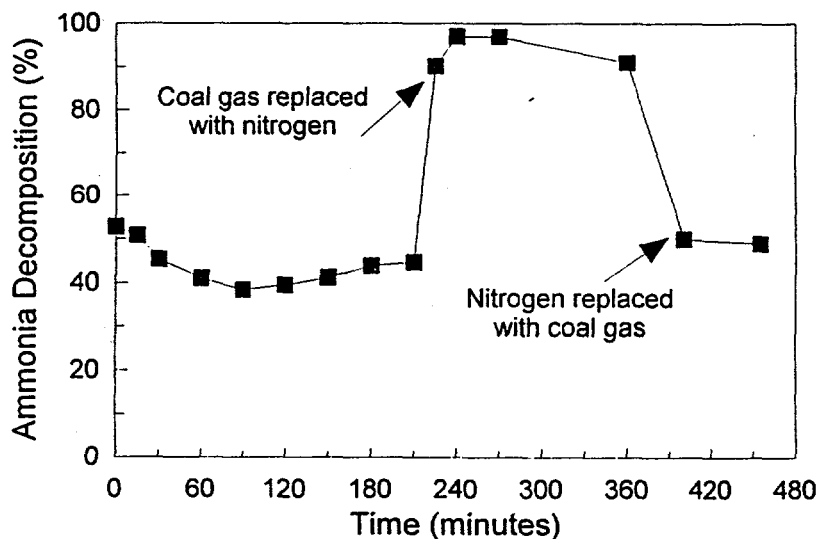


Figure 7. Decomposition of ammonia using UCI C11-9-02 catalyst.

N₂: 1.62%; and H₂O: 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 NH₃ in the outlet gas. We, however, collected the condensate samples at regular intervals to confirm the GC results. These condensate samples were analyzed for NH₄⁺ 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 H₂S 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 super-

ficial 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 NH₃ in the exit gas using the GC, we also collected the condensate samples at regular intervals for NH₄⁺ 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:

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

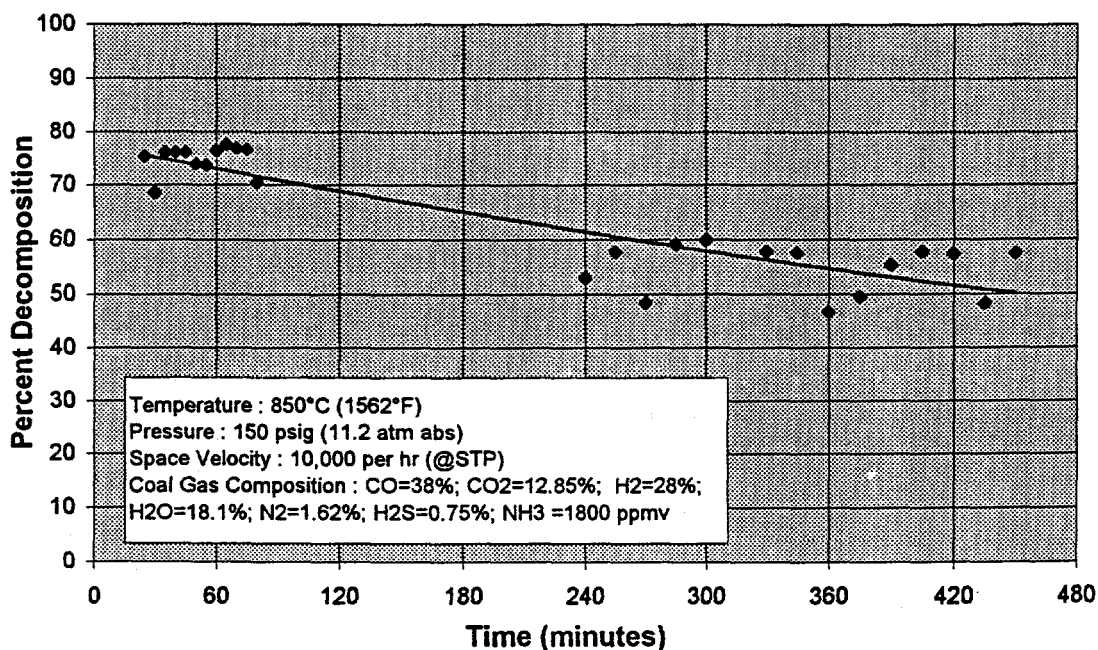


Figure 8. Ammonia decomposition by HTSR-1 catalyst.

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 H₂S on the Performance of HTSR-1 Catalyst

It is well known that H₂S is a strong poison for the Ni-based ammonia decomposition catalysts. Because poisoning by H₂S is quite severe at lower temperatures and leads to almost complete deactivation of the catalyst within the first few hours depending on the H₂S concentration in the coal gas, the recommended operating temperature for the HTSR-1 catalyst is above 800 °C.

Figure 9 shows the effect of H₂S addition in the coal gas. Initially, with 7,500 ppmv of H₂S present in coal gas, the ammonia decomposition was in the vicinity of about 50 percent. After about 3 h, the H₂S 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 H₂S, the H₂S 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, H₂S 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 H₂S 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

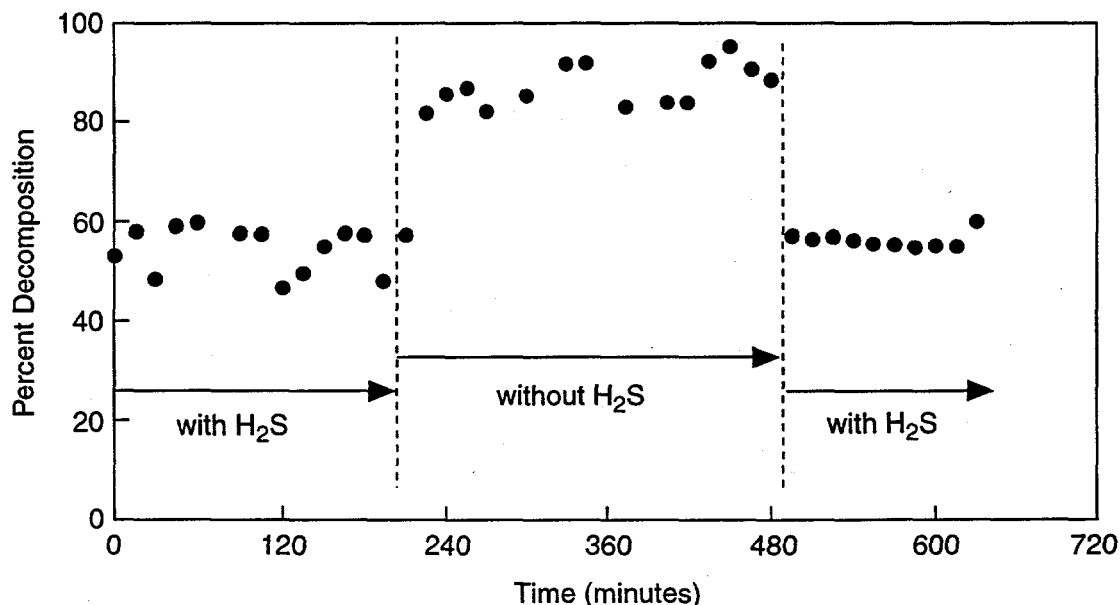


Figure 9. Effect of H₂S on ammonia decomposition by HTSR-1 catalyst.

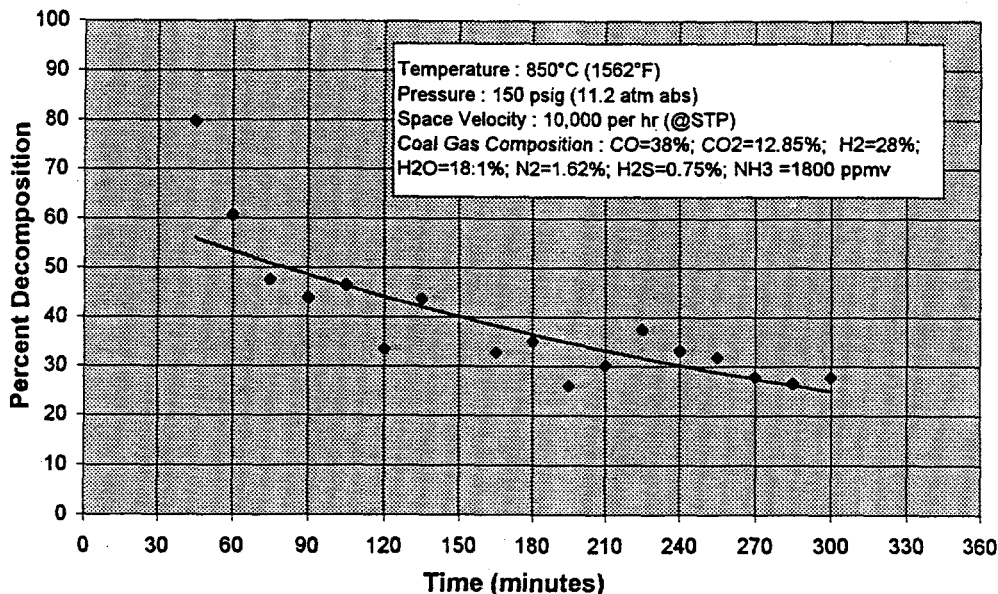


Figure 10. Ammonia decomposition by C100N catalyst.

a direct comparison of performance. As can be seen, 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.