

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 $900\text{ }^\circ\text{C}$ ($1652\text{ }^\circ\text{F}$). Because the reactor wall temperature had to be run at its maximum design limit of $927\text{ }^\circ\text{C}$ ($1700\text{ }^\circ\text{F}$) 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 $10,000\text{ h}^{-1}$ was selected throughout the run except for the last 6 hours during which the space velocity was reduced to $5,000\text{ h}^{-1}$ 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 $10,000\text{ h}^{-1}$, 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 $5,000\text{ h}^{-1}$, 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

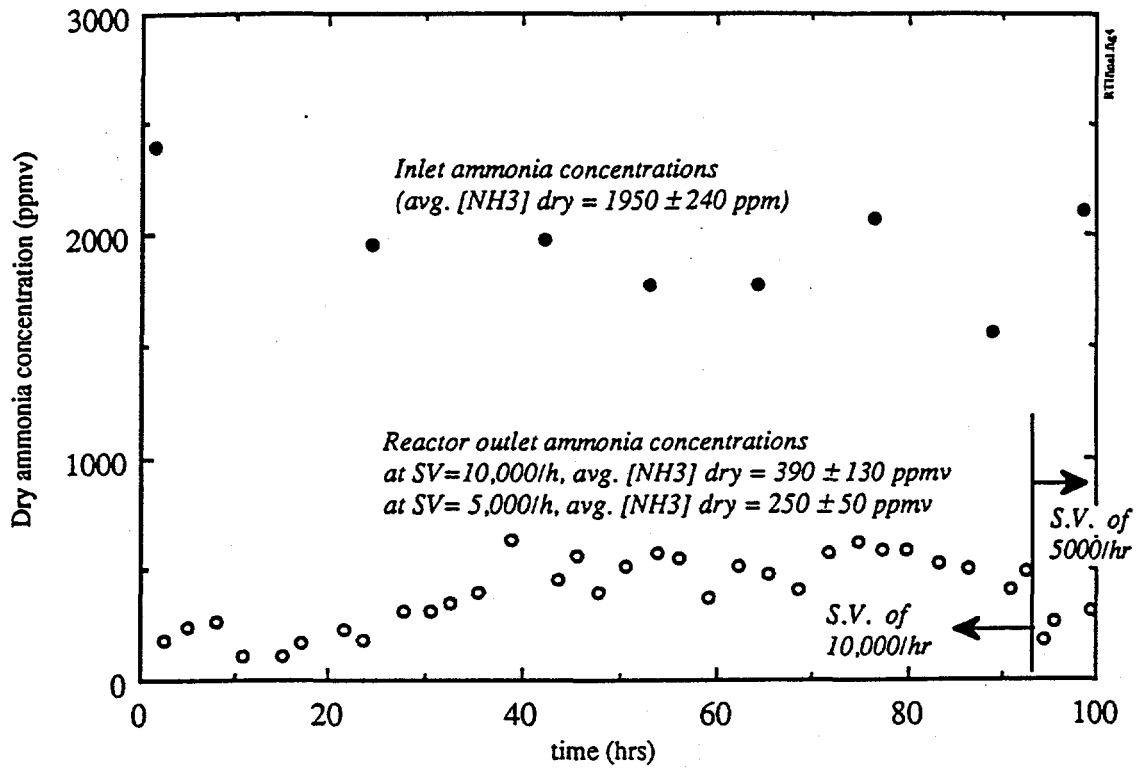
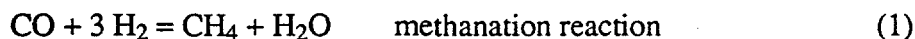


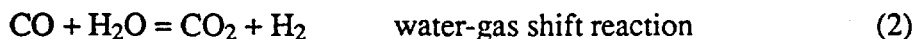
Figure 3.3-1 Ammonia (g) concentrations at reactor inlet and outlet

the methanation and water-gas shift reactions from altering the composition of the gases in the preheater coils, H₂S 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 H₂S 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 H₂S 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 CH₄ 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:



CO₂ concentrations also increased significantly over this same period of time. The increased CO₂ is likely due to the onset of the water-gas shift reaction which would further reduce CO concentrations while increasing CO₂ concentrations:



H₂S 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 H₂S. It is believed that H₂S inhibited the surface reactions on the stainless steel preheater coils which were likely responsible for these side reactions. By periodically flowing H₂S 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 Relevant 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%
CO	38.00	39.6	36.9
CO ₂	12.85	9.1	11.0
H ₂ S	0.75	0.78	0.72 ¹
H ₂ O	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 H₂S measurements were unstable (likely because of insufficient mixing distance from H₂S injection location to the gas sampling location. Used exit H₂S 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 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 calculation 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 calculations⁵ 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 °F), the gases would react adiabatically to reach an equilibrium temperature of 921 °C (1690 °F). 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 Relevant Outlet Gas Compositions

Gas Species	Measured and equilibrium outlet compositions		
	Bench-scale measurements at 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 ₂ S	0.71	0.72	0.72
H ₂ O	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

¹Amount 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.

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

³Constant TP denotes constant temperature and pressure.

Interestingly, a close inspection of the reactor exit gas composition shows that more CO and H₂O were measured and less CO₂ and H₂ 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 H₂O concentrations and higher CO₂ and H₂ 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, CO₂, H₂O, and H₂ is the observation of a black carbonaceous material found

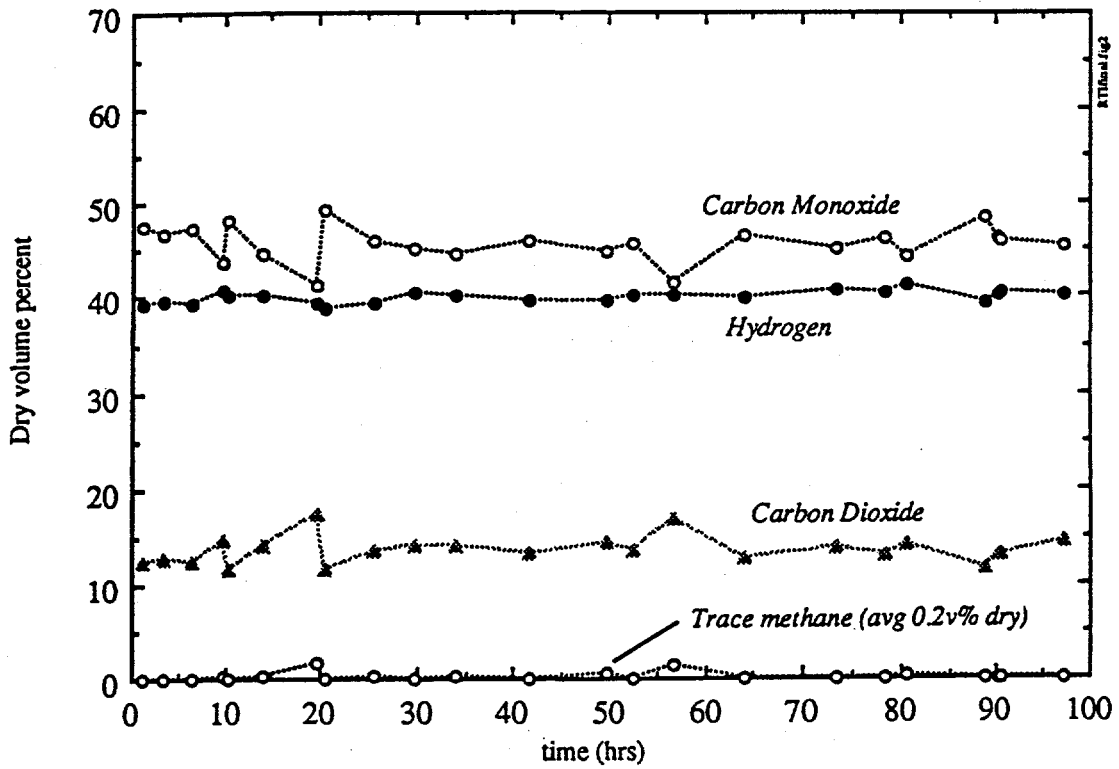


Figure 3.4-1 Reactor inlet dry gas concentrations for 100-hr run

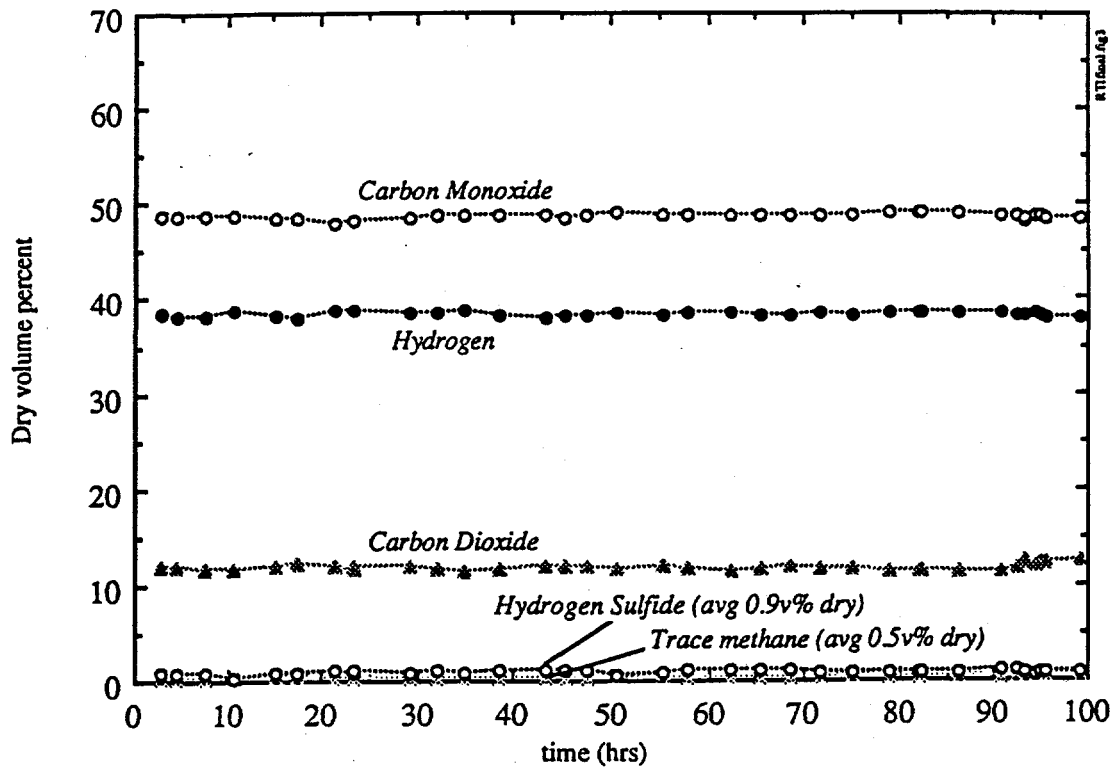


Figure 3.5-1 Reactor Exit dry gas concentration for 100-hr run

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 CO₂ and H₂:



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:



Note that the result of the combination of reactions (3) and (4) is a net reduction in CO₂ and H₂ concentrations and a net increase in CO and H₂O 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, CO₂, H₂O, and H₂ 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 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 $10,000 \text{ h}^{-1}$, 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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