

L-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% H₂, 1750 ppm NH₃, and balance Ar. The measured outlet NH₃ concentrations for the *L-3785M inlet sample* are presented in Figure 2.3.6-1 and show that although a decrease in the NH₃ concentration was measured at 750 °C, no measurable reduction in NH₃ was measured at 650 °C. By comparison, a ~20% reduction in the NH₃ 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 CO₂ in addition to H₂. The gas composition used is similar to that from a Texaco oxygen-blown gasifier, but without the water vapor: 38.8% CO, 13.0% CO₂, 29.5% H₂, 1800 ppm NH₃, and balance Ar. The measured NH₃ outlet concentrations at various temperatures are shown in Figure 2.3.6-3 which only show the NH₃ 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 CO₂ had little measurable influence on NH₃ 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 NH₃ decomposition. The base material for the H₂S 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 MoS₂ as the catalytic additive towards NH₃ decomposition (GE-CRD has previously demonstrated MoS₂ to be catalytically active). It was believed that although MoS₂ was catalytically active towards NH₃ 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 MoS₂ and Al used as the catalyst support in hydrodesulfurization and hydrodenitrication 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

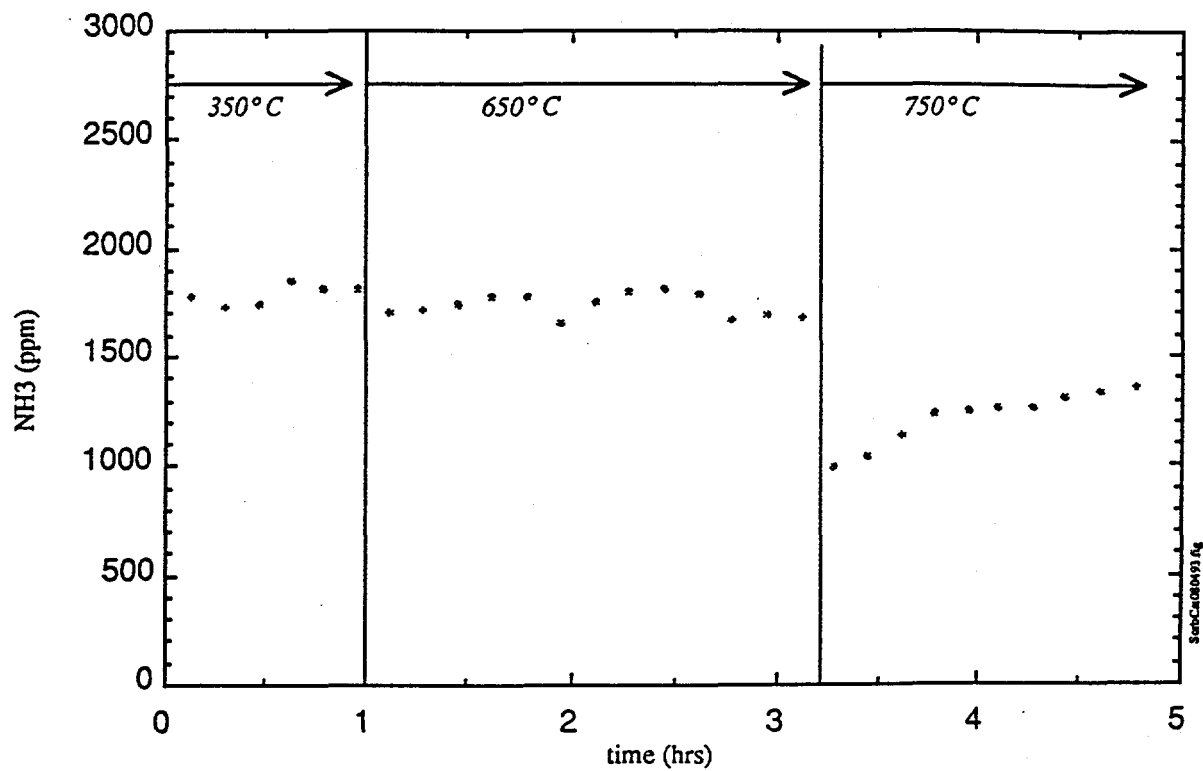


Figure 2.3.6-1 Ammonia Decomposition over L-3785M (Inlet Sample)

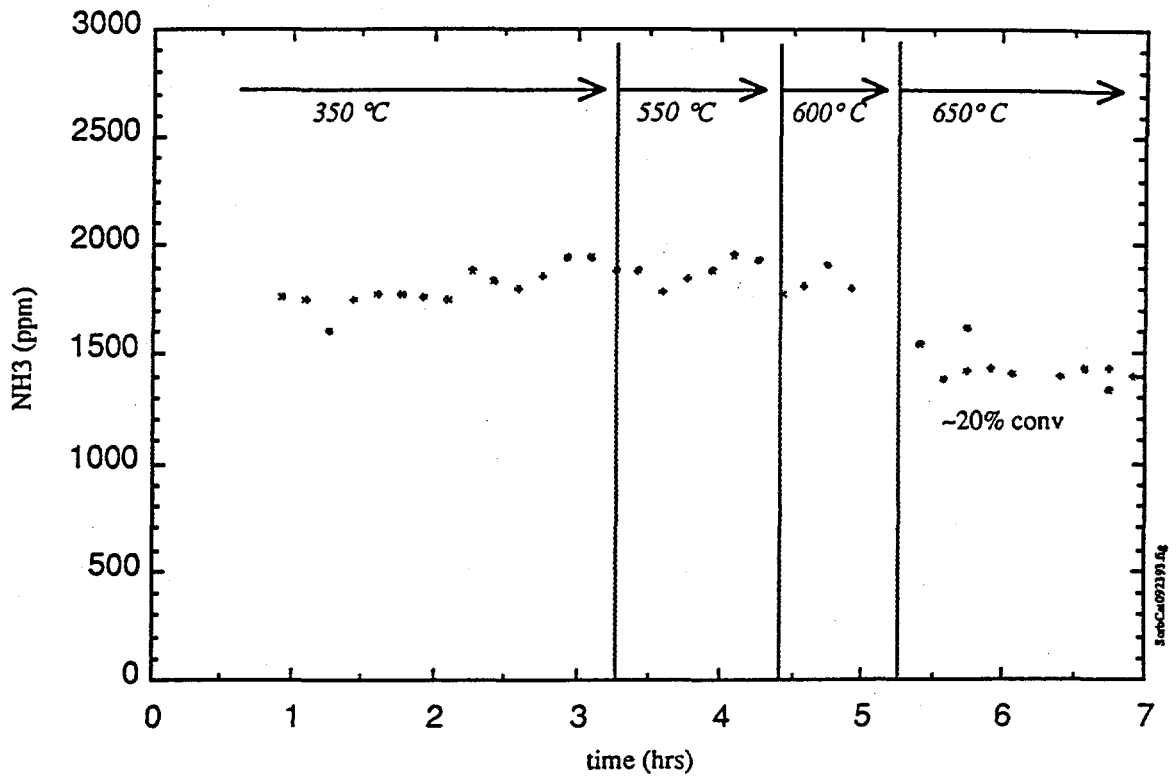


Figure 2.3.6-2 Ammonia Decomposition over L-3785M (Outlet Sample)

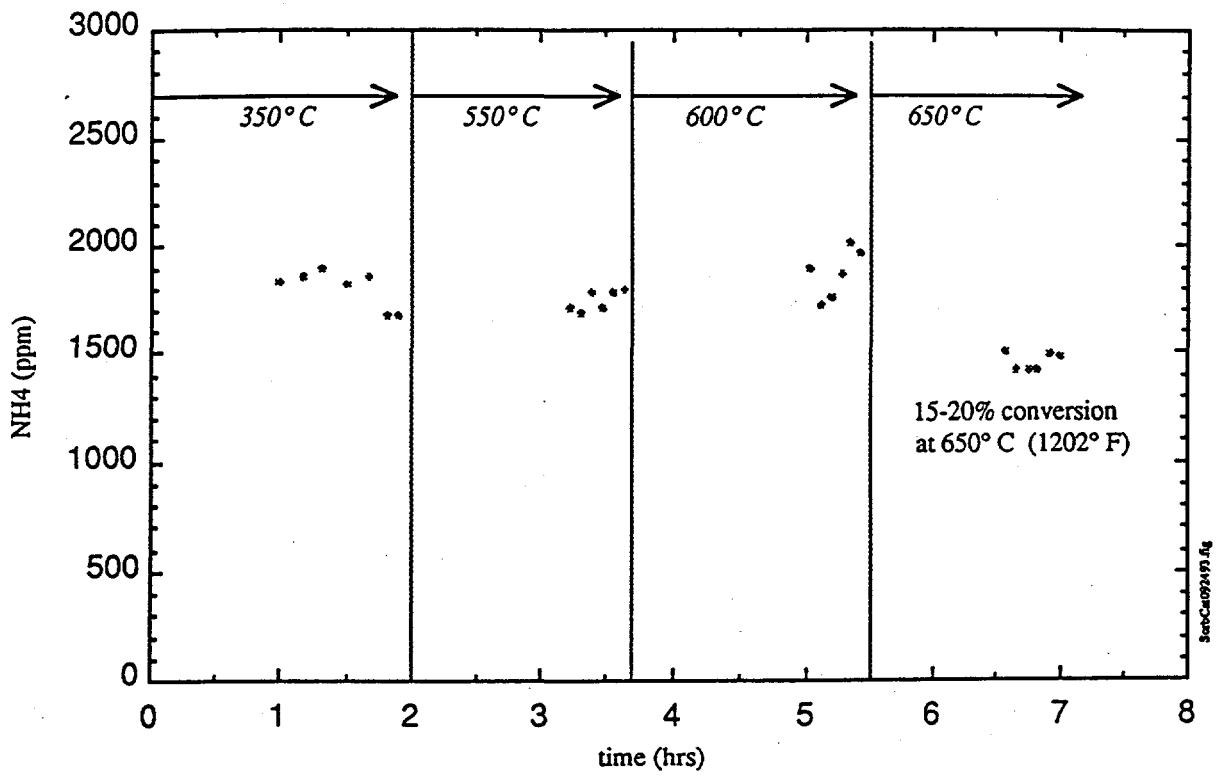


Figure 2.3.6-3 Ammonia Decomposition over L-3785M (Outlet Sample)

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, H₂, CO₂, N₂, H₂S) with NH₃ stored in H₂. 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, H₂S 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 (CH₄) was initially used in the gas mixture, the gas exiting the preheater was measured to contain as much as 5-6% CH₄. 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 occurring in the preheater, the preheater coils were periodically poisoned by sulfiding them with a short pulse of 1% H₂S 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 H₂S through the preheater and to preserve the operational life of the coils, H₂S was injected thereafter downstream of the preheater, keeping the periodic pulsing of the H₂S to suppress methanation. Further testing over several days have thus far shown that methanation of CO and CO₂ in the coal gas continues to be suppressed by the single pulse of H₂S passed through the preheater.

Following the shakedown tests in which NH₃ 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

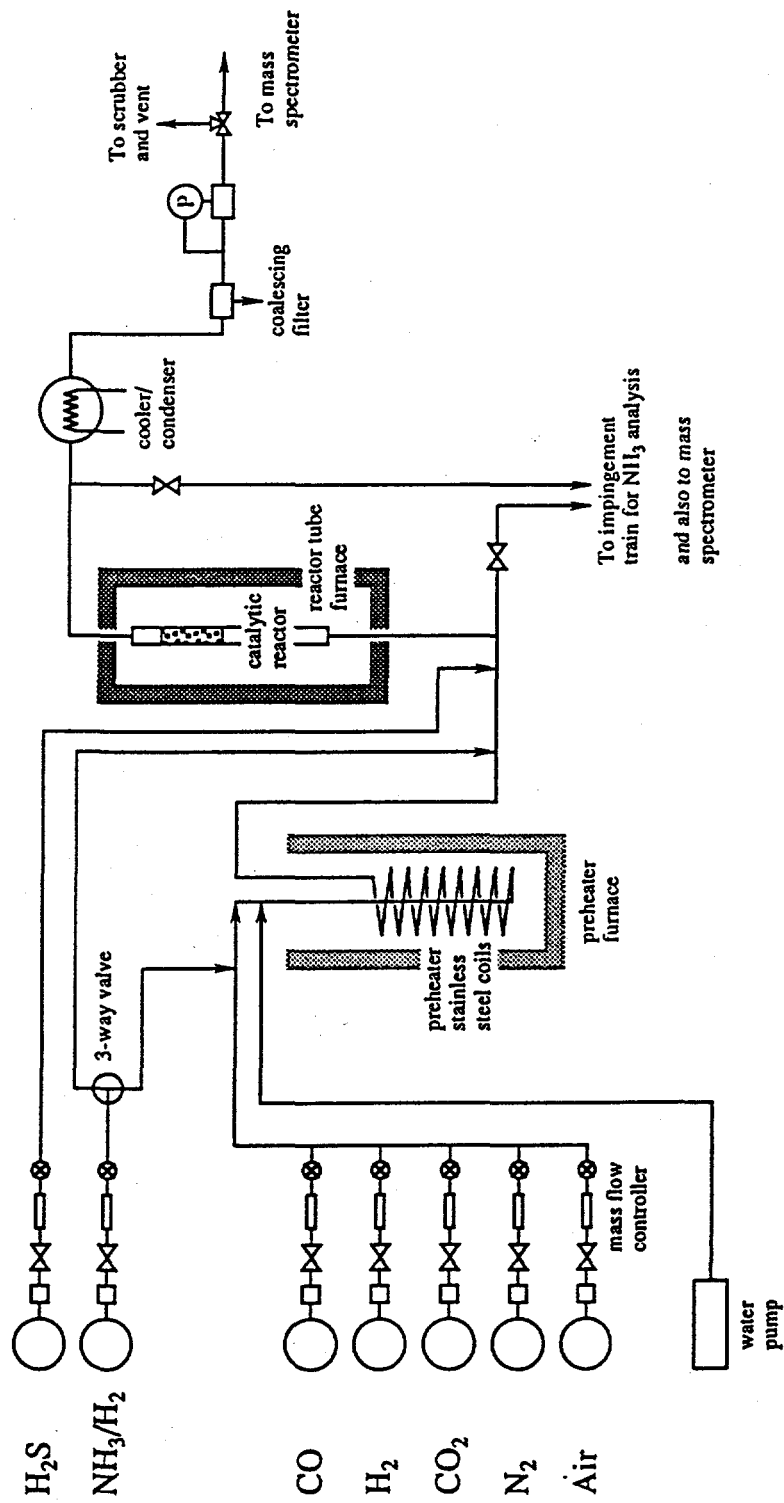


Figure 3.1-1 GE-CRD Bench-Scale Ammonia Decomposition Reactor System