Figure 2.3.3-2 shows that the catalytic activity of the Co-Mo-Al-zinc titanate material diminished as 0.75% H_2S was introduced into the gas mixture at 725 °C. This was surprising as the Co-Mo-zinc titanate (with no alumina) did not show any measurable loss of catalyst activity when H_2S was added (in Figure 2.3.1-1). It was speculated that the presence of alumina in the current Co-Mo-Al-zinc titanate sorbent-catalyst formulation lead to the formation of aluminum sulfate(s) which may have reduced the availability of the catalytic sites by blocking the catalyst surface or the pore channels.

2.3.4 Fresh Mo-doped zinc titanate

Of the three sorbent-catalyst samples discussed thus far, the Co-Mo-zinc titanate was found to be the best catalyst towards NH_3 decomposition. Although the activity of the Co-Mo-zinc titanate was not as high as that of Co-Mo-Al-zinc titanate, its activity did not diminish in the presence of H_2S. Next, a sample of a Mo-doped zinc titanate sample was tested (without the cobalt additive) so that the effect of cobalt on the Mo-zinc titanate material could be determined. Although this sample was prepared in our own lab, the final sorbent-catalyst sample composition was nominally similar to that of L-3787M.

Data taken over the Mo-zinc titanate is presented in Figure 2.3.4-1 and show that at 725 °C, NH_3 levels were reduced from 1800 ppm to 1200-1300 ppm. The activity of this catalyst was comparable to that of Co-Mo-zinc titanate (Figure 2.3.4-1 and Figure 2.3.1-1). Interestingly, NH_3 decomposition may have increased slightly as 0.75% H_2S was added to the gas mixture at 725 °C (see Figure 2.3.4-1).

2.3.5 Cycled L-3787M2 Mo-doped zinc titanate

It has now been shown that Co-Mo-zinc titanate and Mo-zinc titanate were both active towards the catalytic decomposition of NH_3 at relatively high temperatures (>700 °C) and that their activities were not affected by the presence of 0.75% H_2S in the gas mixture. In addition, it was also known from other work[1] that molybdenum doped zinc titanate is active towards NH_3 decomposition and that the activity improved as the material was subjected to multiple cycles of H_2S absorption and subsequent regeneration. Although it was not understood why increasing cycles of absorption and regeneration improved the catalyst activity, the increased activity may be related to the migration of the molybdenum within the zinc titanate material incurred from the operational cycles of the sorbent or the formation of MoS_2.

Tests were conducted to determine whether exposure of the Mo-doped zinc titanate to the operation cycles of adsorption and regeneration produced a more active NH_3 decomposition catalyst. This sample, designated L-3787M2, contained ~2.5% molybdenum oxide and was cycled through ten adsorption/regeneration cycles in GE-
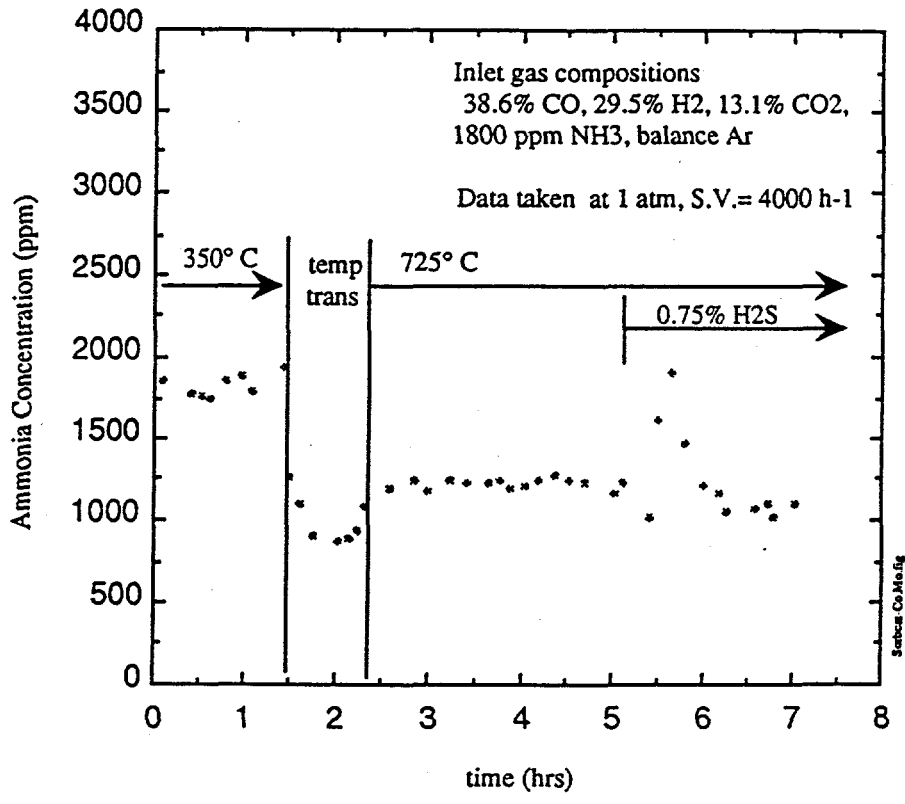
4000

3500   Inlet gas compositions
      38.6% CO, 29.5% H2, 13.1% CO2,
      1800 ppm NH3, balance Ar

3000   Data taken at 1 atm, S.V.= 4000 h-1

Ammonia Concentration (ppm)

2500   350° C   temp   725° C
      trans
                     0.75% H2S

2000

1500

1000

500

0

   0   1   2   3   4   5   6   7   8

time (hrs)

**Figure 2.3.1-1 Preliminary Data of Ammonia
Decomposition over Co-Mo-Zinc Titanate**
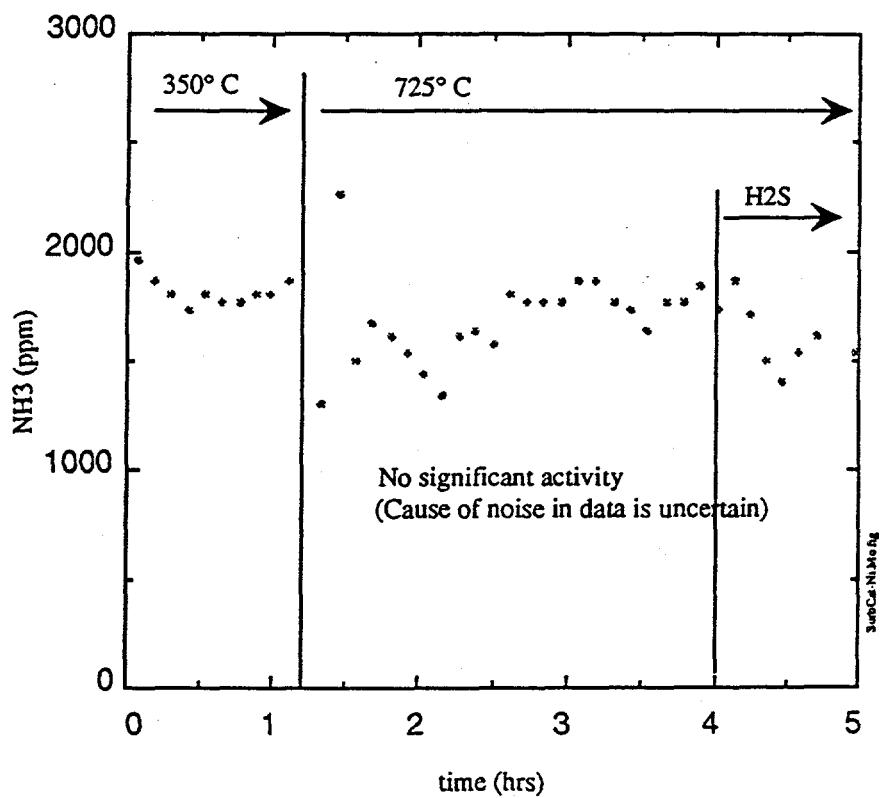
Figure 2.3.2-1 Ammonia Measurements for Ni-Mo-Zinc Titanate
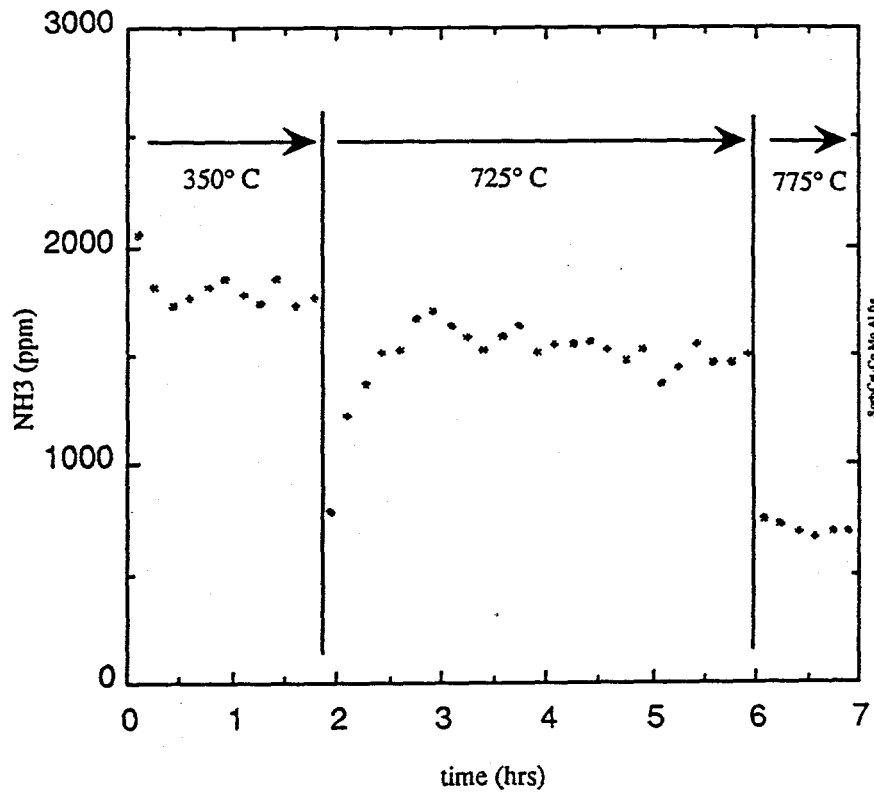
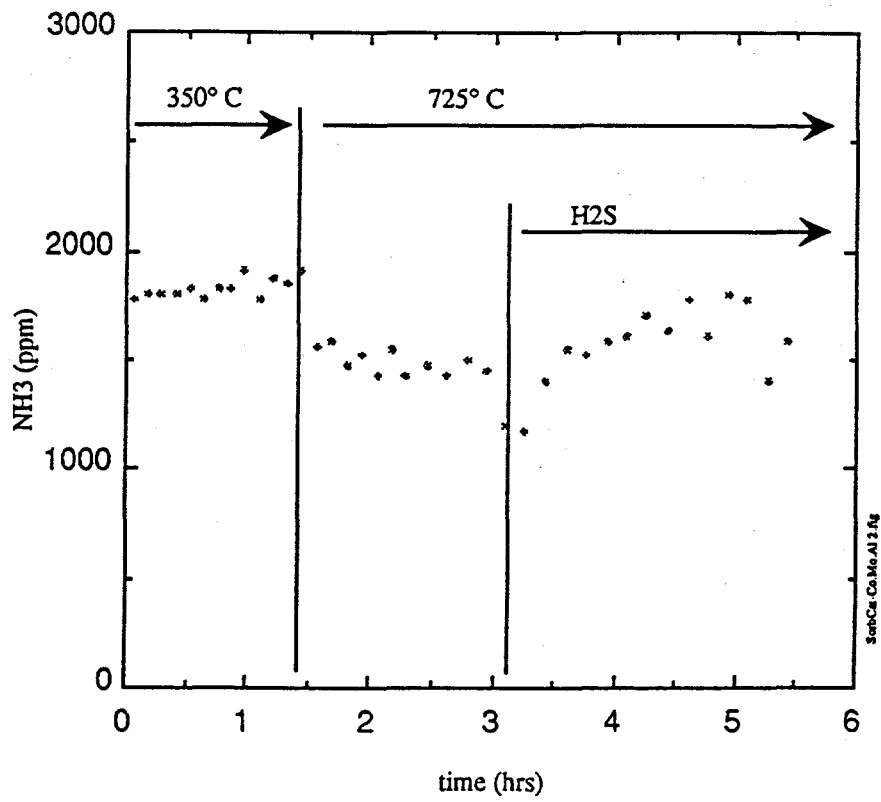Figure 2.3.3-1 Ammonia Measurements for Co-Mo-Al-Zinc Titanate

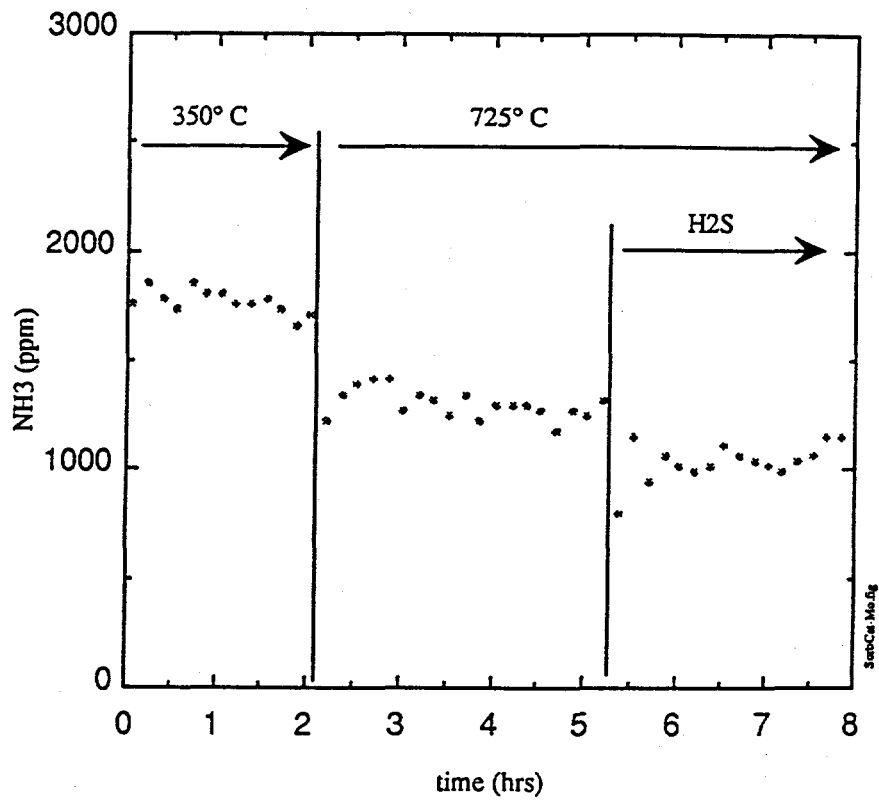**Figure 2.3.3-2 Ammonia Measurements for Co-Mo-Al-Zinc Titanate**

Figure 2.3.4-1 Ammonia Measurements for Mo-Zinc Titanate

CRD's bench apparatus (in pelletized form). Since these samples were previously exposed to H_2S, no presulfidation was used although the addition of H_2S to the feed gas was used to observe its effect on the catalyst activity.

For the microreactor studies, a gas composition of 28.6% H_2, 1750 ppm NH_3, and balance Ar was first used in this test. Using powdered L-3787M2 (in regenerated form) as sorbent-catalyst sample, Figure 2.3.5-1 shows that no measurable NH_3 decomposition was measured at 550 °C. Increasing the reaction temperature to 650 °C, 700 °C, and 725 °C (Figure 2.3.5-2) increased the catalyst activity, but NH_3 conversions remained low.

Next, NH_3 decomposition over the same catalyst was studied using a gas mixture containing 38.8% CO, 13.0% CO_2, 29.5% H_2, 1800 ppm NH_3, and balance Ar. This gas mixture approximates the nominal gas composition from a Texaco oxygen blown gasifier, but without any water vapor. Even at relatively high temperature of 725 °C and 750 °C, however, only limited NH_3 conversions were observed (Figure 2.3.5-3). For example, at 750 °C the NH_3 was reduced by only ~33% as NH_3 was reduced to ~1200 ppm (from 1800 ppm).

The effect of the presence of 0.75% H_2S in the gas mixture on the L-3787M2 catalytic activity was also investigated. Figure 2.3.5-4 shows the addition of 7500 ppm H_2S reduced the activity of the catalyst for NH_3 decomposition. The decrease in catalyst activity as H_2S was added was surprising as previous test data using zinc titanate doped with molybdenum showed the catalyst activity to be unaffected by H_2S over short duration (i.e., several hours; see Section 2.3.4).

2.3.6 Cycled L-3785M Mo-doped zinc titanate

Samples of a molybdenum doped zinc titanate with even higher levels of molybdenum than the L-3787M2 sample described in Section 2.3.5 were tested. This material, called L-3785M contained approximately 5% molybdenum oxide (by weight) and had a zinc to titanium molar ratio of 2 to 1. By contrast, the L-3787M2 material discussed in section 2.3.5 contained ~2.5% molybdenum oxide. The L-3785M samples were taken from a bench-scale packed bed test in which, like the L-3787M2 sample, the samples were previously subjected to ten absorption and regeneration cycles. Two separate L-3785M samples were tested. The first L-3785M sample was taken from the inlet end of the packed bed and the second L-3785M sample from near the outlet end of the packed bed. In the packed bed bench apparatus, the inlet end of the packed bed would be exposed to higher levels of H_2S and would achieve higher degrees of sulfidation then the sorbent near the outlet end. During regeneration, the inlet end of packed bed would be exposed to higher levels of oxygen and be more thoroughly regenerated than the sorbent near the outlet end. The outlet end of the packed bed, on the other hand, would also be exposed to higher concentrations of SO_2 during the regeneration stage. The significance of the differences between the inlet and outlet samples towards the catalytic activity of the L-

13
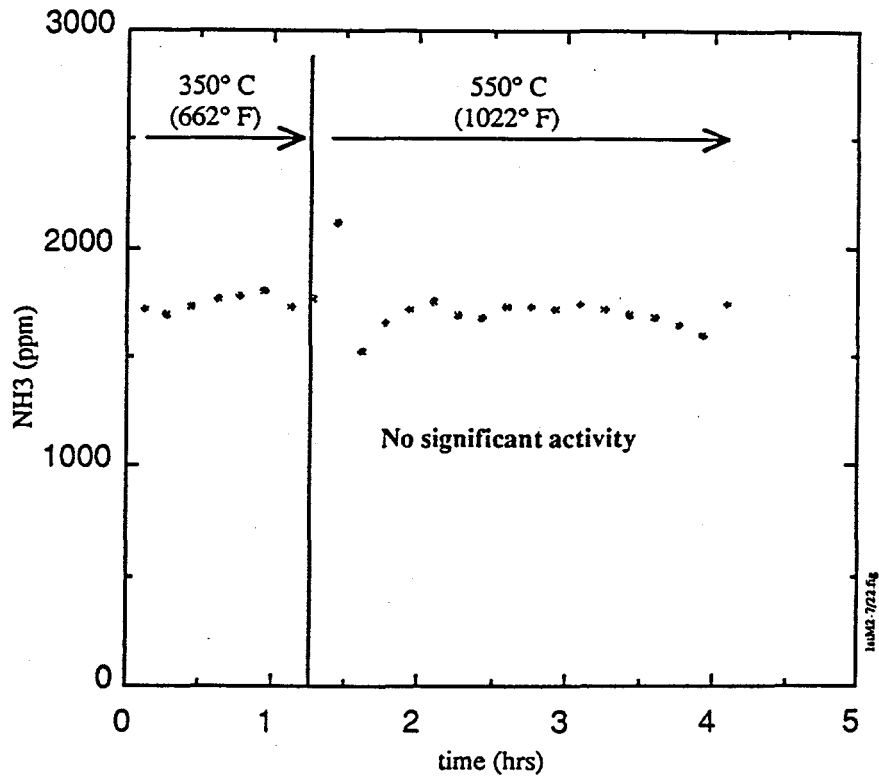
Figure 2.3.5-1 Ammonia Decomposition over L-3787M2 Previously Subjected to Ten Absorption/Regeneration Cycles
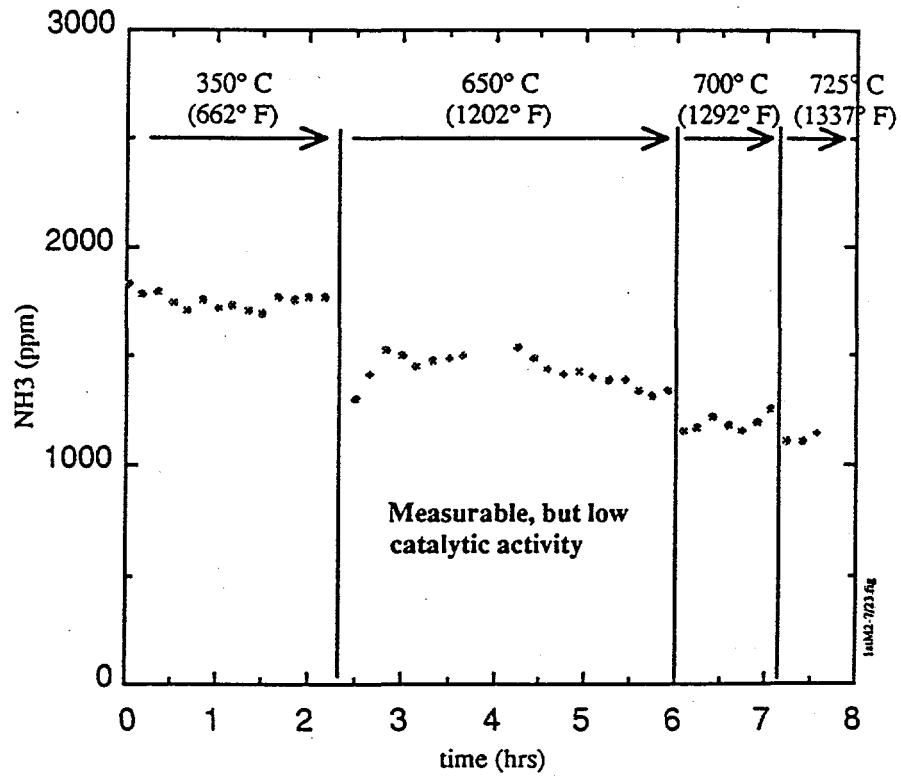
Figure 2.3.5-2 Ammonia Decomposition over L-3787M2
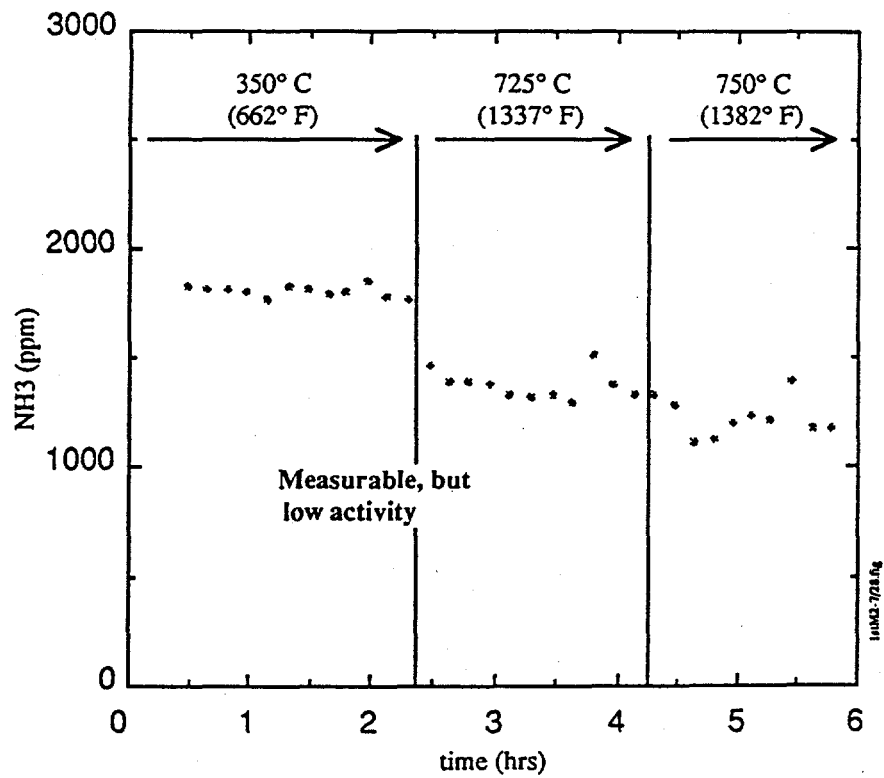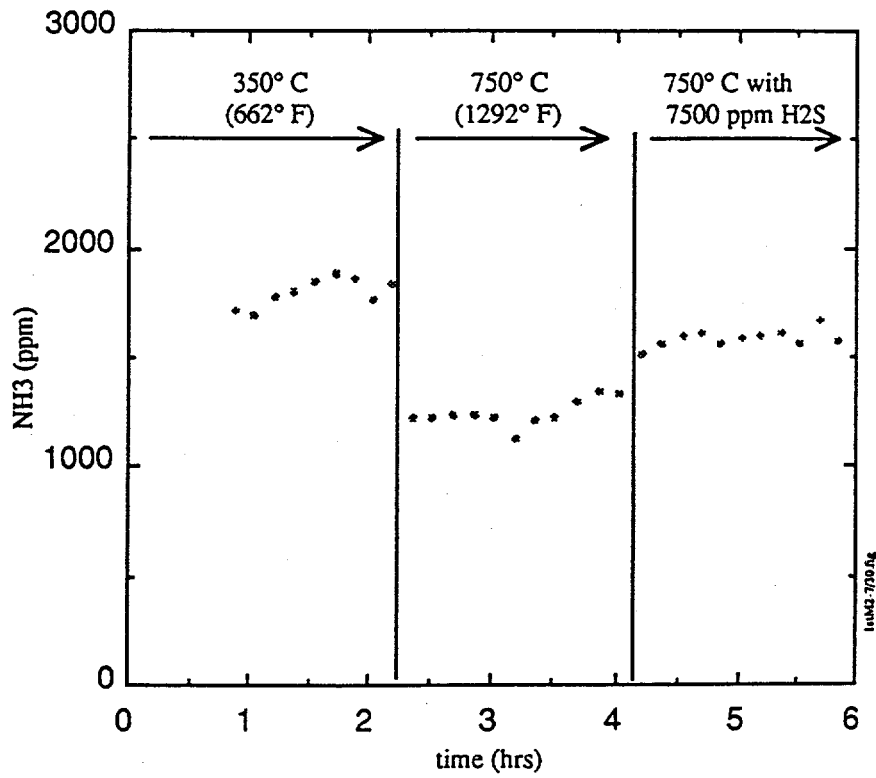Previously Subjected to Ten Absorption/Regeneration Cycles

Figure 2.3.5-3 Ammonia Decomposition over L-3787M2 Previously Subjected to Ten Absorption/Regeneration Cycles

Figure 2.3.5-4 Ammonia Decomposition over L-3787M2 Previously Subjected to Ten Absorption/Regeneration Cycles