

## 1. SUMMARY

The initial objective of this program was the development a material for use in hot gas cleanup of coal gas that will act both as a catalyst towards the decomposition of ammonia ( $\text{NH}_3$ ) as well as a sorbent towards hydrogen sulfide ( $\text{H}_2\text{S}$ ) removal. The focus of the work at General Electric's Corporate Research and Development (GE-CRD) was on the application of the sorbent-catalyst material to a moving-bed hot gas clean-up (HGCU) system. In the first phase of this program, powdered sorbent-catalyst samples were tested in a small scale microreactor to test their effectiveness towards  $\text{NH}_3$  decomposition. The starting base material for all of GE-CRD's sorbent-catalyst formulations was zinc titanate, a material which was being studied as a potential commercial  $\text{H}_2\text{S}$  sorbent in a parallel DOE funded study at GE-CRD.  $\text{MoS}_2$ , which has been reported to be catalytically active towards the  $\text{NH}_3$  decomposition reaction, was studied as the catalytic component. In addition to molybdenum, other species (Co, Ni, and Al) were used in the catalyst formulations in attempts to promote and stabilize the catalytic activity of  $\text{MoS}_2$ . A number of catalyst formulations were tested, and although some levels of  $\text{NH}_3$  decomposition activity were observed, the catalytic activities were limited and incomplete  $\text{NH}_3$  destruction levels were achieved at the operating conditions for desulfurization.

After the initial effort at studying simultaneous desulfurization and ammonia decomposition and showing the need for higher ammonia decomposition activity, GE-CRD focused on the development of a material only for decomposition of ammonia. As necessary, elevated temperatures were to be used to minimize potential catalyst inhibition or poisoning by  $\text{H}_2\text{S}$ . Previous tests at RTI produced encouraging results indicating that a commercially available steam reforming catalyst (HTSR-1 catalyst; Haldor Topsoe, Denmark) was sufficiently active towards the desired  $\text{NH}_3$  decomposition reaction in fluidized-bed, bench-scale tests. In this second phase of work at GE-CRD, the HTSR-1 catalyst was tested and demonstrated to be effective towards the catalytic decomposition of  $\text{NH}_3$  at elevated temperatures ( $900^\circ\text{C}$ ) and pressures (8.5 atm) in a 100-hr bench-scale test. Using an initial  $\text{NH}_3$  concentration of  $\sim 1550$  ppm (wet basis) and operating at a space velocity of  $10,000\text{ h}^{-1}$ ,  $\text{NH}_3$  destruction levels of 80% were measured over extended periods of time. When the space velocity was reduced to  $5000\text{ h}^{-1}$ ,  $\text{NH}_3$  destruction levels further increased to 88%, even in the presence of hydrogen sulfide.

## 2. MICROREACTOR SCREENING TESTS

### 2.1 CATALYST SELECTION

R. Ayala<sup>1</sup> and others<sup>2</sup> have shown molybdenum disulfide ( $\text{MoS}_2$ ) to be active towards the catalytic decomposition of  $\text{NH}_3$  in coal gas.

In the current study, the strategy for developing a stable  $\text{NH}_3$  decomposition catalyst was to stabilize  $\text{MoS}_2$  catalysts from commercial hydrodesulfurization processes to stabilize  $\text{MoS}_2$  onto zinc titanate, a sorbent used for desulfurization of coal gases. Note that although hydrodesulfurization and the current application of the sorbent-catalyst (i.e., for application to HGCU system) are different, the operating conditions for the two processes are similar. In the petroleum refining industry, hydrodesulfurization involves the catalytic reaction of  $\text{H}_2$  with sulfur containing hydrocarbons to form  $\text{H}_2\text{S}$  so that the sulfur may be removed as  $\text{H}_2\text{S}$ . The catalyst is typically a sulfided form of Co-Mo or Ni-Mo on an alumina support. One difference between the two catalysts is that Co-Mo-S will more easily catalyze the exothermic methanation reactions than Ni-Mo-S<sup>3</sup>. It has been cited that some hydrodesulfurization catalysts use tungsten (W) instead of molybdenum (Mo)<sup>4</sup>. The role of the alumina support ( $\gamma\text{-Al}_2\text{O}_3$ ) on the catalytic reaction(s) is unclear, but likely contributes to the stability and activity of the hydrodesulfurization catalyst. Note that while  $\gamma\text{-Al}_2\text{O}_3$  may be stable for the temperatures found in hydrodesulfurization units (200-400 °C),  $\alpha\text{-Al}_2\text{O}_3$  may be the more stable form of alumina at the higher temperatures found in an HGCU gas stream (> 538 °C). The effect of the sorbent material (i.e., zinc and titanium oxides, sulfides, and sulfates) on the Molybdenum-based catalysts is unclear.

During the first phase of the test program, GE-CRD focused its efforts on Molybdenum-based catalysts and the use of additives which may promote and/or stabilize its catalyst activity.

## 2.2 EXPERIMENTAL SETUP FOR MICROREACTOR TESTS

A schematic diagram of GE's microreactor system is shown in Figure 2.2-1. As shown in this figure, mixtures of  $\text{NH}_3/\text{H}_2$ ,  $\text{H}_2\text{S}/\text{Ar}$ ,  $\text{CO}_2/\text{CO}$  were combined with pure gases ( $\text{H}_2$ ,  $\text{CO}_2$ , Ar, and  $\text{N}_2$ ) to give the desired coal gas compositions. The flow rates of these gases were metered using mass flow controllers. Water vapor, when needed, was produced by evaporating the water delivered via a syringe pump. To minimize the possible formation of ammonium carbonate (from  $\text{NH}_3$  and  $\text{CO}$ ) in the inlet gas manifold, the gases were heated to 120 °C prior to the introduction of  $\text{NH}_3$ . The gas composition used as the basis for this study corresponds to that typical from a Texaco oxygen-blown gasifier: 38.00%  $\text{CO}_2$ , 28.50%  $\text{H}_2$ , 12.85%  $\text{CO}$ , 18.10%  $\text{H}_2\text{O}$ , 1.62%  $\text{N}_2$ , 7500 ppm  $\text{H}_2\text{S}$ , and 1800 ppm  $\text{NH}_3$ . In some of the initial microreactor screening tests,  $\text{H}_2\text{O}$  and  $\text{N}_2$  were not used in the gas mixture (Ar was used as the balance instead).

The microreactor was fabricated using a high temperature metallic alloy (800H) with a nominal composition of Ni-Fe-Cr. To minimize chemical interactions between the powdered sorbent-catalyst samples and the reactor, the tubes were coated with a 0.5-1.0 micron thick layer of  $\text{SiO}_2$ . The metallic reactor had an ID of 11 mm and was heated in a tube furnace. The packing arrangement of the powdered sorbent-catalyst samples within the microreactor assembly is shown in Figure 2.2-2.

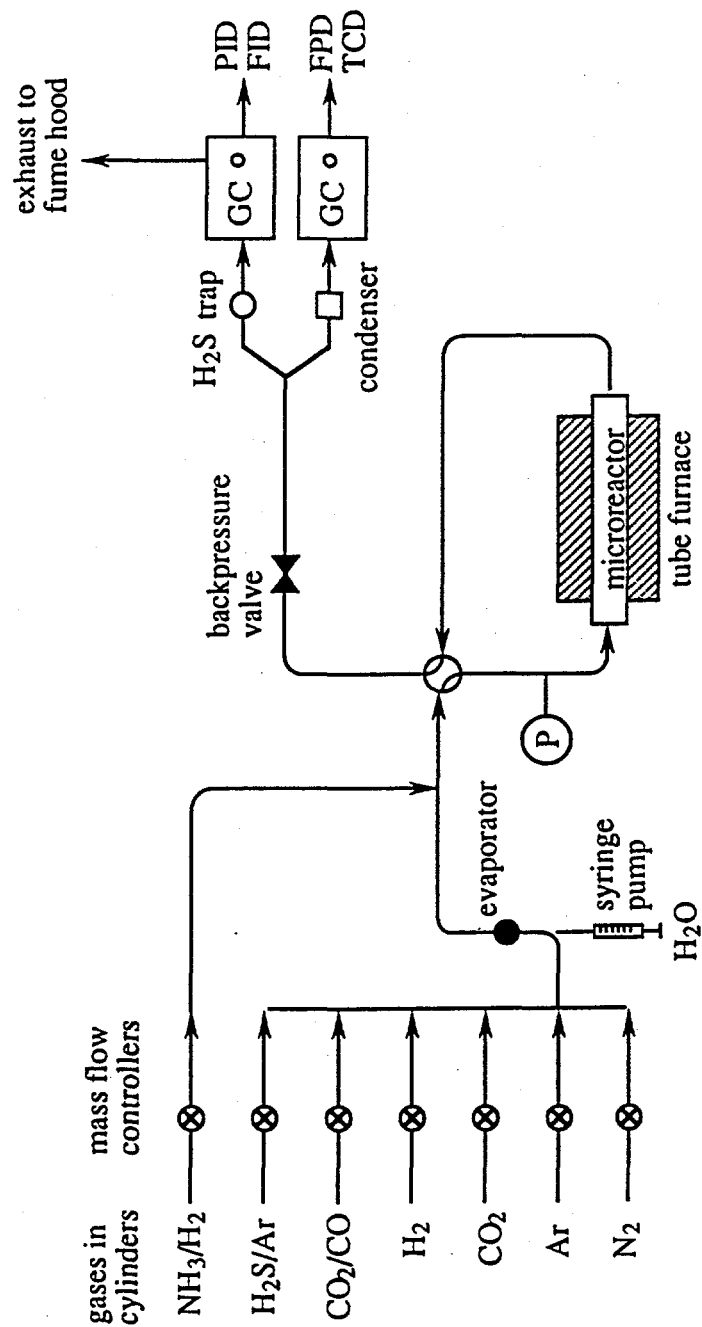


Figure 2.2-1 Microreactor System for Ammonia Decomposition Screening Tests

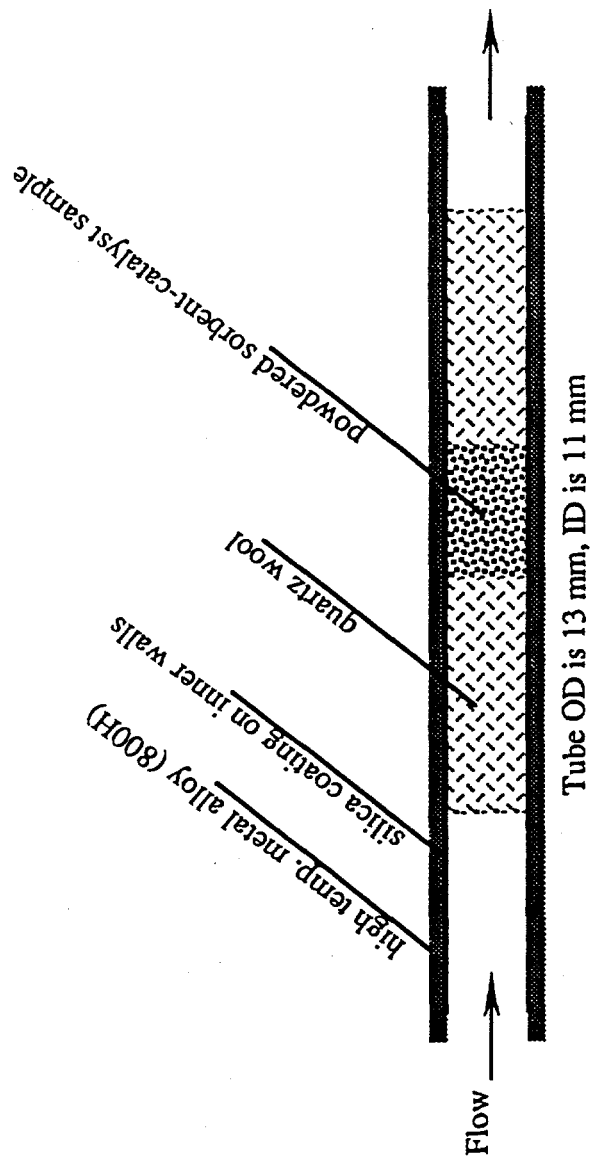


Figure 2.2-2 Schematic Diagram of GE-CRD's High Temperature, High Pressure Microreactor

The exhaust gases were analyzed for  $\text{NH}_3$  using a gas chromatograph equipped with both a photo-ionization detector (PID) and flame ionization detector (FID). The PID was used for  $\text{NH}_3$  analysis and the FID for  $\text{CH}_4$  analysis. When needed, a second gas chromatograph equipped with a flame photometric detector (FPD) was used for  $\text{H}_2\text{S}$  analysis. With the GC/PID (with a Chromosorb 103 packed column), the lower detectable limit of  $\text{NH}_3$  was 50-75 ppm. The present study did not focus on the mechanisms of  $\text{H}_2\text{S}$  adsorption onto the sorbent because the zinc titanate base material has been studied extensively as a desulfurization sorbent in other parallel studies.

## 2.3 RESULTS OF MICROREACTOR SCREENING TESTS

The objective of the initial microreactor tests was to screen various catalyst formulations based solely on their measured catalytic activities towards  $\text{NH}_3$  decomposition. It was intended that other methods for better characterization of sorbent-catalyst materials (i.e., determine dispersion of Mo in the zinc titanate, surface area determination, etc.) would be made only if the materials displayed sufficient activity towards  $\text{NH}_3$  decomposition to justify such extended work.

### 2.3.1 Co-Mo-zinc titanate

Co and Ni are commonly used to promote the activity of  $\text{MoS}_2$  desulfurization and denitrification catalysts. Sorbent-catalyst samples of zinc titanate doped with cobalt-molybdenum were prepared by first crushing and sieving pellets of zinc titanate sorbents (United Catalyst, Inc., formulation L-3774M). The zinc titanate powders were then placed in an aqueous solution having the desired total amount of molybdenum (in the form of molybdic acid). The water was then dried and the powder heated and calcined. To add cobalt to the Mo-coated powder, the powder was then placed into a solution of cobalt nitrate containing the appropriate amount of the cobalt precursor followed by drying and calcination. The samples were then activated (presulfided) by introducing  $\text{H}_2\text{S}$  in a controlled reducing environment (typically 1%  $\text{H}_2\text{S}$ , 5%  $\text{H}_2$ , balance Ar, at 300 °C). The final catalyst, which consisted of cobalt and molybdenum impregnated onto the zinc titanate material, was labeled Co-Mo-zinc titanate.

Using a gas mixture of 1800 ppm  $\text{NH}_3$  and a space velocity of 4000  $\text{h}^{-1}$ , the catalytic decomposition of  $\text{NH}_3$  was measured over Co-Mo-zinc titanate. The gas mixture contained 38.6%  $\text{CO}$ , 29.5%  $\text{H}_2$ , 13.1%  $\text{CO}_2$ , and balance Ar. The test results are presented in Figure 2.3.1-1 and show that  $\text{NH}_3$  decomposition occurred. As the reaction temperature was increased from 350 °C to 725 °C, outlet  $\text{NH}_3$  levels decreased from ~1800 ppm to 1200-1300 ppm. The effect that  $\text{H}_2\text{S}$  would have on the catalytic reaction was examined by adding 0.75%  $\text{H}_2\text{S}$  to the gas mixture. The data in Figure 2.3.1-1 show that after exposing the catalyst to  $\text{H}_2\text{S}$  (at 725 °C), the measured effluent  $\text{NH}_3$  concentration first increased and then decreased. Finally, the  $\text{NH}_3$  concentration leveled

off near 1100 ppm. The cause for the transient increase/decrease in  $\text{NH}_3$  concentration following the addition of  $\text{H}_2\text{S}$  was not clear although it is believed to be related to the accidental introduction of some oxygen (air) in the  $\text{H}_2\text{S}$  supply line when  $\text{H}_2\text{S}$  was introduced. By taking care to purge air from the  $\text{H}_2\text{S}$  lines (and gas regulator) prior to use, the transient response in  $\text{NH}_3$  levels was eliminated in subsequent tests. Although high  $\text{NH}_3$  destruction levels were not measured with this catalyst, the results showed that at  $725^\circ\text{C}$ , the catalytic activity of Co-Mo-zinc titanate towards  $\text{NH}_3$  decomposition was not inhibited by the presence of 0.75%  $\text{H}_2\text{S}$  in the gas mixture.

### 2.3.2 Ni-Mo-zinc titanate

As stated previously, both Co and Ni are used to promote the activity of  $\text{MoS}_2$  hydrodesulfurization and hydrodenitrification catalysts. The effect of Ni added to a Mo coated zinc titanate for  $\text{NH}_3$  decomposition was studied next. Samples of nickel-molybdenum-zinc titanate were prepared in a similar manner as described above (Section 2.3.1) for the preparation of Co-Mo-zinc titanate but by using Ni nitrate instead of Co nitrate.

Data for the Ni-Mo-zinc titanate catalyst were taken under the same conditions as in the tests with Co-Mo-zinc titanate (at  $725^\circ\text{C}$ ; 1 atm; space velocity of  $4000\text{ h}^{-1}$ ; gas composition of 1800 ppm  $\text{NH}_3$ , 38.6%  $\text{CO}$ , 29.5%  $\text{H}_2$ , 13.1%  $\text{CO}_2$ , and balance Ar). The data is presented in Figure 2.3.2-1 and show that although there was considerable noise in this data, the data showed that Ni-Mo-zinc titanate exhibited little or no activity towards  $\text{NH}_3$  decomposition.

### 2.3.3 Co-Mo-Al-zinc titanate

Data taken with the previous two sorbent-catalyst formulations (Co-Mo-zinc titanate and Ni-Mo-zinc titanate) showed Co-Mo-zinc titanate to be more effective towards the catalytic decomposition of  $\text{NH}_3$  when compared to Ni-Mo-zinc titanate. To further study the cobalt-molybdenum zinc titanate system, alumina (Al) was added to the Co-Mo-zinc titanate sorbent-catalyst formulation because alumina is typically used as the catalyst support for  $\text{MoS}_2$  hydrodesulfurization and hydrodenitrification catalysts and may provide beneficial catalyst-support interactions. The catalyst was prepared in a similar manner as described for Co-Mo-zinc titanate.

The data presented in Figure 2.3.3-1 show that  $\text{NH}_3$  concentrations at the reactor outlet decreased from 1700-1800 ppm at  $350^\circ\text{C}$  to approximately 1500-1600 ppm over the Co-Mo-Al-zinc titanate when the temperature was increased to  $725^\circ\text{C}$ . Figure 2.3.3-1 also shows that the catalytic activity of the Co-Mo-Al-zinc titanate sorbent-catalyst toward the  $\text{NH}_3$  decomposition reaction improved significantly when the temperature was further increased to  $775^\circ\text{C}$  ( $\text{NH}_3$  levels were reduced to 700 ppm to achieve a 61% conversion).