

# Advances in Ammonia Removal from Hot Coal Gas

K. Jothimurugesan (jothi@et.hamptonu.edu; 804-727-5817)  
Department of Chemical Engineering  
Hampton University, Hampton, VA 23668.

Santosh K. Gangwal (skg@rti.org; 919-541-8033)  
Research Triangle Institute  
3040 Cornwallis Road  
Research Triangle Park, NC 27709.

## Introduction

Nitrogen occurs in coal in the form of tightly bound organic ring compounds, typically at levels of 1 to 2 wt%. During coal gasification, this fuel bound nitrogen is released principally as ammonia ( $\text{NH}_3$ ). When hot coal gas is used to generate electricity in integrated gasification combined cycle (IGCC) power plants,  $\text{NH}_3$  is converted to nitrogen oxides ( $\text{NO}_x$ ) which are difficult to remove and are highly undesirable as atmospheric pollutants. Similarly, while the efficiency of integrated gasification molten carbonate fuel cell (IGFC) power plants is not affected by  $\text{NH}_3$ ,  $\text{NO}_x$  is generated during combustion of the anode exhaust gas. Thus  $\text{NH}_3$  must be removed from hot coal gas before it can be burned in a turbine or fuel cell.

The product stream from a high-temperature, oxygen-blown gasifier, such as Texaco, contains about 2,000 ppmv of  $\text{NH}_3$ , where as higher concentrations (about 5,000 ppmv) occur when the gasification is conducted at lower temperatures, such as in the Lurgi or GE air-blown gasifier. A range of 1,500 to 3,000 ppmv is considered for this study.

Removal of  $\text{H}_2\text{S}$  using zinc-based mixed-metal oxide sorbents, particularly zinc titanate, to <20 ppmv levels has been well established (Lew et al., 1989; Jothimurugesan and Harrison, 1990; Woods et al., 1990; Gupta and Gangwal, 1993; Jothimurugesan et al., 1995). A previous study indicated that nickel-based catalysts have high activities for  $\text{NH}_3$  decomposition (Krishnan et al., 1988). If desulfurization sorbents such as zinc titanate could be used along with the  $\text{NH}_3$  decomposition catalysts to decompose ammonia present in hot coal gas, then the number of unit processes necessary to clean hot coal gas could be reduced by one. Simultaneous removal of both  $\text{H}_2\text{S}$  and  $\text{NH}_3$  in one process unit would reduce the capital and operating costs of electric power generation from coal.

## Objectives

The objective of this study is to develop a successful combination of an  $\text{NH}_3$  decomposition catalyst with a zinc-based mixed-metal oxide sorbent so that the sorbent-catalyst activity remains stable for  $\text{NH}_3$  decomposition in addition to  $\text{H}_2\text{S}$  removal under cyclic sulfidation-regeneration conditions in the temperature range of 500 to 750 °C.

## Approach

A number of zinc-based sorbents will be prepared in combination with  $\text{NH}_3$  decomposition catalysts. The catalyst candidates include Ni, Co, Mo, and W. Sorbent-catalyst formulations will be screened for  $\text{NH}_3$  decomposition activity and  $\text{H}_2\text{S}$  adsorption reactivity in a fixed-bed reactor using simulated coal gas at 1 to 20 atm and 500 to 750 °C. One of the superior formulations will be tested for long-term durability over at least 30 cycles.

## Project Description

### Experimental

**Sorbent-Catalyst Preparation** . A highly promising method was recently developed in cooperation with a commercial catalyst vendor under this project to prepare suitable sorbent-catalysts. The catalyst vendor provided the required input to keep the preparation procedure on a commercial track by making sure that the techniques used were scalable. Several sorbent-catalysts were prepared using this proprietary technique. The following analytical techniques were used to characterize sorbent-catalysts: (1) X-ray Diffraction (XRD) for the crystalline phase; (2) the standard BET method for surface area measurement; (3) Hg-porosimetry for pore volume, bulk density, average pore diameter and pore size distribution determination; and (4) Atomic Absorption (AA) Spectrometry for elemental composition analysis.

**Experimental Setup** . The materials prepared were tested in a laboratory-scale, high-pressure and high-temperature fixed-bed reactor. Briefly, the experimental setup consisted of a gas delivery system, a fixed-bed reactor, and a gas analysis system. Using the gas delivery system, a simulated fuel gas of any desired composition could be generated with the help of bottled gases, a set of mass flow controllers, and a high-pressure syringe pump. Steam was added to the mixed dry gas by vaporizing liquid water injected into the gas stream at a controlled rate by a high-pressure syringe pump.  $\text{NH}_3$  was added to the gas mixture downstream of the generator where the temperature was high enough to avoid the formation of ammonium carbonates or sulfides. The reactor was constructed of a 316 stainless steel pipe. Inside the pipe there was a removable 316 stainless steel 1.0 cm I.D. tube with a porous alumina plate at the bottom that acted as a gas distributor. The inside of the tube was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The pressure inside the reactor was controlled by a back pressure regulator and measured by an electronic pressure sensor. The thermocouples were positioned to measure the temperatures of the preheated feed gas, the reactor bed, and the product gas. The tests with sorbent-catalyst were conducted with a simulated gas containing 10%  $\text{H}_2$ , 15%  $\text{CO}$ , 5 mol%  $\text{CO}_2$ , 1 mol%  $\text{H}_2\text{S}$ , 15 mol%  $\text{H}_2\text{O}$ , 0.18%  $\text{NH}_3$ , and balance  $\text{N}_2$ . The outlet

H<sub>2</sub>S and SO<sub>2</sub> concentrations were monitored using detector tubes and gas chromatography. The outlet NH<sub>3</sub> concentration was measured using ion selective electrodes and ion chromatography.

A typical run consisted of loading about 1.0 g of the sorbent in a particle size range of -32+ 64 mesh and heating the reactor to a desired temperature of 500 to 750 °C with continuous flow of nitrogen. Once the desired temperature was attained, the flow of fuel gas to the reactor was started and the concentration of H<sub>2</sub>S and NH<sub>3</sub> were measured intermittently in the effluent gas. When the H<sub>2</sub>S concentration reached 300 ppmv, indicating breakthrough, the sulfidation was stopped and the system was prepared for regeneration. The regeneration of sulfided material was carried out at the desired temperature ranging between 500 to 750 °C with 2 to 4 % oxygen in nitrogen. In all runs, the space velocity used was in the range of 2,000-3,000 h<sup>-1</sup>. The regeneration of the sulfided material was carried out until the SO<sub>2</sub> concentration in the reactor effluent dropped below 50 ppm. These sulfidation-regeneration cycles were repeated as many times as desired. Typically each material was tested for 5 to 10 cycles to obtain meaningful data on material durability. At the end of the 5- to 10-cycle run, the material was removed from the reactor and physical and chemical characterizations were carried out on the reacted material to determine changes due to reaction.

## Results

The extent of NH<sub>3</sub> decomposition in a simulated coal gas was determined for several proprietary sorbent-catalyst formulations. The following simulated gas was used in this study, to test the sorbent-catalyst: 10% H<sub>2</sub>, 15% CO, 5% CO<sub>2</sub>, 1% H<sub>2</sub>S, 15% H<sub>2</sub>O, 0.18% NH<sub>3</sub>, and balance N<sub>2</sub> (mol%). The gas hourly space velocity was about 2500 h<sup>-1</sup> in both sulfidation and regeneration. Regeneration between cycles was conducted with 10 mol% air-90 mol% N<sub>2</sub> at 700 °C.

Nickel-containing zinc-based sorbent-catalysts were the initial sorbent-catalysts tested. Figure 1 shows the ammonia decomposition activity of various sorbent-catalysts tested. As seen in Figure 1, HART-38 sorbent-catalyst showed a very high activity (>90%) for about 40 min. After that, the decline in activity was mainly due to the poisoning of the catalyst by H<sub>2</sub>S. In order to increase this 90% decomposition time window, various catalyst additives were tested. Catalysts containing Ni, Co, Mo, and W compounds were candidates for this study. As seen from Figure 1, the window increased from 40 min for HART-38 to about 150 min for HART-49 sorbent-catalyst. The ammonia decomposition activity increased as the temperature was increased from 500 to 700 °C. As shown in Figure 2, however, even at 500 °C, >90% decomposition activity was maintained for nearly 70 minutes.

Life-cycle testing, consisting of 30 cycles of sulfidation, ammonia decomposition, and regeneration was successfully performed on the HART-49 sorbent-catalyst to demonstrate its long-term durability and reactivity. As shown in Figure 3, up to 180 min the sorbent-catalyst showed a very high activity (>90%). The decline in activity after 180 min is mainly due to the poisoning of the catalyst by H<sub>2</sub>S. The pre-breakthrough H<sub>2</sub>S level was below 20 ppm (not shown in figure). Nearly complete sorbent conversion (100%) was observed at breakthrough.

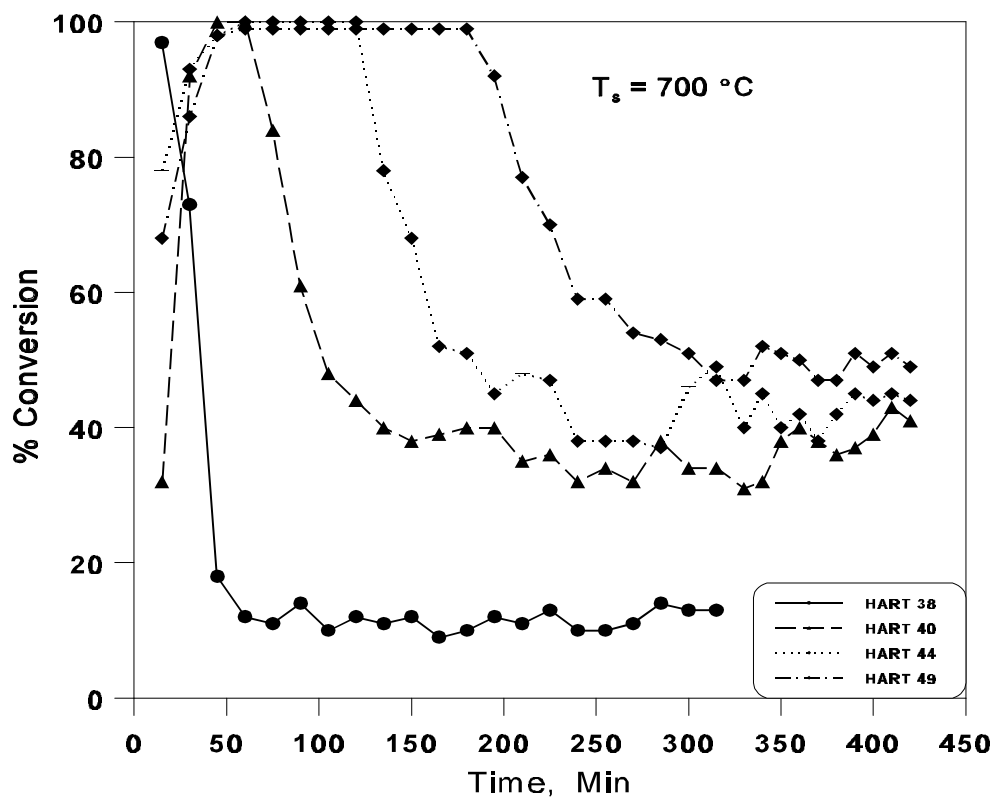


Figure 1. Conversion of Ammonia on HART Sorbent-Catalysts

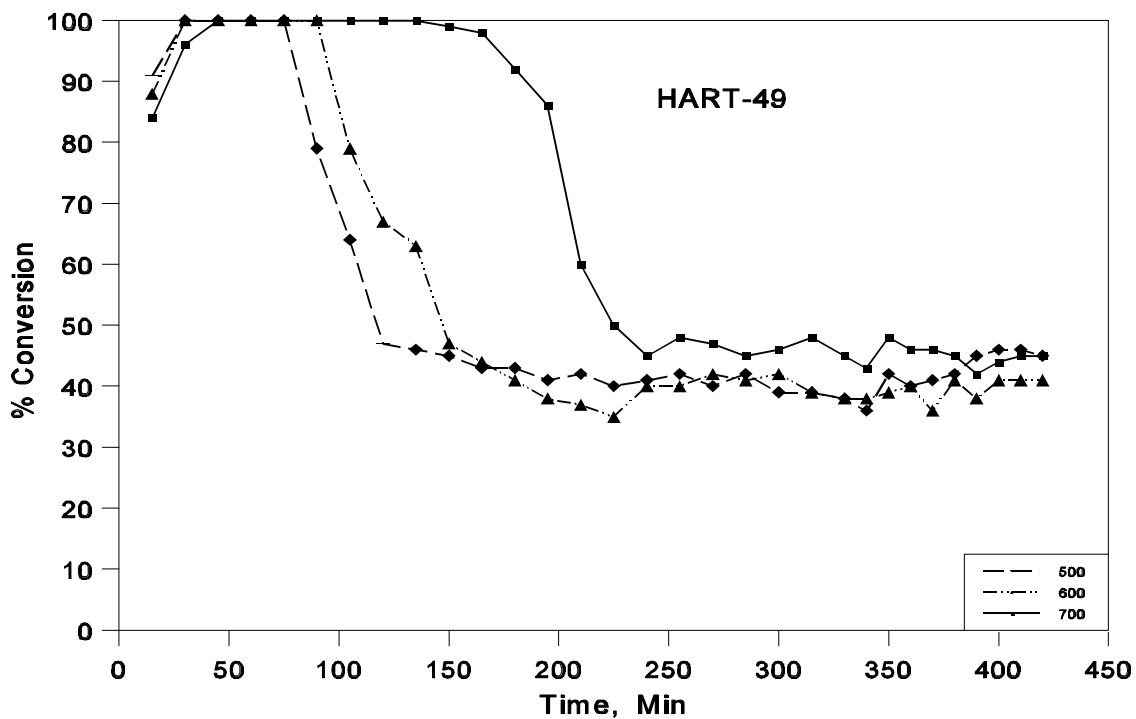


Figure 2. Effect of Temperature on the Activity of HART-49 Sorbent-Catalysts

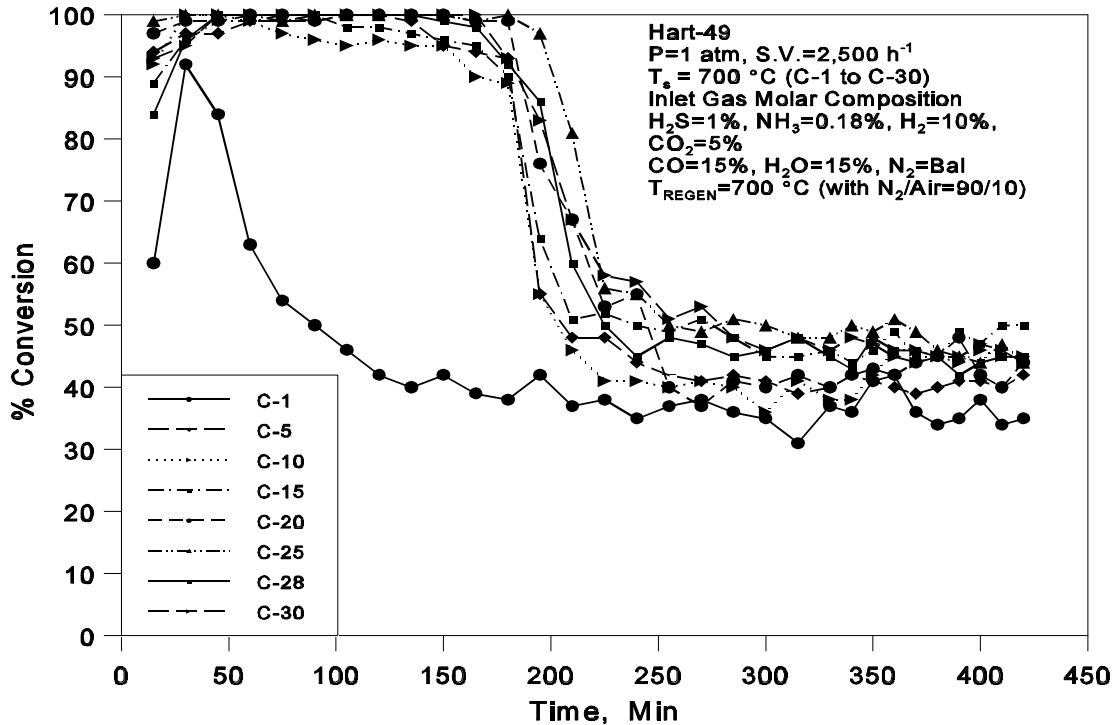


Figure 3. Conversion of NH<sub>3</sub> on HART-49 Sorbent-Catalyst at 700 °C

The 30-cycle test showed that HART-49 sorbent-catalyst developed under this project exhibited superior NH<sub>3</sub> decomposition activity, sulfur adsorption reactivity, and regenerability.

### Application

Nickel-based-catalysts containing zinc-based sorbents have a moderate activity for NH<sub>3</sub> decomposition at 500 to 700 °C in simulated coal gas streams. The sorbent-catalysts prepared to date consistently removed 99% or more of the H<sub>2</sub>S from a simulated coal gas containing 1% H<sub>2</sub>S and were regenerable for multicycle operation. A superior HART-49 formulation demonstrated quite reasonable NH<sub>3</sub> decomposition activity in presence of 1% H<sub>2</sub>S even at temperatures as low as 500 °C. By using the HART-49 formulation, simultaneous H<sub>2</sub>S removal and NH<sub>3</sub> decomposition may become viable at practical IGCC temperatures as low as 500 °C (932 °F). Carrying out these steps simultaneously could result in reduced operating and capital costs of the IGCC plant.

## Acknowledgments

The authors would like to gratefully acknowledge the guidance and assistance of Dr. Kamalendu Das, the Morgantown Energy Technology Center Contracting Officer's Representative. Research Triangle Institute provided subcontract support to the project. The period of performance is from September 2, 1993 to September 1, 1996.

## References

Gupta, R. and S.K. Gangwal, "Fluidizable Zinc Titanate Materials with High Chemical Reactivity and Attrition Resistance," U.S. Patent 5,254,516, 1993.

Jothimurugesan, K, A.A. Adeyiga, and S.K. Gangwal, "Simultaneous Removal of H<sub>2</sub>S and NH<sub>3</sub> from Hot Coal Gas," Twelfth Annual International Pittsburgh Coal Conference Proceedings, pp. 1201-1206, September 11-15, 1995.

Jothimurugesan, K. and D.P. Harrison, "The Reaction Between H<sub>2</sub>S and Zinc Oxide-Titanium Oxide Sorbents: II. Single Pellet Sulfidation Modeling," *Ind. Eng. Chem. Res.*, 29,1167(1990).

Krishnan, G.N., B.J. Wood, G.T. Tong, and J.G. McCarty, "Study of Ammonia Removal in Coal Gasification Processes," Final Report to U.S. DOE/METC. Contract Number DE-AC21-86MC23087, 1988.

Lew, S., K. Jothimurugesan, and M. Flytzani-Stephanopoulos, "High-Temperature H<sub>2</sub>S Removal from Fuel Gases by Regenerable Zinc Oxide -Titanium Dioxide Sorbents," *Ind. Eng. Chem. Res.*, 28,535(1989).

Woods, M.C., S.K. Gangwal, K. Jothimurugesan, and D.P. Harrison, "The Reaction Between H<sub>2</sub>S and Zinc oxide-Titanium Oxide Sorbents: I. Single Pellet Kinetic Studies," *Ind. Eng. Chem. Res.*, 29,1160(1990).