

Final Report • March 1996

# **SIMULTANEOUS REMOVAL OF HYDROGEN SULFIDE AND AMMONIA USING MIXED- METAL OXIDE SORBENTS**

G. N. Krishnan

SRI Project PYD-4151

Prepared for:  
Research Triangle Institute  
Center for Process Research  
P. O. Box 12194  
Research Triangle Park, NC 27709-2194

Attention: Dr. Raghubir Gupta

RTI Contract No. 1-96U5436  
DOE Prime Contract No.: DE-AC21-92MC29011

Approved  
Thomas R. Podoll, Director  
Materials and Chemical Engineering Laboratory

David M. Golden  
Senior Vice President  
Science and Technology Group

**DRAFT**

## SUMMARY

During coal gasification, nitrogen compounds in the coal are primarily converted to  $\text{NH}_3$  and when the coal gas is burnt in a gas turbine to produce electricity  $\text{NH}_3$  is converted to nitrogen oxides. To minimize the formation of these toxic pollutants, removal of  $\text{NH}_3$  from coal gas stream is desirable. Development of sorbents for the removal of  $\text{H}_2\text{S}$  at high temperatures is being actively pursued. Combining removal of both  $\text{H}_2\text{S}$  and  $\text{NH}_3$  in one process unit will reduce the capital and operating costs of coal gas generation.

Catalytic decomposition of  $\text{NH}_3$  into its elements  $\text{N}_2$  and  $\text{H}_2$  is desirable and thermodynamic calculations indicate that decomposition can reduce the level of  $\text{NH}_3$  at temperatures above 900 K. Conventional ammonia decomposition catalysts cannot be used under hot coal gas conditions because  $\text{H}_2\text{S}$  and steam present in the hot coal gas stream act as poisons for these catalysts. Hence, novel catalysts must be developed that can function in steam concentrations greater than 10% and  $\text{H}_2\text{S}$  levels greater than 0.5%. Combining both desulfurization sorbent and  $\text{NH}_3$  decomposition catalyst in the same unit requires that the catalyst not only function in the presence of  $\text{H}_2\text{S}$  but also should survive the oxidative regeneration of the desulfurization sorbent.

In this program, SRI tested several metal-supported catalysts in combination with a zinc titanate sorbent for removing both  $\text{NH}_3$  and  $\text{H}_2\text{S}$  from simulated coal gas streams. Thermodynamic equilibrium calculations were made to determine the stability of the active metal phases in hot coal gas environments and under oxidative regeneration conditions. These calculations indicated that metals like Mo and W will be converted to their corresponding sulfides when exposed to typical coal gas streams. The calculations also showed that only molybdenum oxides have significantly high vapor pressures ( $>1 \times 10^{-4}$  atm) at temperatures above  $725^\circ\text{C}$  to be of a concern. Other oxides such as  $\text{CoO}$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{NiO}$ , and  $\text{W}_2\text{O}_6$  have very low vapor pressures ( $<1 \times 10^{-12}$  atm). Loss of active components by vaporization will not be a problem except in the case of molybdenum.

Alumina, a commonly used catalyst support, could be converted to aluminum sulfate when exposed to  $\text{SO}_2$  and  $\text{O}_2$  present during oxidative regeneration of the spent sorbent. Aluminum sulfate is easily more sinterable than alumina. Thus, it could be expected that the surface area of an

alumina-based catalyst could decrease during cyclic sulfidation-regeneration steps. Oxides such as titania and zirconia are less prone to sulfation than alumina.

Experiments showed that a high surface area ( $>250 \text{ m}^2/\text{g}$ )  $\text{TiO}_2$  powder obtained from Rhone-Poulenc sintered when exposed to a gas stream containing 20% steam at  $725^\circ\text{C}$ . The surface area decreased from about  $280 \text{ m}^2/\text{g}$  to about  $15 \text{ m}^2/\text{g}$  in 24 h. When the titania was intimately mixed with zirconia, the reduction in surface area was much less severe; after 24 h in 20% steam, the surface area was about  $30 \text{ m}^2/\text{g}$ .

SRI identified in a previous program that HTSR-1, a supported Ni catalyst proprietary to Haldor-Topsøe A/S, Copenhagen, Denmark, exhibited excellent activity for  $\text{NH}_3$  decomposition at a temperature of  $800^\circ\text{C}$  even in the presence of 2,000 ppm of  $\text{H}_2\text{S}$ . It also had a superior high temperature stability. Experiments conducted in this program confirmed these observations. At temperatures lower than  $800^\circ\text{C}$ , the steady-state  $\text{NH}_3$  decomposition activity was a function of  $\text{H}_2\text{S}$  concentration. At  $725^\circ\text{C}$ , the catalyst was severely poisoned when exposed to 0.5%  $\text{H}_2\text{S}$ . Mixing the catalyst with a zinc titanate sorbent allowed the catalysts to function for an extended period of time. As the sorbent gets loaded with  $\text{H}_2\text{S}$ , the residual  $\text{H}_2\text{S}$  level increases thereby decreasing the activity of the catalyst for  $\text{NH}_3$  decomposition. The HTSR-1 catalyst could be regenerated by oxidizing in a gas stream containing 2%  $\text{O}_2$ . However, the activity of the regenerated catalyst was less than the original catalyst.

About ten catalytic formulations were synthesized using either Ni, Co, Mo, and W as active components and titania or titania stabilized with zirconia as supports. Both single and dual active component mixtures were prepared. These catalysts were tested at  $725^\circ\text{C}$  in a simulated coal gas mixture representative of a Texaco oxygen-blown gasifier. Although the initial activity of some of these catalysts was high, it declined with time. Under steady-state conditions, less than 20% the feed  $\text{NH}_3$  ( $\sim 1800 \text{ ppm}$ ) decomposed at  $725^\circ\text{C}$ .

The following recommendations are made for further investigation into the removal of fuel-bound nitrogen from hot coal gas streams.

- The HTSR-1 should be tested using hot coal gas streams from an operating coal gasifier. The effects of trace components of the hot coal gas stream that could not be simulated in the laboratory must be determined.
- Alternative catalysts that have a high  $\text{NH}_3$  decomposition activity at a temperature of about  $550^\circ\text{C}$  in the presence of  $\text{H}_2\text{S}$  must be developed.

- The regeneration of sulfur-poisoned HTSR-1 must be investigated. Although this catalyst can tolerate significant levels of H<sub>2</sub>S at 800°C, it is slowly poisoned at low temperatures. Regeneration of the catalyst will allow continued use of this catalyst in a hot coal gas cleanup process.

## CONTENTS

SUMMARY .....	ii
ILLUSTRATIONS .....	vi
TABLES .....	viii
INTRODUCTION .....	1
Fuel-Bound Nitrogen Compounds .....	1
Previous Studies .....	2
Simultaneous Removal of Ammonia and Hydrogen Sulfide .....	3
Scope of the Report .....	6
THERMODYNAMIC CALCULATIONS .....	7
EXPERIMENTAL PROCEDURE .....	16
Fixed-Bed Reactor System .....	16
Preparation of Catalysts .....	20
RESULTS AND DISCUSSION .....	24
Baseline Catalysts .....	24
Nickel on Titania Catalysts .....	33
Cobalt on Titania Catalysts .....	33
Molybdenum on Titania Catalysts .....	36
Cobalt and Molybdenum on Titania Catalysts .....	39
Tungsten Oxide-Zinc Titanate Catalysts .....	48
CONCLUSIONS AND RECOMMENDATIONS .....	51
REFERENCES .....	52
APPENDIX A: THERMODYNAMIC CALCULATIONS OF THE VAPORIZATION OF METAL OXIDES .....	A-1

## ILLUSTRATIONS

1. Equilibrium concentration of ammonia as a function of temperature and pressure in a Texaco coal gasifier gas stream .....	8
2. Equilibrium levels of ammonia as a function of temperature and pressure in GPIF's air-blown gasifier stream .....	9
3. Stability of molybdenum sulfides in hydrogen .....	11
4. Stability of tungsten sulfides in hydrogen .....	12
5. Schematic diagram of the fixed-bed reactor system .....	17
6. Calibration of photoionization detector for NH <sub>3</sub> gas .....	18
7. Calibration of flame photometric detector for H <sub>2</sub> S gas .....	19
8. Change in surface area of a titania support as a function of time at 725°C .....	22
9. The conversion of NH <sub>3</sub> on HTSR-1 catalyst at 725°C in a simulated Texaco gasifier stream .....	25
10. Conversion of NH <sub>3</sub> on HTSR-1 catalyst at 800°C in a simulated Texaco gasifier stream .....	26
11. The conversion of NH <sub>3</sub> on HTSR-1 placed downstream of a zinc titanate bed .....	27
12. The conversion of ammonia on ZT-4T sorbent and HTSR-1 catalyst mixed together ..	29
13. The conversion of NH <sub>3</sub> on a regenerated HTSR-1 mixed with ZT-4 sorbent in a simulated Texaco gasifier stream .....	30
14. Decomposition of NH <sub>3</sub> over HTSR-1 catalyst at 725°C in a simulated coal gas stream	31
15. The conversion of NH <sub>3</sub> and H <sub>2</sub> S on CRC-653 catalyst in a simulated Texaco gasifier stream .....	32
16. Decomposition of ammonia on a zinc titanate (ZT-4) sorbent at 725°C .....	34
17. The conversion of NH <sub>3</sub> on a Ni-TiO <sub>2</sub> catalyst mixed with ZT-4 sorbent in a simulated coal gas stream at 725°C .....	35
18. Decomposition of ammonia on a 7.7 wt% Mo on titania catalyst at 725°C .....	37
19. Decomposition of ammonia on a 10.8 wt% Mo on titania catalyst at 725°C .....	38

20	The catalytic activity of a Co-Mo/titania catalyst at 725°C .....	40
21.	The catalytic activity of a Co-Mo/titania catalyst at 725°C after sulfidation .....	41
22.	X-ray diffraction spectrum of a Co-Mo-titania catalyst .....	42
23.	AES spectrum of a Co-Mo on titania catalyst .....	43
24.	X-ray diffraction pattern of a reacted Co-Mo catalyst mixed with zinc titanate .....	44
25.	X-ray diffraction pattern of a Co-W-titania catalyst after reaction .....	45
26.	Decomposition of NH <sub>3</sub> over W/TiO <sub>2</sub> at 725°C .....	46
27.	Decomposition of NH <sub>3</sub> over Co-W/TiO <sub>2</sub> at 725°C .....	47
28.	The conversion of NH <sub>3</sub> on RTI #82 catalyst in a simulated coal gas stream at 725° C and 200 psig. ....	49
29.	The conversion of NH <sub>3</sub> on RTI #83 catalyst in a simulated coal gas stream at 725° C and 200 psig. ....	50

## TABLES

1. Product gas composition (vol %) in Texaco and GPIF gasifiers .....	7
2. Calculated equilibrium partial pressures of CH <sub>4</sub> , and H <sub>2</sub> at a total pressure of 20 atm in a Texaco gasifier stream .....	10
3. Equilibrium partial pressures of metal oxide vapors in the presence of 2% O <sub>2</sub> at 625° and 725°C .....	13
4. Calculated partial pressures of species over MoO <sub>3</sub> (c) in presence of pure O <sub>2</sub> at 0.02 atm total pressure .....	14
5. Total pressure of Mo-containing species over MoO <sub>3</sub> (c) + MMoO <sub>4</sub> (c) in the presence of pure O <sub>2</sub> at 0.02 atm total pressure .....	15
6. Surface area changes in TiO <sub>2</sub> and TiO <sub>2</sub> -ZrO <sub>2</sub> powders during exposure to steam at 725°C	23