

Simultaneous Removal of H₂S and NH₃ in Coal Gasification Processes

CONTRACT INFORMATION

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OBJECTIVES

The objective of this study is to develop advanced high-temperature coal gas desulfurization mixed-metal oxide sorbents with stable ammonia decomposition materials at 550-800° C (1022-1472° F). The specific objectives of the project are to:

- (i) Develop a combined sorbent-catalyst materials shall be capable of removing hydrogen sulfide to less than 20 ppmv and ammonia by at least 90 percent.
- (ii) Carry out comparative fixed-bed studies of absorption and regeneration with various formulations of sorbent-catalyst systems and select most promising sorbent-catalyst type.
- (iii) Conduct long-term (at least 30 cycles) durability and chemical reactivity in the fixed-bed with the superior sorbent-catalyst.

BACKGROUND INFORMATION

Nitrogen (N₂) occurs in coal in the form of tightly bound organic ring compounds, typically at levels of 1 to 2 wt% on a dry-ash-free basis. During, coal gasification, this fuel-

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bound nitrogen is released principally as ammonia and nitrogen, with smaller levels of HCN. The formation of NH_3 in a coal gasification processes is a function of the fuel gas composition and the gasifier operating conditions. During the use of coal gas to generate electricity in gas-fired turbines, fuel bound(N_2) is converted to nitrogen oxides(NO_x), which are difficult to remove and are highly undesirable as atmospheric pollutants. Recent results indicate that while the efficiency of molten carbonate fuel cell (MCFC) anodes is not effected by exposure to NH_3 , NO_x is generated during combustion of the anode exhaust gas. Thus, NH_3 must be removed from the coal gas before it is used in IGCC or MCFC applications.

The product stream from a high temperature, oxygen-blown gasifier, such as Texaco, contains about 2000 ppmv of NH_3 , where higher concentrations (about 5000 ppmv) occur when the gasification is conducted at lower temperatures, such as in the Lurgi or GE air-blown gasifier. A range of 1500 to 3000 ppmv is considered for this study.

Removal of H_2S using zinc-based 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,). Previous literature study indicated that catalyst have high activities for NH_3 decomposition (Krishnan et al., 1988). If desulfurization sorbents such as zinc titanate could be used along with the 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.

The objective of this project is to develop successful combination of an NH_3 decomposition catalyst with the mixed-metal oxide sorbent so that the sorbent-catalyst activity remains stable for NH_3 decomposition in addition to H_2S removal under cyclic sulfidation-regeneration conditions in the temperature range of $550\text{-}800^\circ\text{C}$ ($1022\text{-}1472^\circ\text{F}$) and pressures up to 20 atm.

PROJECT DESCRIPTION/RESULTS AND ACCOMPLISHMENTS

The project consists of three major experimental tasks (Tasks 1-3) addressing the contract objectives described above.

Task 1: Sorbent - Catalyst Preparation and Characterization

Task 2: Experimental Testing

Task 3: Cyclic Testing

Task 1: Sorbent-Catalyst Preparation and Characterization

Characterization of HART-36, HART-37 and HART-38 samples was performed using BET and X-ray diffraction analyses (XRD). The BET surface area was increased from 17.4 to 26.7 m²/g with increase in nickel content. The XRD results are shown in Table 1 and Figures 1-3. The fresh sorbent-catalysts predominantly contains Zn₂Ti₃O₈ with very little amount of rutile type TiO₂. Even though there is a strong line for NiO (2.109 Å), it was masked by Zn₂Ti₃O₈.

Table 1. Properties of the sorbent-catalysts

Sorbent ^a -catalyst	Wt% of Ni	BET Surface Area, m ² /g	Crystalline Phases
HART 36	5	17.4	Zn ₂ Ti ₃ O ₈ (99.2 %), TiO ₂ [R](0.8%)
HART 37	10	22.1	Zn ₂ Ti ₃ O ₈ (99.1 %), TiO ₂ [R](0.9%)
HART 38	15	26.7	Zn ₂ Ti ₃ O ₈ (98.7 %), TiO ₂ [R](1.3%)

^a Zn/Ti=1.5

Zinc oxide-based sorbent-catalysts containing 5 % nickel showed moderate catalytic activity for NH₃ decomposition. In order to further improve the catalytic activity for ammonia decomposition, zinc oxide based sorbent-catalysts containing 5 wt % nickel various amounts of cobalt (2.5-10 wt %) was prepared as shown in Table 2.

Table 2. Composition of the sorbent-catalysts

Sorbent*-catalysts	Wt % of	
	Nickel	Cobalt
HART 39	5	2.5
HART 40	5	5
HART 41	5	7.5
HART 42	5	10

* Zn/Ti=1.5

Task 2: Experimental Testing

Currently, we are testing the activities of the sorbent-catalysts prepared above in the fixed bed reactor.

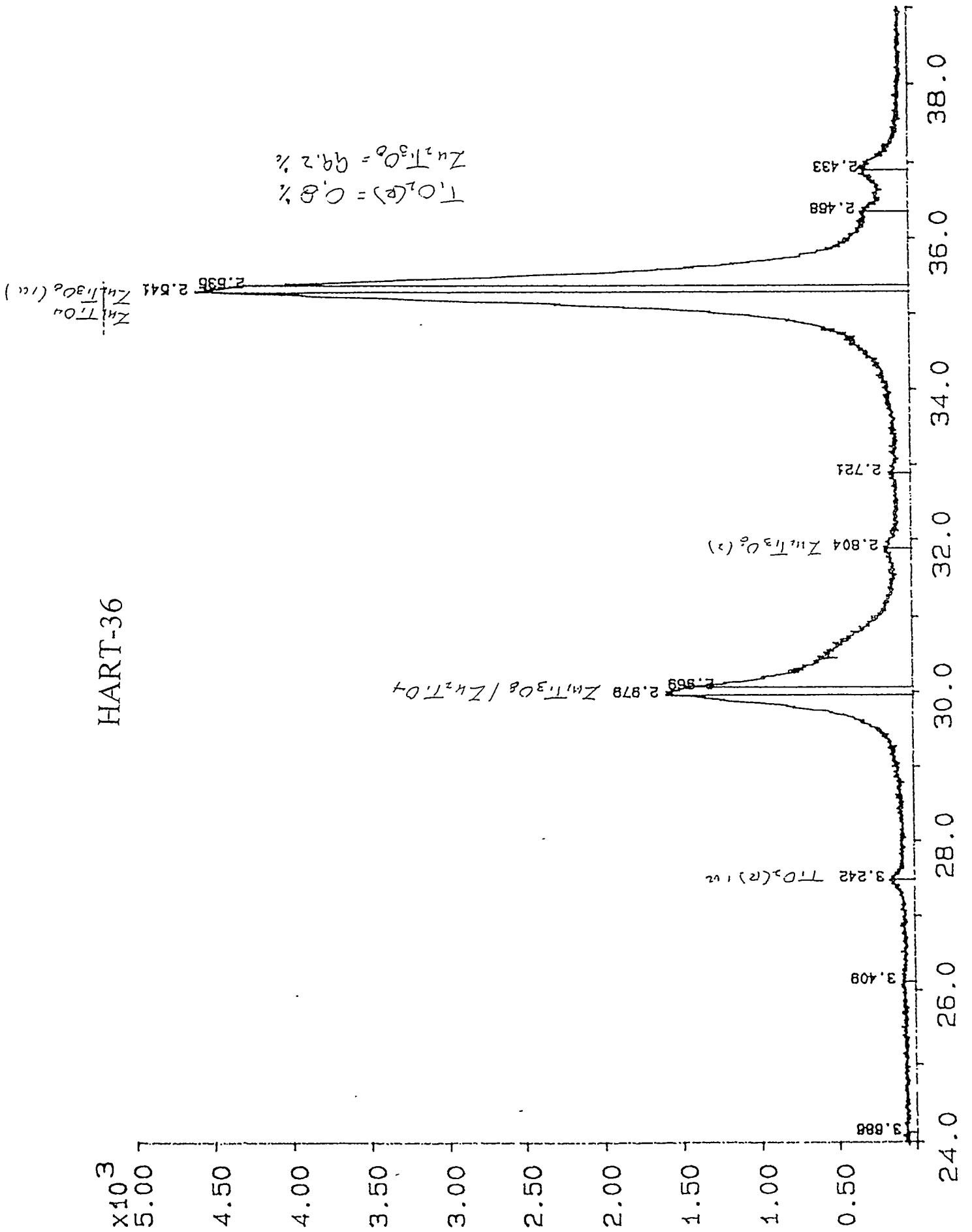
FUTURE WORK

Additional sorbent-catalysts containing Mo and W will be prepared and then it will be tested in the fixed bed reactor.

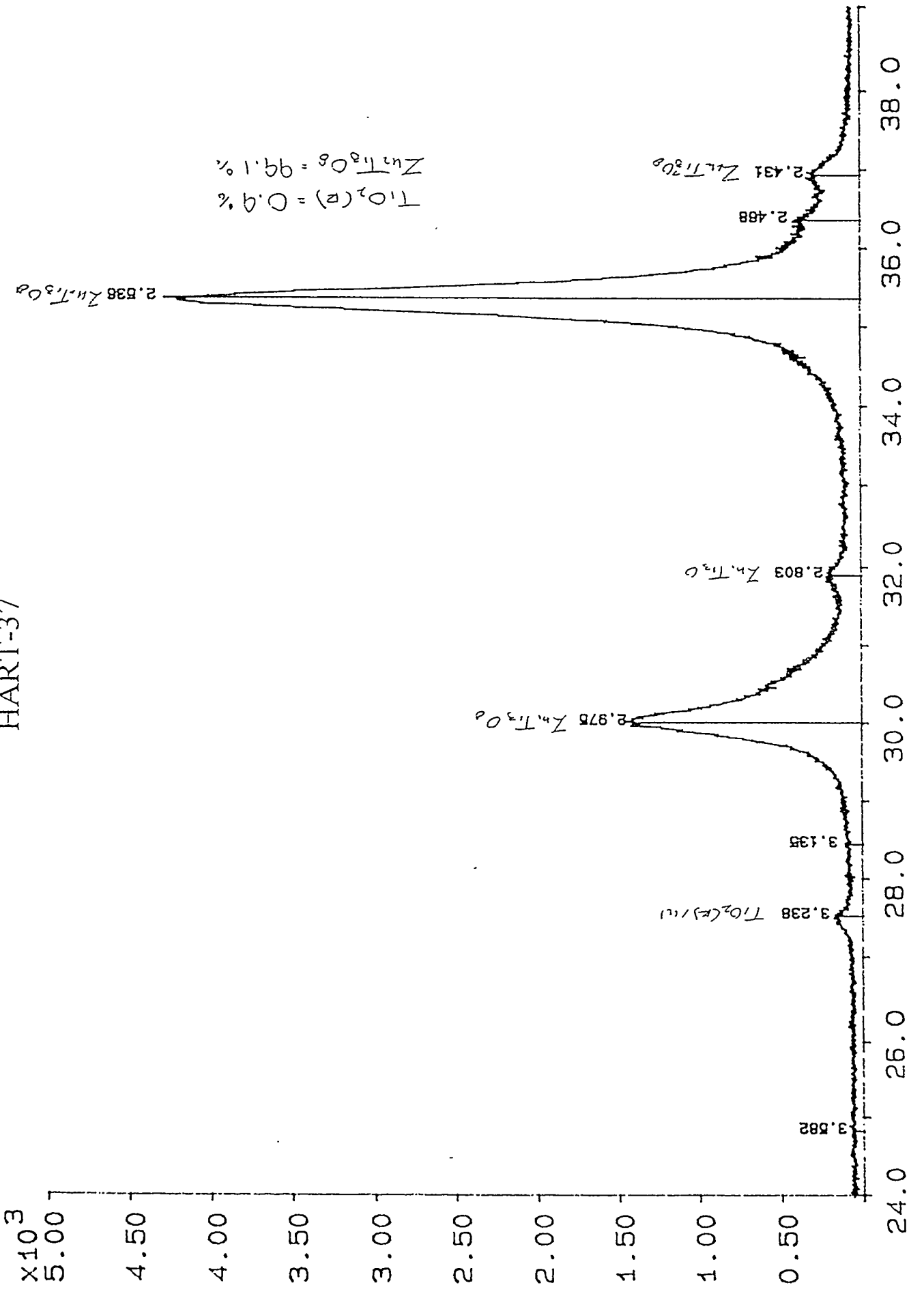
REFERENCES

1. Gupta, R and Gangwal, S.K., "Fluidizable Zinc Titanate Materials with High Chemical Reactivity and Attrition Resistance", U.S. Patent 5,254,516, 1993.
2. Jothimurugesan, K and Harrison, D.P., "The Reaction Between H₂S and Zinc Oxide-Titanium Oxide Sorbents: II. Single Pellet Sulfidation Modelling", Ind.Eng.Chem.Res. 29,1167(1990).
3. Krishnan, G.N., Wood, B.J., Tong, G.T., and McCarty, J.G., "Study of Ammonia Removal in Coal Gasification Processes", Final Report to U.S. DOE/METC. Contract Number DE-AC21-86MC23087, 1988.
4. Lew, S., Jothimurugesan, K and Flytzani-Stephanopoulos, M., "High-Temperature H₂S Removal from Fuel Gases by Regenerable Zinc Oxide -Titanium Dioxide Sorbents", Ind.Eng.Chem.Res. 28,535(1989).
5. Woods, M.C., Gangwal, S.K., Jothimurugesan, K and Harrison, D.P., "The Reaction Between H₂S and Zinc Oxide-Titanium Oxide Sorbents: I. Single Pellet Kinetic Studies", Ind.Eng.Chem.Res. 29,1160(1990).

HART-36



HART-37



HART-38

