

Simultaneous Removal of H₂S and NH₃ in Coal Gasification Processes

DOE/MT/93005-T6

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

Both Task 1 & 2 has been completed.

Task 3: Cyclic Testing

Since HART-49 sorbent-catalysts showed a very promising catalyst activity for ammonia decomposition it was decided to run the multicycle runs using HART-49 sorbent-catalysts.

The HART-49 sorbent-catalyst showed excellent catalytic activity for ammonia decomposition in the 30-multicycle tests as shown in Figure 1. Initially, 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_2S . The pre-breakthrough H_2S level was below 20 ppm as shown in Figure 2. Complete sorbent conversion was observed at breakthrough. The average conversion was increased from 54 to 70 % as the temperature was increased from 500 to 700 °C for HART-49 sorbent-catalysts as shown in Figure 3. Figure 4 shows the scanning electron micrograph of the HART-49 fresh, sulfided and regenerated samples.

FUTURE WORK

Additional multicycle runs will be conducted using HART-51 sorbent-catalysts.

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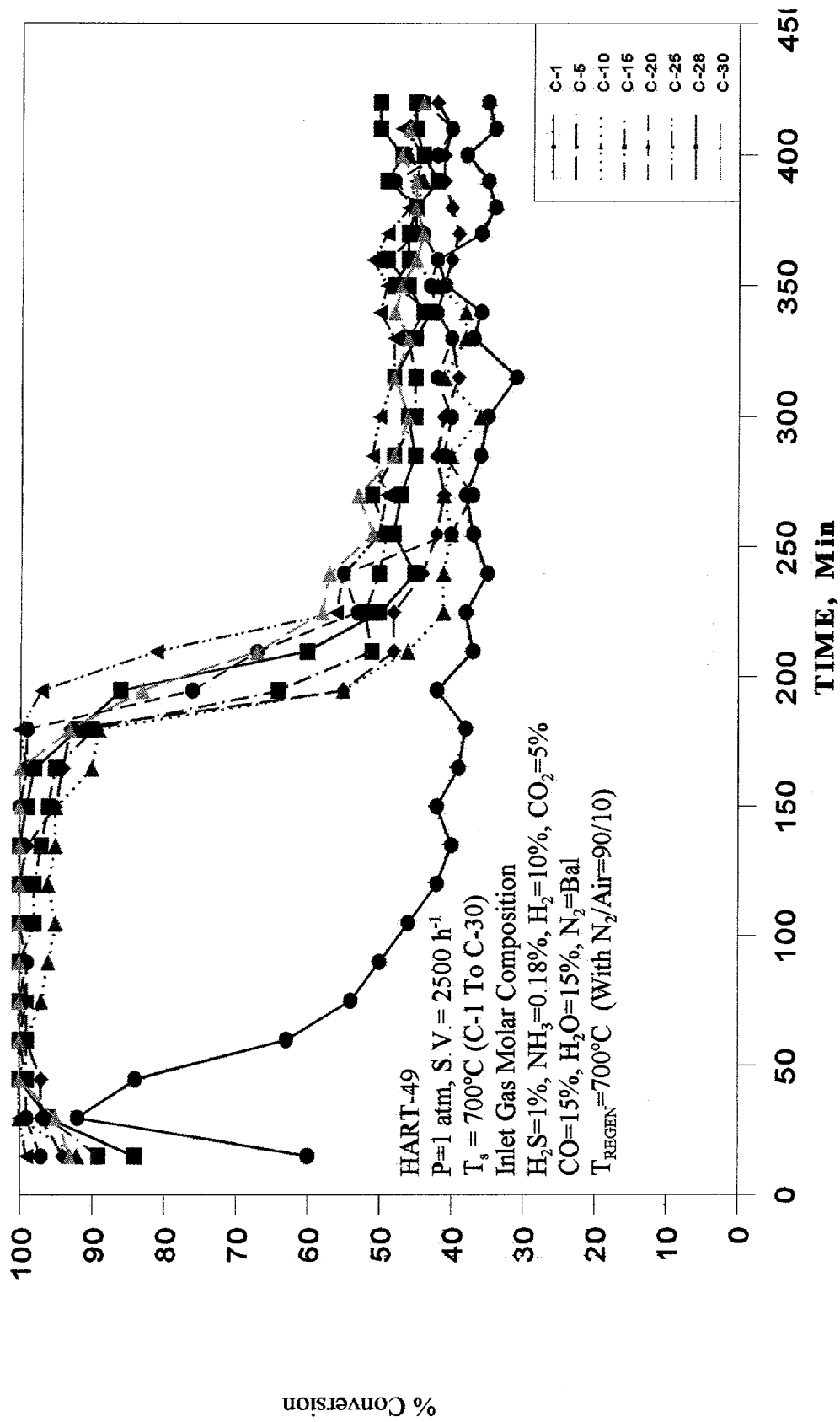


Figure 1. Conversion of ammonia on HART-49 catalyst-sorbents.

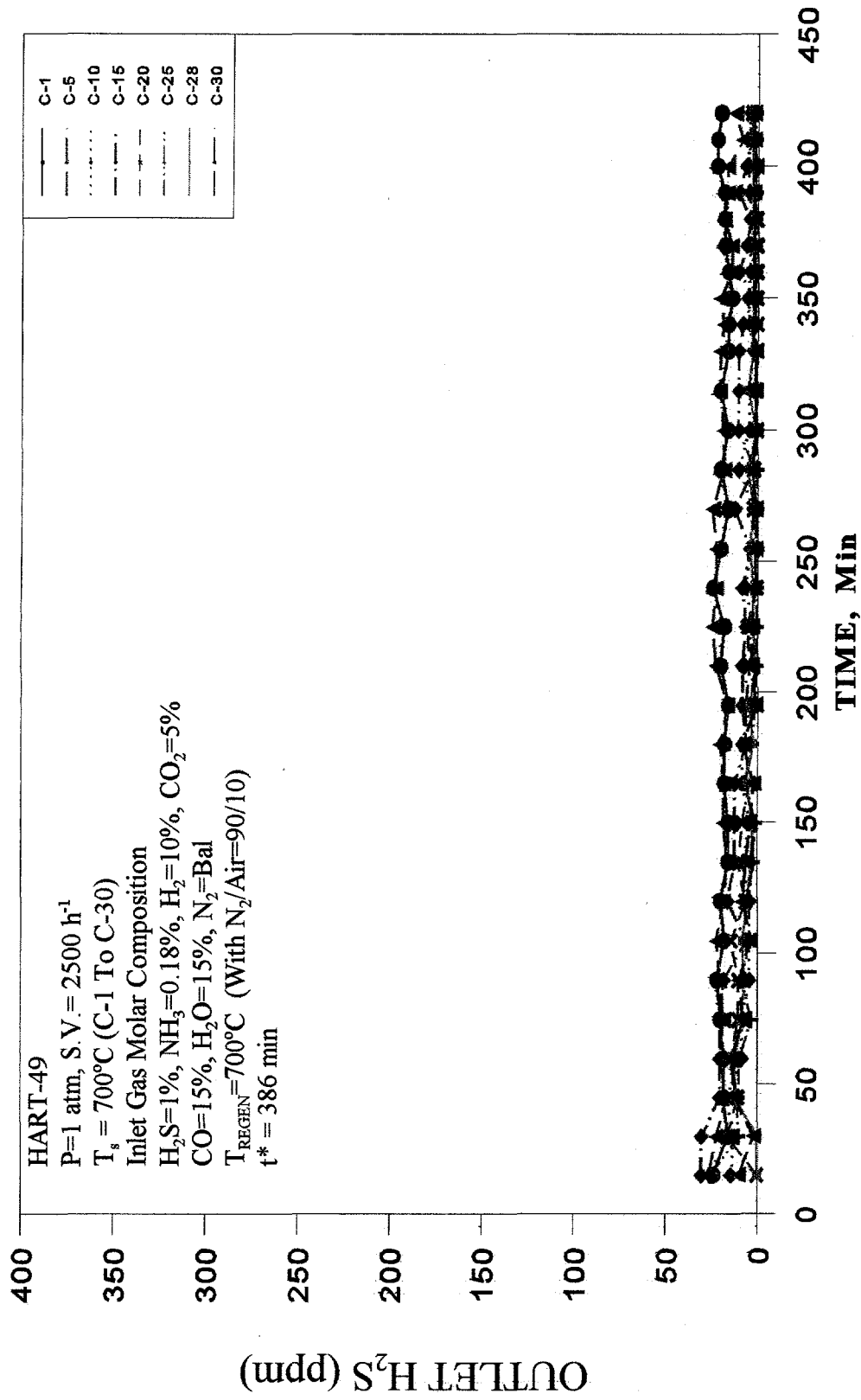


Figure 2. H_2S Breakthrough Curves in Successive Sulfidation Cycles of Sorbent-Catalyst HART-49

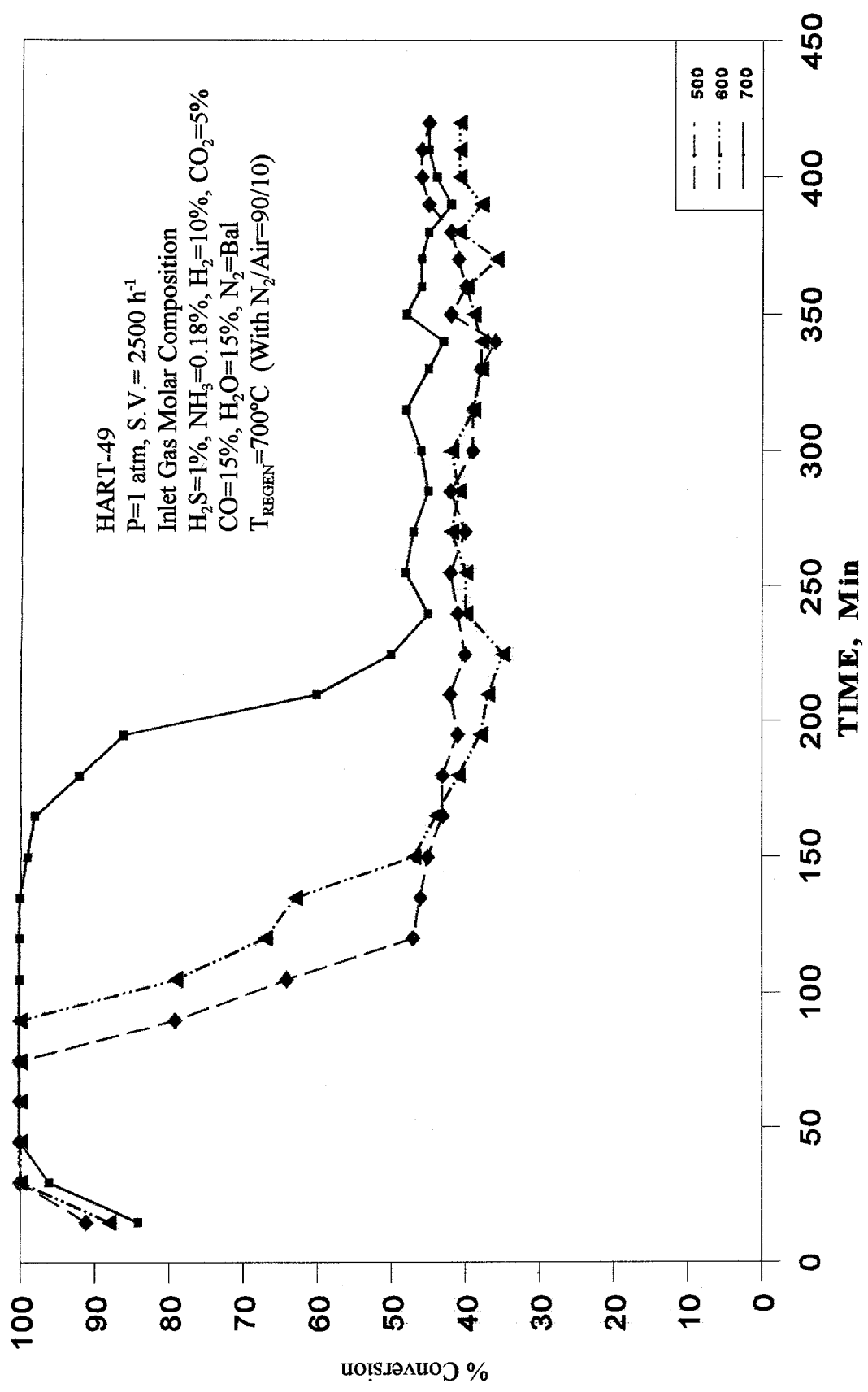


Figure 3. Conversion of ammonia on HART-49 catalyst-sorbents.

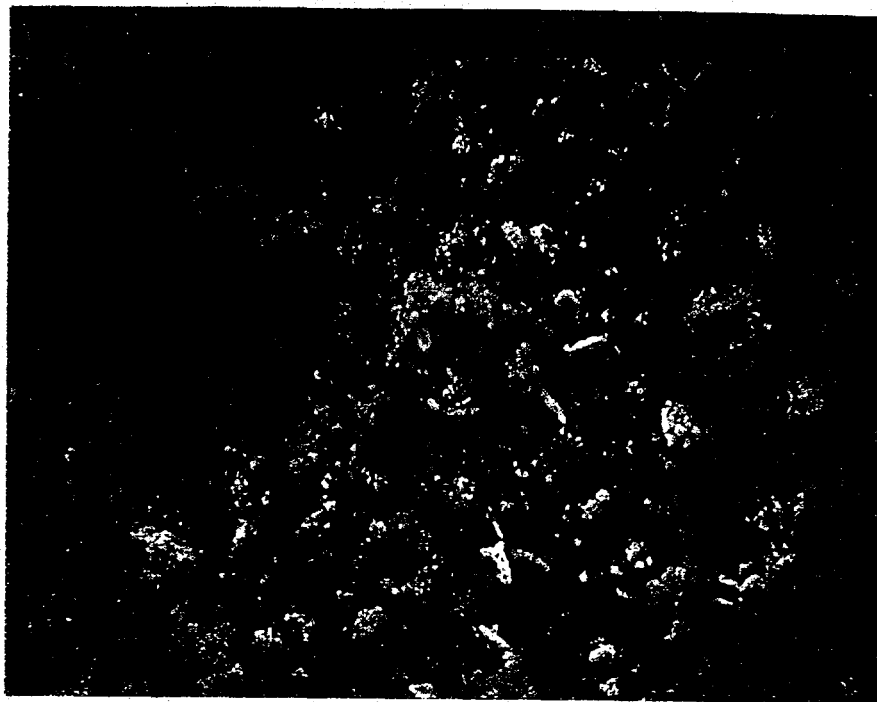


Figure 4a. SEM Micrograph of HART-49 Sorbent-Catalyst (Fresh)

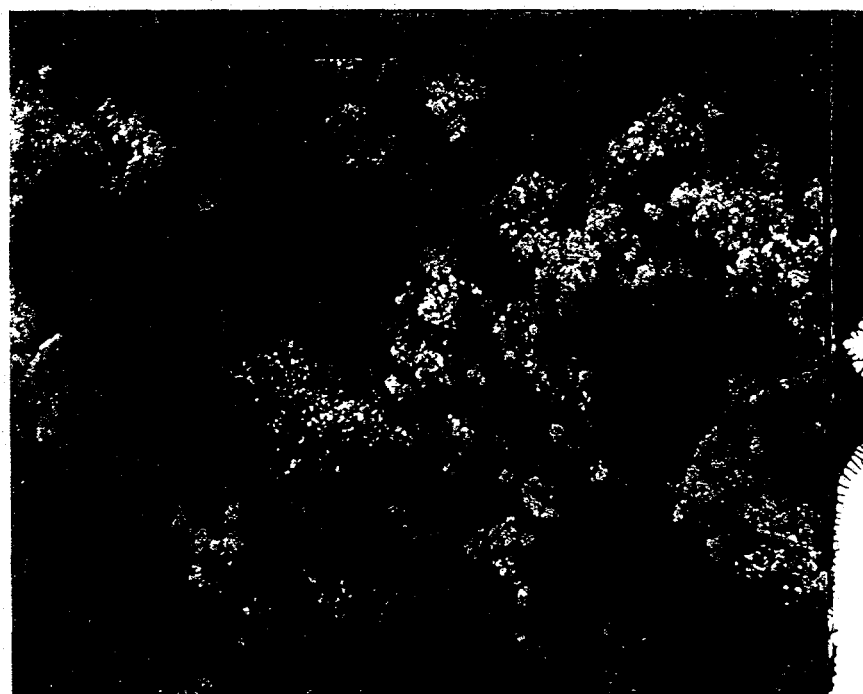


Figure 4b. SEM Micrograph of HART-49 Sorbent-Catalyst (Sulfided)

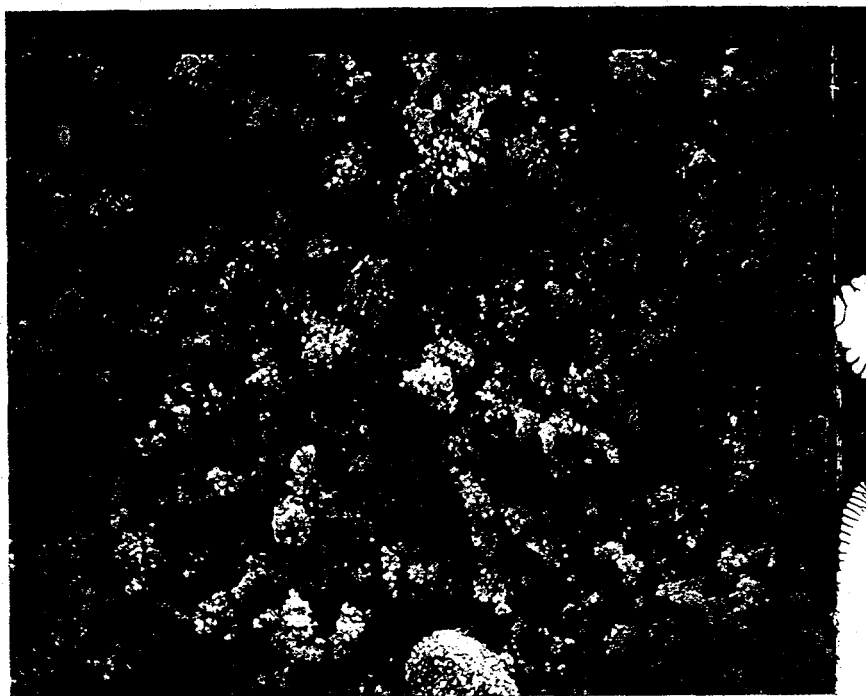


Figure 4c. SEM Micrograph of HART-49 Sorbent-Catalyst (Regenerated)