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Simultaneous Removal of H₂S and NH₃ in Coal Gasification Processes

FINAL REPORT

K. Jothimurugesan
A. A. Adeyiga
Hampton University

S. K. Gangwal
Research Triangle Institute

November 1996

Work Performed Under
Grant No: DE-FG-22-93MT93005

For

U.S. Department of Energy
Office of Fossil Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania 15236-0940

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by

K. Jothimurugesan
Adeyinka A. Adeyiga
Department of Chemical Engineering
School of Engineering & Technology
Hampton University
Hampton, Virginia 23668

Santosh K. Gangwal
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

For

U.S. Department of Energy
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ABSTRACT

Nitrogen (N_2) 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 gasification, this fuel-bound nitrogen is released principally as ammonia. The formation of NH_3 in coal gasification processes is a function of the coal N_2 content and the gasifier operating conditions. During the use of coal gas to generate electricity in gas-fired turbines or molten carbonate fuel cells, fuel bound N_2 is converted to nitrogen oxides (NO_x), which are difficult to remove and are highly undesirable as atmospheric pollutants. Thus it is desirable to remove NH_3 from coal gas in addition to other major contaminants such as hydrogen sulfide (H_2S) and particulates.

The objective of this study was to develop a successful sorbent-catalyst combination of an NH_3 decomposition catalyst with a zinc-based mixed-metal oxide H_2S sorbent with stable NH_3 decomposition and H_2S removal efficiency under cyclic sulfidation-regeneration conditions in the temperature range of 500 to 700°C. Combining the NH_3 and H_2S removal steps is expected to reduce capital and operating costs in an integrated gasification combined cycle (IGCC) power plant.

Sorbent-catalysts were synthesized using a coprecipitation technique. The preparation technique and the formulations are proprietary and pending a patent application. Thus no details regarding the technique are divulged in this report.

Ammonia decomposition studies were conducted in a fully-instrumented packed-bed microreactor under controlled heating so that nearly isothermal operation was possible. Near atmospheric pressure was used in the tests. The gas hourly space velocity was about 2500 h^{-1} . Sulfidations were conducted with gas mixtures containing (volume %): 10 H_2 , 15 CO , 5 CO_2 , 1 H_2S , 15 H_2O , 0.18 NH_3 , balance N_2 . With selected sorbent-catalysts, thirty multicycle

experiment were carried out. Regenerations were conducted at temperatures in the range of 700-750°C with air-N₂ gas mixtures. In the screening phase of the experimental program, fifty one sorbent-catalysts were evaluated at 700°C. Catalysts containing Ni, Co, Mo and W compounds were candidates for this study. Limited tests were also conducted at 500-600°C on the most promising material.

Several sorbent-catalysts showed very high NH₃ decomposition activity (>90%) in the time window of 20-180 minutes depending on the catalyst formulation. The presence of H₂S and steam decreased the activity of the catalyst for NH₃ decomposition. However, the extent of deactivation depended on the temperature. The sorbent-catalysts tested consistently removed 99% or more of the H₂S from a simulated gas containing 1 volume % H₂S and were regenerable for multicycle operation.

A multicycle experiment was performed on a superior HART-49 formulation at 700°C. Up to 180 min, the sorbent-catalyst showed very high NH₃ decomposition activity (> 90%). The decline in activity after 180 min appeared to be due to sulfidation with H₂S in the presence of steam. The activity did not decline in the absence of steam even after nearly complete sulfidation. The pre-breakthrough H₂S level was below 20 ppm. Nearly complete conversion was observed at breakthrough. There was no reduction of sulfur removal reactivity and capacity in 30 cycles in this fixed-bed study. The sulfur capacities during cycles 1 and 30 were 28.9 and 28.9 gS/100 g of sorbent, respectively, corresponding to nearly 100 percent capacity utilization even after 30 cycles. The sorbent also showed reasonable NH₃ decomposition activity at 500-600°C.

Future work should be carried out to fully evaluate HART-49 in the temperature range of 450-550°C at practical IGCC pressures. Also, the HART-49 preparation should be scaled up to produce attrition-resistant sorbent-catalyst in fluidizable or pellet form.

ACKNOWLEDGMENTS

This study was sponsored by the U.S. Department of Energy (DOE) under Grant No: DE-FG-22-93MT93005. The authors would like to acknowledge with gratitude the guidance provided by the DOE Contracting Officers's Representative, Dr. Kamalendu Das, of the Morgantown Energy Technology Center.

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1.0 INTRODUCTION

The removal of hydrogen sulfide (H_2S) to sufficiently low levels from coal-derived fuel gases at elevated temperatures is crucial for the efficient and economic coal utilization in emerging advanced power generation systems such as the integrated gasification-combined cycle (IGCC) and the gasification-molten carbonate fuel cell (MCFC). Both technologies require removal of H_2S and other sulfur compounds from the fuel gas prior to combustion. The sulfur content must be reduced from several thousand parts per million (ppm) to approximately 50-100 parts per million for combined cycle technology and to 1 ppm or less for molten carbonate fuel cell power generation. Commercial desulfurization processes based on liquid scrubbing at or below ambient temperatures result in considerable thermal efficiency loss as well as costly waste water treatment. Ammonia (NH_3) is removed along with H_2S , tar, and other contaminants by dissolution in the quenched water. However, thermal efficiency and the economics of power generation are improved when high temperature devices use a coal gas stream maintained near the operation temperature of the power generating device. In such an operation, contaminants such as NH_3 must be removed at elevated temperatures by methods other than conventional water quenches. Ammonia concentration in raw coal gases could range from 2000 to 5000 ppmv. If this gas is combusted without NH_3 removal, NH_3 would be converted to a nearly equivalent amount of NO_x . This would be in addition to NO_x formed (if any) due to fixation of N_2 at high temperature. The total NO_x formed would be substantially higher than that allowed by current environmental standards. The removal of NH_3 in coal gas at 500 to 700° C is important so that NO_x emission standards can be met during combustion in a turbine.

For about two and a half decades, research on hot-gas desulfurization has concentrated on the use of solid metal-oxide sorbents. There has been more interest in calcium compounds as disposable

sulfur sorbents than any other class of materials, because they are inexpensive and because they are effective under both reducing and oxidizing conditions. CaS forms readily under reducing conditions, and CaSO₄ forms under oxidizing conditions. The principal limitations of Ca-based sorbents are that at low temperatures, the chemical reaction is slow, and at high temperatures, sintering results in slow mass transport of reactants and products, and regeneration of the spent sorbent is difficult (Swisher and Swihwerdtfeger, 1992).

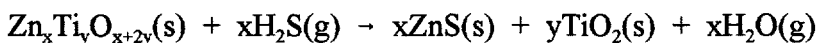
High temperature sulfur removal techniques are based on the reaction of H₂S with solid regenerable sorbents to form solid sulfur compounds. Early work on hot gas desulfurization employed single oxide sorbents, especially iron oxide and zinc oxide (Oldaker et al., 1975; Westmoreland et al., 1977; Gibson and Harrison, 1980). The attractive features of zinc oxide as a sorbent are that it can reduce H₂S concentrations in gas mixtures to very low levels and its reactivity is high, particularly for fine particles. The principal limitation of ZnO is that loss of Zn by vaporization can occur at high temperatures. Iron oxide, on the other hand, has rapid kinetics but its equilibrium constant for sulfidation is not adequate for the degree of H₂S removal required in the IGCC and fuel cell applications.

Recent research has shifted from pure oxides to mixed oxides. Of the several mixed-metal oxide sorbents investigated, ZnO-Fe₂O₃, ZnO-TiO₂, CuO-Al₂O₃, CuO-Fe₂O₃, CuO-Fe₂O₃-Al₂O₃, CoO-TiO₂ (Fahara and Garder, 1980; Grindley and Steinfeld, 1981, 1982, 1983, 1984; Grindley 1986; Grindley, 1989, Anderson and Hill, 1988; Focht et al., 1988; Flytzani-Stephanopoulos et al., 1987, 1988; Flytzani-Stephanopoulos and Jothimurugesan, 1990; Jothimurugesan and Harrison, 1990; Lew et al., 1989, 1992a, 1992b; Sriwardane and Poston, 1990; Tamhanker et al., 1986; Ayala et al., 1991; Gangwal et al., 1988; Patric et al., 1989; Woods et al., 1990, 1991, Baird et al., 1992; Jain et al., 1993), only zinc-and iron based sorbents have emerged as having good potential for application as

regenerable hot-gas desulfurization agents in IGCC systems. Although the feasibility of removing H₂S to very low levels (e.g., <50 ppmv) from coal gases has been shown to be viable in most studies of mixed-metal oxides, the major limitations for large scale use of mixed-metal oxides is the lack of chemical and mechanical stability under reducing gas atmospheres or the difficulty of regeneration over many cycles.

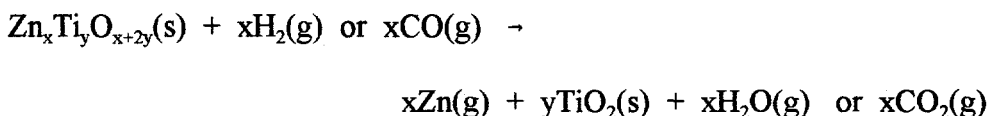
The overall reaction scheme in sulfidation-regeneration of one popular mixed metal oxide, zinc titanate (ZnO-TiO₂) is:

Sulfidation



In addition to sulfidation, some reduction can occur by the reaction

Reduction



Regeneration



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 gasification, this fuel-bound nitrogen is released principally as ammonia and nitrogen, with smaller levels of HCN. The formation of NH₃ in a coal gasification processes is a function of the fuel gas composition and the gasifier operating conditions (pressure and temperature). The product stream from a high temperature, oxygen-blown gasifier, such as Texaco, contains about 2000 ppmv of NH₃, where as higher concentrations (about 5000 ppmv) occur when the gasification is conducted at lower temperatures, such as in the Lurgi or GE air-blown gasifier. During the use of coal gas to generate electricity in gas-fired turbines, fuel bound

(N₂) 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 NH₃, NO_x is generated during combustion of the anode exhaust gas. Thus, NH₃ must be removed from the coal gas before it is used in IGCC or MCFC applications.

Studies of ammonia decomposition under simulated coal gas conditions are relatively few. The Institute of Gas Technology (1983) tested four catalysts under simulated coal gas conditions at temperatures from 425-750° C. ZnO, a bulk iron catalyst, Pt-supported on alumina and Ag-supported on alumina. All the catalysts reduced ammonia concentration at 550° C; zinc-and iron based catalysts were more effective than others. However, these catalysts exhibited a four to six-fold decrease in catalytic activity on exposure to a feed gas containing H₂S.

SRI international (Krishnan et al., 1988) clearly showed that, in the absence of H₂S, decomposition of ammonia can be carried out readily in the temperature range of 550 to 800°C using Ni-based catalysts. The SRI study demonstrated that HTSR-1, a proprietary Ni-based catalyst exhibited excellent activity and high temperature stability. However, its tolerance of H₂S was found to be a function of temperature. At 800°C and above, no catalyst deactivation was observed even in the gas streams containing 2,000 ppmv of H₂S. At lower temperatures, HTSR-1 deactivated rapidly when significant levels of H₂S were present in the coal gas.

U.S. Patent Number 5,188,811 (Ayala,1993) disclosed an invention related to additives to mixed-metal oxides that act simultaneously as sorbents and catalysts in cleanup systems for hot coal gases. Such additives, generally, act as a sorbent to remove sulfur from the coal gases while simultaneously, catalytically decomposing appreciable amounts of ammonia from the coal gases. According to this invention, sorbents for high-temperature desulfurization of coal gases are usually

mixed-metal oxides fabricated from zinc oxide, iron oxide and titanium dioxide, or a combination of these three with other binders and metal oxides. The innovative aspect of the preparation of the sorbents is the addition of molybdenum to the ferrite and titanate sorbents. Molybdenum trioxide (MoO_3) or any other form of molybdenum was added from 0 to 5% by weight to the mixed-metal oxide sorbent to create a base mixture. The pelletized calcinated base mixture was activated, preferably, by subjecting the pelletized base mixture to a calcination process where a gas is passed over the base mixture by conventional gas passing technique such that the gas contains 1% or less by volume of H_2S at approximately 1000°F for approximately one hour. The activation process was repeated several times, if necessary, with interim contact of the catalyst with a gaseous mixture of 1% O_2 in nitrogen at approximately 1000°F for at least one hour. The activated base mixture was then placed in a flow of hot coal gases where the amount of sulfur and NH_3 in the hot coal gases was substantially reduced. During absorption of H_2S from coal gases, the Zn and Fe atoms form sulfides according to well-known reactions found in the literature. Mo was also known to form sulfides, for instance, $\text{MoO}_3 + 2\text{H}_2\text{S} \rightarrow \text{MoS}_2 + 3\text{H}_2\text{O}$. Based on literature data on catalytic activity of MoO_3 and MoO_2 for hydrocracking and methanation reactions, Mo may have activity toward breaking hydrogen bonds with other atoms, and hence, be able to break down the hydrogen-nitrogen bond with ammonia, according to $\text{NH}_3 \rightleftharpoons \text{N}_2 + \text{H}_2$.

More recently, Research Triangle Institute (RTI), (Gangwal et al., 1993) prepared numerous catalyst and catalyst-sorbent combinations and tested them for their NH_3 decomposition activity. These included catalysts based on Ni, Co, Mo and W in various proportions combined with zinc titanate, titania or refractory support. Selected sorbent-catalysts were subjected to bench-scale testing with simulated gas. 40 % or less ammonia decomposition was achieved at $700\text{-}750^\circ\text{C}$ in the presence of 2000 ppmv or higher H_2S . However, when the temperature was increased to 800°C , a

nickel-based HTSR-1 catalyst was able to decompose 80% of the NH_3 in the presence of 0.5% H_2S .

Studies of NH_3 decomposition indicated that Ni, Ir, Co, Mo, Mn and Ru have high catalytic activities (Krishnan et al., 1988, Gangwal et al., 1993). If desulfurization sorbents such as a zinc-based mixed-metal oxide could be used along with above metals 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 H_2S and NH_3 in one process unit would reduce the capital and operating costs of electric power generation from coal.

1.1 PROJECT OBJECTIVES

The objective of this study was to develop a successful combination of an NH_3 decomposition catalyst with a zinc-based 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 500-750° C. The specific objectives of the project were to:

- (i) Develop combined sorbent-catalyst materials 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 a superior sorbent-catalyst.

2.0 DESCRIPTION OF PROJECT TASKS

TASK 1: Sorbent-Catalyst Preparation and Characterization

The objectives of this task were to prepare and characterize various sorbent-catalyst compositions. As indicated earlier, no information about the sorbent-catalyst preparation is divulged, except that they are zinc-oxide based materials. Several parameters were varied in the sorbent-catalyst preparation to study their effects on the physical properties and chemical phases of the sorbent-catalysts. Section 3.1 also describes the various analytical techniques employed for sorbent-catalyst characterization throughout the project.

TASK 2: Experimental Testing

The objectives of this task were to evaluate the performance of various sorbent-catalyst compositions under similar conditions in a fixed-bed microreactor. Section 3.2 describe the experimental apparatus and procedures employed throughout the project. Sorbent-catalyst comparisons were to be carried out at the following operating conditions:

$P=1 \text{ atm}$, $T= 700^{\circ}\text{C}$, $S. V. =2500 \text{ h}^{-1}$

Sulfidation Gas (vol %): 10 H_2 , 15 CO , 5 CO_2 , 1 H_2S , 15 H_2O , 0.18 NH_3 , balance N_2 .

Regeneration gas (vol %): 10 air-90 N_2

At least four to five cycles of sulfidation/regeneration were to be run with each sorbent-catalyst until stabilized performance was attained. Following these tests, the most promising sorbent-catalyst was to be further tested in the multicycles.

TASK 3: Cyclic Testing

The objectives of this task was to determine how well the sulfidation and ammonia decomposition performance of the sorbent-catalyst were retained in many cycles of consecutive sulfidation/regeneration.

3.0 EXPERIMENTAL APPROACH

TASK 1: 3.1 SORBRNT-CATALYST PREPARATION AND CHARACTERIZATION

The sorbents developed to date by a solid-phase synthesis technique have low surface area (typically around 5 m²/g or less). These sorbents show significant loss in chemical reactivity and surface area (down to ~ 1 m²/g) over multiple cycles (Gupta and Gangwal, 1992). Sorbents prepared by a liquid-phase citric acid complexation technique are irreproducible and costly due to complex steps such as vacuum drying and show high active metal loss with simulated gas. It is apparent from the above that there exists a need in the art for developing durable advanced sorbents

The method used to produce novel sorbents in this research involves coprecipitation. A catalyst vendor (United Catalysts, Inc) provided the required input to keep the preparation procedure on a commercial track by making sure that the techniques were scalable.

A detailed physical and chemical characterization of the fresh, sulfided and regenerated sorbent-catalyst materials was carried out using the following analytical techniques.

1. X-ray powder diffraction patterns were obtained using a Phillips PW 1800 X-ray unit using CuK α radiation. Analyses were conducted using a continuous scan mode at a scan rates of 0.05° 2 θ per second.
2. The BET Surface area of the sorbent-catalysts were determined by N₂ physisorption using a Micromeritics Gemini 2360 system. The samples were degassed in a Micromeritics Flow Prep 060 at 120°C for 1 h prior to each measurement.
3. Hg-porosimetry was used for pore volume, bulk density, average pore diameter and pore size distribution determination.
4. Atomic Absorption (AA) Spectrometry for elemental composition analysis.
5. The SEM (Scanning Electron Microscopy) micrograph was taken using a Cambridge

Stereoscan 100.

TASK 2: 3.2 APPARATUS AND PROCEDURES

The materials prepared were tested in a laboratory scale high-pressure and high temperature fixed bed reactor which is shown in Figure 1. Briefly, the experimental setup consists of a gas delivery system, fixed bed reactor and a gas analysis system. In the gas delivery system, a simulated fuel gas of any desired composition can be generated using the bottled gases, a set of mass flow controllers and high pressure syringe pumps. Steam is 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. NH_3 is added to the gas mixture downstream of the generator where the temperature is high enough to avoid the formation of ammonium carbonates or sulfides. The reactor was constructed of stainless steel pipe. Inside the pipe there was a removable 316 stainless steel 1.0 cm I.D pipe with a porous alumina plate in the bottom that acts as a gas distributor. The inside of the pipe was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The pressure inside the reactor was measured by an electronic pressure sensor. The thermocouples were positioned to measure the temperatures of the preheated feed gas, reactor bed temperature and the temperature of the product gas. The tests with sorbent-catalyst were conducted with a simulated gas containing (vol %) 10% H_2 , 15% CO , 5% CO_2 , 1% H_2S , 15% H_2O , 0.18% NH_3 , and balance N_2 . The outlet H_2S and SO_2 concentrations were monitored using detector tubes and gas chromatography. The outlet NH_3 concentration was measured using ion selective electrodes and ion chromatography.

A typical run consists of loading the sorbent-catalyst having a particle size range of -32+ 64 mesh and heating the reactor to a desired temperature of 500-750°C with continuous flow of nitrogen. Once the desired temperature is attained, the flow of fuel gas to the reactor is started and the concentration of H_2S and NH_3 is measured continuously in the effluent gas. Once the H_2S

SCHEMATIC DIAGRAM OF THE LABORATORY-SCALE FIXED-BED REACTOR

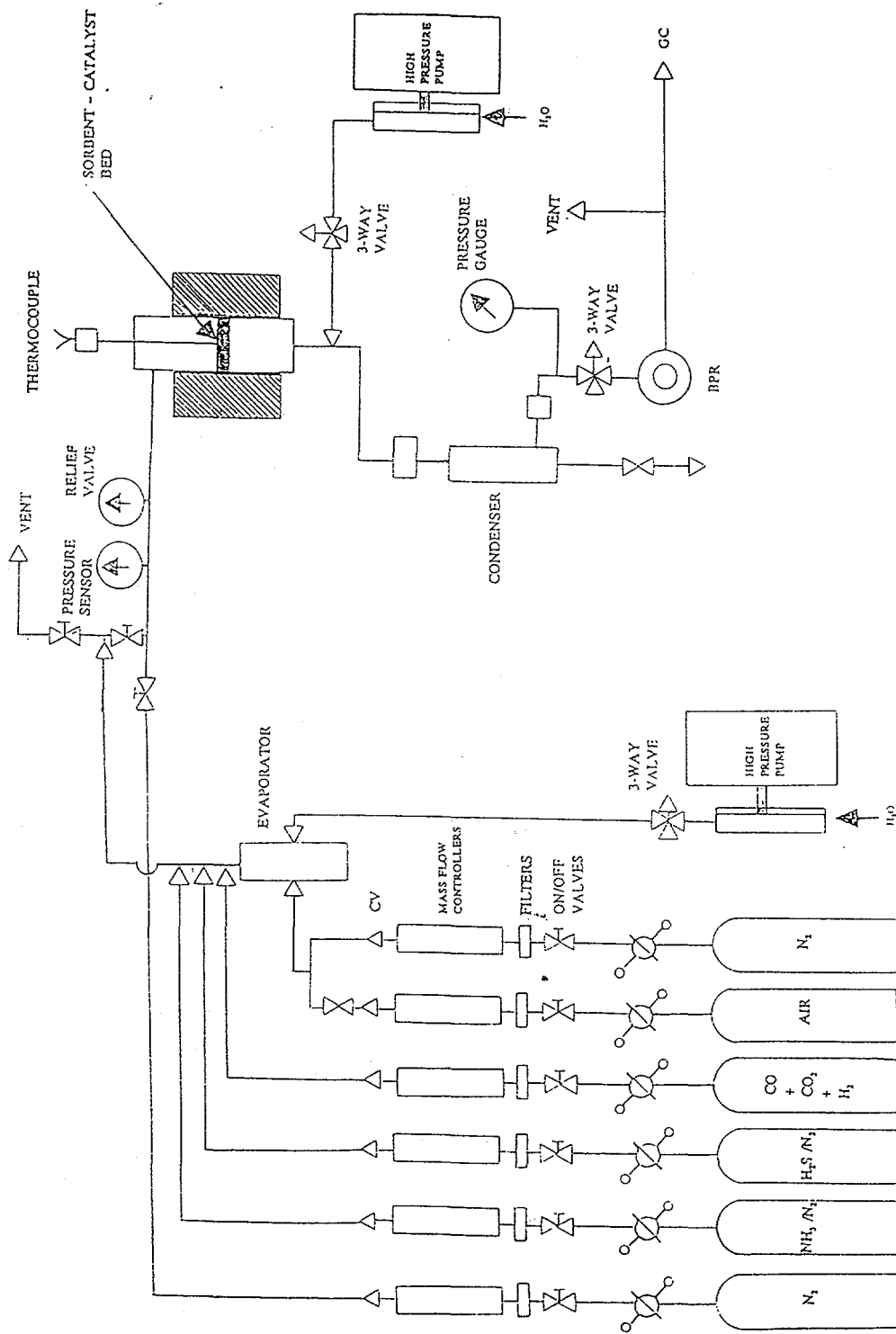


Figure 1. Schematic Diagram of the Laboratory-Scale Fixed-Bed Reactor

concentration reaches 300 ppmv, the run is stopped and the system is prepared for regeneration. The regeneration of sulfided material is carried out at the desired temperature ranging between 500-750°C with 2 -4 % oxygen in nitrogen. In all the runs, space velocity used was in the range of 2000-3000 h⁻¹. The regeneration of the sulfided material is carried out until the SO₂ concentration in the reactor effluent reaches below 50 ppm. These sulfidation-regeneration cycles are repeated as many times as desired. Typically each material is tested for 4-5 cycles to obtain meaningful data on material durability. At the end of a 4-5 cycle run, the material is removed from the reactor and all physical and chemical characterizations, as listed above, are carried out on the reacted material to determine changes due to reaction.

4.0 RESULTS AND DISCUSSIONS

The experimental results are presented and discussed in this section. Data from Tasks 1-2 are combined and presented in this section. Finally, the results of Task 3, involving testing of muticycles of the sorbent-catalyst is presented in section 4.7. Fifty-one sorbent-catalysts were prepared, characterized, and tested in several sulfidation, ammonia decomposition, and regeneration tests aimed at identifying the superior formulation for simultaneous H₂S and NH₃ removal in the temperature range of 500-700°C.

4.1 ZINC - BASED MIXED METAL OXIDE

The effects of preparation conditions on the the physical properties and chemical phases of the fresh sorbents were examined in detail. The SEM morphology of the fresh HART-4, 9, 12, 15, and 18 were depicted in Figure 2 a-e. The surface grains of sorbent were small and well dispersed. Thus considering this surface morphology, an increase of the specific surface area was expected.

As mentioned previously, the sorbent for the desulfurization application must have high chemical reactivity. The chemical reactivity is measured by the total sulfur loading as well as the rate

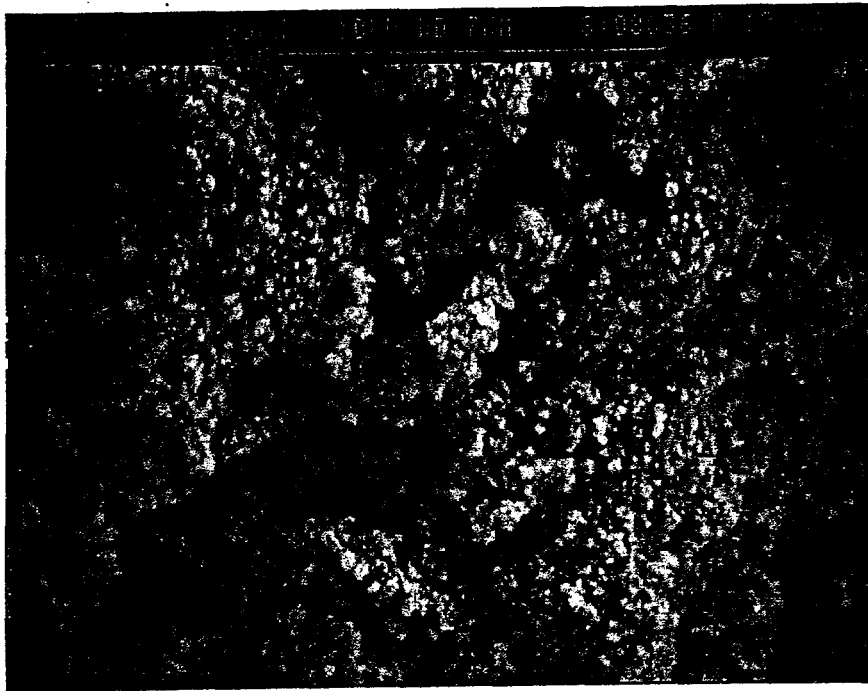


Figure 2. SEM Micrograph of (a) HART-4

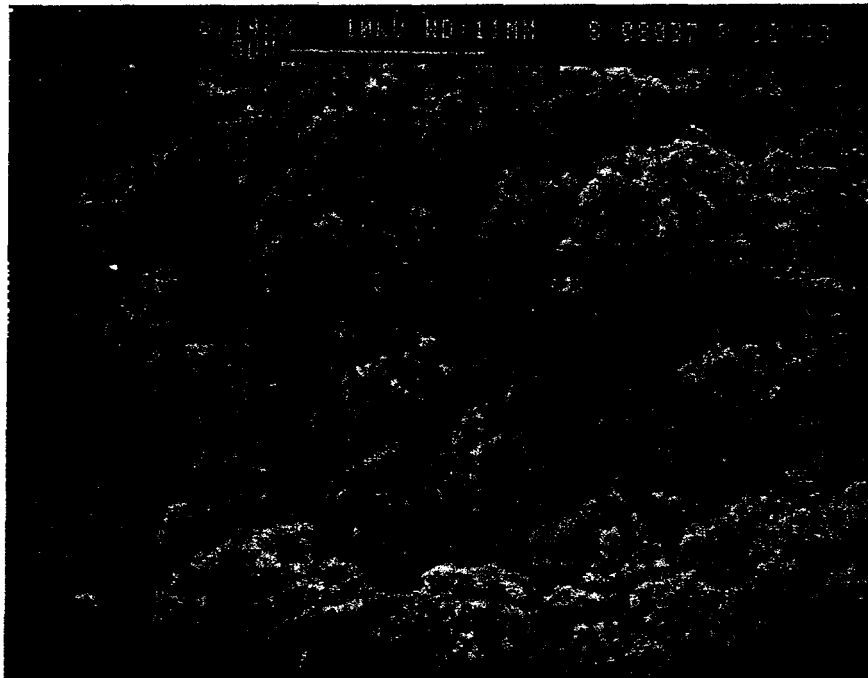


Figure 2. SEM Micrograph of (b) HART-9

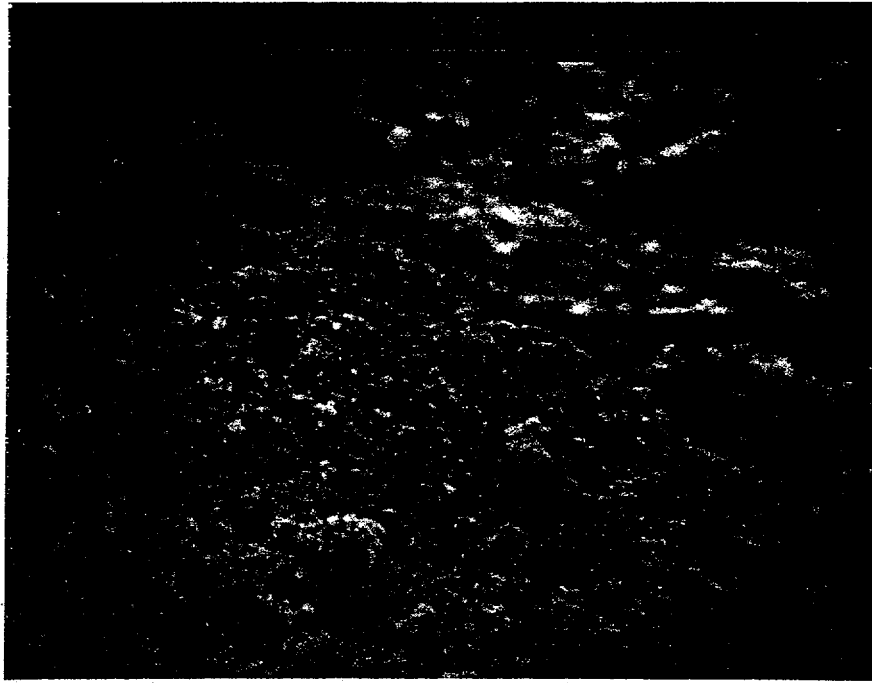


Figure 2. SEM Micrographs of (c) HART-12

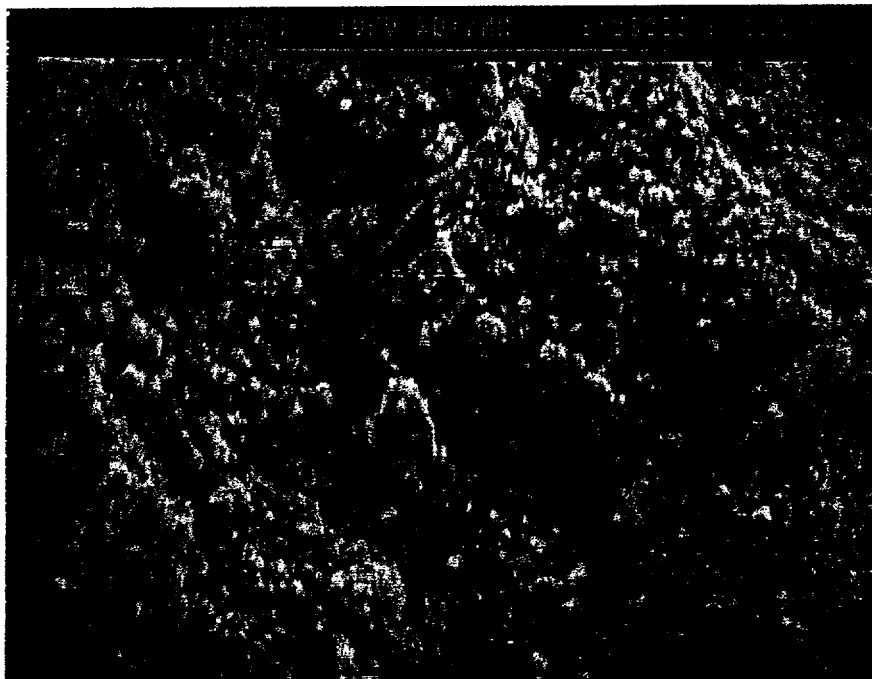


Figure 2. SEM Micrographs of (d) HART-15

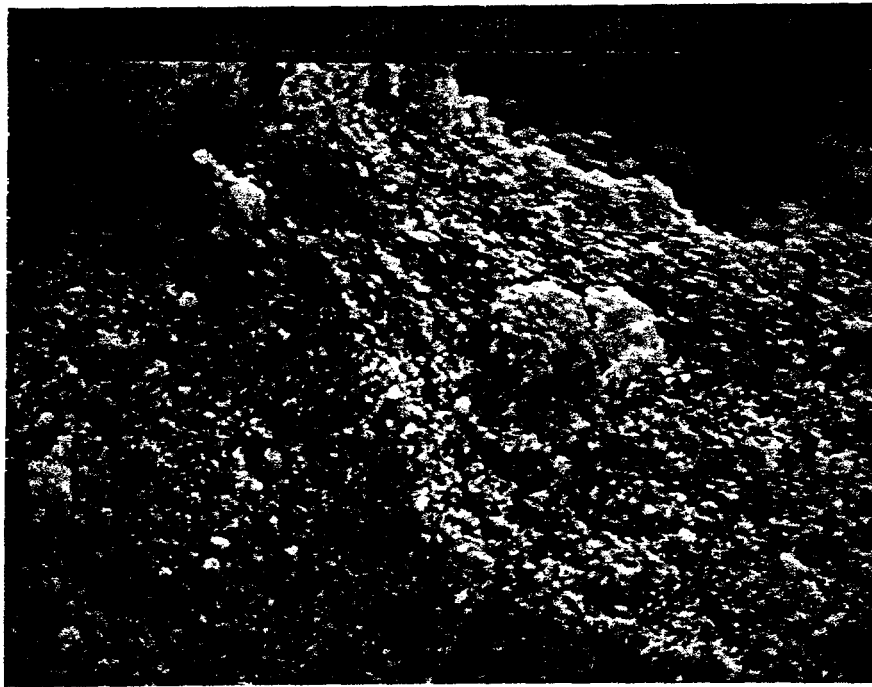


Figure 2. SEM Micrographs of (e) HART-18

of sulfur absorption. In order to measure the latter, standard 1.5 cycle TGA reactivity tests were carried out. The TGA reactivities of HART-5 and HART-19 (as an example) sorbents were measured in simulated gas (which contains 1% H₂S) at 550°C. Each TGA consisted of a 550°C sulfidation, 650°C regeneration with 2% O₂ followed by a second sulfidation. As seen from Figure 3, the HART-19 sample showed excellent reactivity compared to HART-5 following a modification of the basic zinc oxide-based sorbent.

4.2 EVALUATION OF *CLASS A* SORBENT-CATALYST

Class A sorbent-catalysts were prepared by coprecipitation using one set of raw materials. The SEM morphology of the HART-36 fresh sorbent was depicted in Figure 4. The activities of the sorbent-catalysts were tested at two temperatures (650°C and 750°C) using simulated coal gas. The tests with the sorbent-catalyst were conducted with a simulated gas containing (vol %) 10% H₂, 15% CO, 5% CO₂, 1% H₂S, 15% H₂O, 0.18% NH₃, and balance N₂. The ammonia decomposition activity is shown Figures 5-7 and its H₂S removal ability is shown in Figures 8-10. As seen in Figures 5-7, initially the sorbent-catalyst showed a very high activity (>90%) for about 20 minutes. After that, the decline in activity was probably due to the poisoning of the catalyst by H₂S. HART-36 sorbent-catalyst had the highest activity; at steady state about 55% of the feed gas ammonia was decomposed. When the temperature was increased from 650 to 750°C, there is a slight increase in ammonia decomposition activity. As seen from Figures 8-10, the pre-breakthrough H₂S levels for these sorbent-catalyst were less than 120 ppm. Almost complete conversion was achieved at breakthrough. As shown in Table 1, the sulfur capacities of the HART-36, 37, 38 during cycles 2 were 26.3, 25.7 and 28.8 gS/100 g sorbent, respectively. Sulfur capacity was calculated using the concentration of H₂S in the feed, breakthrough time and the amount of sorbent-catalyst used.

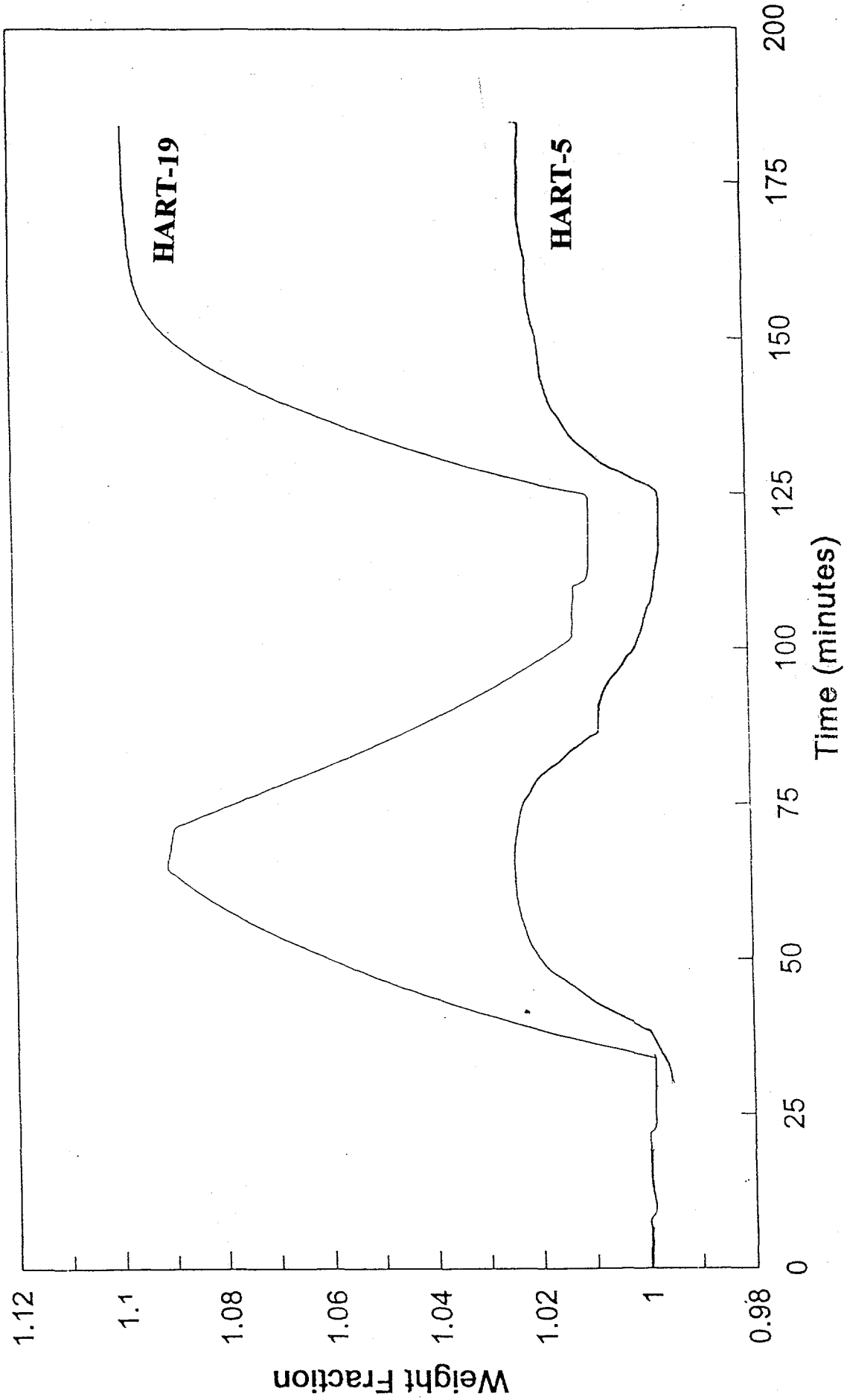


Figure 3. TGA Reactivities of Coprecipitated Zinc Oxide-Based Sorbents

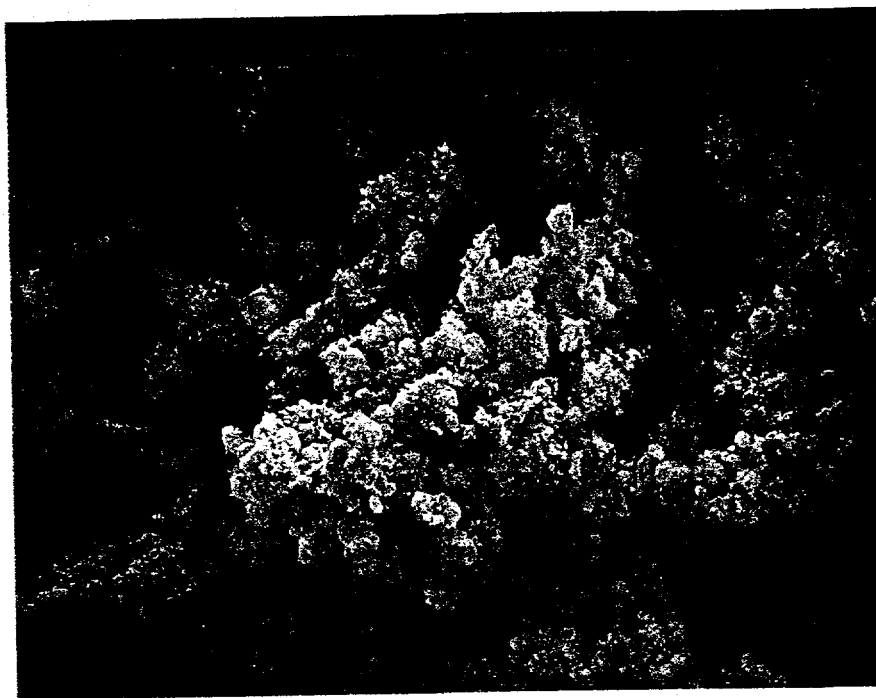


Figure 4. SEM Micrographs of HART-36 Fresh Sorbent-Catalyst

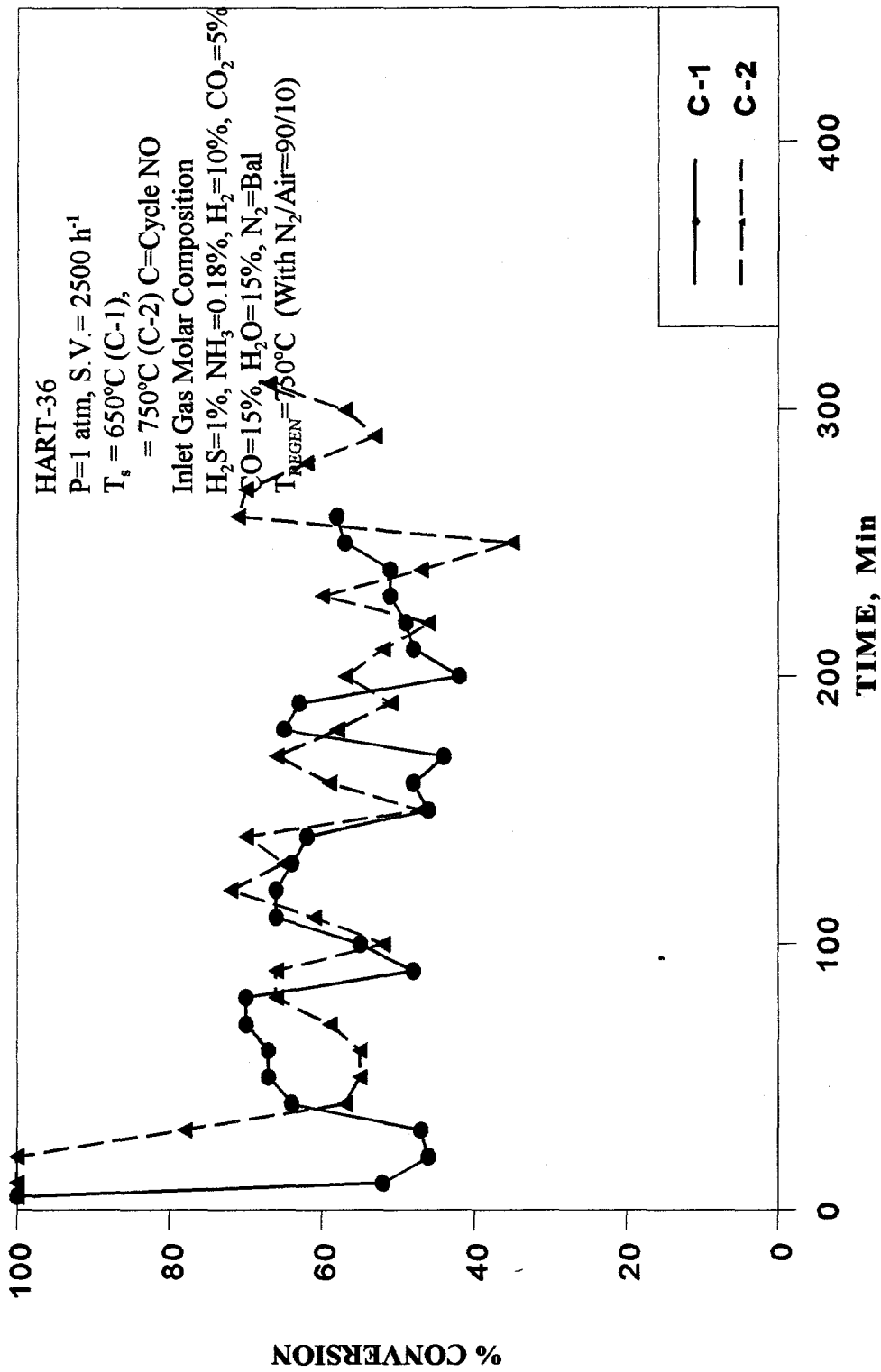


Figure 5. Conversion of Ammonia on HART-36 Sorbent-Catalyst

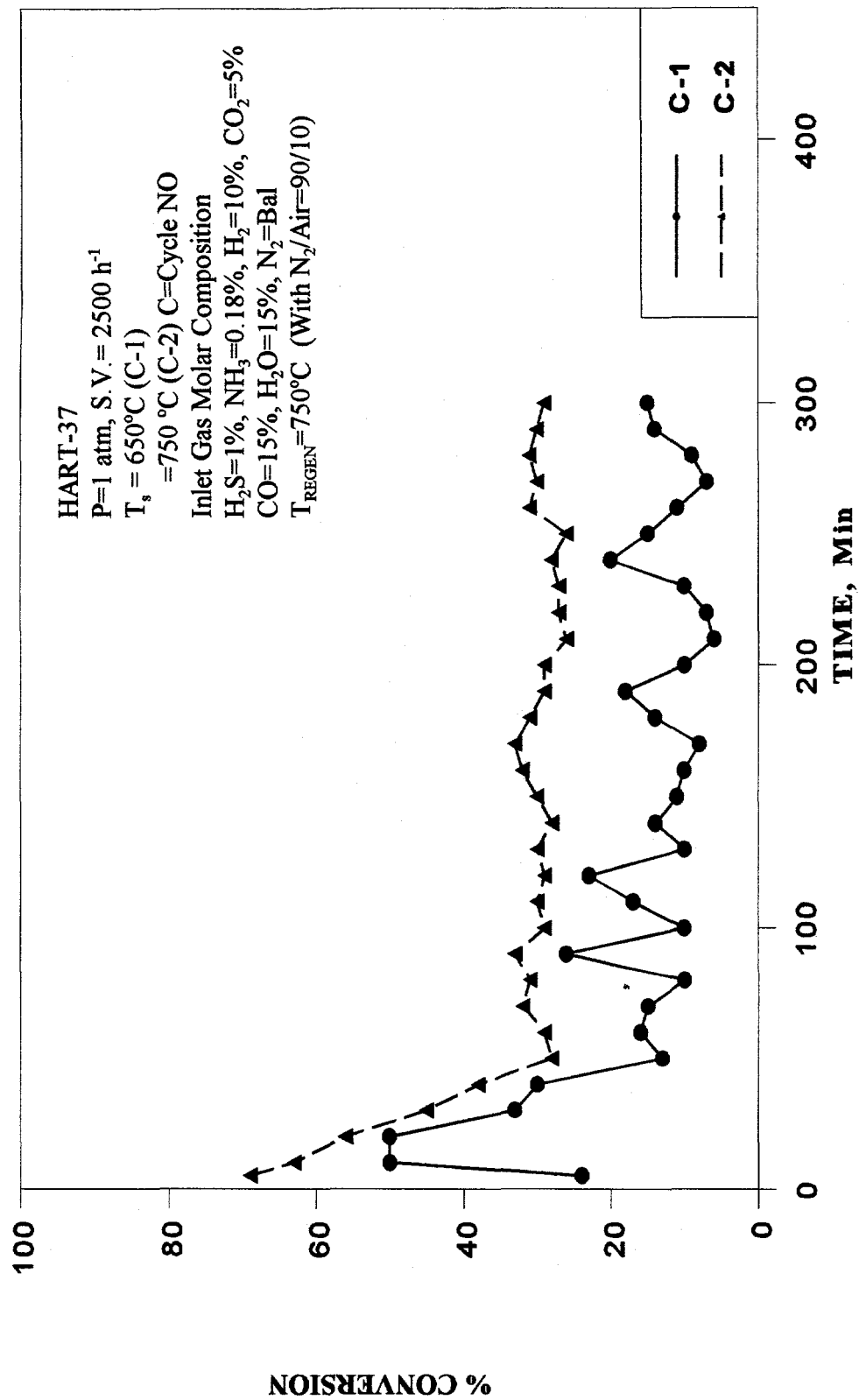


Figure 6. Conversion of Ammonia on HART-37 Sorbent-Catalyst

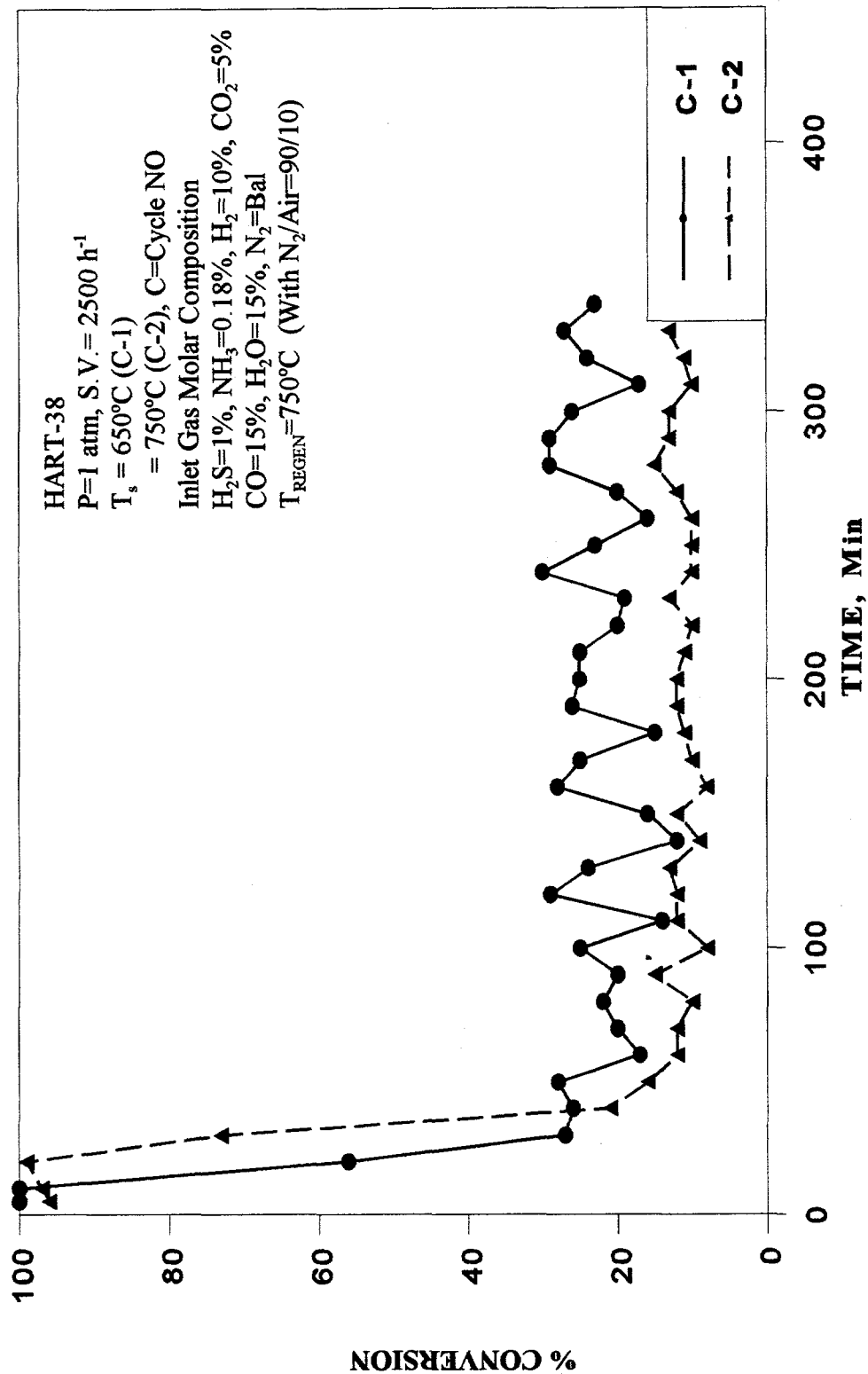


Figure 7. Conversion of Ammonia on HART- 38 Sorbent-Catalyst

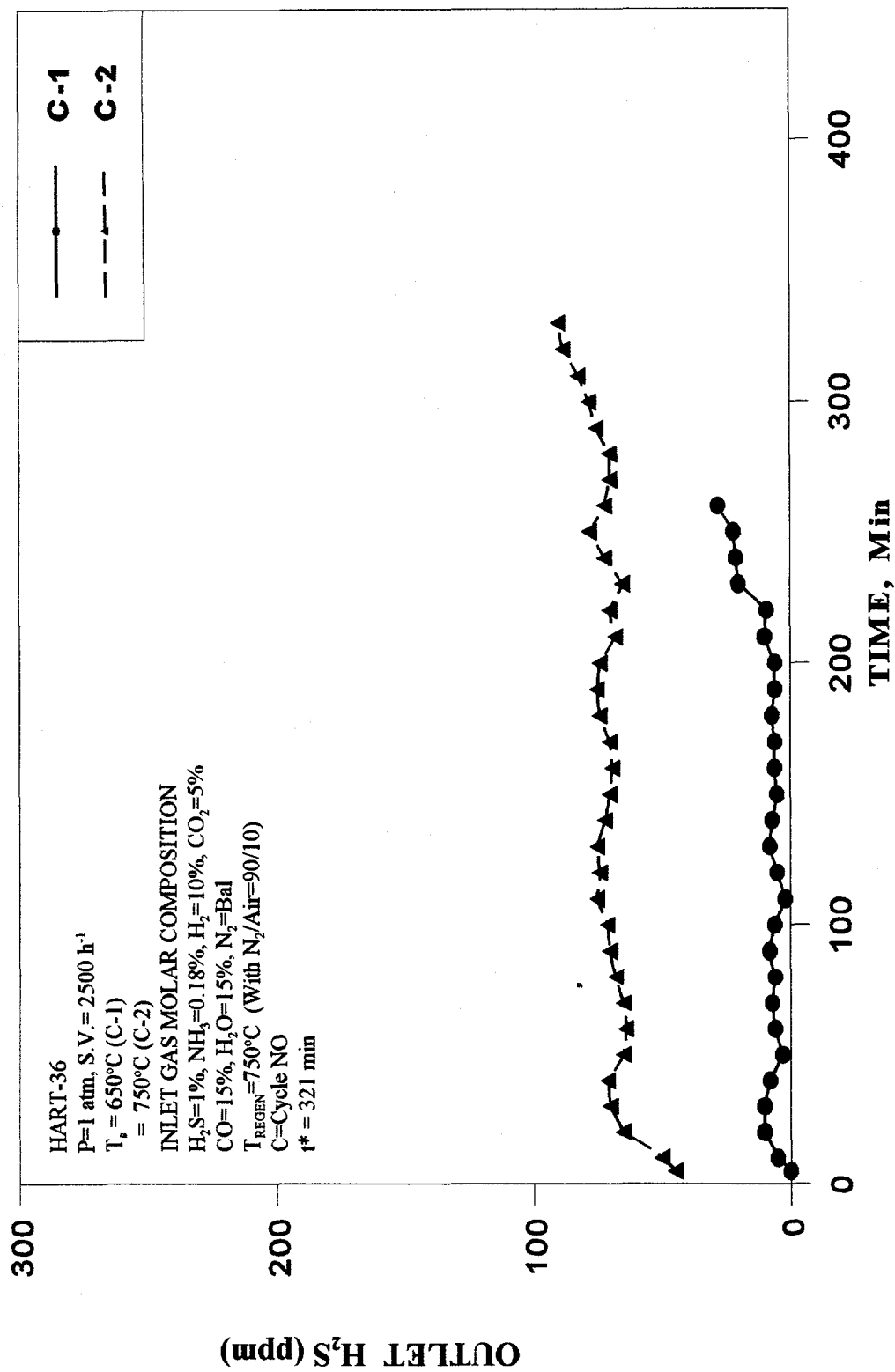


Figure 8. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-36 Sorbent-Catalyst

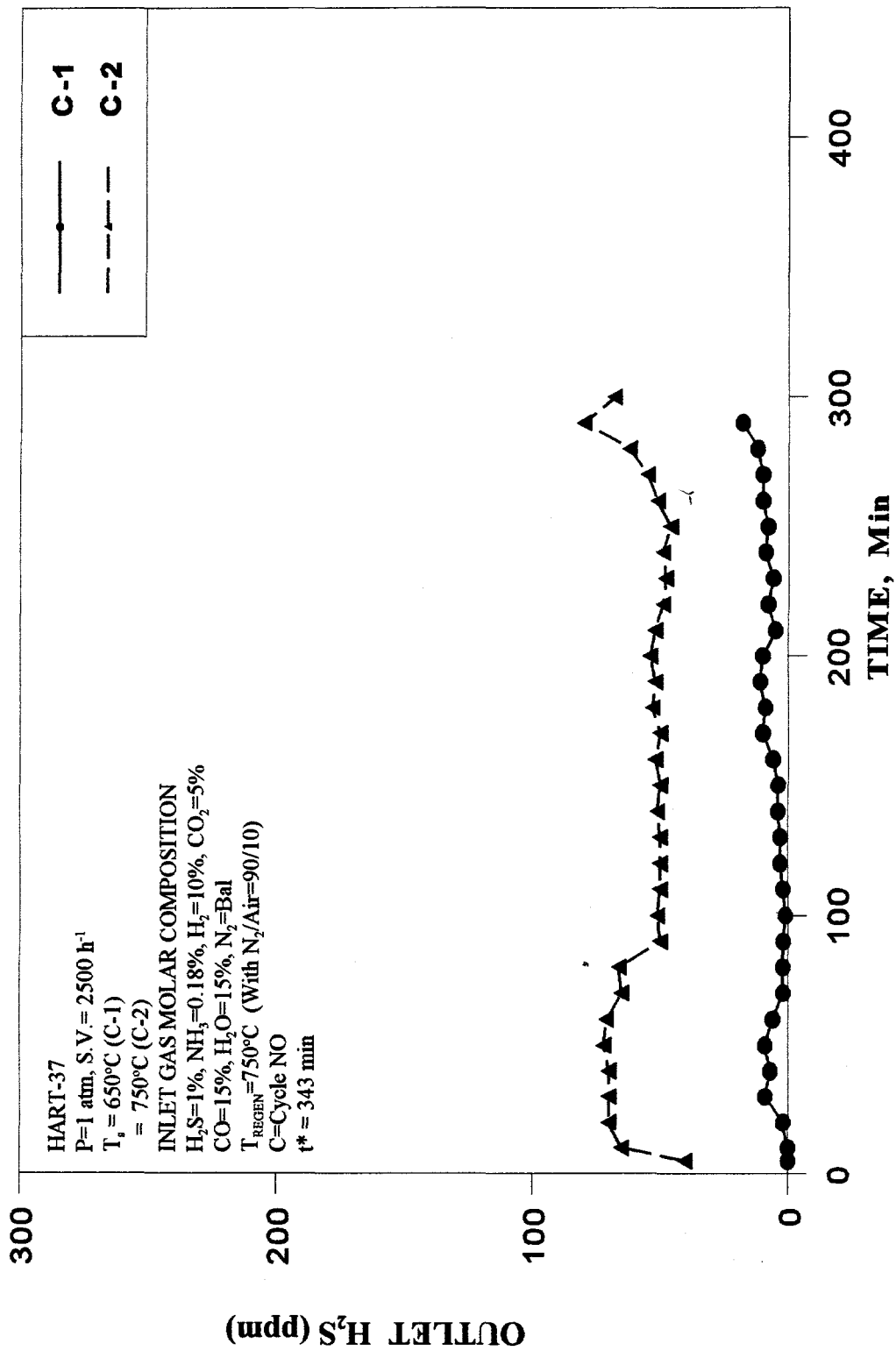


Figure 9. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-37 Sorbent-Catalyst

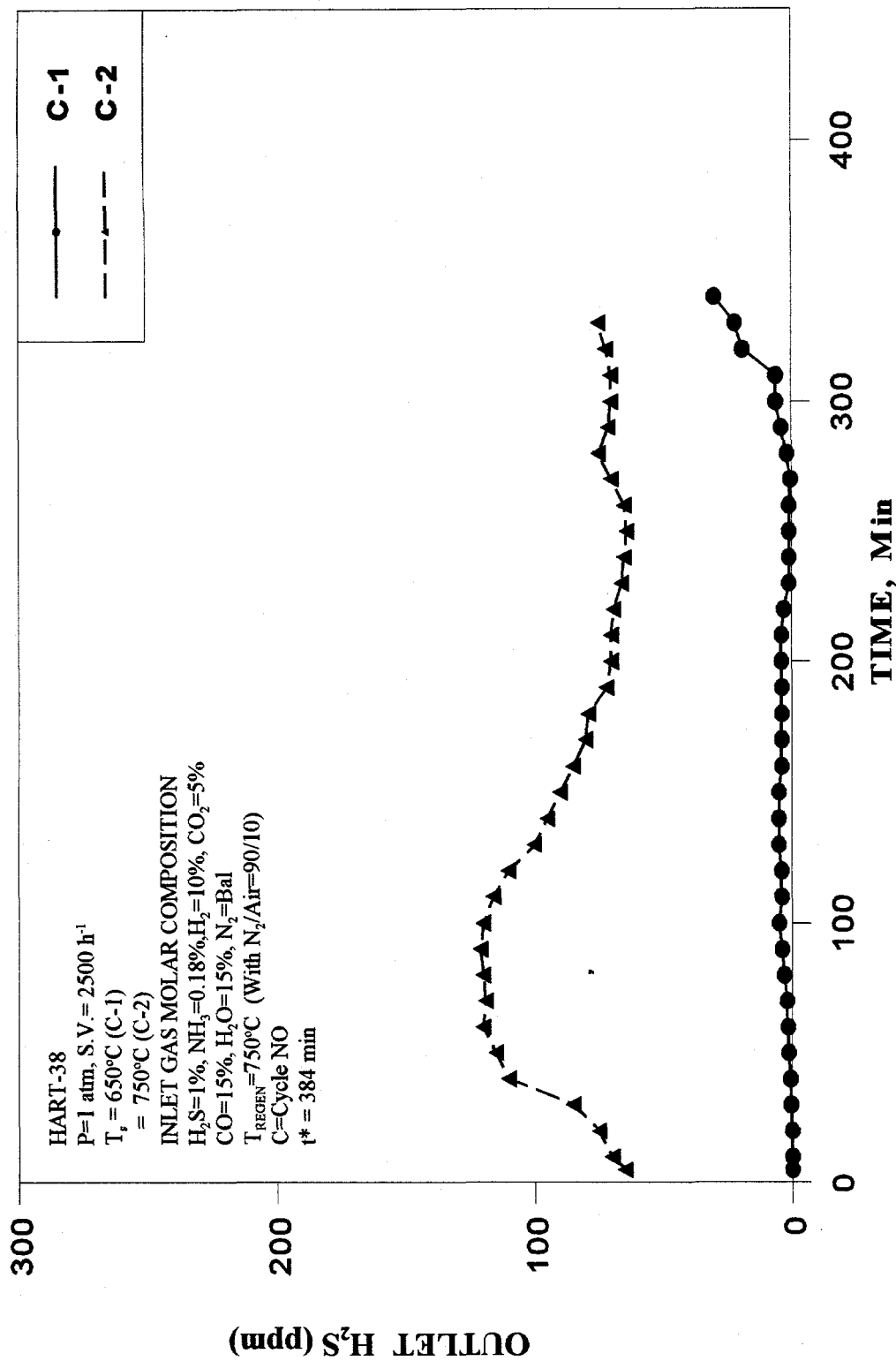


Figure 10. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-38 Sorbent-Catalyst

Table 1. Summary of Sulfidation Tests with HART Sorbent-Catalyst

Sorbent	T _s (°C)	Pre-Break-Through H ₂ S (ppm)	Breakthrough Sorbent Conversion, (t/t*)	Sulfur Loading (gS/100g sorbent)
HART-36	750	80	1.0 at C-2	26.3 at C-2
HART-37	750	80	0.94 at C-2	25.7 at C-2
HART-38	750	120	0.94 at C-2	28.8 at C-2
HART-39	700	110	1.0 at C-4	26.7 at C-4
HART-40	700	90	1.0 at C-4	28.9 at C-4
HART-41	700	80	1.0 at C-4	29.4 at C-4
HART-42	700	80	1.0 at C-4	30.1 at C-4
HART-44	700	60	1.0 at C-4	28.3 at C-4
HART-45	700	60	1.0 at C-4	28.1 at C-4
HART-46	700	60	1.0 at C-4	27.9 at C-4
HART-47	700	60	1.0 at C-4	27.8 at C-4
HART-48	700	50	1.0 at C-4	28.7 at C-4
HART-49	700	20	1.0 at C-4	28.9 at C-4
HART-50	700	NA	NA	NA
HART-51	700	15	1.0 at C-4	29.5 at C-4

4.3 EVALUATION OF *CLASS B* SORBENT-CATALYST

Class B sorbent-catalyst was prepared by coprecipitation using a second set of raw materials. The SEM morphology of the HART-40 fresh sorbent was depicted in Figure 11. The activities of the sorbent-catalysts were tested at 700°C using simulated coal gas. The tests with sorbent-catalyst were conducted with a simulated gas containing (vol %) 10% H₂, 15% CO, 5% CO₂, 1% H₂S, 15% H₂O, 0.18% NH₃, and balance N₂. The ammonia decomposition activity is shown Figures 12-15 and its H₂S removal ability is shown in Figures 16-19. As seen in Figures 12-15, initially the sorbent-catalyst showed a very high activity (>90%) for about 50 minutes. After that, the decline in activity was probably due to the poisoning of the catalyst by H₂S. Compared to class A sorbent-catalyst, for class B sorbent-catalyst, 90% decomposition time window, has been increased from about 20 minutes to 50 minutes. As seen in from Figures 16-19, the pre-breakthrough H₂S levels for this sorbent-catalyst were less than 100 ppm. Almost complete conversion was achieved at breakthrough. The sulfur capacities of the HART-39, 40, 41 and 42 during cycles 4 were 26.7, 28.9, 29.4 and 30.1 gS/100 g sorbent, respectively. Sulfur capacity was calculated using the concentration of H₂S in the feed, breakthrough time and the amount of sorbent-catalyst used.

4.4 EVALUATION OF *CLASS C* SORBENT-CATALYST

Class C sorbent-catalyst was prepared by coprecipitation using a third set of raw materials. The SEM morphology of the HART-46 fresh sorbent was depicted in Figure 20. The activities of the sorbent-catalysts were tested at 700°C using simulated coal gas. The tests with sorbent-catalyst were conducted with a simulated gas containing (vol %) 10% H₂, 15% CO, 5% CO₂, 1% H₂S, 15% H₂O, 0.18% NH₃, and balance N₂. The ammonia decomposition activity is shown Figures 21-24 and its H₂S removal ability is shown in Figures 25-28. As seen in Figures 21-24, initially the sorbent-

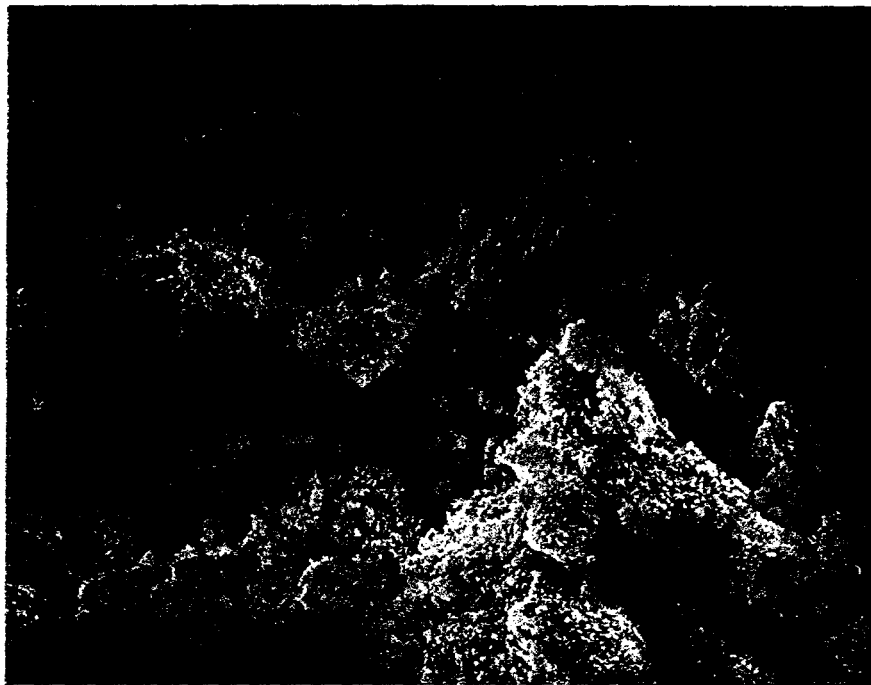


Figure 11. SEM Micrographs of HART-40 Fresh Sorbent-Catalyst

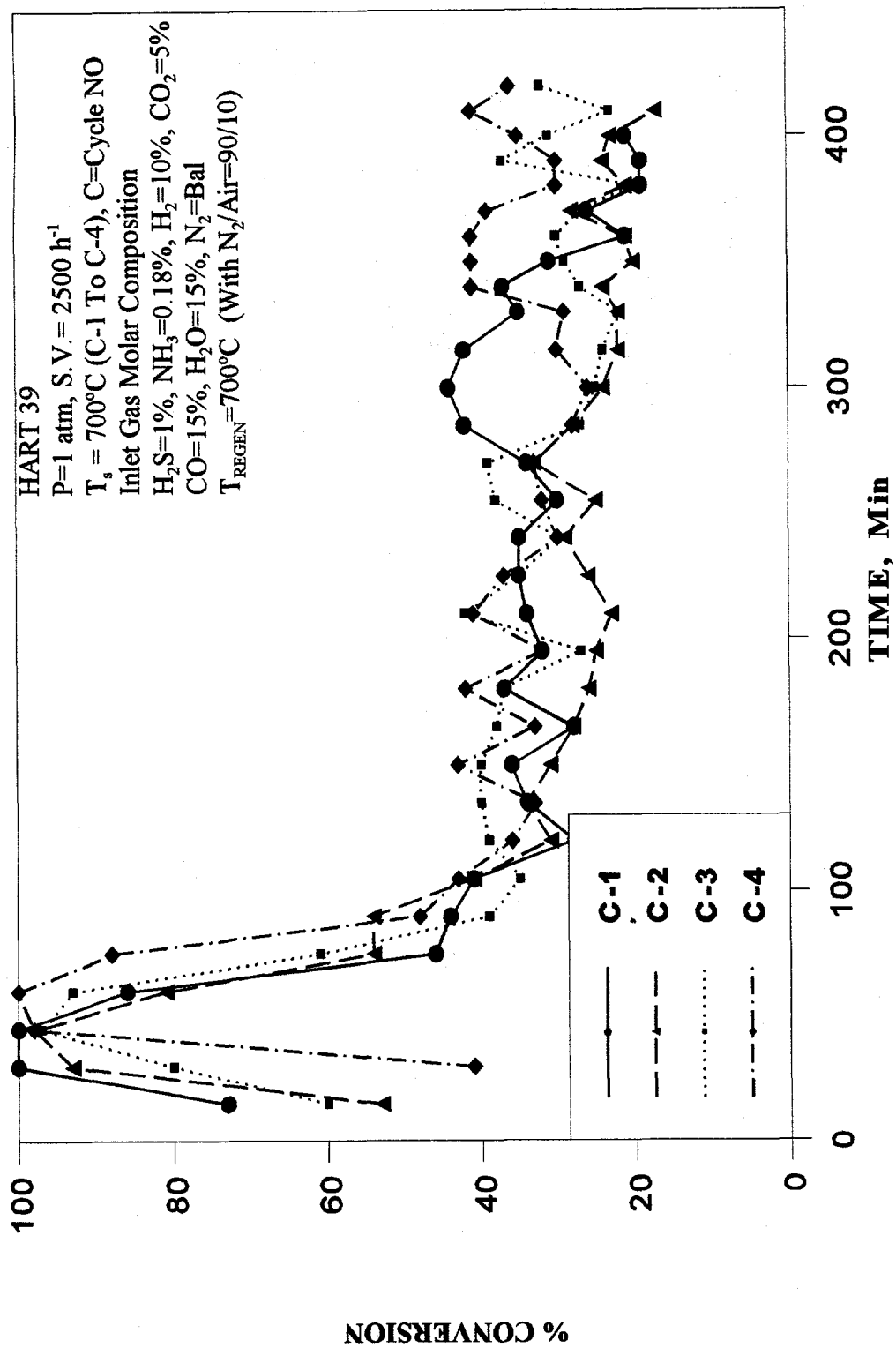


Figure 12. Conversion of Ammonia on HART 39 Sorbent-Catalyst

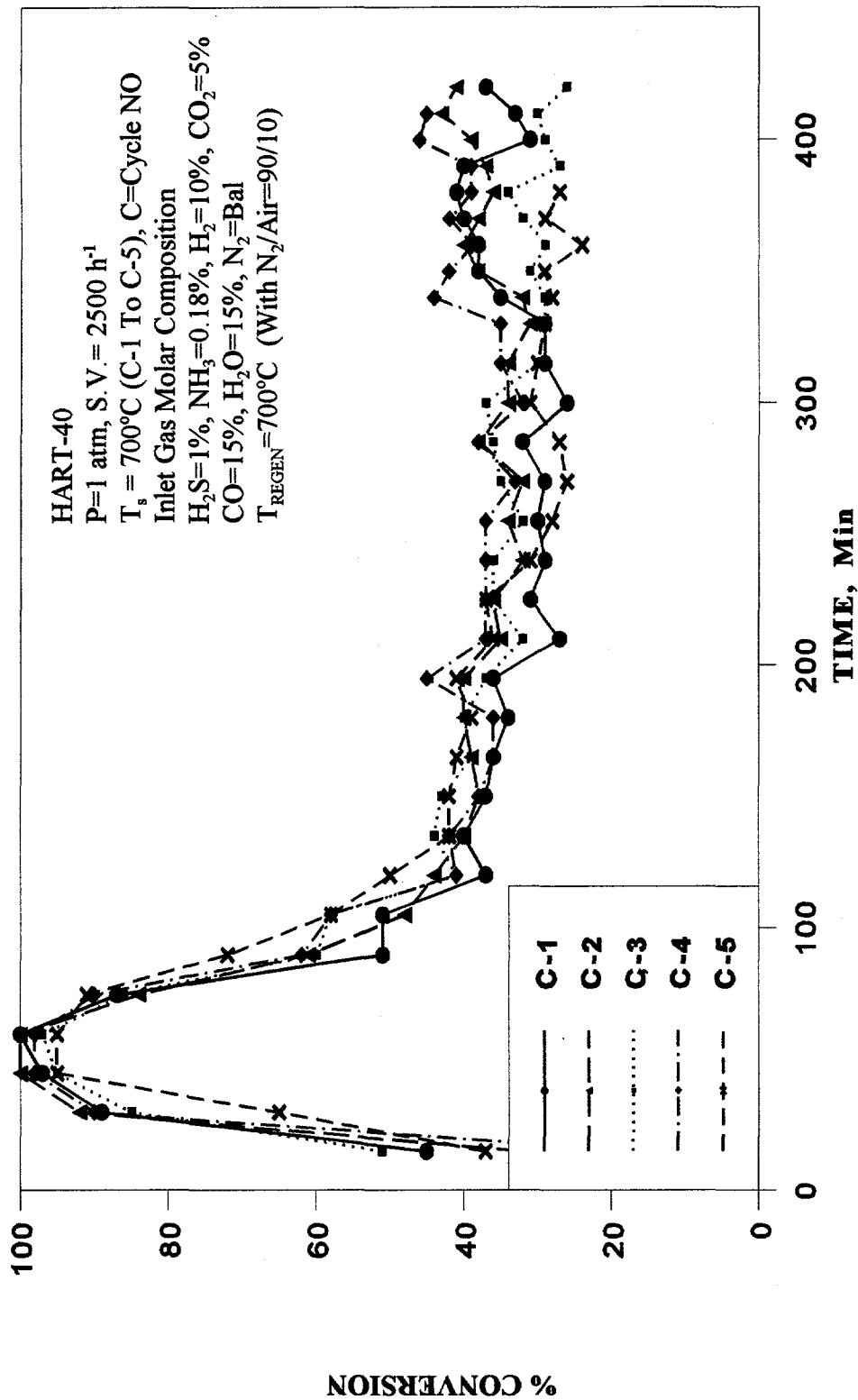


Figure 13. Conversion of Ammonia on HART-40 Sorbent-Catalyst

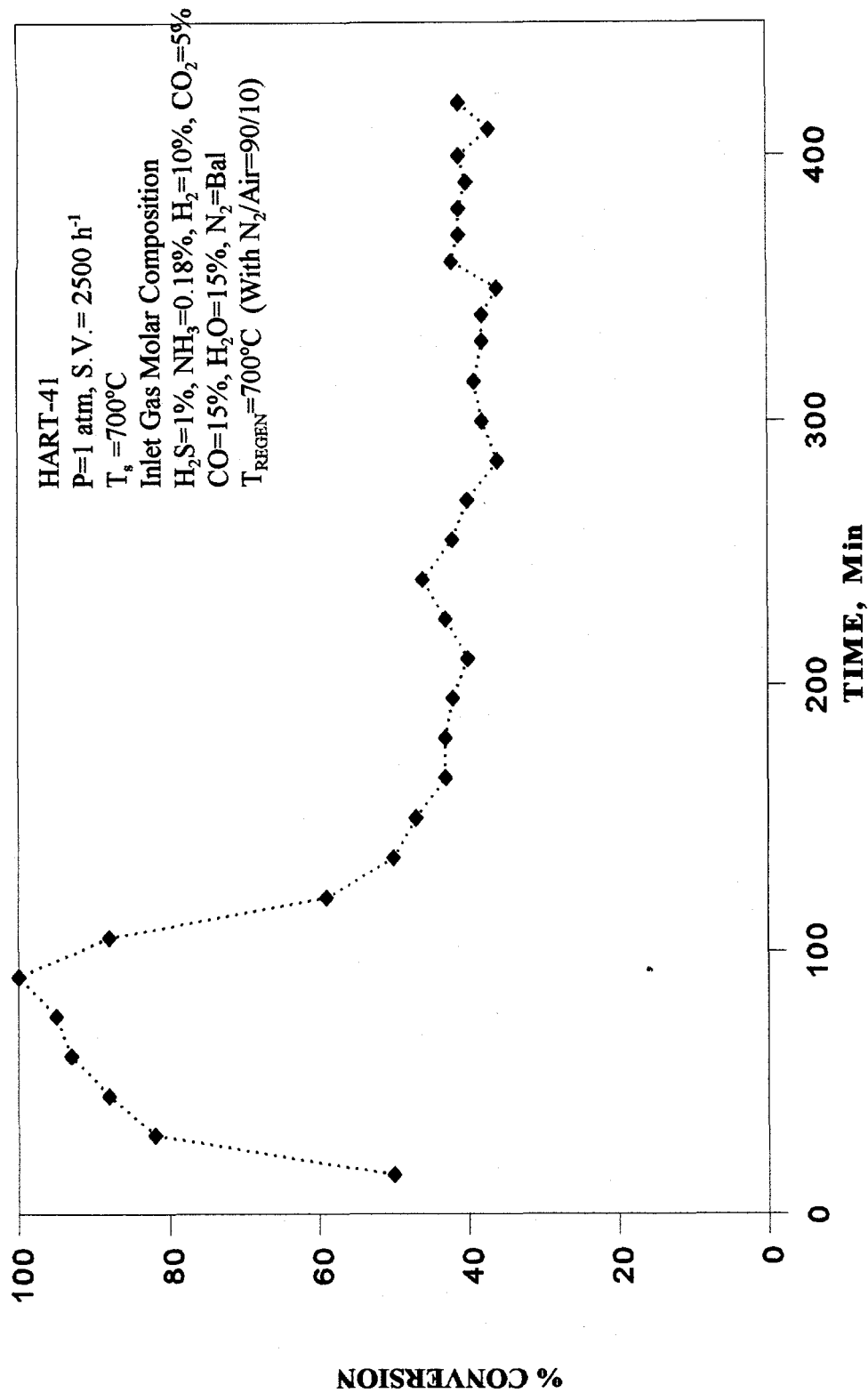


Figure 14. Conversion of Ammonia on HART-41 Sorbent-Catalyst

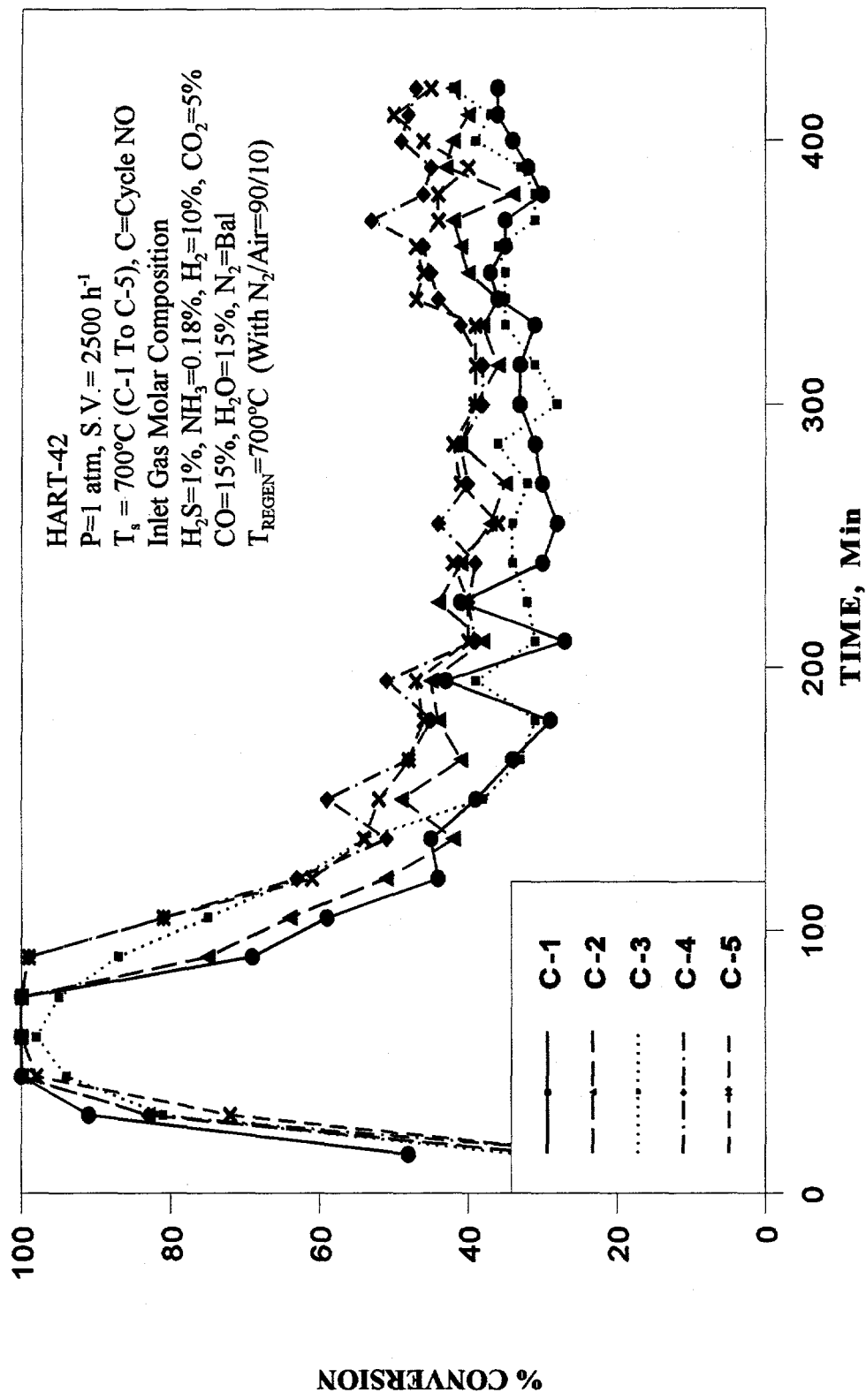


Figure 15. Conversion of Ammonia on HART-42 Sorbent-Catalyst

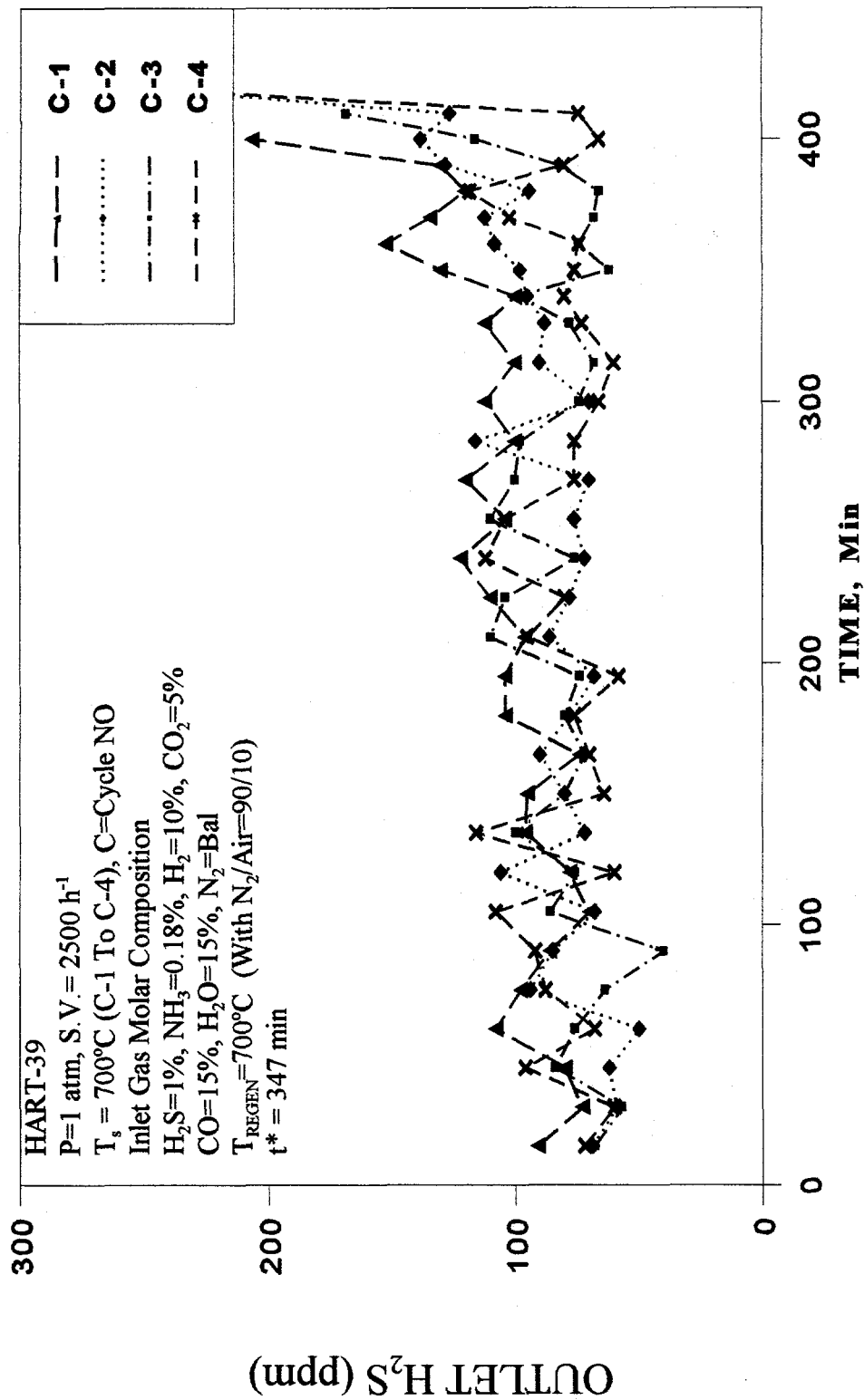


Figure 16. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-39 Sorbent-Catalyst

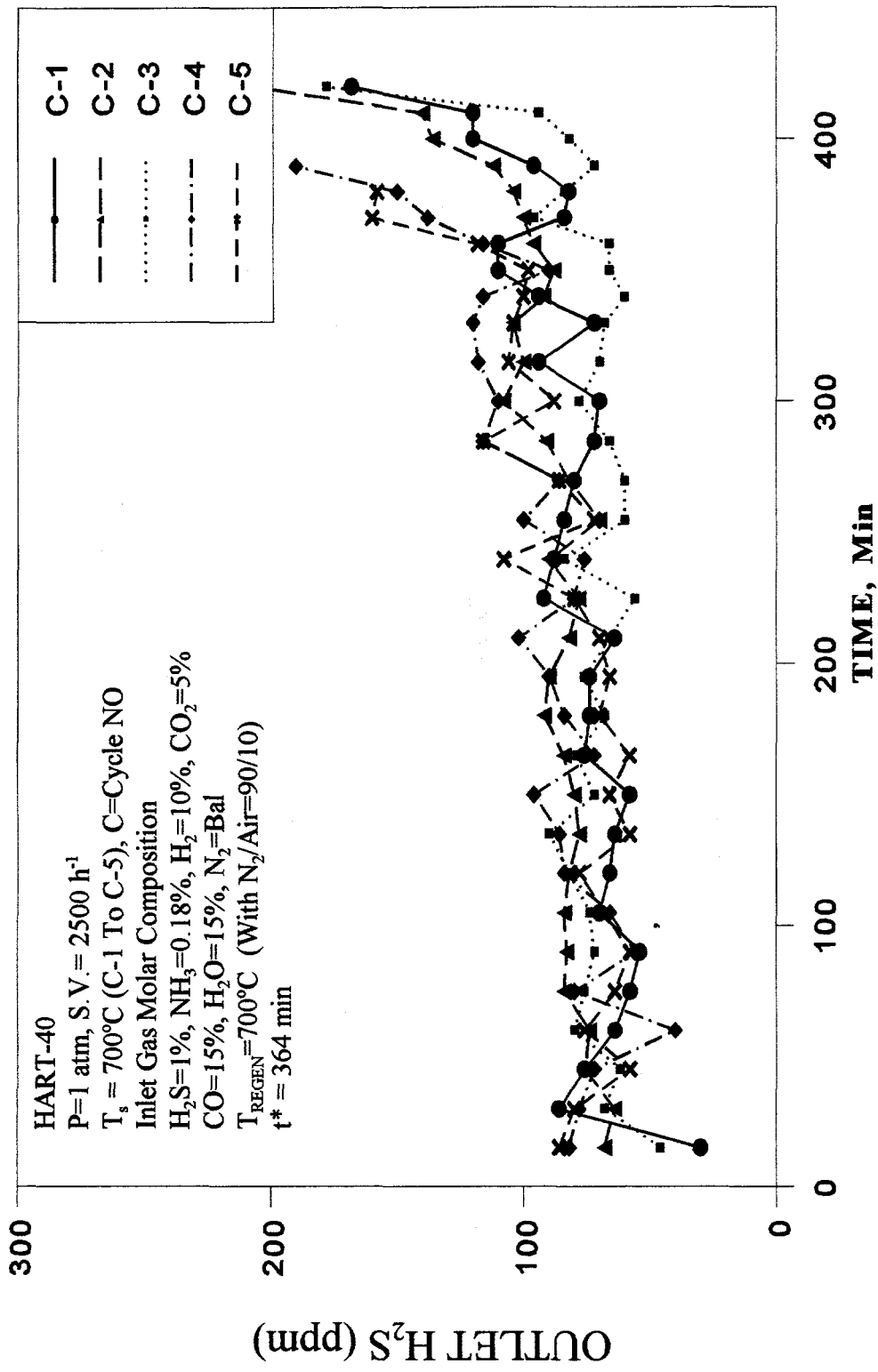


Figure 17. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-40 Sorbent-Catalyst

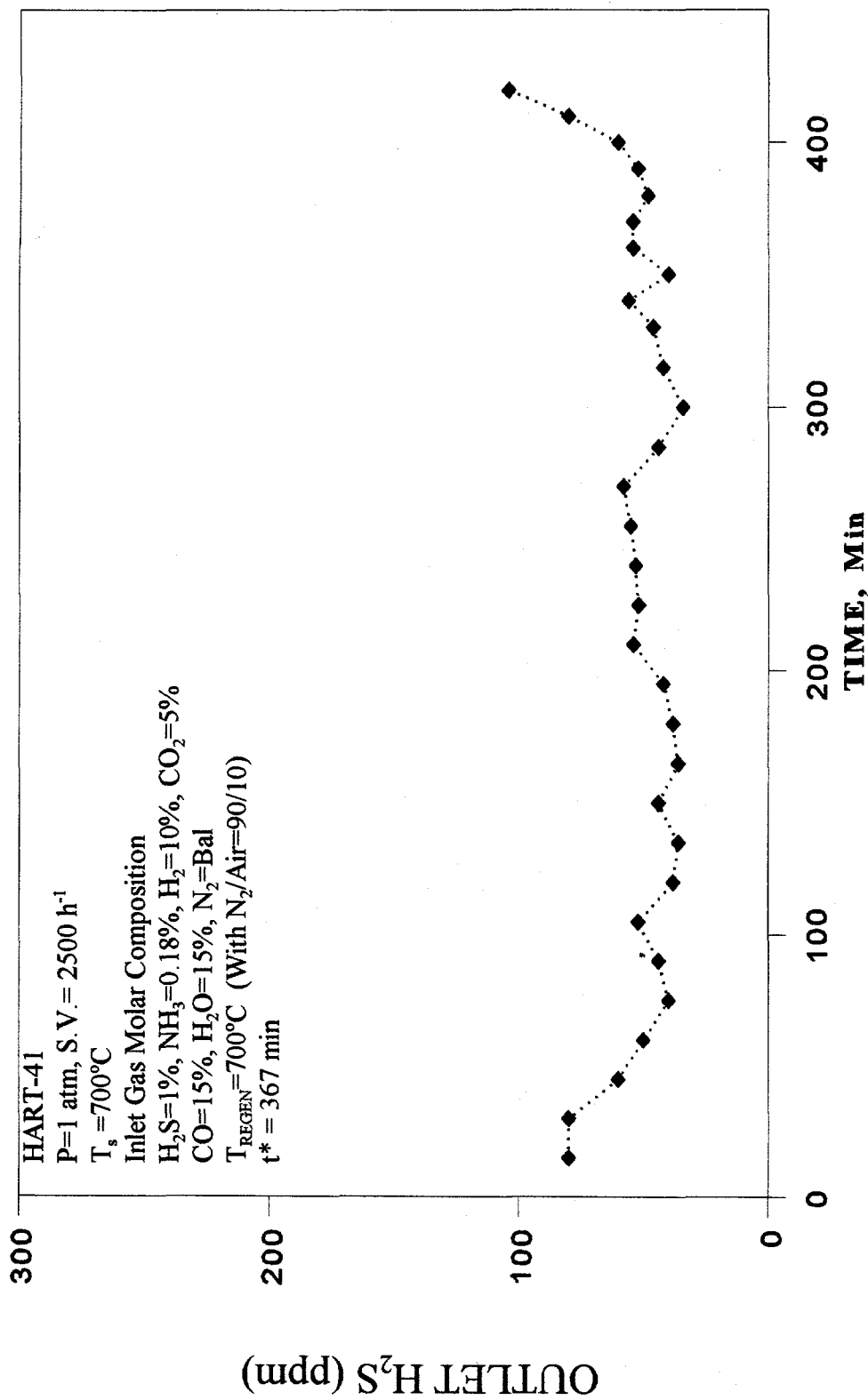


Figure 18. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-41 Sorbent-Catalyst

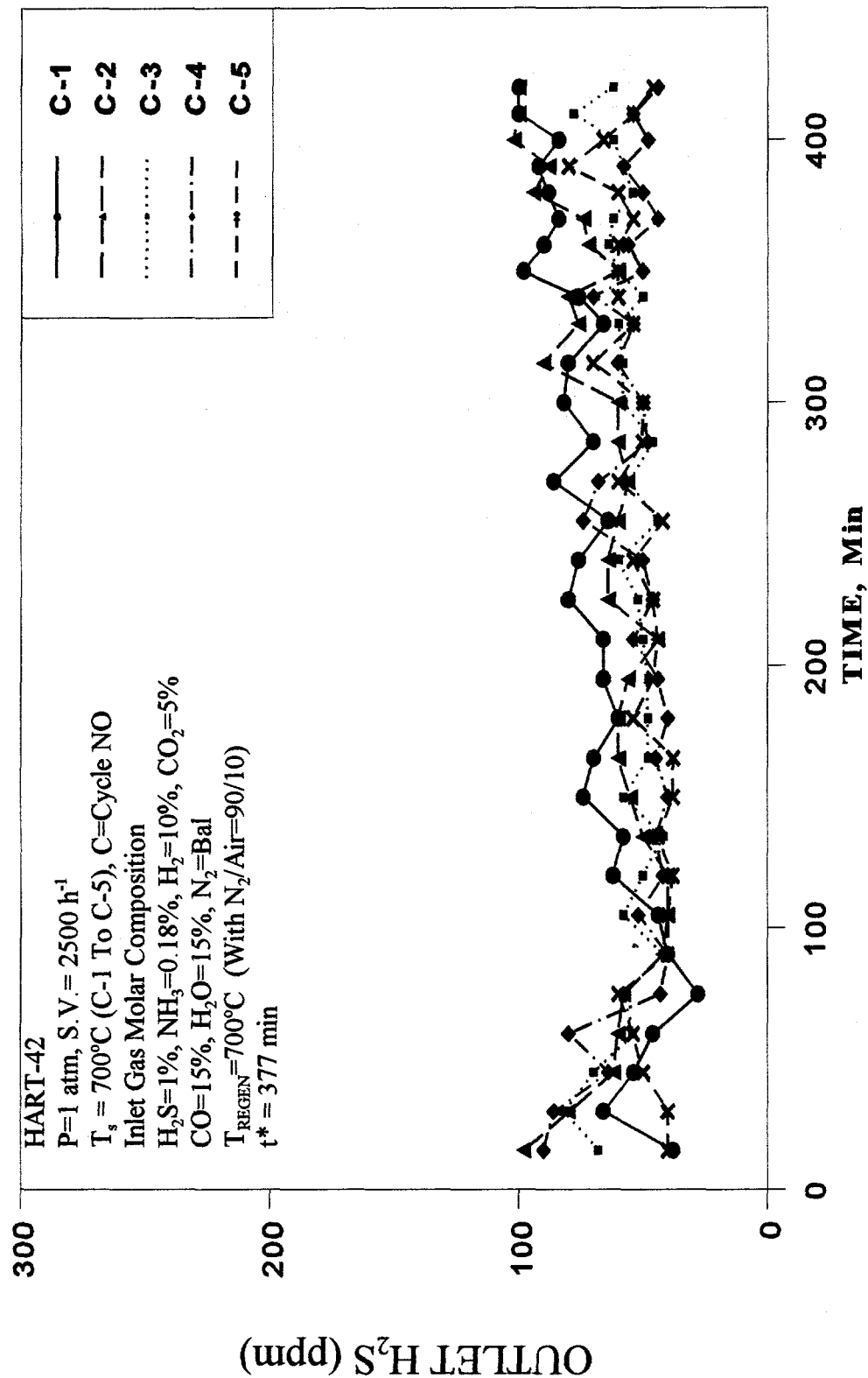


Figure 19. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-42 Sorbent-Catalyst

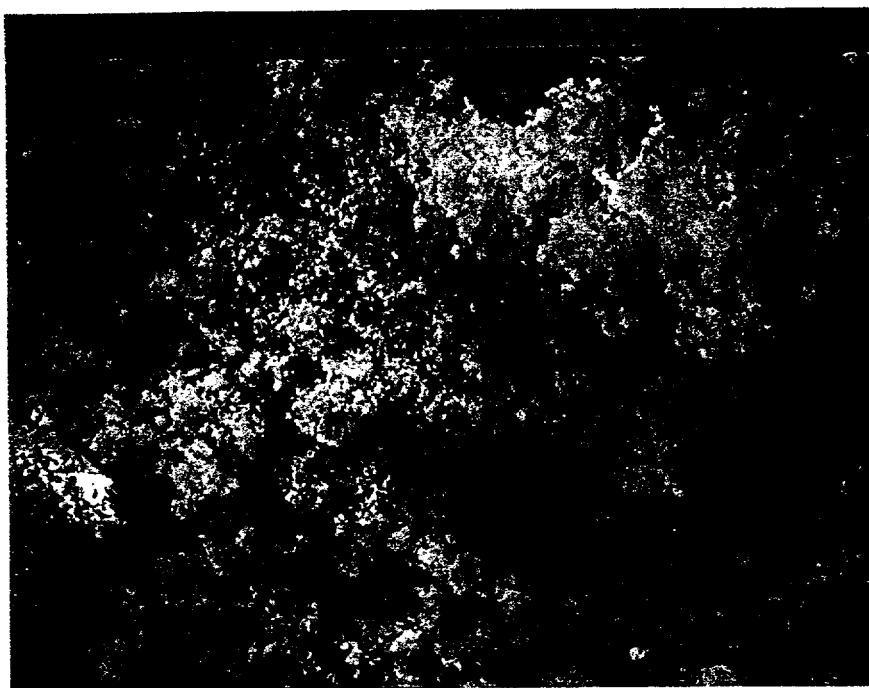


Figure 20. SEM Micrographs of HART-46 Fresh Sorbent-Catalyst

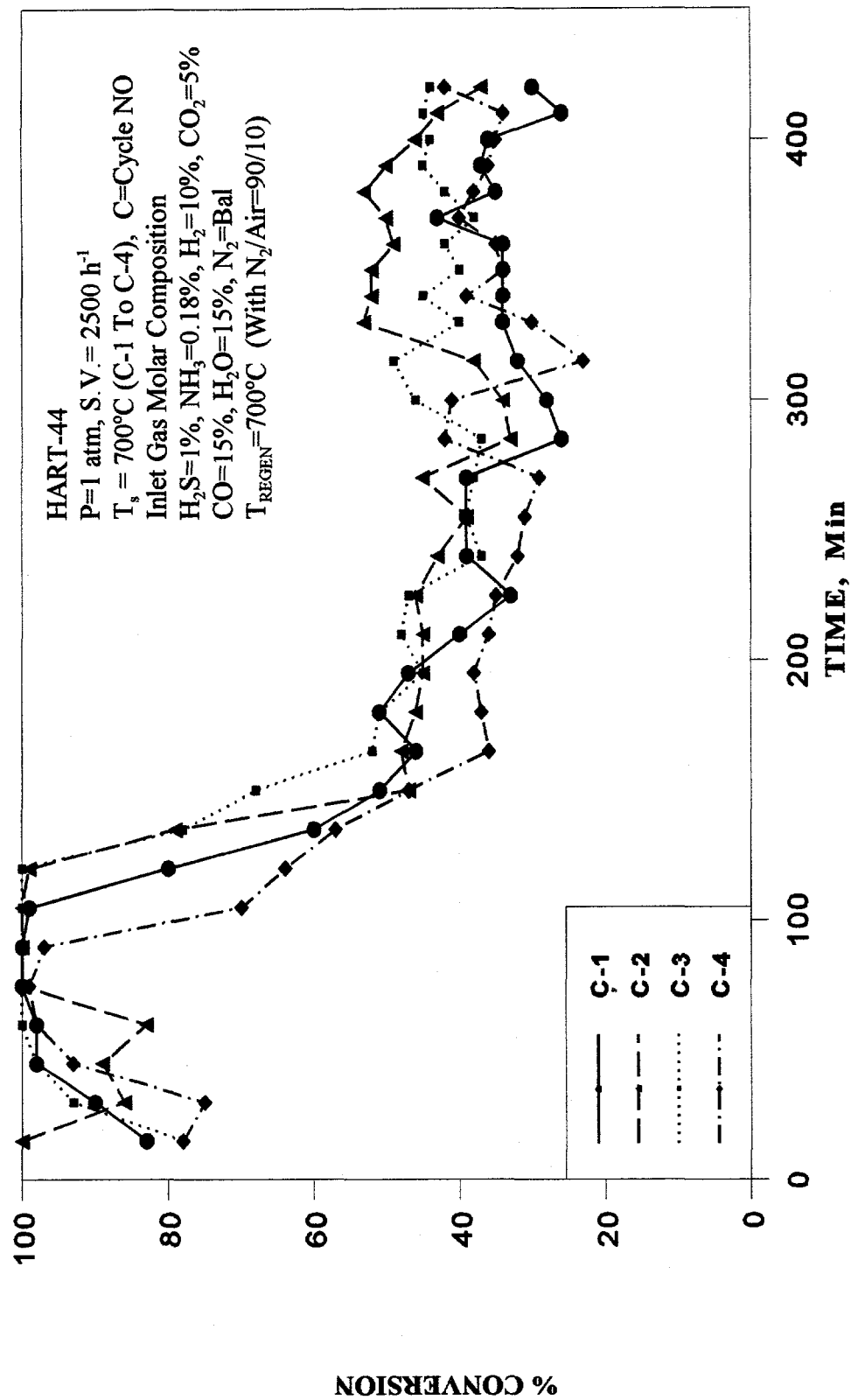


Figure 21. Conversion of Ammonia on HART-44 Sorbent-Catalyst

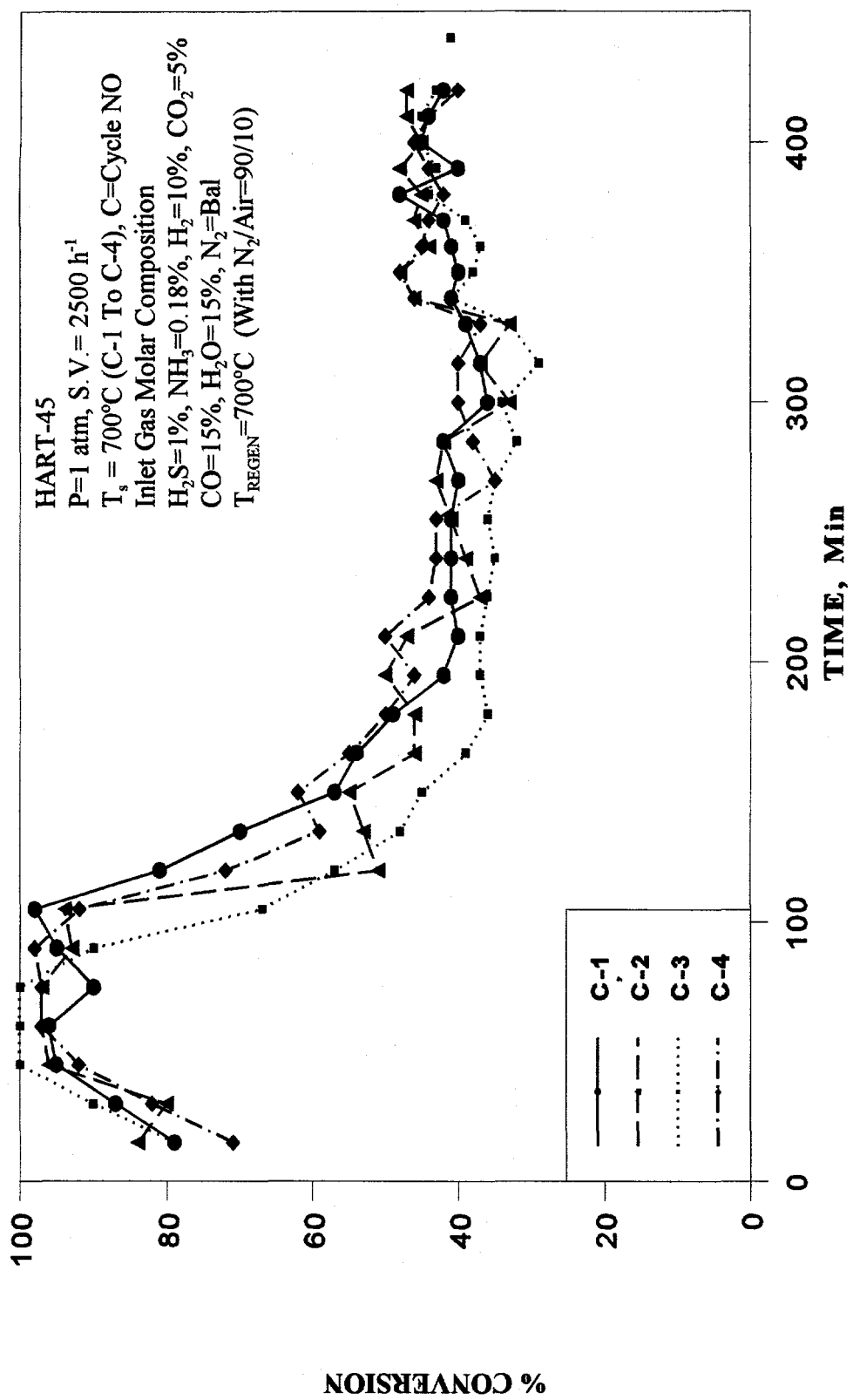


Figure 22. Conversion of Ammonia on HART-45 Sorbent-Catalyst

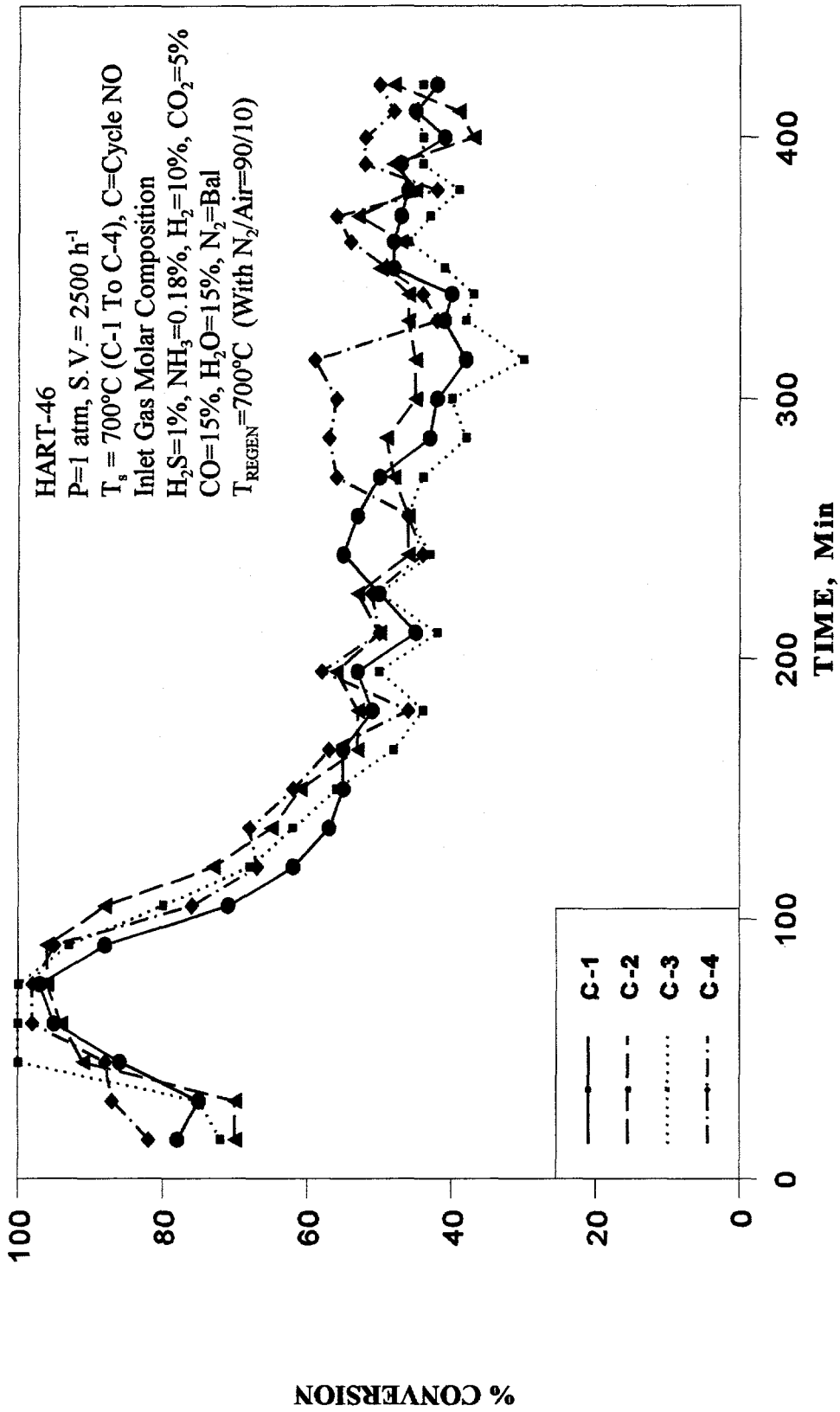


Figure 23. Conversion of Ammonia on HART-46 Sorbent-Catalyst

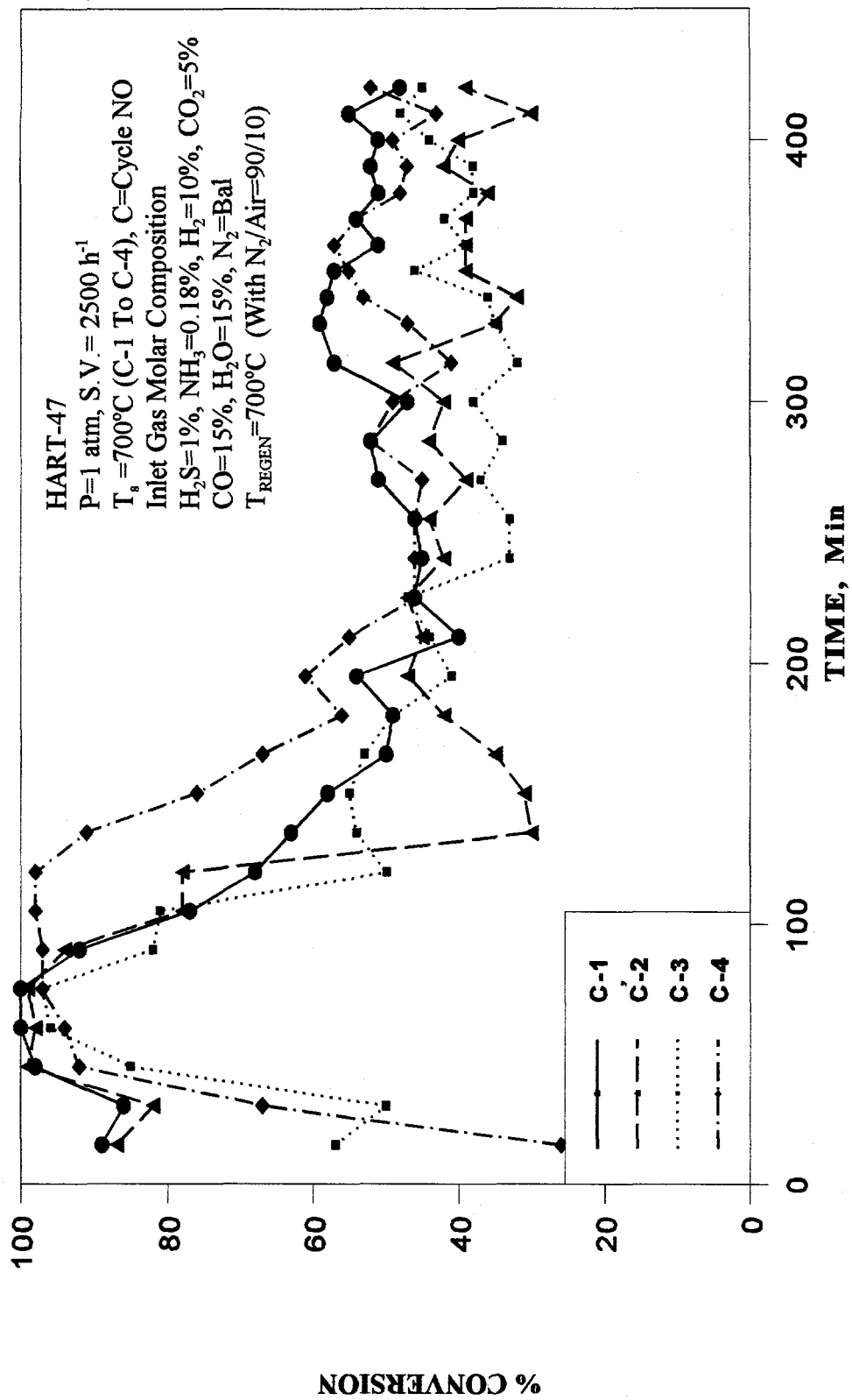


Figure 24. Conversion of Ammonia on HART-47 Sorbent-Catalyst

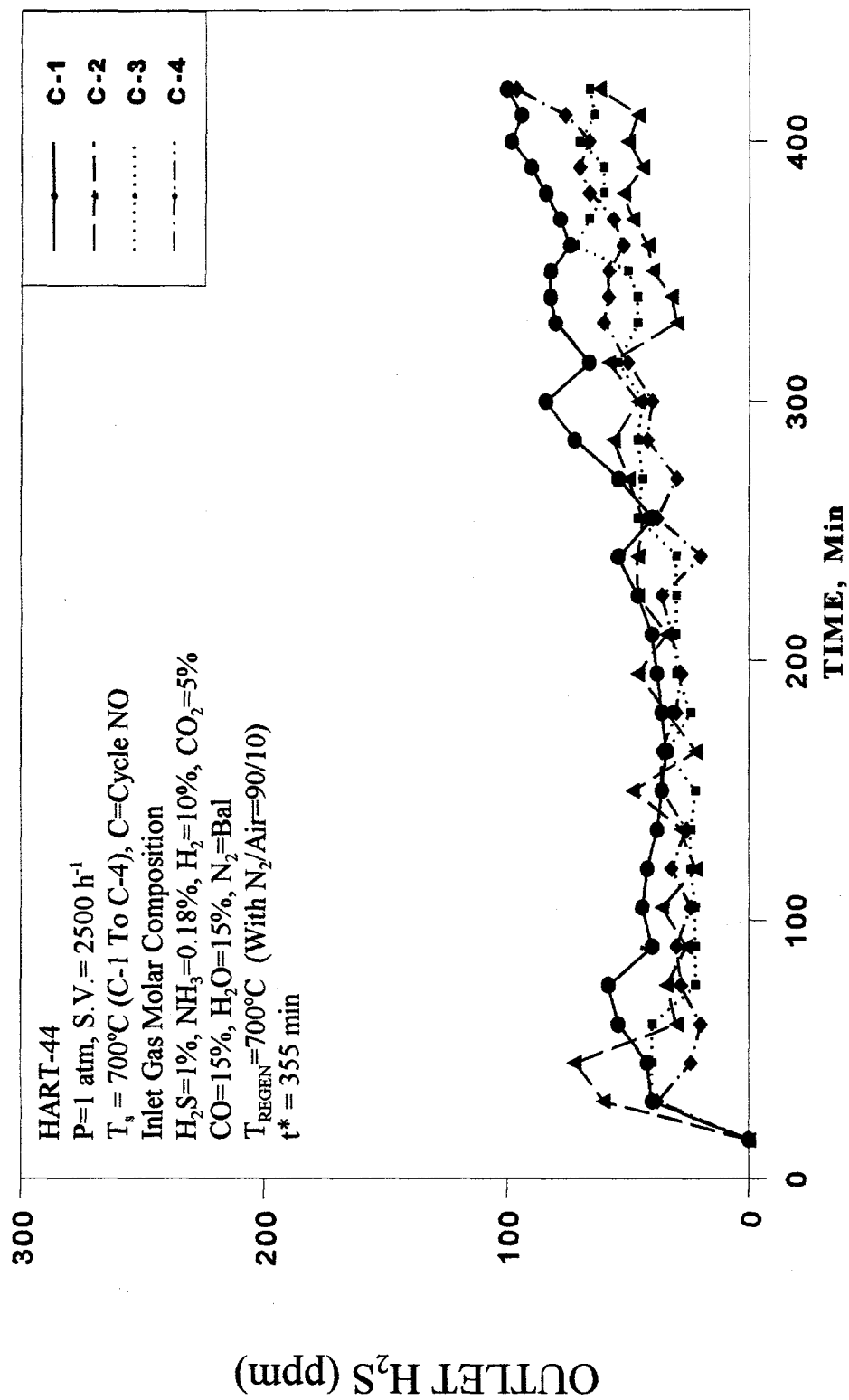


Figure 25. H_2S Breakthrough Curves in Successive Sulfidation Cycles of HART-44 Sorbent-Catalyst

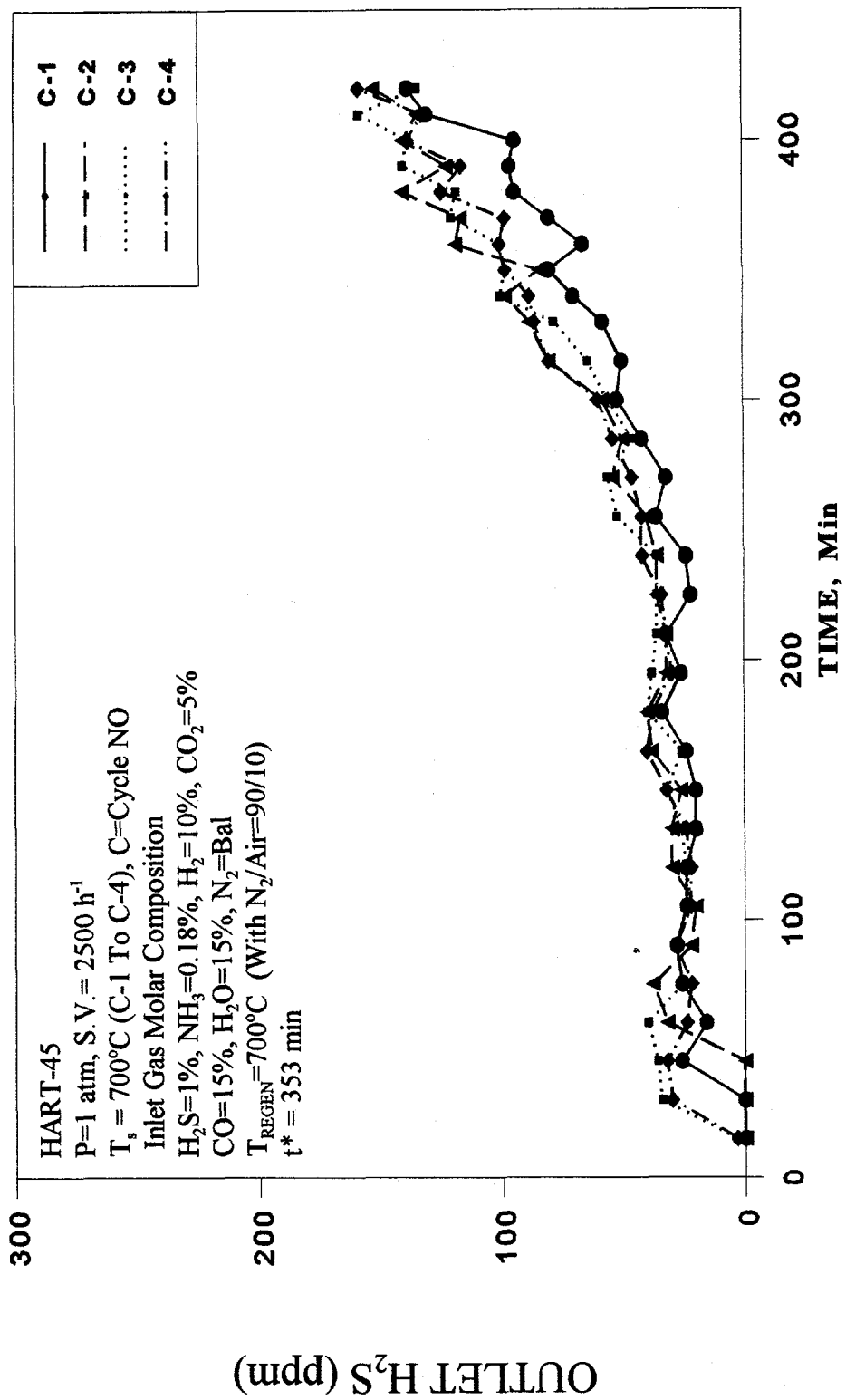


Figure 26. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-45 Sorbent-Catalyst

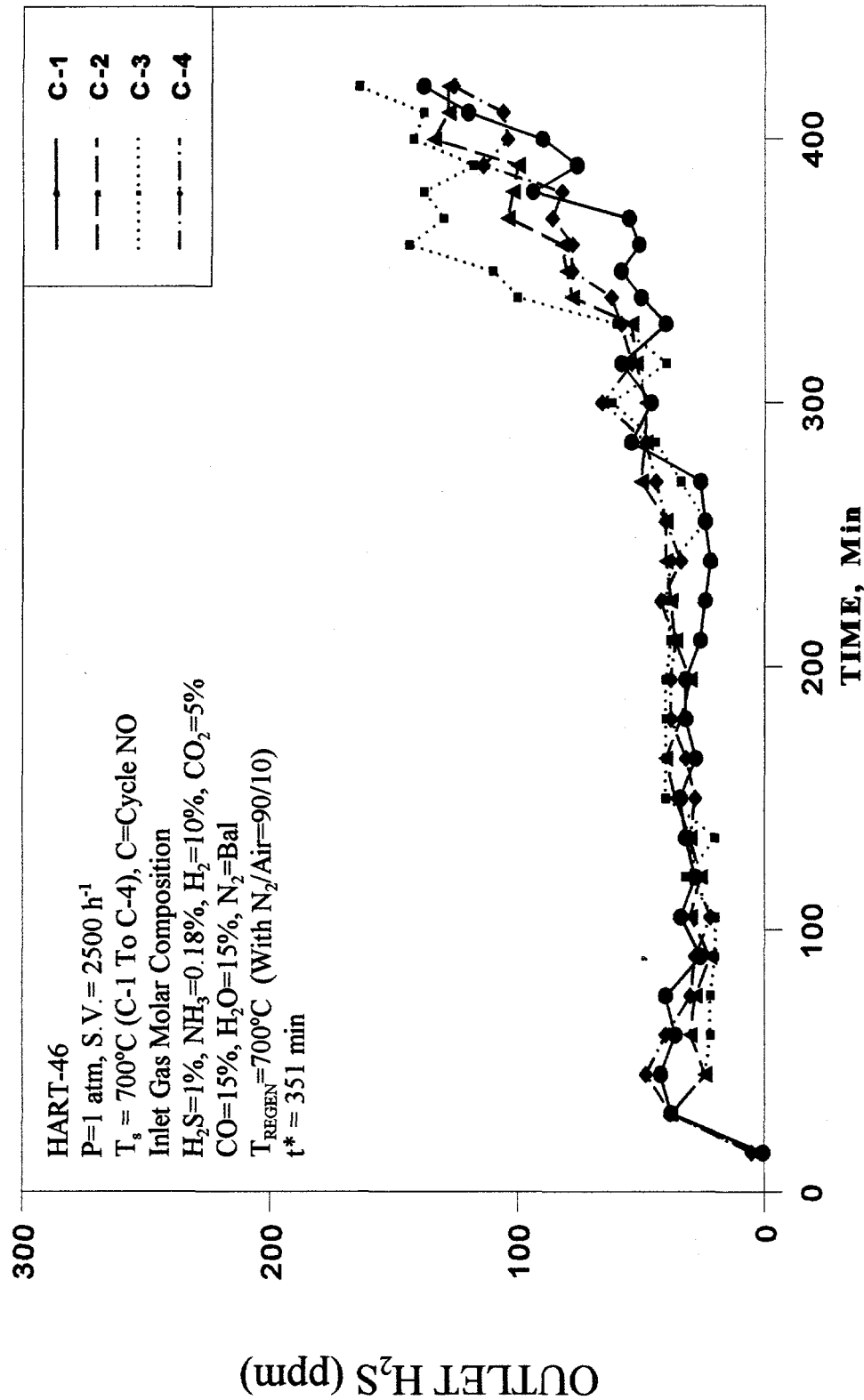


Figure 27. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-46 Sorbent-Catalyst

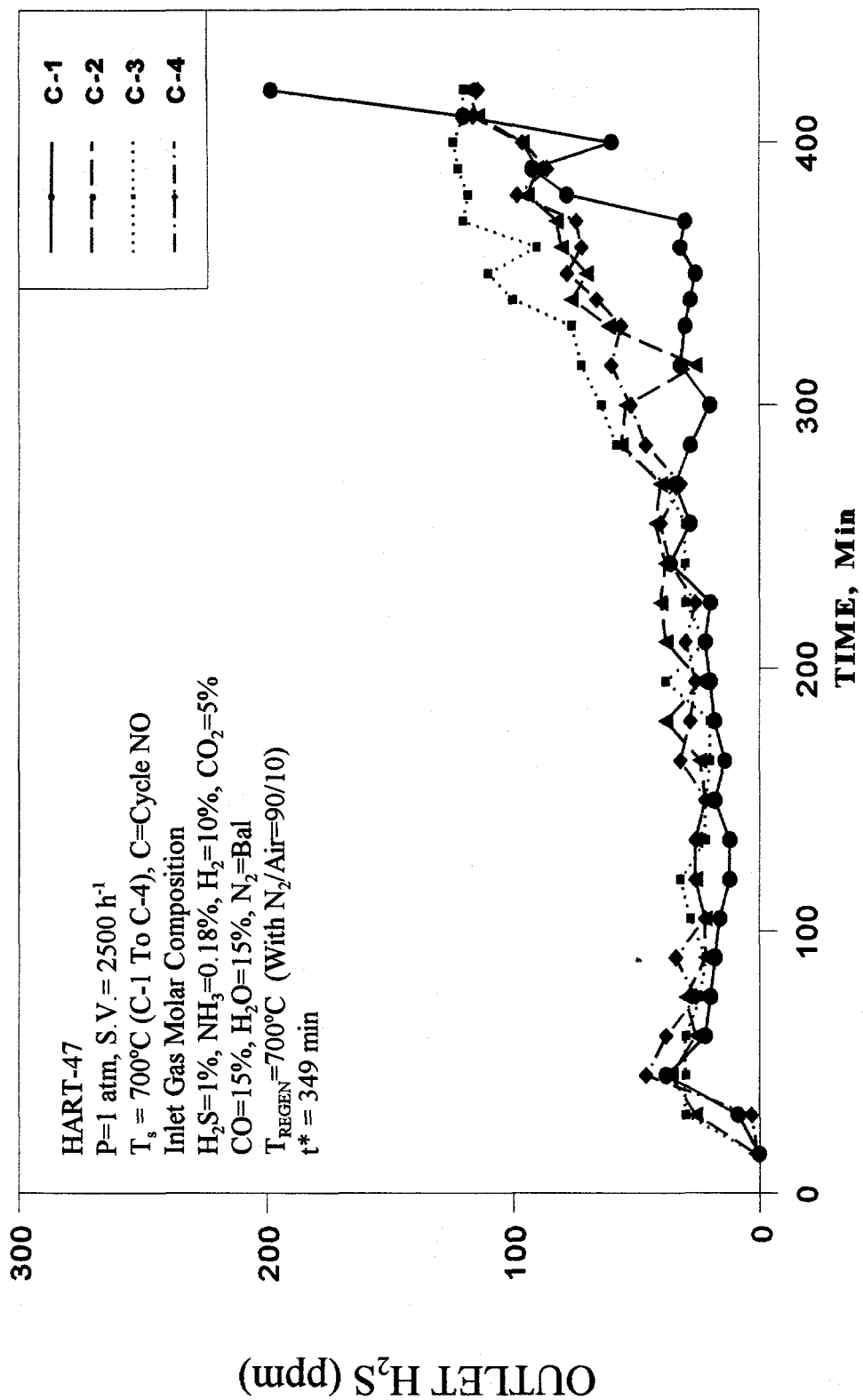


Figure 28. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-47 Sorbent-Catalyst

catalyst showed a very high activity (>90%) for about 60 minutes. After that, the decline in activity was probably due to the poisoning of the catalyst by H₂S. Compared to class B sorbent-catalyst, for class C sorbent-catalyst, 90% decomposition time window, has been increased from about 50 minutes to 60 minutes. As seen in from Figures 25-28, the pre-breakthrough H₂S levels for this sorbent-catalyst were less than 60 ppm. Complete conversion was achieved at breakthrough. The pre-breakthrough level has decreased from 100 ppm to about 60 ppm compare to class B sorbent-catalyst. The sulfur capacities of the HART-44, 45, 46 and 47 during cycles 4 were 28.3, 28.1, 27.9 and 27.8 gS/100 g sorbent, respectively. Sulfur capacity was calculated using the concentration of H₂S in the feed, breakthrough time and the amount of sorbent-catalyst used.

4.5 EVALUATION OF CLASS D SORBENT-CATALYST

Class D sorbent-catalyst was prepared by coprecipitation using a fourth set of raw materials. The SEM morphology of the HART-49 fresh, sulfided and regenerated sorbent-catalyst was depicted in Figure 29 (a-c) and HART-51 in Figure 30.

The activities of the sorbent-catalysts were tested at 700°C using simulated coal gas. The tests with sorbent-catalyst were conducted with a simulated gas containing (vol %) 10% H₂, 15% CO, 5% CO₂, 1% H₂S, 15% H₂O, 0.18% NH₃, and balance N₂. The ammonia decomposition activity of HART-48 is shown Figure 31 and its H₂S removal ability is shown in Figure 32. As seen in Figures 31, initially the sorbent-catalyst showed a very high activity (>90%) for about 100 minutes. After that, the decline in activity was probably due to the poisoning of the catalyst by H₂S. As seen in from Figures 32, the pre-breakthrough H₂S level for this sorbent-catalyst was less than 50 ppm. Complete conversion was achieved at breakthrough.

4.5.1 EFFECT OF STEAM

Although steam is neither a reactant nor a product in the ammonia decomposition reaction,

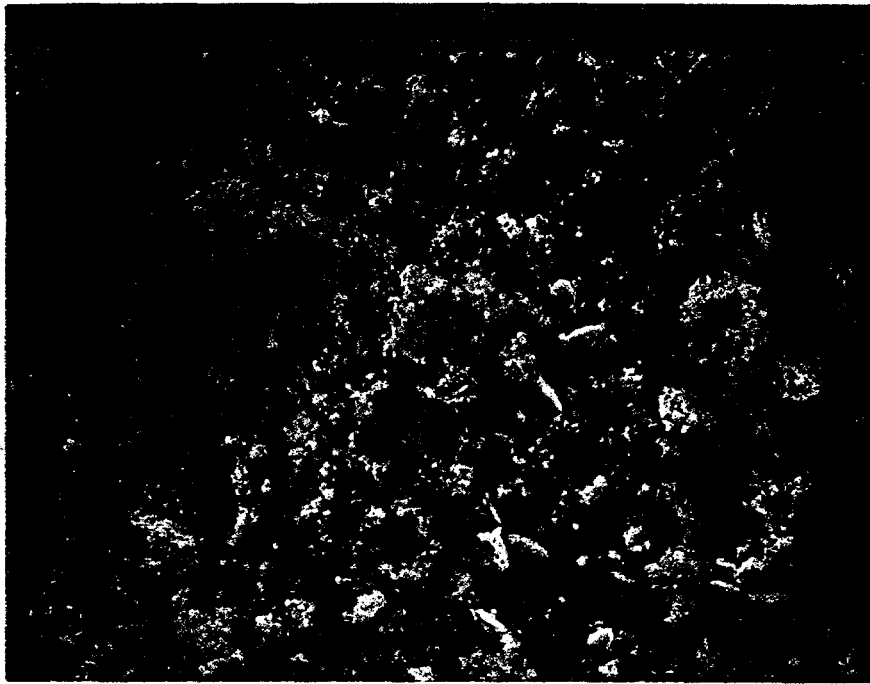


Figure 29. SEM Micrographs of HART-49 (a) Fresh Sorbent-Catalyst

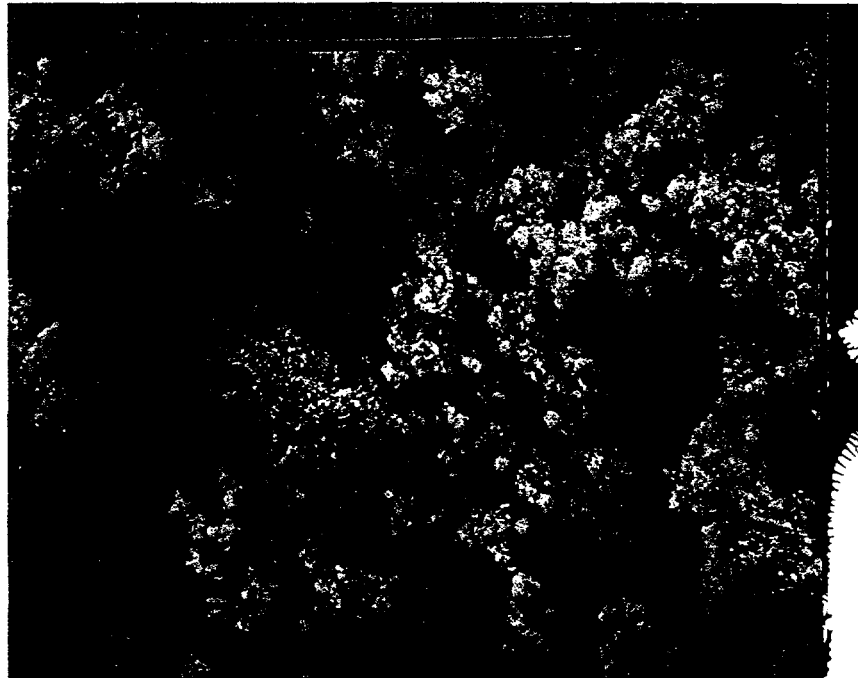


Figure 29. SEM Micrographs of HART-49 (b) Sulfided Sorbent-Catalyst

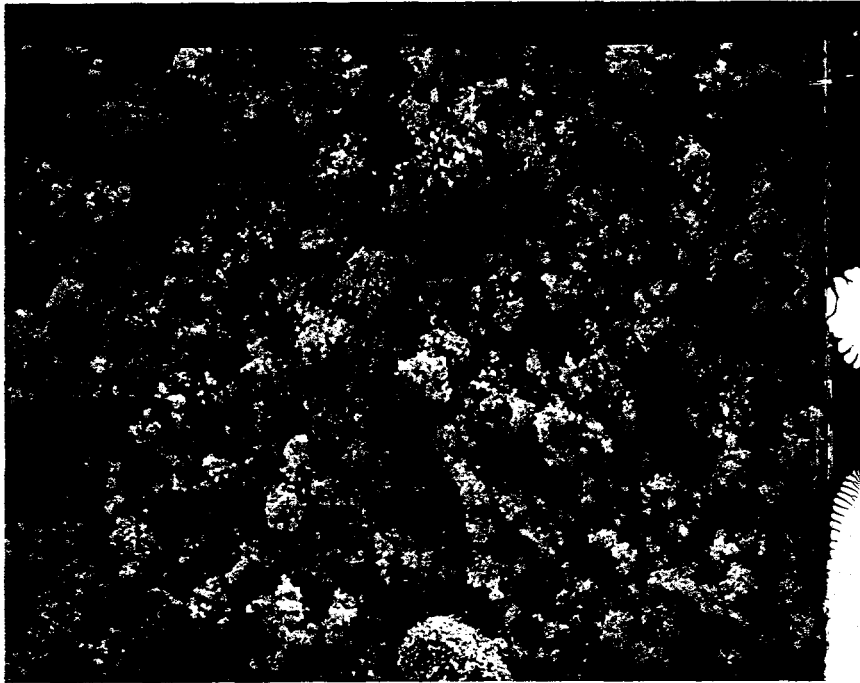


Figure 29. SEM Micrographs of HART-49 (c) Regenerated Sorbent-Catalyst

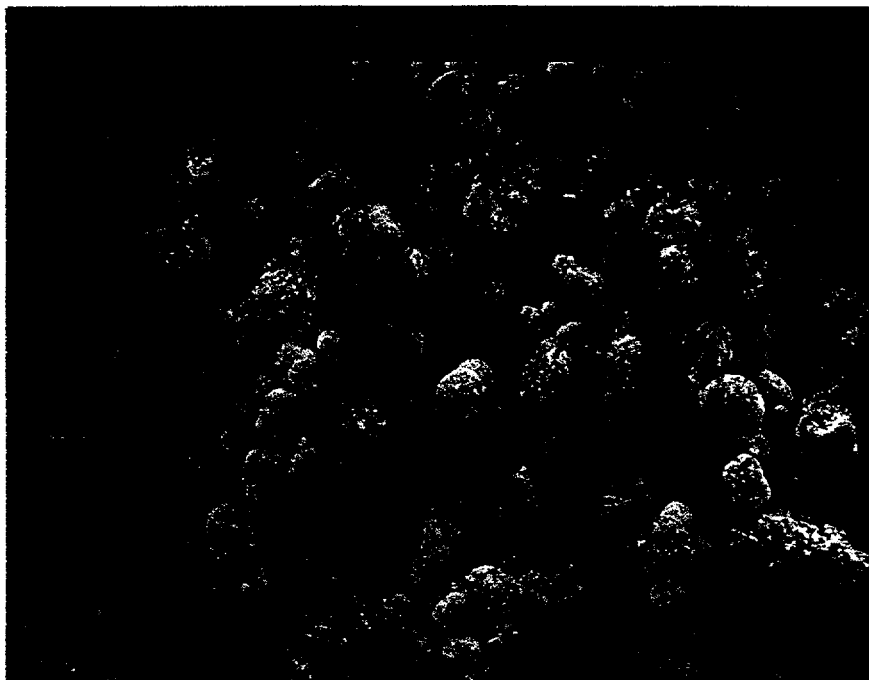


Figure 30. SEM Micrographs of HART-51 Fresh Sorbent-Catalyst

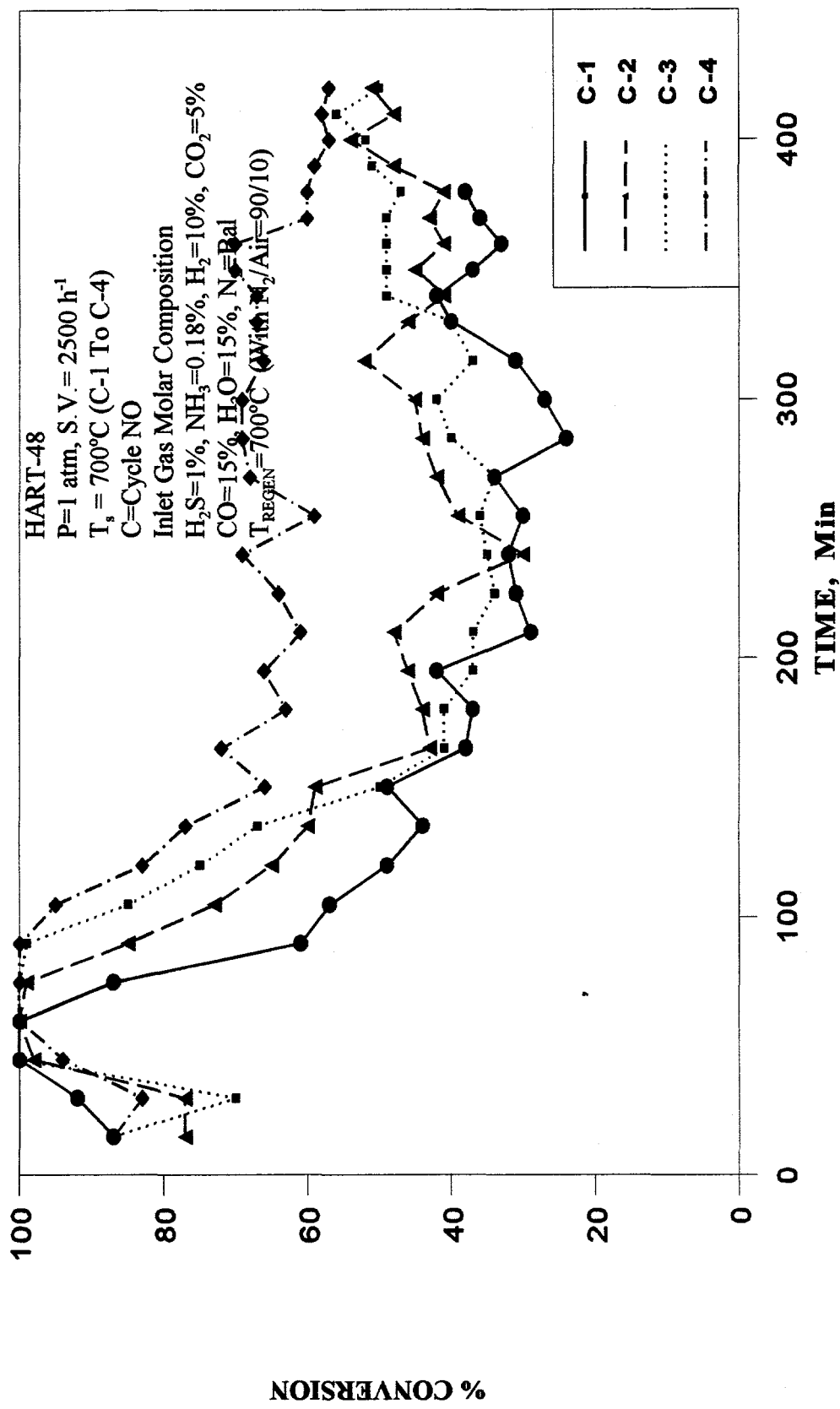


Figure 31. Conversion of Ammonia on HART-48 Sorbent-Catalyst

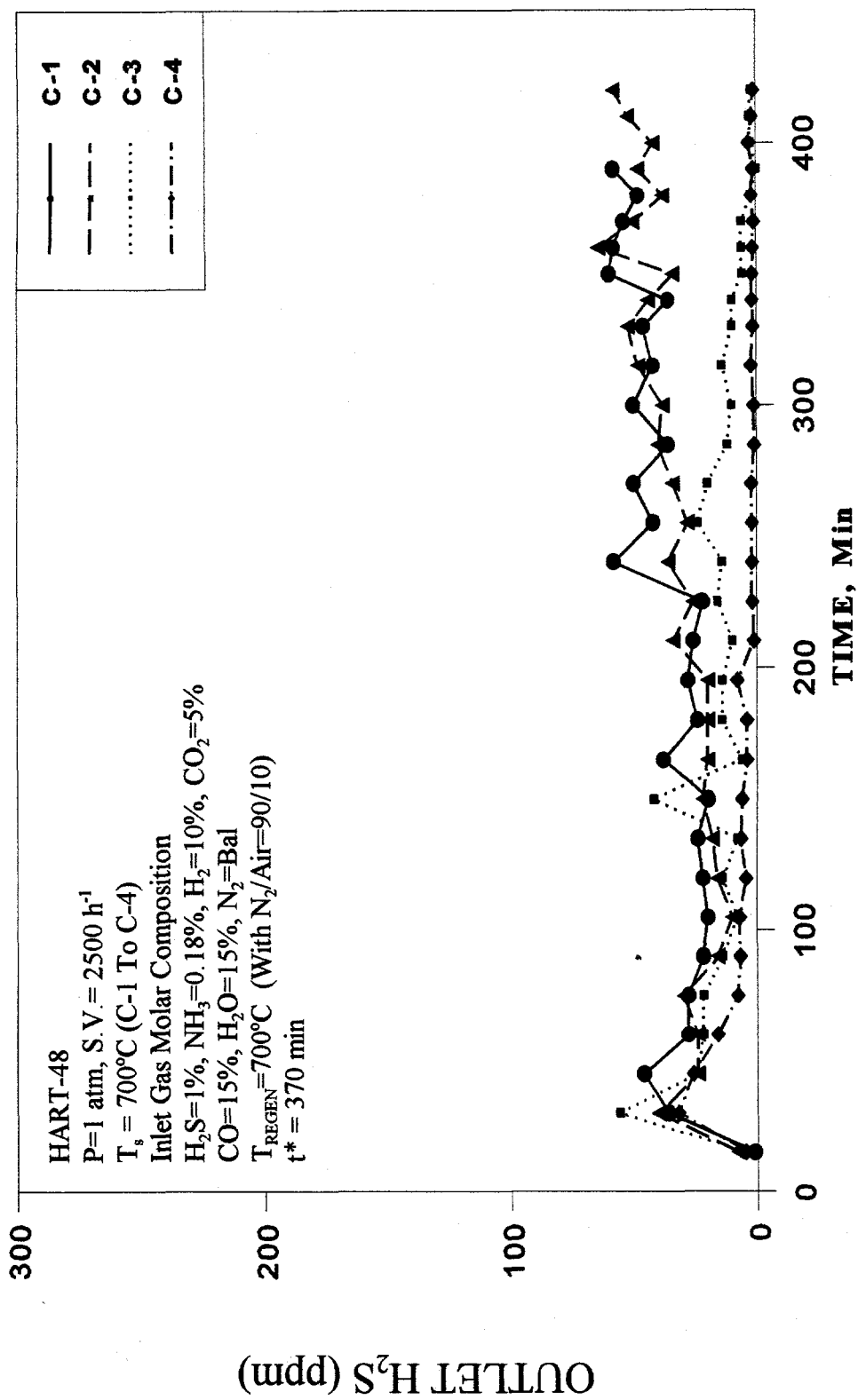


Figure 32. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-48 Sorbent-Catalyst

the presence of steam can affect the decomposition rate in other ways. For example, varying the concentration of steam could change the partial pressure of H_2 in the gas mixture (water gas shift reaction), thereby changing the rate. The catalyst support / sorbent may be chemically altered under high concentrations of steam and elevated temperatures, leading to loss of surface area. The effect of steam was determined experimentally with simulated coal gas mixtures containing 0 and 15%. Figure 33 shows the effect of steam on ammonia decomposition activity of HART-49 sorbent-catalyst.

Cycles 1, 2 was carried out with a simulated gas containing (vol %) 10% H_2 , 15% CO, 5% CO_2 , 1% H_2S , 0.18% NH_3 , and balance N_2 . HART-49 showed >90% decomposition and there was no decline in ammonia decomposition activity for about 400 min. When the temperature decreased from 700 to 625°C (Cycle 6), the window was reduced from 400 min to about 180 min. Further decreasing the temperature to 550° (cycles 3-5) reduced the window to about 140 min. Once again by increasing the temperature to 700°C (cycle -7), the window of operation increased to 400 min. Cycle-8 was carried out with simulated gas containing 15% steam. A marked decrease in catalytic activity was noted and the window now decreased from 400 min to about 180 min. This clearly shows that the steam is more deleterious than H_2S for ammonia decomposition activity. It seems steam is disintegrating the catalyst support/sorbent. The corresponding H_2S breakthrough curves were shown in Figure 34. The pre-breakthrough H_2S is less than 20 ppm. Complete conversion was achieved at breakthrough. The sulfur capacities of the HART-48, 49, and 51 during cycles 4 were 28.7, 28.9, 29.5 gS/100 g sorbent, respectively.

4.5.2 EFFECT OF TEMPERATURE

The effect of temperature on ammonia decomposition activity was investigated over the range from 500-700°C using a simulated coal gas. The ammonia decomposition activity for HART-49 increases as the temperature was increased from 500 to 700° C as shown in Figure 35. The window

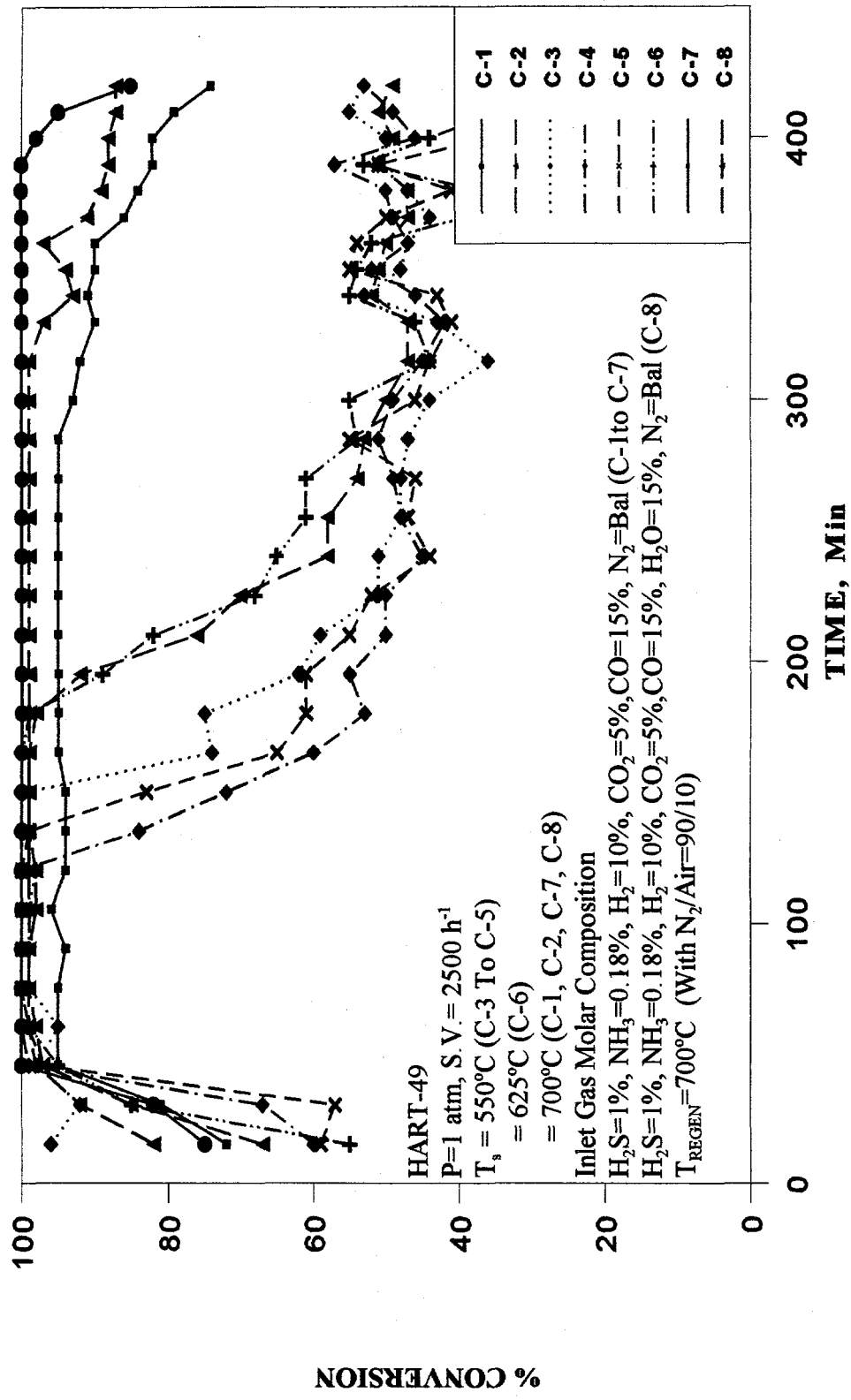


Figure 33. Conversion of Ammonia on HART-49 Sorbent-Catalyst

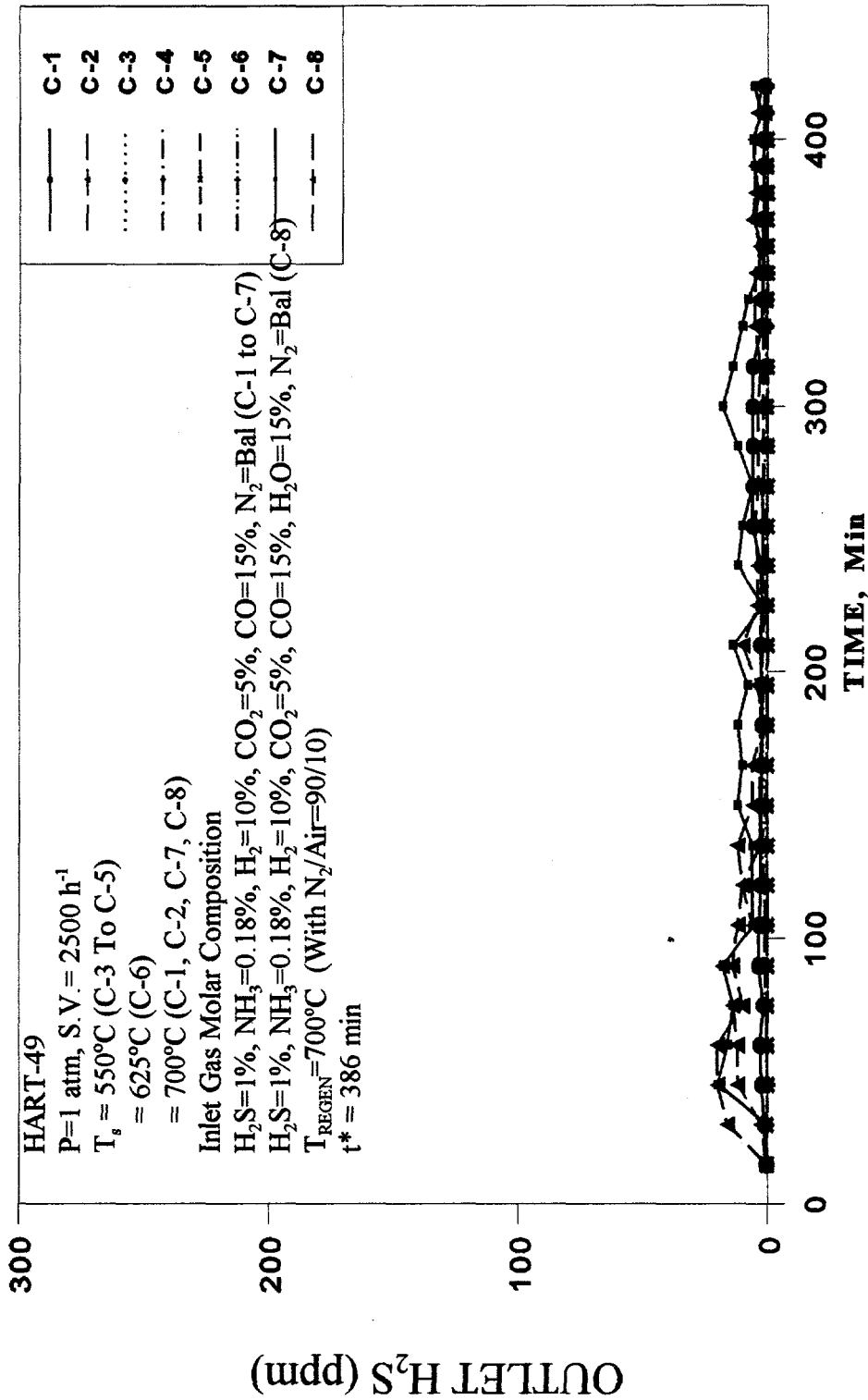


Figure 34. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-49 Sorbent-Catalyst

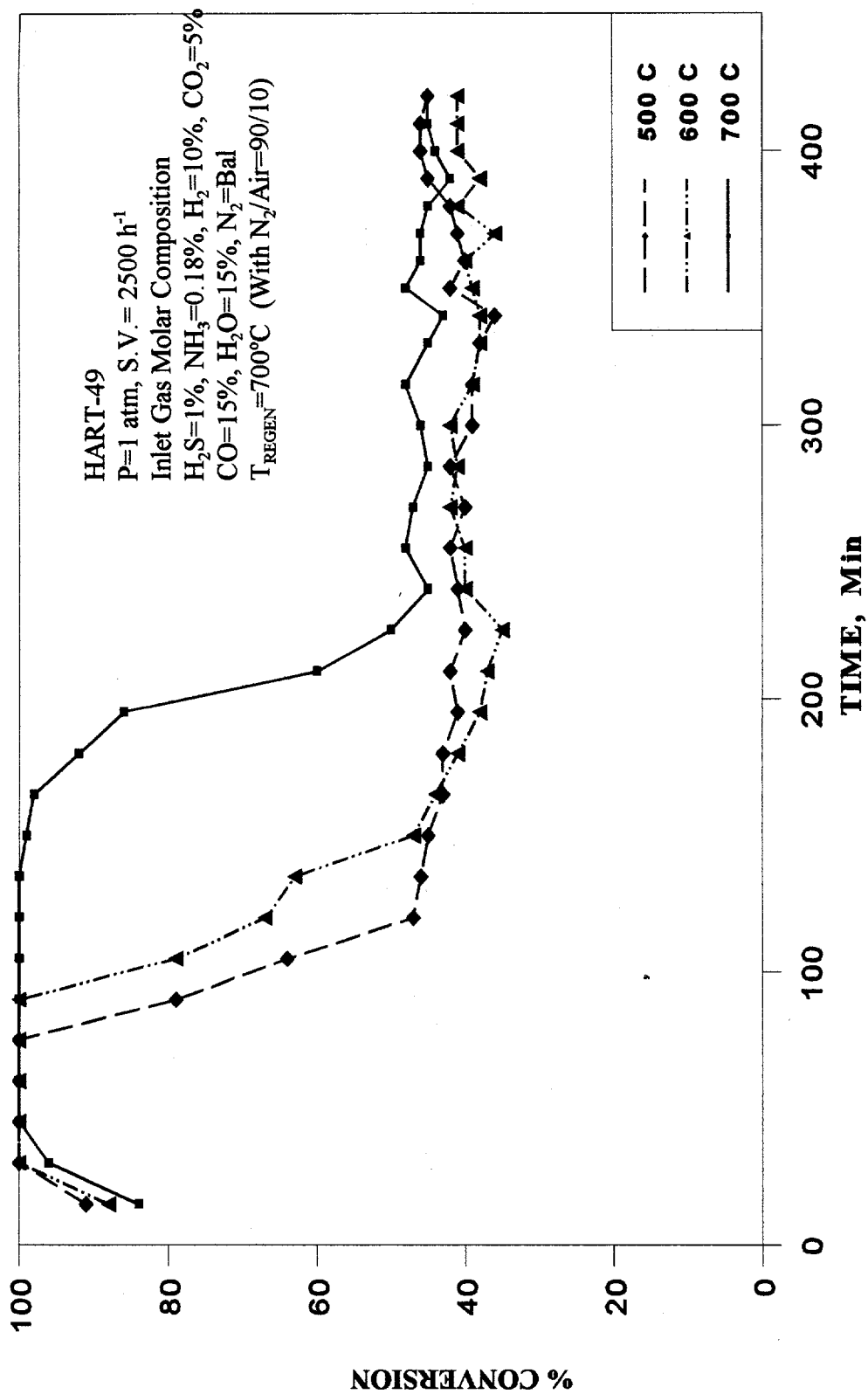


Figure 35. Conversion of Ammonia on HART-49 Sorbent-Catalyst

was increased from 70 to 90 to 180 minutes as the temperature increased from 500 to 600 to 700°C. As shown Figure 35, however, even at 500°C, >90% decomposition activity was maintained for nearly 70 minutes. The corresponding H₂S removal efficiency was shown in Figure 36. Once again the pre-breakthrough H₂S level was less than 20 ppm.

4.6 SORBENT-CATALYST SELECTION

The extensive data base and analysis presented in Section 4.1 to 4.5 were used to guide the selection of the most promising sorbent-catalyst for further studies under Task 3. The criteria used for selection of the sorbent-catalysts were, namely high H₂S removal efficiency and sulfur loading at 700°C with a simulated coal gas, greater than 90% ammonia decomposition, good regenerability performance and good structural stability in cyclic operation.

Figure 37 shows the ammonia decomposition activity of various sorbent-catalyst tested. As seen in Figure 37, HART-38 sorbent-catalyst showed a very high activity (>90%) for about 20 min. After that, the decline in activity was mainly due to the poisoning of the catalyst by H₂S. As seen from Figure 37, the window increased from 20 min for HART-38 to about 180 min for HART-49 sorbent-catalyst. Clearly HART-49 sorbent-catalyst formulation consistently removed 99% or more of the H₂S from a simulated coal gas containing 1% H₂S and was regenerable for multicycle operation. HART-49 sorbent-catalyst formulation demonstrated quite reasonable NH₃ decomposition activity in presence of 1% H₂S even at temperatures as low as 500°C. By using the HART-49 formulation, simultaneous H₂S removal and NH₃ decomposition may become viable at practical IGCC temperatures as low as 500°C. Because of its superior performance, HART-49 was selected for further study in this work for Task 3.

TASK 3: 4.7 MULTICYCLE TEST RESULTS

The ability of a sorbent-catalyst to maintain its reactivity through a number of

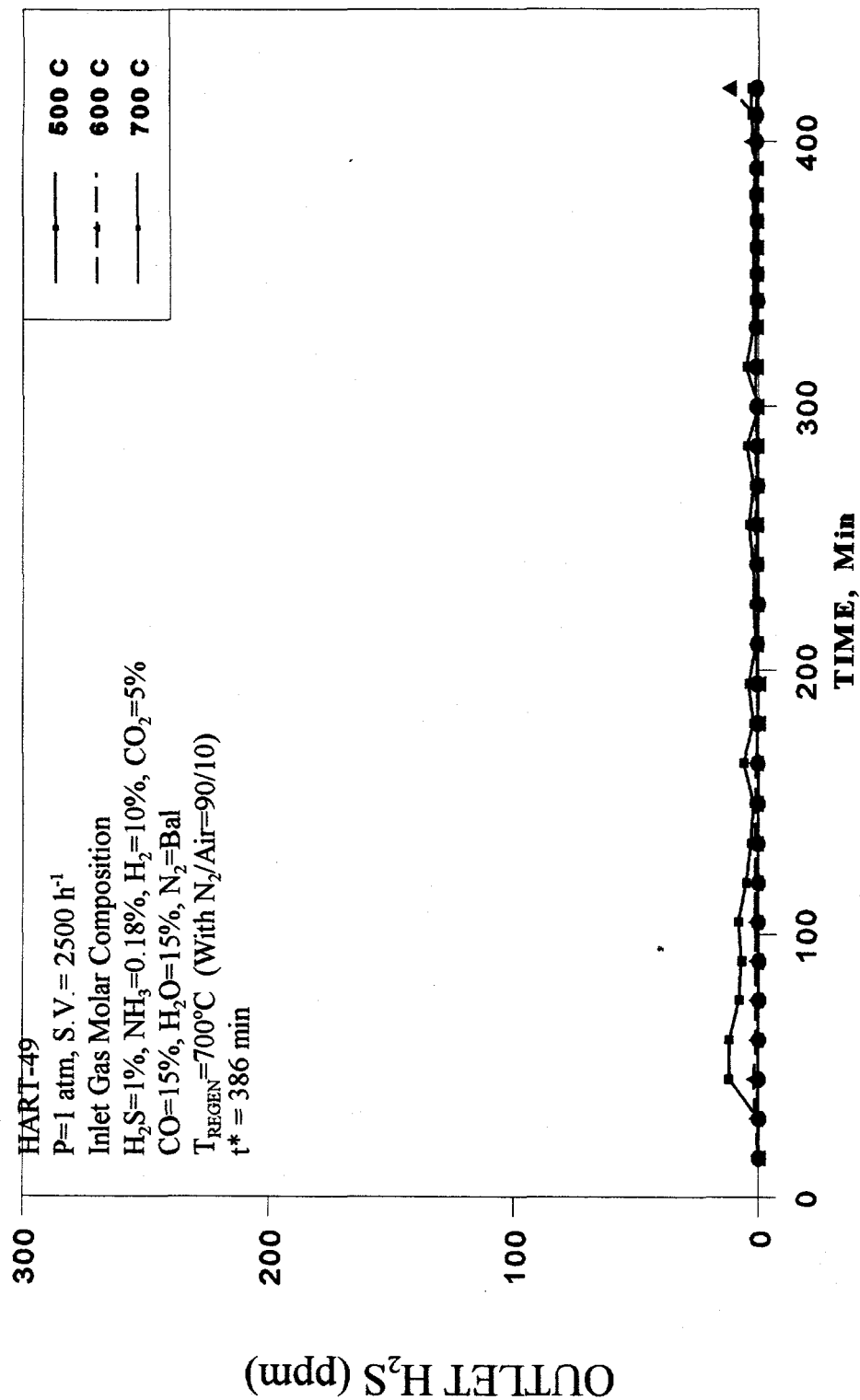


Figure 36. H₂S Breakthrough Curves in Successive Sulfidation Cycles of HART-49 Sorbent-Catalyst

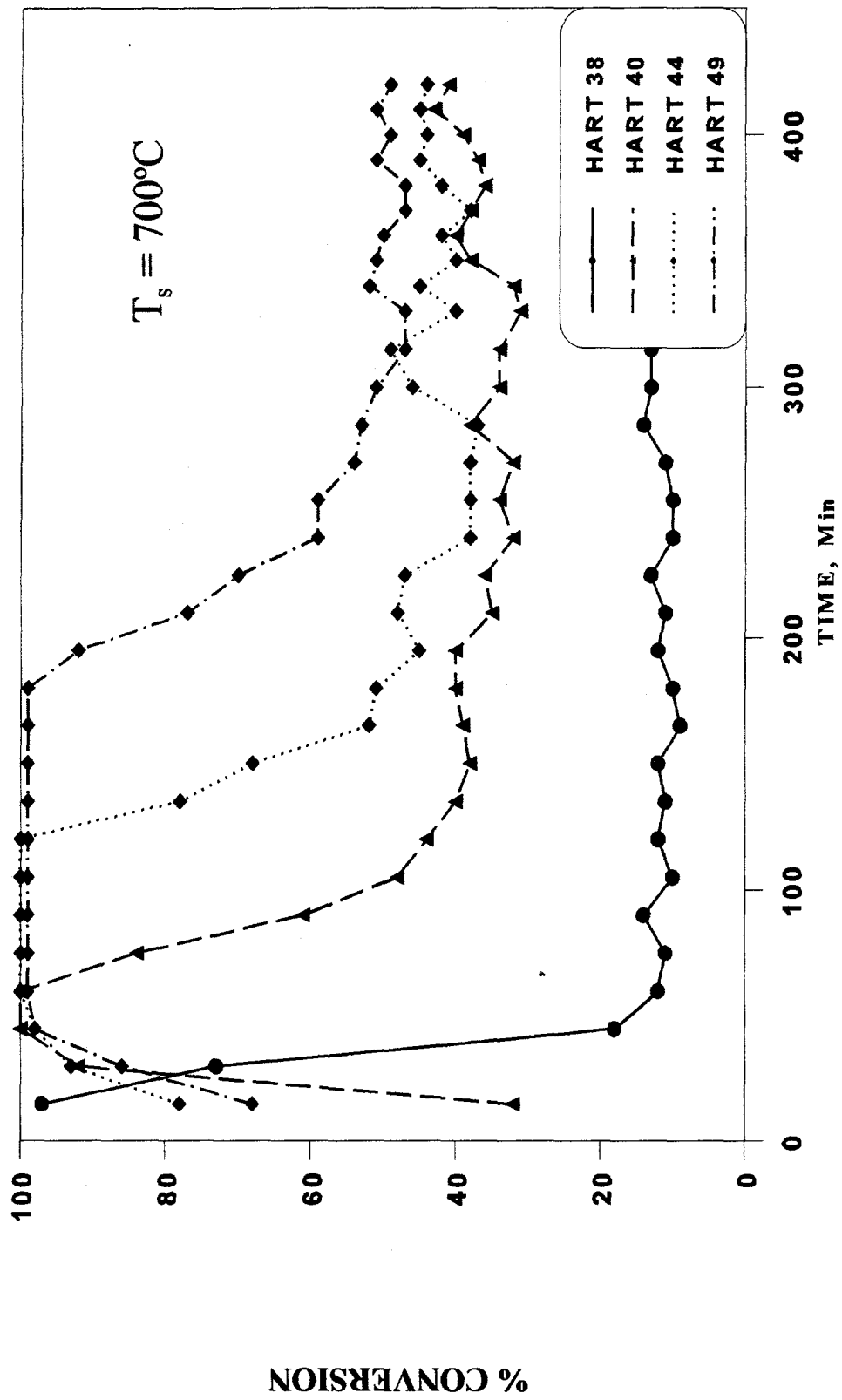


Figure 37. Decomposition of Ammonia Using HART Sorbent-Catalyst

sulfidation/regeneration is of paramount importance. The aim in these tests was to determine how well the sulfidation and ammonia decomposition performance of the sorbent-catalyst were retained in many cycles of consecutive sulfidation/regeneration. Thirty cycles were run with HART-49 and HART-51 sorbent-catalysts. Each sulfidation was approximately 7 hour-long. Sulfidation and ammonia decomposition took place at 700°C with the simulated coal-derived gas containing (in vol%) 10% H₂, 15% CO, 5% CO₂, 15% H₂O, 1% H₂S, 0.18% NH₃, and balance N₂. The gas hourly space velocity was 2500 h⁻¹. Regeneration of the sorbent-catalyst was performed at 700°C with 2% O₂.

Figure 38 shows ammonia decomposition in 30 cycles of sulfidation of HART-49 sorbent-catalyst. After cycle 1, the ammonia decomposition performance was improved. Initially, up to 180 min the sorbent-catalyst showed very high activity (> 90%). The decline in activity after 180 min is probably due to poisoning of the catalyst by H₂S. Figure 39 shows H₂S breakthrough profiles. The pre-breakthrough H₂S level was below 20 ppm. Nearly complete conversion was observed at breakthrough. There was no deactivation in 30 cycles in this fixed-bed study. The sulfur capacity of the HART-49 sorbent-catalyst is plotted in Figure 40. The sulfur capacities during cycles 1 and 30 were 28.9 and 28.9 GS/100 g of sorbent, respectively, indicating a 100 percent capacity utilization even after 30 cycles.

Figure 41 shows ammonia decomposition in 30 cycles of sulfidation of HART-51 sorbent-catalyst. Initially, up to 180 min the sorbent-catalyst showed very high activity (> 90%). Figure 42 shows H₂S breakthrough profiles and the pre-break through H₂S level was below 20 ppm. There was no deactivation in 30 cycles in this fixed-bed study. The sulfur capacity of the HART-51 sorbent-catalyst is plotted in Figure 43. The sulfur capacities during cycles 1 and 30 were 29.5 and 29.5 gS/100 g of sorbent, respectively, indicating a 100 percent capacity utilization even after 30 cycles.

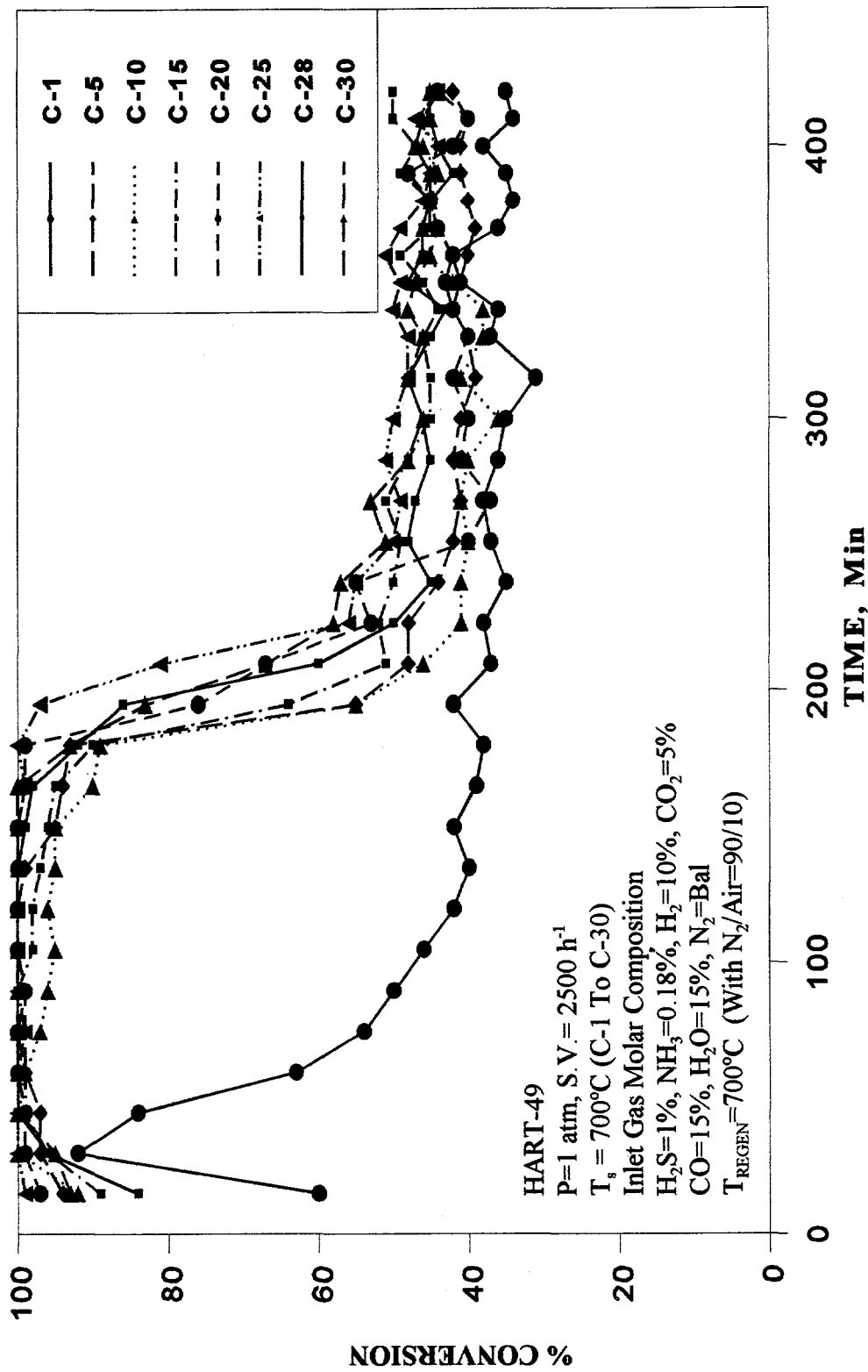


Figure 38. Conversion of Ammonia on HART-49 Sorbent-catalyst in Thirty Sulfidation Cycles

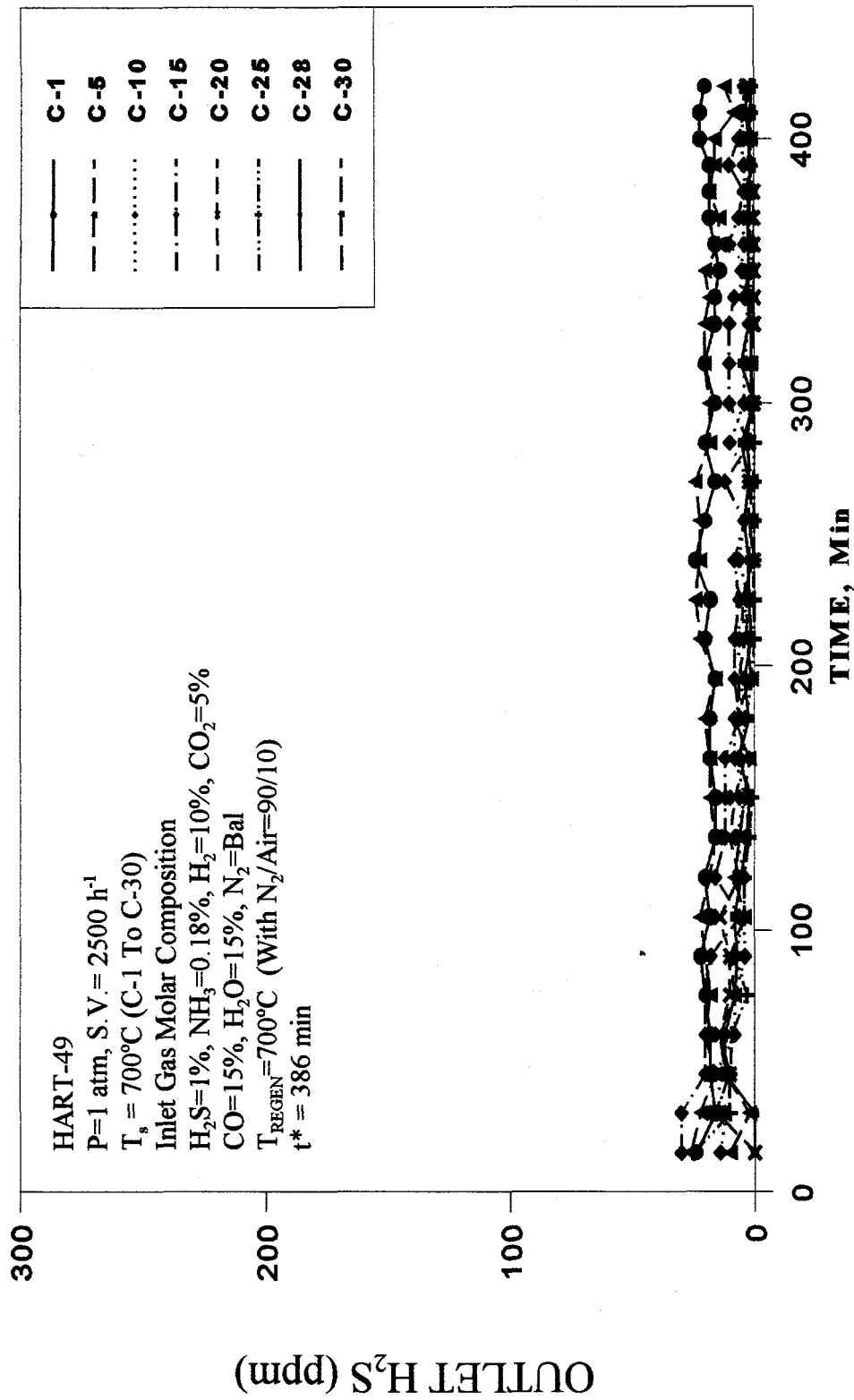


Figure 39. H₂S Breakthrough Curves in Thirty Sulfidation Cycles of HART-49 Sorbent-Catalyst

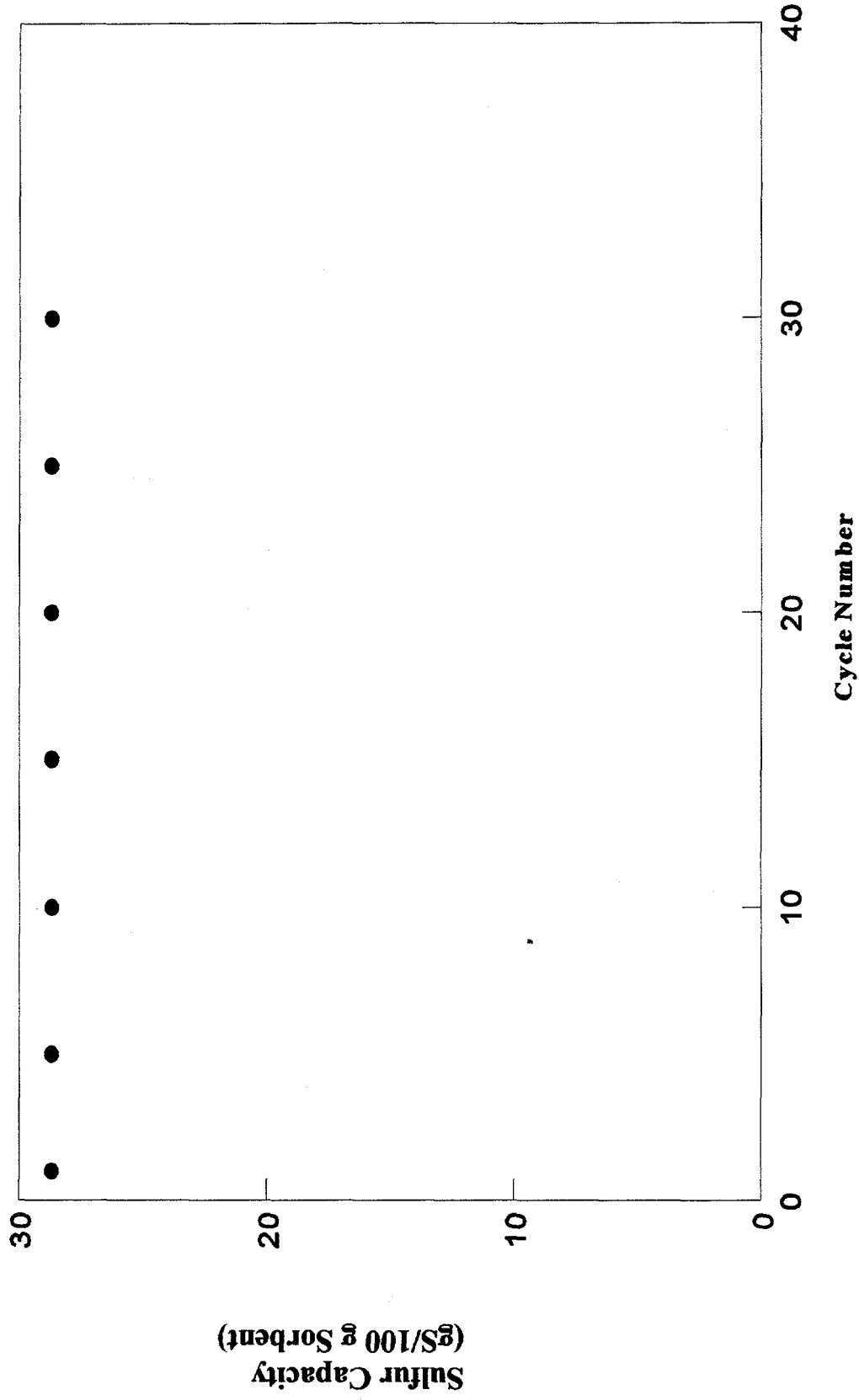


Figure 40. Sulfur Capacity of HART-49 Sorbent-Catalyst

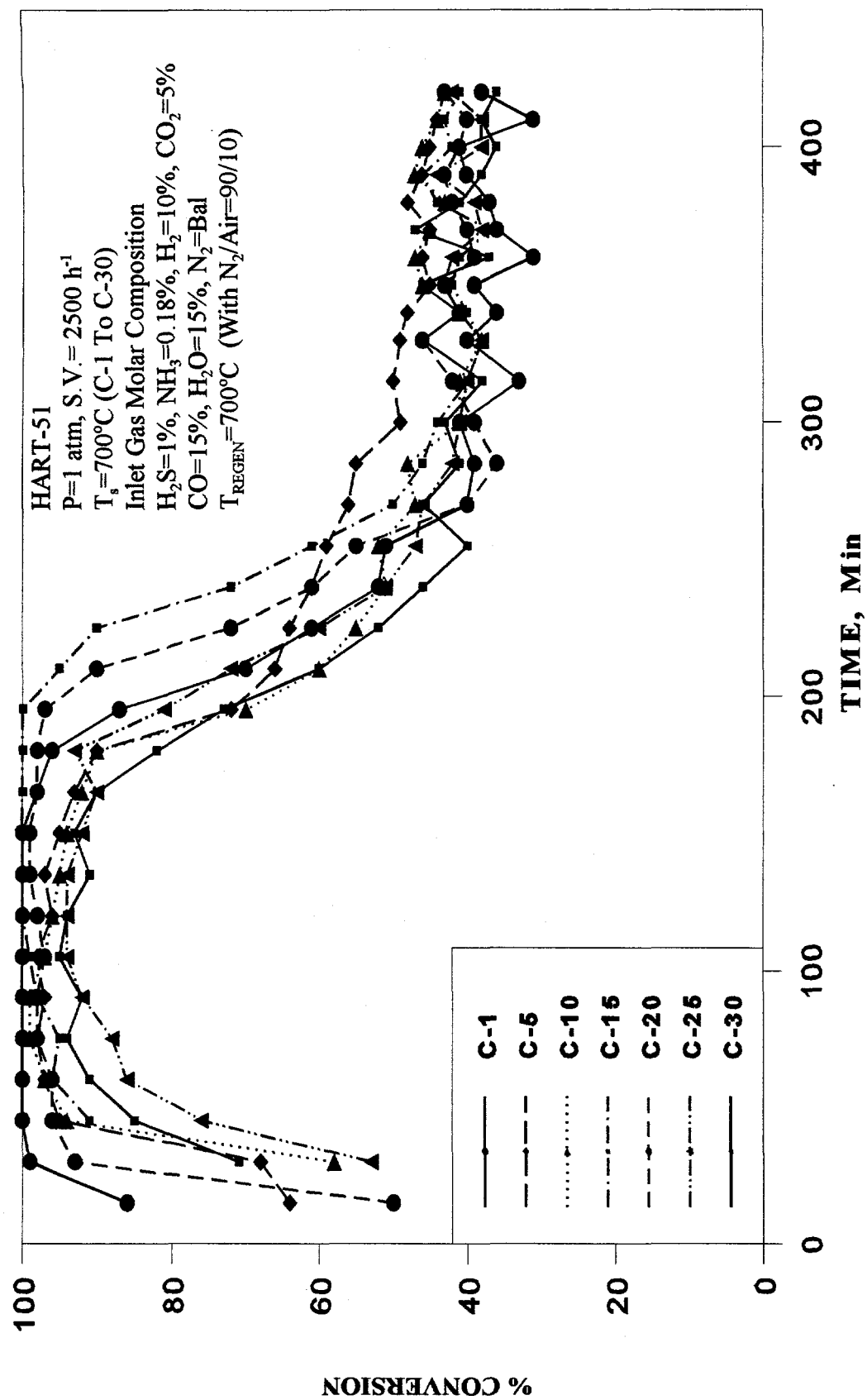


Figure 41. Conversion of Ammonia on HART-51 Sorbent-Catalyst in Thirty Sulfidation Cycles

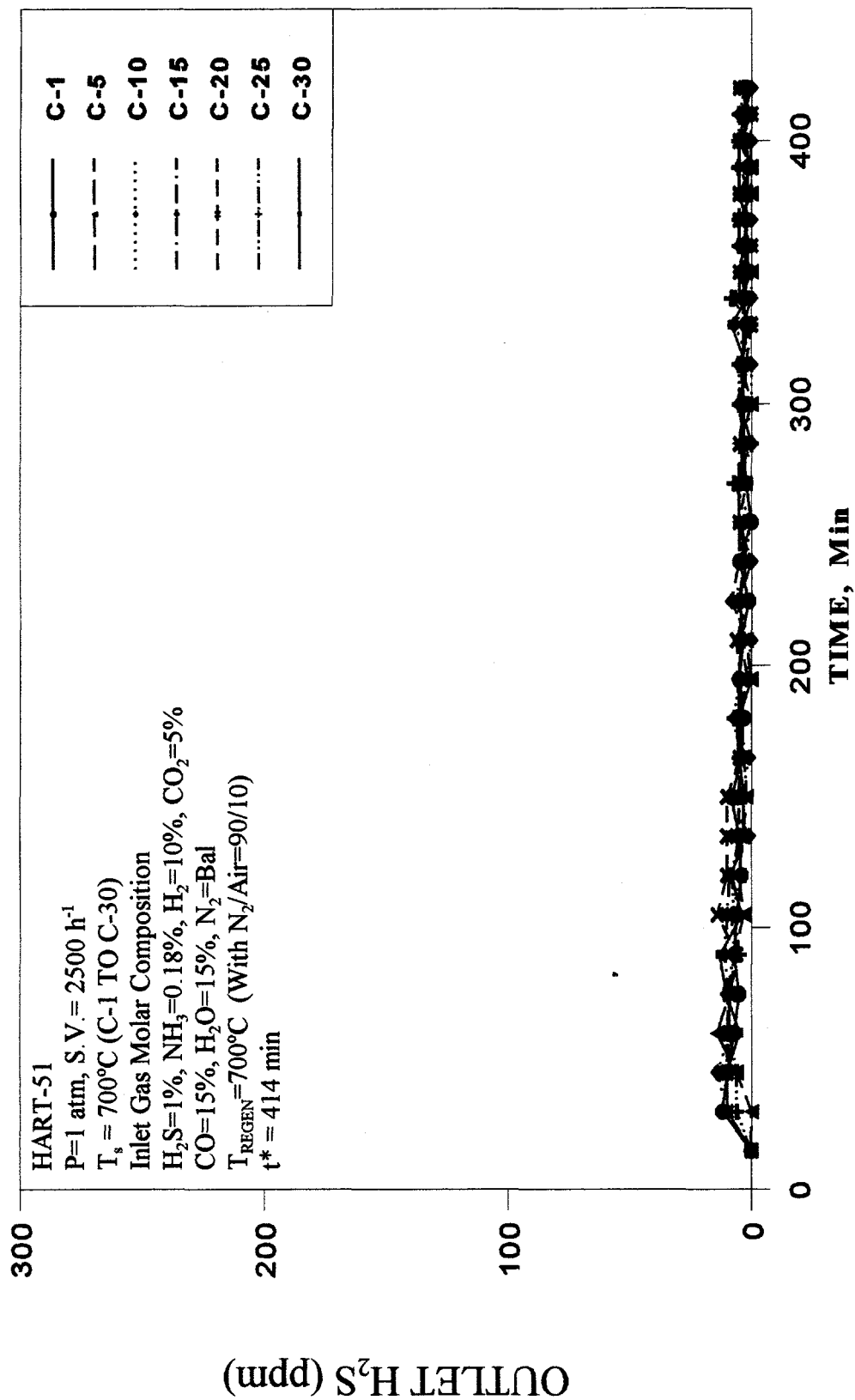


Figure 42. H₂S Breakthrough Curves in Thirty Sulfidation Cycles of HART-51 Sorbent-Catalyst

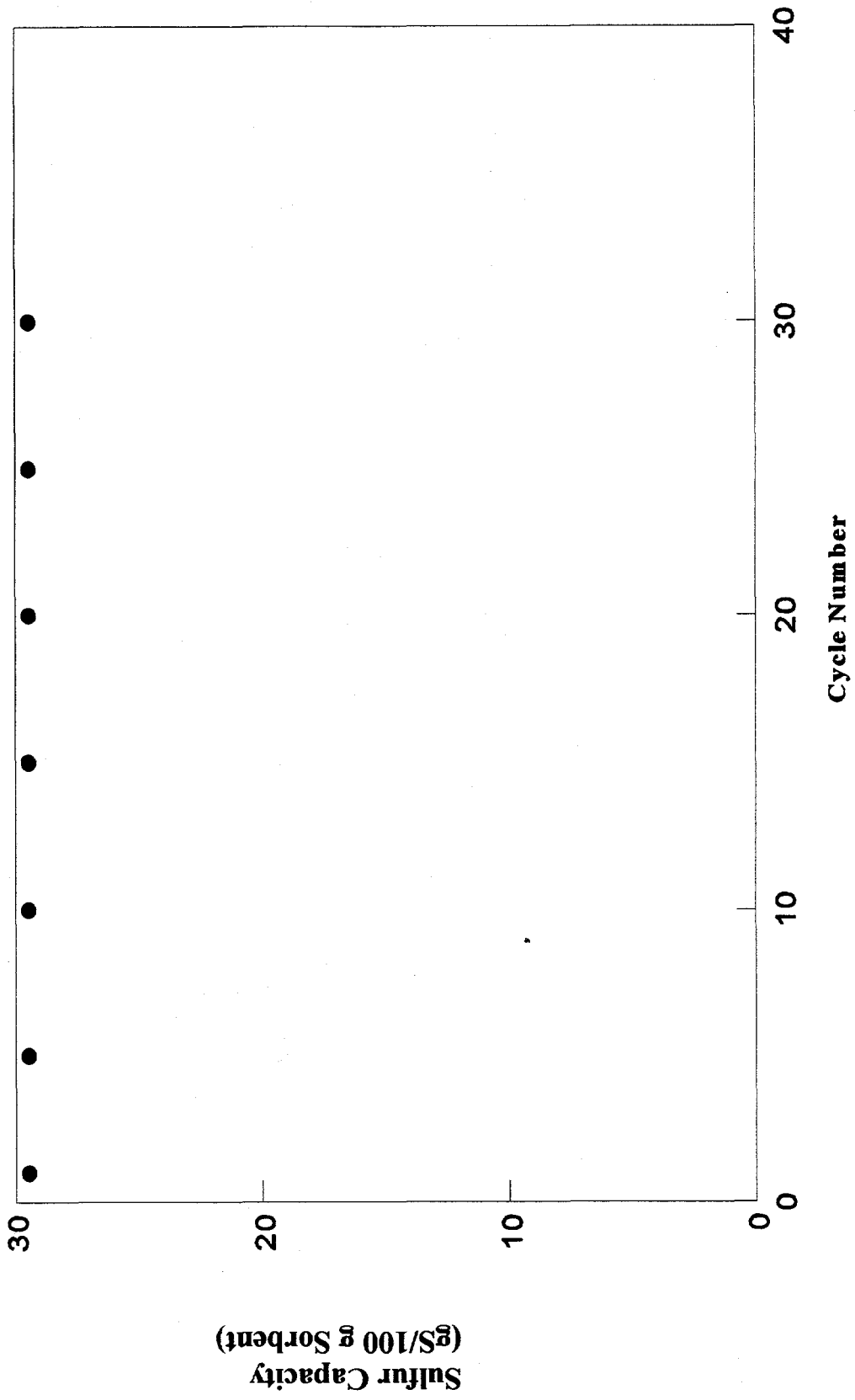


Figure 43. Sulfur Capacity of HART-51 Sorbent-Catalyst

While more extensive multicycle (100-200 cycles) testing is needed, these preliminary results are encouraging. Both the HART-49 and HART-51 sorbent-catalysts appear to possess high reactivity and durability.

5.0 CONCLUSIONS

The feasibility of preparing sorbent-catalysts for simultaneously removing 99% H_2S and 90% NH_3 has been demonstrated. The sorbent-catalysts were prepared by coprecipitation using zinc oxide as the H_2S sorbent and a combination of transition metals (such as Ni, Co, Mo and W) and supports (such as TiO_2 , Al_2O_3 , and SiO_2) as catalyst for NH_3 decomposition. All 51 of the sorbent-catalysts that were prepared successfully removed 99% H_2S and were regenerable for multicycle operation. However the activity of the sorbent-catalysts for NH_3 decomposition exhibited a strong dependence on the type and level of the catalytic transition metal additives. Sorbents HART-36 through 39 showed low activity, HART-40 through 48 showed medium activity, and HART-49 and HART-51 showed high activity for NH_3 decomposition. HART-49 exhibited the highest tolerance to catalyst poisons H_2S and H_2O . In the absence of H_2O , HART-49 maintained over 90% NH_3 decomposition throughout the sulfidation cycle, upto a sorbent sulfur loading of nearly 25%. In the presence of H_2O , HART-49 maintained 90% or higher decomposition of NH_3 up to 6 wt% sulfur loading at 500°C and 12 wt% at 700°C. Furthermore, HART-49 maintained a constant activity for NH_3 decomposition and constant capacity for H_2S over 30 cycles that it was tested. By using the HART-49 formulation, simultaneous H_2S removal and NH_3 decomposition may become feasible at temperatures as low as 500°C.

6.0 RECOMMENDATIONS

The HART-49 sorbent-catalyst should be tested at pressures up to 20 to 30 atm at temperatures from 450 to 550°C over multiple cycles. Based on these results, HART-49 should be developed in an attrition-resistant fluidizable or pellet form using suitable binders and its preparation should be scaled up to several pounds.

Fundamental studies should be conducted to evaluate the effect of pressure under IGCC conditions on the kinetics of the NH_3 decomposition reaction over HART-49 and other Ni-based catalysts. Temperature programmed desorption/reaction studies of the catalyst surface should be carried out to elucidate the mechanism of catalyst poisoning by H_2S in the presence of steam. Based on the results of fundamental studies, the catalyst should be further optimized to extend the period of high NH_3 decomposition activity during cyclic operation in coal gas in presence of steam and H_2S .

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