

EXPERIMENTAL PROCEDURE

THE FIXED-BED REACTOR SYSTEM

A laboratory-scale reactor system was assembled to determine the activity of selected catalyst-sorbent systems for their NH_3 decomposition activity and H_2S removal ability. This system includes a feed gas supply section in which the simulated coal gas components, supplied from standard high pressure cylinders equipped with pressure regulators, are mixed and metered by a bank of electronic mass flow controllers (Figure 5). Steam is added to the feedstock using an in-line stainless steel evaporator to which water is added by a precision liquid-metering pump. All lines downstream from the steam generator are heated to prevent condensation of water. NH_3 is added to the gas mixture downstream of the steam generator where the temperature is high enough to avoid the formation of $(\text{NH}_4)_2\text{CO}_3$. A second reactor was used for pretreating the catalysts.

The product gases from the reactor are analyzed by gas chromatography (GC). For the NH_3 analysis, the product gas, prior to the condensation of steam, first passes through an H_2S trap (copper sponge or zinc oxide kept at a temperature of about 200°C) and is then sampled by a high-temperature injection valve into a GC with a Chromosorb 103 column. This column separates NH_3 from the other components of the sample stream. The effluent from the column first passes through a photoionization detector (PID) for analysis of NH_3 and then through a flame ionization detector for analysis of CH_4 . Of all the components of the sampled gas stream, only NH_3 (and H_2S , if it is not removed) are detected by the photoionization detector. The calibration of the PID for NH_3 is shown in Figure 6. As expected, a linear correlation between the signal intensity and concentration of NH_3 was observed.

The concentration of H_2S in the gas stream is determined on a second sample from which steam is removed by condensation in a trap. This sample flows into a flame photometric detector (FPD) that is sensitive exclusively to sulfur compounds. A thermal conductivity detector used in series with the FPD is used to determine the concentration of the major components of the gas stream. Because NH_3 in this sample is effectively removed during steam condensation, the separation of NH_3 and H_2S is unnecessary. Hence, a Haysep Q column was used to separate the H_2S from the rest of the gases. During sorbent regeneration, the concentration of liberated SO_2 will be measured using this technique. The calibration of the FPD for H_2S is shown in Figure 7.

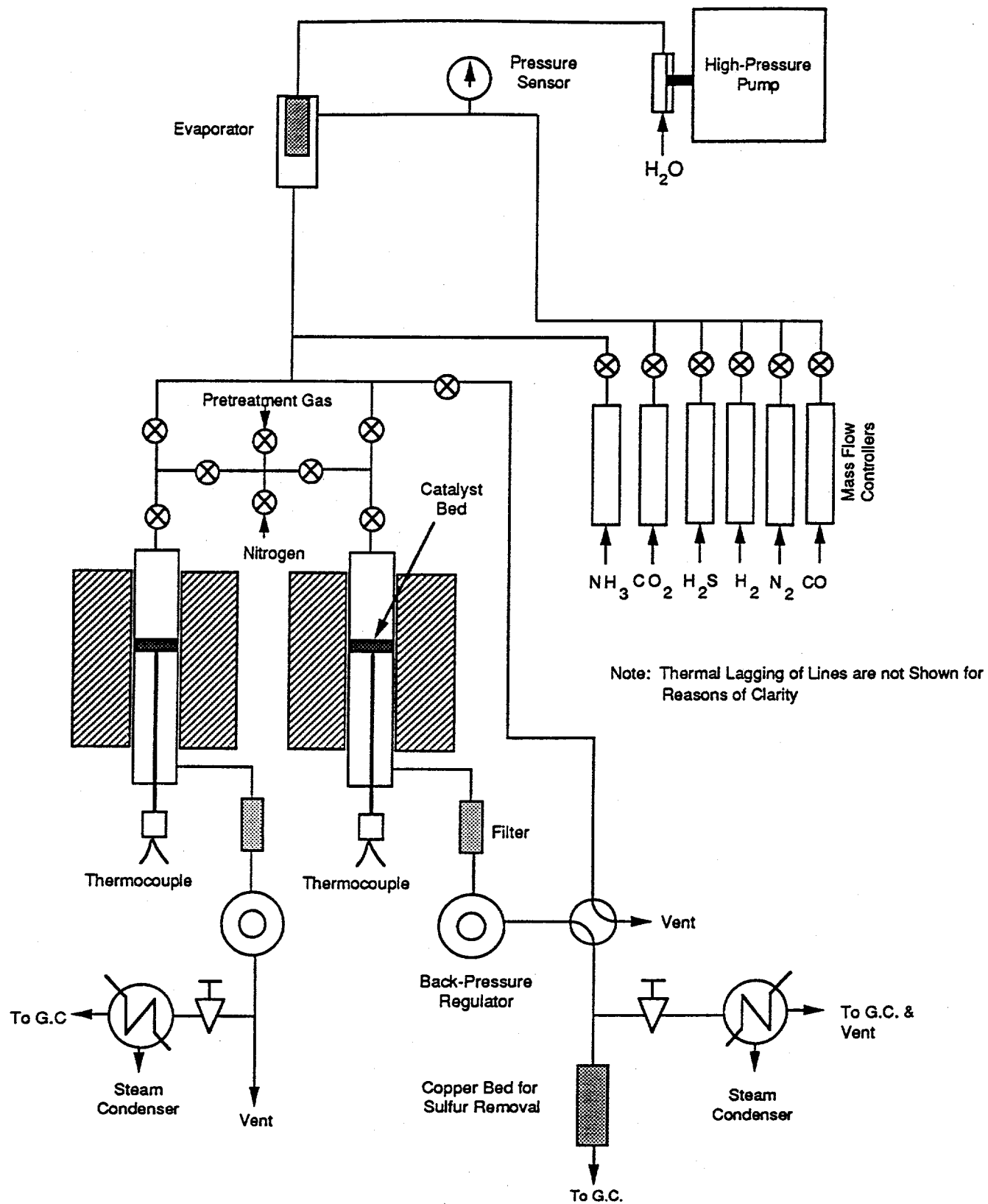


Figure 5. Schematic diagram of the fixed-bed reactor system.

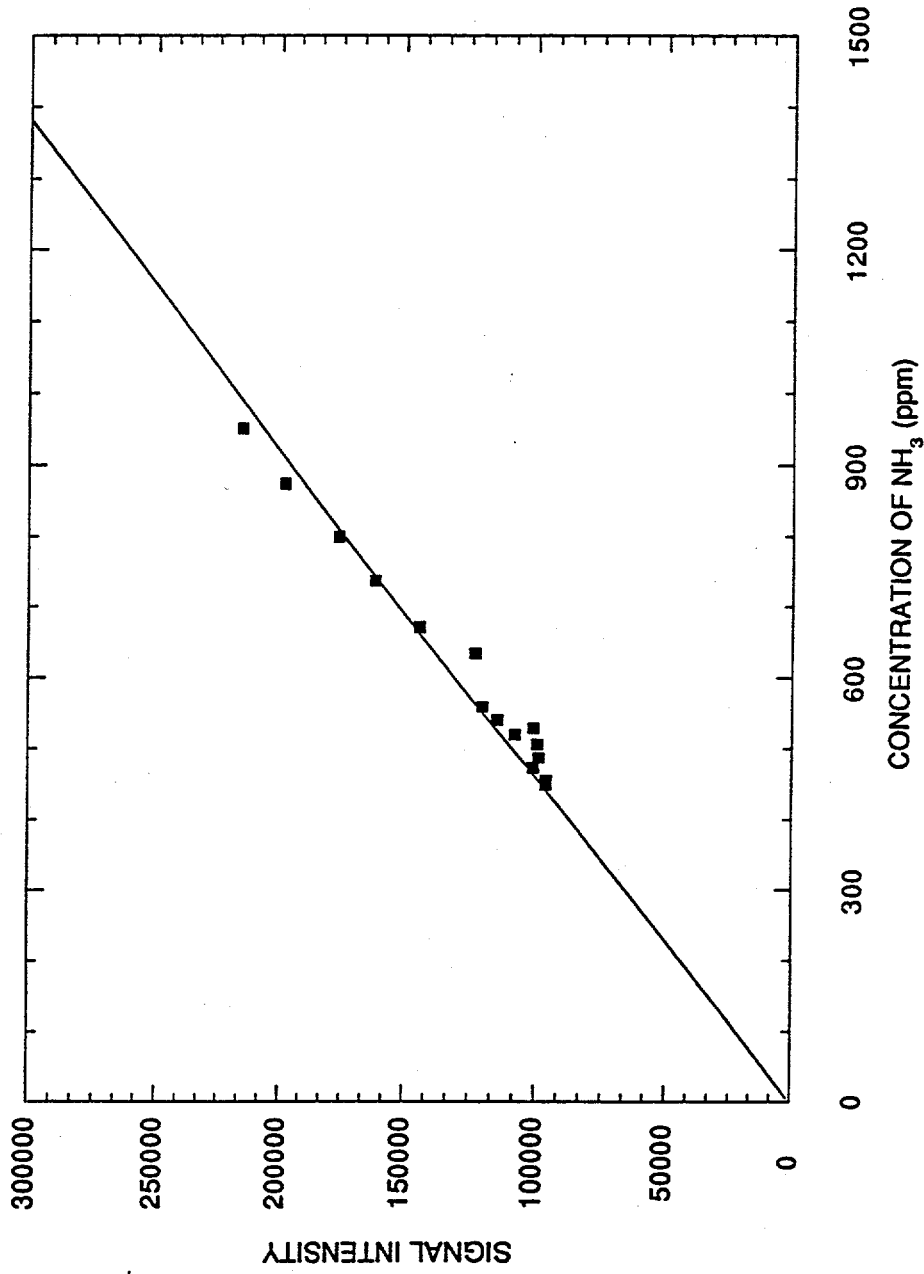


Figure 6. Calibration of photoionization detector for NH₃ gas.

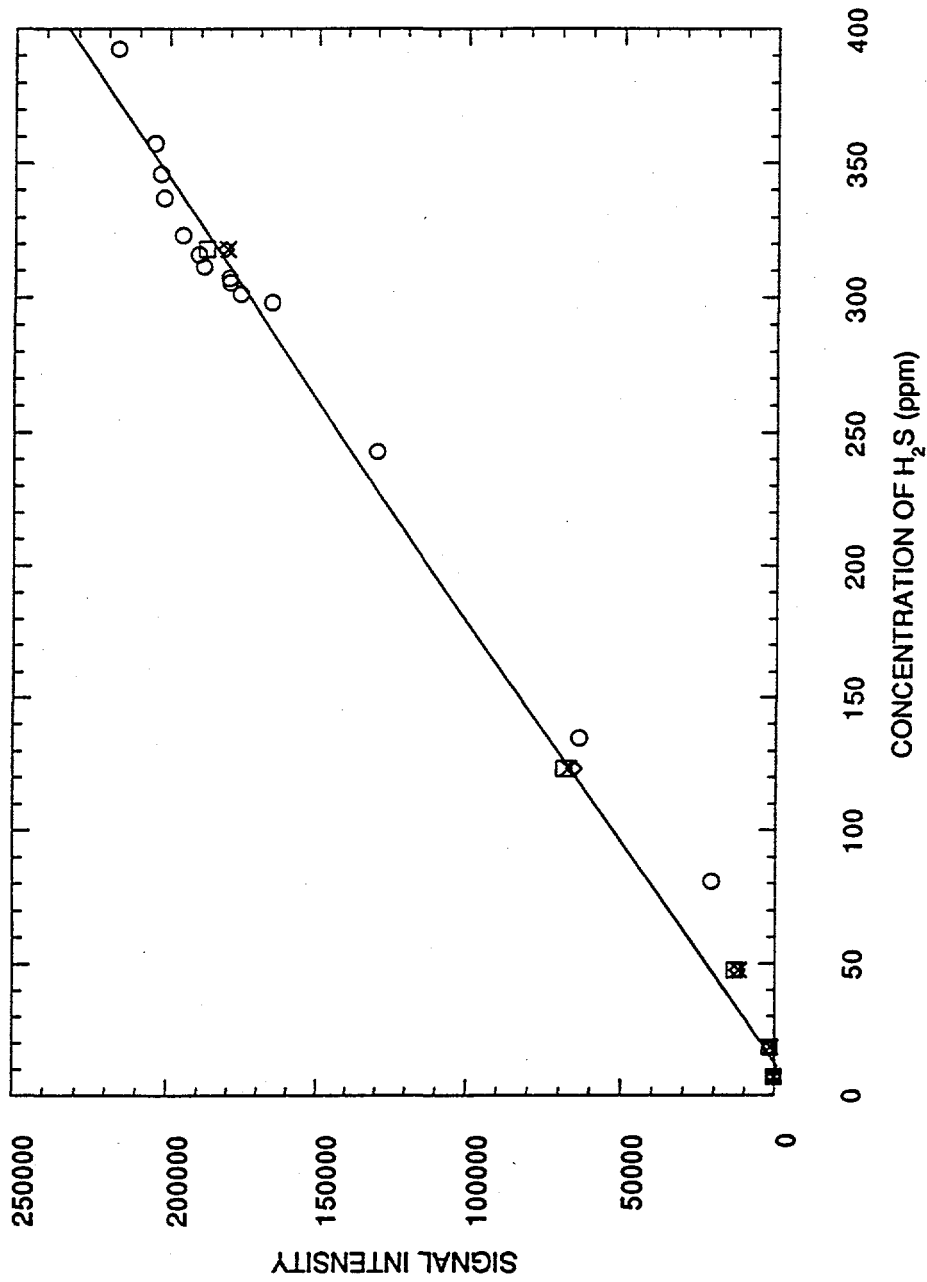


Figure 7. Calibration of flame photometric detector for H₂S gas

A bypass line from the feed gas manifold and a selector valve permits injection of feed gas samples into the chromatographs. Thus the fractional reduction of NH_3 and changes in other components of the simulated coal gas during passage through the reactor can be measured directly. The rate of the ammonia decomposition reaction is calculated from the measured fractional conversion and the space velocity of the gas in the reactor.

PREPARATION OF CATALYSTS

A Ni-supported on a ceramic support (HTSR-1) and a MoS_2 stabilized with zirconia were designated as the baseline catalysts. These two catalysts were tested extensively by SRI in a previous program for NH_3 decomposition. HTSR-1, manufactured by Haldor-Topsoe AG, Copenhagen, Denmark, was found to be an excellent catalyst for decomposing NH_3 . The MoS_2 catalysts (CRC-653 and CRC-530) were prepared by Catalyst Research Corporation, Palisades Park, NJ. CRC-653, which had ZrO_2 as a stabilizing agent, showed a significant catalytic activity for the decomposition of NH_3 in the presence of 0.3% H_2S . CRC-530 did not contain any stabilizing agent.

The HTSR-1 catalyst contains alumina and other oxides that could be converted to sulfates readily when exposed to SO_2 -containing gas streams such as the one expected during oxidative regeneration of the spent catalyst. Titania and zirconia are less prone to sulfate formation than alumina. Hence, several formulations using titania or zirconia as support materials and nickel, cobalt, or molybdenum, and tungsten as active components were prepared.

Catalysts containing Ni as the active component were prepared using a high surface area ($>250 \text{ m}^2/\text{g}$) titania obtained from Rhone-Poulenc. To a slurry of this titania in isopropanol, a solution of zirconyl propoxide (in isopropanol) was added. Zirconium oxide was precipitated by adding water to this mixture resulting in an intimate contact between titania and zirconia. Nickel was incorporated in this substrate by adding a solution of nickel nitrate and precipitating it with ammonium hydroxide. The resulting solid mixture was dried and calcined. The estimated composition of the catalyst (Ni/TiO_2) is 20 wt% NiO, 20 wt% ZrO_2 , and 60 wt% TiO_2 .

The dried catalyst had a surface area of $193 \text{ m}^2/\text{g}$. After calcination in air at 550°C , the surface area was reduced to $115 \text{ m}^2/\text{g}$. Reduction in hydrogen at this temperature did not change the surface area ($118 \text{ m}^2/\text{g}$) significantly. However, calcination in air at 725°C for 2.5 h resulted in a further reduction in surface area to $22 \text{ m}^2/\text{g}$. The measured surface area is less than the manufacturer-specified value of $48 \text{ m}^2/\text{g}$ after calcination in air at 750°C for 2 h.

Catalysts containing either cobalt or cobalt and molybdenum on high surface area titania were prepared. Cobalt (~20 wt%) was deposited on the TiO₂ support by slow precipitation by adding ammonium carbonate to a dilute solution of cobalt nitrate containing the support. The final pH was kept below the isoelectric point for cobalt hydroxide (~11.5) so that the cobalt compound is adsorbed on the TiO₂ support. The catalyst (Co/TiO₂) was then dried and calcined in hydrogen at 500°C for 4 h. The surface area of the calcined catalyst was 63 m²/g.

A batch of Co-Mo supported on TiO₂ was prepared by impregnating the Co-TiO₂ catalyst (prepared as described above) with a solution of ammonium molybdate under incipient wet conditions. The impregnation was performed three times to bring the total amount of Mo to 6.4 wt%. The catalyst (Co-Mo/TiO₂) was calcined in hydrogen at 550°C until all the molybdate was decomposed.

Two Mo-supported on TiO₂ catalysts (Mo-TiO₂) were made by impregnating high surface area TiO₂ powders with an ammonium molybdate solutions. Two W-supported on TiO₂ (W-TiO₂) catalysts were synthesized by impregnating TiO₂ powders with an ammonium tungstate solutions. The impregnated powders were dried overnight at 100°C, reduced in H₂ at 550°C.

Another catalyst containing 5 wt% Co and 15 wt% W on TiO₂ was prepared by impregnating the TiO₂ powder with ammonium tungstate solution three times. The catalyst was dried at 110°C between impregnation. After heating in H₂ at 550°C, cobalt was incorporated into the catalyst with wet impregnation with a cobalt nitrate solution. Finally, the catalyst (W-Co/TiO₂) was treated in H₂ at 550°C until all the nitrate was removed.

At the elevated temperature of 725°C, the TiO₂ support may sinter. The decrease in the surface area of the support due to sintering may contribute to the decline in the catalytic activity with time. To determine the sintering rate of the support, the TiO₂ powder was exposed to a mixture of 80% air-20% steam at 725°C for periods up to 72 h and the change in surface area was measured (Figure 8). These measurements indicated that the surface area of TiO₂ powder decreased from an initial value of about 280 m²/g to about 15 m²/g after 72 h.

To stabilize the surface area of TiO₂, 25 mole% ZrO₂ was added by precipitating the ZrO₂ from a zirconium propoxide solution. This procedure allows intimate contact between the TiO₂ and ZrO₂. The mixture of TiO₂-ZrO₂ was calcined at 350°C for 2h and then exposed to air-steam (25%) mixture at 725°C for periods up to 24 h. Surface area determination of the exposed samples indicated that ZrO₂ addition is beneficial in stabilizing the surface area. The samples containing ZrO₂ have nearly twice the surface area as those which do not contain ZrO₂ (Table 6).

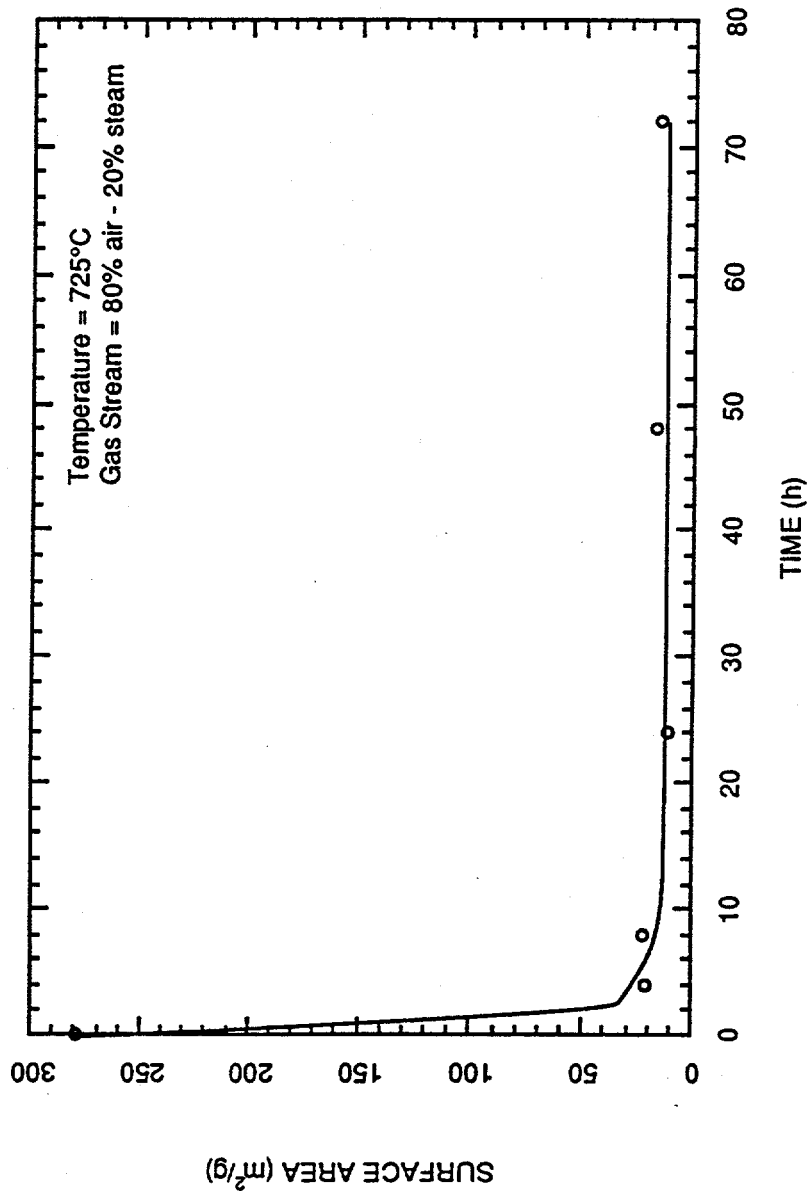


Figure 8. Change in surface area of a titania support as a function of time at 725°C.

TABLE 6
SURFACE AREA CHANGES IN TiO₂ and TiO₂-ZrO₂ POWDERS
DURING EXPOSURE TO STEAM AT 725°C¹

<u>Time (h)</u>	<u>Area of TiO₂ Powder</u> (m ² /g)	<u>Area of TiO₂-ZrO₂ Powder²</u> (m ² /g)
0	279	157
4	21	37
8	22	33
24	11	29
48	17	-
72	16	-

¹ The powders were exposed to a gas stream containing 80% air and 20% steam.

²The initial ZrO₂-TiO₂ sample was calcined at 350°C for 2 h.

RESULTS AND DISCUSSION

BASELINE CATALYSTS

The HTSR-1 catalyst decomposed about 80% of the feedgas NH_3 at 725°C under steady state conditions in the absence of H_2S (Figure 9). Although CH_4 was not added to the feedgas, the reactor effluent contained about 3.5% of CH_4 due to methane formation from CO and H_2 in the feedgas. However, when 0.5% H_2S was added to the feedgas, both the decomposition of NH_3 and the formation of CH_4 were inhibited. The concentration of H_2S in the reactor effluent was initially low, but a breakthrough was observed after about 100 minutes. The concentration of H_2S reached the feedgas value after about 200 minutes of exposure. After this period, the formation of CH_4 and decomposition of NH_3 were negligibly small.

The activity of the poisoned catalyst was not restored even when the catalyst was kept overnight at 725°C in pure H_2 , indicating that the H_2S is irreversibly adsorbed at this temperature. However, when the temperature of the poisoned catalyst was increased to 800°C , the NH_3 decomposition activity was restored (Figure 10). Initially, the concentration of H_2S in the reactor effluent was higher than feedgas level indicating a desorption of adsorbed sulfur on the catalyst. As the catalyst became free of adsorbed sulfur, its activity for the decomposition of NH_3 also increased. At this high temperature and low pressure, the concentration of CH_4 in the reactor effluent was negligibly small.

The effectiveness of HTSR-1 to catalyze the decomposition of NH_3 at low levels of H_2S was also determined by placing the catalyst downstream of a zinc titanate bed and exposing them to a simulated Texaco coal gas containing 0.5% H_2S and 0.18% NH_3 . Under these conditions, when H_2S level was about 10 ppm, nearly 90% of the feed NH_3 was decomposed (Figure 11). These set of experiments demonstrated that HTSR-1 is an effective catalyst for the decomposition of NH_3 at about 725°C when H_2S level is not very high.

An experiment was also performed by mixing both the zinc titanate sorbent and HTSR-1 catalyst in equal proportions and exposing them to the simulated Texaco coal gas at 725°C . When the concentration of H_2S in the reactor effluent was below 10 ppm, nearly 80% conversion of the feed NH_3 was observed. As the quantity of H_2S removed by the sorbent-catalyst bed decreased

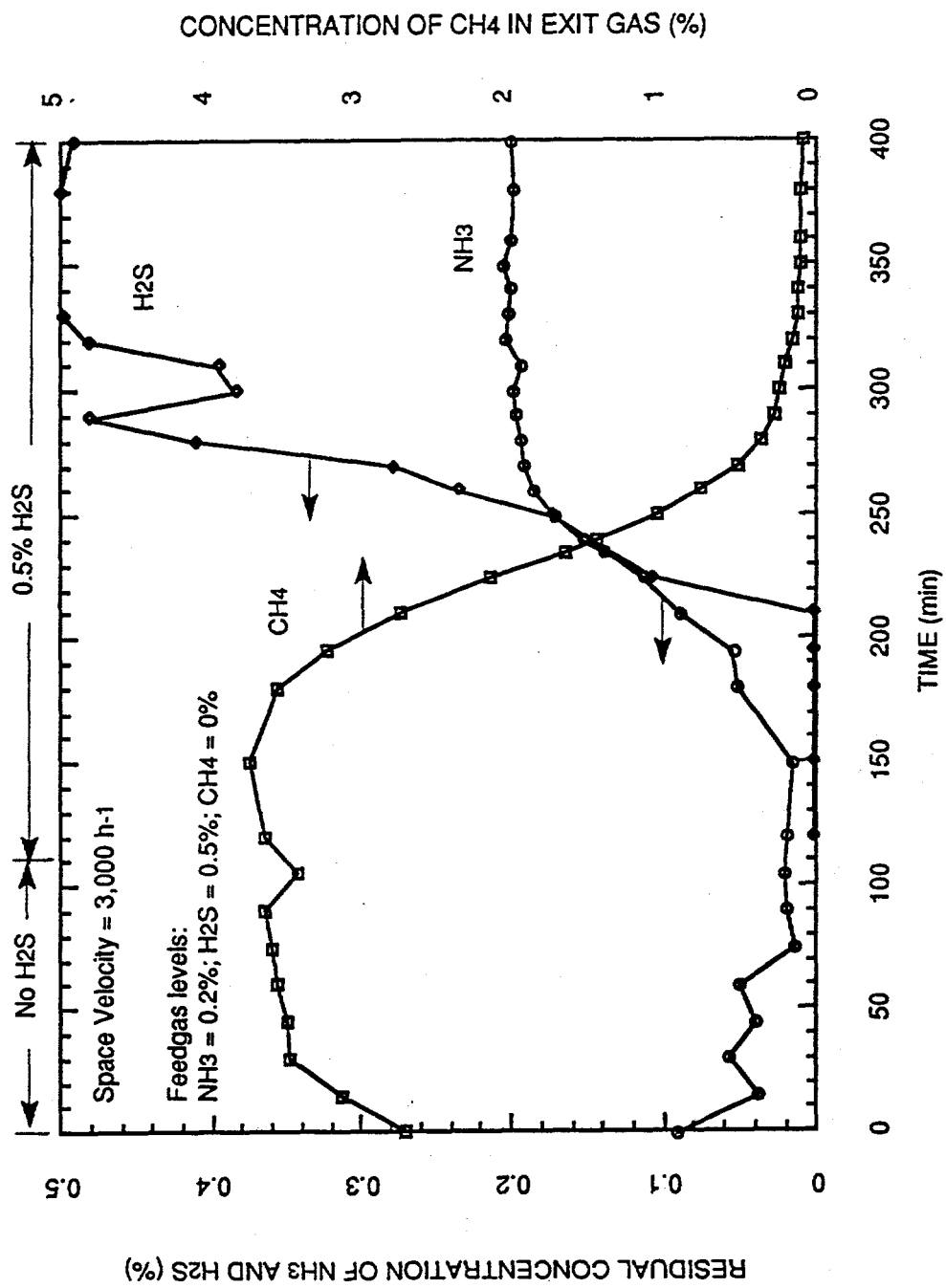


Figure 9. The conversion of NH₃ on HTSR-1 catalyst at 725°C in simulated Texaco gasifier stream.

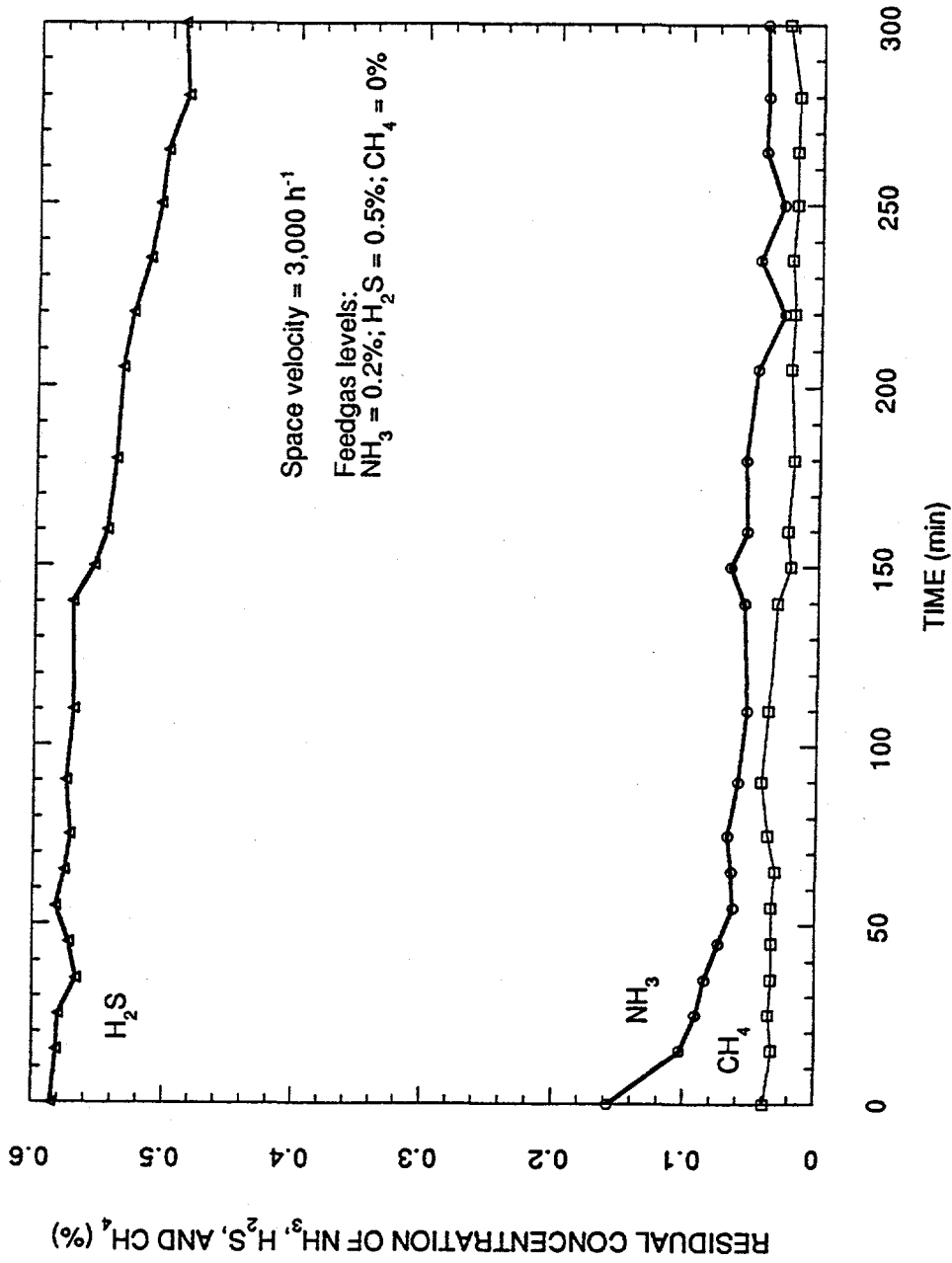


Figure 10. Conversion of NH_3 on HTSR-1 catalyst at 800°C in simulated Texaco gasifier stream.

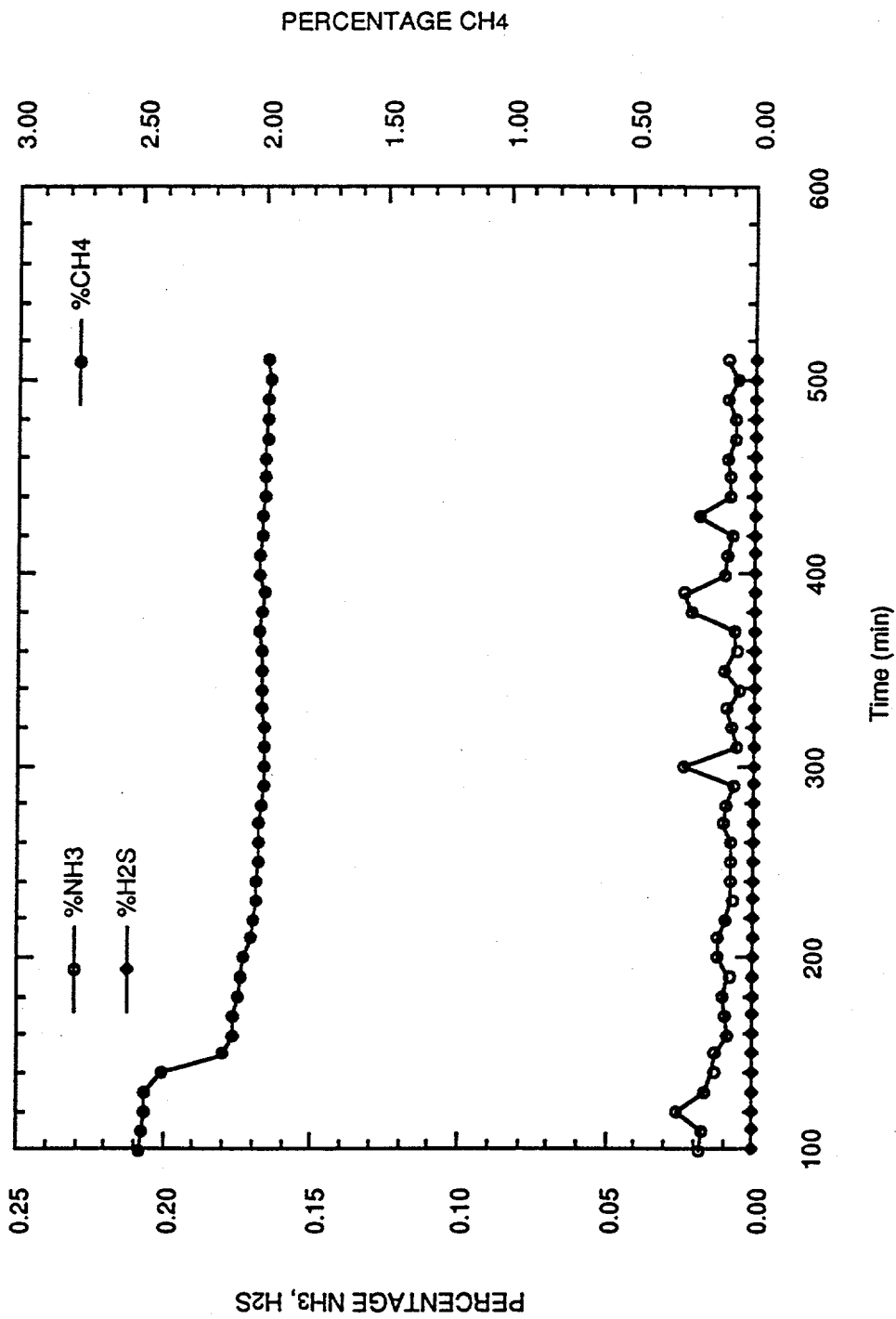


Figure 11. The Conversion of NH₃ on HTSR-1 placed downstream of a zinc titanate bed.

(or the residual H₂S level is increased), the extent of NH₃ decomposition also decreased (Figure 12).

The effect of regeneration on the performance of HTSR-1 catalyst was also determined by exposing the sulfided zinc titanate and HTSR-1 bed to a gas stream of 2% O₂ and balance N₂ at 725°C. The regeneration was terminated when O₂ breakthrough was observed in the effluent gas stream. The regenerated bed was then exposed to the simulated Texaco coal gas stream at the same temperature. During the initial 50 minutes, about 50% of the feed NH₃ decomposed (Figure 13). Subsequently, the conversion of NH₃ decreased with time.

The HTSR-1 catalyst was also tested at a pressure of 200 psig and a temperature of 725°C in the absence of H₂S in the feedgas stream. As shown in Figure 14, the catalyst had decomposed more than 95% of NH₃ in the feedgas. The concentration of CH₄ in the effluent gas was high, about 6.5% (v/v). Thus, the HTSR catalyst promotes both NH₃ decomposition and methanation reactions effectively in the absence of H₂S at 725°C.

MoS₂-based catalysts were also shown to exhibit activity for decomposition of NH₃ in hot coal gas streams. One of this formulations (CRC-653) in which MoS₂ was stabilized with ZrO₂ decomposed nearly 80% of the feedgas NH₃ initially. However, its activity declined with time (Figure 15). However, a second formulation (CRC-530) that did not contain any ZrO₂ did not decompose any measurable quantity of NH₃. These results indicate that although MoS₂ is capable of decomposing NH₃, it could sinter at 725°C unless effective stabilizing agents are added.

Surface area measurements indicated that the initial MoS₂ catalyst had a surface area of about 74.2 m²/g. After exposure to the simulated coal gas stream for about 8 h, the surface area decreased to about 11.7 m²/g. Oxidation of the MoS₂ with 2% O₂ also decreased the surface area, even further, to 6.8 m²/g. But exposure of the oxidized catalyst to a simulated coal gas stream containing H₂S increased the surface area to 19.5 m²/g.

The following conclusions can be derived from the tests with the baseline catalysts :

- HTSR-1, a Ni-based catalyst has a high activity for NH₃ decomposition at 725°C in simulated coal gas streams under low H₂S levels. The tolerance of the catalysts for H₂S increases as the temperature is increased.
- HTSR-1 when mixed with a desulfurization sorbent such as zinc titanate could decompose NH₃ effectively until the removal of H₂S by zinc titanate decreases.
- HTSR-1 continues to exhibit an activity for NH₃ decomposition even after exposure to zinc titanate regeneration conditions.

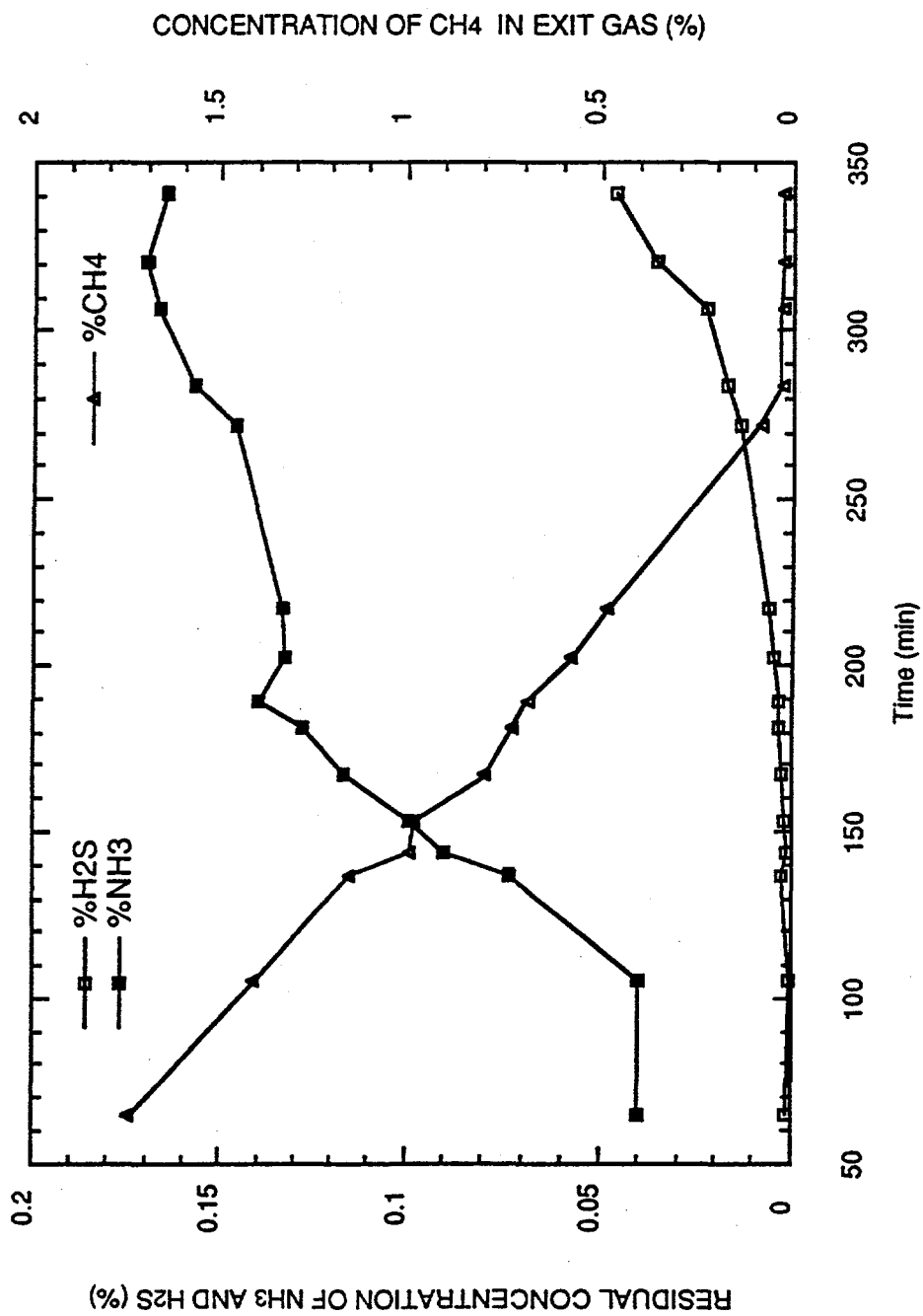


Figure 12. The conversion of ammonia on ZT-4T sorbent and HTSR-1 catalyst mixed together.

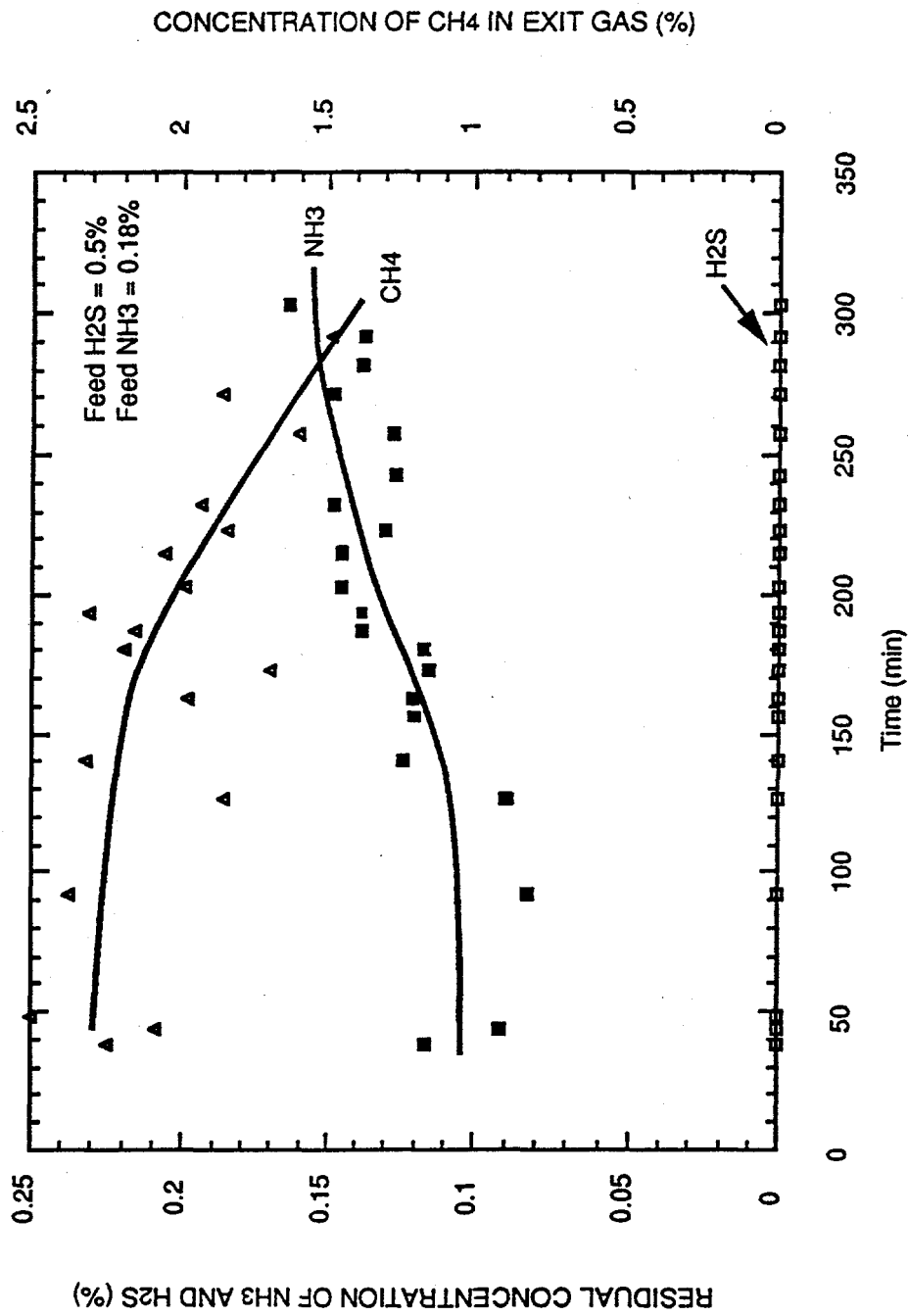


Figure 13. The conversion of NH3 on a regenerated HTSR-1 catalyst mixed with ZT-4 sorbent in a simulated Texaco gasifier stream.

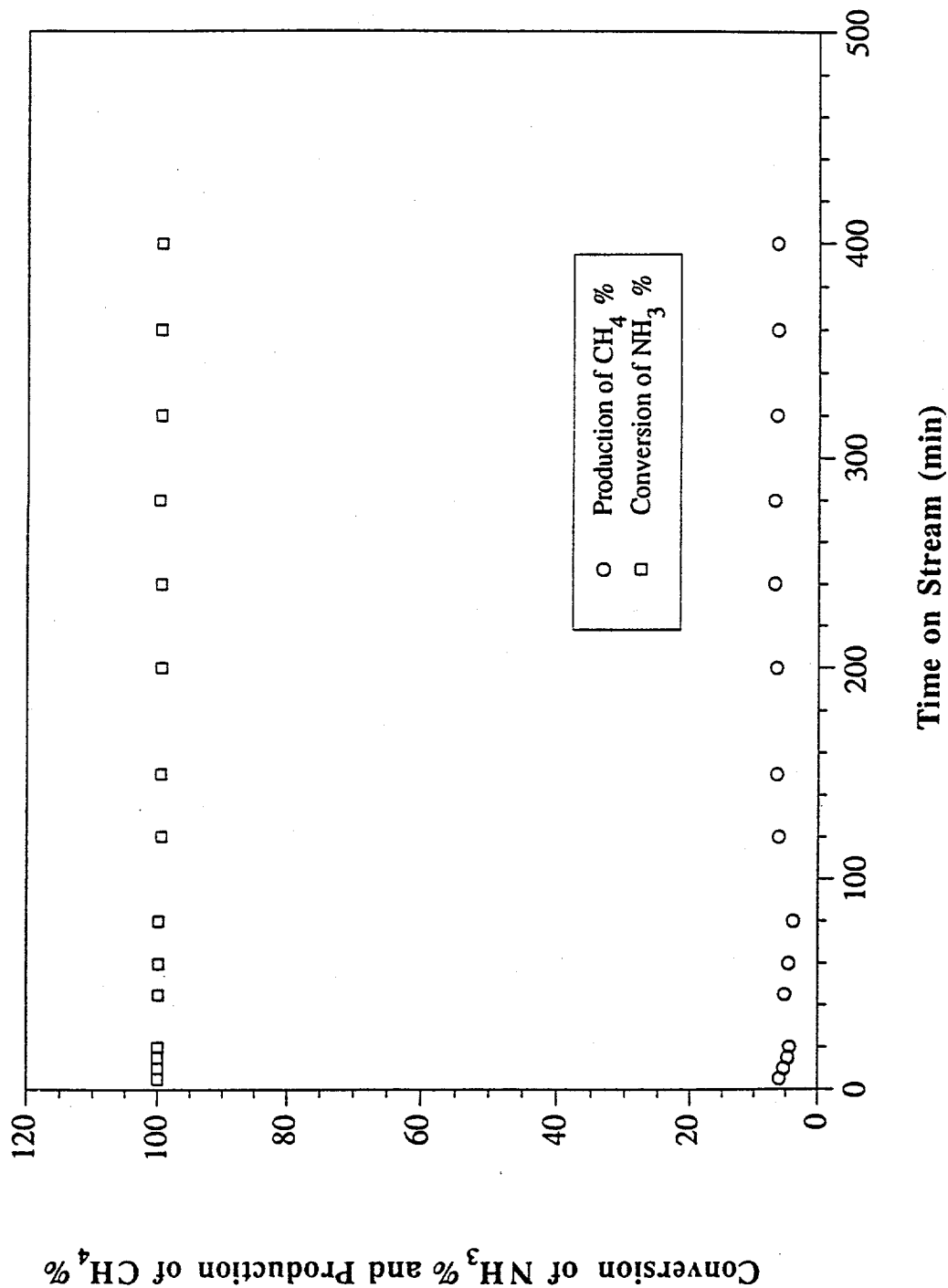


Figure 14. Decomposition of NH₃ over HTSR-1 catalyst at 725°C and 200 psig pressure in a simulated coal gas stream.

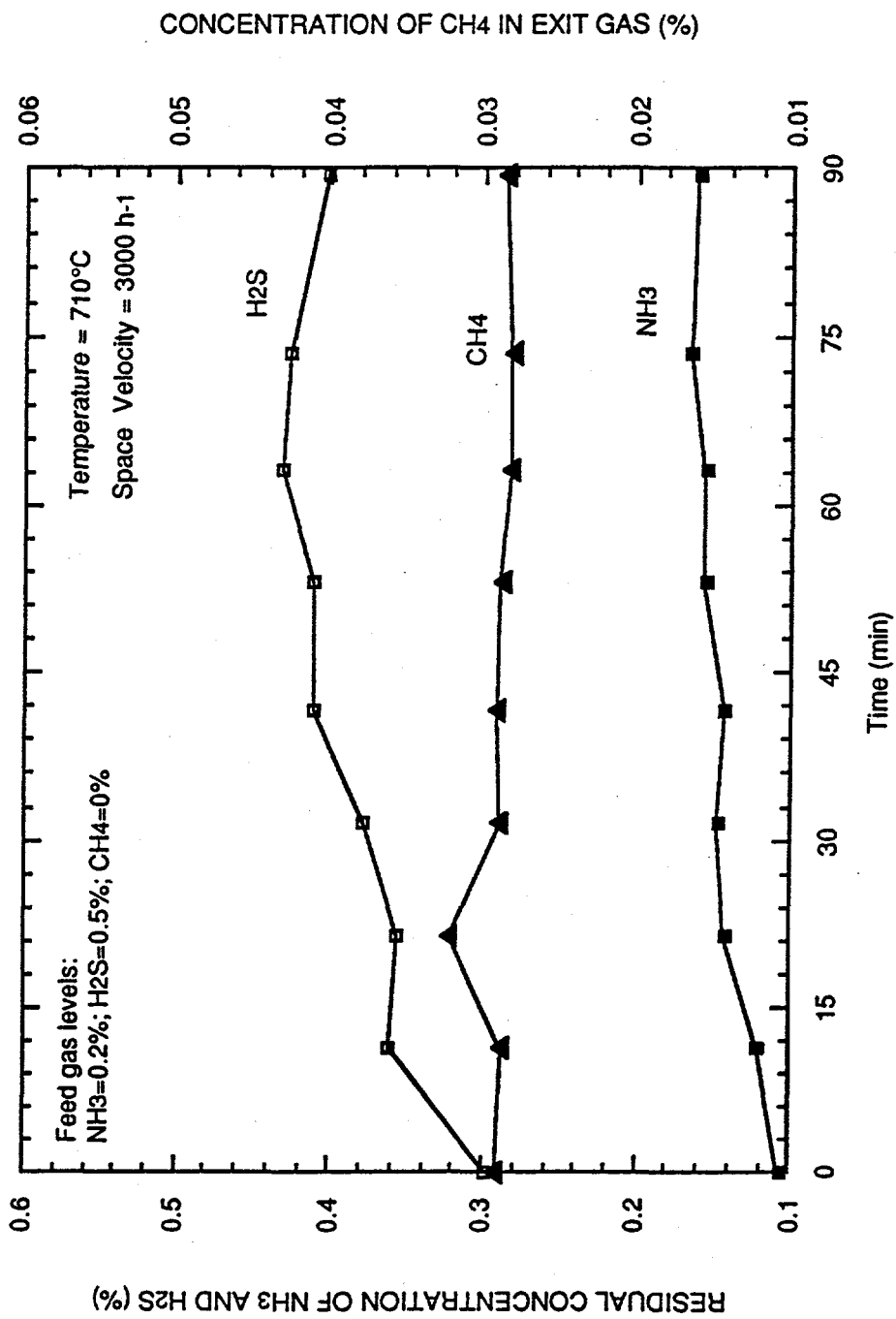


Figure 15. The conversion of NH₃ and H₂S on CRC-653 catalyst in simulated Texaco gasifier stream.