

- MoS_2 is also a catalyst for the decomposition of NH_3 . However, its surface area needs to be maintained by addition of suitable stabilizing agents for sustained activity.

Zinc titanate is one of the best sorbent for removing H_2S in hot coal gas streams. A sorbent formulation (ZT-4) obtained from RTI was tested for its NH_3 decomposition activity. At a temperature of 725°C , its catalytic activity either in the presence or absence of H_2S was low; only less than 10% of the feedgas NH_3 decomposed (Figure 16).

NICKEL ON TITANIA CATALYSTS

The Ni/TiO_2 catalyst (stabilized with ZrO_2) after treatment in hydrogen at 550°C was tested for its NH_3 decomposition activity at 725°C using a simulated coal gas (38% CO , 28.5% H_2 , 12.8% CO_2 , 18.1% H_2O , 0.75% H_2S , 0.18% NH_3 , and 1.6% N_2). Equal quantities of zinc titanate (ZT-4) sorbent and the catalyst were mixed together and exposed to the simulated coal gas at a space velocity of 3000 h^{-1} . The results of this test, shown Figure 17, indicate that the activity of the catalyst for ammonia decomposition and methane synthesis is high initially, but declines with time. This could be attributed to the poisoning of the catalyst by H_2S . When sulfur breakthrough occurred, the extent of ammonia decomposition was observed to be small. Sintering of the catalyst could be also a factor in the decreased activity as the exposed catalyst had a surface area of only $18 \text{ m}^2/\text{g}$.

The Ni/TiO_2 was further modified by incorporating molybdenum. A solution of ammonium molybdate was added to the catalyst by incipient wetness technique. This procedure repeated again to increase the total Mo content to 12 wt%. The catalyst ($\text{Ni-Mo}/\text{TiO}_2$) was then treated in H_2 at 550°C for 3 h until no NH_3 evolution was observed. Then the temperature was increased to 725°C and the gas mixture was changed to the Texaco gas composition with 600 ppm of H_2S and 0.18% NH_3 . The behavior of the catalyst was not different from that of the catalyst containing only nickel. The activity of the $\text{Ni-Mo}/\text{TiO}_2$ catalyst for ammonia decomposition at 725°C under steady state conditions was negligibly small.

COBALT ON TITANIA CATALYSTS

The Co/TiO_2 catalyst was tested for NH_3 decomposition activity at 725°C using a simulated Texaco coal gasifier gas stream. Even in the absence of H_2S in the gas stream, the activity was negligibly small. The presence of 5,000 ppm H_2S did not improve the catalytic activity.

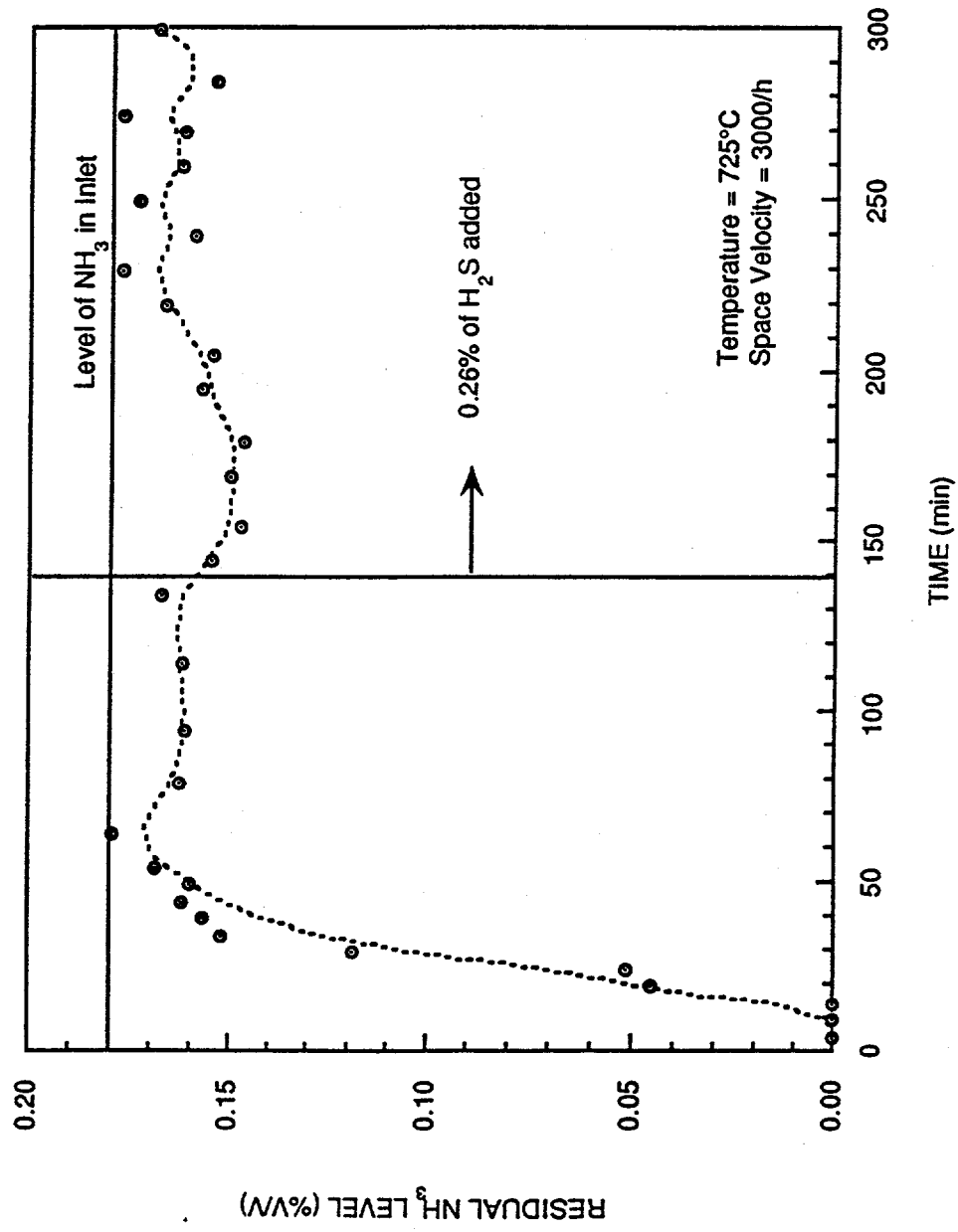


Figure 16. Decomposition of ammonia on a zinc titanate (ZT-4) sorbent at 725°C.

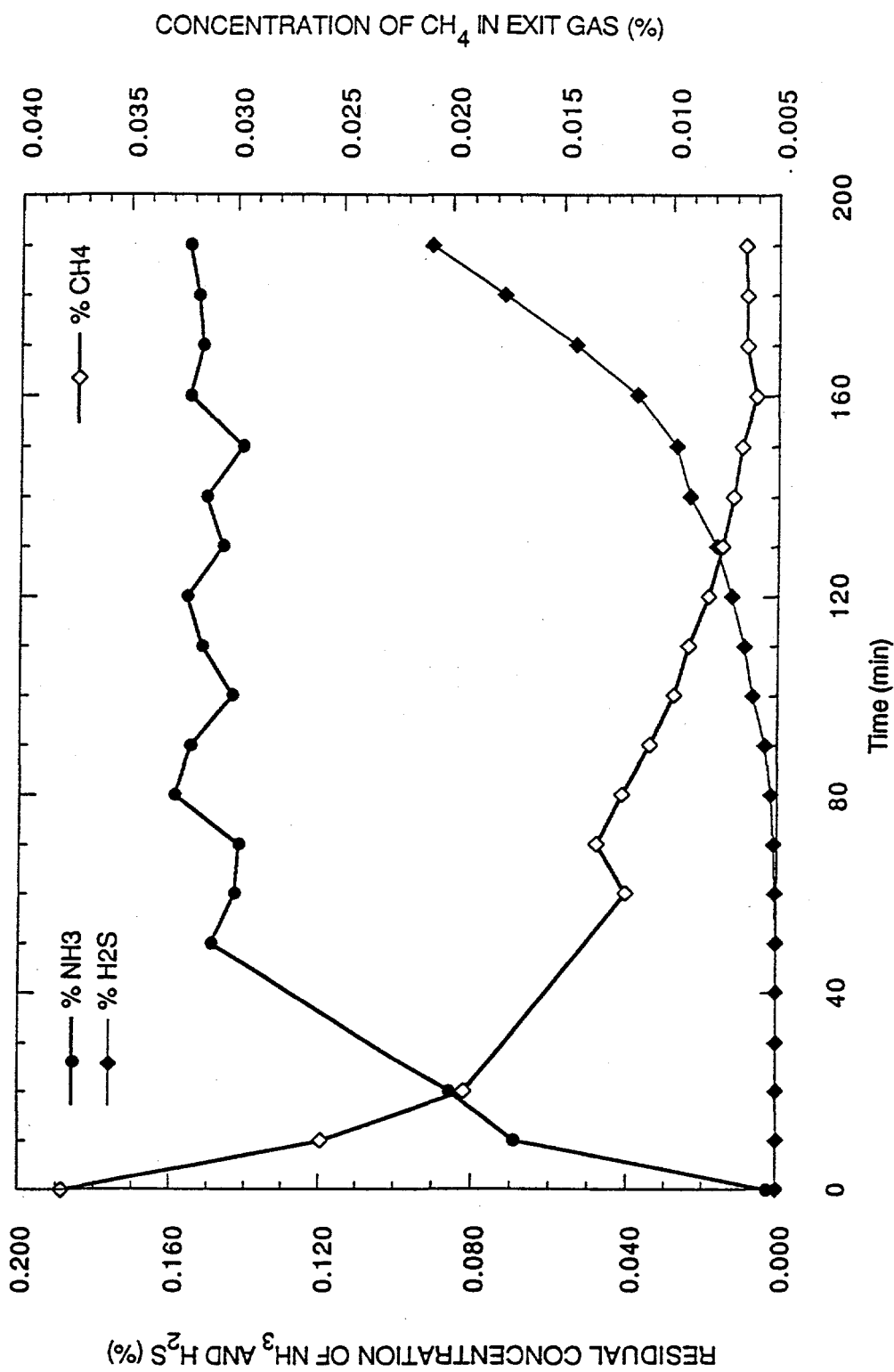


Figure 17. The conversion of NH_3 on a Ni-TiO_2 catalyst mixed with ZT-4 sorbent in a simulated coal gas stream at 725°C .

A batch of Co-Mo supported on TiO₂ was prepared by impregnating the Co-TiO₂ catalyst 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.

The Co-Mo/TiO₂ catalyst showed an initial activity for decomposition of NH₃ at 725°C; about 20% of the feed NH₃ was decomposed. However, the activity declined with time even in the absence of H₂S and became negligibly small after only 4 h.

The Co-Mo catalyst was also sulfided at 550°C using 1% H₂S-H₂ for 7 hours to convert the metals to their sulfide form. The purpose of this experiment to test the assumption that the sulfides could be more active for NH₃ decomposition than the metals. But the catalytic activity of the catalyst at 725°C did not improve with sulfidation; the fraction of the NH₃ decomposed was less than 5%.

MOLYBDENUM ON TITANIA CATALYSTS

A Mo/TiO₂ catalyst was also tested for its NH₃ decomposition activity at 725°C in a simulated Texaco oxygen-blown gasifier gas stream. With a 7.7 wt% Mo on titania, the NH₃ in the reactor exit gas increased steadily reaching the feedstock level in about 400 minutes (Figure 18). In this test, no H₂S was added to the feedgas. However, because the system has been exposed to high levels of H₂S in previous runs, a residual level of about 1 to 10 ppm was detected in the reactor exit gas during the run. This catalyst did not promote the formation of CH₄. The amount of CH₄ formed was less than 0.01% v/v.

A run was also made with a Mo/TiO₂ catalyst containing 10.8 wt% Mo. Initially, the residual level of NH₃ increased rapidly during the initial 50 minutes (Figure 19). After this period, the rate of decrease in ammonia conversion was slow. After about 250 minutes, a near steady state conversion of about 20% was observed. The conditions of this test was similar to the test described above.

The experimental results suggest that Mo-containing catalysts may decompose H₂S at 725°C. However, the surface area of these catalyst appear to decrease with time at that temperature.

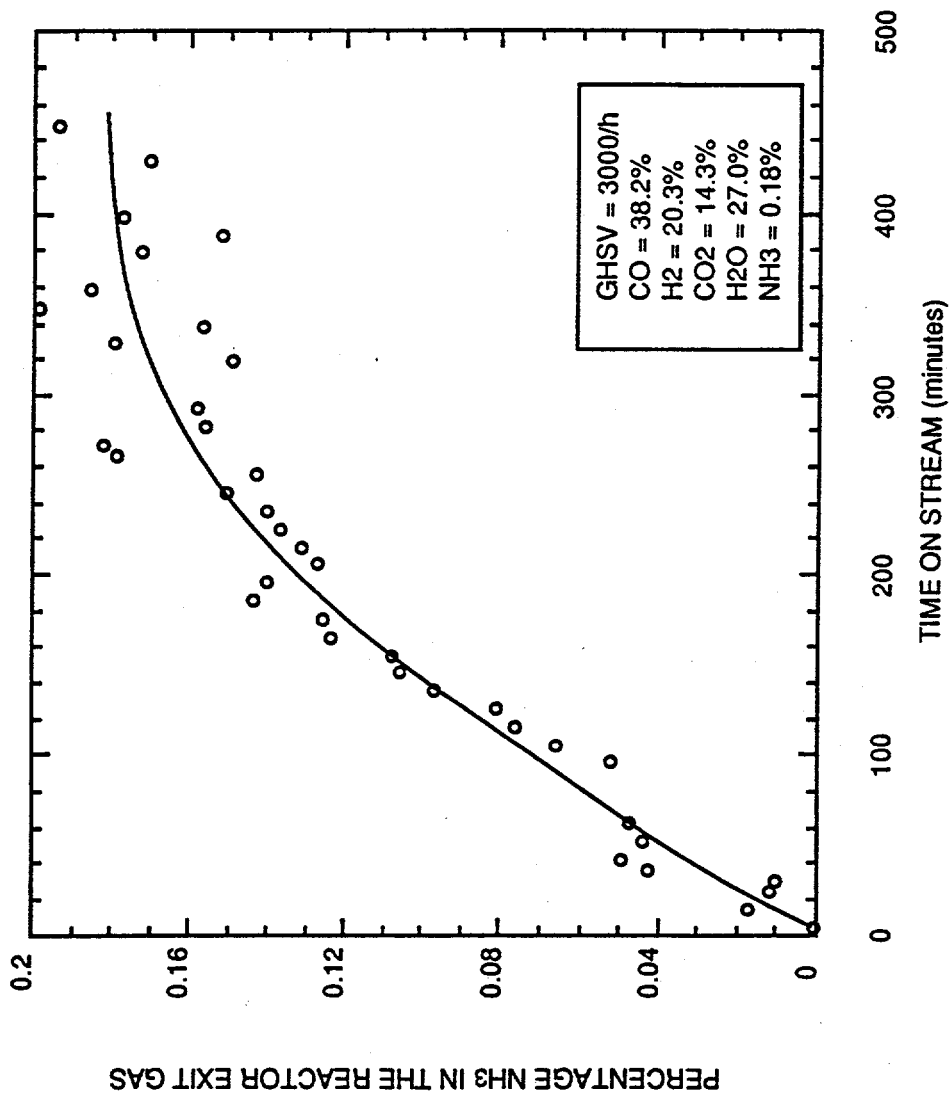


Figure 18. Decomposition of ammonia on a 7.7 wt% Mo on Titania catalyst at 725°C.

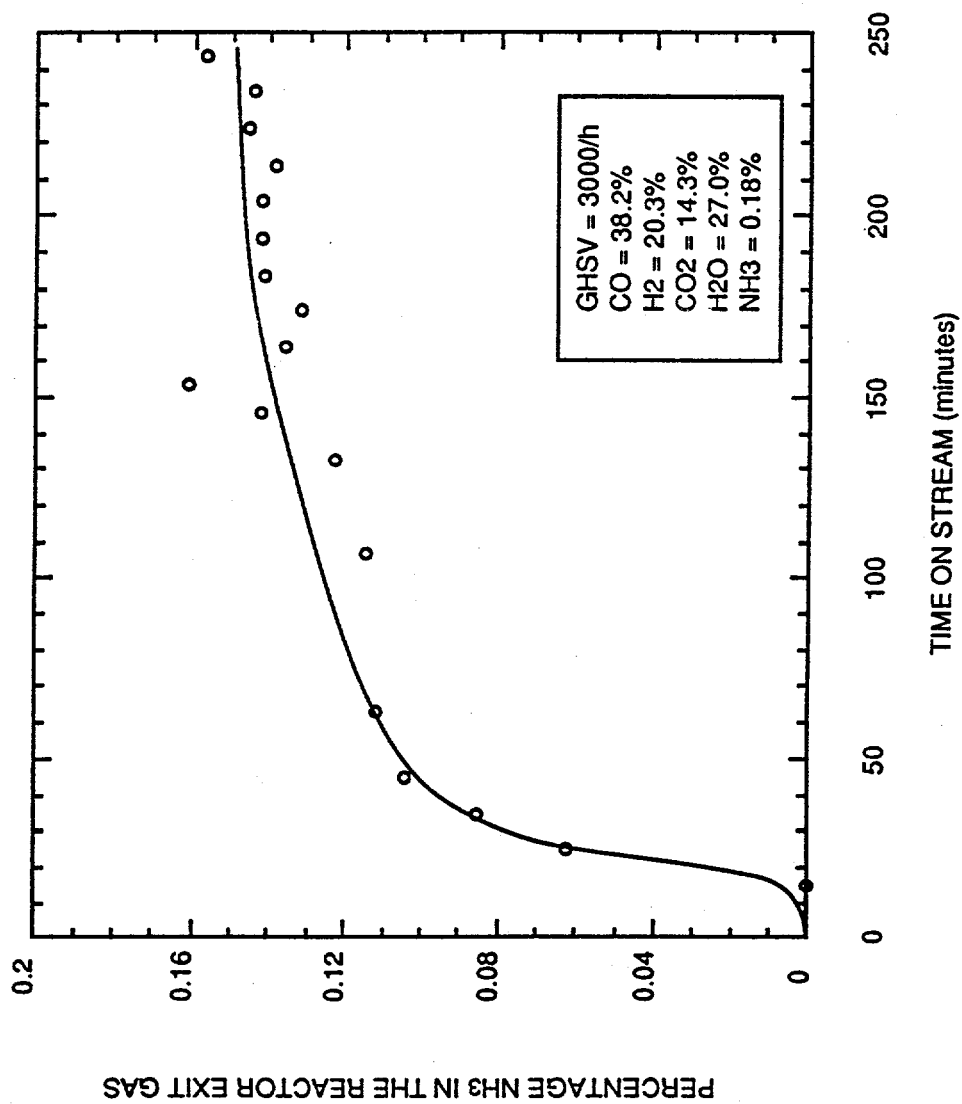


Figure 19. Decomposition of ammonia on 10.8 wt% Mo on titania catalyst at 725°C.

COBALT AND MOLYBDENUM ON TITANIA CATALYSTS

A 100 g batch of 2% Co-10% Mo on titania catalyst was prepared for bench-scale testing at Research Triangle Institute. A sample of this catalyst mixed with additional zinc titanate powder was tested at SRI's laboratory-scale reactor at 1-atm pressure. The results indicated that at a space velocity of 3000 h^{-1} and 725°C , the catalyst reduced the level of NH_3 from about 1700 ppm to about 1500 ppm (Figure 20). Another sample of this catalyst was sulfided overnight and then tested for NH_3 decomposition activity. The activity of the sulfided catalyst was similar to the unsulfided catalyst indicating that Co-Mo/ TiO_2 catalyst has a moderate activity for NH_3 decomposition even after sulfidation (Figure 21).

The catalyst was analyzed using X-ray diffraction (XRD) and Auger electron spectroscopy (AES). The X-ray diffraction pattern of the catalyst under as-prepared conditions indicated peaks corresponding only to titania (Figure 22). This observation suggests that both cobalt and molybdenum are in an amorphous state and presumably finely-dispersed on the titania substrate. Analysis by AES, a technique which is sensitive only to the surface layers ($\sim 2 \text{ nm}$ depth) of a solid material, indicated that both Mo and Co are present on the surface of the titania (Figure 23).

XRD analysis was also performed with catalysts exposed to the simulated hot coal gas streams. The XRD pattern of a Co-Mo/ TiO_2 catalyst mixed with zinc titanate and after a 8-h exposure at 725°C showed the presence of ZnS , MoS_2 , Co_9S_8 , and TiO_2 (Figure 24). This observation indicates that all the active components were sulfided during hot coal gas exposure. The XRD pattern of a tungsten impregnated on titania after reaction to the simulated Texaco coal gas stream at 725°C showed the presence of WS_2 (Figure 25).

TUNGSTEN ON TITANIA CATALYSTS

The W/ TiO_2 catalyst was tested in a simulated Texaco oxygen-blown gasifier gas stream. The residual NH_3 level in the reactor exit gas was low during the initial 50 minutes. After this period it increased to about 1600 ppm and remained at that level for the next two hours. The percentage of decomposition under these conditions correspond to about 10% of the feedstock NH_3 (Figure 26).

The behavior of W-Mo/ TiO_2 catalyst was similar to that W/ TiO_2 catalyst (Figure 27). The steady-state decomposition activity did not differ significantly whether H_2S is present or absent. The conversion of feedstock NH_3 was less than 10% with the W-Mo/ TiO_2 catalyst.

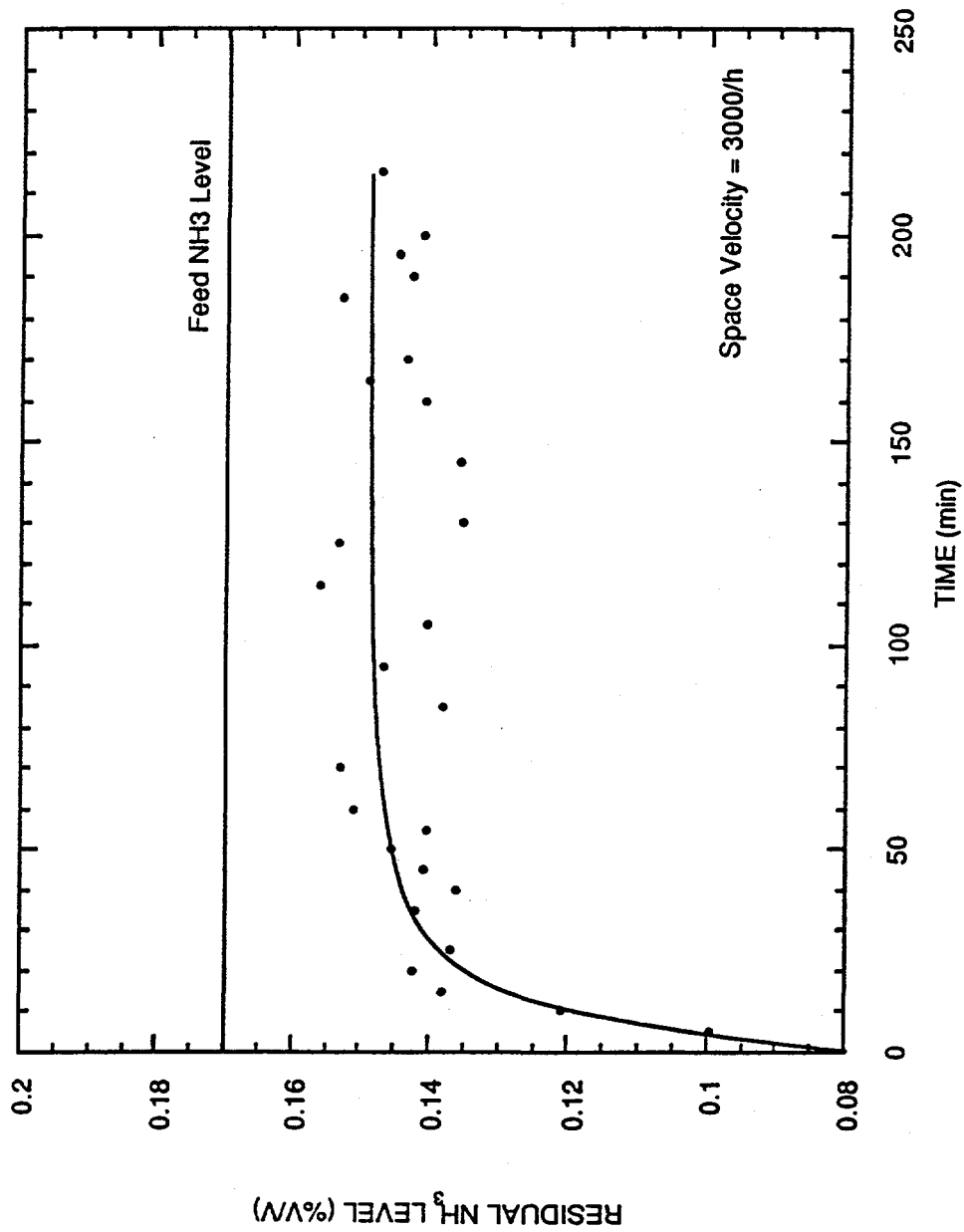


Figure 20. The catalytic activity of a Co-Mo/titania catalyst at 725°C.

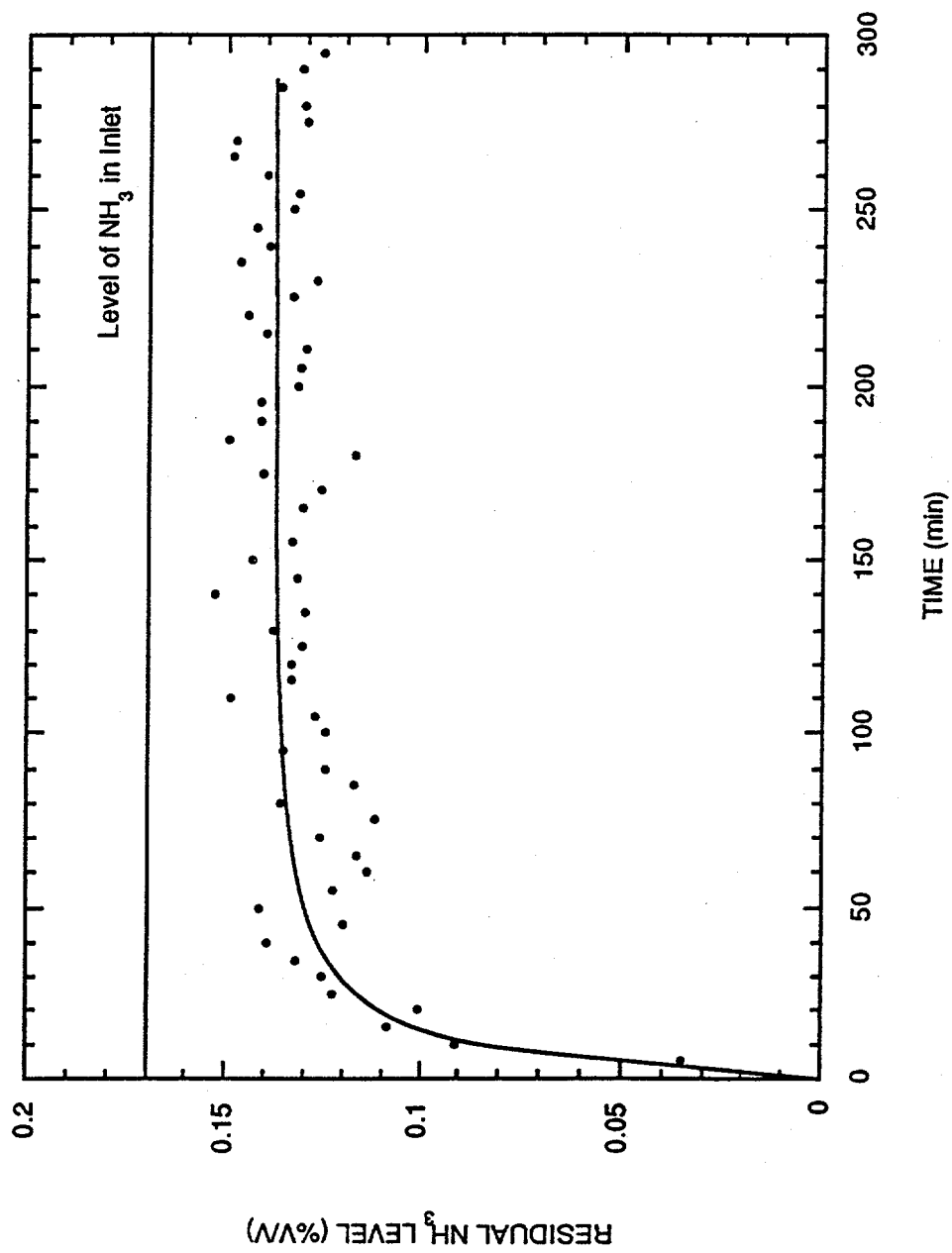


Figure 21. The catalytic activity of a Co-Mo/titania catalyst at 725°C after sulfidation.

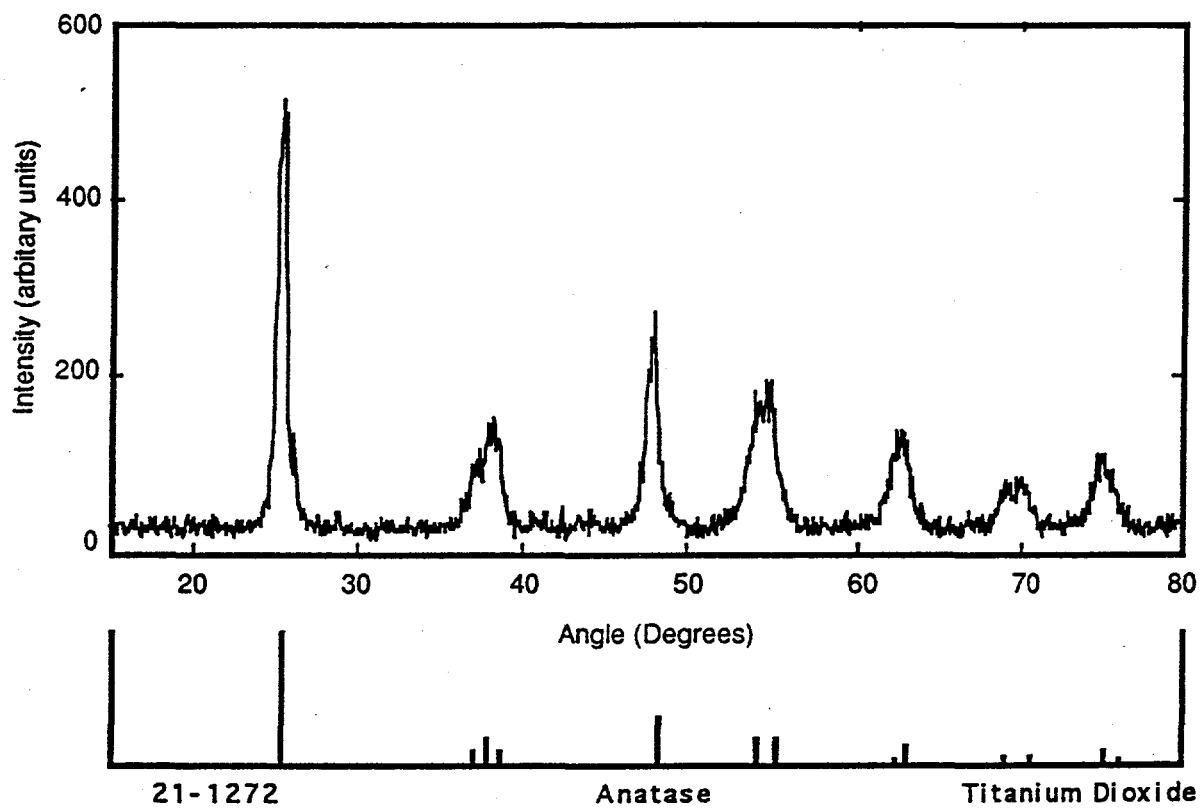


Figure 22. X-ray diffraction pattern of a Co-Mo-Titania catalyst.

400 X-Ray (50 Counts/ Div) File = 6596

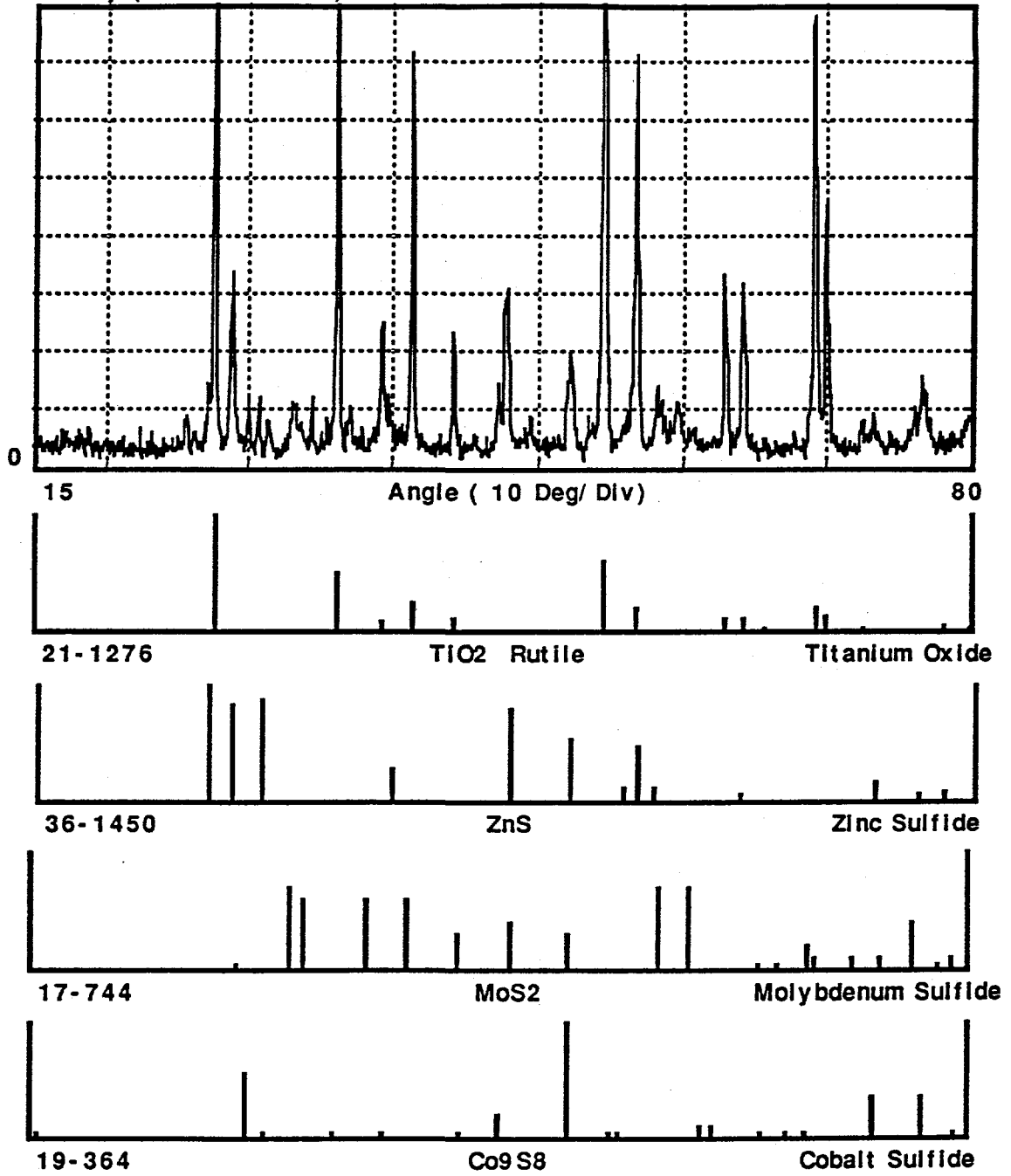


Figure 24. X-ray diffraction pattern of a reacted Co-Mo catalyst mixed with zinc titanate.

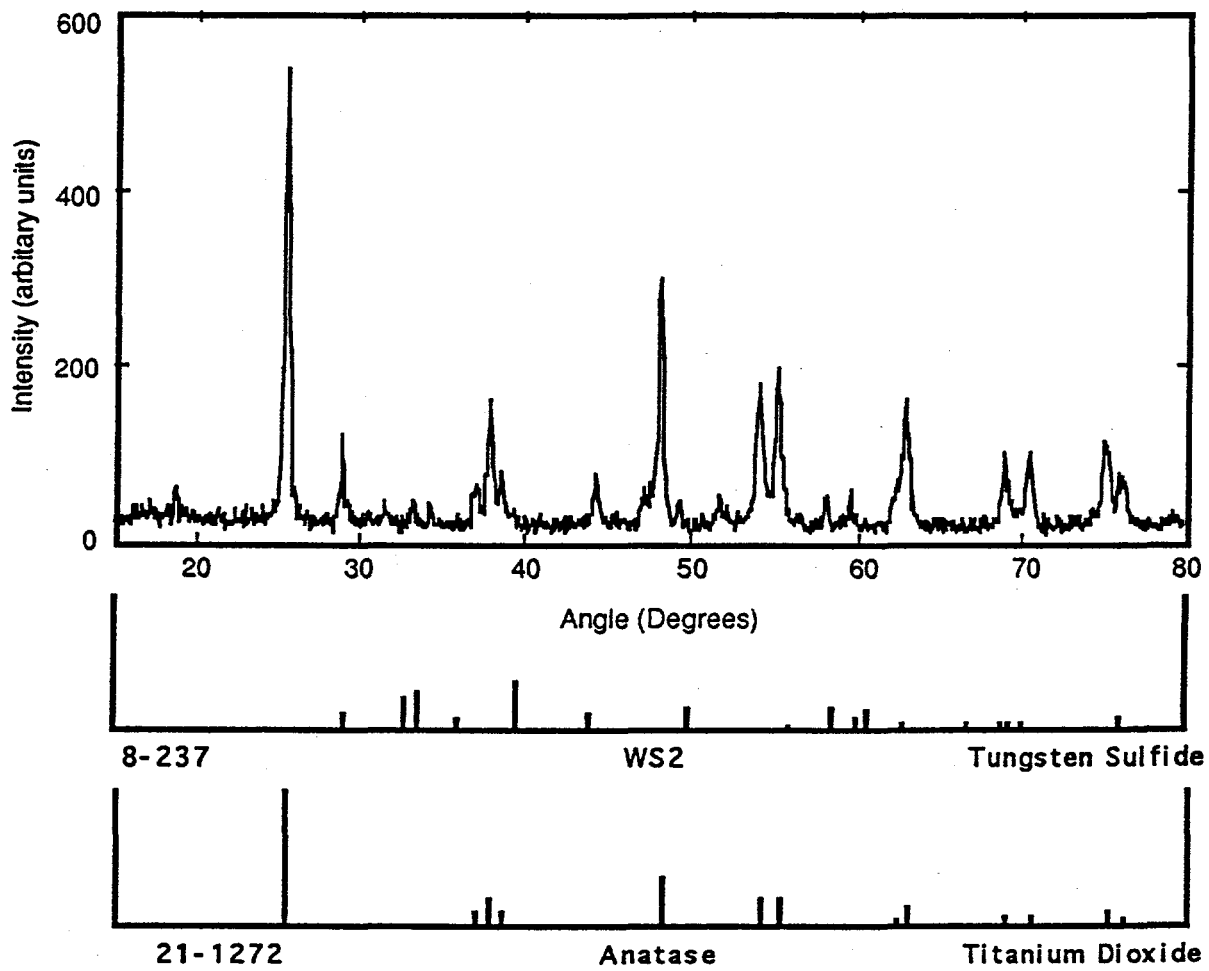


Figure 25. X-ray diffraction pattern of a Co-W-Titania catalyst after reaction.

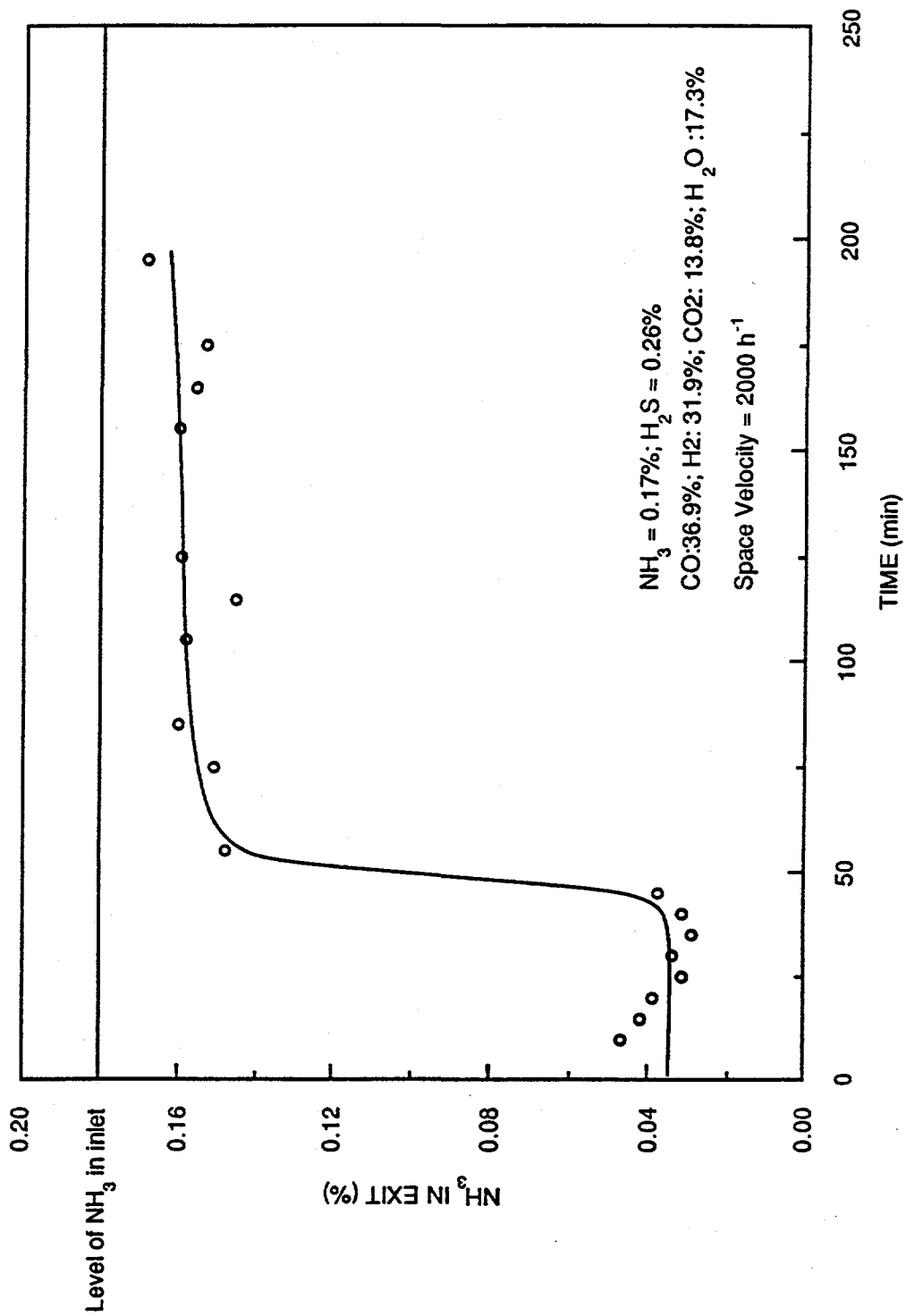


Figure 26. Decomposition of NH_3 over W/TiO_2 at 725°C .

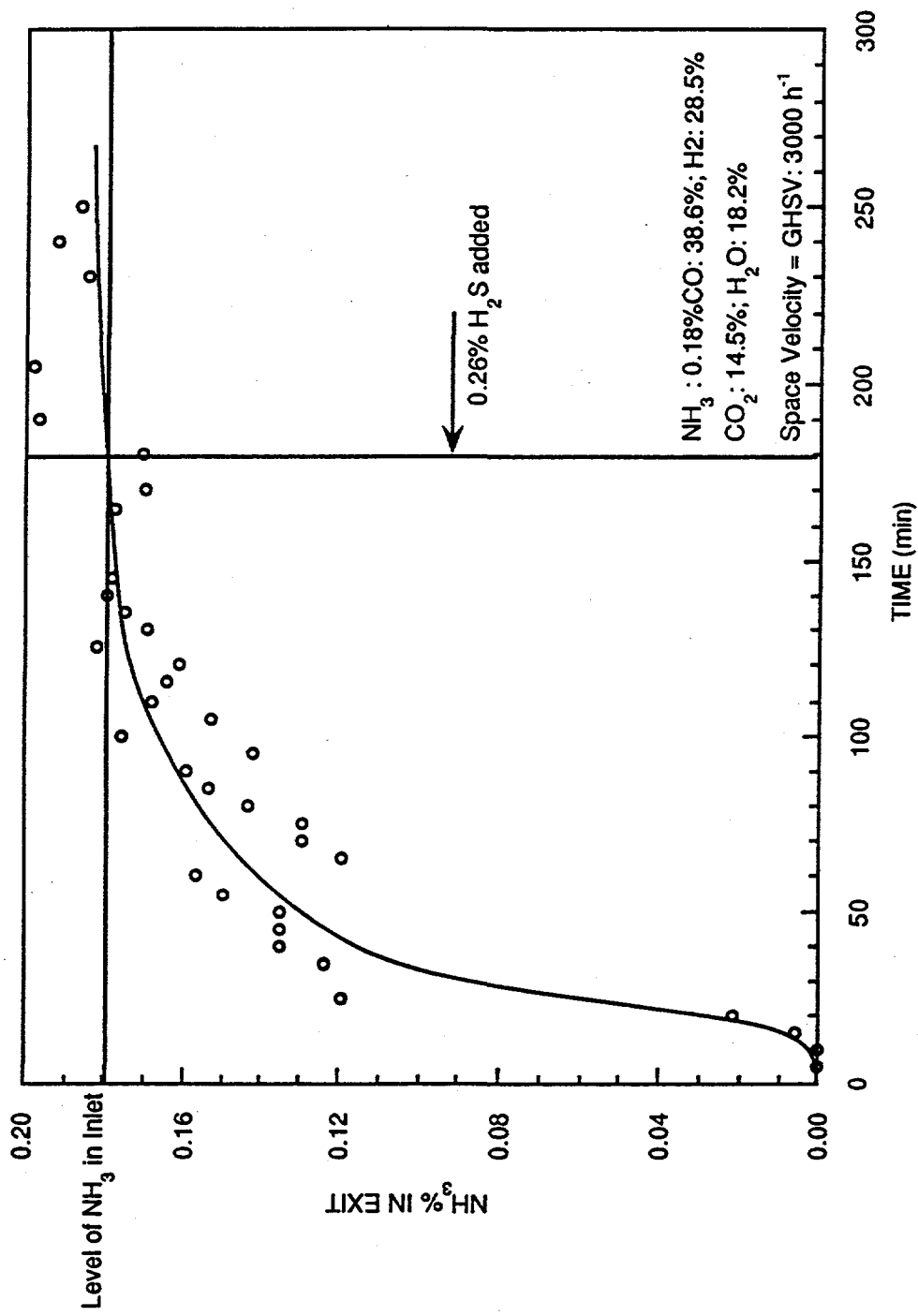


Figure 27. Decomposition of NH_3 over Co-W/TiO₂ at 725°C

The experimental results suggest that W-containing catalysts are not very active for decomposing NH_3 in simulated coal gas stream at 725°C . It is feasible that the surface area of the TiO_2 support decreased with time at the reaction temperature contributing to the decline in catalytic activity.

TUNGSTEN OXIDE-ZINC TITANATE CATALYSTS

RTI supplied two catalysts (#82 and #83) to be tested for their ammonia decomposition activity at a pressure of 200 psig and a space velocity of 3000 h^{-1} . The catalyst #82 contained ZnO and WO_3 in a molar ratio of 1:1. The catalyst #83 was made of ZnO and WO_3 in an equimolar ratio with additions of 5% CoO and 2% ZrO_2 . Although these catalysts decomposed NH_3 initially, the catalytic activities decreased with time at 725°C (Figure 28). No significant activity was observed with the catalyst #82 after 150 minutes. The amount of CH_4 formed with this catalyst was also negligibly small. The #83 catalyst appears to have a higher activity than the #82 for both methanation and NH_3 decomposition reactions (Figure 29). Even with this catalyst, the steady-state rate constant for the decomposition reaction is only 0.02 s^{-1} .

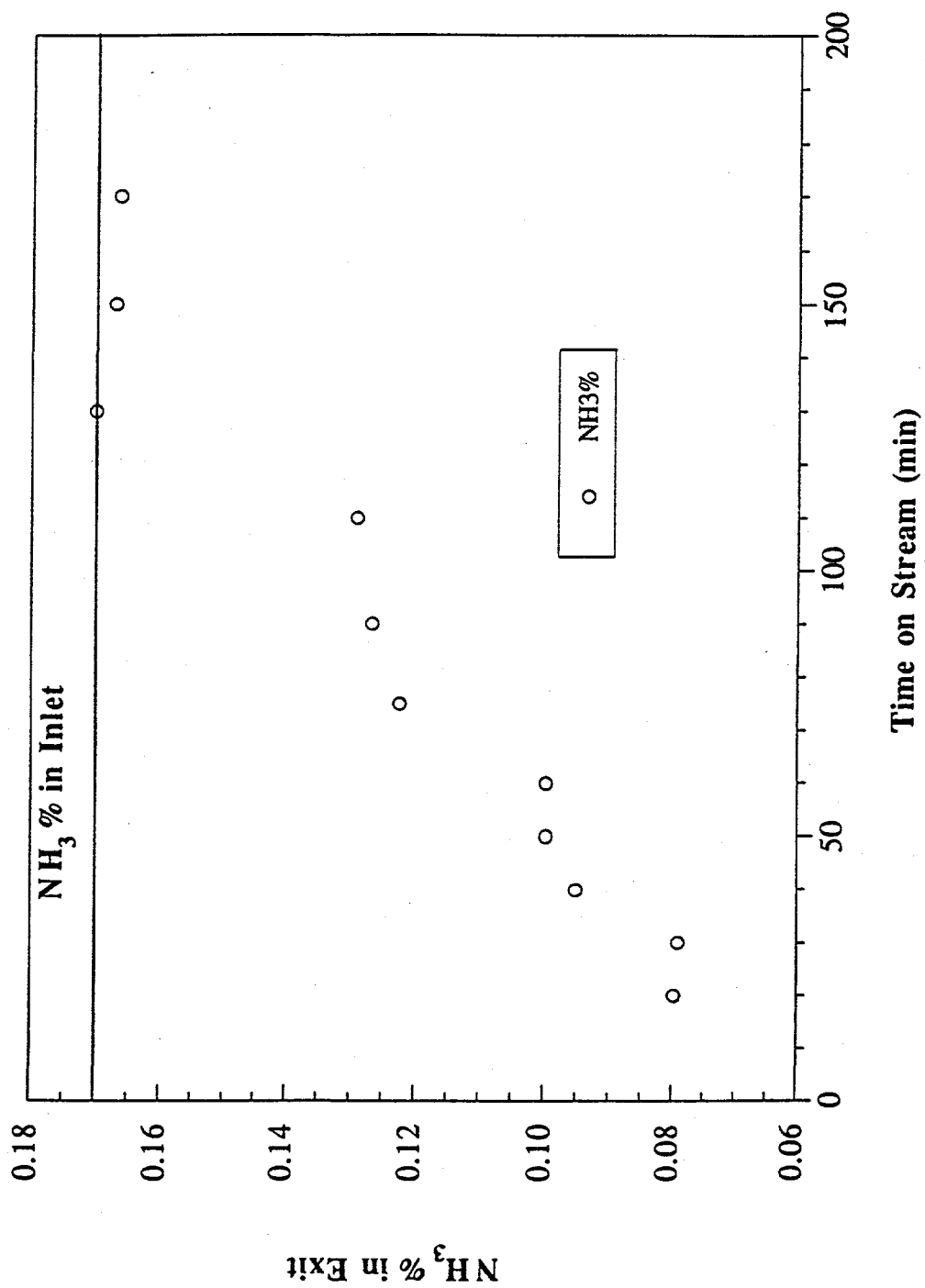


Figure 28. The conversion of NH₃ on RTI #82 catalyst in a simulated coal gas stream at 725°C and 200 psig.

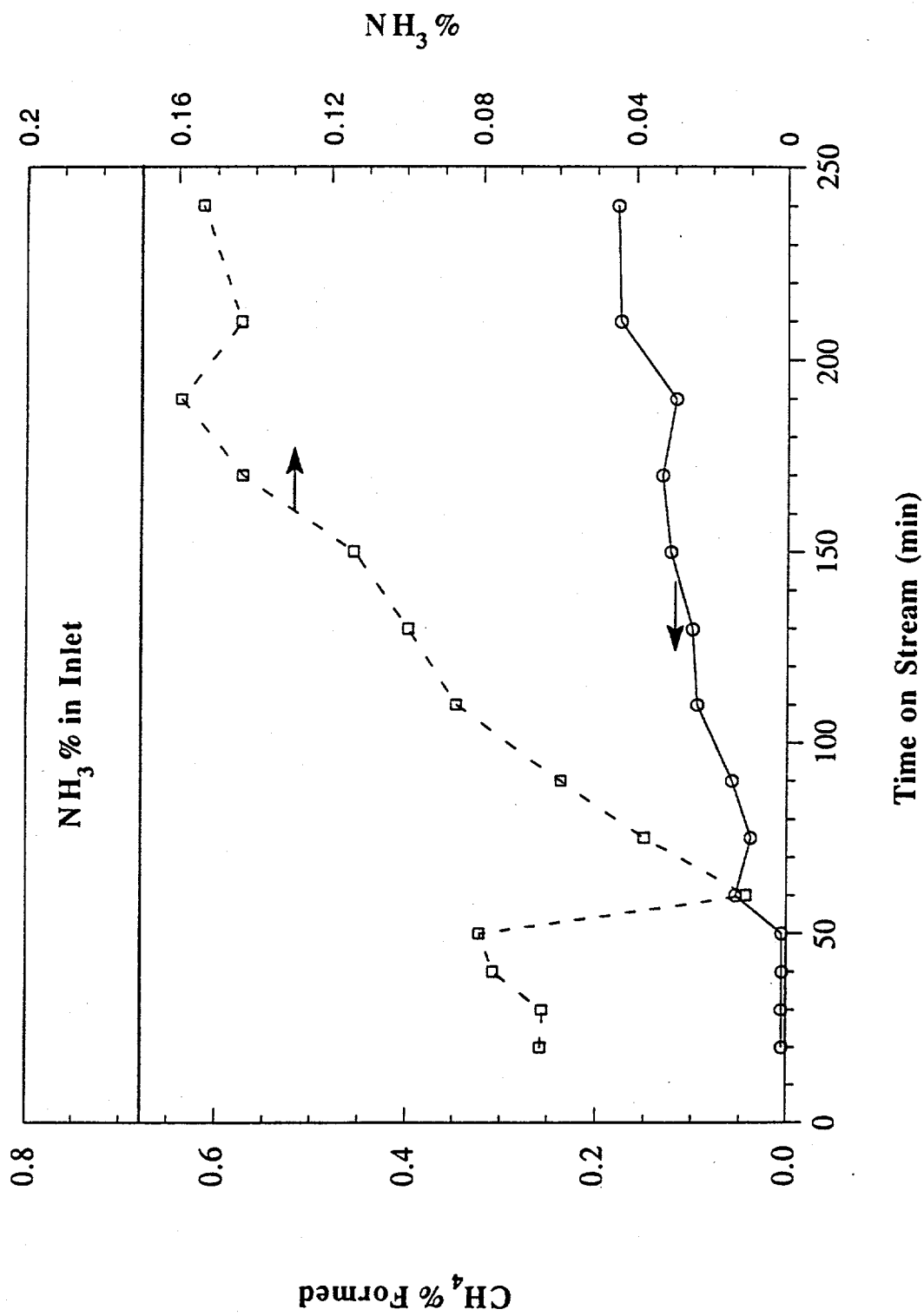


Figure 29. The conversion of NH₃ on RTI #83 catalyst in a simulated coal gas stream at 725°C and 200 psig.