



Sulfur poisoning of methanation catalysts : pulse poisoning with hydrogen sulfide  
by David Jonathon Swanberg

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Chemical Engineering  
Montana State University  
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Abstract:

Because of the sulfur content of coal, synthesis gas produced from it contains sulfur compounds which are poisonous in low concentrations to catalysts used in the conversion of the synthesis gas to methane. In this investigation, methanation catalysts were poisoned with H<sub>2</sub>S by the pulse poisoning method in order to study the deactivation of those catalysts. The measurement of deactivation of various catalysts would aid in the development of sulfur-resistant methanation catalysts.

Methanation was achieved by hydrogenation of CO over supported Ni and Ni-La catalysts. The reaction apparatus incorporated a Berty-type continuous flow mixed reactor. Methanation activity and response to pulse poisoning were studied at 300 degrees C using a feed gas mixture with a H<sub>2</sub> /CO molar ratio of 2.35/1.

Two commercial catalysts, Harshaw Ni-0104 and Ni-3266, were tested for pulse poisoning response at pressures of 85.1, 690, 1380, and 2070 kPa. The response data showed declines in activity for each of the runs, after 11 minutes response time, which were linear in nature. Least-squares linear regressions were applied to the data and were extrapolated back to zero minutes response time to indicate percent of initial activity of the catalysts. This was a measure of the catalyst deactivation which was attributed to H<sub>2</sub> S poisoning. The magnitudes of the slopes of the linear regressions were also noted as extended deactivations of the catalysts, but were not strictly due to sulfur poisoning. Both catalysts had minimum percents of initial activity at 690 kPa, while extended deactivation increased as pressure increased with the exception of the Ni-3266 run at 2070 kPa.

The Ni-3266 and Ni-0104 catalysts, as well as a Ni/Al<sub>2</sub> O<sub>3</sub> catalyst prepared in the laboratory, were tested for pulse poisoning response at 85.1 kPa. The Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-3266 catalysts had 83.5 and 82.6 percent of initial activity respectively, while the Ni-0104 catalyst had 50.2 percent of initial activity.

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MONTANA STATE UNIVERSITY  
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APPROVAL

of a thesis submitted by

David Jonathon Swanberg

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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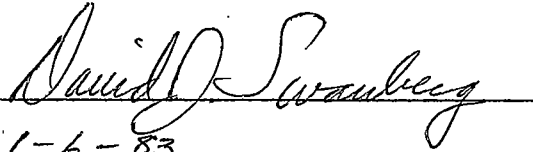
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## ABSTRACT

Because of the sulfur content of coal, synthesis gas produced from it contains sulfur compounds which are poisonous in low concentrations to catalysts used in the conversion of the synthesis gas to methane. In this investigation, methanation catalysts were poisoned with  $H_2S$  by the pulse poisoning method in order to study the deactivation of those catalysts. The measurement of deactivation of various catalysts would aid in the development of sulfur-resistant methanation catalysts.

Methanation was achieved by hydrogenation of CO over supported Ni and Ni-La catalysts. The reaction apparatus incorporated a Berty-type continuous flow mixed reactor. Methanation activity and response to pulse poisoning were studied at 300 degrees C using a feed gas mixture with a  $H_2/CO$  molar ratio of 2.35/1.

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The Ni-3266 and Ni-0104 catalysts, as well as a  $Ni/Al_2O_3$  catalyst prepared in the laboratory, were tested for pulse poisoning response at 85.1 kPa. The  $Ni/Al_2O_3$  and Ni-3266 catalysts had 83.5 and 82.6 percent of initial activity respectively, while the Ni-0104 catalyst had 50.2 percent of initial activity.

## INTRODUCTION

Recently, the disparity between the demand for hydrocarbon fuels and the supply of those fuels from crude oil sources has heightened interest in the production of fuels from coal, a resource of which the United States has plentiful reserves. Commercial processes are available for the gasification of coal which produce synthesis gases of high carbon monoxide (CO) and hydrogen (H<sub>2</sub>) content (Cusumano, Dalla Betta, and Levy, 12:222). From coal synthesis gas it is possible to catalytically synthesize hydrocarbon products including methane. Methane has particular advantages as a fuel because of its higher Btu value than raw synthesis gas and because of its compatibility with existing natural gas pipeline networks. Thus, the catalytic production of methane as a substitute for natural gas is an attractive use of coal energy.

However, because coal contains sulfur, the synthesis gas made from it contains sulfur compounds which are poisonous to methanation catalysts even at very low concentrations. The cost of removal of these sulfur compounds from coal synthesis gas is prohibitive. In addition, characterization of the deactivation of methanation catalysts in the presence of sulfur poison would aid the development of sulfur-resistant methanation catalysts.

The ability to catalytically produce methane from CO and H<sub>2</sub> was first reported near the turn of the century. Also, the synthesis of hydrocarbon fuels from coal-derived gases was carried out extensively by the German scientists, Fischer and Tropsch, circa 1920-1935. Their work involved the catalytic production of methane, as well as various longer chain hydrocarbons, from H<sub>2</sub>/CO mixtures.

Work on the synthesis of hydrocarbon fuels from H<sub>2</sub>/CO mixtures was continued after World War II by several research groups including the British Fuel Research Board.

A major effort was also undertaken by the U.S. Bureau of Mines. Over the past decade the interest in coal conversion in general has increased, and methanation has been the subject of investigation in concert with this trend.

Since the earliest work on methanation, interest has centered around catalysis by the transition metals of Group VIII of the periodic table. Some successful catalysts have consisted of these metals dispersed on porous supports in reduced form. However, the transition metals are highly sensitive to deactivation by exposure to sulfur compounds. Since methanation is usually carried out in a highly reducing atmosphere, a most prevalent sulfur compound encountered in methanation is hydrogen sulfide ( $H_2S$ ). Therefore, many investigations have been directed toward the characterization of the deactivation of methanation catalysts in the presence of  $H_2S$  poison. The methods utilized for this type of study have included catalyst prepoisoning, and *in situ* exposure to continuous, low-level concentrations of  $H_2S$ . In this investigation methanation was carried out at conditions analogous to commercial operations using a Berty-type, continuous flow, mixed reactor. The response of the activity of various methanation catalysts to an *in situ* pulse of  $H_2S$  was measured in an effort to characterize the poisoning of those catalysts.

## REVIEW OF RELATED LITERATURE

Mechanism of Catalytic Methanation

The reaction of CO and H<sub>2</sub> to form methane has been known for some time: Sabatier and Senderens first reported the production of methane from CO and H<sub>2</sub> over Ni and Co catalysts in 1902 (Biloen and Sachtler, 9:167). Also, the catalytic syntheses by Fischer and Tropsch during the 1920s and 1930s, and the work during the past 10-15 years, have contributed to the knowledge of the general methods of methane synthesis. Catalytic methanation may be achieved by several reactions including the following (Trimm, 3:267):



Of the above reactions, (1) has received by far the most attention and was the subject of this study. Reaction (3) has been studied from a similar approach as (1) and most recently reaction (2) has been proposed as a more commercially viable alternative by Meyer et al. (23:10). Because much of the study of catalytic methanation has been by way of reaction (1), and because it was the subject of this particular study, the mechanism of reaction (1) will be discussed here in detail.

A recently proposed mechanism for reaction (1) grew out of the discovery of an important intermediate reaction. An active layer of carbon on the surface of supported Ni catalysts was found by several investigators to be easily hydrogenated to form methane (Sachtler, Kool, and Ponec, 29:285; Wentrcek, Blood, and Wise, 36:235). This reactive surface carbon was identified as the product of the adsorption and subsequent dissociation of

CO, and was distinguished from the much less reactive nickel carbide ( $\text{Ni}_3\text{C}$ ). Thus, the reaction was characterized by the following sequence (Trimm, 32:275):

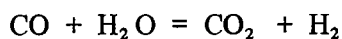


It was questionable whether intermediates (b) and (c) proceeded by means of bulk phase  $\text{H}_2$ , or by adsorbed, or dissociatively adsorbed hydrogen species. However, Vannice has shown enhanced methanation activity with increasing heat of adsorption of hydrogen, which suggests an adsorbed hydrogen species for both the methane formation and water formation reactions (34:468).

Little is known about the form of the surface carbon species which is active for methanation. However, Vannice has noted that the lower the heat of adsorption of CO on a particular catalyst, the higher the activity of that catalyst for methanation (34:465). The ability of a supported catalyst to dissociatively adsorb CO, in order to form the easily hydrogenated surface carbon, has been shown for Ni (Araki and Ponec, 3:439; Rabo, Risch, and Poutsma, 27:295), and less convincingly for Ru and Co (Sachtler, Kool, and Ponec, 29:285). Thus, the likely choice of reactive center for a methanation catalyst should be Ni.

Strongly related to the formation of the active surface carbon species is the degradation of this surface carbon into the much less reactive graphitic carbon or metal carbide forms. This deposition of bulk carbon forms on the surface of a catalyst causes deactivation and is referred to as carbon fouling. Cusumano, Dalla Betta, and Levy suggested that carbon fouling was the most difficult problem in catalytic methanation next to sulfur poisoning (12:55). It has been well noted in the literature that carbon fouling of methanation catalysts is favored at the following reaction conditions: (1) less than stoichiometric ratios of  $\text{H}_2$  to CO in the feed, and (2) moderate temperatures of 250-400 degrees C (Trimm, 32:268; Dalla Betta, Piken, and Shelef, 14:181; Greyson, 17:476).

The reaction of equimolar ratios of CO and H<sub>2</sub> reactants to form CH<sub>4</sub> and CO<sub>2</sub> products, reaction (2) above, has been studied as an alternative to the standard methanation reaction (Meyer et al., 23:110). The reaction itself was of interest because it was observed that the CO product was formed directly rather than by a combination of the methanation reaction with the water-gas shift reaction (Meyer et al., 22:110; Sachtler, Kool, and Ponec, 29:285):



The direct formation of CO<sub>2</sub> was considered an advantage for catalyst design because the use of a sulfur-sensitive, Ni-based, water-gas shift catalyst was avoided. Meyer et al. suggested that a process designed for direct methanation could reduce capital costs by 20% and operation costs by 10% over state-of-the-art methanation processes (23:113).

#### Proven Catalysts

Much progress has occurred in catalytic methanation over the past decade. The application of supported catalysts to methanation gave way to the development of multi-component catalyst formulations for enhanced catalyst performance. Advances in catalyst characterization, by way of selective gas chemisorption and improved catalyst preparation methods, have also contributed to recent progress in catalytic methanation.

Early work on methanation established the catalytic activity of the Group VIII metals. Fischer et al. characterized these metals for their methanation activity. They found the relative activities to be: Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Pd (Vannice, 33:458). The catalysts were the unsupported metals and activities were based on weights of catalytic material. The development of supported catalysts, and the use of chemisorption techniques for measurement of catalyst surface area allowed Vannice to better characterize the specific activities of the Group VIII metals for methanation. The results were: Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir (33:458). Of the Group VIII metals, Ni has been a popular

choice for study because of its reasonable cost and its proven ability to favor the formation of the active surface carbon intermediate of the methanation reaction. In the choice of catalytic material for a methanation process, practical considerations would eliminate Ru because of high cost and Fe due to its high tendency for carbon fouling, leaving Ni as the next best choice for methanation.

### Supported Catalysts

Smith noted that the fine division of a non-porous solid into particles with sufficient surface area for effective catalytic activity was difficult to achieve (31:327-328). Hence, a significant development in catalytic methanation was the application of catalytic material to porous supports. The obvious advantage of the supported catalyst was increased surface area. Boudart noted that a significant characteristic of supported catalysts was the amount of dispersion of the catalytic material; dispersion indicating the fraction of atoms of catalytic material present that were surface atoms and were thus available as reaction sites (10:153). Additionally, Sinfelt noted that the support could provide thermal stability for the catalyst as well as resistance to sintering (30:645). Thermal stability for methanation catalysts was an important consideration due to the high exothermicity of the methanation reaction (Cusumano, Dalla Betta, and Levy, 12:47). Also, Yates and Sinfelt observed that in the hydrogenolysis of ethane over supported catalysts of the Group VIII metals, catalysts with lower dispersions had lower specific activities by as much as one order of magnitude (38:364).

The relationship between activity and degree of dispersion of methanation catalysts has been investigated with the aid of modern characterization techniques including x-ray diffraction, electron microscopy, and gas chemisorption (Cusumano, Dalla Betta, and Levy, 12:30). For Ni-based catalysts, the advantage of a highly dispersed catalyst formulation, which allowed reduced Ni crystallite size, was an increase in catalytic activity

(Carter, Cusumano, and Sinfelt, 17:2257). The relationship between smaller metal crystallite size and catalytic methanation activity was upheld by Vannice in studies of methanation over catalysts of Ni dispersed on alumina supports (35:159). However, Vannice also found that the type of support could affect the methanation activity of a catalyst: the highly dispersed, alumina-supported catalysts showed the highest activities, whereas the silica-supported catalysts with very small crystallite sizes had lower activities (35:155,7). Other investigators noted an optimum range of Ni crystallite sizes for alumina-supported methanation catalysts (Bhatia, Bakhshi, and Matthews, 8:580). They held, as did Vannice, that methanation activity was enhanced by the lower binding energy of adsorbed CO species. In addition, they noted that very small metal crystallites could chemisorb CO strongly and thus inhibit the methanation reaction. Consequently, they concluded that a range of Ni crystallite sizes of 2-15 nm was optimum for methanation activity of alumina-supported Ni catalysts.

#### Multi-Component Catalysts

A significant development in methanation catalysis during the past decade has been the utilization of supported, multi-component catalysts. Cusumano, Dalla Betta, and Levy proposed that for methanation, multi-component systems could be formulated for increased thermal stability and sulfur resistance of the catalyst as well as for control of product distribution in the synthesis of hydrocarbons from  $H_2/CO$  mixtures (12:48). Most multi-component designs have been bi-component or tri-component formulations: highly active metal components such as Ru, Ni, and Co have been promoted with various metals and metal oxides for improved catalyst performance.

Results of catalytic hydrocarbon synthesis from  $H_2/CO$  mixtures have appeared in the literature for many multi-component catalyst formulations. Many catalyst formulations were conceived as highly active catalytic centers augmented with promoters, which were

chosen on a novel basis. Others were conceived in a systematic manner and were subsequently screened for the most successful formulations. The latter method was the most productive for the development of improved methanation catalysts.

Inui et al. (22) tested catalyst formulations of novel combinations of Ni and Ru components, and Lanthanum Oxide ( $\text{La}_2\text{O}_3$ ) and Cerium Oxide ( $\text{Ce}_2\text{O}_3$ ) promoters. The various catalytic materials were dispersed on silica supports. A simple combination of Ni and Ru yielded activity equal to the sum of the activities of the Ni and Ru separately. The  $\text{La}_2\text{O}_3$  did not exhibit methanation activity as a single component, but when added to a Ni + Ru combination the activity was much greater than the sum of the activities of the separate components. A  $\text{Ce}_2\text{O}_3$  promoter was tried but with less success than  $\text{La}_2\text{O}_3$ . The Ni + Ru +  $\text{La}_2\text{O}_3$  combination, with 4.1, 2.5, and 0.7 weight percents respectively, was most active for turnover of CO to methane at 227 degrees C (22:797,801).

The results of activity screening tests of systematically conceived, bi-component methanation catalysts were reported by Bartholomew (5:66). Catalyst formulations were combinations of Ni with other Group VIII metals, as well as with Molybdenum Oxide ( $\text{MoO}_3$ ), and were supported on alumina. Selected single component catalysts of the Group VIII metals were also screened at 250 degrees C. A Ni- $\text{MoO}_3$  formulation, 2.5% Ni and 3.0%  $\text{MoO}_3$  nominal composition, was most active for methane production.

The addition of a promoter to a single component catalyst has also been reported to increase sulfur resistance of the catalyst. Wentreck et al. (37) reported increased sulfur resistance of a catalyst consisting of 25% Ni on alumina, when promoted with 1% Ir. Increased activity for CO conversion was also reported at 426 degrees K for the promoted catalyst (37:232).

Meyer et al. reported the results of the screening of methanation catalyst formulations developed by an iterative process (23:110). Studies were geared toward development of sulfur-resistant methanation catalysts and produced two patented formulations; a Cerium/

Molybdenum catalyst and a Cerium/Molybdenum/Aluminium catalyst. Over a six year period more than 600 new catalyst formulations were tested with the assumption that both composition and morphology of the catalysts contributed to their activity for methanation. The development of the sulfur-resistant methanation catalysts also led to the development of sulfur-resistant catalysts for the alternative, direct methanation reaction,  $2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2$ , which would reportedly reduce the costs of commercial methanation processes and eliminate the need for sulfur-sensitive, Ni-based, water-gas shift catalysts.

### Catalyst Preparation

Since both the composition and the structure of a methanation catalyst are related to the activity of the catalyst, methods of catalyst preparation could be expected to affect the catalyst's methanation activity. Various methods of manufacture of catalytic materials have been presented in the literature (12,30). The preparation of highly dispersed catalytic material can be easily achieved by impregnation of a porous support with solutions of the desired metal components (Carter, Cusumano, and Sinfelt, 11:2258). The advantage of the high dispersion of supported methanation catalysts, achieved by impregnation of a porous support, has been shown by Vannice (35:160). He concluded that greater dispersion of Ni on alumina corresponded to greater methanation activity of the catalyst. However, the preparation of catalysts by the impregnation method has generally involved calcining the catalyst in air at high temperature (450 degrees C), followed by reduction of the metal oxides in flowing  $\text{H}_2$  at high temperature.

Bartholomew and Farrauto (4:42) proposed the elimination of the calcination step for supported Ni catalysts in favor of direct reduction of the catalytic material. They reported decreased reducibility and increased sintering of catalysts that were pre-calcined as opposed to those that were directly reduced: sintering being the agglomeration of catalytic material on the support surface thereby reducing the surface area and dispersion of

the supported catalyst. Similar results were reported for Ni supported on silica, as a result of magnetostatic measurements on both calcined and non-calcined catalysts (Robertson, Kloet, and Sachtler, 28:234). Bartholomew and Farrauto reported twice the surface area and twice the dispersion of a Ni catalyst which was reduced in  $H_2$  at 500 degrees C for 12 hours, over a catalyst that was first calcined, then reduced (4:43). As a final step in catalyst preparation, Bartholomew and Farrauto recommended a passivation routine during which the reduced catalyst was gradually exposed to air at 25 degrees C in order to avoid bulk Nickel Oxide ( $NiO$ ) formation and to allow storage of the catalyst in air (4:51).

#### Sulfur Poisoning of Methanation Catalysts

Poisoning of methanation catalysts by sulfur has been well identified in the literature as the most important obstacle to the feasible conversion of coal synthesis gas to methane. Because of the significant sulfur content of coal (1-4%), synthesis gas made from it carries sulfur compounds which are poisonous to methanation catalysts (Dalla Betta, Piken, and Shelef, 13:54). Generally, an  $H_2S$  level of one ppm in the feed stream of a methanation process has been reported by several investigators to be highly poisonous to transition metal catalysts (1-2,6,14,16). Removal of sulfur compounds to this low level would represent a significant portion of the cost of synthetic natural gas production. Dalla Betta, Piken, and Shelef proposed the development of methanation catalysts which would be capable of withstanding  $H_2S$  levels up to 10 ppm, a concentration attainable without extensive synthesis gas purification schemes (14:174).

In accordance with the fact that low levels of  $H_2S$  are poisonous to methanation catalysts, Dalla Betta and Shelef found that the adsorption of sulfur onto an alumina-supported Ni catalyst deactivated the catalyst irreversibly: bulk nickel sulfide was formed on the catalyst that was highly stable at 250 degrees C (15:45-6). However, in another study which involved methanation over supporting Ni and Ru catalysts at 400 degrees C, the removal of

a 10 ppm  $H_2S$  component of the feed stream resulted in partial recovery of catalyst activity (14:182). Fitzharris, Katzer, and Manogue reported that, in methanation over an alumina-supported Ni catalyst at 661 degrees K, the removal of a portion of the  $H_2S$  component of the feed stream resulted in near total recovery of catalyst activity (16:376).

#### Mechanism of Sulfidation

Although many factors are involved in the poisoning of a transition metal methanation catalyst, one most important factor is the evidence of the formation of a stable, 2-dimensional metal sulfide on the catalyst surface.

Fitzharris, Katzer, and Manogue (16), in a study of methanation over alumina-supported Ni catalysts at 661 degrees K, reported a heat of formation of a 2-dimensional surface nickel sulfide ( $Ni_2S$ ) of  $-109$  kJ/mole. They also reported a heat of formation of bulk nickel sulfide ( $Ni_3S_2$ ) that was at least  $63$  kJ/mole less exothermic than that of the surface nickel sulfide, indicating the surface sulfide was chiefly responsible for catalyst deactivation.

Studies by Wentrcek et al. (37) indicated a sequence of steps involved in the poisoning of the Ni surface of an alumina-supported catalyst by  $H_2S$ . The steps were listed as: (1) molecular adsorption of  $H_2S$  on the catalyst, (2) dissociative chemisorption of  $H_2S$  on the Ni surface, (3) diffusion on the surface, (4) formation of a 2-dimensional nickel sulfur compound ( $Ni_2S$ ), (5) dissolution of the sulfur into bulk nickel sulfide, and (6) precipitation of the  $Ni_3S_2$  phase. The investigators found that sulfur poisoning occurred at 600 degrees K and  $H_2S/H_2$  ratios much lower than simple equilibrium phase boundary conditions for  $Ni_3S_2$  ( $H_2S/H_2 = 85$  ppm). Thus, a major conclusion was that the Ni catalyst was poisoned by means of the 2-dimensional surface sulfide that blocked the catalytic sites. It was further concluded that the poisoned sites were those that facilitated the dissociation of CO, a major step in the mechanism of methanation. The poison species also

tended to favor the formation of carbon-carbon bonds to the extent that a non-reactive, graphitic carbon species was formed on the surface, thus fouling the catalyst.

In addition to the mention of the 2-dimensional site blockage of Ni, Fitzharris, Katzer, and Manogue (16) also indicated a constant activation energy for methanation of 100 kJ/mole for both poisoned and unpoisoned catalysts. The resultant conclusion was that site blockage was a geometric effect and that the poison species had no electronic effects on neighboring active sites. They were in agreement with Wentreck et al. (37) in that they reported that the sites affected by poisoning were those which facilitated the dissociation of adsorbed CO and thus methanation was halted at the reactive surface carbon formation step.

In similar steps, Agrawal, Katzer, and Manogue (2) reported a constant activation energy for methanation between poisoned and unpoisoned Ru on alumina. A 2-dimensional site blockage was also reported as the poisoning mechanism at 663 degrees K. In yet another study from the same laboratory, Agrawal, Katzer, and Manogue (1) noted that the behavior of Co on alumina, in regard to the activation energy of methanation between poisoned and unpoisoned catalysts, was quite different from the behavior of the alumina-supported, Ni and Ru catalysts of the later studies. This observation gives support to Trimm's proposal that Ni and/or Ru should be the main component(s) of the successful methanation catalyst: both metals have the ability to easily dissociate CO to form an active surface carbon species which, in turn, can be easily hydrogenated to form methane (32:278).

## EXPERIMENTAL EQUIPMENT AND PROCEDURE

### Experimental Equipment

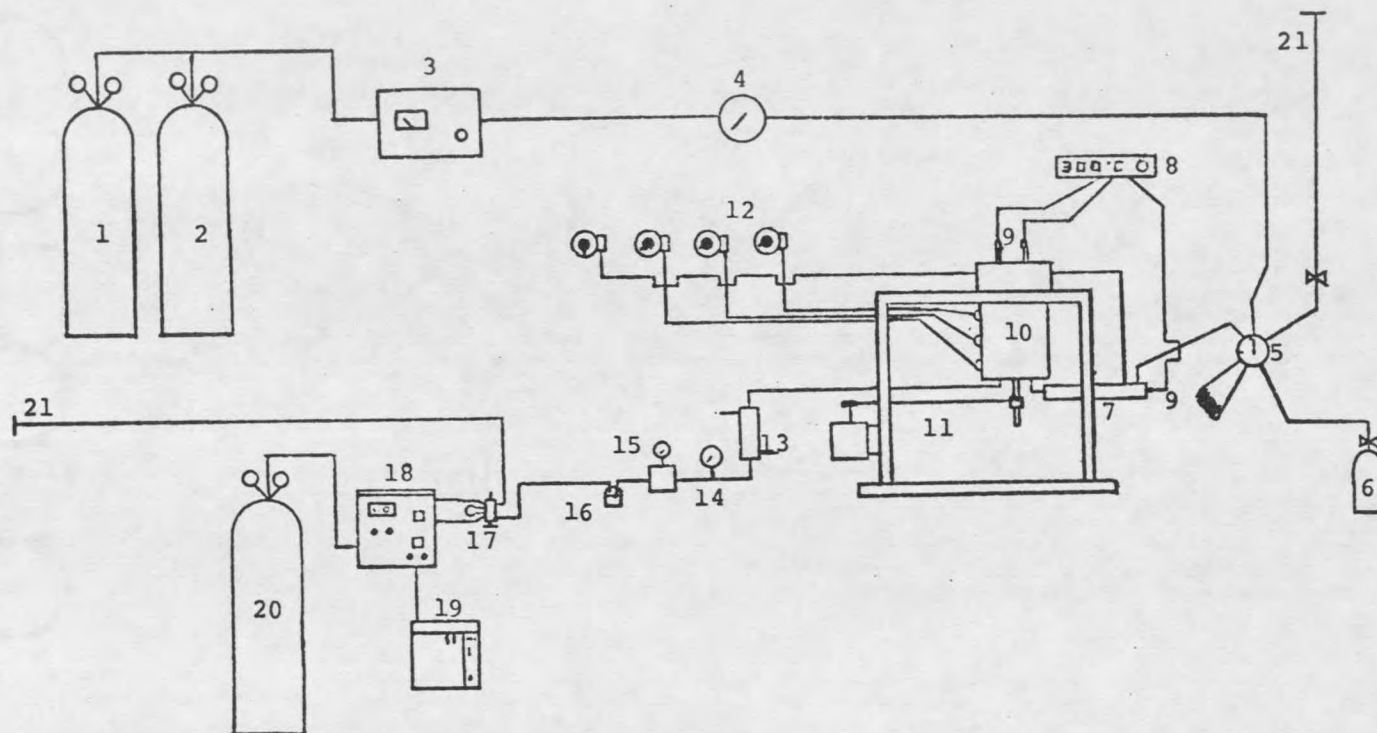
A schematic diagram of the experimental apparatus, with brief descriptions of the separate components, appears in Figure 1. Detailed descriptions of the constituent sub-systems follow.

#### Reactant Feed Stream

The reactant mixture, with  $H_2/CO$  molar feed ratio of 2.35/1, was stored in a high pressure gas cylinder from Matheson Company. Outlet pressure was controlled by a Victor regulator. A Nupro micrometering valve was used to control the reactant gas flow rate. The flow rate was measured via a Brooks, model 5810-1H2K5B mass-flowmeter coupled with a Brooks, model 5820-1H1A flow rate indicator; both from Brooks Instrument Division, Emerson Electric Company. Flow rate was indicated as 0-2000 standard cubic centimeters of hydrogen per minute (SCCM  $H_2$ ).

#### Pressure Control and Monitoring Equipment

Pressure in the experimental apparatus was controlled by a Grove, model S-91XW back pressure regulator fitted with a teflon diaphragm and Matheson pressure gauge. Pressure was monitored in both the feed line to the reactor as well as the outlet line. The inlet gauge was from U.S. Gauge and the outlet gauge was by Acragage. Both gauges indicated pressures of 0-3447 kPa in 69 kPa increments. All accessory lines between the reactant gas inlet and the back pressure regulator were stainless steel rated at 13790 kPa pressure.



- (1) H<sub>2</sub>/CO feed gas mixture (2) H<sub>2</sub> (3) mass-flowmeter/needle valve assembly  
 (4) pressure gauge (5) pulse poisoning valve (6) H<sub>2</sub>S (7) inlet preheater  
 (8) digital pyrometer (9) thermocouples (10) Berty-type reactor (11) impeller  
 drive assembly (12) Powerstats (13) effluent gas cooler (14) pressure gauge  
 (15) back pressure regulator (16) water trap (17) chromatograph injection  
 valve (18) gas chromatograph (19) chart recorder (20) Helium carrier gas  
 (21) outlets to ventilation hood

Figure 1. Schematic diagram of experimental apparatus.

### Temperature Control and Monitoring Equipment

Temperature was controlled by means of four Powerstat variable dc transformers, 140 volt maximum output, from Superior Electric Company. Three of the Powerstats serviced the reactor furnace while one was used for the inlet preheater. Reactor temperature was easily maintained within two degrees C of the 300 degrees C operating temperature by proper settings on the reactor and preheater Powerstats. Temperature was monitored via three Chromel-Alumel pencil thermocouples. One thermocouple was fitted in the preheater and two were inserted into the reactor through its removable cover. Of the reactor thermocouples, one was inserted into a thermowell in the catalyst basket and the other extended into the draft-tube void space above the catalyst bed. Temperature was indicated by a Cole-Parmer, model 8530-05 digital pyrometer in degrees C.

### Pulse Poisoning Apparatus

The main component of the pulse poisoning apparatus was a Rheodyne Incorporated, model 7010 sample injection valve. The valve was a rotary-type, six-port unit that allowed free flow of either the reactant feed stream or the poison load stream in either LOAD or INJECT positions (24). The sample loop was 5.1 cc. The H<sub>2</sub> poison gas was 99.5% purity from Matheson Company and was stored in a pressurized cylinder.

### Reactor System

The reactor system consisted of an Autoclave Engineers' catalytic reactor which had Berty-type internals and was fitted with an inlet preheater and had an outlet heat exchanger to cool the effluent gas stream.

The major component of the experimental apparatus was the reactor itself. The reactor was a continuous-flow, 7.6 cm i.d. model with bolted closure and Berty-type internal components (25). The impeller was driven by an Autoclave Engineers' MagneDrive II assembly which incorporated an ImPak V\*S Drive dc drive motor and control unit, both

from Reliance Electric Company (21). The reactor was equipped with a jacket-type furnace and two pencil thermocouples.

The Berty-type reactor was an improved model of a catalytic recycle reactor designed by Berty (7). The reactor was designed with integral draft-tube recycle, and had a total mixed volume of 320 cc. The catalyst basket had a maximum capacity of 100 cc, yet the reactor was designed for operation with catalyst volumes as low as a single pellet (Berty, 7:84). While the design of the Berty reactor utilized a fixed catalyst bed, recycle ratios of at least 20/1 could be achieved, even at high flow rates, by adjusting the speed of the impeller located just beneath the catalyst basket. The impeller's agitation provided mixing action that assured uniform composition throughout the mixed volume of the reactor.

The inlet preheater fitted to the reactor consisted of a 1.25 cm stainless steel pipe which was 30.5 cm long and was wrapped with nichrome heating tape. A Chromel-alumel pencil thermocouple was inserted longitudinally into the center of the preheater and extended 29 cm into the preheater from the inlet end. The outlet of the preheater was connected to the inlet of the reactor.

The outlet of the reactor was connected to a 54 cm length of 0.64 cm stainless steel tubing which led to the effluent gas cooler. The gas cooler was constructed of a single length of 0.64 cm stainless steel tubing, 23 cm long, with a shell that had inlet and outlet ports for tap water coolant. The outlet of the gas cooler led to the back pressure regulator, after which the effluent gas stream was bubbled through de-ionized water at room temperature to prevent water condensation in the lines leading to the chromatograph.

#### Effluent Gas Analysis Equipment

Effluent gas compositions were determined by means of a Varian Aerograph, model 1420-10 gas chromatograph with a Porapak Q column. The chromatograph detector was a thermal conductivity bridge and the output was indicated on a Varian, model 9176 recorder

with integrator. Effluent samples were injected into the chromatograph with a sampling valve fitted with a 0.65 cc sample loop. The carrier gas was Helium.

The majority of the experimental runs were analyzed with the following chromatograph settings: 80 degrees C column and detector temperatures, 150 ma detector current, and 45 cc/min Helium carrier gas flow rate. Three of the runs were analyzed with the following settings: 24 degrees C column and detector temperatures, 200 ma detector current, and 80 cc/min Helium flow rate. The latter conditions were those used initially in the investigation. However, the conditions were changed in order to eliminate fluctuations due to variations in room temperature and to minimize water vapor condensation. In both cases conditions were such that samples could be analyzed at one-minute intervals.

### Experimental Procedure

#### Preliminary Operations

Preliminary operations of the experimental procedure included preparation of the 2.35/1 molar ratio, H<sub>2</sub>/CO feed gas mixture; calibration of the Brooks mass-flowmeter for the prepared gas mixture; and calibration of the gas chromatograph.

The feed gas mixture was prepared in the Chemical Engineering Laboratory at Montana State University (MSU). A high pressure cylinder of laboratory grade CO from Matheson Company was brought to 3447 kPa pressure. Laboratory grade H<sub>2</sub>, from National Cylinder Gas Division of Chemetron Corporation, was pumped into the cylinder until a final pressure of 11550 kPa was reached. The 2.35/1 molar ratio of H<sub>2</sub>/CO was confirmed with a known volume analysis of the feed gas by the chromatograph.

Calibration of the Brooks mass-flowmeter was performed at various settings over the entire range of the 0-2000 SCCM flow rate indicator. The corresponding volumetric flow rates of the feed gas mixture, at 25 degrees C and 85.1 kPa, were measured with a wet test

meter from Precision Scientific Company. Several readings were taken at each setting. The relationship of actual gas flow rate to SCCM  $H_2$  was linear.

Calibrations of the gas chromatograph with the Porapak Q column were performed with samples of laboratory grade carbon monoxide and methane. Single component samples of the gases were injected into the chromatograph with a 1.0 cc gas syringe from Precision Sampling Corporation. Both gases were sampled from 0.1 cc to 1.0 cc in 0.1 cc increments. Peak areas were determined by the integrator on the Varian recorder. The relationships between sample volume and the product of the peak area and chromatograph attenuation were determined for both gases, at both sets of conditions, and were linear in all cases.

#### Experimental Program

The details of the experimental runs were as follows. Information on the four catalysts studied appears in Table 2 (see Appendix).

- a) All runs were performed with the 2.35/1 molar ratio,  $H_2/CO$  feed gas mixture.
- b) An initial screening was done with the Harshaw Ni-0104 catalyst to find a relationship between reaction temperature and catalytic activity. Pulse poisoning was not performed.
- c) Each of the following poisoning experiments were done at 300 degrees C, and had a 10.2 cc  $H_2S$  poison pulse (pulse volume at 25 degrees C and 85.1 kPa).
- d) Four poisoning experiments were done with the Harshaw Ni-0104 catalyst at pressures of 85.1, 690, 1380, and 2070 kPa. Each experiment had 560 cc/min feed gas flow rate (measured at 25 degrees C and 85.1 kPa) and 0.5 g catalyst charged (total weight of catalyst plus support).

- e) Four poisoning tests were done with the Harshaw Ni-3266 catalyst at pressures of 85.1, 690, 1380, and 2070 kPa. Each experiment had 1120 cc/min feed gas flow rate and 1.0 g catalyst charged.
- f) Four experiments were done for comparison of specific activities as well as sulfur poisoning responses, of various catalysts. The experiments were done at 560 cc/min feed gas flow rate and 85.1 kPa pressure. Specific catalyst charges for each experiment were: 0.5 g Ni-0104, 1.5 g Ni-3266, 2.0 g Ni/Al<sub>2</sub>O<sub>3</sub>, and 2.0 g Ni-La/Al<sub>2</sub>O<sub>3</sub>.

### Experimental Procedure

The procedure for a typical experimental run was as follows.

- a) The reactor was loaded with specified catalyst charge at room temperature and was then sealed.
- b) The Powerstats for the preheater and reactor heating jacket were turned on. The preheater powerstat was set at 18 V and the reactor Powerstats were set at 100 V.
- c) Laboratory grade H<sub>2</sub> from Chemetron Corporation was bled through the system at low flow rate (< 50 cc/min).
- d) After approximately two hours the reactor had reached 300 degrees C. The reactor Powerstats were set to 50 V, H<sub>2</sub> flow rate was set to 300 cc/min, and the impeller was run at maximum speed of about 2500 rpm. This was the final catalyst reduction procedure. The reactor generally reached a maximum temperature of 350 degrees C during this procedure.
- e) After the two hour reduction procedure, the impeller was shut off and H<sub>2</sub> was again bled through the system until the reactor returned to 300 degrees C.

- f) When the reactor reached operation temperature, the  $H_2$  flow was stopped and the feed gas mixture was introduced. The system was brought to specified operating pressure and feed gas flow rate. The impeller was started and run at 2500 rpm.
- g) The reactor was operated at specified conditions until the methanation rate was fairly constant. Then the  $H_2S$  poison was admitted.
- h) Effluent samples were analyzed by chromatograph at one minute intervals for 10-20 minutes after the  $H_2S$  poison pulse was admitted. Subsequent samples were taken periodically until the run was terminated.
- i) Effluent composition data were analyzed for initial reaction rates before poisoning, as well as for catalyst deactivation in response to the  $H_2S$  pulse.

#### Catalyst Preparation

Two catalysts were prepared in this laboratory in order to test their methanation activity as well as deactivation response to  $H_2S$  pulse poisoning. Both catalysts were prepared by impregnation of an alumina support from Davison Chemical Company. The support was in the form of high surface area alumina spheres, .32 cm diameter, with a pore volume of  $0.90 \text{ cm}^3/\text{g}$  (Insley, 20:20). The catalyst metal loadings were 18% Ni, and 17% Ni + 4% La for the respective catalysts. Both were prepared using direct reduction of the impregnated support, a method proposed by Bartholomew and Farrauto (4), in order to reduce sintering and increase surface area and dispersion.

The Ni/ $Al_2O_3$  catalyst was prepared by impregnation with an aqueous solution of reagent grade, hydrated nickel nitrate from Apache Chemicals Incorporated. The Ni-La/ $Al_2O_3$  catalyst was impregnated in two stages. First the support was impregnated with an acidic La solution, which was prepared from industrial grade  $La_2O_3$  (American Potash and Chemical Company) dissolved in nitric acid (Baker Chemical Company). The impregnated support was then dried in air at 110 degrees C, and was subsequently impregnated

with an aqueous nickel nitrate solution. Both catalysts were dried in air, reduced, and passivated for storage in air.

A description of the catalyst preparation procedure is as follows.

- a) An aqueous solution of the desired catalyst component was prepared, the volume of the solution slightly in excess of the total pore volume of the support to be impregnated (1 cc solution/g support).
- b) A measured amount of the alumina support was impregnated with the aqueous solution for one hour.
- c) The catalyst was dried in air at room temperature until it was visibly dry, then dried in air at 110 degrees C for eight hours.
- d) Steps a-c were repeated for the second component of the bi-component catalyst.
- e) The catalyst was reduced overnight in flowing H<sub>2</sub> at 350 degrees C.
- f) The catalyst was passivated at 25 degrees C by gradual exposure to air over a two hour period.

## RESEARCH OBJECTIVE

The intent of the investigation was the development of the *in situ*, pulse poisoning method for the study of methanation catalyst poisoning by  $H_2S$ . The practical application of this objective involved two modes of experimentation; the development of catalytic methanation activity in an experimental system which utilized the Berty mixed reactor, and the poisoning of the methanation catalysts with a pulse of  $H_2S$  to determine what deactivation characteristics could be observed.

The Berty reactor was used because of its versatile temperature and pressure capabilities as well as its continuous flow design. It was desired to operate the reactor at flow rates and pressures that were analogous to commercial reactor conditions while the operation temperature was to be specified by the demands of the methanation reaction. The most important feature of the Berty reactor was its ability to approach perfectly mixed, CFSTR behavior.

With the operation of the Berty reactor system reasonably optimized for methanation, catalyst poisoning experiments were proposed. The objective of the poisoning experiment was to measure the deactivation of methanation catalysts in response to pulse poisoning by  $H_2S$ . It was proposed to test conventional, commercial methanation catalysts at a specified operating temperature and at several operating pressures. Also, it was proposed to compare both commercial catalysts and catalysts which were prepared in the laboratory for deactivation characteristics when poisoned with a pulse of  $H_2S$ .

## RESULTS AND DISCUSSION

### Reactor Behavior

As previously mentioned, the reactor employed was a continuous flow, Berty-type, catalytic mix reactor from Autoclave Engineers Incorporated. The concept of the Berty reactor was based on the principle of the old recycle or loop reactor. The design of the reactor specified a recycle ratio of at least 20/1 in order to duplicate CFSTR behavior (Berty, 7:78). The reactor used in this investigation was a refined model of Berty's original design and was capable of operation at up to 24820 kPa at 525 degrees C (25).

A test was performed on the reactor, using a pulse of inert tracer, in order to determine the extent of mixing. The reactor was operated at 300 degrees C, 85.1 kPa, maximum impeller speed, and a feed rate of 560 cc/min. A blank of alumina catalyst support was charged in place of the catalyst. A pulse of methane was introduced and the reactor effluent was analyzed for methane concentration as a function of response time. The result of the test appears in Figure 2. The residence time distribution function was determined by the method of Smith (31:274) and the average residence time was 27 s at the test conditions. This value of average residence time was used to generate the theoretical response of a perfectly mixed reactor to a pulse input. The model response also appears in Figure 2, with a 5 s lag to account for flow through the accessory lines. The actual response indicated some dispersion in the flow, which most likely occurred in the inlet preheater because of its relatively large diameter compared to the diameters of the exit lines.

In addition to approximation of perfect mixing behavior, Berty (7) recommended operation at high flow rates comparable to commercial processes as in his test reaction, the hydrogenation of ethylene. The high flow rates minimized temperature and concentration

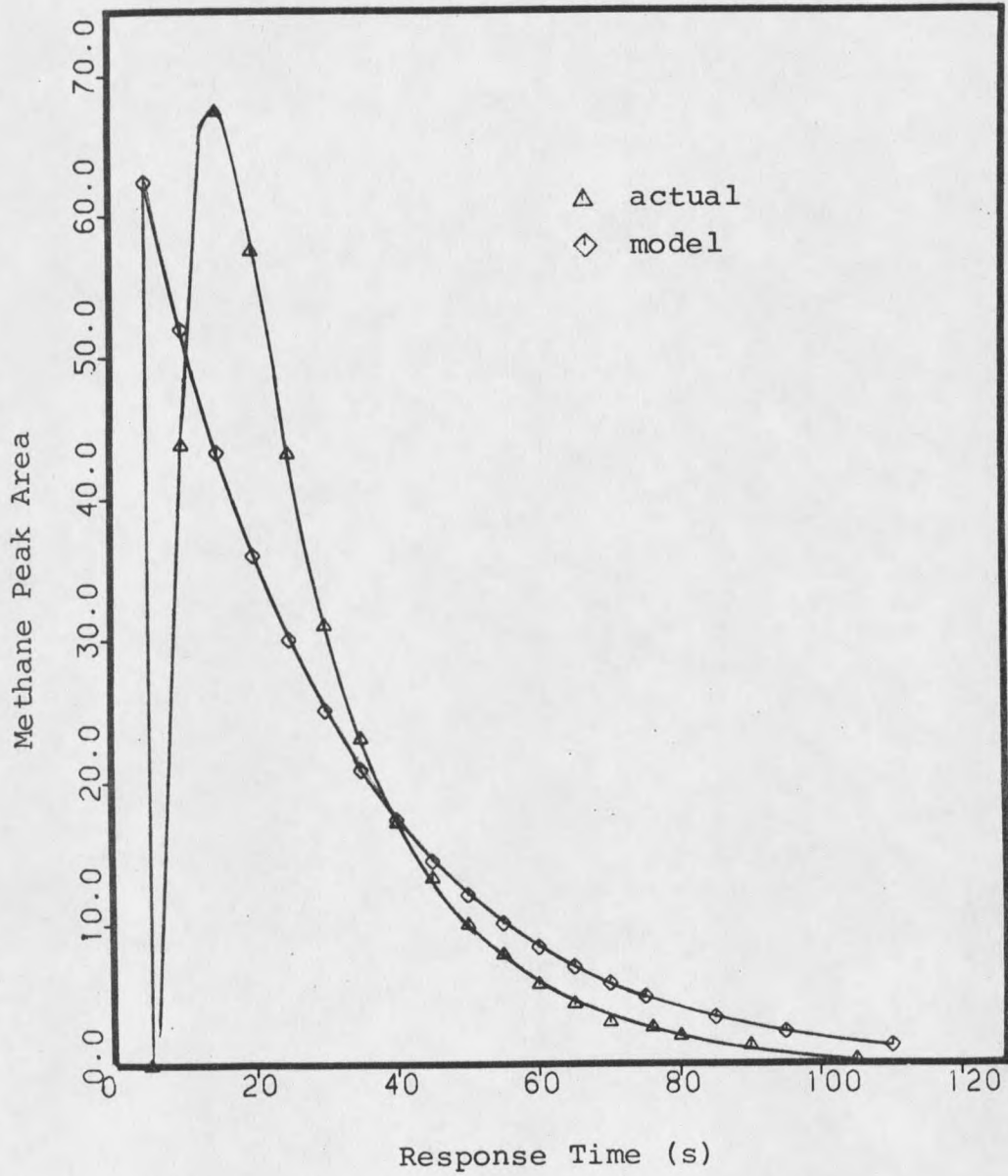


Figure 2. Response to pulse input of methane tracer.

gradients in the boundary film of flow past the catalyst (7:81). The advantages of the Berty design for this study were: the ability to operate at high flow rates analogous to commercial reactor conditions, the versatile temperature and pressure capabilities of the reactor, and the approximation of perfectly mixed reactor behavior.

#### Determination of Reaction Temperature

The Harshaw Ni-0104 catalyst was the first tested in the experimental apparatus. To determine a proper temperature for methanation, a continuous run was carried out under varied temperature conditions. The reactor was charged with 3.0 g of Ni-0104 catalyst and operated at 560 cc/min feed gas flow rate and 85.1 kPa pressure. Temperature was increased from 200 degrees C to 400 degrees C at an average rate of two degrees C per minute. The effluent was sampled at one minute intervals and analyzed by the chromatograph. The results, in terms of conversion, appear in Figure 3. From the results it was determined that subsequent runs would be done at a temperature of 300 degrees C.

#### Pressure Runs

Two commercial methanation catalysts were tested for their response to pulse poisoning by  $H_2S$ . Both catalysts were from Harshaw, Ni-0104 and Ni-3266. They were each tested in separate runs at four pressures: 85.1, 690, 1380, and 2070 kPa. The data from the runs were compared in terms of initial activity before poisoning, as well as the time-dependent response of methanation activity to the  $H_2S$  pulse. The pulse responses were represented on both 2-dimensional and 3-dimensional plots.

The 3-dimensional plots of catalyst poisoning responses were generated by computer programs that were available through the Honeywell CP-6 computer at Montana State University. The programs, SYMAP and SYMVU, were developed by the Harvard Center for Environmental Design Studies (19). The SYMAP program generated a grid matrix from

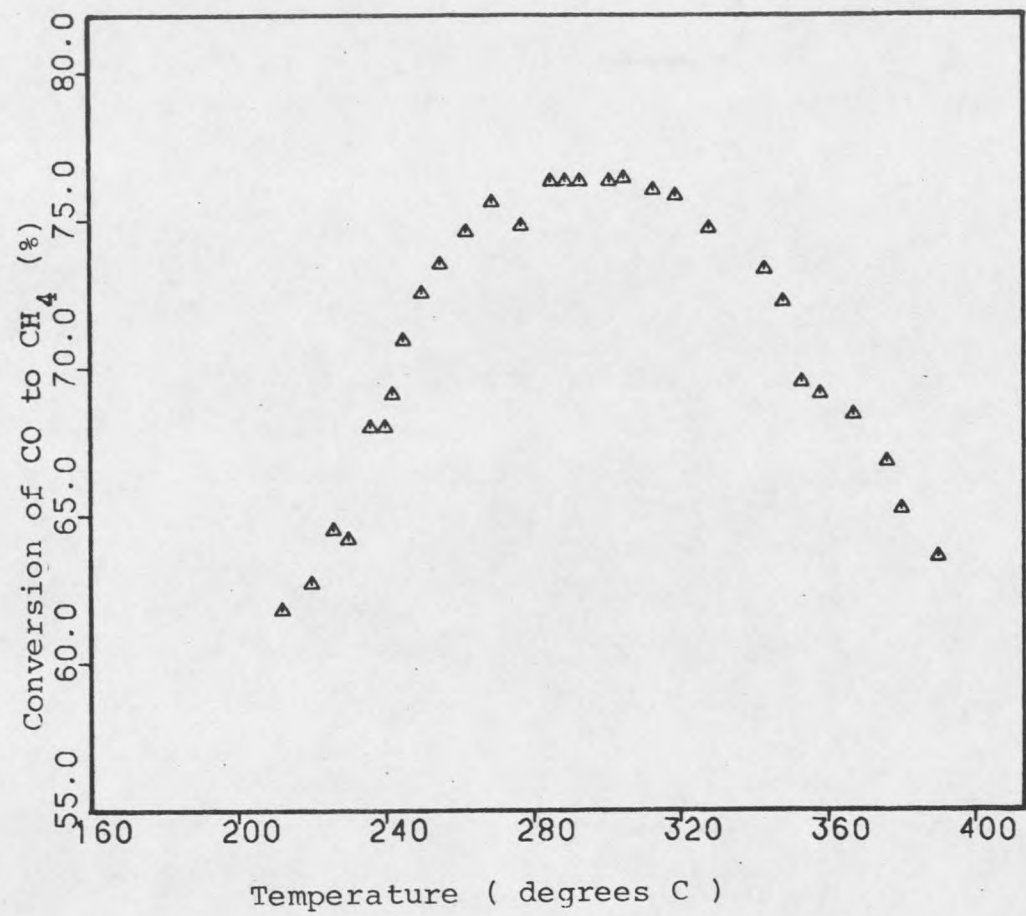


Figure 3. Temperature screening run for Ni-0104 catalyst at 85.1 kPa.

input data values by interpolation between each of the points. The SYMVU program then utilized the grid matrix generated by SYMAP to produce a 3-dimensional display, in the form of a continuous surface, on a CALCOMP plotter. This study used the above programs to generate 3-dimensional surfaces of pulse poisoning response data. The borders of the grid matrix produced by the SYMAP program appeared as the base of the 3-dimensional surfaces, and for the Harshaw Ni-0104 and Ni-3266 catalysts, had the coordinates of pressure and response time. In all cases the raised portions of the plots represented methanation activity. The advantage of the 3-dimensional display was that trends in the data due to either pressure or response time were easily identified.

The activities of the Harshaw Ni-0104 catalyst, before poisoning, for the various pressure runs appear in Figure 4. The methanation rate at 85.1 kPa was  $6.14 \times 10^{-5}$  (moles  $\text{CH}_4$  / g catalysts-s). The rate increased by 45% at 690 kPa and at 1380 kPa the activity was 79% greater than at 85.1 kPa. However, at 2070 kPa methanation rate was 6% greater than the rate at 85.1 kPa.

The responses of the Ni-0104 catalyst to pulse poisoning, in terms of methanation rates for the four different pressures, appear in Figures 5 and 6. It should be noted that Figure 6 represents poisoning responses at four different pressures, and therefore does not represent a continuous surface with respect to pressure. In all cases the response to the pulse of  $\text{H}_2\text{S}$  showed a sharp decline in activity immediately after the pulse, followed by a gradual decline, after 11 minutes response time, which was fairly linear. The 85.1 kPa run showed the sharpest decline in activity immediately after the pulse whereas the 690, 1380, and 2070 kPa runs showed progressively less immediate declines in activity immediately after the pulse.

At 30.5 minutes after the pulse the 1380 kPa run maintained the highest activity, the 85.1 and 690 kPa runs had nearly equal activities, and the 2070 kPa run indicated the lowest activity.

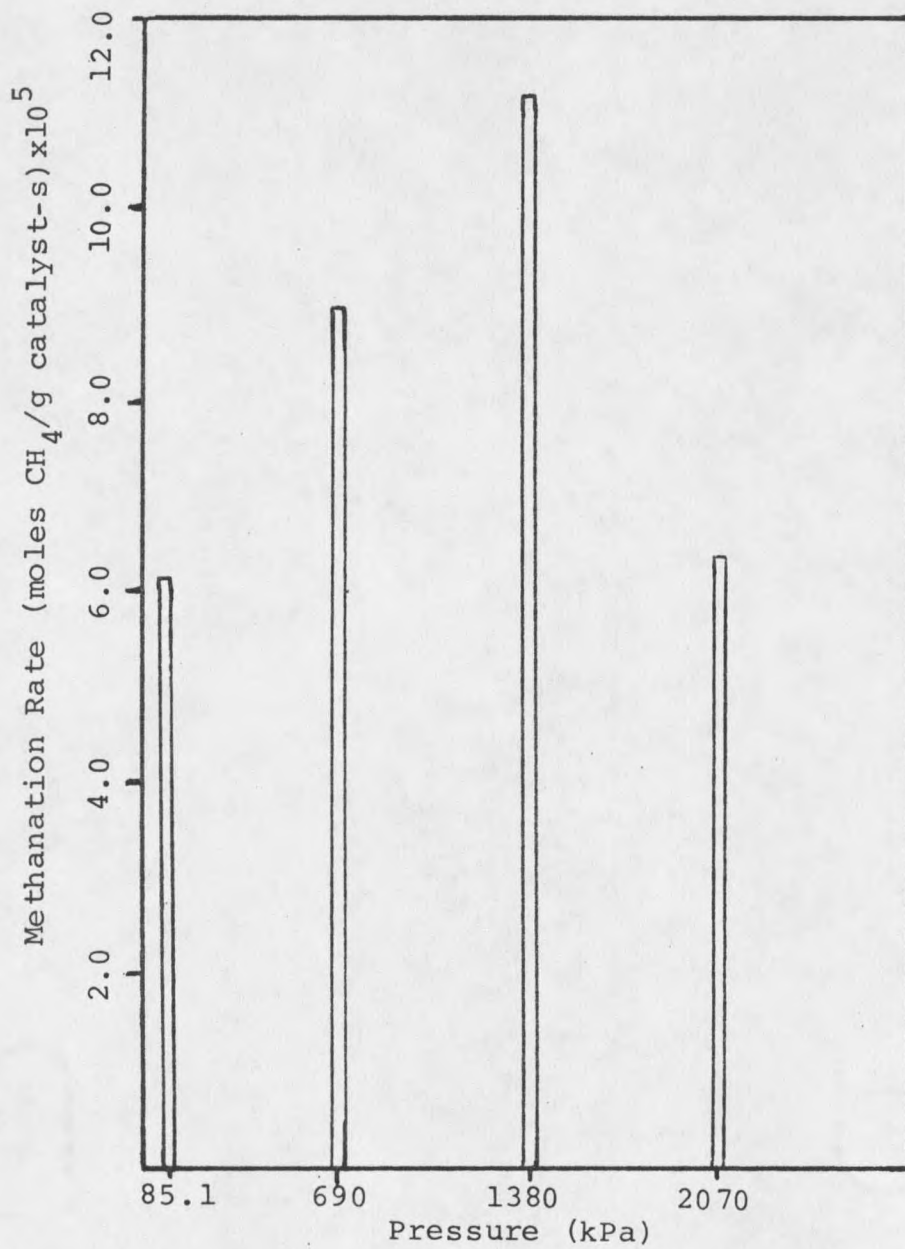


Figure 4. Initial activity of Ni-0104 catalyst at various pressures.

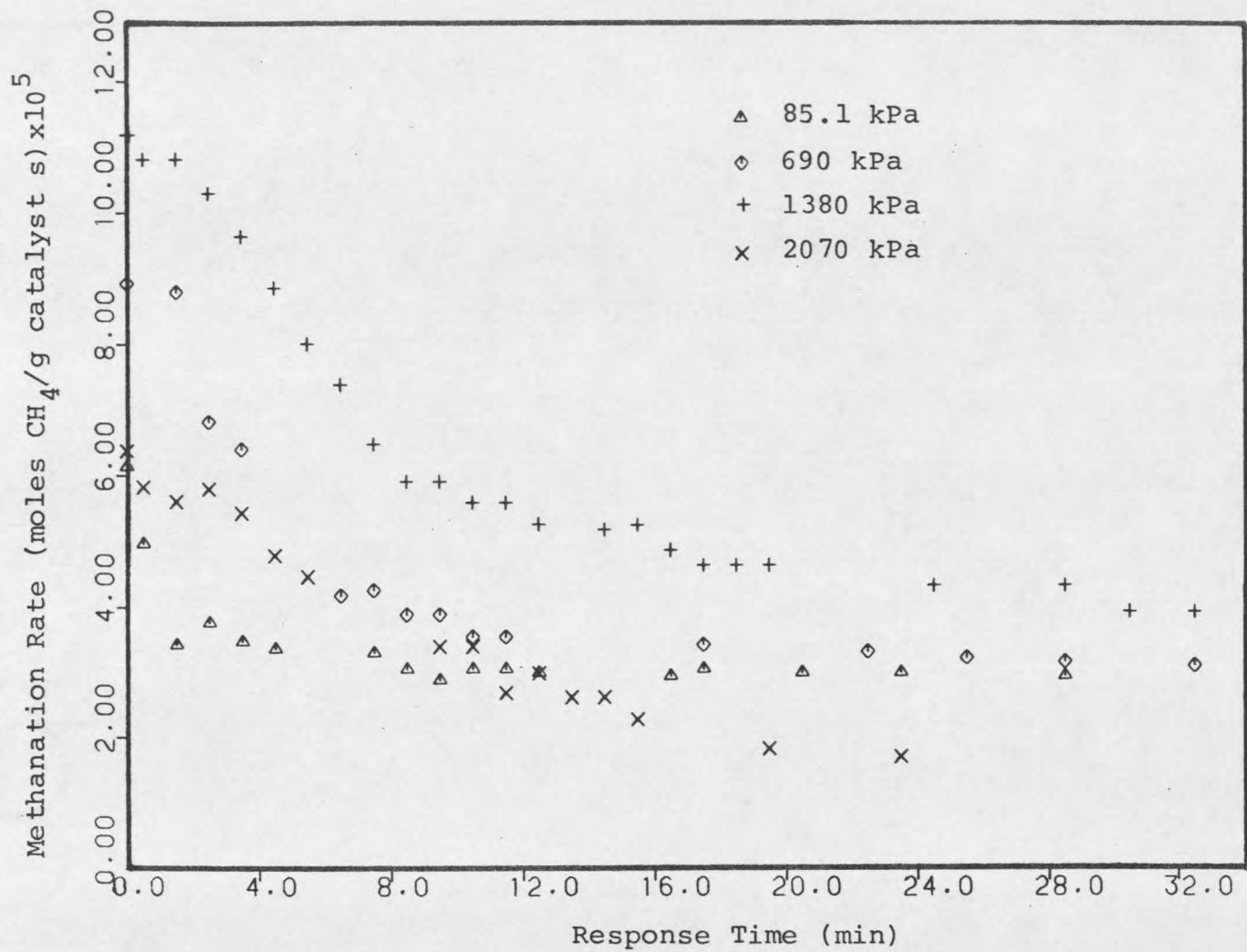


Figure 5. Poisoning response of Ni-0104 catalyst at various pressures.

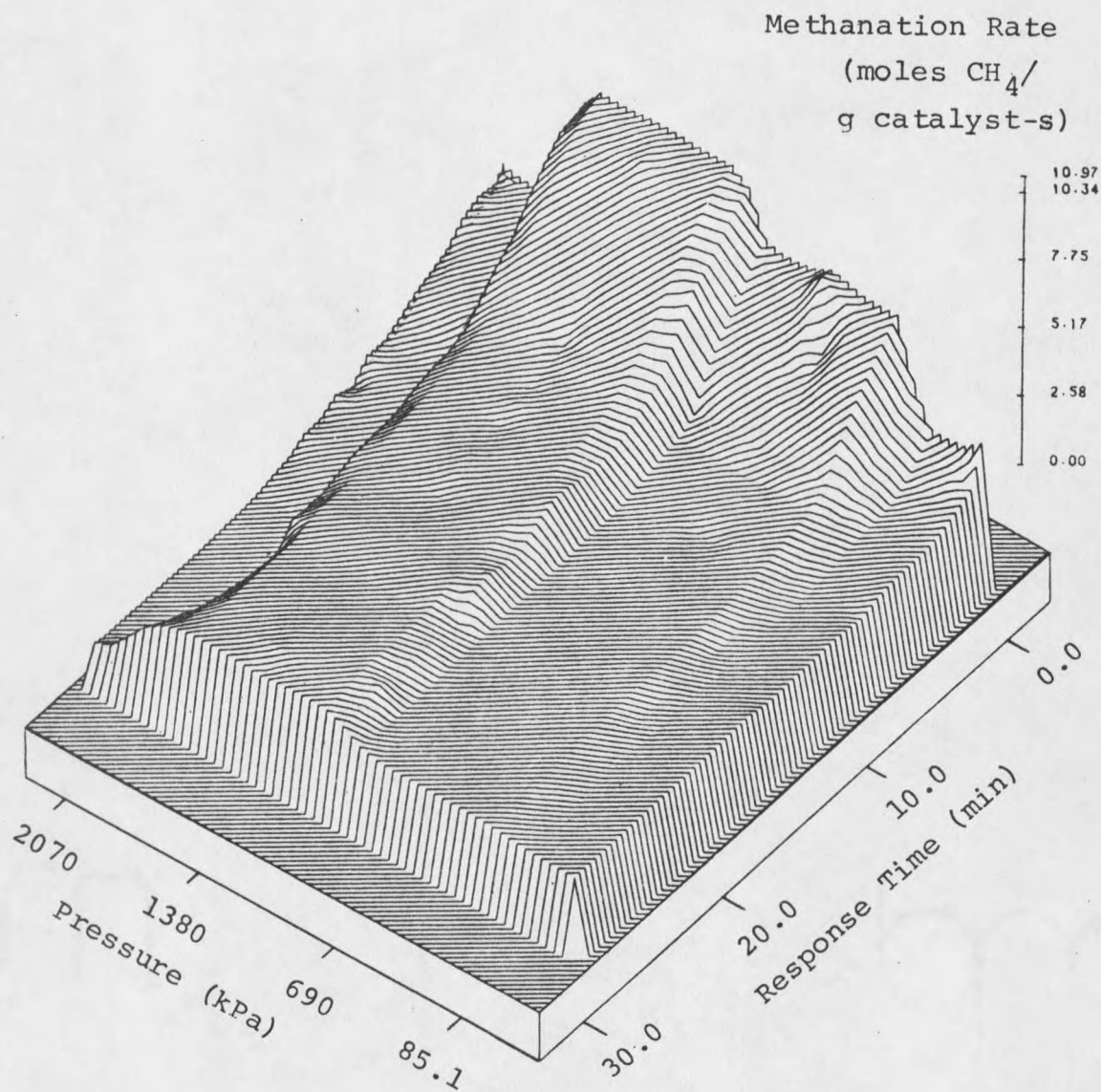


Figure 6. Poisoning response of Ni-0104 catalyst at various pressures.

The Harshaw Ni-3266 catalyst was tested in a manner similar to the Ni-0104 catalyst. Again, four runs were made at 85.1, 690, 1380, and 2070 kPa operating pressures, but the feed rate was doubled to 1120 cc/min. The data were analyzed for initial rates of methanation before poisoning and the responses of the four runs to H<sub>2</sub> pulse poisoning were plotted and displayed on a 3-dimensional surface as with the Ni-0104 catalyst.

The initial rates of methanation for the Ni-3266 catalyst at the four pressures appear in Figure 7. The reaction rate at 85.1 kPa was 8.4 E-5 (moles CH<sub>4</sub> /g catalyst-s). The rate at 690 kPa was a 51% increase over the 85.1 kPa run and the rate at 2070 kPa was a 28% increase.

The responses of the Ni-3266 catalyst to the pulse poisoning are shown in Figures 8 and 9. All of the runs showed sharp declines in catalyst activity immediately after the pulse of H<sub>2</sub>S followed by gradual, linear declines after 11 minutes response time. As with the Ni-0104 runs, the sharpest activity decline immediately after the pulse was at 85.1 kPa and the most gradual decline was at 2070 kPa. The 690 and 1380 kPa runs showed similar rates of decline during the first 11 min after poisoning.

For both the Ni-0104 and Ni-3266 catalysts, the responses to pulse inputs of H<sub>2</sub>S showed sharp deactivations immediately after the pulse followed by gradual declines in activity that were linear in nature. The primary portion of the pulse response of these catalysts gave qualitative information about poisoning while the secondary portion was analyzed by least-squares linear regression for quantitative results.

Linear regressions were applied to the response data of both catalysts at the four operating pressures, after response times of 11 minutes, and including all points up to run termination. The results appear in Figures 10 and 11.

The linear nature of the extended deactivations of the catalysts indicated a deactivation mechanism which was not directly related to pulse poisoning. Extended deactivation was likely due to carbon deposition or sulfur-enhanced carbon deposition, although data

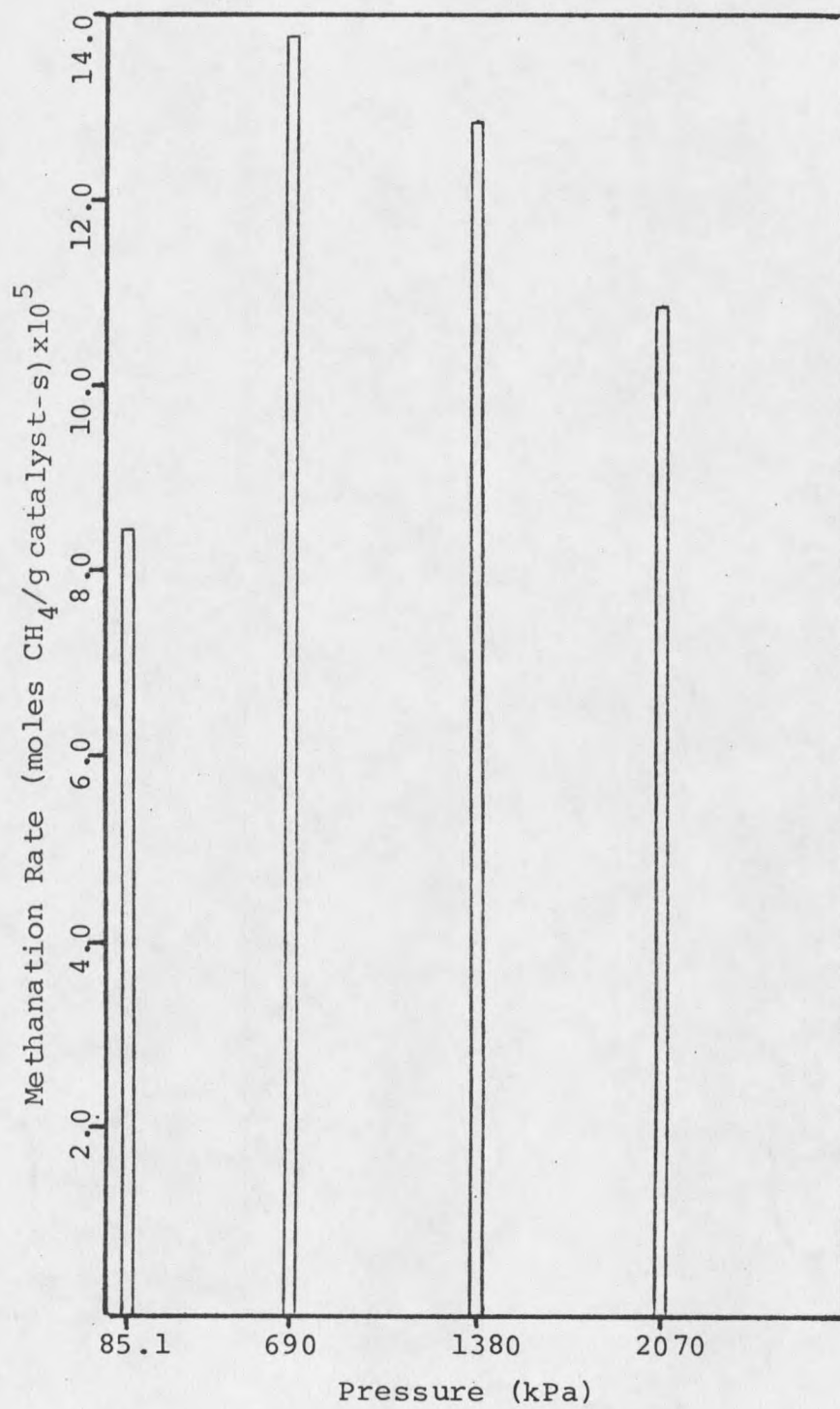


Figure 7. Initial activity of Ni-3266 catalyst at various pressures.

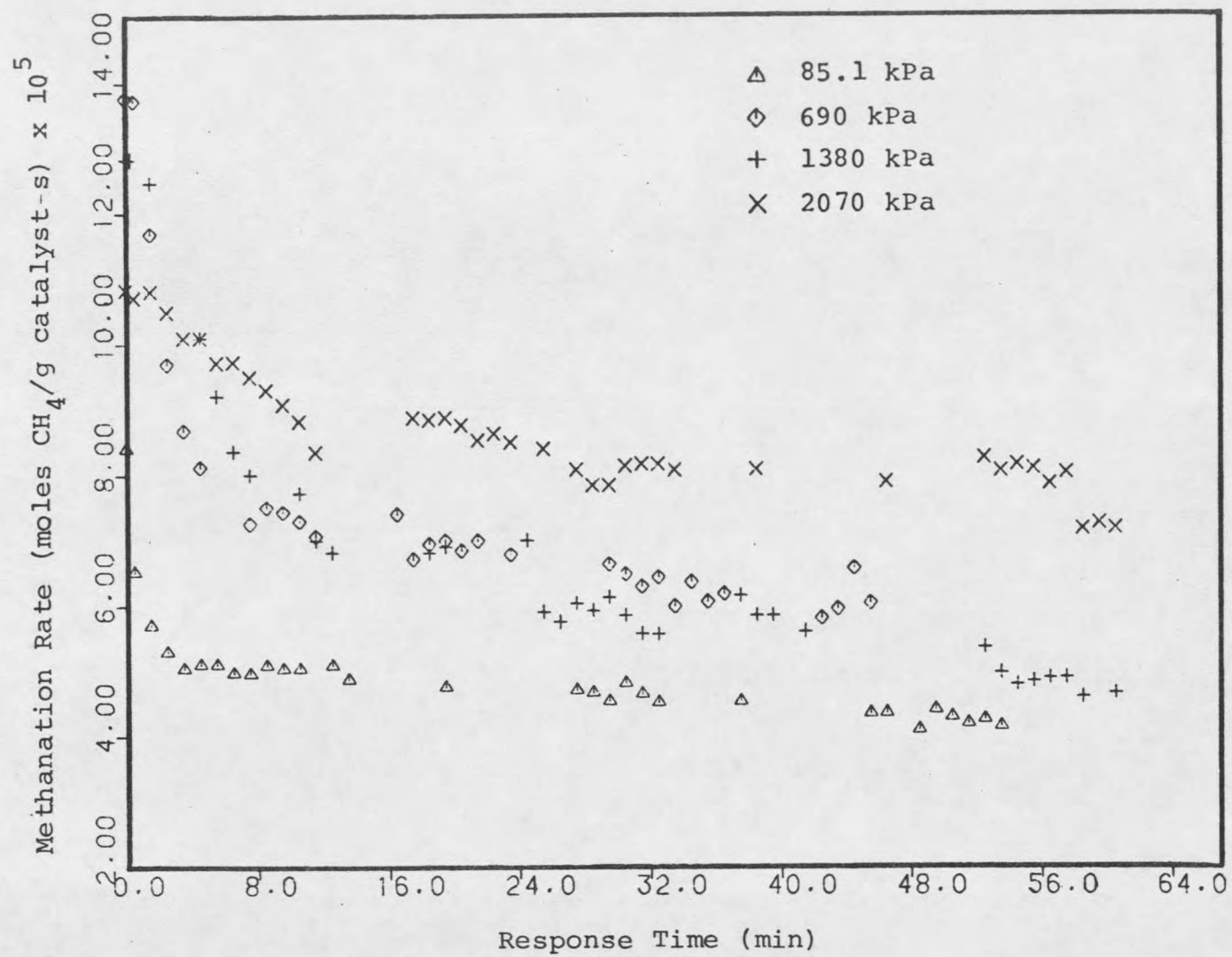


Figure 8. Poisoning response of Ni-3266 catalyst at various pressures.

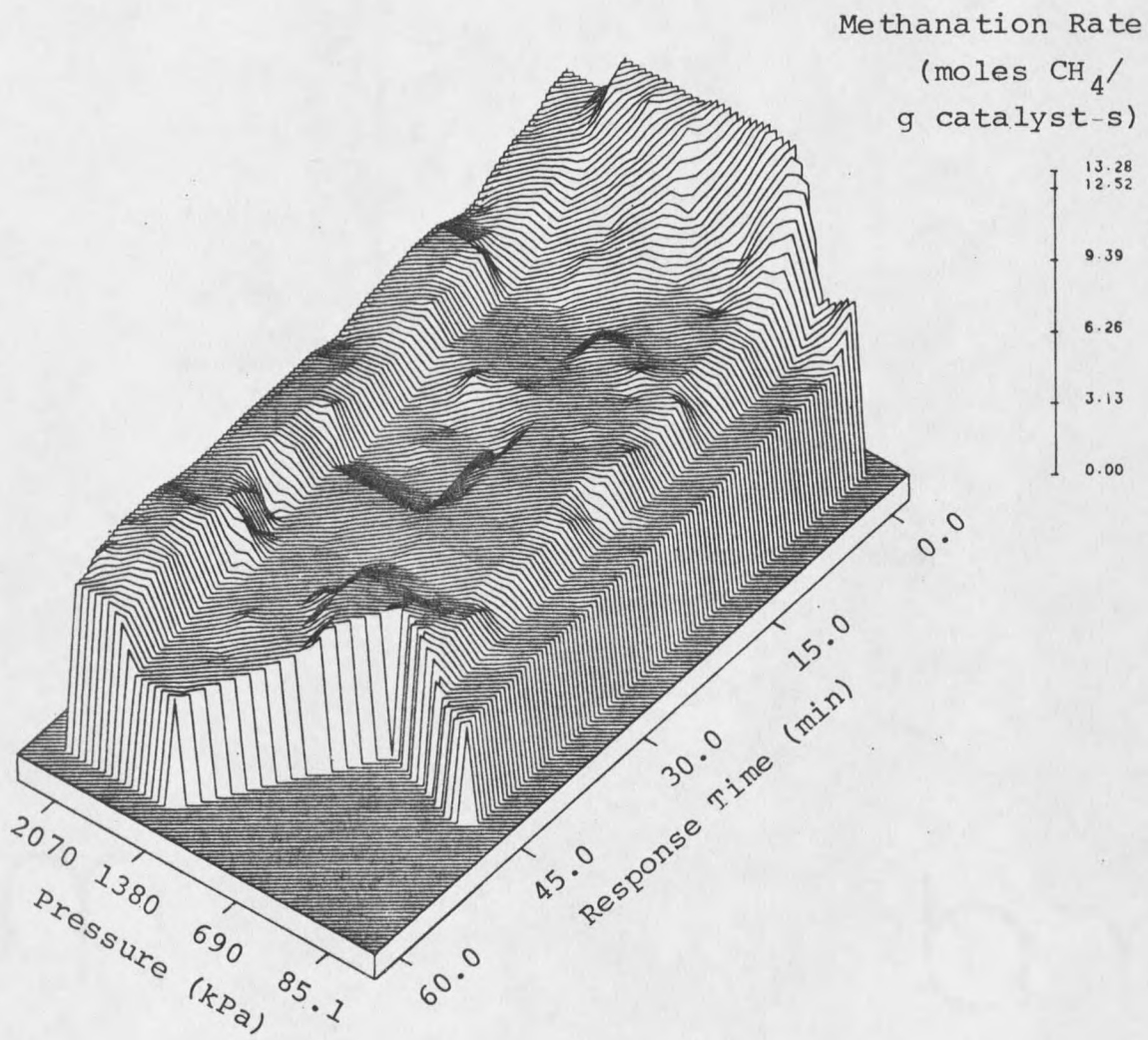


Figure 9. Poisoning response of Ni-3266 catalyst at various pressures.

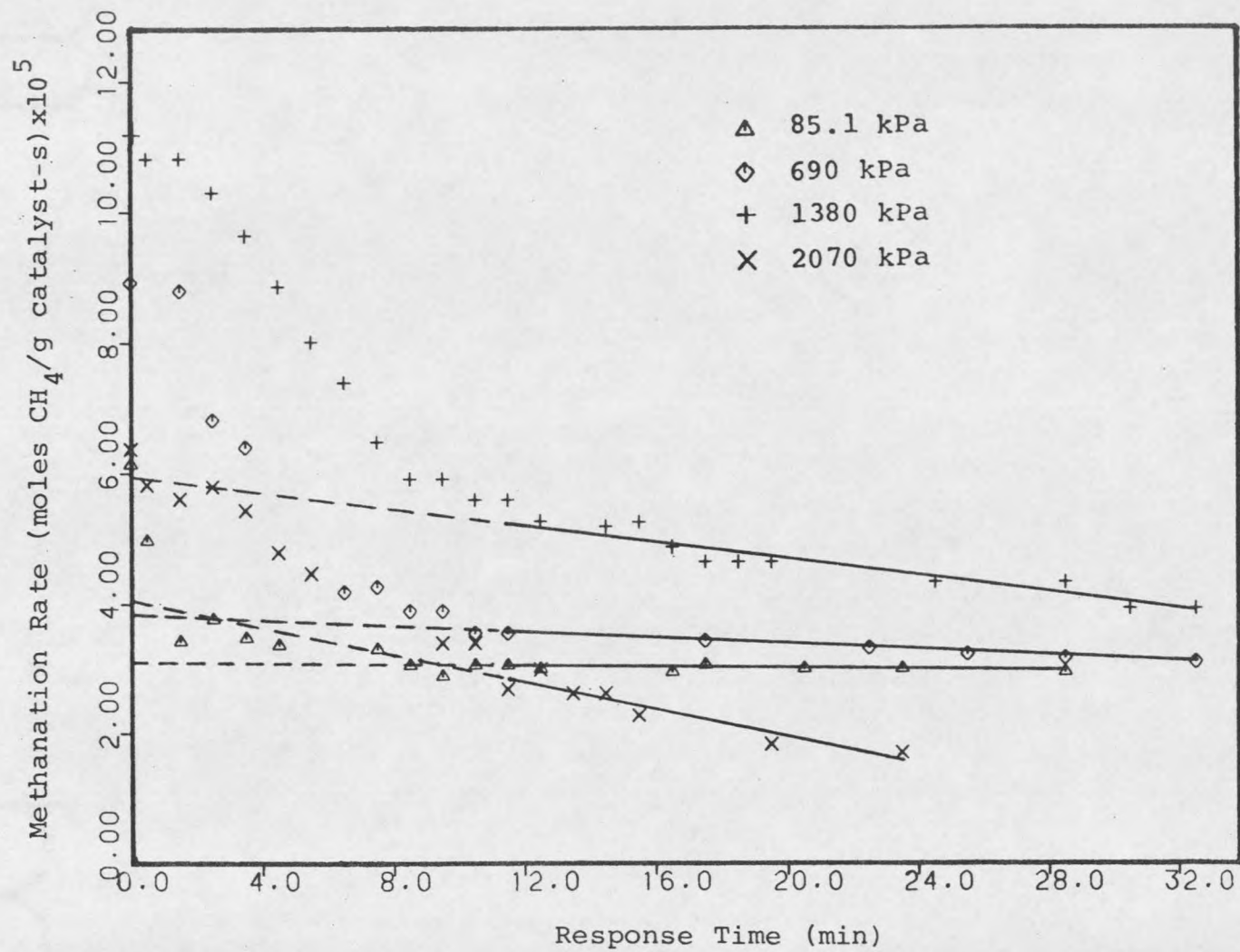


Figure 10. Results of linear regression analysis of Ni-0104 poisoning response.

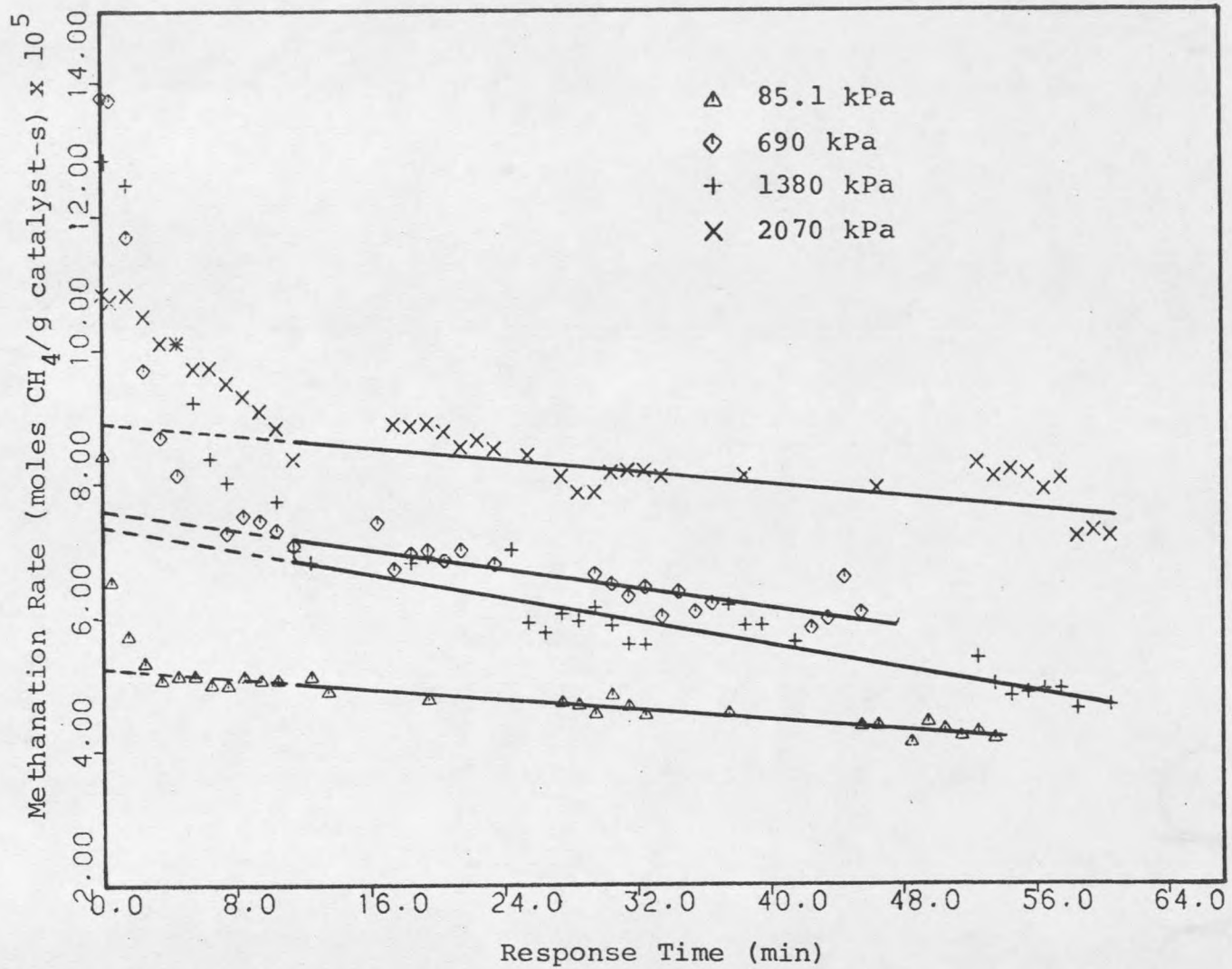


Figure 11. Results of linear regression analysis of Ni-3266 poisoning response.

which confirmed this were not available. In order to isolate catalyst deactivation due to pulse poisoning, the linear regressions of extended deactivation of the catalysts were extrapolated back to zero minutes response time. Those values were then expressed as percent of initial activity for each of the various runs. They indicated catalyst deactivation due to pulse poisoning in the absence of extended, linear deactivation of the catalysts.

The amount of extended deactivation of the catalysts was also noted. This was indicated, for each run, by the magnitude of the negative slope of the linear regression.

The percents of initial activity were calculated for each of the runs and the results appear in Figure 12. At each pressure, values of percent of initial activity for the Ni-3266 catalyst were higher than those for the Ni-0104 catalyst. Also, both catalysts showed the same trend in percent of initial activity across the range of pressures, and had a minimum percents of initial activity at 690 kPa.

Higher values of percent of initial activity for the Ni-3266 runs over the Ni-0104 runs were likely due to a couple of factors. First, 67% more Ni was charged for each of the Ni-3266 runs as was charged for the Ni-0104 runs while the amount of H<sub>2</sub>S poison was equal for each run (10.2 cc at 85.1 kPa and 25 degrees C). Also, due to the higher flow rate of feed gas for the Ni-3266 runs, the H<sub>2</sub>S/H<sub>2</sub> ratios for those runs were likely lower than those for the Ni-0104 runs: lower H<sub>2</sub>S/H<sub>2</sub> ratios would suppress the dissociation of H<sub>2</sub>S and thus inhibit catalyst poisoning.

In regard to the trends in percent of initial activity of the catalysts over the range of pressures, increases in percent of initial activity as pressure increased could be explained by the fact that pulse characteristics changed as pressure increased. Evidence of these changed pulse characteristics can be seen in Figures 10 and 11, where immediate responses of activity to pulse poisoning, from zero to 11 min response time, became more gradual as pressure increased. This was likely due to longer residence times of the poison pulses at higher pressures. With respect to pulses of equal amounts of H<sub>2</sub>S, the pulses with longer residence

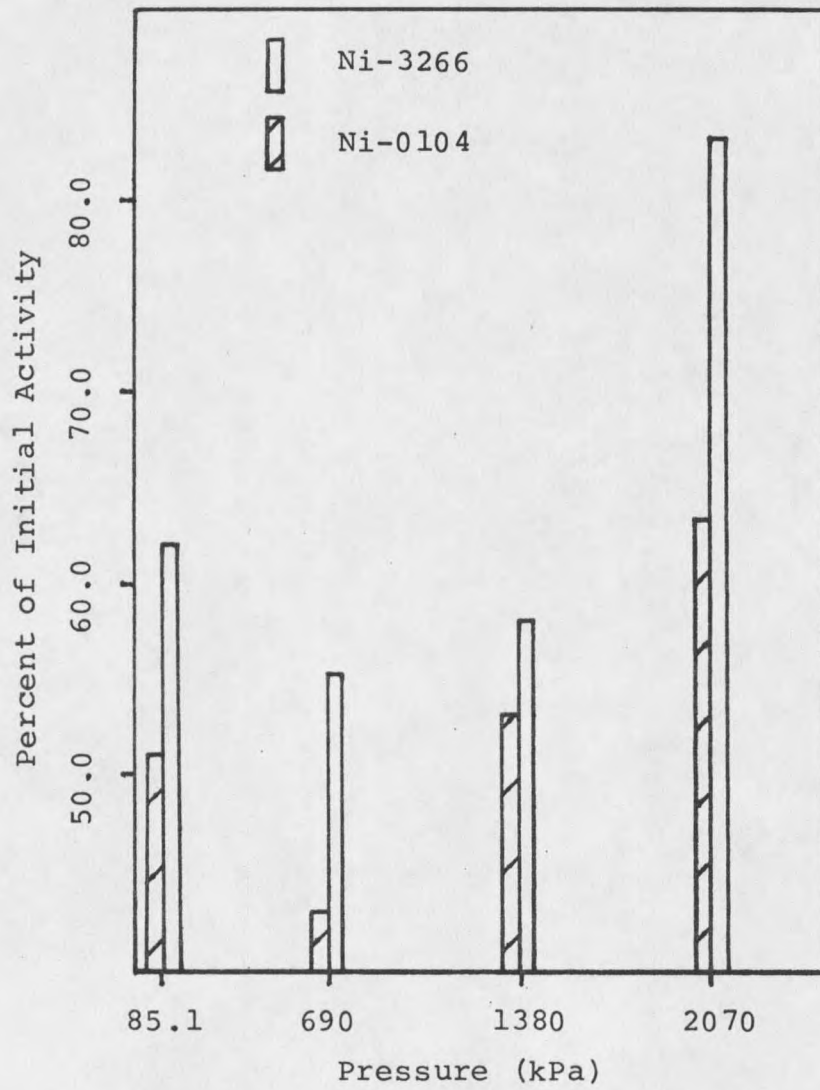


Figure 12. Percent of initial activity of Ni-0104 and Ni-3266 catalysts at various pressures.

times would have lower  $H_2S/H_2$  ratios at any given time, and thus sulfur poisoning would be inhibited. The above explanation, however, cannot account for percents of initial activity at 85.1 kPa, which were higher than those at 690 kPa.

With regard to extended catalyst deactivation, the negative slopes of the linear regressions were also noted and appear in Figure 13. The negative slopes increased in magnitude as pressure increased for all runs except that of Ni-3266 at 2070 kPa. This indicated a pressure dependence of the long term deactivation of the catalysts if the Ni-3266 run at 2070 kPa were not considered. That particular run showed both a low rate of extended deactivation and a high percent of initial activity, which indicated less sulfur poisoning than expected. The lesser amount of sulfur poisoning was probably due to the high flow rate of feed gas, longer residence time of the pulse, and possible high resistance to mass diffusion at the high reaction pressure.

On the basis of the above results, it was concluded that comparison of the deactivation of various catalysts would be done at identical conditions of pressure, temperature, and flow rate in order to reproduce  $H_2S$  pulse characteristics for each run. Thus, specific characteristics of catalyst deactivation could be more easily identified.

#### Comparison of Specific Activity of Methanation Catalysts

The characterization of methanation activity of unpoisoned methanation catalysts was advanced by Vannice (33) and Bartholomew (5) who measured the specific activity of supported methanation catalysts on the basis of active catalytic surface area. Modern techniques of selective gas chemisorption allowed the determination of the surface area of the active catalytic material. Methanation rates were then expressed as turnover numbers (N, molecules  $CH_4$ /catalytic site-second). Other investigators expressed turnover numbers in modified fashion (molecules  $CH_4$ /surface atom-second) (Dalla Betta, Piken, and Shelef, 14; Fitzharris, Katzer, and Manogue, 16). The catalysts of this study were compared on a

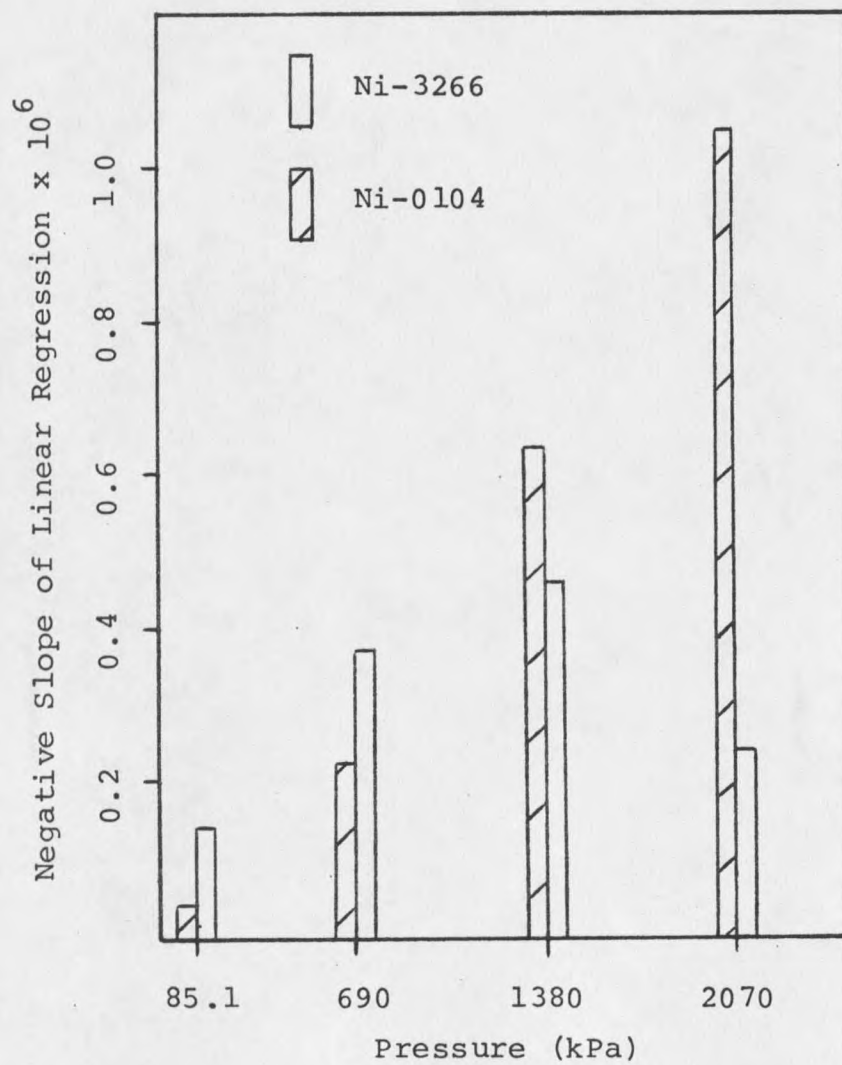


Figure 13. Extended deactivation of Ni-0104 and Ni-3266 catalysts at various pressures.

similar basis. However, since chemisorption experiments were not performed on the catalysts of this study, turnover numbers were based on the amount of catalytic material present (molecules  $\text{CH}_4$  /metal atoms loaded-second). This method could not account for bulk formation of loaded metals or for incomplete reduction of loaded metal atoms. However, it did provide an order-of-magnitude comparison of the specific activities of the catalysts of this study with those of other studies. Turnover numbers for some of the catalysts of other studies, as well as for those of this study appear in Table 1.

The four catalysts of this study were compared according to initial methanation activity and  $\text{H}_2\text{S}$  pulse poisoning response. The comparison of the initial turnover numbers and conversions for the four runs appears in Figure 14. The  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst showed the highest turnover number at a conversion of 0.665. The Ni-3266 showed the lowest turnover number of the four catalysts but, at a conversion of 0.697, may have been inhibited by limited quantities of available reactants. The  $\text{Ni-La}/\text{Al}_2\text{O}_3$  catalyst showed a lower turnover number than the  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst even though the La was expected to promote methanation. This was likely due to its preparation with acidic impregnation solution. The generally higher initial turnover numbers for the alumina-supported catalysts were probably a result of higher dispersion of the catalytic material due to lower metal compositions.

The responses of the four catalysts to the  $\text{H}_2\text{S}$  poison pulse appear in Figures 15 and 16. All responses, except for the  $\text{Ni-La}/\text{Al}_2\text{O}_3$  run, showed a rapid decline in methanation rate immediately after the pulse, which was followed by a gradual decline in activity at later times. The  $\text{Ni-La}/\text{Al}_2\text{O}_3$  run showed no sharp decline immediately after poisoning, but had a continuous decline in turnover number.

The extended deactivations of each of the catalysts, with the exception of the  $\text{Ni-La}/\text{Al}_2\text{O}_3$ , were analyzed by least-squares linear regression and the results appear in Figure 17. The regressions were extrapolated back to zero minutes response time and the

Table 1. Comparison of Specific Activity of Various Catalysts.

Catalyst	Nominal Composition (wt. %)	Turnover no. $\times 10^3$	H <sub>2</sub> /CO Feed	Temp.	Press. (kPa)	Reactor	Ref.
Ni/Al <sub>2</sub> O <sub>3</sub>	.22% Ni	55.0	24/1	300°C	111.5	CFSTR	(16)
Ni/Al <sub>2</sub> O <sub>3</sub>	2% Ni	51.9	3.8/1	400°C	76.0	single pass flow	(14)
Ni/Al <sub>2</sub> O <sub>3</sub>	14% Ni	14.21 2.2*	4.0/1	250°C	137.9	packed bed	(5)
Ni/Al <sub>2</sub> O <sub>3</sub>	18% Ni	10.4	2.35/1	300°C	85.1	CFSTR	this study
Ni-La/Al <sub>2</sub> O <sub>3</sub>	17% Ni 4% La	8.8	2.35/1	300°C	85.1	CFSTR	this study
Ni-0104	60% Ni on Kieselguhr	6.0	2.35/1	300°C	85.1	CFSTR	this study
Ni-3266	50% Ni proprietary support	5.2	2.35/1	300°C	85.1	CFSTR	this study

\*Turnover no. calculated based on amount of Ni loaded.

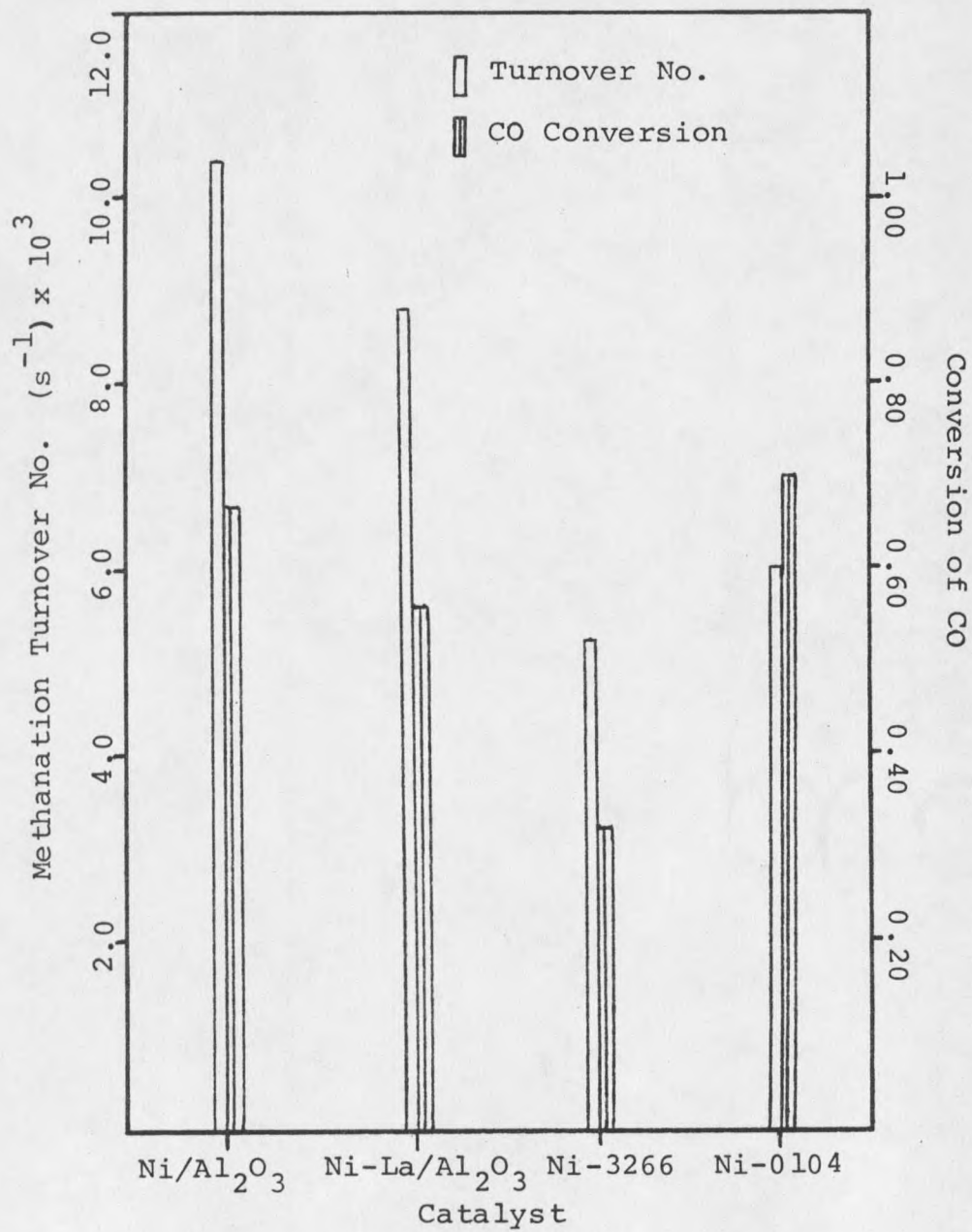


Figure 14. Initial turnover and conversion of CO for various catalysts.

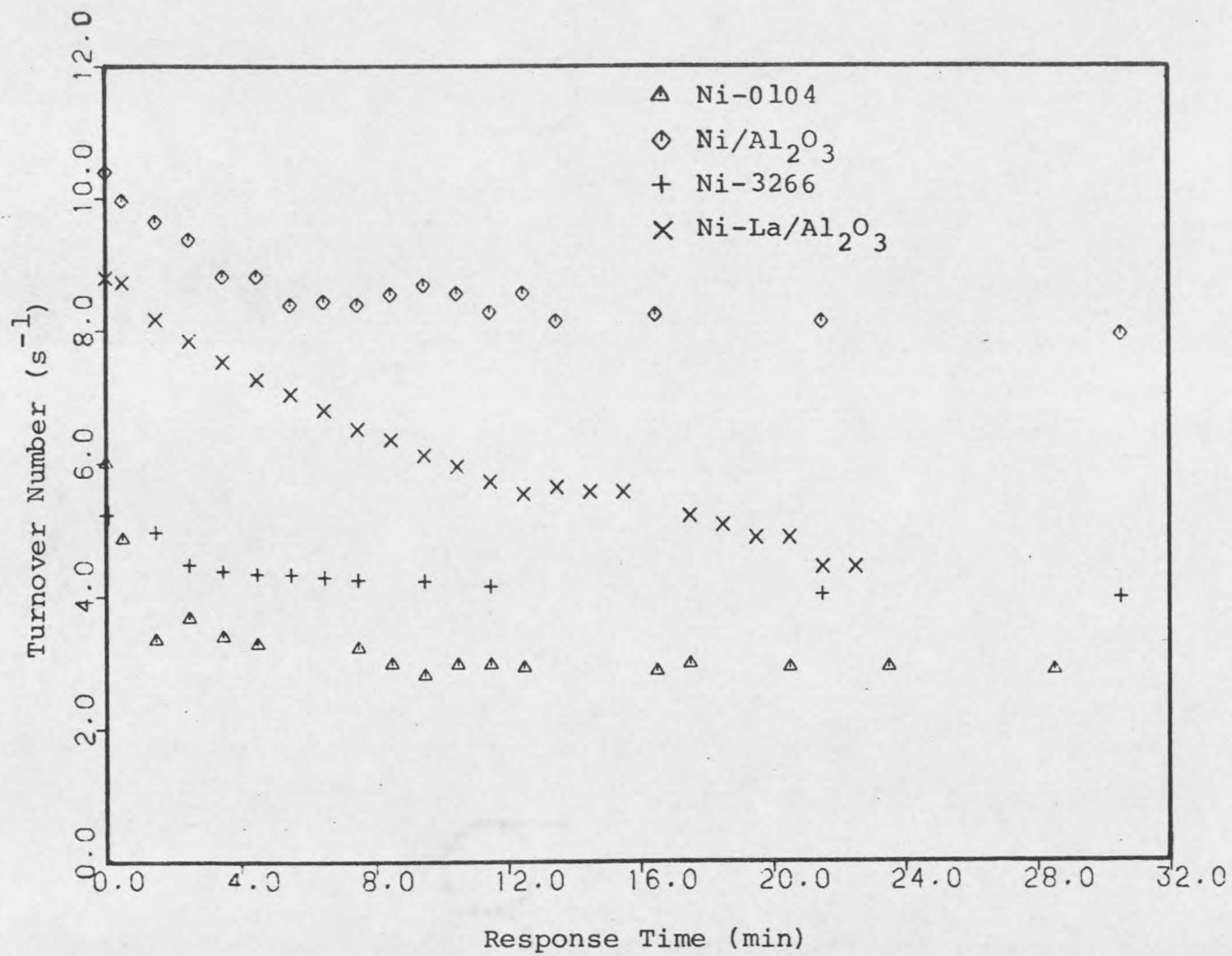


Figure 15. Comparison of poisoning response at 85.1 kPa.

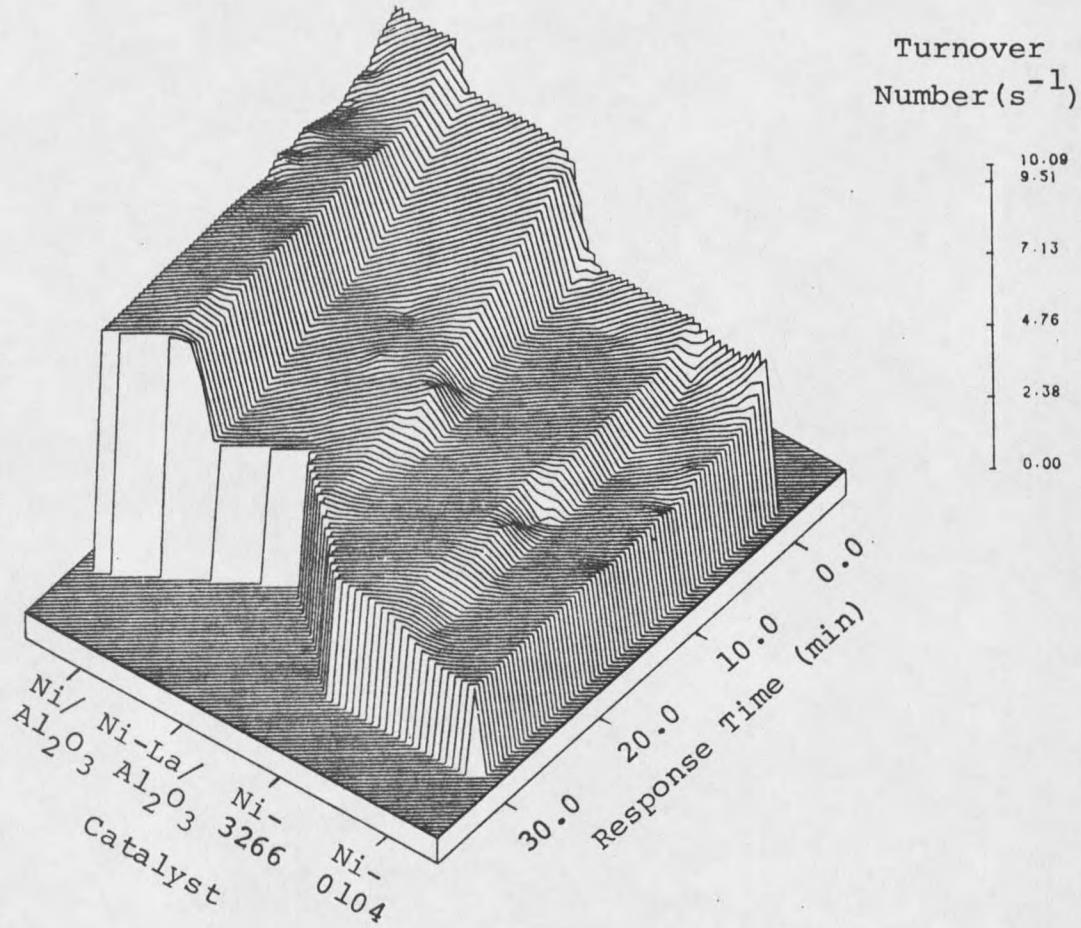


Figure 16. Comparison of poisoning response at 85.1 kPa.

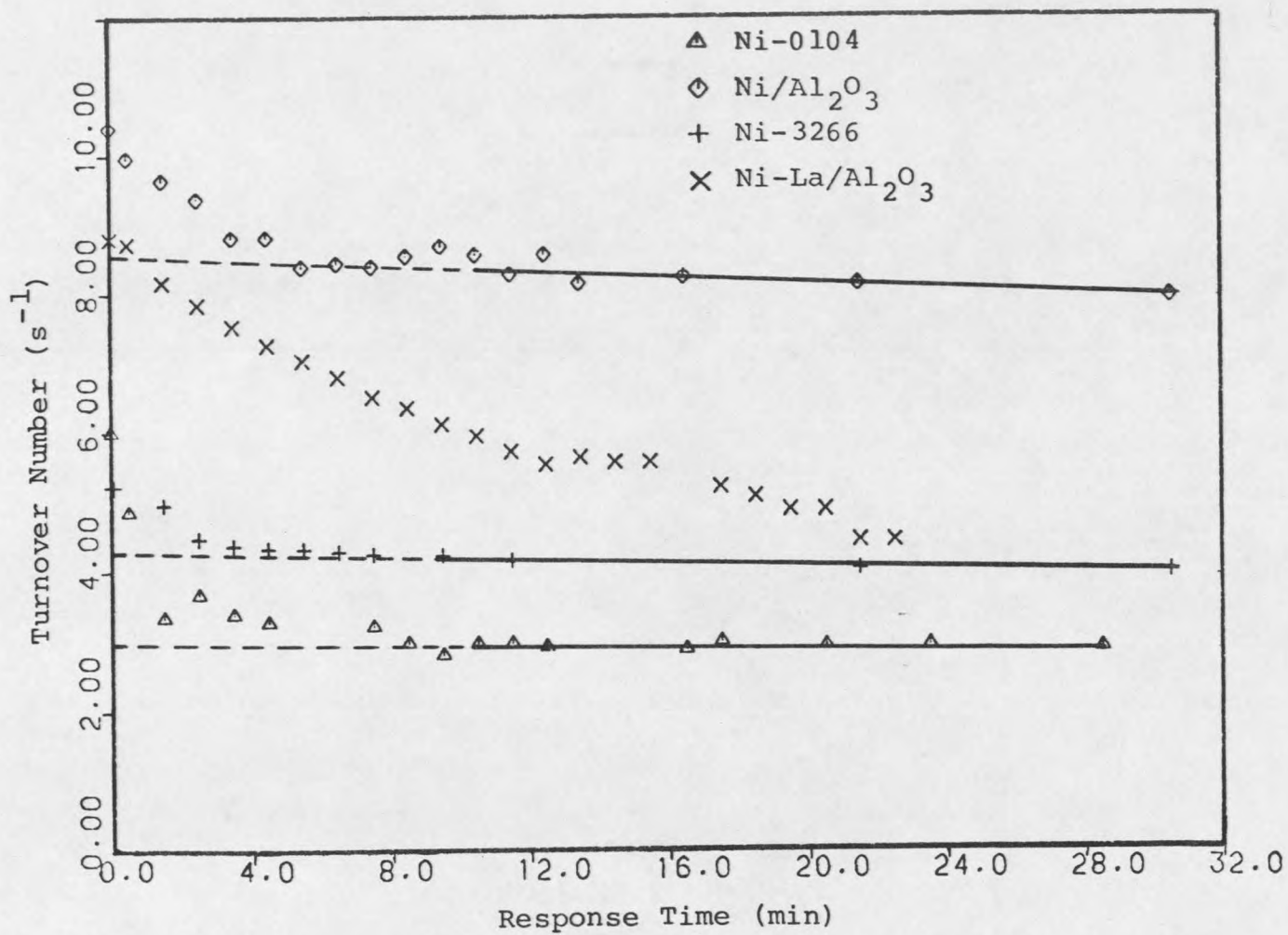


Figure 17. Results of linear regression analysis of poisoning response at 85.1 kPa.

values obtained were expressed as percent of initial activity of the catalysts. Those results appear in Figure 18. Also, the slopes of the extended deactivation periods for the three remaining runs appear in Figure 19. The Ni-3266 and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts had nearly equal percents of initial activity after poisoning of 82.6 and 83.5 respectively, while the Ni-0104 catalyst had a value of percent of initial activity of 50.2. However, the slope of the extended deactivation of the Ni-0104 catalyst was much smaller in magnitude than those of the Ni-3266 and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

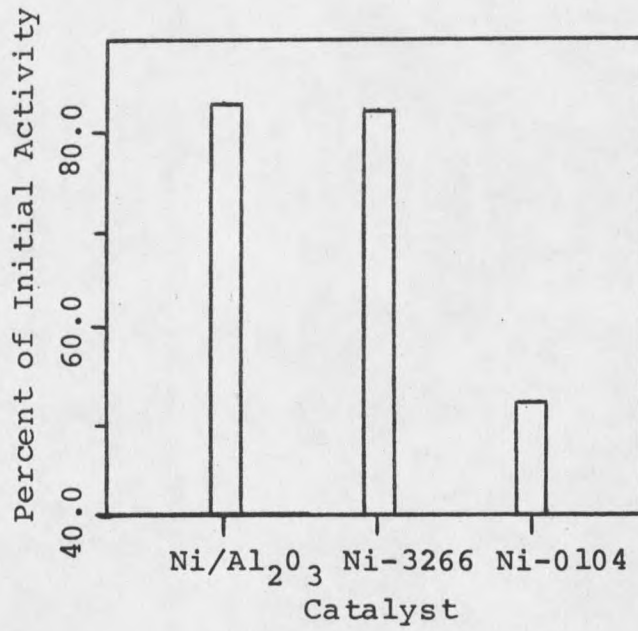


Figure 18. Percent of initial activity for various catalysts.

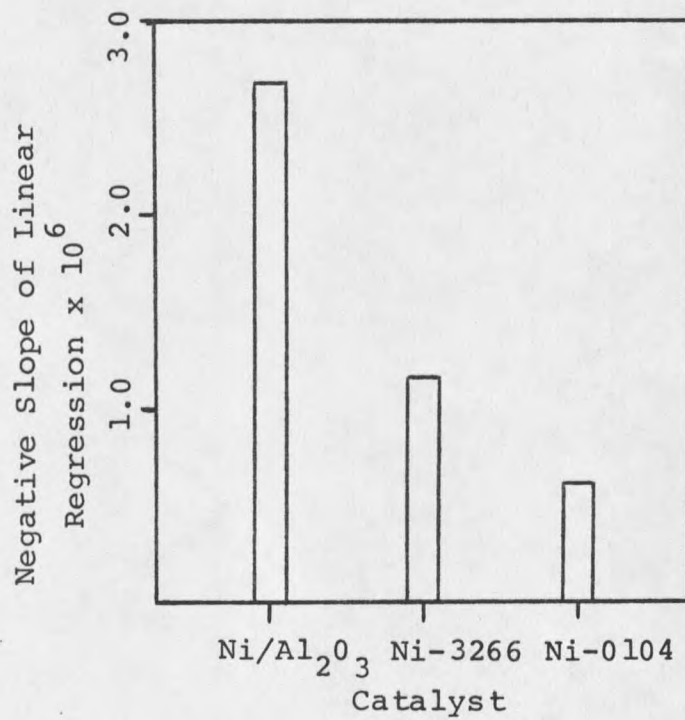


Figure 19. Extended deactivation for various catalysts.

## SUMMARY AND CONCLUSIONS

The catalytic formation of methane from a 2.35/1 molar ratio of  $H_2/CO$  feed was performed over commercial methanation catalysts as well as catalysts which were prepared in the laboratory. A Berty-type, continuous-flow, mixed reactor was used as the main component of the experimental apparatus. The various operation pressures and high flow rates were analogous to commercial reactor conditions, whereas the temperature was chosen according to the requirements of the methanation reaction at 85.1 kPa pressure. The reactor was tested for mixing behavior by a pulse-tracer experiment from which the actual and theoretical responses to a pulse input were generated. The response of the reactor to the pulse of tracer indicated good approximation of perfectly mixed, CFSTR behavior.

The methanation catalysts of this study were tested for deactivation response to a pulse input of  $H_2S$  poison. The two commercial catalysts, Harshaw Ni-0104 and Ni-3266, were tested at pressures of 85.1, 690, 1380, and 2070 kPa and a temperature of 300 degrees C. The catalysts at all conditions exhibited rapid rates of deactivation within 11 minutes after the  $H_2S$  pulse. At times later than 11 minutes, the catalysts exhibited linear declines in activity, which increased in magnitude with increasing pressure for all runs except the Ni-3266 run at 2070 kPa. The major characteristic of deactivation by pulse poisoning was percent of initial activity at zero minutes response time. Those values were obtained from linear regressions of extended deactivation of the catalysts by extrapolation back to zero minutes response time. Both catalysts had minimum percents of initial activity at 690 kPa pressure. The values of percent of initial activity for the Ni-3266 runs were higher at each pressure than the values for the Ni-0104 runs. This was likely due to a greater amount of nickel charged and lower  $H_2S/H_2$  ratios for the Ni-3266 runs.

Both the Ni-0104 and Ni-3266 catalysts and the two catalysts prepared in this laboratory were compared according to their specific activities at 85.1 kPa and 300 degrees C. Although chemisorption experiments were not performed on the catalysts of this study in order to determine the fraction of metal present that was catalytically active, specific activities were based on the total number of metal atoms loaded onto the catalyst. The specific activities of the catalysts of this study were of the same order of magnitude as those of other studies at similar conditions.

In the comparison of the initial turnover numbers of the four catalysts tested at 85.1 kPa and 300 degrees C, the Ni-0104 (60% Ni) and the Ni-3266 (50% Ni) catalysts showed lower specific activities than the Ni/Al<sub>2</sub>O<sub>3</sub> (18% Ni) and the Ni-La/Al<sub>2</sub>O<sub>3</sub> (17% Ni, 4% La) catalysts. The higher initial activities of the catalysts with lower Ni compositions were likely due to greater dispersion and more complete reduction than the catalysts with higher Ni compositions. The catalysts with lower Ni compositions were prepared by direct reduction and were not calcined, as in conventional catalyst preparation.

The responses of the four catalysts to the H<sub>2</sub>S pulse poisoning were similar, except for the Ni-La/Al<sub>2</sub>O<sub>3</sub> catalyst, in that they showed high rates of deactivation shortly after the pulse followed by gradual, linear declines in activity at later times. In contrast, the Ni-La/Al<sub>2</sub>O<sub>3</sub> catalyst showed a continuous rate of deactivation after the poison pulse. Linear regressions of the extended deactivations of the catalysts were extrapolated back to zero minutes response time in order to isolate deactivation due to pulse poisoning. Those values were expressed as percents of the initial activities of the catalysts. The runs were all made at the same temperature, pressure, and feed gas flow rate in order to duplicate H<sub>2</sub>S poison pulse characteristics for each of the runs. The Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-3266 catalyst runs showed 83.5 and 82.6 percents of initial activity respectively, whereas the Ni-0104 run showed 50.2 percent of initial activity at zero minutes response time.

Generally, the pulse poisoning method of this investigation was useful for comparison of the activity-response of methanation catalysts to  $H_2S$  poison. The percent of initial activity of a given catalyst was the fundamental characteristic of the response to pulse poisoning with  $H_2S$ . The pulse poisoning method could be useful for the development of sulfur-resistant methanation catalysts. New catalyst formulations could be screened by use of this method, and those formulations that showed highest percents of initial activity after poisoning could then be tested more extensively. One method of extensive testing of a catalyst would be the measurement of deactivation in response to a step input of  $H_2S$  poison. Another method would involve catalyst deactivation in response to various pulse poisoning schemes such as: (1) a series of pulses of  $H_2S$ , and (2) various pulses of unequal amounts of  $H_2S$ . The extensive testing of methanation catalysts would provide more information on the sulfur resistance of various catalysts and may provide information regarding the nature of sulfur poisoning.

## RECOMMENDATIONS FOR FURTHER STUDY

Recommendations for further study are geared toward the refinement of the study of methanation catalyst poisoning by  $H_2S$ , particularly by the pulse poisoning method. The goal of continued study would be the characterization of the sulfur poisoning of methanation catalysts. One result would be the ability to screen new catalyst formulations in the development of sulfur-resistant catalysts. Recommendations are here limited to the most significant experimental factors.

Characterization of the amount and morphology of supported catalyst material would provide more accurate results in regard to the specific methanation activity of supported catalysts. Gas chemisorption of CO and  $H_2$  for the determination of catalytic surface area, as well as spectroscopic techniques for determination of crystallite size and dispersion of catalytic material should be utilized.

The gas feed mixture should be altered to  $H_2/CO$  ratios which are much greater than reaction stoichiometry requires. This would discourage carbon deposition on the catalyst, and thus help isolate deactivation characteristics due to  $H_2S$  poisoning.

The CO content of the feed gas should be diluted. Reaction stoichiometry indicates that higher pressure tends to favor the right hand side of the methanation reaction. Feed stream diluent such as Helium or a large excess of  $H_2$  would reduce the pressure effects on the reaction and thereby reduce the variations in CO conversion over a range of pressures. Thus, the contribution of  $H_2S$  poisoning to catalyst deactivation over a range of operating pressures, including those commonly found in commercial processes, could be easily identified.

Although the Berty reactor is particularly well suited for kinetic studies because of its mixing behavior, good kinetic data is not assured unless interior and exterior temperature and concentration gradients of the catalyst are effectively eliminated. Usually operation at differential conditions helps eliminate these gradients. However, the methanation reaction is quite exothermic at 300 degrees C (-79 kJ/mole) and high pressure tends to move the resistance to mass diffusion into the bulk regime (Smith, 31:454). Therefore greater care must be taken in methanation to insure negligible heat and mass transfer effects. In general, Berty (7) recommended high recycle ratios and high flow rates for his reactors. He also proposed several tests to determine if a catalytic reaction was independent of heat and mass transfer effects, including pore diffusion.

In the case where such tests on the experimental apparatus of this investigation indicate negligible concentration and temperature gradients, new catalyst formulations can be easily screened for deactivation characteristics by the pulse poisoning method. More promising catalyst formulations can then be tested for long term deactivation with constant levels of  $H_2S$  incorporated into the feed stream.

As was mentioned in reference to the mechanism of sulfidation, activity recovery of poisoned methanation catalysts has been reported at or near 400 degrees C reaction temperature. An attempt to confirm those results in this investigation was inconclusive: recovery of methanation activity at 400 degrees C was masked by extended deactivation of the catalyst, probably due to carbon deposition. Tests should be run at or near 400 degrees C to confirm, or refute activity recovery. If recovery is confirmed, characterization of that recovery for various catalyst formulations could be done, for which the pulse poisoning method could be utilized.

Preparation of catalysts would be improved by the addition of an apparatus for reduction of impregnated catalysts. The equipment should be capable of reduction with flowing  $H_2$  at various temperatures in the general range of 300-600 degrees C. Adequate means for

passivation of reduced catalysts should be arranged so that catalysts can be stored in air. A catalyst preparation technique which would likely increase the dispersion of supported catalytic material should be investigated. That technique is the evaporation of catalytic material, under vacuum, onto the catalyst support material.

In reference to the experimental apparatus, two major changes should be made in order to facilitate a more extensive study of the poisoning of methanation catalysts. Those changes would be: (1) the addition of an effective water removal system for the effluent gas stream, and (2) the addition of temperature control for the reactor and preheater. The effective removal of water from the effluent gas stream would allow operation of the gas chromatograph at conditions tailored for carbon monoxide and hydrocarbon analysis. Removal of water would also allow use of a flame ionization detector which would increase sensitivity by several orders of magnitude over the thermal conductivity bridge detector (Purnell, 26:323). Flame ionization detection may not be an essential improvement: during the course of this investigation, methane concentrations as low as 1.5% of the effluent stream were detected with reasonable accuracy. Temperature control for the reactor and preheater of the experimental system would be required in order to operate the system isothermally for extended periods of time. The present system requires repeated adjustment for experimental runs longer than a couple of hours.

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## LITERATURE CITED

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APPENDICES

APPENDIX A

TABLES

Table 2. Table of Nomenclature

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btu	British Thermal Unit
C	Centigrade (e.g., degrees Centigrade)
cc	cubic centimeter
CFSTR	Continuous Flow Stirred Tank Reactor
cm	centimeter
dc	direct current
E	base 10 exponent (e.g., $1 \text{ E}-5 = 1 \times 10^{-5}$ )
g	gram
K	Kelvin (e.g., degrees Kelvin)
kJ	kiloJoule
kPa	kiloPascal
L/D	Length/diameter
ma	milliampere
min	minute
N	Turnover number ( $\text{s}^{-1}$ )
nm	nanometer
ppm	parts per million
rpm	revolutions per minute
s	second
SCCM	standard cubic centimeters per minute
V	volt

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Table 3. The Group VIII Metals.

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Fe	Iron
Co	Cobalt
Ni	Nickel
Ru	Ruthenium
Rh	Rhodium
Pd	Palladium
Os	Osmium
Ir	Iridium
Pt	Platinum

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Table 4. Catalyst Properties.

Catalyst	Composition (wt. %)	Size	Pore Volume (cc/g)	Surface Area (m <sup>2</sup> /g)	Ref.
Harshaw Ni-0104 T 1/8"	60% Nickel on Kiedelguhr	1.8" tablets	0.2	125	(18:23)
Harshaw Ni-3266 E 1/8"	50% Nickel on proprietary support	1/8" extrudates	0.52	145	(18:24)
Ni on alumina	18% Nickel	1/8" spheres	—	—	this study
Ni-La on alumina	17% Nickel 4% Lanthanum	1/8" spheres	—	—	this study
alumina support (Davison Chemical SMR 7-6052)	98% Al <sub>2</sub> O <sub>3</sub>	1/8" spheres	0.90	—	(20:20)

Table 5. Results of Linear Regression Analysis for Pressure Runs.

Pressure (kPa)	Initial Rate*	Linear Regression Analysis			Percent Initial Activity
		Intercept*	Slope	Straight Line Correlation	
Harshaw Ni-0104					
85.1	6.14 E-5	3.08 E-5	-0.41 E-7	-0.54	50.1
690	8.93 E-5	3.83 E-5	-2.25 E-7	-0.96	42.9
1380	11.19 E-5	5.95 E-5	-6.37 E-7	-0.85	53.2
2070	6.38 E-5	4.05 E-5	-10.47 E-7	-0.94	63.5
Harshaw Ni-3266					
85.1	8.41 E-5	5.22 E-5	-1.90 E-7	-0.94	62.1
690	13.77 E-5	7.61 E-5	-3.65 E-7	-0.86	55.3
1380	12.83 E-5	7.45 E-5	-4.47 E-7	-0.92	58.1
2070	10.84 E-5	9.02 E-5	-2.39 E-7	-0.80	83.2

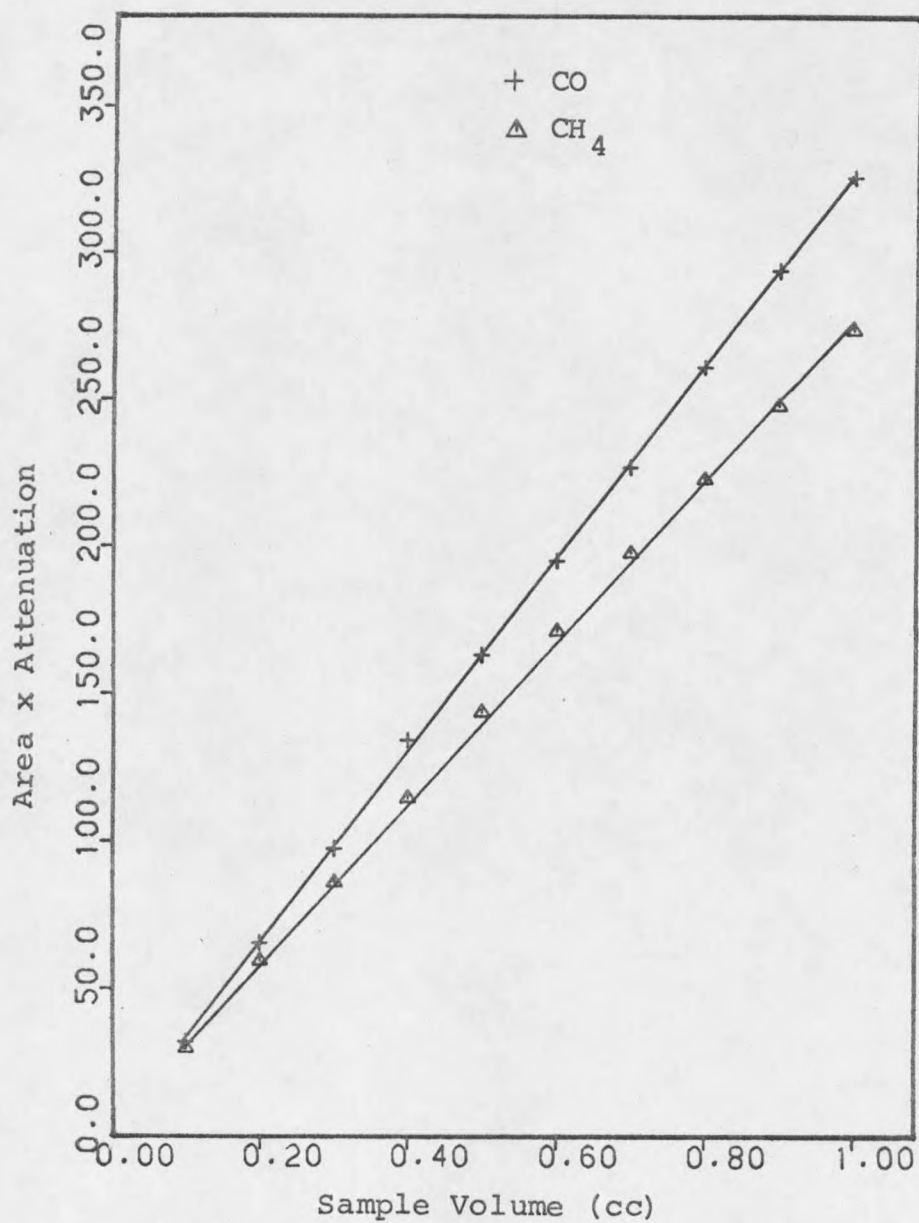
\*Indicates (mole CH<sub>4</sub> /g catalyst-s).

Table 6. Results of Linear Regression Analysis for Various Catalysts at 85.1 kPa.

Pressure (kPa)	Initial Turnover Number (s <sup>-1</sup> )	Linear Regression Analysis			Percent Initial Activity
		Intercept (s <sup>-1</sup> )	Slope	Straight Line Correlation	
Ni/Al <sub>2</sub> O <sub>3</sub>	10.40 E-3	8.69 E-3	-2.67 E-5	-0.81	83.5
Ni-3266	5.22 E-3	4.31 E-3	-1.18 E-5	-0.96	82.6
Ni-0104	6.00 E-3	3.01 E-3	-0.42 E-5	-0.61	50.2
Ni-La/Al <sub>2</sub> O <sub>3</sub>	8.80 E-3	—	—	—	—

APPENDIX B

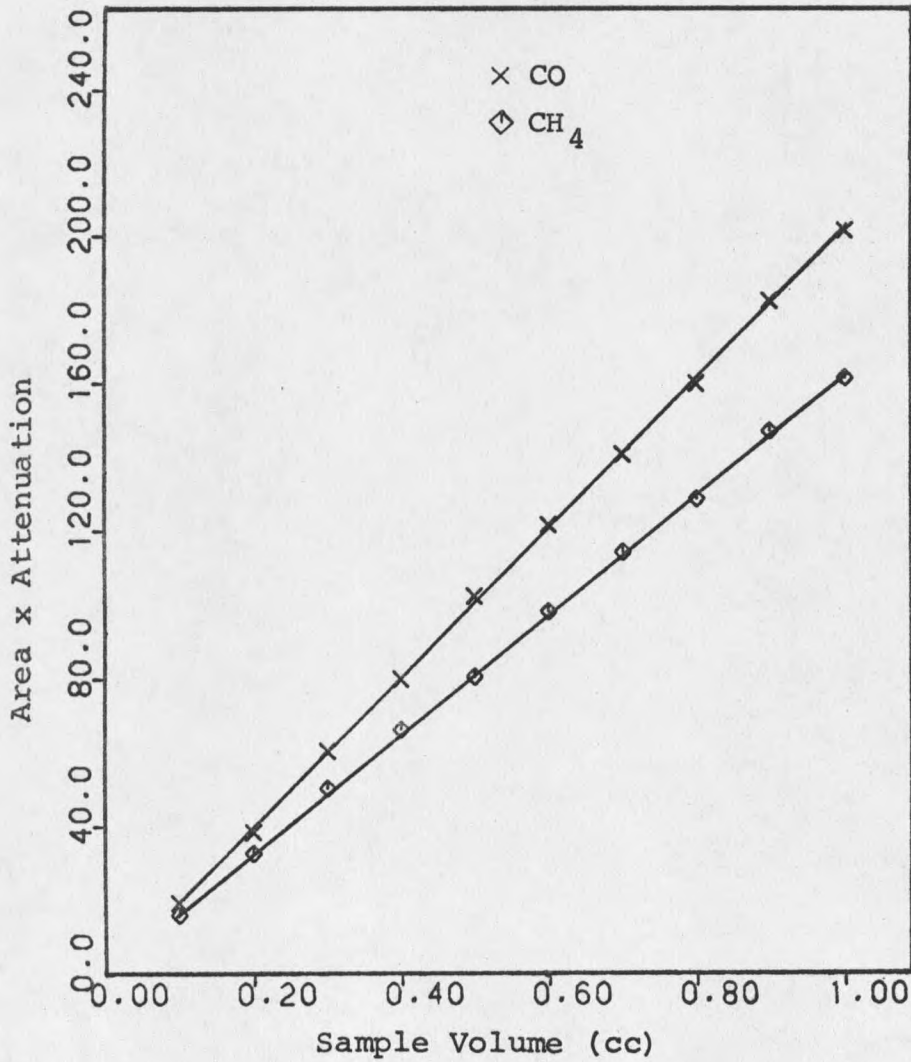
FIGURES



Chromatograph Settings:

25 degrees C column temp.  
200 ma detector current  
45 cc/min He<sub>2</sub> flow rate

Figure 20. Chromatograph calibration I.



Chromatograph Settings:  
80 degrees C column temp.  
150 ma detector current  
80 cc/min He<sub>2</sub> flow rate

Figure 21. Chromatograph calibration II.

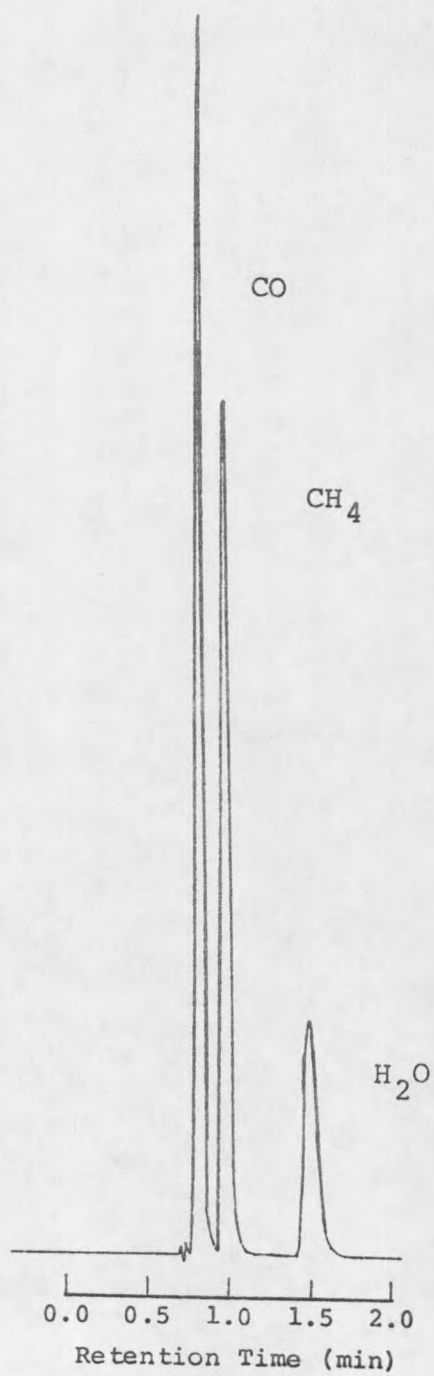


Figure 22. Sample chromatogram.

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Sulfur poisoning of methanation catalyst



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Sw24

cop.2

Swanberg, D. J.

Sulfur poisoning of  
methanation catalysts

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