



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
© Copyright by David Jonathon Swanberg (1983)

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 H₂S 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 H₂ /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 H₂ 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/Al₂ O₃ catalyst prepared in the laboratory, were tested for pulse poisoning response at 85.1 kPa. The Ni/Al₂O₃ 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.

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
Bozeman, Montana

January 1983

MAIN LIB.
N378
Sw24
cop.2

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.

1-6-83
Date

J.P. McCandless
Chairperson, Graduate Committee

Approved for the Major Department

Jan 6, 1983
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

1-18-83
Date

Michael P. Malone
Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his/her absence, by the Director of Libraries when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature



Date

1-6-83

ACKNOWLEDGMENT

The author wishes to thank the faculty, graduate students, and staff of the Department of Chemical Engineering at Montana State University for their assistance which helped make this project possible.

Special thanks to Dr. F. P. McCandless for his advice, assistance, and support throughout the course of the study.

The author also wishes to thank Gerald Paulson and Jim Bratsky for assistance with the computer graphics.

TABLE OF CONTENTS

	Page
APPROVAL	ii
STATEMENT OF PERMISSION TO USE	iii
ACKNOWLEDGMENT	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	x
INTRODUCTION	1
REVIEW OF RELATED LITERATURE	3
Mechanism of Catalytic Methanation	3
Proven Catalysts	5
Supported Catalysts	6
Multi-Component Catalysts	7
Catalyst Preparation	9
Sulfur Poisoning of Methanation Catalysts	10
Mechanism of Sulfidation	11
EXPERIMENTAL EQUIPMENT AND PROCEDURE	13
Experimental Equipment	13
Reactant Feed Stream	13
Pressure Control and Monitoring Equipment	13
Temperature Control and Monitoring Equipment	15
Pulse Poisoning Apparatus	15
Reactor System	15
Effluent Gas Analysis Equipment	16
Experimental Procedure	17
Preliminary Operations	17
Experimental Program	18
Experimental Procedure	19
Catalyst Preparation	20
RESEARCH OBJECTIVE	22

TABLE OF CONTENTS—Continued

	Page
RESULTS AND DISCUSSION	23
Reactor Behavior	23
Determination of Reaction Temperature	25
Pressure Runs	25
Comparison of Specific Activity of Methanation Catalysts	39
SUMMARY AND CONCLUSIONS	49
RECOMMENDATIONS FOR FURTHER STUDY	52
LITERATURE CITED	55
APPENDICES	59
Appendix A—Tables	60
Appendix B—Figures	65

LIST OF TABLES

Tables	Page
1. Comparison of Specific Activity of Various Catalysts	42
Appendix Tables	
2. Table of Nomenclature	61
3. The Group VIII Metals	62
4. Catalyst Properties	63
5. Results of Linear Regression Analysis for Pressure Runs	64
6. Results of Linear Regression Analysis for Various Catalysts at 85.1 kPa	64

LIST OF FIGURES

Figures	Page
1. Schematic diagram of experimental apparatus	14
2. Response to pulse input of methane tracer	24
3. Temperature screening run for Ni-0104 catalyst at 85.1 kPa	26
4. Initial activity of Ni-0104 catalyst at various pressures	28
5. Poisoning response of Ni-0104 catalyst at various pressures	29
6. Poisoning response of Ni-0104 catalyst at various pressures	30
7. Initial activity of Ni-3266 catalyst at various pressures	32
8. Poisoning response of Ni-3266 catalyst at various pressures	33
9. Poisoning response of Ni-3266 catalyst at various pressures	34
10. Results of linear regression analysis of Ni-0104 poisoning response	35
11. Results of linear regression analysis of Ni-3266 poisoning response	36
12. Percent of initial activity of Ni-0104 and Ni-3266 catalysts at various pressures	38
13. Extended deactivation of Ni-0104 and Ni-3266 catalysts at various pressures	40
14. Initial turnover and conversion of CO for various catalysts	43
15. Comparison of poisoning response at 85.1 kPa	44
16. Comparison of poisoning response at 85.1 kPa	45
17. Results of linear regression analysis of poisoning response at 85.1 kPa	46
18. Percent of initial activity for various catalysts	48
19. Extended deactivation for various catalysts	48

Figures	Page
Appendix Figures	
20. Chromatograph calibration I.....	66
21. Chromatograph calibration II.....	67
22. Sample chromatogram.....	68

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.

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_2S 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_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 (H₂) 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 H₂ 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 H₂/CO mixtures.

Work on the synthesis of hydrocarbon fuels from H₂/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 H₂ to form methane has been known for some time: Sabatier and Senderens first reported the production of methane from CO and H₂ 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 (Ni_3C). Thus, the reaction was characterized by the following sequence (Trimm, 32:275):

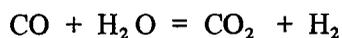


It was questionable whether intermediates (b) and (c) proceeded by means of bulk phase H_2 , or by adsorbed, or dissociatively adsorbed hydrogen species. However, Vannice has shown enhanced methanation activity with increasing heat of adsorption of hydrogen, which suggests an adsorbed hydrogen species 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 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 H₂ reactants to form CH₄ and CO₂ 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 CO₂ 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 (La_2O_3) and Cerium Oxide (Ce_2O_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 La_2O_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 Ce_2O_3 promoter was tried but with less success than La_2O_3 . The Ni + Ru + La_2O_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 (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- MoO_3 formulation, 2.5% Ni and 3.0% 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 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

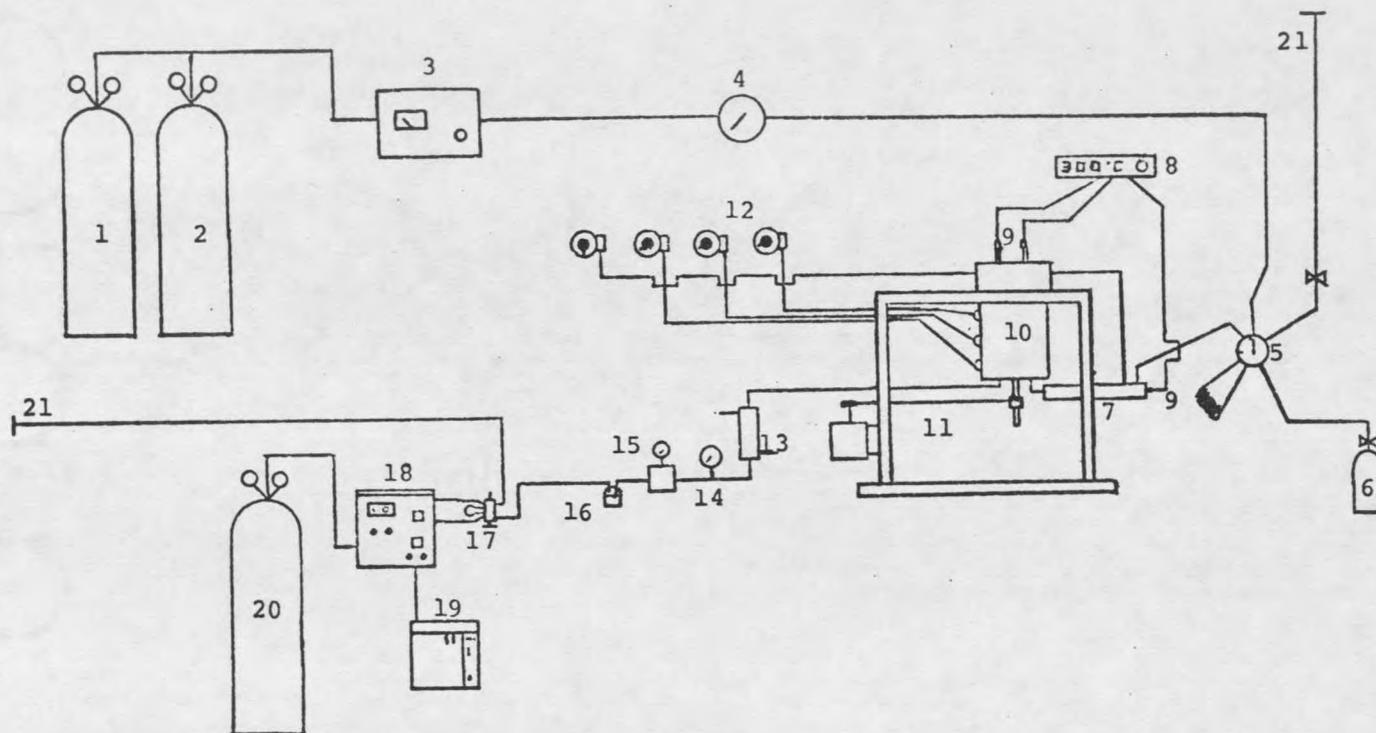
A schematic diagram of the experimental apparatus, with brief descriptions of the separate components, appears in Figure 1. Detailed descriptions of the constituent sub-systems follow.

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) H₂/CO feed gas mixture (2) H₂ (3) mass-flowmeter/needle valve assembly
 (4) pressure gauge (5) pulse poisoning valve (6) H₂S (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 H₂ 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, H₂/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 H₂, 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 H₂/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/Al₂O₃, and 2.0 g Ni-La/Al₂O₃.

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 H₂ 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, H₂ 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 H₂ 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_2 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

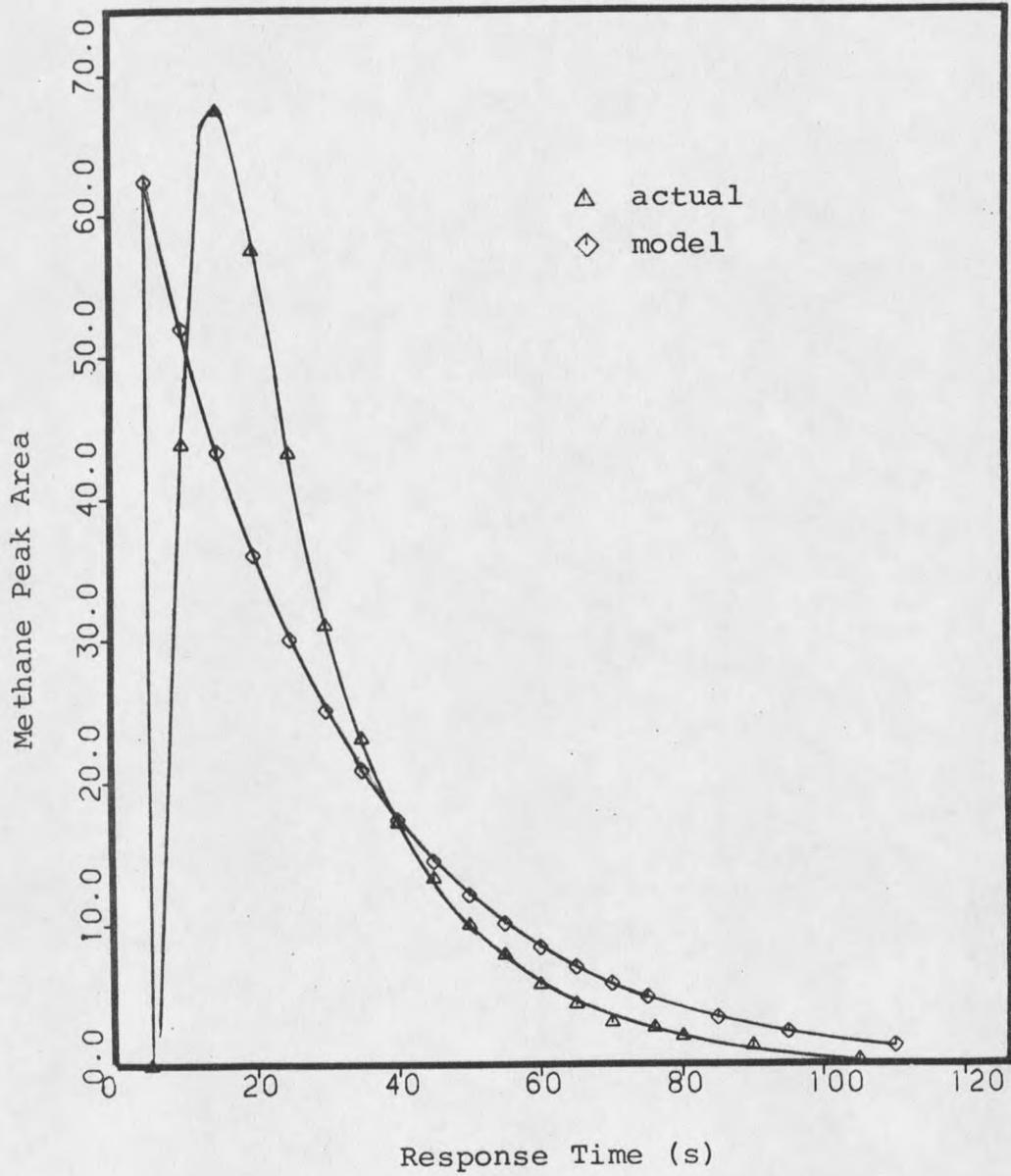


Figure 2. Response to pulse input of methane tracer.

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

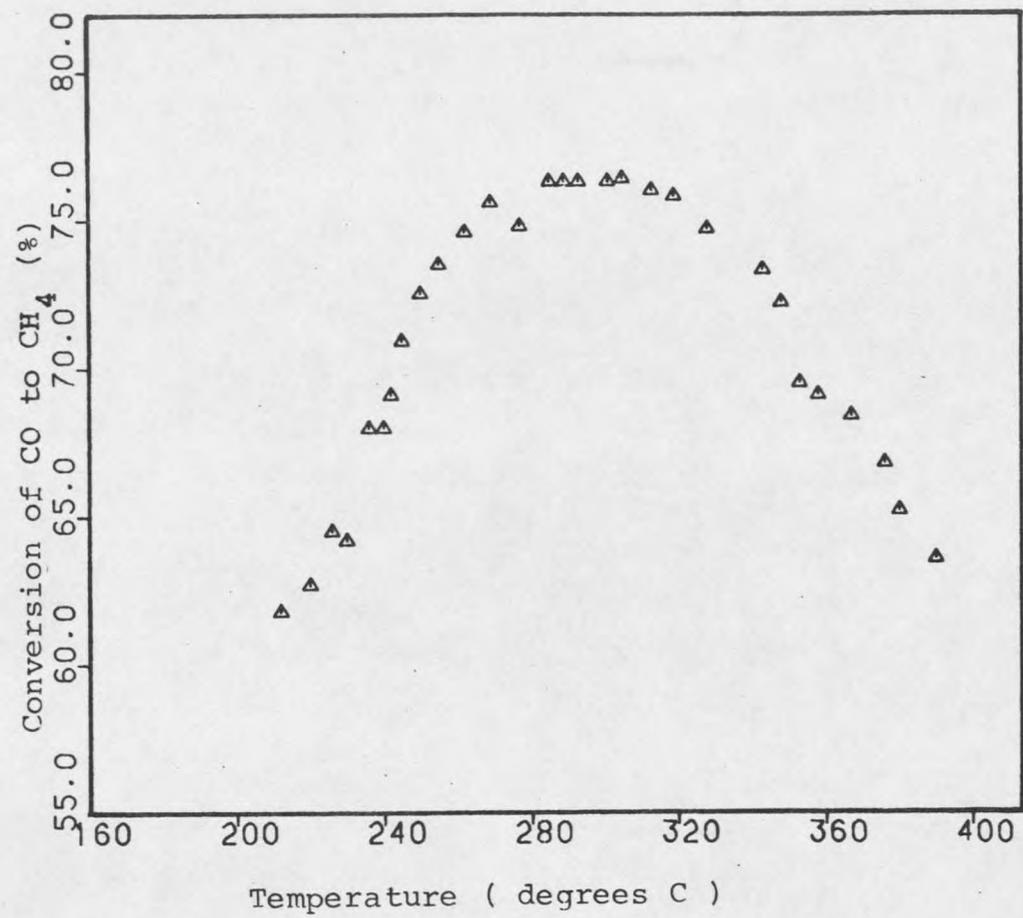


Figure 3. Temperature screening run for Ni-0104 catalyst at 85.1 kPa.

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 6.14×10^{-5} (moles 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 H_2S 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.

