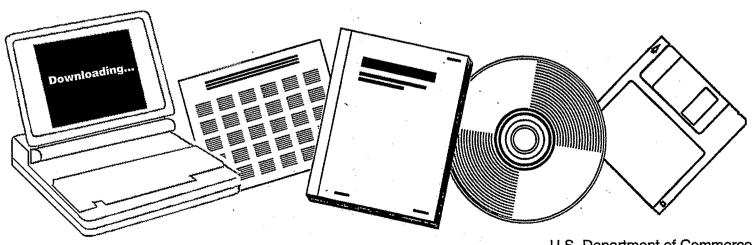




## METHANE PRODUCTION FROM CARBON OXIDES OVER BOROHYDRIDE-REDUCED TRANSITION METALS

NEW MEXICO ENERGY INST., ALBUQUERQUE

**JAN 1978** 



U.S. Department of Commerce National Technical Information Service

## **One Source. One Search. One Solution.**

NTZS



# **Providing Permanent, Easy Access to U.S. Government Information**

National Technical Information Service is the nation's largest repository and disseminator of governmentinitiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.





#### Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **www.ntis.gov.** You now have access to information on more than 600,000 government research information products from this web site.

#### Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

#### **Download Publications (1997 - Present)**

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

# www.ntis.gov



U.S. DEPARTMENT OF COMMERCE Technology Administration National Technical Information Service Springfield, VA 22161

PB286385

#### Final Report .

METHANE PRODUCTION FROM CARBON OXIDES OVER BOROHYDRIDE-REDUCED TRANSITION METALS

#### by

Thomas W. Russell, Ph.D.

Chemistry Department Division of Natural Science Eastern New Mexico University Portales, New Mexico 88130

#### NMEI Report No. 76-173

January 1978

NTIS

New Mexico Energy Institute at The University of New Mexico grants permission to the National Technical Information Service to reprint this publication for sale.

> REPRODUCED BY: N. U.S. Department of Commerce National Technical Information Service Springfield, Virginia 22161

Exercise       PARET - 76/173       PARET - 76/173         The and Exercise       Author Prom Carbon Oxides Over Borohydride-Reduced Transition Metals         Mathiane Production Form Carbon Oxides Over Borohydride-Reduced Transition Metals       5         Anthorio       Thomas W. Russeell, Ph.D.         Thomas W. Russeell, Ph.D.       76-173         Anthorio       76-173         New Maxico Energy Institute       76-173         The Information Form Carbon Oxides       10         New Maxico Brangy and Minerals Department       76-173         Prior Static Oxide States       10         New Maxico Barsey and Minerals Department       76-173         Prior State Oxide States       10         New Maxico Barsey and Minerals Department       76-173         Prior State Oxide Core       11         This Study was undertaken to continue the examination of the utility of borohydrid         This study was undertaken to continue the examination of carbon oxides to produce         Synthetic fuels.       While most related efforts deal only with carbon monoxide (the predominant oxide state valiable core).         Note the cost related efforts deal only with carbon monoxide (the predominant oxide state valiable core).       11         Supported the carbon doxide being only slightly less productive than carbon doxides or product formad (beast orelabet formad continues methanation over coball		I DEFORT NO	<u></u>	2.	3. Peripient's A	ccession No
Mathema Production From Carbon Oxides Over Borohydride- Reduced Transition Metals       January, 1978         Anthofd Thomas W. Russell, Ph.D.       6         Anthofd Thomas W. Russell, Ph.D.       76-173         New Mexico Energy Institute The University of New Mexico 117 Richmond Dr., N.E.       10. Protection/Werk Unit Ne. 76-173         Albuquerue, New Mexico S7006       10. Content(0) Ne. (o) 76-173         2. Spennoting Organization Name and Adverse New Mexico Energy and Minerals Department P.O. Box 2770 Santa Pe, New Mexico 87501       13. Type of Heard Energy Final Report         3. Supplementary Nets       13. Type of Heard Energy Final Report       14.         4. Supplementary Nets       13. Type of Heard Energy Final Report       14.         5. Supplementary Nets       13. Type of Heard Energy Final Report       14.         6. Statuse (Link: 200 word)       14.       14.         This study was undertaken to continue the examination of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to produ synthetic fuels.       15. Statuse (Link: Energy Netset and Jourde as wall in our work.         Work with cobalt, copper, Nickel and palledum has resulted in methane productive than carbon monoxide. From the last three metals, methane is the only product formal (heasi water). This is a definite inprovement over many of the catalysts reported in the sci- entific Literature, where a major problem is the production of numerous carbon-contains tow-week run.         17. Document Analysis a. Desc	EFORT DOCUMENTATION	<u>NMEI - 76/173</u>	$\sum$		PBC	86385
Reduced Transition Matals       6         Anterdo Thomas W. Russell, Ph.D.       8. Performing Organization Raps N. 76-173         Performing Organization Name and Address       10. Project Provide Organization Raps N. 76-173         New Mexico Energy Institute The University of New Mexico 117 Richmond Dr., N.E. Albuquerque, New Mexico 87106       11. Centract() or Cenn(1) Ne. (C) 76-173         Assession Wew Mexico Energy and Minerals Department P.O. Box 2770 Santa Fe, New Mexico 87501       13. Type of Report & Period Govern Final Report         A demond Unit 200 works       The study was undertaken to continue the examination of the utility of borohydrin box available copy.         A demond Unit 200 works       This study was undertaken to continue the examination of carbon oxides to produce synthetic fuels.         While most related efforts deal only with carbon monoxide (the predominant oxide : coll gasification processes), we have included carbon dioxide as well in our work.         Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide heim only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besin from both carbon oxides, with carbon dioxide heim only slightly less production the esti- stice there a major problem is the production of numerous carbon-contain products.         Completion of construction of a second flow system has allowed several questions completion during a two-week run.         7. Dearment Analysis = Descriptors         2. Mentifiers/Opent Ended Terms			0.1	The sea to a dead deal		. 10.79
Animation       4. Performing Organization Names and Address       5. Performing Organization Names and Address         New Mexico Emergy Institute       11. Project/Des/Work Uol No.         The University of New Mexico 87106       11. Contract(0) or Grant(0) No.         6 spreaming Organization Names and Address       11. Project/Des/Work Uol No.         6 spreaming Organization Name and Address       11. Contract(0) or Grant(0) No.         6 spreaming Organization Name and Address       11. Description Official Project Address         8 spreaming Organization Name and Address       11. Description Official Project Address         8 spreaming Organization Name and Address       11. Description Name and Address         11 Rickico Emergy and Minerals Department       7.6-173         9. Obsort 2770       Santa Fe, New Mexico 87501         14. Empoduced from sent address organization of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to produce arganization processes were and include a carbon monoxide (the predominant oxide : coal grasification processes), we have included carbon dioxide as well in our work.         While most related efforts deal only with carbon monoxide (the predominant oxide : acrbon work with cobalt, copper, nickel and palladium has resulted in methane product forme (besident).         Work the Carbon oxides, with carbon dioxide being only slightly less product forme (besident).         Toroh both carbon oxides, with carbon dioxide being oxides as allowed several questions acrli			Oxides Over	Boronyariae-		, 1970
Thomas W. Russell, Ph.D.       76-173         Fedoration Nama and Address       10. Project/TextWork Unit Nam.         Mere Mexico Chargy Institute The University of New Mexico 117 Richmond Dr., N.E.       11. Contraction of the utility of borohydrif.         Albuquere, New Mexico 87501       11. Type of Report & Period Courter Final Report         Associate the second of the utility of borohydrif.       11. Type of Report & Period Courter Final Report         Associate the second of the utility of borohydrif.       14.         Associate the second of the utility of borohydrif.       14.         Association metals as catalysts for the hydrogenation of the utility of borohydrif.       16.         This study was undertaken to continue the examination of the utility of borohydrif.       16.         This study was undertaken to continue the examination of carbon oxides to production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besin control of of a second flow system has allowed several questions in mathane production of a second flow system has allowed several questions in mathane production during two-week run.         A bounder the sciention of sulfur dioxide has shown an increase in methane production during two-week run.         A bounder the sciention         A bounder the sciention         A bounder theres	Reduced Transiti	Lon Metals	• •		6.	
Performing Organization Name and Address New Mexico Energy Institute The University of New Mexico 117 Richmond Dr., N.E. Albuquerque, New Mexico 87106 . Genergy and Minerals Department P.O. Box 2770 Santa Re, New Mexico 87501 . The Study was undertaken to continue the examination of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc synthetic fuels. With cobit, copper, include and palladium has resulted in methane productive than action processes), we have include carbon dioxide as well in our work. With cobit, copper, include and palladium has resulted in methane productive than action of a second flow system has allowed several questions carbon increase in methane production of a second flow system has allowed several questions completion during a two-week run. Continuous methanation over nickel has shown no deer in methane production during a two-week run. Continuous methanation over cobalt in the presence of Lopen Ended Terms b. MentHimer/Open-Ended Terms 2. Availability Statement		L1, Ph.D.				
New Mexico Energy Institute       11. Contract(0) or Genent(0) No.         111 Richmond Dr., N.E.       11. Contract(0) or Genent(0) No.         12 Spendong Organization Nume and Address       13. Type of Report & Paried Ecore         New Mexico Energy and Minerals Department       13. Type of Report & Paried Ecore         P.O. Box 2770       14.         Samplementery Nats       14.         A symplementery Nats       15. Type of Report & Paried Ecore         Final Report       14.         A symplementery Nats       14.         A symplementery Nats       14.         A symplementery Nats       16. Approximation of the utility of borohydrin         A symplementery Nats       16. Approximation of carbon oxides to produce you have a specific copy.         A symplementery Nats       16. Approximation of carbon oxides to produce you have a specific copy.         A symplementery Nats       16. Approximation of carbon oxides to produce you have a specific copy.         A symplementery Nats       16. Approximation of carbon oxides to produce you have a specific copy.         A symplementery Nats       16. Approximation of carbon oxides to produce you have a specific copy.         A symplementery Nats       16. Approximation of carbon oxides to produce you have a specific copy.         This is a definite improvement over many of the cataloystis proofuct formed have production of numerous carbon-contain produ	Performing Organization Name ar	nd Addrass		•		•
The University of New Mexico 117 Richmond Dr., N.E. Albuquerque, New Mexico 87106 Seconsoting Organization Name and Address New Mexico Energy and Minerals Department F.O. Box 2770 Santa Fe, New Mexico 87501 Santa Fe, New Mexico 87501 Construction Mexico 87501 Construction Mexico Reproduced from Best available copy. Construction of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc Synthetic fuels. While most related efforts deal only with carbon monoxide (the predominant oxide : Coal gasification processes), we have included carbon dioxide as well in our work. Work with cohalt, copper, nickel and pailadium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besin water). This is a definite improvement over many of the catalysts reported in the sci- earlier work (1) to be answered. Continuous methanation over nickel has shown on deer in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Decument Analyts a Descriptors a. Availability Satement 2. Availability Satement Descriptors A valiability Satement Descriptor (2. No. of Fages Descriptors Descriptors Descriptors Descriptor (2. No. of Fages Descriptors Descript	New Mexico Ener	ev Institute				
117 Richmond Dr., N.E.       IS 76-173         Albuquerque, New Mexico 87106       IS         Seconduct Organization Nume and Address       New Maxico Energy and Minerals Department         P.O. Box 2770       Santa Fe, New Mexico 87501         Samphomentary Nozs       Is Type of Record & Period Cover Final Report         A barnet Unmit 200 word)       Reproduced from bot available copy.         This study was undertaken to continue the examination of the utility of borohydrin reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc synthetic fuels.         While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work.         Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besin water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products.         Completion of construction of a second flow system has allowed several questions in methane production during a two-week run. Continuous methanation over cobalt in the presence of Hopm of sulfur dioxide has shown an increase in methane production during two-week run.         A beentifiers/Open-Ended Terms       19. Security Class (file Ropert) Unclassified       21. No. ef Pages			· .	4		
Spensoring Organization Name and Address New Mexico Energy and Minerals Department P.O. Box 2770 Santa Fe, New Mexico 87501 Beproduced from Dast available copy. Adstract (Lunk 200 words) This study was undertaken to continue the examination of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to produce synthetic fuels. While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production than carbon monoxide. From the last three metals, methane is the only product formed (beain matrix). This is a definite improvement over many of the catalysts reported in the sci- earlier work (1) to be answered. Continuous methanation over nickel has shown no deer in methane production during a two-week run. Continuous methanation over cobalt in th presence of loppm of sulfur dioxide has shown an increase in methane production during two-week run. b. MentHern/Open-Ended Terms b. MentHern/Open-Ended Terms b. MentHern/Open-Ended Terms coalt Field/Group z. Availability Statement Unclassified 21. No. of Fages	-				(C) 76-17	73
New Mexico Energy and Minerals Department P.O. Rox 2770 Santa Fe, New Mexico 87501       Final Report         Image: Second State St	Albuquerque, New	w Mexico 87106	•		(G)	
New Maxico Emergy and Minerals Department P.O. Box 2770 Santa Fe, New Mexico 87501       Final Report         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Fe, New Mexico 87501       Image: Santa Fe, New Mexico 87501         Image: Santa Feider Santa Feider Fermination Mexico Research Provide Fermination Oper Santa Feider Ferms       Image: Santa Feider Ferms         Image: Santa Feider Ferms       Image: Santa Feider Ferms       Image: Santa Feider Ferms         Image: Santa Feider Ferms       Image: Santa Feider Ferms       Image: Santa Feider Ferms         Im	O	ad Addracc			13. Type of Rei	oort & Pariod Covered
P.O. Box 2770         Santa Fe, New Mexico 87501         It         Supplementary Notes         Exproduced from Dest available copy.         This study was undertaken to continue the examination of the utility of borohydric reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc synthetic fuels.         While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with coalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besident). Completion of construction of a second flow system has allowed several questions in methane production during a two-week run.         Completion of construction of a second flow system has allowed several questions in methane production during a two-week run.         To Decument Analysis a Descriptors         is. Identifiers/Open-Ended Terms         is. Availability Statement	New Mexico Ener	gy and Minerals	Department			-
Santa Fe, New Mexico 87501           3. Supplementary Notes           3. Supplementary Notes           3. A Autrast (Umit 200 words)           This study was undertaken to continue the examination of the utility of borohydric reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc synthetic fuels.           While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon doxide being only slightly less product formed (beside water). This is a definite improvement over many of the catalysts reported in the sci- eartific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during two-week run.           7. Decument Analysis a Descriptors         19. Security Class (This Report)         21. No. ef Pagers Unclassified			-	•	F III F	L REPOIL
Supplamentary Notes     Best available copy.     Best available copy.     This study was undertaken to continue the examination of the utility of borohydrin reduced transition metals as catalysts for the hydrogenation of carbon oxides to produ     wynthetic fuels.     While most related efforts deal only with carbon monoxide (the predominant oxide :     coal gasification processes), we have included carbon dioxide as well in our work.     Work with cohalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than     carbon monoxide. From the last three metals, methane is the only product formed (besi     water). This is a definite improvement over many of the catalysts reported in the sci-     entific literature, where a major problem is the production of numerous carbon-contain     products.     Completion of construction of a second flow system has allowed several questions     im methane production during a two-week run. Continuous methanation over cobalt in the     presence of lOppm of sulfur dioxide has shown an increase in methane production during     two-week run.      b. Identifiers/Open-Ended Terms      te Availability Statement		exico 87501		•	14.	•
A Sutrat (Umit 200 words)  A Astrat (Umit 200 words)  A Astrat (Umit 200 words)  This study was undertaken to continue the examination of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to product synthetic fuels.  While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work.  Work with cobalt, copper, mickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less product ive than carbon monoxide. From the last three metals, methane is the only product formed (besi water). This is a definite improvement over many of the catalysts reported in the sci entific literature, where a major problem is the production of numerous carbon-contain products.  Completion of construction of a second flow system has allowed several questions earlier work (1) to be answered. Continuous methanation over nickel has shown no deer in methane production during a two-week run. Continuous methanation over cobalt in the presence of loppm of sulfur dioxide has shown an increase in methane production during two-week run.  A Decument Analysis a. Descriptors  a. cosATI Field/Group  a. Availability Statement  15. Security Class (This Report) Chiclassified  21. No. of Pages Containing Completion of the rems  b. Identifiers/Open-Ended Terms  Completion of the rems  Completion of the rems  Completion of the rems  Containing the re	-	- ·				. ·
best aveilable copy.     Asstrant (Umit 200 words)     This study was undertaken to continue the examination of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc synthetic fuels.     While most related efforts deal only with carbon monoxide (the predominant oxide :     coal gasification processes), we have included carbon dioxide as well in our work.     Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than     carbon monoxide. From the last three metals, methane is the only product formed (besi water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products.     Completion of construction of a second flow system has allowed several questions :     earlier work (1) to be answered. Continuous methanation over nickel has shown no deer     in methane production during a two-week run. Continuous methanation over nickel has shown no deer     two-week run.  7. Decument Analysis a. Descriptors      descriptors      descriptors      descriptors      descriptors	i. Supplementary Notes		· · ·			
best available copy.     S Astract (Limit 200 words)     This study was undertaken to continue the examination of the utility of borohydrid reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc     gynthetic fuels.     While most related efforts deal only with carbon monoxide (the predominant oxide :     coal gasification processes), we have included carbon dioxide as well in our work.     Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than     carbon monoxide. From the last three metals, methane is the only product formed (besi     water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products.     Completion of construction of a second flow system has allowed several questions :     earlier work (1) to be answered. Continuous methanation over nickel has shown no deer     in methane production during a two-week run. Continuous methanation over nickel has shown no deer     the subject run.     Austration of sulfur dioxide has shown an increase in methane production during     two-week run.     b. Identifiers/Open-Ended Terms     b. Identifiers/Open-Ended Terms						
This study was undertaken to continue the examination of the utility of borohydric reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc synthetic fuels. While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besit water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions earlier work (1) to be answered. Continuous methanation over nickel has shown no decr in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Document Analysis a Descriptors b. Identifiers/Open-Ended Terms 2. COSATI Field/Group 2. Availability Statement 2. Availability Statement 2. Availability Statement 2. Availability Statement		☐ Reproduced from best available com	ру.			•
This study was undertaken to continue the examination of the utility of borohydric reduced transition metals as catalysts for the hydrogenation of carbon oxides to produc synthetic fuels. While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besit water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions earlier work (1) to be answered. Continuous methanation over nickel has shown no decr in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Document Analysis a Descriptors b. Identifiers/Open-Ended Terms 2. Availability Statement 3. Availability Statement 2. Availability Statement 2. No. of Pages Unclassified 2. No. of Pages						· · · ·
reduced transition metals as catalysts for the hydrogenation of carbon oxides to product synthetic fuels. While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less product than carbon monoxide. From the last three metals, methane is the only product formed (beside water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions : earlier work (1) to be answered. Continuous methanation over nickel has shown no deer in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Decument Analysis a Descriptors b. Identifiers/Open-Ended Terms 2. COSATI Field/Group 2. Availability Statement 15. Security Class (This Report) 21. No. of Pages Unclassified 21. No. of Pages		1			E the utility	of borobydride-
synthetic fuels. While most related efforts deal only with carbon monoxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besix water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions : earlier work (1) to be answered. Continuous methanation over nickel has shown no deer in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Decument Analysis a. Descriptors b. identifiers/Open-Ended Terms 2. Availability Statement 2. Availability Statement 15. Security Class (This Report) Unclassified 21. No. of Pages	This study was	undertaken to co	bucinue ine	examination U.	of arrhon ovi	dos to produce
While most related efforts deal only with carbon monxide (the predominant oxide : coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (beside water). This is a definite improvement over many of the catalysts reported in the scientific literature, where a major problem is the production of numerous carbon-contain products.         Completion of construction of a second flow system has allowed several questions : earlier work (1) to be answered. Continuous methanation over nickel has shown no decr in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during two-week run.         7. Decument Analysis a. Descriptors       b. Identifiers/Open-Ended Terms         b. Identifiers/Open-Ended Terms       19. Security Class (This Report)       21. No. of Pages Unclassified		letais as catalys	sts for the	inverogenation .	OT CALDOIL OXE	ies to produce
<ul> <li>coal gasification processes), we have included carbon dioxide as well in our work. Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (beside water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions : earlier work (1) to be answered. Continuous methanation over nickel has shown no decr in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run.</li> <li>7. Document Ansiysis a. Descriptors</li> <li>a. Mentifiers/Open-Ended Terms</li> <li>b. Identifiers/Open-Ended Terms</li> <li>19. Security Class (This Report) Unclassified</li> </ul>	synthetic fuels.	· · · · · · · · · · · · · · · · · · ·	1	aarhan manavi	do (the predom	inant ovide in
Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besive water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions : earlier work (1) to be enswered. Continuous methanation over nickel has shown no decr in methane production during a two-week run. Continuous methanation over cobalt in th presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run.         7. Decument Analysis a. Descriptors         b. Identifiers/Open-Ended Terms         c. COSATI Field/Group         12. Availability Statement	While most rela	ted efforts dea	c onty with	Carbon monoard		
from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (beside water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions : earlier work (1) to be answered. Continuous methanation over nickel has shown no decr- in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Decument Analysis a Descriptors 8. Identifiers/Open-Ended Terms 19. Security Class (This Report) 11. No. of Pages Unclassified 21. No. of Pages	COAL GAGITICATION DT		the frequencies	arrhon diavid		ur work.
carbon monoxide. From the last three metals, methane is the only product formed (beside water). This is a definite improvement over many of the catalysts reported in the sci- entific literature, where a major problem is the production of numerous carbon-contains products. Completion of construction of a second flow system has allowed several questions : earlier work (1) to be answered. Continuous methanation over nickel has shown no decr- in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 17. Document Analysis a Descriptors b. Identifiers/Open-Ended Terms 18. Availability Statement 19. Security Class (This Report) Unclassified 21. No. of Pages	COAL gastication pi	ocesses), we have	ve included	carbon dioxid	e as well in o	ur work.
water). This is a definite improvement over many of the catalysts reported in the scientific literature, where a major problem is the production of numerous carbon-contains products.         Completion of construction of a second flow system has allowed several questions :         earlier work (1) to be answered. Continuous methanation over nickel has shown no decreating methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run.         17. Decument Ansiysis a. Descriptors         b. Identifiers/Open-Ended Terms         18. Availability Statement         19. Security Class (This Report)         11. No. of Pages	Work with cobal	t, copper, nick	el and palla	carbon dioxid dium has resu	e as well in ou lted in methan	ur work. e production
entific literature, where a major problem is the production of numerous carbon-contain products. Completion of construction of a second flow system has allowed several questions : earlier work (1) to be answered. Continuous methanation over nickel has shown no decr in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 17. Document Ansiys's a. Descriptors b. Identifiers/Open-Ended Terms 18. Availability Statement 19. Security Class (This Report) Unclassified 21. No. of Pages Unclassified	Work with cobal from both carbon oxi	t, copper, nick des, with carbo	el and palla n dioxide be	carbon dioxid dium has resulting only slig	e as well in ou lted in methand htly less produ	ur work. e production uctive than
products.       Completion of construction of a second flow system has allowed several questions a earlier work (1) to be answered. Continuous methanation over nickel has shown no decrin methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during two-week run.         17. Document Analysis a. Descriptors         b. Identifiers/Open-Ended Terms         18. Availability Statement         19. Security Class (This Report)         21. No. of Pages	Work with cobal from both carbon oxi carbon monoxide. Fr	t, copper, nick des, with carbo on the last thr	el and palla n dioxide be ee metals, π	carbon dioxid dium has resu ing only slig wethane is the	e as well in or lted in methand htly less prod only product	ur work. e production uctive than formed (beside:
Completion of construction of a second flow system has allowed several questions earlier work (1) to be answered. Continuous methanation over nickel has shown no decr in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Document Analysis a. Descriptors b. Identifiers/Open-Ended Terms c. COSATI Field/Group 18. Availability Statement 19. Security Class (This Report) Unclassified 21. No. of Pages	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c	t, copper, nick des, with carbo on the last thr lefinite improve	el and palla n dioxide be ee metals, m ment over ma	carbon dioxid dium has resu ing only slig wethane is the my of the cat	e as well in ou lted in methand htly less prod only product alysts reporte	ur work. e production uctive than formed (besides d in the sci-
earlier work (1) to be answered. Continuous methanation over nickel has shown no decr- in methane production during a two-week run. Continuous methanation over cobalt in the presence of lOppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Document Analysis a. Descriptors b. Identifiers/Open-Ended Terms c. COSATI Field/Group 18. Availability Statement 19. Security Class (This Report) Unclassified 21. No. of Pages Unclassified	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature,	t, copper, nick des, with carbo on the last thr lefinite improve	el and palla n dioxide be ee metals, m ment over ma	carbon dioxid dium has resu ing only slig wethane is the my of the cat	e as well in ou lted in methand htly less prod only product alysts reporte	ur work. e production uctive than formed (besides d in the sci-
in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during two-week run. 7. Document Analysis a. Descriptors b. Identifiers/Open-Ended Terms c. COSATI Field/Group 18. Availability Statement 19. Security Class (This Report) Unclassified 21. No. of Pages Unclassified	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature, products.	t, copper, nick des, with carbo on the last thr lefinite improve where a major p	el and palla n dioxide be ee metals, m ment over ma roblem is th	carbon dioxide dium has resu- ing only slig methane is the any of the cat- ne production	e as well in ou lted in methand htly less prod only product alysts reporte of numerous ca	ur work. e production uctive than formed (besides d in the sci- rbon-containing
presence of 10ppm of sulfur dioxide has shown an increase in methane production during two-week run.         7. Document Analysis a. Descriptors         b. Identifiers/Open-Ended Terms         c. COSATI Field/Group         18. Availability Statement         19. Security Class (This Report)         21. No. of Pages         Unclassified	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature, products. Completion of c earlier work (1) to	t, copper, nick des, with carbo om the last thr lefinite improve where a major p construction of be answered. C	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me	carbon dioxide dium has resu ing only slig wethane is the my of the cat he production w system has wethanation ove	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas
two-week run. 7. Document Analysis a. Descriptors 5. Identifiers/Open-Ended Terms c. COSATI Field/Group 18. Availability Statement 19. Security Class (This Report) 21. No. of Pages Unclassified 4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature, products. Completion of c earlier work (1) to in methane production	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two-	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 19. Security Class (This Report) 21. No. of Pages Unclassified 4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature, products. Completion of c earlier work (1) to in methane production	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two-	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 8. Availability Statement Unclassified 21. No. of Pages	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of lOppm of	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two-	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 2. Availability Statement 2. Availability Statement 2. Availability Statement 2. Availability Statement 2. No. of Pages Unclassified	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of loppm of	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two-	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 3. Availability Statement 19. Security Class (This Report) Unclassified	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of loppm of	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two-	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (beside d in the sci- rbon-containin l questions fr hown no decrea cobalt in the
c. COSATI Field/Group 3. Availability Statement Unclassified 21. No. of Pages	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of lOppm of two-week run.	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two- 5 sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containin l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 8. Availability Statement 19. Security Class (This Report) 21. No. of Pages Unclassified 4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a construct products. Completion of construction earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two- 5 sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 8. Availability Statement Unclassified 21. No. of Pages	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature, products. Completion of c earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two- 5 sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 8. Availability Statement Unclassified 21. No. of Pages	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature, products. Completion of c earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two- 5 sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
c. COSATI Field/Group 8. Availability Statement Unclassified 21. No. of Pages	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a c entific literature, products. Completion of c earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo on the last thr lefinite improve where a major p construction of be answered. C on during a two- 5 sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
8. Availability Statement       19. Security Class (This Report)       21. No. of Pages         Unclassified       4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
8. Availability Statement       19. Security Class (This Report)       21. No. of Pages         Unclassified       4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
8. Availability Statement       19. Security Class (This Report)       21. No. of Pages         Unclassified       4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
8. Availability Statement       19. Security Class (This Report)       21. No. of Pages         Unclassified       4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
18. Availability Statement       19. Security Class (This Report)       21. No. of Pages         Unclassified       4	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
Unclassified	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a co- entific literature, products. Completion of co- earlier work (1) to in methane production presence of 10ppm of two-week run.	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig wethane is the any of the cat- be production ow system has chanation ove Continuous met	e as well in ou lted in methand htly less prod- only product alysts reporte of numerous ca allowed severa r nickel has s hanation over	ur work. e production uctive than formed (besides d in the sci- rbon-containing l questions fro hown no decreas cobalt in the
Onclassified	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run. 17. Document Analysis a. Descrip b. Identifiers/Open-Ended Term c. COSATI Field/Group	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig methane is the may of the cat- ne production ow system has ethanation ove Continuous met an increase in	e as well in on lted in methand htly less prode alysts reported of numerous ca allowed several r nickel has s hanation over methane produ	ur work. e production uctive than formed (besides d in the sci- rbon-containing 1 questions fro hown no decreas cobalt in the ction during a
Zu. Security Glass (tims roge)	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run. 17. Document Analysis a. Descrip b. Identifiers/Open-Ended Term c. COSATI Field/Group	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu ing only slig methane is the my of the cat he production ow system has thanation ove Continuous met in increase in 19. Security C	e as well in on lted in methand htly less prode only product alysts reporter of numerous ca allowed severa r nickel has s hanation over methane produ	ur work. e production uctive than formed (besides d in the sci- rbon-containing 1 questions fro hown no decreas cobalt in the ction during a
Unclassified,	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run. 17. Document Analysis a. Descrip b. Identifiers/Open-Ended Term c. COSATI Field/Group	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig methane is the my of the cat- ne production ow system has thanation ove Continuous met in increase in 19. Security C Unclass	e as well in on lted in methand htly less prode only product alysts reported of numerous can allowed severa r nickel has so hanation over methane produ	ur work. e production uctive than formed (besides d in the sci- rbon-containing 1 questions fro hown no decreas cobalt in the ction during a
ee ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 2 (Formerly NTIS-35	Work with cobal from both carbon oxi carbon monoxide. Fr water). This is a d entific literature, products. Completion of d earlier work (1) to in methane production presence of 10ppm of two-week run. 7. Document Analysis a. Descrip b. Identifiers/Open-Ended Term	t, copper, nick des, with carbo com the last thr lefinite improve where a major p construction of be answered. C on during a two- sulfur dioxide	el and palla n dioxide be ee metals, m ment over ma roblem is th a second flo ontinuous me week run. (	carbon dioxide dium has resu- ing only slig methane is the my of the cat- ne production ow system has ethanation ove Continuous met in increase in 19. Security C Unclass 20. Security C	e as well in on lted in methano htly less prode only product alysts reporter of numerous ca allowed severa r nickel has so hanation over methane produ lass (This Report) sified lass (This Page)	ur work. e production uctive than formed (besides d in the sci- rbon-containing 1 questions fro hown no decreas cobalt in the ction during a

#### METHANE PRODUCTION FROM CARBON OXIDES OVER BOROHYDRIDE REDUCED TRANSITION METALS

#### Thomas W. Russell, Ph.D. Principal Investigator

#### TECHNICAL COMPLETION REPORT Project ERB No. 76-173

New Mexico Energy Resources Board New Mexico Energy Institute at UNM in cooperation with Division of Natural Science Eastern New Mexico University Portales, New Mexico

January, 1978

#### SUMMARY

This study was undertaken to continue the examination of the utility of borohydride-reduced transition metals as catalysts for the hydrogenation of carbon oxides to produce synthetic fuels.

While most related efforts deal only with carbon monoxide (the predominant oxide in coal gasification processes), we have included carbon dioxide as well in our work. This has resulted in our being contacted by personnel at Jet Propulsion Laboratory to discuss possible incorporation of this work into a Viking Landing on Mars in the 1980's. This may develop into a NASA grant to develop a process to convert components in the Martian atmosphere into a combustible fuel.

Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besides water). This is a definite improvement over many of the catalysts reported in the scientific literature, where a major problem is the production of numerous carbon-containing products.

Our discovery that copper, prepared from sodium borohydride reduction of cupric salts, produces both methane and methyl alcohol is without comparison in the literature. Detailed studies on copper are just beginning.

Completion of construction of a second flow system has allowed several questions from earlier work (1) to be answered. Continuous methanation over nickel has shown no decrease in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during a two-week run.

This last result was instrumental in obtaining a 16-month grant from the Four Corners Regional Commission to study the effects of sulfur on borohydride-reduced metal methanation catalysts (2).

ii

This work was presented at a Colloquium at New Mexico State University in June and will be presented at the National Conference on Technology for Energy Conservation in Albuquerque in January (3). Two manuscripts for submission to the "Journal of Catalysis" are nearing completion.

The Principal Investigator has received unsolicited offers of scientific assistance and collaboration from researchers at the University of New Mexico, Texas Tech University and the University of South Florida as well as Ventron Corporation and Catalysts and Chemicals International. He has recently been invited to present this work before the Second International Conference on Organic Synthesis sponsored by the International Union of Pure and Applied Chemistry (IUPAC) in Jerusalem in September. (Travel funds were, however, not offered.)

Three Masters Theses are resulting from this project. One student is now successfully enrolled in a Ph.D. program at Michigan State University; one ex-student now owns and runs a private chemical lab in Albuquerque; one ex-student has just started working for Diamond Shamrock in Dumas, Texas (4). No undergraduate students working on the projects have as yet graduated.

Travel funds permitted the Principal Investigator to attend the Rocky Mountain Fuel Symposium in Salt Lake City in February. (A paper submitted for the program was never received.) Personnel contacted during other grant-sponsored travel included chemical engineers working on energy research, ERDA contract holders for synthetic fuels research and an ERDA proposal reviewer. Also, a chemist from the University of Oklahoma was brought in as a consultant concerning possible high pressure studies.

Work is continuing on all aspects of the project. A flow system designed to operate at pressures up to 1500 psi should enhance results when finished. Publications, increased publicity, and information obtained during travels and meetings should result in federal funding with the new fiscal year in October.

iii

#### RESULTS AND DISCUSSIONS

#### I. Palladium Catalyst

#### 1. Preparation

Palladium chloride was used exclusively as it was the most accessible source of palladium for this research. It was easily dissolved in small amounts of water, so a 95% ethanol solution was easy to prepare. Further, it has been found that borohydride can chemically reduce certain other common anions, i.e. nitrate, acetate, etc.

In the preparation of an aqueous solution of palladium, a metallic mirror was formed along the beaker walls after a minute amount of borohydride was added. This was witnessed also of nickel by Sterlyadkina (5) and Hofer, et.al., (6). When prepared in an ethanol solution (95%) no metallic mirror was oberved, instead a fine gray material settled to the bottom of the beaker. Sodium borohydride was added until the evolution of gas was complete. When the first catalyst was allowed to drip dry and then placed immediately in the catalyst bed and flushed with hydrogen at 200°C, the glass catalyst bed shattered, sending glass shrapnel through the heating tape and asbestos tape. It was found that the catalyst must air dry for at least 48 hours before it is sufficiently "deactivated". to not cause an explosion of the catalyst bed. It is possible that if the catalyst is indeed deactivated by the 48-hour air dry process, then a stainless steel reactor may be able to contain a catalyst not allowed to set for 48 hours with better methane yield than the catalyst which has been allowed to set. No x-ray studies (which would show % palladium, palladium boride or palladium chloride) were made to determine exact catalyst composition. This combination may be a relevant factor in the methane production.

Production of methane was expressed as percentage with respect to a standard peak, or as percentage composition. Only two carbon-containing compounds (carbon monoxide and methane) were observed.

l

#### 2. Continuous Flow Studies

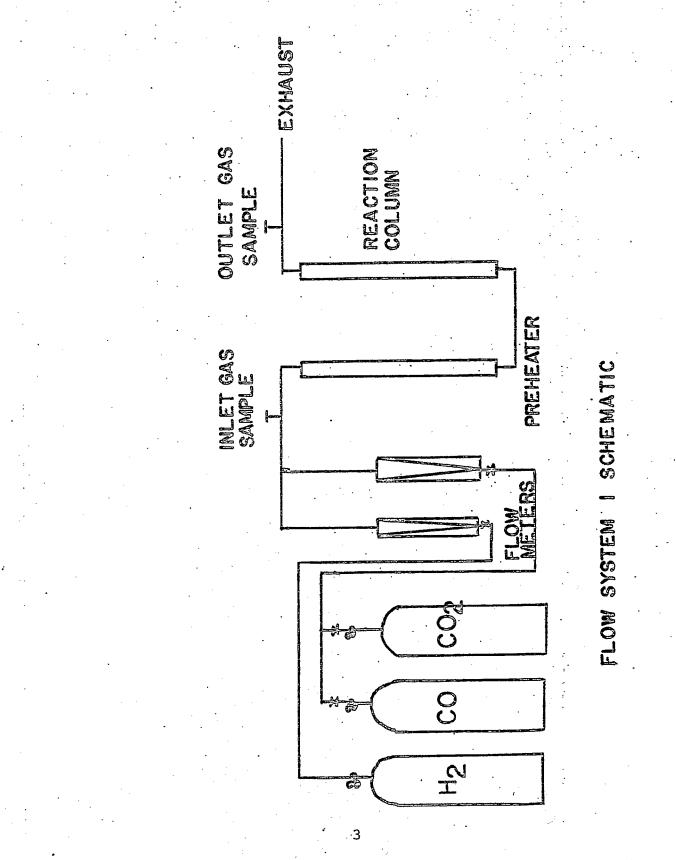
All work was done in the continuous flow systems designed and constructed from Energy Institute funds (Figures 1 and 2). Temperatures were allowed to stabilize before an analysis was made. Effect of temperature on methane production is shown in Figure 3, where the conversion is 48% methane with a 0.36\% supported catalyst at  $420^{\circ}$ C.

Since 0.36% supported catalyst seemed to be a very small percent load, it was decided to see what, if any, effect increasing and decreasing the loading would have on methane yield. Figure 4 shows 33% methane yield on the 9.36% supported catalyst, while a catalyst of 1% loading could not produce 10% methane at what was thought to be an optimum temperature of  $420^{\circ}$ C. A catalyst of 1.02% palladium produced zero percent methane which indicates that of the three, the 0.36% loading is indeed optimum. The actual percentage CO<sub>2</sub> converted to methane on the 1.02% support is shown in Figure 5.

Reactant ratio was a question of concern in previous work and was investigated in this research. Figure 6 indicates that the stoichiometric ratio of four hydrogen to one carbon dioxide produces the best yield of methane. Again, optimum temperature is 420°C. Lower ratios (3:1,2:1) were run which showed no methane production.

Two other parameters were studied. These were solvent and support. Water was used as a solvent for catalyst preparation, but the catalyst so generated afforded less than 1% methane under identical conditions to which the ethanol catalysts were subjected. Two supports were tried also, silica gel and alpha alumina. Figures 3,4,5 and 6 and all silica gel supports. Alpha alumina yielded less than 1% methane under conditions identical to those reported for silica gel.

Another variable studied was flow rate. Original work was done at 7-10 liters per hour. Later, it was decided to reduce the flow to 0.8 liters per hour



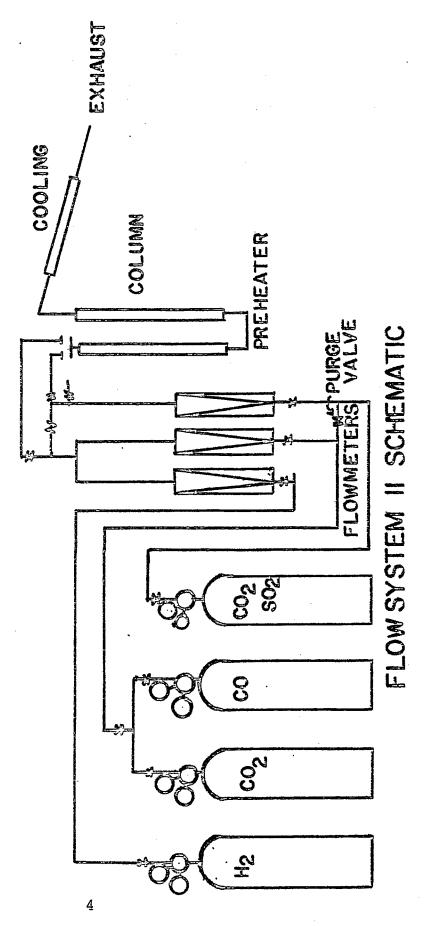
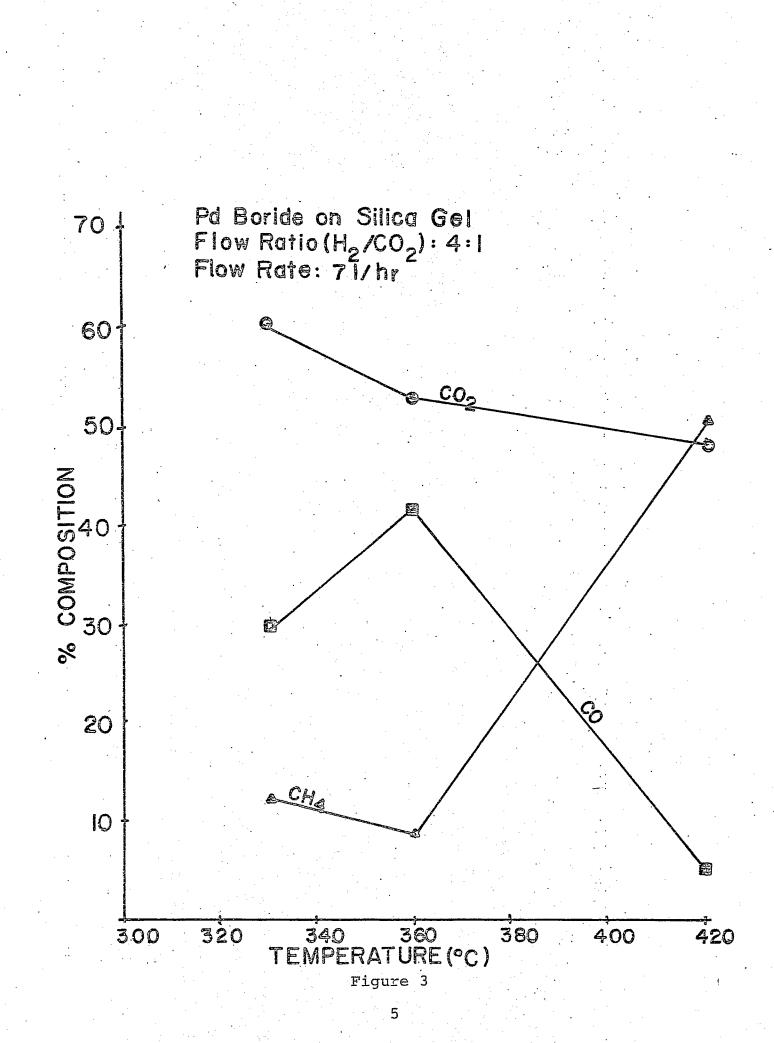
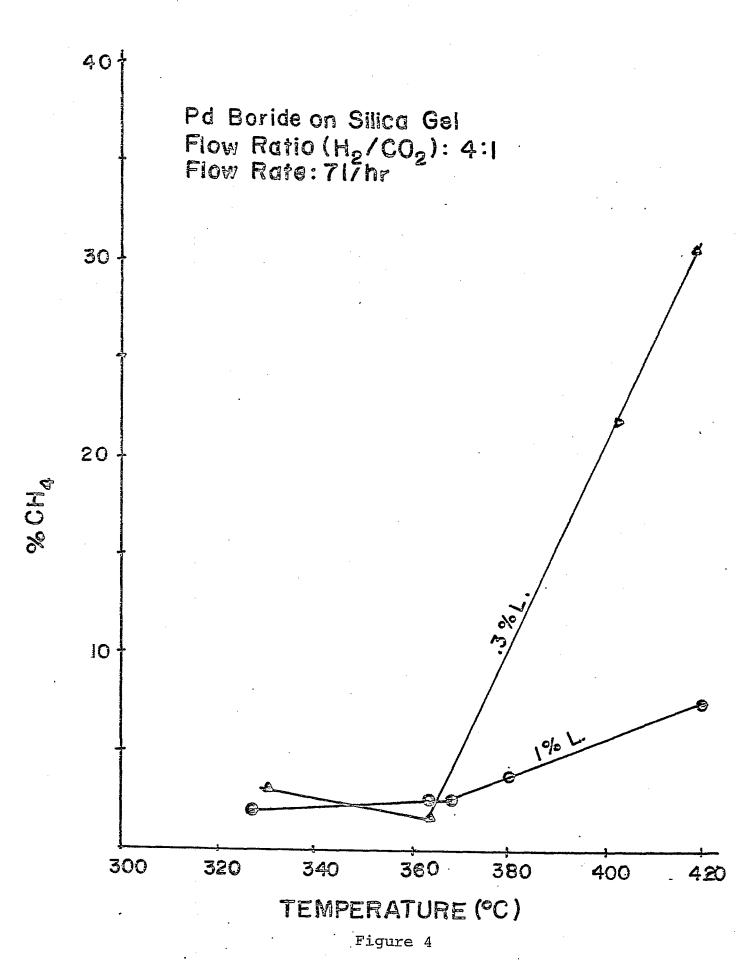
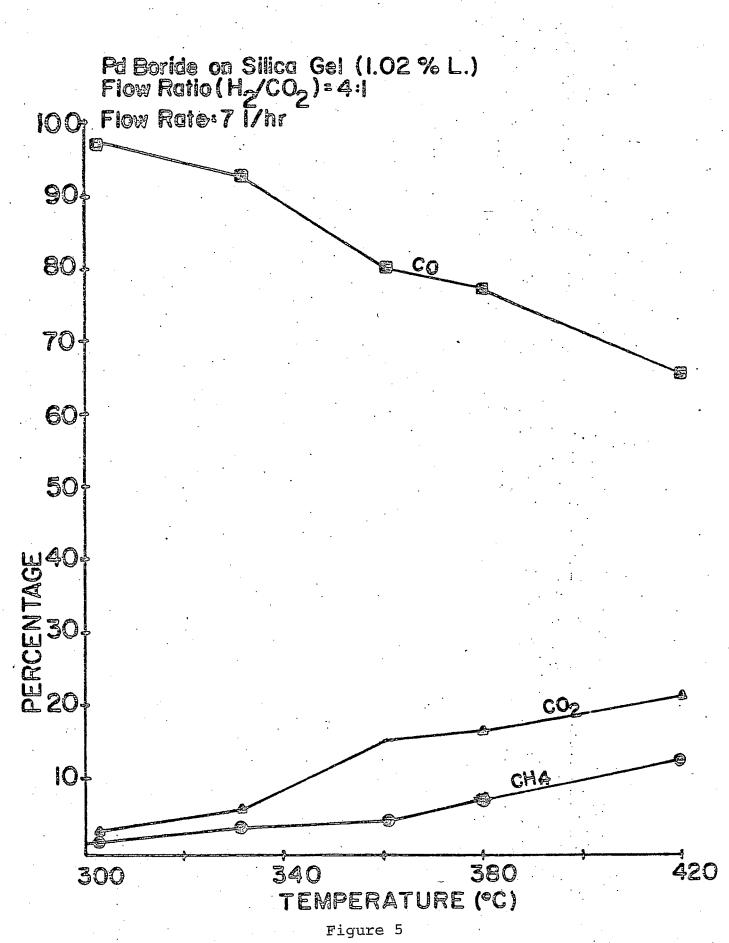


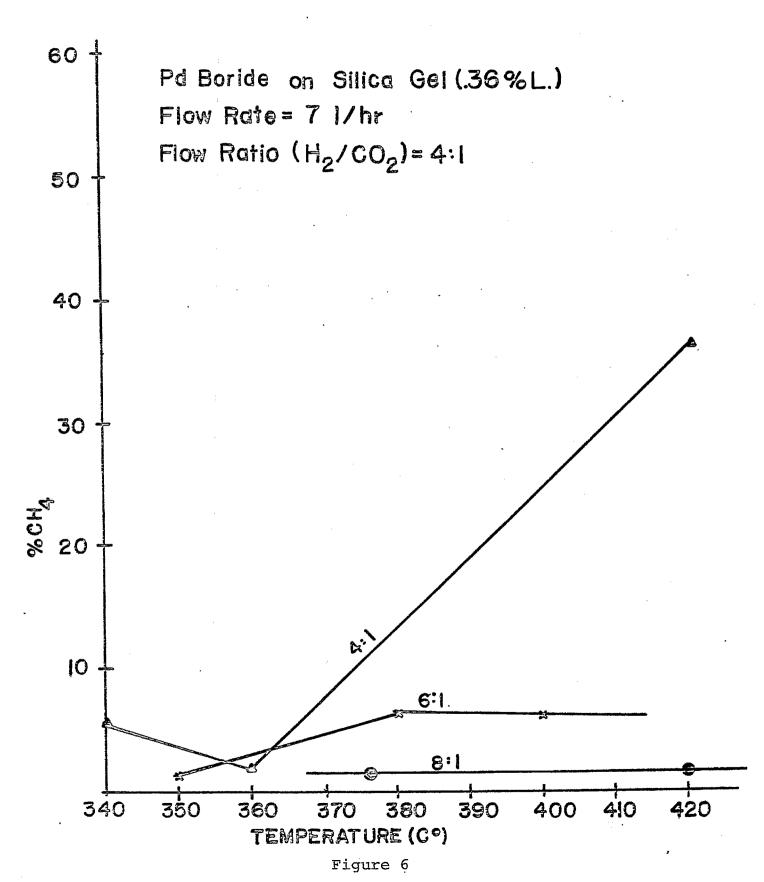
Figure 2













#### Reproduced from best available copy.

with a resultant yield of no methane. However, there was total conversion of carbon dioxide to carbon monoxide at 410°C with reactant ratio 4:1. The catalyst used for this study was 0.36% support.

Work with palladium has ceased pending efforts to ascertain the explosive nature of "new" catalyst.

II. Cobalt Catalyst

1. Preparation

Cobaltous chloride was used exclusively for the same reasons as elaborated for palladium. The preparation of supported cobalt boride in water did not have the metallic sheen as reported with nickel or palladium.

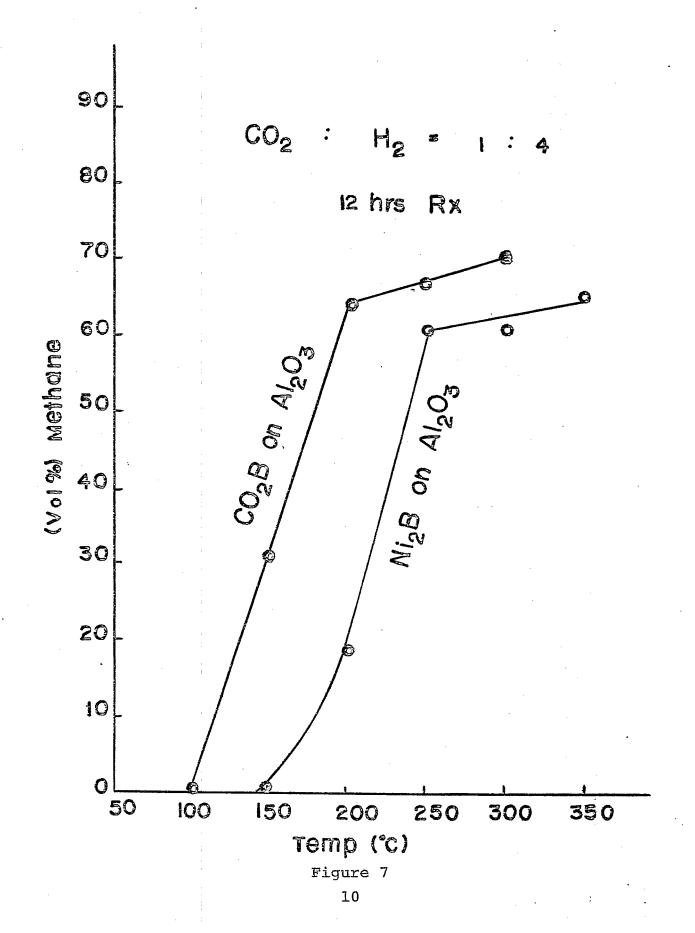
The preparation of the 95% ethanolic catalyst did not show this metallic sheen but produced a fine black catalyst in the beaker and on the support.

The formula for cobalt boride is not known; but for purposes of calculations, the formula  $(CO_2B)_5$ .H<sub>3</sub>(proposed by Maybury, et. al. (7)) was used in calculation of the hydrogen to the weight of catalyst.

2. Static Reactions for Carbon Dioxide

Silica supported cobalt boride made from ethanolic solution was gray at the start of the reactions. The static reactions were carried out in the Parr reactors with appropriate reactant gas ratios of 4 moles hydrogen per mole of carbon dioxide. Temperatures were varied from 100°C to 350°C at an initial pressure at room temperature of 150 psig. All runs were carried out for 12 hours.

Production of methane is expressed as percent composition. The only other products noted were carbon monoxide and water. Percentage compositions of methane are shown in Figure 7. The maximum production noted was 6.8% at 350°C, with production of mathane starting with the 100°C run. Also shown on Figure 7 are the results reported previously from nickel. These comparative results are the basis for the supplemental request for funds to construct a flow system to operate at pressures up to 1500 psi.



3. Continuous Reaction for Carbon Dioxide

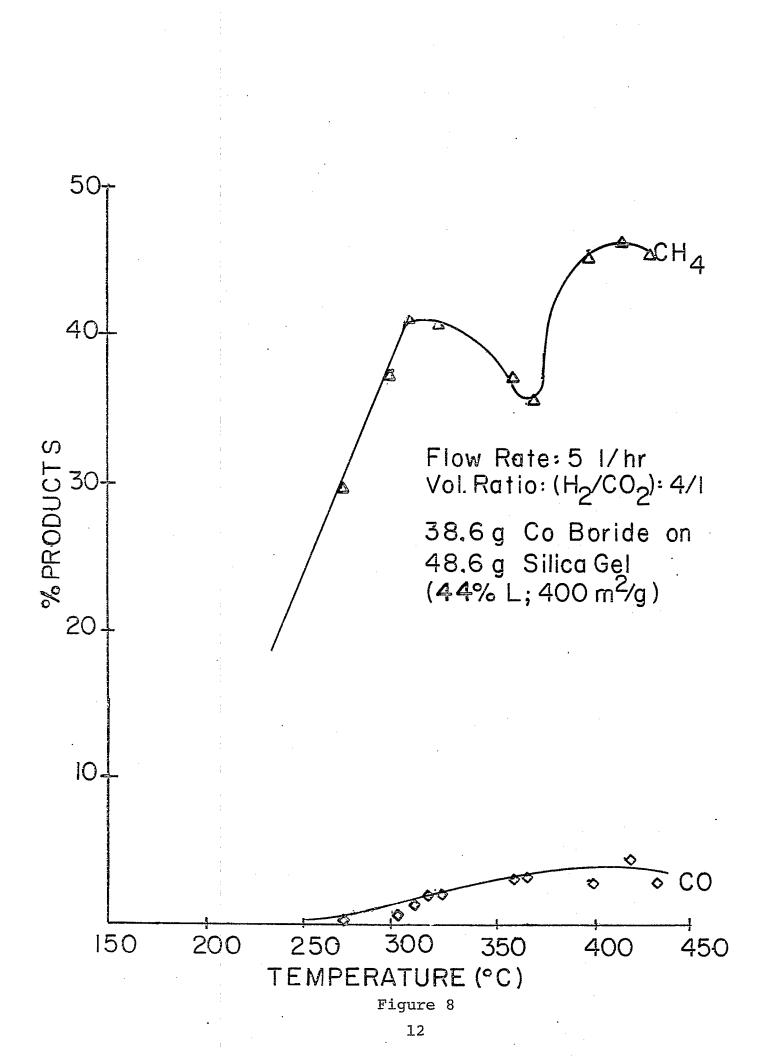
Because of the results from the hydrogenation of carbon dioxide over cobalt boride in the static reactor, cobalt boride was expected to exhibit significant methane production in a practical continuous reaction at atmosphere pressure. The flow systems shown in Figures 1 and 2 were used for cobalt studies, also.

All attempts to produce active aqueous solution catalysts proved unsuccessful. All cobalt catalysts used in the continuous flow system were made in 95% ethanol. The catalyst was also made by an immersion process. The process of flash evaporation process proved to be of little importance in comparison. This was probably due to the drawing of the hydrogen blanket by the vacuum placed on the evaporation apparatus and the inevitable replacement of it with air.

A. Reactions at Various Temperatures

A 44% cobalt boride catalyst on silica gel  $(400m^2/g)$  was used with the stoichiometric reactant ratio of 4 moles of hydrogen to one mole of carbon dioxide with a flow rate of 5 l/hr. The conversion of carbon dioxide to methane and carbon monoxide are plotted versus temperatures in Figure 8. The maximum conversion of carbon dioxide to methane in the temperature range covered was about 47%. Infrared spectra of the gas products showed methane production beginning around  $170^{\circ}$ C. The conversion of carbon dioxide to carbon monoxide seemed noncompetitive. It started at about 230°C and increased until about 400°C, about which it started to decrease with increasing temperature.

Another catalyst was made having 4% of cobalt boride on micron silica gel. The methane and carbon monoxide production of this catalyst is shown in Figure 9. This shows that there is tendency of the carbon dioxide to carbon monoxide conversion to follow the methane production. The maximum conversion that was seen was 18% for the low-loaded catalyst. The maximum efficient temperature was not indicated by this study.



#### B. Reactions at Various Flow Rates

With the 4% loaded catalyst and a volume ratio of 4 moles of hydrogen to each liter of carbon dioxide. The comparison of the reaction at 5 liters/hour (with various temperatures as shown in Figure 9) to the 10 liters/hour runs with various temperatures as shown in Figure 10, show what was expected that increased flow rate would decrease reaction conversion, (Figure 11).

C. Reactions at Various Reactant Ratios

With the 4% loaded catalyst and 10 liters per hour flow rate, the number of moles of hydrogen per mole of carbon dioxide was varied from 1 to 10 by units. The conversion increased rapidly to a ratio of about 8 and tended to level off above that. The amount of conversion to carbon monoxide also increases with increased amount of hydrogen, (Figure 12).

D. Reactions in Relationship to Sulfur Dioxide Poisoning

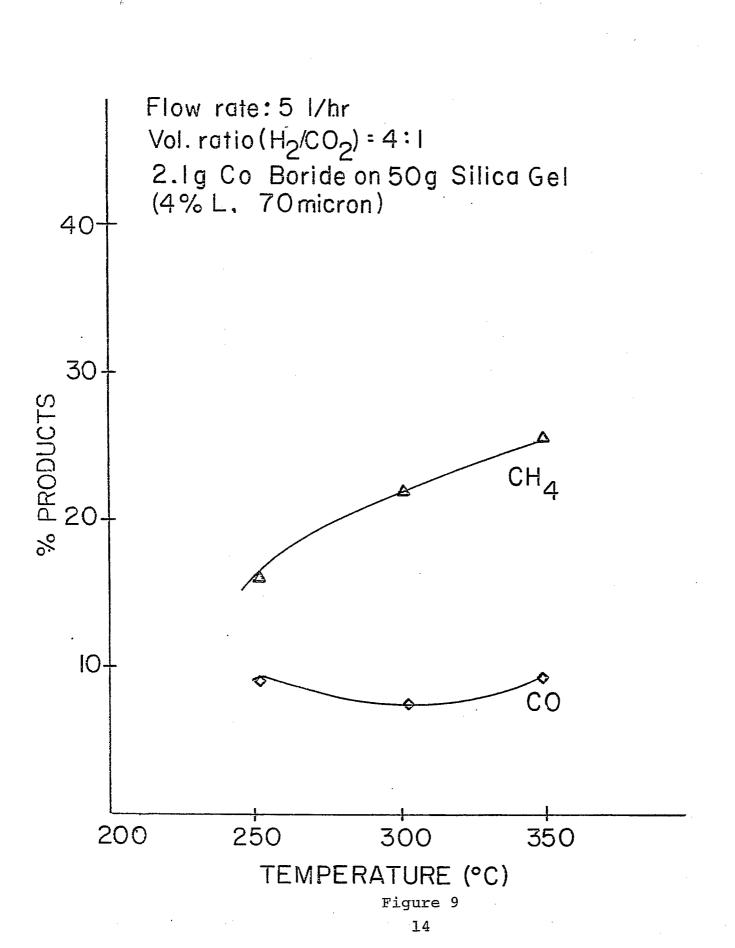
Dalla Betta, et. al. (8) reported that sulfur compounds had a marked decrease in the activity of many methanation catalysts. A study of the effect of sulfur dioxide was initiated with silica gel supported cobalt catalyst (8%). It was found with a reactant ratio of 4 liters of hydrogen to each liter of carbon dioxide with 10 ppm sulfur dioxide as sulfur poison that no decrease in methane production and no conversion of the sulfur dioxide to sulfur or hydrogen sulfide was found, Table 1.

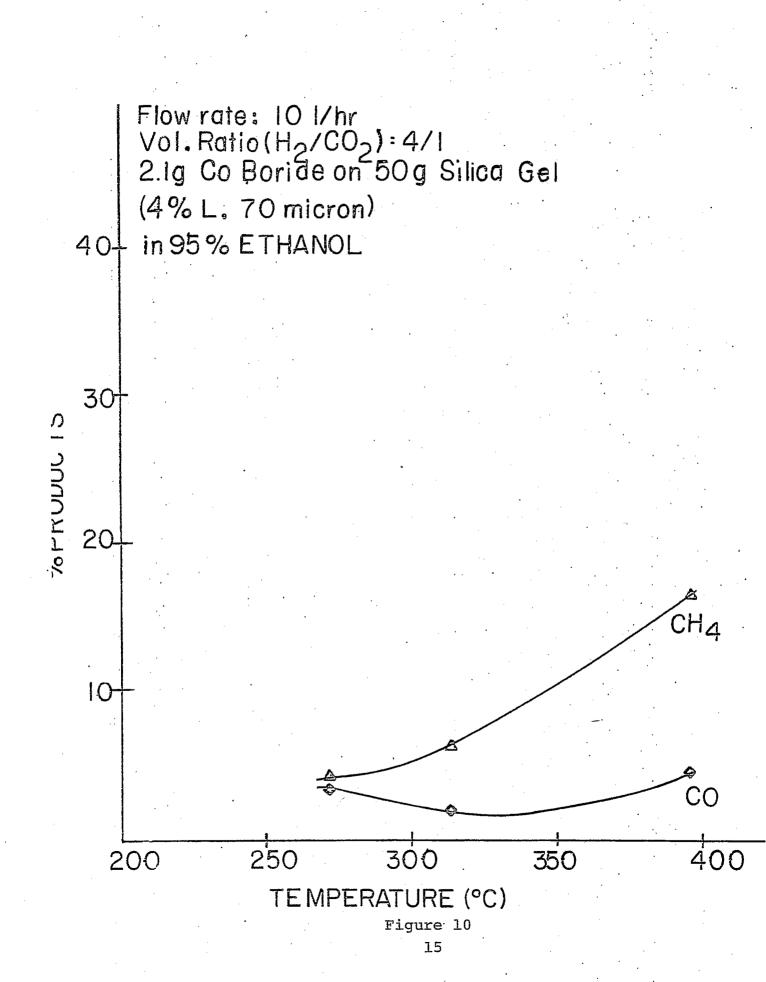
This run is the basis for the contract from the Four Corners Regional Commission to continue study in this area.

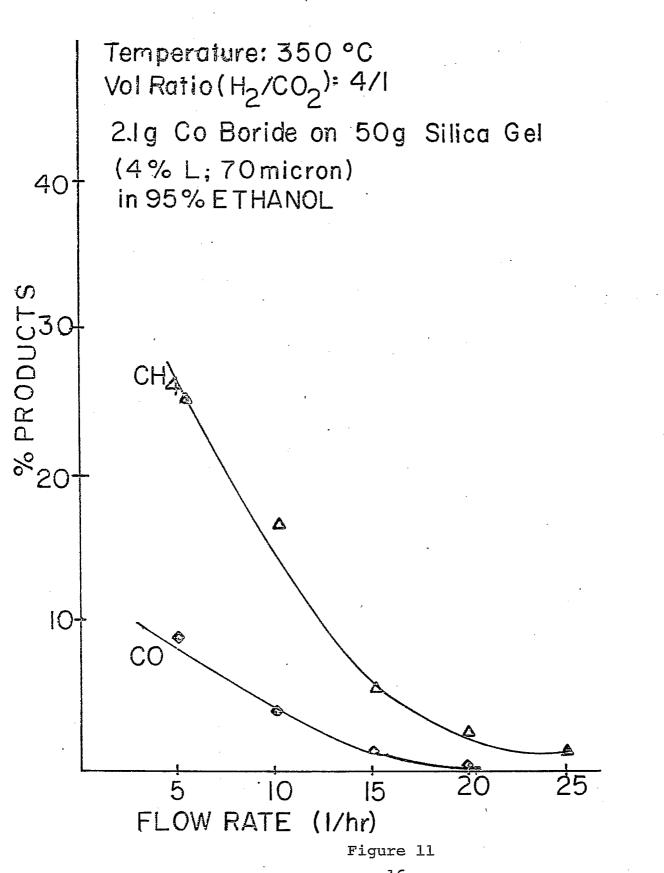
4. Continuous Reactions of Carbon Monoxide

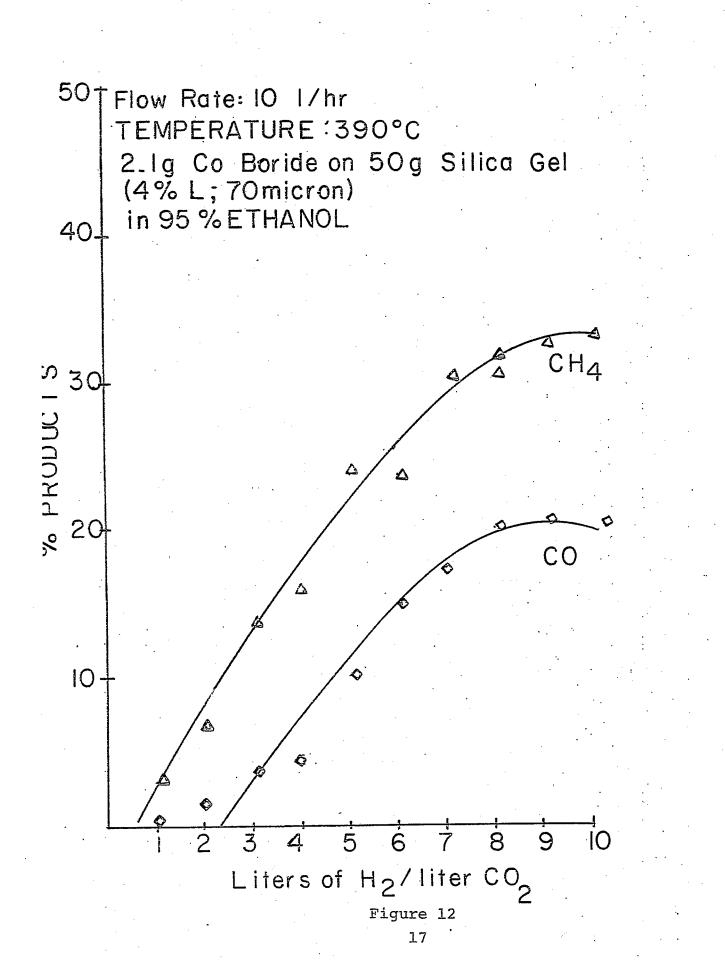
A. Reactions at Various Temperatures

The 4% loaded catalyst was run with a volume ratio of 3 moles of hydrogen to each mole of carbon monoxide. The conversion of carbon monoxide to methane and carbon dioxide is shown in Figure 13.





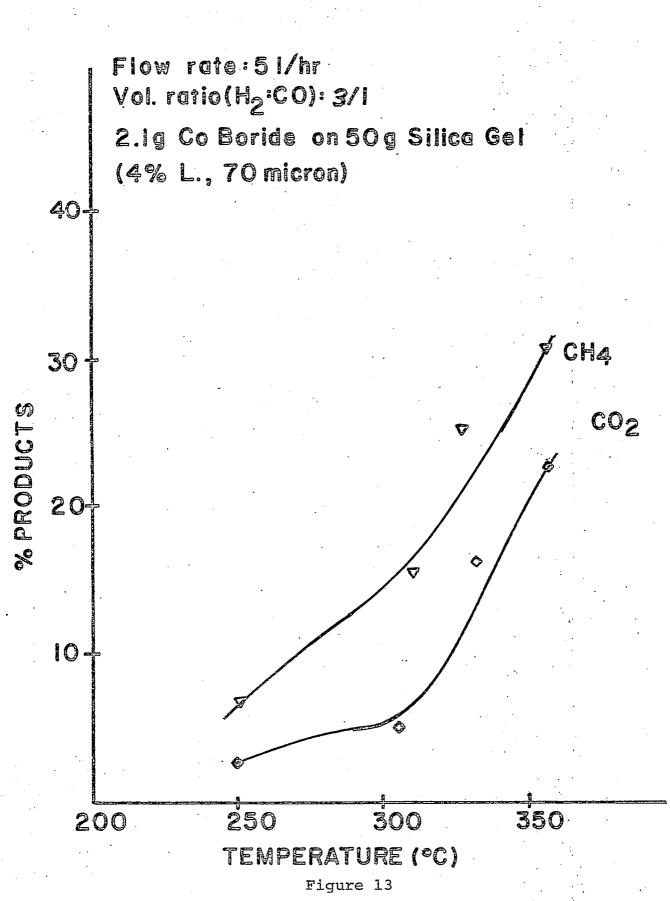




Time in Hrs.	Temp. <sup>O</sup> C	%CO	%сн <sub>ц</sub>	~ %co <sub>2</sub>
0	385	7.18	I64	92.17
10	418	15.11	1.27	83.62
25	397	13.69	1,17	85.13
29	401	13.11	1.00	85.88
58	400	16.21	1.24	79.39
60	415	24.11	2.04	73.83
70	390	14.47	1,46	84.06
76	412	19.50	1.87	78.75
97	388	31.71	3.74	65.54
101	358	30.78	3.29	65.92
106	364	31.54	3.51	65.3

Table I

#### Effects of Sulfur Poisoning of Methanation of Carbon Dioxide





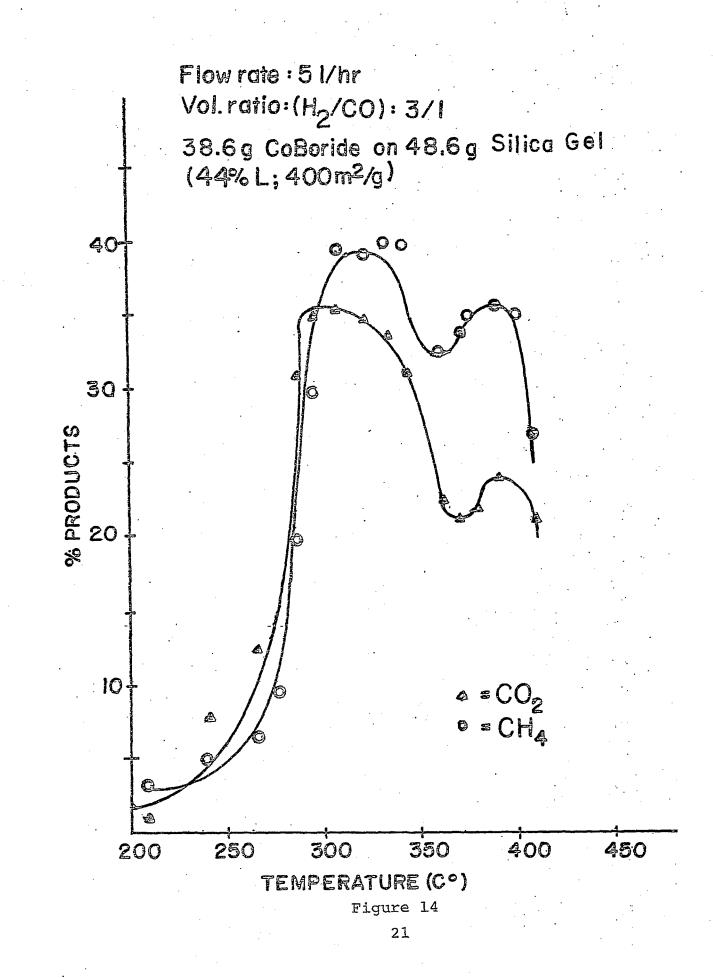
The 44% catalyst was run with a volume ratio of 3 moles hydrogen to 1 mole of carbon monoxide having a maximum conversion to methane of 40% at  $346^{\circ}$ C and with another smaller peak at  $397^{\circ}$ C and 35% methane conversion (Figure 14). This curve is similar to one reported by Kurita in 1961 (9).

B. Reactions at Various Flow Rates

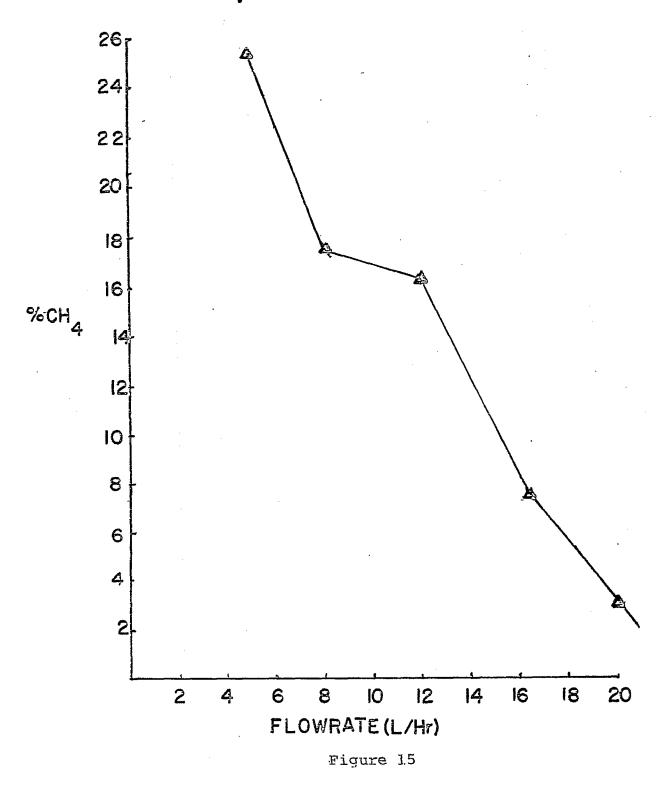
Using a 30% cobalt boride catalyst supported on #70-micron silica gel, reactant gas flow rate was varied from 1 to 10 liters per hour. The gases again produced a decrease in methane production with an increase in flow rate (Figure 15).

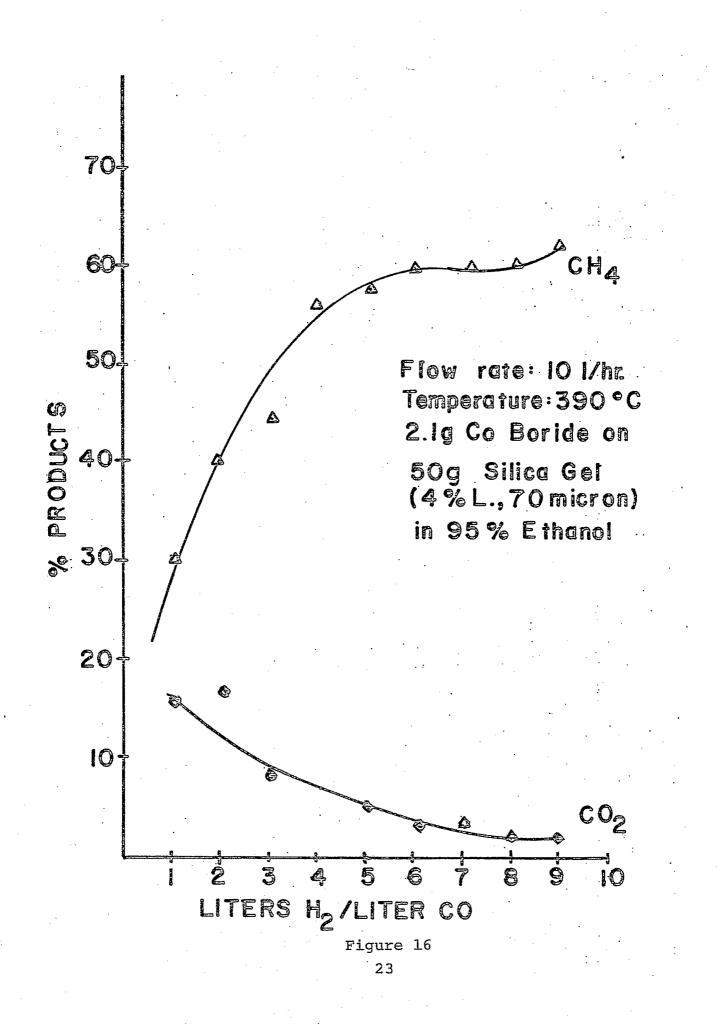
C. Reactions at Various Reactant Ratios

With the 30% cobalt catalyst supported on 70-micron silica gel, reactant ratios were varied from 1 to 10 liters of hydrogen for each liter of carbon monoxide. The increase of hydrogen resulted in a steady increase in methane production (Figure 16).



Temperature 352° Vol Ratio 3:1 Cobalt boride on Silica gel 34% L, 70 miCron





#### Esperimental

#### I. Equipment

Parr Model 4563 minireactors with automatic temperature controls (purchased on a previous ERB contract) were used for all static reactions. Two flow systems were designed and built for the continuous flow work. One flow system is used for flow gas studies only (Figure 1). Both are equipped with semi-automatic temperature control. At present, 2.5 x 25cm columns are being used for catalyst bed containers. Catalyst column, preheater column and cooling condensors are all Pyrex glass. Some rubber and copper tubing are used in the first system. The second system was designed to allow for study on the effects of sulfur compounds, and is constructed of stainless steel, (Figure 2). Rotometers are used to determine flow rates.

Fisher 2400 and Aerograph Model A-90-P gas chromographs were used for most qualitative and quantitative analyses using thermal conductivity detectors. Perkin-Elmer Model 281 infrared spectrophotometer (purchased with this grant) was used to confirm qualitative analyses.

Gas-tight 5ml syringes were used to obtain gas samples directly from the static and flow reactors for gas chromatographic analysis. Liquid phase sampling was done using Hamilton 701-N microliter syringes. The gas chromographic columns used for gas analyses were Molecular Sieve 13 x ( $\frac{1}{4}$ " x 8'), Porapak Q 100/200 ( $\frac{1}{4}$ " x 8') and Spherocarb 100/120 ( $\frac{1}{8}$ " x 4'). Ethofat 1% on Fluoropak ( $\frac{1}{4}$ " x 5m) was for formaldehyde, water, and methanol analysis. Carbowax 20M 20% on Chromosorb W and XF-1150 15% on Chromosorb W were prepared for analysis of possible higher molecular-weight hydrocarbons.

#### II. Materials

All chemicals used were reagent grade, except the raw systhesis gases. Cobaltous chloride, methanol and formaldehyde were from Fisher Scientific. Ethanol was from U.S. Industrial Chemicals. Sodium borohydride, silica gel aluminum oxide and palladium chloride were products of Ventron Corporation. Molecular Sieve 13X was from Linde. Ethofat 80, Chromosorb W-AW 45/60, Carbowax 20M, and XF-1150 were from Supelco Company. Spherocarb 100/120 was from Analabs.

The raw systhesis gases were commercial grade gases from Linde Division of Union Carbide Corporation. Hydrogen had almost no impurities, as determined by gas chromotography and infrared spectroscopy. Carbon dioxide contained only trace amounts of nitrogen and oxygen. Carbon monoxide contained only trace amounts of methane and carbon dioxide. Helium was used as carrier gas for gas chromotography. Methane and dimethyl ether were high purity gases obtained from Linde for standards. All stainless steel used was type 316 or 304. Temperature monitoring was by iron-constantan thermocouples.

III. Preparation of Catalysts

1. Palladium

Fifty grams of support were immersed in 100 ml of solvent and palladium chloride was added to yield a chosen percentage of supported catalyst i.e., 0.5g PdCl<sub>2</sub> added would yield 0.60% supported catalyst. The resultant mixture was stirred frequently and kept in a dessicator until all solvent had evaporated. Absorption/ adsorption was complete. A solution of sodium borohydride, dissolved in a small quantity of water with absolute ethanol added to yield a 95% solution, was added to the supported palladium (II) until the reduction was complete. The reaction was believed to be complete when the evolution of gas did not occur when more borohydride solution was added. The catalyst was allowed to air dry and was then placed in the flow system.

2. A cobalt catalyst prepared from aqueous solutions (similar to one prepared for nickel in previous work) proved ineffective in the methanation process, so this method was abandoned. All cobalt catalysts were prepared in 95% ethanol solutions.

3. Cobalt Catalyst by Immersion Process

A selected support of known weight was immersed in a solution of 5ml of 1M cobaltous chloride in 95% ethanol solution per gram of support for 4-5 hours. The supported metal salt was then drip-dried of excess cobalt chloride solution. It was then cooled and 25ml of freshly prepared 0.1M 95% ethanolic sodium borohydride solution was allowed to react for 2-4 hours in a refrigerator. The liquid phase was then decanted and discarded.

Another 125ml of freshly prepared sodium borohydride solution per 100 of support was then added and again allowed to react for 2-4 hours. This was repeated until there was no more reaction, as evidenced by evolution of hydrogen gas. The catalyst was washed twice with water, then three times with 95% ethanol. It was predried to a powder at  $70^{\circ}$  to  $80^{\circ}$ C. It was then packed into the catalyst column of the flow system and dried under hydrogen flow at temperatures between  $150^{\circ} - 200^{\circ}$ C for 4 hours.

4. Cobalt Catalyst by Flash Evaporation

A selected support of known weight was placed in a flask of sufficient size to hold the support and liquid cobalt chloride solution without loss of part of contents when placed on the flash evaporator. A solution of 5ml of cobaltous chloride in 95% ethanol solution per gram of support was then placed in the flask. The flask was placed on the flash evaporator for stirring to insure sufficient mixing of support. After about 4 hours, a vacuum was placed on the solution and the water under the flask heated to 70°C to remove excess solvent.

When solvent evaporated, the flask was removed and 125ml of .IM sodium borohydride in 95% ethanol solution per 100g of support was added to the flask for reaction. The flask was returned to the evaporator for reaction under constant stirring and a slight vacuum. Cool water was run over the flask until completion of the reaction.

The flask was again removed and the solution decanted. Fresh sodium borohydride solution was introduced and the above method repeated until fresh borohydride solution no longer gave a reaction with cobalt salt.

The flask was again removed and the solution filtered. The catalyst was washed twice with water and three times with 95% ethanol. The wet catalyst was returned to the evaporator and dried under a vacuum at 70°C until powder dry.

The catalyst was then placed in a flow system column and dried at  $150^{\circ} - 200^{\circ}$ C under hydrogen flow for 4-5 hours.

5. Preparation of Unsupported Cobalt Catalyst

Previous work indicated that unsupported nickel catalyst was colloidial in nature and unusable as a flow system catalyst. A cobalt catalyst with a large particulate size was produced by the following procedure: A 300ml aloquot of a LM solution of cobaltous chloride in 95% ethanol was placed in a beaker. Sodium borohydride (.15 mole) was added in small amounts to the beaker allowing time for the reaction to slow. The beaker was cooled in an ice water bath. The solution was allowed to react to completion with the settling of the cobalt catalyst. The catalyst was then filtered and washed as before. The catalyst was dried in an oven at  $70^{\circ} - 80^{\circ}$  until powder dry and then under hydrogen flow at  $150^{\circ} - 200^{\circ}C$  for 4-5 hours.

6. Determination of Catalyst Loading on Support

The support was weighed before preparing the catalyst. The catalyst was made, dried and weighed; and the catalyst loading was calculated by the formula:

% loading =  $\frac{(wt \text{ of supported catalyst}) - (weight of support)}{(wt of supported catalyst)} x 100$ 

IV. Static Reactions with Cobalt

1. Hydrogenation of Carbon Dioxide

A Parr reaction bomb was charged with wet supported catalyst made in 95% ethanol. The catalyst was dried at 150<sup>°</sup> under 100 psig of hydrogen by releasing and charging every half hour and repeating this three to four times. Finally, it was cooled to room temperature in a hydrogen atmosphere.

The hydrogen was vented. Carbon dioxide was introduced and vented several times, finally charged to 30 psig. Then, hydrogen was introduced to 150 psig. This set a reactant ratio that was close to the stoichiometric relationship of 4 moles hydrogen to 1 mole carbon dioxide. The reactor was turned on and the reaction temperature selected. The reaction was considered started at the time the desired temperature was reached. At this time, time and pressure were recorded and at regular intervals until reaction time was completed.

2. Hydrogenation of Carbon Monoxide

The catalyst was introduced and dried as described above. Carbon monoxide was introduced and vented several times, finally being charged to 40 psig. Hydrogen was then added to 150 psig to bring the reactant reaction to approximately 3 moles hydrogen to 1 mole carbon monoxide. The reactor was turned on and the reactor temperature selected. Time and pressure were recorded at regular intervals.

V. Continuous Reactions

The flow systems shown in Figure 1 and 2 were used for the continuous reactions. The flow rate, reactant ratio, preheater temperature and column temperature were selected. After the temperature had been reached and system parameters had stabilized the outlet gases were sampled.

Experiments were performed varying the parameters of reaction temperature reactant, flow rate, reactant ratios and the carbon oxide.

VI. Analysis

1. Qualitative

Porapak Q had a good performance in the separation of methane and carbon dioxide. Hydrogen, air, and carbon monoxide peaks were not separable in this column. Molecular sieve 13X separated carbon monoxide and air. The separation order was hydrogen, oxygen, nitrogen, carbon monoxide and methane, with carbon dioxide coming out as an insignificant peak.

Spherocarb was selected later because it would separate all the gases. Using temperature programming from  $60-200^{\circ}C$ , the order of separation was hydrogen, oxygen, nitrogen, carbon monoxide, methane, carbon dioxide and water.

The operating condition of the columns were: Poropak Q ( $\frac{1}{4}$ " x 8') and Molecular Sieve 13X ( $\frac{1}{4}$ " x 8') temperatures of 200° for the injector, 50° for the column and 250° for the detector. The filament current to the thermoconductivity detector was 150 mA with helium as the carrier gas at a flow rate of 40-45ml/min.

Spherocarb 100/120 (1/8" x 4') had operating temperatures held at  $60^{\circ}$ C for 3 minutes programmed at a rate of  $20^{\circ}$ C per minute to  $200^{\circ}$ C; then held for 4 minutes at a temperature of  $250^{\circ}$  and an injector temperature of  $200^{\circ}$ C. The thermal conductivity detector filament current was 150 mA with helium as carrier gas at a flow rate of 25-30ml/min.

The qualitative analyses were confirmed by infrared. The individual spectrums were compared with the spectrum of an authentic sample for each suspected component of the gas sample mixture. The infrared sample was in a locm gas cell.

2. Quantitative Analysis

Composition of gas sample was computed as a corrected area:

gas A peak area of authentic gas sample std

The gas-corrected areas were added to get a gas total area and used to obtain percentage compositions. One ml was used as sample size for the reaction gas

mixtures and standards of methane air, carbon monoxide, and carbon dioxide. Since there were difficulties in setting up internal standards, response factors were used for each of the gases. These response factors were checked frequently and one of the standards was run each time. Percentage conversion of carbon dioxide or carbon monoxide to methane was calculated from the following equation:

%conversion to methane = <u>%methane</u> x 100 sum of % all gas products

The percent conversion of carbon monoxide or carbon dioxide to other carboncontaining products could be calculated with similar equations by substitutions in the numerator the appropriate percent composition.

All reactions were repeated and reproducable data were obtained. VII. Palladium Recovery Procedures

When the catalyst was found to yield less than 10% methane, when compared to previous runs, it was removed from the flow system. More sodium borohydride solution was added until the evolution of gas was complete. All "dead" palladium catalysts reacted with the borohydride. After the catalyst was again air dried, it was placed in the catalyst column once and another run was made. The results were the same as when the catalyst was initially run. The catalyst is active at flow ratios of 4:1 ( $H_2:CO_2$ ) for about 15 days, but for peak performance it should be regenerated every 6-7 days.

Such degeneration has not been noted with cobalt or nickel.

The palladium can be recovered by adding aqua regia and dissolving the palladium. The palladium-containing solution is decanted from the support and is then reduced with borohydride to produce what is believed to be palladium boride.

#### VIII. Blank Runs

To determine the effect of the catalyst (proof that the metal and borohydride are necessary), a catalyst support with sodium borohydride and one of support and metal chloride were run as blanks. The blanks yielded less than 1% methane at the optimum conditions and less yield at other temperatures and ratio of reactants. No other products were observed during these runs.

#### REFERENCES

- 1. T. W. Russell, Technical Completion Report, Project BEF No. 152, New Mexico Energy Institute at the University of New Mexico, Albuquerque, September, 1976.
- T. W. Russell, "Methane by Recycling Fossil Fuels," Technical Assistance Grant Four Corners Regional Commission, Albuquerque, January 1, 1978, to April 20, 1979.
- 3. T. W. Russell, T. L. Bogey and H. S. Tung, "Borohydride Reduced Metal Catalysts in Methanation Studies," Second National Conference and Exhibition on Technology for Energy Conservation, Albuquerque, January, 1978.
- 4. H. S. Tung, "Methanation of Carbon Oxides over Borohydride Reduced Nickel Salts", Master of Science Thesis, Eastern New Mexico University, Portales; J. P. Grover, "Methanation of Carbon Dioxide over Borohydride Reduced Palladium Salts", Master of Science Thesis, Eastern New Mexico University, Portales; T. L. Bogey, "Methanation of Carbon Oxides over Borohydride Reduced Cobalt Salts", Master of Science Thesis, Eastern New Mexico University, Portales.
- 5. Z. K. Steryladkina, N. N. Mal'tseva, G. D. Frangulyan, B. D. Polkovnikov, and V. M. Bakulina, Izv. Akad. Nauk., SSR., Ser. Khim., 1240 (1972).
- L. J. E. Hoffer, J. F. Shultz, R. D. Panson, and R. B. Anderson, <u>Inorg. Chem.</u>, <u>3</u>, 1783 (1964).
- 7. P. C. Maybury, R. W. Mitchell, and M. F. Hawthorne, J.C.S., Chem. Comm., 534 (1974).
- 8. R. A. Dalla Betta, A. G. Piken and M. Shelef, J. of Catal, 40, 173 (1975).
- 9. H. Kurita and Y. Tsutsumi, Nippon Kagaku Zasshi, 82, 1461 (1961).

# SATISFACTION GUARANTEED

the item you receive NTIS strives to provide quality products, reliable service, and fast delivery if we have made an error in filling your order. Please contact us for a replacement within 30 days if E-mail: info@ntis.gov is defective or

Phone: 1-888-584-8332 or (703)605-6050

# Reproduced by NTIS

National Technical Information Service Springfield, VA 22161

# This report was printed specifically for your order from nearly 3 million titles available in our collection.

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

### About NTIS

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at <u>http://www.ntis.gov</u>.



**Ensuring Permanent, Easy Access to U.S. Government Information Assets** 



.

U.S. DEPARTMENT OF COMMERCE Technology Administration National Technical Information Service Springfield, VA 22161 (703) 605-6000

.