



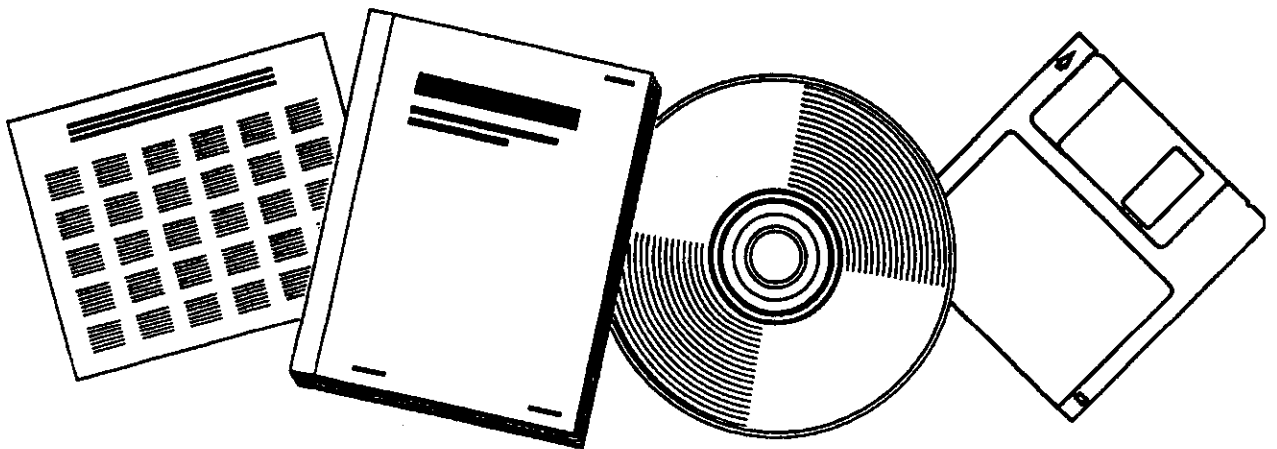
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DEVELOPMENT OF CATALYSTS FOR COAL CONVERSION

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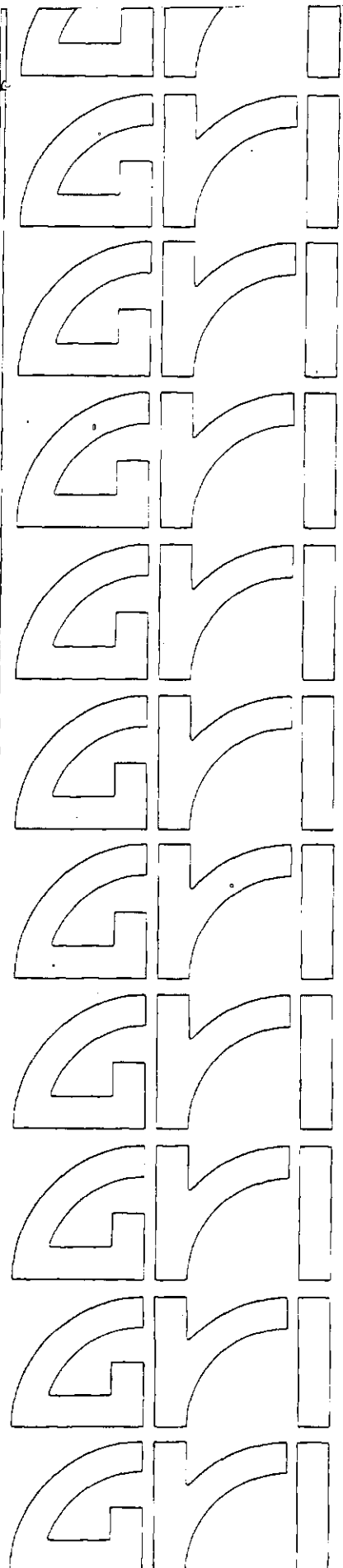
**DEVELOPMENT OF CATALYSTS FOR
COAL CONVERSION**

ANNUAL REPORT FOR 1979

**Gas Research Institute,
10 West 35th Street,
Chicago, Illinois 60616**

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DEVELOPMENT OF CATALYSTS FOR
COAL CONVERSION

ANNUAL REPORT FOR 1979

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FOR

GAS RESEARCH INSTITUTE

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RESEARCH SUMMARY

Title: Development of Catalysts for Coal Conversion
GRI Code: 79/0078
GRI Contract number: 5014-322-0115

Contractor: Catalysis Research Corp.

Principal Investigator: John Happel

Time Span: 12 months

Major Achievements: A major breakthrough was accomplished in the development of a new family of catalysts. These formulations have such high activity in the presence of high concentrations of CO₂ that they can be used in a process cycle to produce syngas with only one acid gas removal step. Steam consumption will also be reduced from that required in conventional methanation processes.

Recommendations: Catalyst development work should be continued since there is the possibility of achieving still higher activity in the presence of CO₂. Bench scale tests should be instituted as soon as adequate economic studies can be made to indicate optimum preliminary process design.

Description of Work Completed: Eighty six new catalyst formulations and one hundred seventy three reduction and evaluation tests were conducted. A wide variety of potential catalytic material was tested. The best catalysts were further tested at high pressures and with gas feeds simulating raw syngas from several different types of processes.

GRI COMMENT

This report documents the ongoing research work performed during this period on the development of catalysts for the direct conversion of synthesis gas to methane. A major breakthrough was accomplished in the development of a new family of sulfur tolerant catalysts that have high methanation activity in the presence of high concentration of CO_2 . With these catalysts the ratio of CO_2 to H_2O production is much higher implying that methane is produced directly from equal amounts of H_2 and CO without employing steam.

This work is conducted in conjunction with work being performed at the Institute of Gas Technology and at SRI International. Therefore, this report represents only a part of the complete study in the ongoing development program.

Overall Project Objective

Present goals are aimed at the development of processes which will methanate synthesis gas directly without removal of the acid gases hydrogen sulfide and carbon dioxide before methanation. The objective of the methanation process itself is to convert synthesis gas directly without combining this process with the water gas shift reaction. In this way substantial economies will be effected due to reduced steam consumption and capital requirement.

Summary of Previous Work

- a. Work performed - Almost 400 catalyst formulations were made and tested with syngas feed containing 400-1200 ppm of hydrogen sulfide. Higher pressure tests up to 1000 psia have been made on the most promising catalysts. During these five years since the inception of the project steady catalyst improvement was realized. Patent applications have been filed on catalyst preparation and on process concepts using the catalysts developed.
- b. The first major technical problem encountered was the preparation of catalysts which were not sensitive to poisoning by sulfur. A second major problem was the reduction of tendency to carbon deposition. A third problem which appeared as process concepts

were developed was the importance of separating water gas shift activity from methanation rather than continuing these steps.

c. Major accomplishments - Progress was made in solving all major technical problems though further improvement is expected. Catalysts were developed with sufficient activity in the presence of sulfur to have commercial promise. Problems of coke deposition which are faced by users of nickel catalyst were overcome. High selectivity catalysts for direct methanation were developed.

d. Conclusions and significant findings - The development of improved catalysts moved forward rapidly. The results indicated possibilities of replacement of the major bulk of the methanation process by use of the new type catalysts.

Specific Objectives of the Current Year

In view of continuing steady progress additional screening tests were planned to take advantage of findings of previous research. It was thought that preparation of catalysts starting with the sulfide state rather than the oxide state would be desirable. It was planned to synthesize and characterize novel formulations varying not only composition but methods of pretreatment. Additional special tests were planned to facilitate patent coverage.

Work with C.F. Braun was anticipated which would hopefully be of help in narrowing down process objectives. It was planned to build and operate an adiabatic reactor assembly to characterize catalysts under development. It was also planned to develop rate equations which hopefully could

be employed in process studies. A testing program at Columbia University was to be undertaken in order to obtain fundamental information on the reasons for good catalyst performance.

Work Plan (Tasks) for the Current Year

The proposed program was subdivided into seven tasks as follows:

Task I - Formulation, synthesis, and evaluation of novel catalysts.

Task II - Analysis of data obtained; the most promising catalysts to be further evaluated using advanced techniques.

Task III - Making new formulations, which incorporate results from Tasks I and II and conducting additional screening tests.

Task IV - Design and construction of an adiabatic reactor evaluation apparatus.

Task V - Conduct tracer studies to elucidate the nature of the methanation mechanism, using special technique developed by CRC staff.

Task VI - Conduct experiments to obtain kinetic data to characterize the methanation process.

Task VII - Work with C.F. Braun in development of process sequences for producing pipeline gas.

Task VIII - Coordinate CRC research with that being conducted at SRI and IGT.

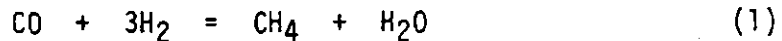
Task IX - Prepare technical process reports, papers and patent applications.

Work Activity Performed During Current Year and Detailed Discussion of Results and Findings

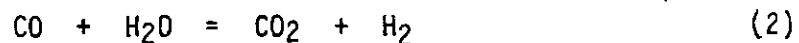
Major emphasis on research during the current year was devoted to the first three tasks involving the development of catalysts for direct methanation. During the year eighty six catalyst formulations and one hundred seventy three evaluation runs were performed. This work led to the discovery of a family of new catalysts with substantially improved properties for application to pipeline gas production.

As Massey has noted (L.G. Massey, Chapter IV, "Coal Conversion Technology", Ed. Wen & Lee, Addison-Wesley, Reading, Mass (1979)) much debate has occurred with respect to shift conversion before or after acid gas removal. In any case even with sulfur insensitive shift catalysts the usual processes for pipeline gas production require two acid gas removal steps which account for a considerable proportion of the total investment. Thus the dry bottom Lurgi process (Eisenlohr & Moeller, *Advances in Chemistry Series 146*, Amer. Chem. Soc, 1975) employs four steps after gasification two of which involve acid gas removal. Application of the slagging Lurgi to synthetic natural gas production (Roberts, Hebden, Brooks and Sudbury, 14th World Gas Conference, Toronto, 1979) employs three steps after gasification two of which involve acid gas removal. A more economical process sequence should be possible by use of only one acid gas removal step..

As conducted over nickel catalyst the methanation reaction follows essentially the equation:

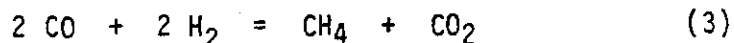


Thus it is necessary to use three volumes of hydrogen for every volume of carbon monoxide methanated. Even the dry ash Lurgi type process, which produces syngas with the highest H_2/CO ratio falls far short of meeting the necessary hydrogen requirement of Reaction (1). The dry ash Lurgi process produces a syngas with a ratio of $\text{H}_2/\text{CO} = 2/1$. Other processes produce less and in some cases the ratio of H_2/CO is less than 0.5/1. Thus considerable water gas shift is required to upgrade the synthesis gas as follows:



Since Reaction (2) uses water and Reaction (1) produces it, it is clear that in conventional methanation an expensive cycle is involved in which large quantities of steam are consumed in a step producing hydrogen. This is followed by the methanation step which consumes large quantities of hydrogen and produces water.

Some efforts have been made to develop a more economical processing sequence by so called combined shift-methanation schemes in which Reactions (1) and (2) occur in the same system. In this way the overall result is the following, obtained by adding Reactions (1) and (2):



With nickel catalysts this is not readily accomplished. Firstly, one still has the problem of removing H₂S before the operation. Secondly, if low H₂/CO ratio gases are processed over nickel coke formation occurs. It is therefore necessary to add considerable steam even though the overall Reaction (3) does not involve H₂O.

Although many calculations have been made of the equilibrium between C, H & O to establish regions in which coke formation may be a problem, the formation of coke is not basically one of thermodynamics but of kinetics ("Catalyst Handbook," ICI, p 73, Springer, N.Y. 1970). The composition of a gas can be such that thermodynamic theory predicts the formation of carbon by one of the carbon forming reactions and its removal by another. The question of whether there is a net build up of carbon is thus a kinetic one. In the case of nickel it is now established that the mechanism of methanation itself (Goodman, et al, J.Catal 58, 95 (1979); Happel et al, J. Catal. 65, 59 (1980)) involves a balance between carbidic carbon deposition by dissociation of carbon monoxide followed by its removal by hydrogenation to form methane. If removal is not sufficiently rapid carbon buildup will occur in a short period of time.

Hydrodesulfurization catalysts based on formulations of Co/Mo/Al and Ni/Mo/Al have also been proposed but have not found wide acceptance. Although these catalysts are not sulfur sensitive, it is necessary to still add considerable steam to avoid consumption of hydrogen by the reverse of the water gas shift Reaction (2).

Initial research at CRC during the current year was devoted to developing catalysts with higher methanation activity than the Co/Mo/Al type catalysts and which would not be poisoned by sulfur or carbon deposition like nickel catalysts. We were successful in these attempts.

Tests extending several hundred hours on Catalyst (GRI-C-578) demonstrated that carbon formation will not be a problem with gases containing H_2/CO ratios as low as 1, which is below the conditions we expect to operate.

Further studies than proceeded to the third goal of catalyzing Reaction (3) directly. Fundamental studies at Columbia had indicated that even over nickel catalyst Reaction (3) would occur. Furthermore, it occurred to a greater extent at low H_2/CO feed ratios such as are present in many gasifier syngas effluents. Since carbon formation did not present a problem with our catalysts, it was possible to conduct studies at much lower H_2/CO ratios than can be tolerated with nickel in the absence of steam. We found that even with H_2/CO ratios below 0.5/1 formulations could be made which did not suffer from coke formation such as (GRI-C-318).

The next step was to prepare catalysts with a minimum of water gas shift activity. It was found that certain formulations had this desirable property. In fact an entire family of catalyst components was discovered which catalyzed Reaction (3) without catalyzing the water gas shift activity.

Typical of these catalysts is (GRI-C-484). To further investigate this finding, a series of special high pressure runs was conducted with this catalyst, using a feed composition of synthesis gas containing a low hydrogen/carbon monoxide ratio such as might correspond to that produced by the HYGAS process. Three gas feed compositions were employed as shown in Table I. In one of these (Run GRI-717) a feed high in methane was used. In a second run (Run GRI-709) a gas high in CO_2 was used and it was shown that a product containing almost 50% CO_2 could be reached. Finally a gas corresponding exactly to the HYGAS synthesis gas product was used. Conversion of CO of over 75% was achieved. This furnished the basis for a preliminary process concept furnished to C.F. Braun.

Note that the amount of water produced is substantially less than that corresponding to water gas shift equilibrium, thus indicating that Reaction (4) is occurring to a substantial extent rather than Reaction (1) which usually predominates over nickel catalyst.

In view of the importance of this finding, Task IV, the design and construction of an adiabatic reactor was deferred because it was felt to be premature to initiate bench scale tests while the catalyst development itself was undergoing rapid change. Furthermore, economic studies had not progressed as fast as anticipated so that the optimum choice of methanation reactor is still undecided.

Table 1

Effect of CO₂ in the Feed
Catalysts (GRI-C-484)

Run #	<u>GRI-711</u>		<u>GRI-709</u>		<u>GRI-710</u>	
Space Vel. v/v/hr (STP)	2000		2000		2000	
Temperature, °C	530		520		540	
Pressure, psig	980		980		900	

Flow Stream	<u>Feed</u>	<u>Product</u>	<u>Feed</u>	<u>Product</u>	<u>Feed</u>	<u>Product</u>
Gas Analysis, Dry Basis Comp. Vol.%						
H ₂	32.0	7.3	32.7	9.9	28.5	7.9
CO	28.4	4.7	30.0	11.8	25.1	7.6
CH ₄	24.8	52.0	11.2	28.9	21.5	40.0
CO ₂	14.8	36.0	26.1	49.6	24.9	44.5

Water Content			
H ₂ O by Hydrogen Bal.	4.4	6.1	4.2
H ₂ O by Oxygen Bal.	3.4	0	0
H ₂ O Thermodynamic Equil.	13.2	7.6	13.6

Task V involving the conduct of transient isotopic tracing at Columbia University was carried forward to gain further insight into reasons for improved performance of the catalysts being tested. Details of the experimental equipment and procedure were presented in the Annual Progress Report for 1978. Tests were conducted in which the characteristics of nickel were compared with those of new catalysts developed at the beginning of 1979. In these tests a Ce/Mo/Al catalyst (GRI-C-318) was employed. Further details of the study are given in a paper presented at the New Orleans Meeting of the Organic Chemistry Section of the Catalysis Society in 1980. It was found that reaction of CO with adsorbed oxygen produced by initial dissociation of CO is fast as compared with nickel catalysts. This is evidenced by rapid approach of $^{13}\text{CO}_2$ marking to that of the ^{13}CO introduced with the feed after steady state overall operation is achieved. This contrasts with the behavior of nickel in which case water production is larger than production of CO_2 . The same delay in appearance of $^{13}\text{CH}_4$ marking in the product occurs as in the case of nickel indicating that slow steps in the process involve hydrogenation of carbonaceous intermediates rather than the initial CO dissociation. Thus formulations with high hydrogenation activity should be explored. These findings in fact led to feedback which produced important improvements in catalyst formulations.

Task VI, obtaining kinetic data was held in abeyance until further catalyst development is completed. In view of the complex nature of the kinetics, it was considered more useful to obtain high pressure data closely related to proposed process conditions rather than attempt the development of rate equations.

In principal the rates of production of CO_2 , H_2O and CH_4 from H_2 and CO should be a function of the proportions of those five components as well as the temperature and pressure. Adequate rate data for any single set of conditions could be obtained by use of a gradientless re-circulating reactor but it would be difficult matter to express rates in term of conventional rate equations because at least two overall reactions are occurring simultaneoulsy. Often (Happel, AI ChE Journal 24, 368 (1968)) it is in fact not possible to accurately describe kinetics by such equations. This is especially the case as equilibrium is approached and in the present case at very high conversion, equilibrium may be a factor. Therefore it seems safer as well as more economical to defer the task of development of rate equations to express conversions until process conditions are more closely established.

Task VII proposed work with C.F. Braun engineers to explore the economics of preliminary process sequences for production of pipeline gas. Several such sequences were furnished to Braun and some useful ideas were developed. It appears that a major cost in the methanation sequence is related to acid gas removal steps. By reducing the need for acid gas scrubbing substantial economies should be possible. Braun's studies are still in progress so detailed discussions of their findings would be premature. Economic studies conducted with lower activity catalysts than those more recently available showed that extensive scrubbing facilities for CO_2 removal must be avoided. The data in Table 1 show that this can be done by using more recent formulations.

Task VIII involved coordination of our efforts with those sponsored by GRI at the Institute of Gas Technology and Stanford Research Institute. Separate reports are prepared for GRI by IGT and SRI giving details and justification for their programs.

Studies have been started at SRI on the best catalyst developed to date (GRI-C-486) at CRC. An unusual property of this catalyst is that the methanation reaction is much less inhibited by CO_2 and water than the previously tested Ce/Mo/Al catalyst (GRI-C-318). These results agree with similar tests conducted at CRC. Other tests at SRI indicate that high partial pressures of H_2S , up to 2500 ppm, result in improvement in activity of Ce/Mo/Al catalyst (GRI-C-318). Studies at IGT at 1000 psig show a similar effect except that maximum activity is attained at 200 ppm of H_2S . Possibly a similar effect will be reached with the new (GRI-C-486) catalyst .

(GRI-C-486) catalyst has been tested at IGT and exhibited high activity (84% conversion at 2100 v/v/hr.) with a synthesis gas containing 22 vol.% of CO_2 . Activity was maintained for a period of over 900 hrs.

A process sequence based on the runs shown in Table 1 was developed and submitted to Braun engineers. In this sequence there is no need to recycle partially methanated gas to reach acceptable conversions as had been necessary in earlier process concepts. Based on newer catalysts developed while Braun was conducting these economics studies, it should be possible to effect much greater process improvements.

Major Achievements during the Current Year

A new family of catalysts has been developed which represents a real breakthrough in the possibilities for substantial improvement in methanation. An entire group possessing a range of characteristics has been synthesized. These materials are all sulfur insensitive. They do not present problems of coke formation which characterize nickel and other metal based catalysts. Formulations have been developed with low water gas shift activity and high activity in the presence of CO₂ which seem ideally adapted to improved process sequences.

Major Technical Problems which have been Encountered

The major technical problem to be solved in the development of a process for the direct methanation of raw syngas was that the process sequence should only employ one acid gas removal step. Doubts which had been expressed earlier regarding water poisoning of the catalysts under development turned out to be unfounded based on further tests at SRI and IGT.

Conclusions

An exciting new catalyst development has been brought forward to the point where the next scale in process development should be undertaken, as described in the following section of this report.

The results which we have obtained might very well be incorporated into a variety of new processes under consideration for pipeline gas production.

Specific Objectives and Work Planned for next Year

Additional screening tests will be needed to establish the optimum formulations. Several desirable properties are now becoming clearer following recent developments. Of great importance is the achievement of higher activity in the presence of CO_2 so as to minimize the amount of catalyst required. Another item is the continued development of catalysts with minimum sensitivity to poisoning by water. Finally of greatest importance is the development of catalysts with the maximum useful life connected with high activity over a range of temperature. This will involve formulations aimed at preventing or retarding formation of crystallites in the catalyst mass.

Since the methanation reaction is highly exothermic, it seems likely that a preliminary high conversion in a fluidized bed containing coils for heat removal could be a promising alternative. Studies by Braun, however, indicate that a series of adiabatic beds may be more attractive. This matter may need to be resolved before proceeding with bench scale tests.

Assuming that the alternative involving a series of adiabatic beds is selected, bench scale tests should be conducted in a adiabatic unit simulating the actual feed stocks to be used. A unit of this type should contain at least 40 ml of catalyst pellets (as compared with the present 10 ml capacity of our present integral reactors used for evaluation purposes).

The catalyst should be distributed in a series of several beds with provisions to measure temperature rise across each bed. In such a unit it would be possible to accurately determine catalyst ignition temperature and allowable catalyst temperature rise. Information obtained from a unit of this type could be used with some confidence for engineering design purposes.

Further fundamental studies using the tracer techniques developed at Columbia should be useful in gaining insight into the effect of changes in catalyst formulation on improvement of critical reaction steps.

Tasks

The following specific tasks are envisaged for work during the coming year:

- Task I - Formulation, synthesis and evaluation of novel catalysts.
- Task II - Analysis of the data; the newer promising catalysts will be further evaluated, using advanced research techniques.
- Task III - Making new formulations, incorporating the results of I and II and conducting additional screening tests.
- Task IV - Conduct tracer studies to elucidate the mechanism of methanation over new catalysts and suggest further formulation possibilities.
- Task V - Conduct experiments for obtaining preliminary process design data. It would be desirable to optimize process design for other gases than that produced by the HYGAS process.
- Task VI - Work with C.F. Braun to develop a process sequence for producing pipeline gas, employing the best catalyst developed to date.
- Task VII - Coordinate work with SRI and IGT.
- Task VIII - Reporting: Progress Reports, Monthly Reports, Annual Report, Patent write-ups, technical papers