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INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

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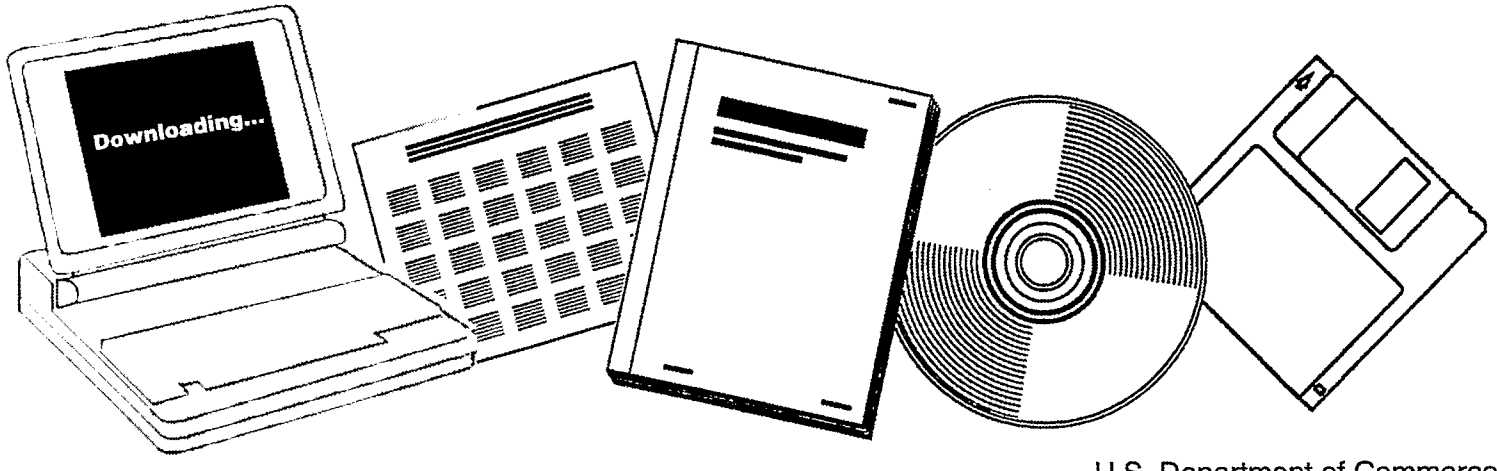

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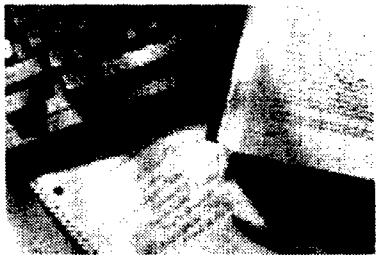

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EVALUATION OF COAL CONVERSION CATALYSTS

ANNUAL REPORT
(January-December 1984)

Prepared by

Anthony L. Lee

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IGT Project No. 30523

for

GAS RESEARCH INSTITUTE

Contract No. 5014-322-0139

GRI Project Manager
Howard S. Meyer, Manager
Associated Coal Gasification Technology

January 1985

This is an interim report; hence, the data, conclusions, and calculations are preliminary and should not be construed as final.

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16. Abstract (Limit: 200 words)

A novel family of sulfur-resistant, low-carbon fouling hydrogenation catalysts were discovered by Catalysis Research Corporation for GRI. These catalysts promote the direct methanation reaction in which equal molar concentrations of H_2 and CO react to produce CH_4 and CO_2. IGT evaluated these catalysts. The work performed during 1984 includes the following:

- Concurrent life tests of the GRI-C-500 and GRI-C-600 catalysts were completed.
- The steam reforming of a sulfur-containing natural gas using the GRI-C-318 catalyst was conducted.
- The evaluation of the GRI-C-700A and GRI-C-700B catalysts was completed.
- The effect of low sulfur concentration in the feed on the life and activity of direct methanation catalysts was studied.
- A set of first-cut design data using an underground coal gasification type raw gas was obtained.

17. Document Analysis a. Descriptors

Catalysts; Sulfur Resistant; Hydrogenation; Steam Reforming.

b. Identifiers/Open-Ended Terms

Methanation; High Btu Gas; Coal Conversion; Lurgi Process; Westinghouse Gasification Process; Underground Coal Gasification Process.

c. COSATI Field/Group Catalysis, Chemical Engineering, Process Engineering.

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RESEARCH SUMMARY

Title	Evaluation of Coal Conversion Catalysts GRI Contract Number: 5014-322-0139 GRI Accession Code: GRI-85/0113
Contractor	Institute of Gas Technology
Principal Investigator	Anthony L. Lee
Time Span	January-December 1984 Annual Report
Objective	To develop new raw-gas process schemes that will improve the catalytic conversion steps in coal conversion processes.
Technical Perspective	This new raw-gas process, the direct methanation process, could decrease both capital and operating costs because the final SNG can be produced with equimolar carbon monoxide and hydrogen, and the methanation catalyst is sulfur-resistant. To ensure that the direct methanation process is applicable to existing coal conversion processes, simulated quench gases of Lurgi, BGC Slagger, underground coal gasification, and Westinghouse processes are used. To ensure that the catalysts have adequate life expectancies, they are subjected to long periods of continuous reactions with a Lurgi-type raw gas.
Results	Concurrent life tests of the GRI-C-500 and GRI-C-600 catalysts were completed. The steam reforming of a sulfur-containing natural gas using the GRI-C-318 catalyst was conducted. The evaluation of the GRI-C-700A and GRI-C-700B catalysts was completed. The effect of low sulfur concentration in the feed on the life and activity of direct methanation catalysts was studied. A set of first-cut design data using an underground coal gasification type raw gas was obtained.
Technical Approach	Life tests of the GRI-C-500 and GRI-C-600 catalysts were conducted in a dual-reactor system where the performance of one catalyst was compared with that of the other concurrently. These two catalysts were on-stream for 2300 hours and the process conditions were: 950°F, 450 psig, and 6000 SCF/h-ft^3. A Lurgi-type raw gas (CO 17 mol %; CO_2 28%; H_2 39%; CH_4 12%; C_2-C_4 1%; H_2S-COS-CH_3SH-CS_2 1%; N_2 1.5%; H_2O 0.5%) was used.

- A set of experiments was conducted to study the steam reforming of a sulfur-containing natural gas using the GRI-C-318 catalyst. The process conditions were 900°, 1000°, 1100°, 1200°, 1400°, and 1600°F; 0 psig; 18 ppm sulfurs; and a H_2O/C molar ratio of 3:1. The catalyst was active in promoting the steam reforming reaction.

- The evaluation of GRI-C-700A and GRI-C-700B catalysts, which were formulated by a new technique, was completed. These two catalysts were on-stream for about 250 hours. The process conditions and the feed gas composition were identical to those used in the life test of the GRI-C-500 and GRI-C-600 catalysts.

- The effect of low sulfur concentration in the feed on the life and activity of the direct methanation catalysts was studied. The catalysts used were the GRI-C-700A and GRI-C-700B, and the process conditions and feed gas composition were the same as those used in the evaluation of these two catalysts except that the sulfur concentration was reduced to 450 ppm (v). No change in the catalysts' activities were detected for 190 hours.

- A set of data was obtained using an underground coal gasification type raw gas (CO 23 mol %; CO_2 34%; H_2 34% CH_4 7%; H_2S 0.13%; C_2, C_3, C_4, N_2, COS, CH_3SH, balance). The process conditions were 750°, 850°, and 950°F, 506 psig, 3000; 6000; 10,000; and 15,000 SCF/h-ft^3, and 0, 2, and 10 mole percent of steam in the feed. The GRI-C-600 catalyst was used in this study. This set of data should provide sufficient information for a first-cut design of a direct methanation process to be used with an UCG system.

Project Implications

This ongoing project is an integral part of GRI's overall program for developing the direct methanation process. Previous results from this project were used by CF Braun & Co. to perform preliminary technical and economic evaluations of the direct methanation process in Westinghouse, BGC/Lurgi, and Lurgi gasification facilities.

During 1984, IGT life tests of the Series 500, 600, and 700 series catalysts, together with previous catalyst testing, indicate that the catalyst can maintain constant activity for over 1 year in commercial application. The low sulfur testing data indicate that the direct metnanation process should not be affected by variations in the sulfur content of the coal fed to the gasifiers.

Work on this project will be completed in 1985. Catalysts fabricated by Catalysis Research Corporation will be evaluated and design data will be obtained for Lurgi, Shell, and KRW-type raw synthesis gases.

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OVERALL OBJECTIVE OF THE PROGRAM

The overall objective of this program is to develop new raw-gas process schemes that will improve the present catalytic conversion steps in coal conversion processes, resulting in a reduction of the cost of SNG production.

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SUMMARY OF ALL PREVIOUS WORK PERFORMED ON THE CONTRACT

Work Performed

The following 16 tasks were completed or are being continued since the initiation of this project in 1978 through 1984:

- Task I. Establishment of consistency of catalyst performance (1978).

  The initial activity of the catalysts was tested with a 17-component simulated gasifier effluent; the effect of various concentrations of sulfurs (H_2S, COS, CH_3SH) on the activities of these catalysts was also measured.

- Task II. Measurement of the effect of temperature, pressure, and feed composition on the methanation reaction (1981).

  The methanation reaction was measured at temperatures from light-off to 1150°F, pressures from 50 to 1000 psig, and feed CO concentrations from 4 to 30 mole percent.

- Task III. Measurement of the effect of space velocity on conversion (1982).

  At constant temperature, pressure, and feed composition, the methanation reaction was measured at space velocities from 1000 to 16,000 SCF/h-ft^3.

- Task IV. Measurement of the effect of H_2/CO ratios and H_2O on conversion (1979).

  The methanation reaction was measured with feed mixtures containing H_2/CO molar ratios of from 0.5:1 to 3:1, and with H_2O concentrations from 0 to 16 mole percent.

- Task V. Measurement of the effect of benzene, phenol, and ammonia on conversion (1980).

  The methanation reaction was measured with feed mixtures containing up to 2 mole percent benzene; 0.05 mole percent phenol; and 0.3 mole percent ammonia.

- Task VI. Determination of the reaction order of the major reactants and products (1980).

  A first-cut rate analysis was conducted based on the integral data obtained from the packed-bed reactors.

- Task VII. Reporting.

  Monthly, quarterly, and annual reports have been and are being completed, as contracted.

- Task VIII. Technical service.

  GRI was assisted in the preparation of technical reports during 1979 and 1980.

- Task IX. Obtain design data (1982).

  First-cut direct methanation process design data were obtained for the dry-bottom Lurgi, British Gas Corporation Slagging gasification, and Westinghouse cases.

- Task X. Design and construct an adiabatic reactor system (1980).

  An adiabatic reactor system was designed and constructed.

- Task XI. Obtain adiabatic design data for evaluation of raw-gas process schemes.

- Task XII. Test direct methanation catalysts (1984).

  Newly developed sulfur-resistant catalysts, fabricated both on a laboratory scale and on a commercial scale, were and are being tested at process conditions and with feed mixture compositions that simulate the raw gas from an established gasifier.

- Task XIII. Determine catalyst life. (1984)

  Life tests were and are being conducted on a number of catalysts with feed mixture compositions that simulate those of raw gasifier effluents.

- Task XIV. Determine kinetics of reaction(s).

  The kinetics of reactions (direct methanation and reverse water-gas shift) are being determined.

- Task XV. Support process development (1984).

  A number of experiments were conducted to provide design data: COS hydrolysis/hydrogenation reactions, water-gas shift reactions, steam reforming reactions, and catalyst regeneration.

- Task XVI. Storage of chemical by-products (1984).

  IGT provides storage, security, and management for the by-products derived from the gasification of Illinois basin coal by the Lurgi process.

Major Technical Problems Encountered

In the absence of steam, the presence of 0.05 mole percent of C_6H_5OH and 2 mole percent of C_6H_6 promoted carbon formation reactions at temperatures higher than 1000°F for the four catalysts tested (GRI-C-284, GRI-C-318, CRL-T-1, and CB-79-57).

Major Accomplishments

- Seven sulfur-resistant catalysts were evaluated with feed gases simulating raw gasifier effluents for extended periods: GRI-C-284 (5,232 hours on stream), GRI-C-318 (1,048 hours), GRI-C-486 (1,542 hours), GRI-C-525 (10,000 hours), GRI-C-600 (1,000 hours), CRL-T-1 (1,520 hours),

and CB-79-57 (846 hours). The feed gases contained H_2, CO, CO_2, N_2, He, Ar, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, C_6H_5OH, NH_3, H_2S, COS, CH_3SH, C_2H_5SH, C_3H_7SH, C_4H_4S, and H_2O. These catalysts are sulfur-active and were active in the presence of sulfurs up to 3 mole percent.

- Some of these sulfur-resistant catalysts (GRI-C-486, GRI-C-525, and GRI-C-600) were able to promote the methanation reaction at H_2/CO ratios of from 0.5:1 to 3:1. The optimum range of H_2/CO ratios is between 1.1:1 and 1.3:1 for the raw-gas process schemes considered.

- With quenched gases, simulating those from the dry-bottom Lurgi, BGC Slagger, Westinghouse, and HYGAS processes, direct methanation with a high CO conversion (85 mol %) was obtained using the GRI-C-525 catalyst with feed gases containing H_2/CO ratios of 1.1 to 1.3 and a CO_2 concentration of 25 mole percent. The equilibrium conversion for this test condition was 95%. In addition, the presence of less than 5% steam had no detrimental effect on the methanation reaction. This GRI-C-525 catalyst is the best direct methanation catalyst tested from 1978 to 1982.

- With quenched gases, simulating those from the BGC Slagger process, a preconditioning shift from a 0.5 H_2/CO ratio to a 1.1:1.3 H_2/CO ratio was required prior to direct methanation. This shift was achieved by using the GRI-C-318 catalyst and controlling the feed steam concentration and space velocity in the preconditioning step.

- The initial light-off temperature of the GRI-C-525 catalyst was measured at 480°F. This temperature is within the start-up capability of commercial plants.

- Acquisition of the first-cut design data for the direct methanation process using a BGC-Slagging-type raw gas was completed.

- Acquisition of the first-cut design data for the direct methanation process using a Westinghouse-type raw gas was completed.

- Acquisition of the first-cut design data for the direct methanation process using a dry-bottom Lurgi-type raw gas was completed.

- The GRI-C-600 catalyst, which was developed by CRC with the intention of maintaining high activity in the presence of a high concentration of CO_2 (40+ mol %), was evaluated with both the first-stage and the third-stage Lurgi-type raw gases and the standard gas mixture. The 600 catalyst showed an average of 34% higher conversion than the 500 catalyst.

- A microprocessor-controlled reactor system was modified to include two parallel reactors so that life tests of two catalysts can be conducted simultaneously.

- Detectors were installed and calibrated (FI, FP, TC) in the Perkin-Elmer Sigma I chromatograph analyzer to measure C_2H_6, C_2H_4, C_3H_8, H_2S, COS, and mercaptans in the 1 to 20 ppm range.

- The COS hydrolysis and hydrogenation reactions were determined at conditions of the shift convertor of a Westinghouse base case and those of the post conditioner of a Westinghouse/CRC case. The catalyst used was United Catalysts, Inc.'s C25-2-02, a shift catalyst similar to the old Girdler G-93 catalyst.

- The steam reforming of a sulfur-containing natural gas was conducted at 700° to 1100°F, 0 psig, 21 ppm H_2S, and a H_2O/C molar ratio of 3:1. The catalyst used was the GRI-C-318.

- A single reactor system was modified to include a low-flow, high-pressure pump (6.5 cm^3/h, 8000 psig) for introduction of potential poisons (BTX, naphtha, and Lurgi oils) in the ppm range to the feed mixtures.

- Life tests of both GRI-C-500 and GRI-C-600 catalysts in the dual-reactor system were begun. The catalysts were screen-tested by CRC and were found to have activities consistent with those of the catalyst prepared before.

- Fresh GRI-C-500 and GRI-C-600 catalysts were loaded in new 316 SS reactors and were evaluated one at a time in the microarc reactor system, which was used in obtaining the first-cut design data.

Conclusions and Significant Findings

- The seven sulfur-resistant catalysts have much higher upper temperature limits than conventional nickel-based catalysts. Catalysts with a high upper temperature limit (1200°F) decrease the possibility of sintering and permit higher quality steam generation than do those with a low upper temperature limit. Conventional nickel-based catalysts have an upper temperature limit of about 950°F. Because the design operating temperature is about 850°F, a high recycle ratio is required.

- The sulfur-resistant catalysts are much more durable and are easier to handle than conventional nickel-based catalysts. No pretreatment is needed to activate the catalytic surfaces, and no special precaution is needed to shut down the reactors. These catalysts can be exposed to air at room temperature after use and still retain their original activity upon restarting.

- The direct methanation process is an improvement over current methanation conversion processes because it minimizes the total steam usage and reduces loads on acid-gas removal systems.

- The GRI-C-600 catalyst has higher activity than the GRI-C-500 catalyst. More important, the GRI-C-600 catalyst promotes a much higher total CO conversion in the presence of high concentrations of CO_2 than the GRI-C-500 catalyst.

SPECIFIC OBJECTIVES FOR THE CURRENT YEAR

The Gas Research Institute (GRI) has sponsored a team approach to the development of raw-gas processes using sulfur-resistant direct methanation catalysts. This team consists of three members:

1. Catalysis Research Corporation (CRC) — to develop the screen-test catalysts and propose process schemes
2. Institute of Gas Technology (IGT) — to evaluate these catalysts using feeds that simulate coal gasifier effluents after a water quench
3. Kellogg-Rust Synfuels, Inc. (KRSI) — to assist in process development and make economic analyses.

The following items are to be accomplished by IGT in 1984:

- Life tests of the GRI-C-500 and GRI-C-600 catalysts
- Steam reforming of a sulfur-containing natural gas using the GRI-C-318 catalyst
- Steam reforming of a sulfur-containing natural gas using the GRI-C-600 catalyst
- Evaluation of the GRI-C-700A and GRI-C-700B catalysts
- Evaluation of the effect of sulfur concentration on the activity of the direct methanation catalysts.

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WORK PLAN FOR THE CURRENT YEAR

The following tasks were planned to be continued/conducted during 1984:

Task XI. Obtain Adiabatic Design Data

Data will be obtained with an adiabatic reactor system to provide information for a second-cut design and economic analysis. The mode of reactor control and the light-off temperature of both the fresh and the temperature-cycled catalysts as a function of feed composition will also be determined.

Task XII. Test Direct Methanation Catalysts

Newly developed sulfur-resistant direct methanation catalysts, fabricated both on a laboratory scale and on a commercial scale, will be tested at process conditions and with feed mixture compositions simulating those of the raw gas from an established gasifier. The catalysts will be tested for their light-off temperatures and activities as a function of temperature, pressure, and steam concentration.

Task XIII. Determine Catalyst Life

Life tests will be conducted on the existing GRI-C-500 and GRI-C-600 series catalyst and any newly developed and commercially fabricated catalysts that have successfully passed the tests outlined in Task XII. During each life test, the catalyst will reach temperatures of from 480° to 1150°F, pressures from 450 to 600 psig, feed compositions ranging from raw gasifier effluents to fourth-reactor-stage gases, and any other conditions, such as sintering temperature, as directed by GRI.

Task XIV. Determine Kinetics of Reaction(s)

This task will be carried out by CRC, assisted by IGT.

Task XV. Support Process Development

The support tasks are listed here for completeness and to give an overall view. Only the ones that are marked by an asterisk were to be conducted during 1984.

*XV-1. The reaction of the steam reforming of a sulfur-containing natural gas will be studied at temperatures up to 1650°F at atmospheric pressure using the GRI-C-318 and the GRI-C-600 catalysts.

*XV-2. The effect of low sulfur concentration in the feed on the life and activity of GRI-C-500 and GRI-C-600 catalysts will be studied.

*XV-3. The method of regeneration of the spent catalysts will be studied.

XV-4. The CO_2 reforming of a sulfur-containing natural gas will be conducted at various temperatures and pressures using the GRI-C-600 catalyst.

XV-5. The fate of COS in the post conditioner will be determined as a function of a combination of water-gas shift and COS hydrolysis catalysts and steam concentration.

XV-6. The steam requirement in a COS hydrolyzer will be determined as a function of temperature, pressure, and steam concentration.

XV-7. A skid-mounted mini-PDU (process development unit) will be constructed so that it can be transported to various gasification sources to test the catalysts with real effluents and to prove that the direct methanation process is applicable to any and all gasification processes.

Task XVI. Provide Storage of Chemical By-Products Derived From the Gasification of Illinois Basin Coal by the Lurgi Process

IGT will provide storage, security, and property management functions for the samples and for additional by-products up to a total of 200 55-gallon drums, if such storage is required by GRI.

WORK ACTUALLY PERFORMED DURING THE CURRENT YEAR

Summary

Life tests of the GRI-C-500 and the GRI-C-600 catalysts were completed. These two catalysts were on-stream for approximately 2300 hours. A Lurgi-type raw gas (western coal) with a sulfur content of 0.5 mole percent, a CO_2 content of 28 mole percent, and a H_2/CO ratio of 2.4:1 was used.

The steam reforming of a sulfur-containing (18 ppm) natural gas was also conducted using the GRI-C-318 catalyst.

The evaluation tests of the GRI-C-700A and GRI-C-700B catalysts were completed. These two catalysts have been on-stream for about 250 hours. A Lurgi-type raw gas (western coal) with a sulfur content of 0.5 mole percent, a CO_2 content of 28 mole percent, and a H_2/CO ratio of 2.4:1 was used.

The effect of low sulfur concentration in the feed on the life and activity of these catalysts is being studied. The same Lurgi-type raw gas, except with a sulfur content of about 450 ppm (v), as the ones previously used was prepared and used in the evaluation of the two 700 series catalysts. No change in activity was detected at the end of 190 hours.

A set of first-cut design data was obtained using an Underground Coal Gasification type raw gas. The catalyst used was GRI-C-600.

2000-Hour Life Test of the GRI-C-500 and the GRI-C-600 Catalysts

- The GRI-C-500 series (525) catalyst was on stream for more than 10,000 hours and was used to obtain the first-cut design data for the British Gas Corporation Slagging gasification (October 1980 to October 1981), the Westinghouse gasification (October 1981 to January 1982), and the Dry-Bottom Lurgi gasification (January 1982 to March 1982). During this 18-month period of design data generation, this catalyst was subjected to high steam concentrations (37 mol %), high temperatures (1150°F), low H_2/CO molar ratios (0.5:1), and multiple exposures to atmospheric air. The total CO conversion was changed from 63% when the GRI-C-525 catalyst was fresh to 50% at the end of the 18-month test period when this catalyst was subjected to the standard test. The loss in activity of this catalyst would have been much smaller if it were operated under steady-state, optimum design conditions. Therefore, this catalyst is considered to be durable and satisfactory.

  The GRI-C-600 series catalyst was developed by CRC for high activity in the presence of a high concentration of CO_2. It was screen tested by CRC first and showed higher activity than the GRI-C-500 series catalyst. IGT evaluated this catalyst with both the first-stage and the third-stage Lurgi-type raw gases and the GRI-C-600 catalyst has about 30% higher

activity than the GRI-C-500 catalyst at comparable conditions. However, the life expectancy of this catalyst was not known.

To determine the life of the GRI-C-600 catalyst and to be able to compare the test results fairly with that obtained using the GRI-C-500 catalyst, a microprocessor controlled reactor system was modified to include two reactors in parallel so that life tests of these two catalysts can be conducted simultaneously.

The life tests of these two catalysts were discontinued after about 2300 hours on-stream and the following results were measured.

- Based on the 2000-hour test and the knowledge of the formulation and the method of preparation of the GRI-C-600 and the GRI-C-500 catalysts, we conclude that the GRI-C-600 catalyst is as durable as and has higher activity than the GRI-C-500 catalyst.

- The total CO conversion for the GRI-C-600 catalyst started at about 78%, stabilized at about 65% and remained steady for the entire test period. The light-off temperature was 510°F, and the CH_4 selectivity was about 84%.

- During the 2000-h test of the GRI-C-500 and GRI-C-600 catalysts, check runs were made with a standard feed mixture at standard conditions. The initial total CO conversions were 72% for the GRI-C-500 catalyst, and 80% for the GRI-C-600 catalyst.

- Hydrogenation reactions were detected; that is, the olefins were hydrogenated to their corresponding paraffins. Hydrogenolysis reactions were not detected.

Although the tests were conducted on a 24-hour-per-day basis and continually, the actual time on-stream was only about one-half of this year. The overall reason for this shortage of run-time was the meticulous manner in which these experiments were conducted. For example —

- Two of the feed gas components, H_2 and CO, were obtained directly from the producing plants and stored in IGT's own aluminum cylinders to minimize the possibility of metal carbonyl formation. It was not always possible to synchronize the date of gas production with that of cylinder availability. To alleviate this problem, more aluminum cylinders are being ordered so that a larger supply of "clean" gases can be stored and more gas cylinders can be circulated.

- More time was required to prepare this 15-component mixture containing a high concentration of CO_2 (30 mol %) than was required previously, when the CO_2 content was low and the CH_4 selectivity was not as sensitive to the H_2/CO ratio. At pressures higher than 900 psig, CO_2 is either stratified and/or exists in a two-phase region in a constant volume cylinder. During the preparation of the 15-component mixture, each component is added one at a time. The component with the lowest concentration, and therefore the lowest partial pressure, is added to the

evacuated cylinder first, and so on. Hydrogen is added last to bring the total pressure of the feed supply tanks to about 1800 to 2000 psig. After CO_2 has been introduced, the remaining components must be added gradually and the cylinder must be mixed from time to time during addition. These steps are necessary to assure the homogeneity of the composition and to ensure that the desired composition is achieved. Short-cut methods were tried, but the result was mixtures with undesirable compositions that could not be adjusted. Premixed gases can be purchased from a number of suppliers (Scott Specialty Gases, Linde Specialty Gases, Air Products, Matheson, Fred Peters Welding Supply Co.), although they are reluctant to make a sulfur-containing gas mixture with more than six components. Also, 2 to 3 weeks are required for delivery, and the suppliers will not guarantee the final composition.

- When the pressures of the feed-mixture-containing cylinders fall below 500 psig, they are no longer sufficient for runs conducted at 450 psig. These gases are compressed, combined, and mixed in one or two cylinders for the continued experiments. The gases in the remaining cylinders are vented through NaOH solutions to trap the sulfur compounds. The vented cylinders are evacuated to minimize the moisture that came with the supply gases.

- Due to the formation of sulfide soot in the system, the mass flow controllers, gas regulators, and wet test meters were cleaned — disassembly was frequently necessary — and calibrated. The columns in the gas chromatography analyzers were regenerated when the deviation of the calibration factor exceeds 3% of the mean, and recalibrated or replaced if the deviation exceeds 5%.

Steam Reforming of a Sulfur-Containing Natural Gas

For all reversible reactions, if a catalyst is active in promoting the forward reaction, it has the potential to promote the reverse reaction. All of the GRI catalysts have shown that they are active in promoting the methanation reaction, and they are sulfur-resistant. It is logical to assume that they can also promote steam reforming and/or CO_2 reforming of methane in the presence of sulfurs.

A set of experiments was conducted in 1983 to study the steam reforming of a sulfur-containing natural gas. The conditions were 700° to 1100°F, 0 psig, 21 ppm sulfur, and a H_2O/C molar ratio of 3:1. The catalyst used was GRI-C-318. This work was continued during 1984 by extending the temperature range to 1600°F.

Evaluation of the GRI-C-700A and the GRI-C-700B Catalysts

The initial total CO conversion for the GRI-C-700A catalyst was about 78%, which was higher than that for the GRI-C-500 (65%) and was the same as

that for the GRI-C-600 (78%). The conversion stabilized at about 58% after 180 hours which is lower than that of the GRI-C-500 catalyst (60%) and the GRI-C-600 catalyst (65%) for the same time duration. The light-off temperature was 482°F (GRI-C-500: 485°F; GRI-C-600: 510°F) and the methane selectivity was 85% (GRI-C-500: 82%; GRI-C-600: 84%).

The total CO conversion for the GRI-C-700B catalyst started at about 74%, stabilized at about 55% after 180 hours and remained steady for the test period of about 260 hours. The light-off temperature was 490°F and the methane selectivity was 85%. Standard runs were conducted when the activities of these catalysts were changing to assure that the experimental procedure was conducted correctly. Also, it provided a record of the catalyst activity during start-up which can be compared with that from all the other catalysts evaluated previously.

The results obtained from the standard runs followed the pattern set by using the Lurgi-type raw gas. To make certain that the catalysts were not deactivated, the control temperature was increased from 950° to 975°F at 250 hours of this experiment. The total CO conversion responded quickly from 56% to 60% which was a signal that the catalyst was not deactivated. The GRI-C-700A catalyst showed better activity than the GRI-C-700B catalyst at steady state, but it was not significantly better.

Effect of Low Sulfur Concentration

The same Lurgi-type raw gas as the ones used previously, except with a sulfur content of 450 ppm, was used to evaluate the effect of low sulfur concentration on the activity of the GRI-C-700A and the GRI-C-700B catalysts. No change in catalyst activity was detected for 190 hours. When the temperature was intentionally changed from 950° to 975°F and back to 950°F during this run, the total CO conversion responded by changing from 57% to 63% and back to 57%, correspondingly. This corresponding movement of the conversion with the temperature indicated that the catalysts were active. Within the range tested, the catalyst activity does not appear sensitive to the sulfur concentration.

The total CO conversion remained steady and constant for the entire test period. The reactors were purged with inert gas (He) and locked up under pressure. These two catalysts, GRI-C-700A and GRI-C-700B, can be used in the

future for additional evaluation studies. It is planned to test the effect of sulfur concentration at lower levels on activity.

First-Cut Design Data for the First Reactor Stage of the Direct Methanation Process Using an UCG-Type Raw Gas

A set of data was obtained using an underground coal gasification type raw gas. The gas composition simulated the quenched gas which was at 125°F and 211 psia, and, subsequently it was compressed to 321°F and 521 psia. The GRI-C-600 catalyst was used for this study.

The total CO conversion was quite high, even at space velocities as high as 10,000 SCF/h-ft^3, and therefore, should provide flexibility in process design. However, the H_2/CO molar ratios in the product were less than 1:1 after the first pass and is considered to be deficient in hydrogen content for the final polishing reactor stage. The presence of steam promoted the water-gas shift reaction and the product H_2/CO molar ratio was increased to about 3 at 6000 SCF/h-ft^3 with the addition of 10 mole percent of steam in the feed. These experiments showed that the product H_2/CO ratio can be adjusted according to design by carrying steam in the feed. One important, and pleasant, observation was that the methanation reaction was not reduced in presence of the water-gas shift reaction. The methane yield, the portion of carbon monoxide that was converted to methane, was unaffected by the concentration of steam in the feed.

MAJOR ACHIEVEMENTS DURING THE CURRENT YEAR

- Concurrent life tests of the GRI-C-500 and GRI-C-600 catalysts were completed in a dual-reactor system. These two catalysts have been on-stream for about 2300 hours. A Lurgi-type raw gas (CO 17 mol %; CO_2 28%; H_2 39%; CH_4 12%; C_2-C_4 1%; H_2S-COS-CH_3SH-CS_2 1%; N_2 1.5%; H_2O 0.5%) was used.

- A set of experiments was conducted to study the steam reforming of a sulfur-containing natural gas using the GRI-C-318 catalyst. The catalyst was active in promoting the steam reforming reaction.

- The evaluation of GRI-C-700A and GRI-C-700B catalysts which were formulated by a new technique, was completed. These two catalysts were on-stream for about 250 hours. The process conditions and the feed gas composition were identical to those used in the life test of the GRI-C-500 and GRI-C-600 catalysts. The GRI-C-700 catalysts are at least equivalent to the GRI-C-500 catalysts within the temperature ranges tested.

- The effect of low sulfur concentration in the feed on the life and activity of the direct methanation catalysts was studied. The catalysts used were the GRI-C-700A and GRI-C-700B, the process conditions and feed gas composition were the same as those used in the evaluation of the GRI-C-500 and GRI-C-600 catalysts except that the sulfur concentration was reduced to 450 ppm (v). No change in the activities of the catalysts were detected for 190 hours.

- A set of data was obtained using an underground coal gasification type raw gas (CO 23 mol %; CO_2 34%; H_2 34%; CH_4 7%; H_2S 0.13%; C_2, C_3, C_4, N_2, COS, CH_3SH, balance). The GRI-C-600 catalyst was used in this study. This set of data should provide sufficient information for a first-cut design of a direct methanation process to be used with an UCG system.

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MAJOR TECHNICAL PROBLEMS ENCOUNTERED DURING THE YEAR

No major technical problems were encountered during the year.

CONCLUSIONS

The following conclusions were reached during this reporting period:

- The GRI-C-600 catalyst averages about 30% more active in total CO conversion than the GRI-C-500 catalyst.

- In the presence of 40 mole percent of carbon dioxide, the GRI-C-600 catalyst is about 20% more active than the GRI-C-500 catalyst, and is about 40% more active than the GRI-C-200 and GRI-C-300 catalysts.

- The GRI catalysts are capable of promoting the steam reforming of a sulfur-containing natural gas. The GRI-C-318 catalyst was tested for this application and the conversion was comparable to that reported by other investigators who used "sulfur-resistant" catalysts. It is not clear that those catalysts reported by other investigators were truly sulfur-resistant because the life expectancy of those catalysts is not reported. The GRI catalysts are proven to be sulfur-resistant and sulfur-tolerant.

- The presence of steam in the feed dictated the product distribution when the GRI-C-600 catalyst was used, and the total methane yield was unaffected.

SPECIFIC OBJECTIVES AND WORK PLAN FOR THE NEXT YEAR

GRI has sponsored a team approach to the development of raw gas processes using sulfur-resistant methanation catalysts. This team consists of the following three members:

1. Catalysis Research Corporation (CRC) — to develop and screen-test catalysts and propose process schemes
2. Institute of Gas Technology (IGT) — to evaluate these catalysts using feeds that simulate coal gasifier effluents after quench
3. Kellogg-Rust Synfuels, Inc. (KRSI) — to assist in process development and make economic analyses.

The following tasks will be continued/conducted during 1985.

Task XII. Test Direct Methanation Catalysts

Newly developed sulfur-resistant direct methanation catalysts, fabricated on both a laboratory scale and a commercial scale, will be tested at process conditions and with feed mixture compositions simulating those of the raw gas from an established gasifier. The catalysts will be tested for their light-off temperatures and activities as a function of temperature, pressure, space velocity, and steam.

Task XIII. Determine Catalyst Life

Life tests will be conducted on the newly developed and commercially fabricated catalysts that have successfully passed the tests outlined in Task XII. During each life test, the catalyst will reach temperatures of from 480° to 1150°F, pressures of from 450 to 600 psig, space velocities of 1,000 to 16,000 SCF/h-ft^3, feed compositions ranging from raw gasifier effluents to fourth-reactor-stage gases, and any other conditions, such as sintering temperature, as directed by GRI.

Task XIV. Determine Kinetics of Reactions

This task will be carried out by CRC, assisted by IGT.

Task XV. Support Process Development

The support tasks are listed here for completeness and to give an overall view. Only the ones that are marked by an asterisk will be conducted during 1985.

*XV-1. The reaction of the steam reforming of a sulfur-containing natural gas will be conducted at temperatures up to 1650°F at atmospheric pressure using the GRI-C-318 and the GRI-C-600 catalysts.

*XV-2. The effect of low sulfur concentration in the feed on the life and activity of the GRI-C-500 and GRI-C-600 catalysts will be studied.

*XV-3. The method of regeneration of the spent catalysts will be studied.

XV-4. CO_2 reforming of a sulfur-containing natural gas will be conducted at various temperatures and pressures using the GRI-C-600 catalyst.

XV-5. The fate of COS in the post conditioner will be determined as a function of a combination of water-gas shift and COS hydrolysis catalysts and steam concentration.

XV-6. The steam requirement in a COS hydrolyzer will be determined as a function of temperature, pressure, and steam concentration.

XV-7. A skid-mounted mini-PDU (process development unit) will be constructed so that it can be transported to various gasification sources to test the catalysts with real effluents and to prove that the direct methanation process is applicable to any and all gasification processes.

*XV-8. Obtain first-cut design data using an UCG-type raw gas.

*XV-9. Obtain first-cut design data to provide information for the evaluation of alternate options for the direct methanation process to CRC and KRSI.

Task XVI. Provide Storage of Chemical By-Products Derived From the Gasification of Illinois Basin Coal by the Lurgi Process

IGT shall provide storage, security, and property management functions for the samples and for additional by-products up to a total of 200 55-gallon drums, if such storage is required by GRI.

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