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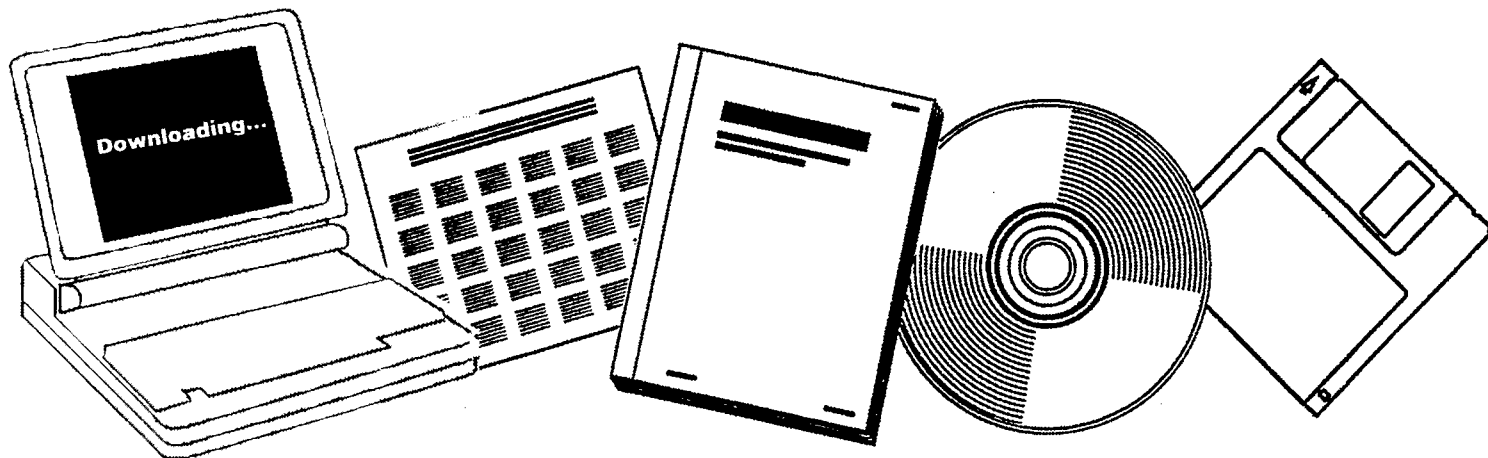
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EVALUATION OF COAL CONVERSION CATALYSTS

INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

MAY 1984



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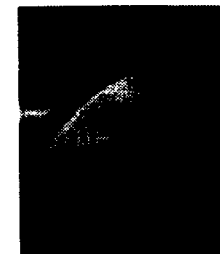
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EVALUATION OF COAL CONVERSION CATALYSTS

ANNUAL REPORT
(January-December 1983)

Prepared by

A. L. Lee

INSTITUTE OF GAS TECHNOLOGY
IIT CENTER
CHICAGO, ILLINOIS 60616

IGT Project No. 30523

for

GAS RESEARCH INSTITUTE

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GRI Project Manager
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RESEARCH SUMMARY

Title Evaluation of Coal Conversion Catalysts

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Time Span January-December 1983
Annual Report

Objective To evaluate direct methanation catalysts and 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 assure that the direct methanation process is applicable to existing coal conversion processes, simulated quench gases of Lurgi, BGC Slagger, and Westinghouse processes are used in the evaluation of catalysts. To assure that the catalysts have adequate life expectancies, they are subjected to long periods of continuous reactions with a Lurgi-type raw gas.

Results The GRI-C-600 catalyst has higher activity (30+%) than the GRI-C-500 catalyst in the presence of a high CO₂ (40%) concentration. Life tests of both catalysts were continued. The catalysts have been on-stream for more than 1000 hours, using a Lurgi-type raw gas (Western coal).

The sulfur-resistant GRI-C-318 catalyst was evaluated for the steam reforming of a sulfur-containing (21 ppm H₂S) natural gas at low temperatures (700° to 1100°F). The results are comparable to those reported by other investigators using other types of sulfur-tolerant catalysts.

To provide design data for the economic/process evaluation of both the base case and the direct methanation case in a Westinghouse gasification process, a set of experiments was conducted to study the COS hydrolysis and hydrogenation reactions. Near-equilibrium (50°F approach) conversions were measured for the water-gas shift reaction, but away-from-equilibrium (250°F approach) conversions were measured for the COS hydrolysis/hydrogenation reactions.

Technical
Approach

Life tests of both GRI-C-500 and GRI-C-600 catalysts in the dual-reactor system were continued, using a dry-bottom Lurgi-type raw gas. The catalysts have been on-stream for over 1000 hours. The total CO conversion stabilized at 62% for the GRI-C-600 catalyst and at 54% for the GRI-C-500 catalyst.

The COS hydrolysis/hydrogenation reactions for the Westinghouse/CRC case at the process conditions of the post-conditioning stage were measured. The catalyst used was United Catalysts, Inc.'s C25-2-02, which is a water-gas shift catalyst. The water-gas shift reaction has a 10°F approach to the equilibrium; the COS hydrolysis reaction has a 50°F approach to the equilibrium by API data, or a 250°F approach to the equilibrium by JANAF data.

The steam reforming of a sulfur-containing natural gas was conducted at 700° to 1100°F, 0 psig, 300 to 1000 SCF/h-ft³, 21 ppm H₂S, and a H₂O/C molar ratio of 3:1. The catalyst used was the GRI-C-318, and the highest total CH₄ conversion was 8% (equilibrium conversion is 66%). However, the activation energy is similar to that in the data reported by UTC (PSD-6002 catalyst).

Project
Implication

This ongoing project is an integral part of GRI's overall program for developing the direct methanation process. The results obtained during 1983 allowed C F Braun and Co. to perform preliminary technical and economic evaluations of the direct methanation process in a Westinghouse and in dry-bottom Lurgi gasification plants. The results obtained indicate a significant advantage for direct methanation over conventional methanation technology for the dry-bottom Lurgi plant. The proposed configuration for the Westinghouse process did not show an advantage, primarily because of the large steam consumption required for COS hydrolysis.

Work on this project will continue during 1984. Life-testing of the GRI-C-500 and 600 series catalysts will be performed. The effect of trace quantities of liquid hydrocarbon gasification by-products on the catalysts' behavior will be determined. New process sequences will be tested to mitigate the cost penalties associated with the need for COS hydrolysis steam.

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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.

SUMMARY OF ALL PREVIOUS WORK PERFORMED ON THE CONTRACT

Work Performed

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

- Task I. Establishment of consistency of catalyst performance.

The initial activity of the catalysts was tested with a simulated 17-component 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.

The methanation reaction was measured at temperatures from light-off to $1150^{\circ}F$, 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 the conversion.

At constant temperature, pressure, and feed composition, the methanation reaction was measured at space velocities from 1,000 to 16,000 $SCF/h-ft^3$.

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

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 the conversion.

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.

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.
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.
An adiabatic reactor system was designed and constructed.
- Task XI. Obtain adiabatic design data for evaluation of raw-gas process schemes.
Design data are being obtained.
- Task XII. Test direct methanation catalysts.
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.
Life tests were and are being conducted on a number of catalysts with feed mixture compositions that simulate that 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.
Based on the feedback from CRC and KRISI, various types of experiments were conducted to provide design data: COS hydrolysis/hydrogenation reactions, water-gas shift reactions, steam reforming reactions, catalyst regeneration, and CO₂ reforming reaction.
- Task XVI. Storage of chemical by-products.
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 C₆H₅OH and 2 mole percent of C₆H₆ promoted carbon formation reactions at temperatures higher than 1000°F for all catalysts. The presence of CO₂ inhibited the methanation reaction when four catalysts (CRC's GRI-C-284 and GRI-C-318, Union Carbide's CRL-T-1, and Shell Oil's CB-79-57) were used, although the catalysts were not poisoned.

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, 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.
- With quenched gases, simulating those from the dry-bottom Lurgi, BGC Slagger, Westinghouse, and HYGAS processes, direct methanation with a high CO conversion (85 mole percent) 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 following design operating conditions for this preconditioning step were developed: 580°F, 500 psig, 3000 SCF/h-ft³, and approximately 16 mole percent steam in the feed.
- 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 a CO_2 (40+ mole percent), 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.

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 coal conversion processes because it minimizes the total steam usage and reduces loads on acid-gas removal systems.

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 four 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. SRI International (SRI) -- to study the fundamental catalyst properties
4. Kellogg-Rust Synfuels, Inc. (KRSI) -- to assist in process development and make economic analyses.

WORK PLAN FOR THE CURRENT YEAR

The following tasks are planned for 1983.

Task XI. Obtain Adiabatic Design Data

Data are to be obtained with an adiabatic reactor system to provide KRSI and CRC information for second-cut design and economic analysis. The catalyst to be tested first will be the GRI-C-500 series. Newly developed and commercially fabricated catalysts that have fulfilled the requirements outlined in Task XII will also be tested with this system.

Task XII. Test Direct Methanation Catalysts

Newly developed sulfur-resistant direct methanation catalysts, fabricated both on a laboratory scale and on a commercial scale, are to be tested at process conditions and with feed mixture compositions that simulate the raw gas from an established gasifier. The type of gasifier to be used can be the dry-bottom Lurgi, the Westinghouse, or the BGC Slagger. The catalysts are to be tested for their light-off temperatures, high-temperature resistance, and activities as a function of temperature, pressure, space velocity, steam, ammonia, BTX, sulfur compounds, hydrogen chloride, hydrogen cyanide, and oils.

Task XIII. Determine Catalyst Life

Life tests are to be conducted on the existing GRI-C-500 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 is to be exposed to temperatures from 480° to 1150°F, pressures from 450 to 600 psig, feed compositions from raw gasifier effluents to the last reactor stage gases, steam concentrations from 0 to 20 mole percent, BTX concentrations from 0 to 2 mole percent, ammonia concentrations from 0 to 1 mole percent, and any other conditions such as sintering temperature, oils, and tars as directed by GRI.

Task XIV. Determine Kinetics of Reaction(s)

The kinetics of reactions are to be obtained isothermally in a continuous stirred-tank reactor. Data obtained from this study can be expressed in both the rate of CO conversion and the rate of CH₄ formation. These rate equations can be used in the material and energy balance of the process design. Rates of deactivation resulting from poisoning, aging, and fouling will also be determined if directed by GRI.

Task XV. Support Process Development

Design data are to be continually supplied to KRSI and CRC to assist in process design and development. Close communication is to be maintained among KRSI, CRC, and IGT, as it has been in the past. Data are to be obtained on the performance of each direct methanation stage. The product from the first reactor stage will be simulated and used as feed to the second reactor stage, etc., through the needed stages. The CO conversion will be determined for each reactor stage, with its corresponding feed composition as a function of space velocity in the range of 2,000 to 16,000 SCF/h-ft³, and the process operating conditions. The design information is to be determined by used feed mixtures that simulate the compositions of the raw gases from the dry-bottom Lurgi, the Westinghouse, the BGC Slagger, or any other coal conversion process as directed by GRI.

WORK ACTUALLY PERFORMED DURING THE CURRENT YEAR

The cocurrent life tests of the GRI-C-500 and the GRI-C-600 series catalysts (Tasks XII and XIII) were continued. In the support of process development work (Task XV), the COS hydrogenation/hydrolysis reactions at operating conditions of the shift convertor of a Westinghouse base case and at operating conditions of the post conditioner of a Westinghouse/GRC case were measured; a single reactor system was modified to include facilities for introducing "oils" in the ppm(v) range to the feed mixtures; and the steam reforming of a sulfur-containing natural gas was conducted using the GRI-C-318 catalyst.

Life Tests of the GRI-C-500 and GRI-C-600 Series Catalysts

Several additions and improvements were made to facilitate the operation of the microprocessor-controlled dual reactor system:

- A multipoint temperature recorder was added to record all furnace, line, and reactor temperatures continuously, providing immediate visual observation of the behavior patterns of all the temperatures in the reactor system over the previously unattended two shifts.
- The Brooks mass flow controllers were replaced by a combination of a Barber Coleman proportional controller, a Brooks E/I convertor, a Validyne power supply and transducer, and RCI control valves. The Brooks mass flow controller's capillary tubing can be plugged by solids and/or liquids more readily, and this controller is more difficult to disassemble and clean than the RCI control valves. It must be reassembled at the factory because of its electronic sensing devices, whereas the RCI valves can be reassembled at IGT's laboratory by IGT technicians.
- A Fisher gas chromatograph detector with the same sample size loop as that of the Perkin-Elmer Sigma I was added to the sample system to measure hydrogen concentration. It provides an improved hydrogen balance; previously, the measurement of water had not been accurate due to the hold-up in the transfer lines.
- Five computer chips for temperature control were replaced with new programs to extend the upper temperature limit from 1200° to 1800°F to evaluate the catalysts at high temperatures.

The GRI-C-500 and GRI-C-600 catalysts were loaded into the reactor system and tested with a standard gas at standard conditions. The data obtained from this test and those obtained from a previous batch of the same type of catalysts checked, and the standard tests were repeated after the holiday season and just before the life tests began. The initial life test conditions

are a dry-bottom Lurgi-type raw gas using a Western coal, 450 psig, 950°F, and 6000 SCF/h-ft³. The total CO conversions of both catalysts increased in the beginning, then gradually decreased. They were still decreasing after more than 500 hours on-stream; the CO conversion of the GRI-C-600 catalyst was 46%, and that of the GRI-C-500 catalyst was 37%.

Total CO conversion continued to decline after 600 hours on-stream. Informal discussions were conducted among GRI/CRC/IGT personnel to determine the cause(s) of the deactivation. The feed gas supply, especially the CO, was analyzed for metals by the X-ray fluorescence method, and Fe and Ni were detected. Quantitative analysis was done by flame atomic absorption; 330 µg of iron and 2.4 µg of nickel were found in each liter of gas. The chromium content was less than 0.1 µg per liter and was beyond the detection limit. For comparison purposes, the feed gas that was used in the previous 10,000-hour runs to obtain the first-cut design data was analyzed for metals content. The concentrations of Fe, Ni, and Cr were 2.7, 1.2, and 0.1 µg per liter, respectively. The present gas supplier, Fred Peters Welding Company, obtained its gases from Union Carbide, Linde Division, and stored them in carbon steel tanks. It is possible that metal carbonyls formed during storage.

Arrangement was made with the Matheson Company to purchase gases (CO, CO₂, CH₄, H₂) directly from its plants and to store the gases in IGT's own aluminum cylinders. Teflon balls were inserted into each cylinder to improve mixing of gases during preparation of the needed multicomponent feed mixtures. The metal content in this batch of feed gas was analyzed; 0.7 to 1.7 µg of Fe and 1.2 to 1.7 µg of Ni per liter of gas were found. These concentrations are lower than those found in the feed gases used in the 10,000-hour runs.

Fresh GRI-C-500 catalyst was loaded into the reactor, and fresh GRI-C-600 catalyst was prepared by CRC. Hot and cold traps were installed to filter out residual metal carbonyls, and the life test was continued.

A newly prepared Lurgi-type raw gas was introduced; the total CO conversion declined from 57% to 40% within 300 hours, and the CH₄ selectivity increased from 85% to 100%. Some of the CO₂ in the feed was also converted to CH₄. The standard gas was used to check the catalyst activity, and runs were continued for about 150 hours. The total CO conversion (53% to 55%) and the CH₄ selectivity (53%) remained consistent with those obtained previously.

To pinpoint the catalyst/reactor behavior, two blank runs, one on an empty reactor with inerts only and another on the empty reactor after the reactor system was thoroughly sulfided with H_2S , were conducted. No reaction was detected in either case. The catalyst was reloaded and sulfided thoroughly, and the same Lurgi-type raw gas was reintroduced.

This life test of the GRI-C-500 catalyst, which was begun on March 25, 1983, was continued with the same Lurgi-type raw gas. The total CO conversion decreased continually from 55% to 35% and was steady at about 35% for 120 hours after being sulfided with a mixture of 6 mole percent H_2S /94 mole percent H_2 , at 400 psig, 350°F, and 0.1 ft³/h for about 30 hours. The CH_4 selectivity remained at 100%; about 5% of the CO_2 in the feed was also methanated.

This GRI-C-500 catalyst-containing reactor was cooled, purged, locked, and relocated from the dual-reactor system to the microarc reactor system, which was used in obtaining the first-cut design data. The catalyst was evaluated with the same feed at the same conditions, and the results agreed with those obtained from the dual-reactor system. It appeared that the catalyst was encroached by some additional active species, such as iron. It was deduced that these species (Fe, Ni, Cr) came from the transfer lines that were previously contaminated by metal carbonyls, because the feed gases were clean and were passed through traps. It is mandatory, in the future, that all the tubings, valves, regulators, and flow controllers be either replaced or thoroughly cleaned once they have been exposed to metal carbonyls or any other poisons.

Fresh GRI-C-500 and GRI-C-600 catalysts were loaded in new reactors and were evaluated one at a time. Under standard conditions with the standard gas, the total CO conversion for the GRI-C-500 catalyst was 68%; CRC reported 66%, and previous work also reported 66%. The total CO conversion for the GRI-C-600 catalyst was 79%; CRC reported 75%, and previous work reported 76%.

The Lurgi-type raw gas that has been used in the life test was introduced. After 70 hours on-stream, for the GRI-C-500 catalyst, the total CO conversion was 60% and steady, and the CH_4 selectivity was 80%. These conversions are higher than those obtained during the first-cut design data. However, when the first-cut dry-bottom Lurgi-type design data were taken, the catalyst was on-stream for about 15 months; had gone through cyclings of

temperature, pressure, steam, and feeds with H_2/CO ratios of 0.5:1 to 2:1; and had been exposed to air twice.

The same Lurgi-type raw gas was introduced to the GRI-C-600 catalyst. The total CO conversion stabilized at 66% after 100 hours; the CH_4 selectivity was about 80%. The mass flow controller was stuck at a fixed narrow range, giving space velocities of from 4300 to 4900 SCF/h-ft³. Both the microprocessor and the pneumatic hardware were examined while the life test was continued. The space velocity could not be adjusted to the required 6000 SCF/h-ft³ without shutting down the total reactor system. After about 200 hours on-stream, the total CO conversion remained steady and the reactor system was cooled, purged, and locked. The flow controller was overhauled and is functioning smoothly. It was found that the stem of the control-metering valve had picked up a few speckles of soot, which, in turn, caused seizure between the stem and its packings. The soot was analyzed and found to be sulfides of copper, nickel, and iron.

In previous work by IGT and CRC, measurements showed that the higher the H_2/CO ratio in the feed, the more pronounced the reverse water-gas shift reaction. The bottom line is that the higher the H_2/CO ratio in the feed, the higher the CH_4 selectivity. In general, it may be concluded that, for the Lurgi-type raw gas studied here —

- The higher the H_2/CO ratio, the higher the CH_4 selectivity.
- The higher the temperature (for the same H_2/CO), the higher the CH_4 selectivity.
- The higher the pressure (same H_2/CO), the higher the CH_4 selectivity.
- The higher the CO_2 concentration, the lower the CH_4 selectivity.

This life test, which began on August 24, 1983, was continued to date. It is estimated that these two catalysts have been on-stream for more than 1000 hours. The total CO conversion is stabilizing at about 62% for the GRI-C-600 catalyst and about 54% for the GRI-C-500 catalyst. The methane selectivity varies from 86% to 94% for the GRI-C-600 catalyst and from 74% to 80% for the GRI-C-500 catalyst.

The changes in ethane, ethylene, propane, and butanes were measured. The increase in the mass of ethane was equivalent to the decrease in the mass of ethylene. It appeared that the hydrogenation reaction had taken place and the

hydrogenolysis reaction had not. A slight increase in the mass of propane and no change in butanes were noted. The reason for this behavior is not known. Some reverse water-gas shift reaction was detected, and the approach to equilibrium is about 120°F for the GRI-C-500 catalyst. In all prior work, the reverse water-gas shift reaction was measured whenever the feed H₂/CO ratios were more than 1.5:1.0.

COS Hydrolysis/Hydrogenation Reactions

This set of experiments was conducted to provide design data for the economic/process evaluation of both the base case and the direct methanation case in a Westinghouse gasification process.

The United Catalysts, Inc.'s C25-2-02 water-gas shift catalyst, which was used in the design by C.F. Braun and Co., was used in the experimental work for both cases. For the Westinghouse base case, based on the design specifications provided by CFB, the test conditions were 600 psig, 600°-800°-900°F, and 3000-5000-7000 SCF/h-ft³. The water-gas shift reaction has a 50°F approach to equilibrium, and the COS hydrolysis reaction has a 100°F approach to equilibrium (based on API 44 data). To meet the design specifications of the COS content in the shift convertor of a Westinghouse base case, the shift convertor temperature must be kept below 600°F at a space velocity of 7000 SCF/h-ft³, or below 690°F at 3000 SCF/h-ft³.

For the post conditioner of a Westinghouse/CRC direct methanation case, conditions were 600 psig, 600°-800°-900°F, and 3000-5000-7000 SCF/h-ft³. The water-gas shift reaction had a 10°F approach to equilibrium, and the COS concentration was 350 ppm at 600°F and 800 ppm at 900°F.

For this catalyst (C25-2-02), which was not designed for COS hydrolysis, and at the steam concentration (13.9%) of the feed to the post conditioner, the COS concentration was 350 ppm(v) at 600°F and 800 ppm(v) at 900°F.

Single-Reactor System

In 1982 GRI decided that both the 500 and the 600 series catalysts will be tested simultaneously within Task XII of the present contract so that the results obtained from the evaluation of these two catalysts can be compared directly. In addition, it was and still is desired, by GRI, that the effect of BTX, naphtha, phenol, and Lurgi oils (potential poisons) on the activity and life of the direct methanation catalysts will be determined in a separate

reactor system that is not within the present contract. The advantages of this cocurrent, separate testing method are —

- The activity and selectivity of the catalysts can be compared immediately.
- The effect of these potential poisons can be pinpointed accurately.
- The catalyst in the single-reactor system can be unloaded for examination without disturbing the long-term life test in the dual reactor system.

The GRI-C-500 series catalyst will be used. Steady-state measurements will be made at all times; these results will be compared with those obtained from the dual-reactor system. Upon detection of changes in activity, the flow of the potential poisons will be discontinued and measurements will be continued to determine if the deactivation reactions are reversible. If not, regeneration steps will be taken to determine the regeneration procedure. The spent catalyst will be forwarded to Catalysts Research Corporation for analysis.

A single-reactor system was modified, and a low-flow high-pressure pump was installed for the introduction of BTX, naphtha, phenol, and Lurgi oils. This work was discontinued at the end of February 1983 because of budget limitations.

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-C 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 CO₂ reforming of methane in the presence of sulfurs.

A set of experiments was conducted to study the steam reforming of a sulfur-containing natural gas. The conditions were 700° to 1100°F, 0 psig, 21 ppm sulfur, 300 to 1000 SCF/h-ft³, and a H₂O/C molar ratio of 3:1. The catalyst used was GRI-C-318. Most of the steam-reforming systems in present-day hydrogen and ammonia plants are operated at temperatures near 1650°F.

A direct comparison with the data reported by United Technologies Corporation cannot be made because UTC did not report its data in terms of percent of methane converted. The data were reported as "reaction rate constants." Nevertheless, a set of reaction rate constants was calculated

from our data. The activation energies, the slopes, of these two sets of data (GRI-C-318 and PSD-6002) are not vastly different.

MAJOR ACHIEVEMENTS DURING THE CURRENT YEAR

- A single reactor system was modified to include a low-flow, high-pressure pump for introduction of potential poisons 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. Under standard conditions with the standard gas, the total CO conversion was 68% for the GRI-C-500 catalyst (CRC reported 66%; previous work also reported 66%). The total CO conversion was 79% for the GRI-C-600 catalyst (CRC reported 75%, and previous work reported 76%).
- The dry-bottom Lurgi-type raw gas was introduced to these catalysts. The total CO conversion stabilized at 62% after 1000 hours on-stream, and the CH_4 selectivity varied from 86% to 94% for the GRI-C-600 catalyst. The total CO conversion was 54% after 1000 hours on-stream, and the CH_4 selectivity varied from 74% to 80% for the GRI-C-500 catalyst.
- The COS hydrolysis/hydrogenation reactions for the Westinghouse/CRC case at the process conditions of the post-conditioning stage were measured. The catalyst used was United Catalysts, Inc.'s C25-2-02, which is a water-gas shift catalyst. The water-gas shift reaction has a 10°F approach to the equilibrium; the COS hydrolysis reaction has a 50°F approach to the equilibrium by API data, or a 250°F approach to the equilibrium by JANAF data.
- The steam reforming of a sulfur-containing natural gas was conducted at 700° to 1100° , 0 psig, 300 to 1000 SCF/h-ft³, 21 ppm H_2S , and a $\text{H}_2\text{O}/\text{C}$ molar ratio of 3:1. The catalyst used was the GRI-C-318, and the activation energy is similar to that in the data reported by UTC (PSD-6002 catalyst).

MAJOR TECHNICAL PROBLEMS ENCOUNTERED DURING THE YEAR

Metal carbonyls (iron and nickel), which were detected in the feed mixtures, caused deactivation in the catalysts. Because the gas supplier stored the gases (CO, H₂, CO₂, CH₄, etc.) in carbon steel tanks, it is possible that metal carbonyls formed during storage. An arrangement was made with gas suppliers to purchase gases directly from their plants and to store them in IGT's own aluminum cylinders. Hot and cold traps were installed in IGT's reactor feed systems to further eliminate metal carbonyls.

CONCLUSIONS

The following conclusions were reached during this reporting period:

- The presence of iron and/or nickel carbonyls deactivates the activity of direct methanation catalysts.
- 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 CO₂ (40 mole percent) than the GRI-C-500 catalyst.
- If the JANAF equilibrium were approached, the COS concentration in the product at 600°F would be 105 ppm instead of 350 ppm. It would not require as much steam as in the CFB's design of the COS-hydrolyzer in the process analysis, or the COS hydrolysis reaction may be conducted concurrently with the water-gas shift reaction in the shift convertor with the addition of COS hydrolysis catalyst and steam.

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 1984 and 1985.

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 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 existing GRI-C-500 and GRI-C-600 series catalysts 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 of from 450 to 600 psig, space velocities of 1000 to 16,000 SCF/h-ft³ 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 1984 and 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 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 CO₂ 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 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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