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DIRECT CONVERSION OF METHANE TO C_2's AND LIQUID FUELS

Third Quarterly Technical Progress Report for the Period April 1 - June 30, 1988

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CONTENTS

I. CONTRACT OBJECTIVES

Methane is expensive to transport, so it is often flared or reinjected[1]. It is also a byproduct from coal gasification. Conversion of methane to liquid hydrocarbon transportation fuels in an energy efficient, economical process would represent important technology for extending natural hydrocarbon fuel reserves. One route from methane to liquid fuels involves the conversion of methane through light hydrocarbon gases rich in ethylene to liquid fuels. Other routes, including one through methanol, are considered less technologically feasible[2]. The technological hurdle in the route through light hydrocarbon gases rich in ethylene is the direct conversion of methane to this ethylene-rich mixture. The light olefins may then, ideally, with little or no separation of products, be converted over molecular sieve catalysts to gasoline and distillates using Mobil's Olefins to Gasoline and Distillate (MOGD) Process[3].

The objectives of the project are to discover and evaluate novel catalytic systems for the conversion of methane or by-product light hydrocarbon gases (from natural gas, Lurgi Dry Bottom Gasifiers, or Fischer-Tropsch processes) either indirectly (through intermediate light gases rich in C_2's) or directly to liquid hydrocarbon fuels, and to evaluate, from an engineering perspective, different conceptualized schemes. The approach is to carry out catalyst testing on several specific classes of potential catalysts for the conversion of methane selectively to C_2 products, including metal oxide catalysts, catalysts containing metals in unusual oxidation states, and other novel catalysts and process ideas, and to provide appropriate engineering support to the catalyst design and testing effort. Promising catalysts and process ideas will be further explored.

II. ABSTRACT

Promoted metal oxide catalysts were tested. Several of these exhibited similar high ethylene to ethane ratios and low carbon dioxide to carbon monoxide ratios observed for the NaCl/α-alumina catalyst system reported earlier. More experimental results were obtained consistent with an interaction between the support and supported catalyst components which results in the observed catalytic properties including the activity and the high ethylene to ethane ratios. Catalyst deactivation was confirmed in certain cases to be due to the loss of supported catalyst components. Addition of volatile chloride to the feed stream retarded or reversed catalyst deactivation; however, loss of alkali eventually resulted in catalyst deactivation. New catalysts containing alkaline earth additives were prepared which were less likely to lose catalyst components, and these catalysts were observed to exhibit slower deactivation. The type of catalyst support was found to be critical to selectivity, activity, and catalyst stability.

Research on catalysts containing potentially activated metals began with testing of metal molecular sieves. All tested were unselective, and some were unreactive. Silver catalysts were shown to be promising as low temperature catalysts and gave higher yields to C_2's at 650 °C than have been reported in the literature.

In the Second Quarterly Report[4], homogeneous oxidation of methane was shown to be significant under certain reaction conditions. Process conditions were found to minimize the homogeneous reaction component for catalyst screening, including the design of new reactors with reduced void volumes. A designed set of experiments showed how large the homogeneous reaction contribution is under different process conditions, and showed how high C_2 yields and C_2 selectivities could be with only the homogeneous reaction. Quartz chips were found to quench gas-phase reactions, especially at temperatures below 700 °C.

Perovskites were tested as potential methane coupling catalysts. Most of these were active for conversion of methane but unselective for C_2 formation. A layered perovskite ($K_2La_2Ti_3O_{10}$) of unique crystal structure gave the the highest C_2 yield of the complex metal oxides tested.

Economics of a Comparison Case process are being developed so as to establish a baseline against which processes developed using methane coupling technology can be compared. It consists of conversion of methane to synthesis gas, synthesis gas to methanol, and methanol to liquid fuels via olefins. This work is nearly completed.

Work has continued on the economic evaluation of a hypothetical process converting methane to ethylene. An engineering model of the methane coupling system has been prepared which will facilitate studies of the sensitivities of key economic to independent process variables.

Engineering support of the experimental program consisted of discussions of heat transfer, reactor design, and possible gas phase reactions contributing to observed results.

III. SCHEDULE

This program is planned as a 24-month research and development effort, from September 17, 1987 through September 16, 1989.

The contract work is composed of two tasks. Task 1 work involves the set-up of reactor equipment, the chemical investigation of novel and existing catalysts for the direct conversion of methane to light hydrocarbon gases rich in C_2's (ethylene and ethane), and the integration of the conversion of methane to C_2's with the conversion of C_2's to liquid hydrocarbon fuels. Task 2 involves development of and economic evaluation of conceptual processes for converting methane to C_2's and C_2's to fuels, and engineering assistance to catalyst design and testing. Tasks 1 and 2 will proceed during the entire duration of the program.

In Task 1, research on metal oxide catalysts (promoted metal oxide and rare earth catalysts) has continued. Research on catalysts containing metals in unusual oxidation states and other novel catalysts and process ideas has begun with tests of metal containing molecular sieves and complex and mixed metal oxides of particular structures, including perovskites. During the last six months of the contract, methane to C_2's with C_2's to fuels steps will be integrated and the use of typical by-product gas mixtures (from Lurgi Dry Bottom Gasifier and Fischer-Tropsch processes) will be demonstrated.

During the first year of Task 2, preliminary economics of a Comparison Case which uses established technologies for the conversion of methane to liquid fuels shall be developed to provide process performance targets (the minimum productivity and selectivity) which any new catalyst must meet to be economically attractive. The economics of the Comparison Case are nearly completed. Preliminary material, heat, and economic evaluations of a hypothetical methane to ethylene process (Case 1) and a process to convert methane to C_2's then liquid fuels case (Case 2) will identify promising process configurations, define catalyst performance criteria, and provide information to assist in designing catalysts and test reactors. A study to determine the sensitivity of the process economics to process variables on Case 1 will be started next quarter. Results from process configuration studies and sensitivity analyses shall be used to establish catalyst performance targets such as desirable ranges for conversions, selectivities, pressures, and temperatures.

During the second year of Task 2, catalysts or systems identified in Task 1 as having the most potential shall undergo engineering evaluation. The most suitable catalysts and reactor configurations will be identified and developed taking into consideration mass, heat, and diffusion characteristics of catalysts of interest. The commercial and economic impact of any significant new developments shall be explored, and shall be used to guide the research along the path of maximum commercial significance. Case 2 will be pursued during the final nine months of the two-year contract.

During this first 15 months of the contract, the catalyst design, preparation, testing, and performance evaluation work under Task 1 is being conducted by 1.8 full-time catalyst chemists and 2 full-time laboratory technicians (5 days/week, 1 shift/day) with additional part-time technical direction from the members of the technical management team and support from analytical, applied math, separations, and site services (maintenance) personnel. During the last 9 months of the contract, the catalyst design, preparation, testing and evaluation work will be conducted by 1.3 full-time catalyst chemists and 1.5 full-time laboratory technicians.

Three engineers will be involved in Task 2. Two of the engineers will be concerned mainly with process conceptualization, process integration, economic guidance, and input into the laboratory program on hydrocarbons, separations, equipment, and thermodynamics. The third engineer will be concerned with engineering assistance in the design of catalysts and reactor configurations, and in catalyst testing and interpretation of results. During the second, third, fourth, and fifth quarters of the contract, three engineers will provide a total of 6 man-months of effort. During the final nine months of the contract, 7 man-months of engineering support will be provided. This will include economic evaluation of the most promising catalysts, continued support for catalyst testing, and assistance in writing the final report.

IV. ORGANIZATION

The catalyst development, catalyst evaluation, and conceptual process design efforts for converting methane or by-product light hydrocarbon gases either indirectly or directly to liquid hydrocarbon fuels are being pursued by a group within the Solvents and Coatings Materials Division (SCMD) of Union Carbide with funding and engineering support provided by the Industrial Chemicals Division. During the initial portion of the contract, this SCMD group was part of the Engineering, Manufacturing and Technology Services Division of Union Carbide.

The work is performed at Union Carbide's South Charleston Technical Center, South Charleston, West Virginia 25303.

Project Manager and Principal Investigator is Dr. Barbara Knight Warren.

Program Manager is Dr. Donald C. Best.

V. SUMMARY OF PROGRESS

A. Task 1: Catalyst Design and Testing

Task 1 work involves the set-up of reactor equipment and the development and testing of catalysts for the direct conversion of methane to C_2's (ethylene and ethane). Later in the contract, efforts to convert C_2's to liquid fuels will be initiated.

Some new promoted metal oxide catalysts showed higher C_2 selectivity, higher activity and/or lower deactivation rates than the NaCl/α-alumina catalyst system reported last quarter. Several catalysts exhibited the high ethylene to ethane ratios and low carbon dioxide to carbon monoxide ratios typical of the NaCl/α-alumina catalyst system. More experimental results were obtained consistent with an interaction between the support and supported catalyst components which results in the observed catalytic properties including the activity and the high ethylene to ethane ratios. Deactivation was confirmed in certain cases to be due to the loss of supported catalyst components. Addition of volatile chloride to the methane feed stream retarded or reversed catalyst deactivation; however, loss of alkali eventually resulted in catalyst deactivation. New catalysts containing alkaline earth additives were prepared which were less likely to lose catalyst components. These catalysts exhibited slower catalyst deactivation rates. The type of catalyst support was found to be critical to selectivity, activity, and catalyst stability.

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In the Second Quarterly Report[4], homogeneous oxidation of methane was shown to be significant under certain reaction conditions. Process conditions were found to minimize the homogeneous reaction component for catalyst screening, including the design of new reactors with reduced void volumes. A designed set of experiments showed how large the homogeneous reaction contribution is under different process conditions, and showed how high C_2 yields and C_2 selectivities can be with only the homogeneous reaction. Quartz chips were found to quench gas-phase reactions, especially at temperatures below 700 °C.

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B. Task 2: Process Conceptualization

Task 2 covers all of the engineering studies. It involves evaluation and development of conceptual processes for converting methane to C_2's and C_2's to fuels, and also includes engineering assistance to catalyst design and testing. The intention is that engineering participation in economic evaluation, process conceptualization, and experimental design will speed up the development of the optimum process.

For Task 2, the Comparison Case consists of conversion of methane to synthesis gas, synthesis gas to methanol, and methanol to liquid fuels via olefins. All of the components of this technology have been demonstrated on a commercial or pilot scale. Economics of the Comparison Case process are being developed so as to establish a baseline against which processes developed using methane coupling technology can be compared. This work is nearly completed.

Work has continued on the economic evaluation of a hypothetical process converting methane to ethylene (Case 1). A model of the methane coupling system has been prepared which will facilitate studies of the sensitivities of process economics to key independent process variables.

Case 2 will be of a process which involves the conversion of methane to C_2's followed by the conversion of the C_2's to liquid hydrocarbon fuels. These two cases address the primary interests of UCC and DOE, respectively.

Work to support the experimental program has continued with attention to heat transfer and gas phase kinetics.

VI. FUTURE WORK

Work during the next quarter will continue on Tasks 1 and 2, as described in the schedule of Section III. Task 1 work will continue with the preparation and testing of new catalysts within the classes of complex and mixed metal oxides, promoted metal oxides, catalysts stabilizing metals in unusual oxidation states or energies, and new catalyst and process concepts.

In the next quarter, the plan for Task 2 is to complete most of the work on the Comparison Case and Case 1 and to provide guidance for the experimental program. In the following quarter, these cases will be completed, and initial economic sensitivity studies for Case 1 will be conducted. The economics of Case 2, the conversion of methane to C_2's and further to liquid hydrocarbon fuels, will be pursued the last nine months of the contract.

VII. TECHNICAL AND EXPERIMENTAL RESULTS

By K. D. Campbell and B. K. Warren
Contributions from K. E. Carmichael, G. L. Culp, and J. L. Matherne

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

VII. TECHNICAL AND EXPERIMENTAL RESULTS

TASK 1: Catalyst Design and Testing

INTRODUCTION:

Background

Direct conversion of methane to C_2's is an increasingly active area of research internationally[5], industrially[6], academically[7], and in government laboratories[8]. Although several different mechanisms have been proposed for the catalytic oxidative coupling of methane, Lunsford and coworkers[9-12] have elegantly and convincingly demonstrated, and others[13-17] have agreed, that the mechanism for conversion of methane to ethane and ethylene over the metal oxides studied (and probably over other selective methane oxidation catalysts for this reaction) involves abstraction of hydrogen from methane by the catalyst to produce methyl radicals and surface hydroxyls, followed by release of the methyl radicals into the gas phase where they couple to form ethane. Methyl radicals can also be produced in the gas phase without a catalyst, by initiation on surfaces, by direct reaction with oxygen, or by cracking of higher hydrocarbon impurities in the methane. Ethane produced by catalyzed or uncatalyzed reactions may be converted to ethylene through known gas phase free radical chemistry. The sequence for the conversion of methane to ethylene is shown in Figure 1.

Figure 1. Methane to Ethylene Current Technology

$$\text{Catalyst-O}^{*} + CH_4 \longrightarrow CH_3\bullet + \text{Catalyst-OH}$$

$$CH_3\bullet\ \text{(adsorbed)} \longrightarrow CH_3\bullet\ \text{(gas phase)}$$

$$2\,CH_3\bullet \longrightarrow C_2H_6$$

$$C_2H_6 \longrightarrow C_2H_4$$

This mechanism shows that much of the product distribution is dictated by gas phase chemistry, largely independent of catalyst, but dependent on the temperature and operating conditions. With this mechanism, one might at best approach C_2 yields above 50% if certain reported models of the mechanism are correct. Others (J. Labinger and J. McCarty) have proposed a yield barrier closer to 30%. Practically, literature results above a 30% yield to C_2's are very rare, and these are probably transient results which cannot be maintained over practical periods of time.

Methane can be converted to C_2's by a two-step process in which methane is reacted with a metal oxide to produce C_2's, then the reduced metal oxide is reoxidized[18-20] with air. Methane can also be converted to C_2's in a cofeed mode, where methane and oxygen, with or without a diluent, are fed simultaneously[21,22] to a reactor containing catalyst. Active sites on the catalyst are continuously regenerated by the oxygen present in this mode. In both cases, the major inefficiencies are the formation of CO and CO_2. Smaller amounts of C_3's, and some minor amounts of (especially in the sequential rather than the cofeed mode) C_4's and higher hydrocarbons are formed. Reactions are usually conducted at temperatures in the 700-950 °C range and operated at low pressures (5-50 psig), in fixed bed or fluidized bed reactors. Oxygen concentration is limited to about mole 10% in any stream to avoid operation within the explosive limits. The cooxidation mode of operation was preferred for all studies and used for all experiments in this Quarterly Report, although the sequential mode of operation is planned to be explored.

No stable catalysts have been reported in the literature. Almost all of the reported literature catalysts rapidly deactivate. A few metal oxide catalysts which are less volatile (e.g., Sm_2O_3) undergo phase changes resulting in deactivation. Most frequently, catalysts lose critical components due to volatilization at the high temperatures used for methane oxidation. Catalysts containing alkali metals lose the metal salts, e.g., the lithium is lost from the Li/MgO catalyst. Often, initial results from literature catalysts indicate transient high selectivities and/or yields of C_2's.

Approach

The plans at the beginning of this project were to explore simple catalyst systems which might be more active and/or stable than existing catalyst systems. Literature catalyst systems were predominantly variations on Li/MgO, the Mn-based ARCO catalyst, or lanthanide oxide systems. Catalysts which might provide high (greater than 1/1) ethylene to ethane ratios were of particular interest. Studies began with the exploration of a very simple NaCl on α-alumina catalyst discovered, but not reported, by Union Carbide's G. E. Keller and M. M. Bhasin in the late 1960's. They explored this catalyst only in a pulsed, rather than a continuous mode. Initial results obtained with NaCl on α-alumina catalysts operated in the cofeed mode were reported in the First and Second Quarterly Reports. These catalysts were coded UCC-S (powders requiring dilution with quartz chips) and UCC-A:N1 (larger mesh) catalysts. Further exploration of alkali/metal oxide catalysts was of interest, and new catalysts were sought, both to understand what was unique about alkali/metal chloride catalysts, as well as to provide catalysts superior to these. In addition to promoted metal oxides and mixed metal oxide catalysts, catalysts with highly reactive metals which might operate at low temperatures were also of interest, including metal containing molecular sieve catalysts and silver catalysts containing silver.

In the Second Quarterly Report[4], homogeneous oxidation of methane was shown to be significant under certain reaction conditions, and conditions were found to minimize the homogeneous reaction component during catalyst screening. The homogeneous reaction was minimized by utilizing reactors with low void volumes, and by appropriate choices of process conditions, especially reactor temperatures.

Recently, literature reports have addressed the question of the importance of the homogeneous oxidation of methane during catalytic oxidative coupling studies. Yates and Zlotin[23] studied methane coupling over lithium/magnesium oxide (Li/MgO) catalyst at atmospheric pressure and reported the formation of significant quantities of ethane and ethylene in the absence of a catalyst. They concluded that Li/MgO was mainly a combustion catalyst that produced more C_2's than the homogeneous reaction but at the cost of converting carbon monoxide to carbon dioxide. Hutchings[24] compared the homogeneous gas phase oxidation of methane to the reaction over Li/MgO at elevated pressures. At 520 °C and 5.8 atmospheres, they found that the catalyst appeared to have only limited effects. The catalyst enhanced the production of carbon oxides and hydrogen without significantly affecting the production of C_2's. Wolf and Lane[25] reported that at one atmosphere significant homogeneous gas -phase, oxidative coupling of methane occurred under certain experimental conditions. At a methane conversion of 2%, a hydrocarbon (C_{2+}) selectivity of 65% was reported. When the methane conversion was increased to 32%, a C_{2+} selectivity of 30% resulted with a C_{2+} yield of 9.6%. Asami[26,27] reported that the noncatalytic oxidative coupling reaction of methane was enhanced under pressurized conditions (up to 15.8 atm) in a temperature range from 650 to 800 °C. However, the best C_2 yields reported were less than 6%.

In order to measure the extent and importance of the homogeneous gas phase reaction for the experimental conditions and reactor systems currently used in the second Union Carbide laboratory (the KDC laboratory), a designed sequence of experiments was performed. The experiments were designed to measure the effects of changing reaction temperature, methane to oxygen ratio, total pressure, and reactor flow rate (residence time). Data for the statistically designed set of experiments was analyzed by linear regression analysis. The effect of pressure on the homogeneous reaction was of sufficient interest to warrant further experiments. Additional experiments were also carried out to measure the effects of surface area on the extent of the homogeneous reaction.

Perovskites have a number of physical and chemical characteristics which make them among the most promising of catalysts proposed. For years, perovskites were largely unexplored for catalytic reactions[28]. They were then explored as oxidants in the automobile emissions area. More recently they have been explored as catalysts for several specific reactions. At Union Carbide[29], perovskites were found to catalyze some syngas conversions. A large number of perovskites were synthesized and characterized for this project and were available to be screened for methane coupling.

Imai[30] had reported $LaAlO_3$ to be highly active (48% selectivity) for the oxidative coupling of methane. This was the only example of a perovskite structure reported as a methane oxidation catalyst, it was not stated to be a perovskite, and perovskite features of interest were not discussed. The use of perovskites for methane coupling catalysts had not been proposed elsewhere at the time this work was proposed[31].

EXPERIMENTAL:

Catalyst tests carried out under this contract are assigned notebook ID numbers which identify the appropriate researcher and the notebook reference of the experiment. Codes including KDC indicate that work was done in the KDC laboratory, which has one operating reactor. Codes including BKW indicate that work was done in the BKW laboratory, which became operational this last reporting quarter, and which contains two operating reactors. The laboratory reactor systems are illustrated in Figures 1 and 2 of the Second Quarterly Report, and analytical procedures for the two laboratories are described in the Experimental Section, Tables 1-9, and Figures 3 and 4 of the Second Quarterly Report.

Linde oxygen, nitrogen, and ultra high-purity methane were used in all experiments unless noted otherwise. CP Grade ethyl chloride from Linde at 2% by volume is mixed in methane by Union Carbide's Automated Analytical Systems Gas Mixing Laboratory. Quartz wool is obtained from Alltech Company, and quartz chips are obtained from either National Scientific or Thomas Scientific. Molecular sieves and metal molecular sieves were used as obtained from UCC's Molecular Sieve Department (now part of UOP).

Supported catalysts were usually prepared using the incipient wetness technique. In this procedure, the amounts of components required to give the desired loading were dissolved in a quantity of distilled water necessary to just fill the pores of the support. The solution was then added to the support particles, and the resulting material was dried in a vacuum oven at 130 °C for several hours. The dried catalysts were tested without further treatment. In some cases, if the dopants were not easily soluble, suspensions of the finely ground components were added to a mixture of water which was stirred with the support with heating (with or without vacuum) to distribute the material in and on the support.

The reactor systems used for catalyst testing in both laboratories consist of gas feed-mix systems, steam feed systems, tubular reactors, Lindberg tube furnaces, liquid collection vessels, and gas analyzers connected directly to the product streams.

Reaction conditions used for catalytic runs included:

temperature	200 - 850 °C
reactant flow rate	25 - 165 cc/min
weight of catalyst	0.25 - 30.00 grams
methane	5 - 28%
methane/oxygen ratio	1.1 - 15
water	0%
nitrogen	balance

Reactions coded with KDC were run at 5 psig. Reactions coded with BKW were run at about 11 psig.

In both laboratories, the gas mixtures entering and exiting the reactor system were analyzed by gas chromatographic methods (vpc) using Hewlett-Packard Model HP-5880A gas chromatographs equipped with thermal conductivity detectors. Ultrapure helium was used for vpc analyses. Calibrations were done in the HP ESTD mode using calibration gases (Tables 5 and 9 of the Second Quarterly Report) prepared by Union Carbide's Automated Analytical Services group. Injections of calibration gases, product streams, and reactant streams were accomplished using a Valco valve with a fixed volume sample loop. Details of the analytical procedures may be found in the Experimental Section, Tables, and Figures of the Second Quarterly Report. In both laboratories, the components analyzed included methane, oxygen, nitrogen, ethane, ethylene, propane, propene, carbon monoxide, and carbon dioxide. Analyses for C_4's were not necessarily carried out unless there were large amounts of C_3's. Carbon balance calculations indicated that other hydrocarbon products and oxygenates were not present in significant quantities; thus, analyses of heavier hydrocarbons and oxygenates were not performed during these screening experiments. However, analyses for heavier hydrocarbons and oxygenates will be carried out in the future by gas chromatography coupled with mass spectrometry.

The numbers from the ESTD mode from reactant streams were used as read from the vpc. The numbers as read from the vpc for product components were adjusted to correct for volume changes by multiplying by nitrogen in the reactants divided by nitrogen in the products. The Key in Appendix A shows how these numbers were used.

BKW Laboratory

For all BKW laboratory results described in the Results and Discussion Section below, or in Tables and Figures, the Experimental section and Appendix D describe catalyst preparation procedures, and Appendix E describes catalyst compositions. The key to abbreviations used in Tables or Figures, and to terms used in the Results and Discussion section appears in Appendix A.

Catalyst compositions are described in Appendix D. For those catalysts prepared from adding components, these were generally high purity (99.99+) components added by one of two general procedures, Procedure A or Procedure B. In Procedure A, supported catalysts are prepared using the incipient wetness technique. In this procedure, the amounts of components required to give the desired loading are dissolved in a quantity of deionized, distilled water necessary to just fill the pores of the support. The solution is then added to the support particles. In some cases, if the dopants are not easily soluble, suspensions of the components are added to the support. The resulting material is dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa for 1 to 50 hours (usually 18 20 hours). The dried catalysts are either tested without further treatment or first calcined in air. Metal or inorganic compound loadings are expressed as weight percent based on the weight of the support.

In Procedure B, supported catalysts are prepared by adding the proper amount of component(s) to a mixture of water which is stirred with the support, while heating in a glass container on a hotplate for 2 to 3 hours (or until almost no water is left), to distribute the material in and on the support. If the dopants are not easily soluble, they are finely ground first. Deionized, distilled water is used (50 mL unless stated otherwise). The resulting material is dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa for 1 to 50 hours (preferred 18-20 hours). The dried catalysts are then calcined in air.

Elements contained in various molecular sieve catalysts tested include oxygen (O), aluminum (Al), phosphorus (P), cobalt (Co), magnesium (Mg), manganese (Mn), and/or silicon (Si). Abbreviations for these catalysts will be followed in this Experimental section by second abbreviations listing these elements. All molecular sieves were powders. In each case, 0.5 grams (0.55 mL) of catalyst was diluted with 5 mL (5.5 grams) of 30 to 40 mesh quartz chips (from Thomas Scientific). Catalysts were obtained from Union Carbide's Molecular Sieves Department, and included:

29-BKW-142	MnAPSO-5	MnAlPSiO-5	U. S. Patent 4,686,092
29-BKW-143	CoAPSO-34	CoAlPSiO-34	U. S. Patent 4,744,970
29-BKW-146	MnAPSO-34	MnAlPSiO-34	U. S. Patent 4,686,092
29-BKW-147	MAPO-34	MgAlPO-34	U. S. Patent 4,567,029
29-BKW-151	CoAPSO-34	CoAlPO-34	U. S. Patent 4,567,029
30-BKW-66	AlPO4-5	AlPO4-5	U. S. Patent 4,310,440
30-BKW-67	SAPO-5	SiAlPO-5	U. S. Patent 4,440,871
30-BKW-80	MAPO-36	MgAlPO-36	U. S. Patent 4,567,029
30-BKW-95	highly acidic molecular sieve		

A catalyst of 9.1 weight percent silver on alpha alumina (30-BKW-115) for reaction 30-BKW-123 is prepared by the following procedure. 600 grams of 88% aqueous lactic acid are added to a glass beaker and heated to 80 °C with stirring (30 minutes). The temperature of this mixture is between 80 and 85 °C while 220 grams of silver oxide (available from either Ames Goldsmith Corporation, Glens Falls, New York) are slowly added, with stirring. The mixture is stirred an additional 30 minutes at 80-85 °C, then 10 milliliters of CP grade hydrogen peroxide from J. T. Baker are added. The clear solution is slowly added from a 1000 milliliter glass separatory funnel over a period of 5 minutes to 300 grams of Norton SA5502 hollow cylinder supports. These are first evacuated under a vacuum of from less than 1 kPa to 70 kPa pressure at 80 °C for 120 minutes in a 5.7 cm i. d.(5.9 o. d.) glass tube, which is 36 cm long. This tube is fitted with a stopcock on the bottom and on the top, through a two-hole, black rubber, size 12 stopper, with a separatory funnel and a vacuum adapter. The glass tube is heated with a 6 foot

Thermolyne heat tape, controlled by a Variac. The impregnating solution remains in the tube with the support at 81 °C for 60 minutes, then is drained. The resulting material is dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa for 1 to 50 hours (preferred 18-20 hours). The dried catalysts are then calcined in air. Metal or inorganic compound loadings are expressed as weight percent based on 100 weight percent support.

A catalyst of 2 weight percent potassium chloride and 9.1 weight percent silver on alpha alumina is prepared for reaction 31-BKW-9 by use of Procedure A (above) with the catalyst of 9.1 weight percent silver on alpha alumina, 30-BKW-115. In a similar manner, catalysts of 1.5% $BaCl_2$ and 9.1 weight percent silver on alpha alumina (for 31-BKW-2) and of NaCl and 9.1 weight percent silver on alpha alumina (for 31-BKW-1) are prepared.

The reactor system in the BKW laboratory contains two parallel reactors which may be fed with a variety of gases. It consists of a gas feed system, two tubular microreactors (a steam feed system to one of these), two Lindberg tube furnaces, two liquid collection systems, an on-line gas analyzer with a stream selector, and a separate liquids analyzer. All the lines to the reactors are made of 1/8" and 1/4" SS tubing unless otherwise stated. The tubular reactors are operated outside the hood behind a safety shield.

Methane, oxygen, nitrogen, and other gases are fed through a feed system which controls flows with Brooks mass flow meters and which controls pressure with a Grove back pressure regulator. The Grove regulator sends excess gases to a vent in the hood. The system is designed so that gas ratios may be set independently from flow rates and reactor pressures (controlled by GO Regulators after the reactors and collection pots), and flow rates with all of these parameters easily and independently changed. Relief valves are present between the gas regulators and the Brooks mass flow meters. A relief valve (vented to the hood) set at 25 psig is installed immediately before each quartz reactor so that the pressure in the reactor cannot exceed 25 psig. Low flow switches after the reactors and before the liquid traps activate an emergency shut down system which passes nitrogen over the reactors and turns off heaters if there is a leak or plug in the reactor.

Two Lindberg Mini-Mite, model 55035, tube furnaces (800 watts, 115 volts, 1100 °C maximum operating temperature) were used for heating the tubular microreactors. The entire cylindrical heated chamber is comprised of two halves, making up the split-hinge furnace design. Each half is a composite unit of Moldatherm, Lindberg's high temperature ceramic fiber insulation, and a helically coiled alloy heating element. The furnaces were equipped with a chromel-alumel (type K) thermocouple (centrally positioned within the heated region) which was used to measure the temperature of the furnace. The heated region is 31 cm long and the hottest point is 2 cm above the center of this region. Athena temperature controllers were used to control the furnace temperatures. The temperature controllers have built-in overtemp devices which turn the furnace off when the operating temperature exceeds the set temperature by 80 °C.

Two cold traps, cooled with a circulating cooling fluid (50/50 mixture of propylene glycol and water) pumped through coiled copper tubing by a Haake A81 refrigeration unit, were used in parallel for each reactor so that one cold trap could be removed and sampled while the other one was collecting product. These traps were located after the reactor outlet (after the low flow switches) and before the reactor back pressure regulator. Another trap was present in the line after the back pressure regulator. This third trap was not cooled.

Compounds which were not trapped were analyzed on an HP 5880A vpc equipped with a thermal conductivity detector and column switching (including a molecular sieve column), utilizing four Valco valves and a 10-port stream selector, programmed to operate from the HP 5880A keyboard. Initial and final column temperatures of 85 °C and 170 °C were used for the analyses. Details of the analytical procedures may be found in the Experimental Section, Tables, and Figures of the Second Quarterly Report. Feed streams were periodically analyzed before, during, and after runs. Analyses of trapped liquids by gc-ms indicated only water. The water was acidic (<pH 3) by litmus paper. By ir, traces of carbonyls could be detected.

Thermocouples, heating tape, and glass insulating tape are present on the steam feed system and lines before and after the reactors. Brooks mass flow meters were calibrated in place.

Quartz reactors used included Reactor A, Reactor C, Reactor D, and Reactor E. Reactor A (Figure 5 of the Second Quarterly Report) was constructed of 1.5 cm i. d. quartz tubing (1.7 cm o. d.) with thermocouple wells of 0.3 cm i. d. quartz tubing (0.5 cm o. d.) positioned along the center of the reactors. Reactors were operated vertically as shown in Figure 5 of the Second Quarterly Report. All quartz tubing used in the construction of all reactors was obtained from National Scientific Company. Reactor A was 56.5 cm long, and the thermocouple well extended 33.75 cm into the reactor. The bottom of the heated region of the reactor was 12.75 cm above the bottom of the reactor. The top of the heated region was 46.75 cm above the bottom of the reactor. The post-catalyst volume was packed with 20/40 or 14/30 mesh quartz chips in order to minimize the high temperature post-catalyst residence time of the products, and to hold the catalyst in place. The "O"-ring joints were supplied by Quartz Scientific Inc. The bottom end of the reactor is connected to 1.0 cm i. d. (1.2 cm o. d.) quartz tubing at a right angle to the reactor. The ends of the reactor were made of quartz "O"-ring joints (1.5 cm i. d. at the inlet ; 0.9 cm i. d. at the outlet) which allowed easy placement of the reactor into the system. "O"-ring joints for all reactors were supplied by Quartz Scientific Inc. The joints were connected using FETFE "O"-rings obtained from Ace Glass Incorporated.

For reactors A, C, D, and E in the BKW laboratory, the center of the catalyst bed is 18.5 cm above the bottom of the oven, or 31.25 cm above the bottom of the reactor. When this point is heated to 802 °C under typical flow rates of gases, it is 800 °C at 2-2.5 cm above this point and 800 °C at 2 cm below this point. 5 cm below this point, it is 793 °C, and 10 cm below this point, it is 773 °C. 18.5 cm below this point (at the bottom of the heated portion of the reactor, the temperature is 645 °C. Figure 7 of the Second Quarterly Report presented a heat profile for Reactor A when it is heated to 800 °C. It may be seen that there was a significant temperature drop from the catalyst bed to the bottom of the reactor.

Reactor C (Figure 2) was constructed of 0.9 cm i. d. quartz tubing (1.1 cm o. d.) to minimize void volume. Reactor C was 56.5 cm long. The bottom of the heated region of the reactor was 12.75 cm above the bottom of the reactor. The top of the heated region was 46.75 cm above the bottom of the reactor. The post-catalyst volume was packed with 20/40 or 14/30 mesh quartz chips in order to minimize the high temperature post-catalyst residence time of the products, and to hold the catalyst in place. The bottom end of the reactor is connected to 1.0 cm i. d. (1.2 cm o. d.) quartz tubing at a right angle to the reactor. The ends of the reactor were made of quartz "O"-ring joints (1.5 cm i. d. at the inlet ; 0.9 cm i. d. at the outlet) which allowed easy placement of the reactor into the system.

The top 30.5 cm of Reactor D (Figure 3) was constructed of 0.9 cm i. d. quartz tubing (1.1 cm o. d.). This was connected to 26 cm of 3 mm i. d. (5 mm o. d.) quartz tubing to minimize void volume even more than did Reactor C. Reactor C was 56.5 cm long. The bottom of the heated region of the reactor was 12.75 cm above the bottom of the reactor. The top of the heated region was 46.75 cm above the bottom of the reactor. The post-catalyst volume of the wider part of the reactor was packed with 20/40 or 14/30 mesh quartz chips, quartz wool, or both quartz chips and quartz wool in order to minimize the high temperature post-catalyst residence time of the products, and to hold the catalyst in place. The bottom end of the reactor is connected to 1.0 cm i. d. (1.2 cm o. d.) quartz tubing at a right angle to the reactor. The ends of the reactor were made of quartz "O"-ring joints (1.5 cm i. d. at the inlet ; 0.9 cm i. d. at the outlet) which allowed easy placement of the reactor into the system.

The top 29.5 cm of Reactor E (Figure 4) was constructed of 1.5 cm i. d. quartz tubing (1.7 cm o. d.). This was connected to 27 cm of 3 mm i. d. (5 mm o. d.) quartz tubing. The reactor was designed to hold larger amounts of catalyst in a given vertical segment of the reactor while minimizing the void volume after the catalyst zone. Reactor C was 56.5 cm long. The bottom of the heated region of the reactor was 12.75 cm above the bottom of the reactor. The top of the heated region was 46.75 cm above the bottom of the reactor. The post-catalyst volume of the wider part of the reactor was packed with 20/40 or 14/30 mesh quartz chips, quartz wool, or both quartz chips and quartz wool in order to minimize the high temperature post-catalyst residence time of the products, and to hold the catalyst in place. The bottom end of the reactor is connected to 1.0 cm i. d. (1.2 cm o. d.) quartz tubing at a right angle to the reactor. The ends of the reactor were made of quartz "O"-ring joints (1.5 cm i. d. at the inlet ; 0.9 cm i. d. at the outlet) which allowed easy placement of the reactor into the system.

Catalysts for reactions coded BKW were not first preconditioned with oxygen. The reactors were filled with washed quartz chips above and below the catalyst bed. Tubing of 0.3 cm i. d. in Reactors D and E were not filled with quartz. Quartz wool was used to separate quartz chips from the catalyst bed and to hold quartz chips in the reactor. Undiluted catalysts of varying mesh sizes were used except in cases where the catalyst was only available as a fine powder. In these cases, it was diluted with quartz chips.

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Charged reactors were flushed with nitrogen during heating. After the experiment the reactant flow was terminated and the reactor was flushed with nitrogen while cooling. The reactor was cleaned between experiments by thoroughly rinsing with acid followed by distilled water. New reactors were frequently used.

KDC Laboratory

Substances tested for catalytic methane coupling activities this quarter included mixed and complex metal oxides, such as ABO_3 perovskites. The catalysts were either obtained from suppliers, obtained from a previous Union Carbide Corporation project, or prepared using a high temperature migration technique. In the high temperature migration technique, mixtures of metallic oxides and/or carbonates having the correct stoichiometric ratio of metals were ground to fine powders and placed in alumina crucibles. The crucibles were then heated in air to 1050 °C for approximately 6 hours. The samples were then ground again, and the heating process was repeated. After three heating cycles, the samples were ground to powder and tested without further treatment.

Doped mixed metal oxide catalysts were prepared by grinding to a fine powder the correct proportions of dopant (or dopant precursor) and mixed metal oxide necessary to give the desired dopant loading. The mixture was then heated to 800-900 °C for several hours and tested without further treatment.

Some supported catalysts were made by complexing components with organic compounds in water, adding this mixture to the support, draining and drying the support, followed by oven drying the catalysts precursors at 130 °C. Next these were roasted in an air flow at 600 °C, then these were used directly, or additional dopants were added in water by the incipient wetness technique.

Reactors A (described above) and B were used in the KDC laboratory. Reactor B was constructed by enlarging to 1.3 cm o.d. the outlet end (26.7 cm) of the thermocouple well in Reactor A (Figure 5 of the Second Quarterly Report). This reactor was charged with catalyst by adding 20 to 40 mesh washed quartz chips around the enlarged thermocouple well (post-catalyst region), quartz wool, catalyst bed, quartz wool, and a solid 1.3 cm o.d. quartz rod with 20 to 40 mesh washed quartz chips around the outside (preheater region). This modified reactor had approximately 50% less void volume than Reactor A.

The reactors were filled with washed quartz chips above and below the catalyst bed. Quartz wool was used to separate quartz chips from the catalyst bed and to hold quartz chips in the reactor. The catalyst beds were composed of 0.25 - 3.00 grams of catalyst (fine powder) mixed with enough washed 20/40 mesh quartz chips to make a total volume of 4 cc. The quartz chips were obtained from National Scientific Company.

Charged reactors were flushed with nitrogen during heating. The reactor temperature was raised to 465 °C and the catalyst was preconditioned with flowing air (100 cc/min) for 1 hour. After preconditioning the air flow was terminated, the reactant flow was started, and the reactor temperature was raised to the desired value. Product stream analysis was carried out at one-hour intervals using gas chromatography. After the experiment the reactant flow was terminated and the reactor was flushed with nitrogen while cooling. The reactor was cleaned between experiments by thoroughly rinsing with acid followed by distilled water.

Modifications currently being carried out on the KDC laboratory system will allow greater flexibility in the experimental variable settings and will add a second reactor to this system.

RESULTS AND DISCUSSION:

BKW Laboratory

Control Studies

Control studies were done to determine temperatures, reactors, and reaction conditions where methane reactions were slow enough that the homogeneous reaction would not interfere with catalyst results. Initial studies reported in the Second Quarterly Report showed that new reactors were needed to reduce void volume in order to minimize the homogeneous component of the reaction. Studies were continued to compare results of the new reactors with those of Reactor A, and to determine the effect of added volatile chloride (ethyl chloride) on the homogeneous (uncatalyzed) reaction, so that volatile chloride could be added to methane coupling reactions to replace chloride which might be lost from catalyst compositions containing chloride.

Results from all conditions (see Table 1) of four control runs without catalyst but with quartz chips (using three reactors) are presented in Figure 5 (selectivity vs. temperature) and in Figure 6 (conversion vs. temperature). The observed results are from homogeneous (uncatalyzed) gas phase oxidation of methane. Quartz surface area from the reactor and quartz chips is low (with the surface area of 14/30 Thomas Scientific quartz chips measured at 0.08 m^2/g), but quartz initiation and quenching reactions are expected to contribute to some degree. Figure 5 shows that selectivity to C_2's was low at 700 °C and rose to the 25-45% range at 750 °C. Further increases in temperature did not improve the selectivity. Figure 6 shows that methane conversion rose as the reaction temperature was increased.

The table below shows the highest methane conversions for each experiment without added volatile ethyl chloride (ECl) in the gas feed. Results depend on the history of the reactor (temperature and ethyl chloride level), and complete results are presented in Table 1. The top part of Reactor E is the same width as Reactor A, but Reactor E narrows to a 3-mm i.d. capillary tube after the catalyst bed. Reactor D has the same capillary tube in the lower part of the reactor and is narrower in the top part of the reactor as well (for the least void volume).

Blank Runs

Reaction	ECl	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	Time	Reactor
30-49	0	750	50	6.76	26.3	1.73	9.2	0.63	195	A
30-79	0	750	50	4.12	43.7	1.75	6.54	0.27	400	D
30-82	0	750	50	9.92	35.1	3.38	12.8	1.05	1455	E
29-139	0	800	50	17.04	28.8	4.92	35.3	2.48	4260	A
30-79	0	800	50	6.63	41.2	2.68	12.1	0.65	315	D

The amount of reaction is smaller in Reactor D with the smaller void volume. At 750 °C and 50 sccm flow rate, reaction is at a sufficiently low level with this reactor that the homogeneous reaction would not interfere with catalyst testing (at this temperature or lower temperatures with a 50 sccm or higher flow rate, with 10% methane and 5% oxygen at 11 psig pressure). Reactor D will be used preferentially in the BKW laboratory unless large amounts of catalysts are used; then Reactor E can provide a smaller axial temperature differential for the catalyst bed.

Although methane conversions are higher with Reactors A and E at 750 °C, these methane conversion levels are low enough for catalyst testing under these conditions if necessary. Reactor A cannot be used under these conditions at 800 °C, since methane conversion is high at this temperature. Although Reactor E has a narrower diameter after the reaction zone, the void volume in the hottest part of the reactor is the same as that for Reactor A, so conversions are similar between the two reactors. The reactors used for these runs are described in the Experimental Section, and are illustrated in Figure 5 of the Second Quarterly Report and Figures 3 and 4 of the current Quarterly Report.

Figures 7, 8, and 9 show the effect of addition of 100 ppm ethyl chloride to reaction 30-BKW-49. The table below shows results with three reactors at two temperatures for the gas phase, uncatalyzed reaction with added ethyl chloride. Addition of ethyl chloride increases the ethylene to ethane ratio (Figure 7), the selectivity to C_2's (Figure 8), and the methane conversion (Figure 9). At 750 °C in Reactor D with 50 ppm ethyl chloride, methane conversion is only 2%, which is an acceptable level for testing catalysts. Methane conversions with Reactors A and E at 750 °C or 800 °C are too high for catalyst testing unless higher flow rates are used.

Blank Runs

Reaction	ECl	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	Time	Reactor
30-82	50	800	50	27.18	23.6	6.26	54.7	3.43	330	E
30-79	50	750	50	2.15	41.8	0.89	0	0.54	540	D
30-82	50	750	50	12.77	33.2	4.01	19	1.17	420	E
30-49	100	750	50	12.53	29.2	3.54	20.4	1.6	1410	A
30-82	100	750	50	12.14	35.1	4.06	13.9	1.07	1545	E

Alkali Chloride/Metal Oxide Catalysts

The NaCl/α-alumina catalyst system, identified in the First Quarterly Report, showed high initial methane conversions and C_2 selectivities, atypically high ethylene to ethane ratios (3 to 20), low carbon dioxide to carbon monoxide ratios, catalyst deactivation, and changing product selectivities as a function of on-stream time. The high ethylene to ethane ratios are desirable since ethylene is a more valuable product than ethane and the conversion of ethylene into other products such as liquid fuels is possible. The low carbon dioxide to carbon monoxide ratios are advantageous for several reasons: less oxygen is required for the same methane conversion; the heat produced per unit of methane converted is lower when carbon monoxide rather than carbon dioxide is the product; and carbon monoxide is a more valuable product. Deactivation was observed to occur at different rates on these catalysts.

It was known that the support is not active or selective for C_2 production, but it was not known whether the alkali or chloride catalyst components were unique in some way, whether all of the catalyst components present were needed, or whether an unsupported catalyst would be active. Successful methane coupling with sodium chloride/α-alumina indicates that redox metals are not needed for this reaction, and it reasonable to assume that an oxide of sodium may abstract hydrogen from methane in the rate determining step of this reaction. It was therefore likely that oxides of other alkali metals might activate methane. Catalysts similar to and different from the NaCl/α-alumina system were designed to identify what made NaCl/α-alumina catalysts unique. The importance of component/support interactions in these catalysts was studied.

Catalysts with NaCl and KCl (UCC-A:P1, last Quarterly Report) exhibited results competitive with literature catalysts in methane conversion and C_2 selectivity, but showed product distributions containing ethylene to ethane ratios of over 2.5, rather than the ethylene to ethane ratios of about 1 which were typical for literature catalysts. Catalysts deactivate rapidly under cooxidation conditions. It was thought that this might be due to the loss of chloride or alkali, so both possibilities were explored. Alkaline earth salts are less volatile, and oxides derived from alkaline earth compounds were considered good candidates for methane coupling catalysts.

The alkali chloride/α-alumina catalysts were shown in the last Quarterly Report to have interesting selectivity patterns, e.g., high ethylene to ethane ratios and low carbon dioxide to carbon monoxide ratios compared with literature catalysts like the Li/MgO catalyst. Both sodium and potassium chloride catalysts were tested. The effect of these and other alkali salts on activity, selectivity, and catalyst deactivation was of interest. The uniqueness of the alkali, the chloride, and the support components, and the effect of catalyst loadings and other catalyst and process variables on C_2 selectivity and methane conversion was also of interest.

The catalyst in 29-BKW-99 was 3.85% NaCl on Norton 5551 α-alumina. This is a relatively inactive catalyst (see Table 2). More catalyst was used (30 g) in order to obtain high conversions at low temperatures. 29-BKW-81 (Second Quarterly Report) used 1 gram and 29-BKW-95 used 5 grams. Only 3.5 times the O_2 conversion was observed although 6 times the amount of catalyst as in 29-BKW-95 was used. This is presumed to be due to the temperature gradient over the 31 cc heated portion of the reactor. There is a 42 °C temperature difference over 11.5 cm of the reactor length when the hottest part of the reactor is at 802 °C (from 6.5 cm to 18 cm from the bottom of the heated zone). A yield (selectivity x methane conversion) of 17.9% was obtained at 700 °C at 50 sccm. In this experiment (run for 5 days) the methane to oxygen ratio was changed from 1.9 to 9.3 and the selectivity rose from 42% (C_2 yield was 16%) to 60% (C_2 yield was 7.2%) at 700 °C and 50 sccm. The oxygen conversion went from 77 to 99% but the methane conversion dropped from 37 to 12%. With a methane to oxygen ratio of 1.2 and a flow rate of 35 sccm the C_2 selectivity dropped to 31% and the oxygen conversion was 87% (C_2 yield of 17.5% and methane conversion of 55%). Because larger amounts of catalysts could not be tested at uniform temperatures due to the temperature gradients in existing ovens, ir ovens were ordered because they were claimed to have only a 2 °C difference over 5 or 10 inches of oven length. They were not used in this reporting period.

The concentration of NaCl on Norton 5551 α-alumina was increased from 3.85% in 29-BKW-95 (Second Quarterly Report) to 13.8% in 29-BKW-101. The catalyst with more NaCl was a lot less active under the same conditions (see Table 10 of the Second Quarterly Report, and Table 2 of the current Quarterly Report). This might indicate an interaction of the NaCl with the support which requires optimum amounts of both to be exposed for higher activity.

KCl (4.85%) on Norton 5551 α-alumina in 29-BKW-106 was compared with an equal molar amount of NaCl on Norton 5551 α-alumina. Under the same conditions, the KCl catalyst was slightly less active and deactivated much faster than the NaCl catalyst. C_2 selectivities were approximately the same (See Table 2). The catalyst histories were slightly different because the NaCl catalyst (Norton 5551 α-alumina, 29-BKW-95, Table 10 of the Second Quarterly Report) had been run briefly at 100 sccm flow rate at 700 °C before changing to the conditions under which these catalysts were compared (first at 700 °C and 25 sccm).

In 29-BKW-107, a CsCl (7.06%) on Norton 5551 α-alumina catalyst (Table 2) was compared with a NaCl (3.85%) on Norton 5551 α-alumina catalyst (29-BKW-95, Table 10 of the Second Quarterly Report). Under the same conditions, the CsCl catalyst was slightly less active and selective to C_2's than the NaCl catalyst, but the deactivation rates were similar. The catalyst histories were slightly different.

LiCl (2.82%) on Norton 5551 α-alumina (29-BKW-111, Table 2) was compared with an equal molar amount of NaCl on Norton 5551 α-alumina (29-BKW-95, Table 10 of the Second Quarterly Report). Under the same conditions, the LiCl catalyst was much more active but less selective than the NaCl catalyst. A doubling of the flow rate lowered the conversion but did not result in a change in the C_2 selectivity.

Temperatures of 600-750 °C and space velocities of 146 to 1098 hr^{-1} were examined for 5 grams of LiCl on Norton 5551 α-alumina (2.82% LiCl, 29-BKW-115, Table 2 and shown below). A 16.8% yield (selectivity x methane conversion) of C_2's was obtained at 750 °C with a 75 sccm flow rate. The outstandingly high C_2 yields at temperatures below 700 °C are considered transients (results not able to be maintained, even with vapor phase additives) due to the decomposition of LiCl on the catalyst surface, with release of high concentrations of chlorine radicals into the gas phase to catalyze methane oxidation and conversion of the product ethane to ethylene. Space velocities were very low at the lower temperatures. At 750 °C with more typical space velocities, rapid catalyst deactivation was observed.

2.8% LiCl/Norton 5551 α-Alumina

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl
600	46.3	23.9	7.7	32.6	0.7	10.0	4.8	55	146	0
650	33.6	20.0	6.6	11.5	0.4	10.0	4.8	145	146	0
675	38.9	26.2	10.1	11.5	0.5	10.0	4.8	235	293	0
725	44.1	33.6	14.7	9.2	0.4	10.0	4.8	325	878	0
750	47.0	36.1	16.8	19.7	0.3	10.0	4.8	430	1098	0
750	39.7	34.2	13.9	15.1	0.4	10.2	5.1	565	1098	0
750	21.7	28.6	6.2	1.6	1.0	10.2	5.1	715	1098	0

In 29-BKW-119, the catalyst was 3.85% NaCl on Norton 5551 α-alumina (impregnation method), as in 29-BKW-99. 30 g of catalyst were used in order to obtain high conversions at low temperatures. 29-BKW-99 also used 30 grams (Table 2). In 29-BKW-119 (Table 2 and below), the space velocity at a given temperature was lowered until about 95% oxygen conversion was obtained so as to maximize yield. A yield (selectivity x methane conversion) of 20.65% was obtained. This is the highest yield obtained to date. The highest C_2 yields reported in the literature at the time this reaction was run included few above 20% and only two over 30%. There is a temperature gradient of 42 °C from 6.5 cm to 18 cm from the bottom of the heated zone when the center of the reactor is at 800 °C (see the Experimental Section and Figure 7 of the Second Quarterly Report). Five grams of catalyst occupies about 5 to 6 cc of the reactor length. The catalyst did not deactivate as fast as other catalysts. This is presumed to be due to the larger amount of catalyst used. Volatilization of alkali and/or chloride from the top of the 30 g catalyst bed might result in deposition of the alkali at a lower point in the bed, or it might simply take more time to lose that much more alkali and/or chloride.

3.8% LiCl/Norton 5551 α-Alumina

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl
700	43.6	37.0	16.5	15.1	0.2	10.2	5.3	75	93	0
700	42.8	38.0	16.6	12.9	0.3	10.2	5.3	165	93	0
700	41.8	38.2	16.5	11.7	0.4	10.2	5.3	255	93	0
800	47.4	42.7	20.4	27.3	0.4	10.2	5.3	450	186	0
800	48.0	43.2	20.7	25.2	0.5	10.2	5.1	585	186	0
800	47.4	41.5	19.5	25.2	0.5	10.3	5.1	1515	186	0
800	46.1	40.7	18.7	28.5	0.5	10.1	5.0	1815	186	0
800	46.9	37.7	17.3	33.0	0.4	10.1	5.0	1905	233	0
800	45.8	35.7	16.0	24.4	0.4	10.1	5.0	1995	279	0
800	45.4	36.6	15.6	43.6	1.2	10.1	5.0	2085	58	0
700	25.4	42.6	10.3	4.7	0.3	10.1	5.0	2175	93	0
700	25.8	42.5	10.4	4.5	0.4	10.1	5.0	2280	93	0
700	20.1	42.6	8.7	4.2	0.4	10.0	4.7	3105	93	0

Reactions 30-BKW 64 and 74 tested RbCl/α-alumina catalysts for methane coupling, reactions 30-BKW- 65 and 83 test CsCl/α-alumina catalysts, and reactions 30-BKW 71 and 73 use KCl/α-alumina catalysts. Reaction 30-BKW-70 uses a LiCl/α-alumina catalyst. Ethyl chloride (50 ppm) was added to these reactions in the gas phase to replace chloride lost during reactions (see discussion below). The catalysts containing Rb and Cs exhibited C_2 yields below 14% under conditions tested, they deactivated rapidly, and they exhibited lower activity at 750 °C than similar Na or Li catalysts. Initial C_2 selectivities were over 50% at the low conversions. An initial selectivity of 65% was obtained with the KCl/α-alumina catalyst in reaction 30-BKW 71. In reaction 30-BKW-65, after only a few hours of operation, the reactor (Reactor D, which contains a 3 mm quartz tube after the catalyst bed) plugged in the narrow region with large, clear crystals which were found (by powder x-ray diffraction) to be cesium chloride. The LiCl/α-alumina catalyst showed an initial C_2 yield of 20.2% (41% C_2 selectivity) with an ethylene to ethane ratio of nearly 20 (at 750 °C and a GHSV of 1463 hr^{-1}). Catalyst deactivation was rapid.

A NaOH/α-alumina catalyst was shown to have initial activity and selectivity (at 35 minutes after the start of the experiment) comparable to a NaCl//α-alumina catalyst, but results after the initial analysis were indistinguishable from homogeneous reaction results (30-BKW-188, Table 2).

Results for alkali catalysts with other anions, e.g., one with $LiBO_2$ (30-BKW-118, Table 2), showed selectivities and activities which were not comparable to those of the catalysts containing NaCl.

A catalyst consisting of NaCl on Ga_2O_3 (30-BKW-132, Table 2) showed methane conversions, C_2 selectivities, and C_2 yields at least as good as similar catalysts on Norton SA5551 α-alumina.

It was concluded that alkali metal/metal oxide catalysts deactivated too rapidly for them to be practical catalysts for methane coupling. This was the case even when volatile chloride was added in the gas phase to replace any lost from the catalyst (see discussion below). The CsCl/α-alumina catalyst was shown to lose CsCl, and the catalyst used in reaction 29-BKW-95 (see the Second Quarterly Report), which was analyzed by ICP to contain 1.33% sodium prior to reaction, was found by ICP to contain 0.134% sodium after reaction for 46 hours at temperatures of 700-800 °C.

Pure Components

Since NaCl/α-alumina catalysts provided active catalysts, NaCl alone was tested as catalyst in reactions 30-BKW-23 and 30-BKW-48. (Table 3). Two forms of pure sodium chloride were tested for activity in methane coupling (30-BKW-27 and 28). Selected results below show that activity is low at temperatures of interest (750 °C and below).

Pure NaCl

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	Ref.
700	4.5	39.6	1.8	0.5	0.2	10.5	5.0	90	652	0	30-23
700	4.4	25.4	1.1	0.4	0.2	10.0	4.9	15	423	0	30-48
750	12.3	46.5	5.7	2.0	0.1	10.5	5.0	270	652	0	30-23
750	9.9	40.4	3.9	1.5	0.1	10.0	4.9	105	423	0	30-48
800	33.0	26.5	8.8	9.1	0.1	10.5	5.0	360	326	0	30-23

Zinc chloride was also tested as a methane coupling catalyst (Table 3). The table below shows that methane coupling results with zinc chloride are similar to results from alkali and alkaline earth/metal oxide catalysts, all exhibit the high ethylene to ethane ratios. Deactivation occurs, but it can be reversed with addition of ethyl chloride. Further work on zinc chloride and catalysts containing zinc chloride is of interest

Pure $ZnCl_2$

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	R
750	23.3	46.6	10.5	2.5	1.8	10.0	5.4	45	878	0	C
750	15.8	41.8	6.7	1.6	0.9	10.0	4.9	1005	878	0	C
750	19.5	48.5	9.4	2.4	1.2	10.1	4.7	1185	878	50	C
750	26.3	50.1	13.4	5.9	0.3	10.5	4.8	4060	878	500	C
750	25.8	49.8	13.1	5.8	0.2	10.5	4.8	4140	878	500	C
750	24.8	46.5	11.7	6.2	0.1	10.5	4.8	4325	878	500	C

Alkaline Earth Chloride/Metal Oxide Catalysts

It was not known whether the alkali or chloride catalyst components were unique in some way, whether all of the catalyst components present were needed, or whether an unsupported catalyst would be active. Since it was shown that deactivation of catalysts with alkali chlorides occurred, and that these catalysts lost alkali metal components, catalyst components with higher melting points, which might be less volatile, were sought. Several alkaline earth chlorides have higher melting points than the alkali chlorides (Table 4).

$BaCl_2$ (12.43%) on Norton 5551 α-alumina (29-BKW-110, Table 5) was compared with an equal molar amount of NaCl on Norton 5551 α-alumina (29-BKW-95, Table 10 of the Second Quarterly Report). Under the same conditions, the $BaCl_2$ catalyst was more active and selective to C_2's than the NaCl catalyst, and the deactivation rate appeared to be at least as good as that for the NaCl catalyst. The catalyst histories were slightly different. The catalyst in 29-BKW-110 is essentially the same as that in 29-BKW 128 (Table 5), but 29-BKW-110 showed higher yields under similar conditions than 29-BKW-128. This is presumed to be due to the longer time which 29-BKW-128 was operated (catalyst deactivation) prior to being compared under the same conditions with 29-BKW-110.

Temperatures from 700 to 820 °C and space velocities from 146 to 1317 hr^{-1} were examined for 5 grams of $BaCl_2$ on Norton 5551 α-alumina (12.43% $BaCl_2$, 29-BKW-114,

Table 5). A 17% yield (selectivity x methane conversion) of C_2's was obtained at 820 °C with a 90 sccm flow rate.

The catalyst of 29-BKW-118 was 12.43% $BaCl_2$ on Norton 5551 α-alumina (impregnation method). This is a relatively inactive catalyst similar to the NaCl catalyst 29-BKW-99 (Table 10 of the Second Quarterly Report), with the same interesting selectivity pattern (the ethylene to ethane ratio is high and the carbon dioxide to carbon monoxide ratio is low compared with literature catalysts like the Li/MgO catalyst). More catalyst was used (30 g) than in 29-BKW-110 (5 grams) in order to obtain high conversions at low temperatures. There is a 42 °C temperature difference from 6.5 cm to 16.5 cm from the bottom of the heated zone of the reactor when the center of the reactor is at 800 °C (see Experimental Section and Figure 7 of the Second Quarterly Report). A yield (selectivity x methane conversion) of 18.0% to C_2's was obtained.

Concentration Studies

In experiments 29-BKW-124, 29-BKW-125, 29-BKW-128, and 29-BKW-129, four concentrations of $BaCl_2$ on Norton 5551 α-alumina are compared under the same conditions (Table 5 and below). The 0.145% $BaCl_2$ catalyst (29-BKW-129) was the most active. The 1.41% $BaCl_2$ (29-BKW-124) catalyst was more active than the 12.43% catalyst (29-BKW-128) and the 0.019% $BaCl_2$ catalyst (29-BKW-125, the lowest activity).

Different Concentrations of $BaCl_2$ on Norton 5551 α-Alumina

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	Ref.	Conc.,%
700	15.9	54.6	8.6	1.7	0.7	9.8	4.7	135	714	0	29-124	1.41
700	5.1	17.3	0.9	0.7	0.6	9.8	4.7	180	714	0	29-125	0.02
700	13.3	58.5	7.6	1.3	0.7	10.1	5.1	180	714	0	29-128	12.4
700	20.2	57.6	11.4	3.0	0.4	10.1	5.1	135	714	0	29-129	0.15
800	42.6	39.2	17.3	11.9	0.5	9.8	4.7	420	1143	0	29-124	1.41
800	11.0	26.1	2.9	1.6	0.5	9.8	4.7	465	1143	0	29-125	0.02
800	40.8	40.7	16.9	10.9	0.4	10.1	5.1	465	1143	0	29-128	12.4
800	37.3	36.1	13.7	9.2	0.5	10.1	5.1	405	1143	0	29-129	0.15

This might indicate an interaction of the $BaCl_2$ with the support which requires optimum amounts of both to be exposed for higher activity, as was proposed above for a catalyst containing NaCl.

Mesh Studies

Catalysts of three different meshes were compared for 1.41% $BaCl_2$ on Norton SA5551 α-alumina in experiments 29-BKW-124 (14/30 mesh), 29-BKW-132 (100/140 mesh), and 29-BKW-138 (30/60 mesh). As shown in the table below, the smallest mesh catalyst was the most active, and the largest mesh catalyst was the least active.

Different Catalyst Meshes

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	Ref.	Mesh
700	15.9	54.6	8.6	1.7	0.7	9.8	4.7	135	714	0	29-124	14/30
700	26.7	48.8	13.1	3.3	1.0	10.0	5.2	125	682	0	29-132	100/140
700	19.5	55.5	11.0	2.5	0.8	9.9	5.0	135	714	0	29-138	30/60
800	42.6	39.2	17.3	11.9	0.5	9.8	4.7	420	1143	0	29-124	14/30
800	48.8	45.7	22.2	13.3	0.6	10.0	5.2	410	1705	0	29-132	100/140
800	45.6	41.8	19.7	14.5	0.4	9.9	5.0	225	1286	0	29-138	30/60

Measured surface areas (BET method) of the different mesh supports were similar for the different sized particles (14/30 mesh was $0.24 m^2/g$, 100/140 mesh was $0.27 m^2/g$, and 30/60 mesh was $0.25 m^2/g$), so differences in activity were not due to differences in surface area. Differences in activity could have resulted from mass transfer problems or slightly different pressure drops across the different mesh catalysts. Slight changes in pressure result in significant differences in activity. Pressure drops are larger over smaller particles. Experiments 30-BKW-3, 5, and 7 compare 30/60 to 60/100 mesh catalyst.

Different Catalyst Meshes

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	Ref.	Mesh
700	15.9	42.6	6.7	2.2	0.7	9.9	4.9	120	714	0	30-3	30/60
700	18.4	43.1	7.8	2.8	0.8	9.9	4.9	165	698	0	30-5	60/100
700	16.2	43.0	7.0	2.2	1.0	10.0	4.7	210	714	0	30-7	30/60
800	44.6	30.8	13.9	19.4	0.4	9.9	4.9	210	857	0	30-3	30/60
800	44.7	30.7	13.8	19.5	0.4	9.9	4.9	255	837	0	30-5	60/190

In each case, 5 g of catalyst is diluted with 25 cc of 14/30 quartz chips. Results show that 30/60 mesh catalysts are insignificantly different from 60/100 mesh catalysts, so it is thought that differences in 29-BKW-124, 29-BKW-132, and 29-BKW-138 were due to slight differences in pressure drops. Table 5 shows complete results for these experiments, and it is evident that catalyst deactivation occurs rapidly at 800 °C, even with barium catalysts. Loss of chloride is considered a possible cause for this.

Different Reactors

A narrow reactor without a thermocouple well (Reactor C, see Experimental Section) was used in experiment 29-BKW-152 to determine if the linear velocity of the gas had an effect on the rate of the reaction (if there were mass transfer limiting conditions). The same amounts of 1.41% $BaCl_2$ on Norton 5551 α-alumina catalyst of 30/60 mesh (5 g) under the same conditions were run in this experiment and in 29-BKW-138, which used the larger diameter Reactor A, with the thermowell. Since the rates of oxygen conversion were the same (35% for 29-BKW-138 and 34% for 29-BKW-154), it is tentatively concluded that there were not significant mass transfer limits to the rates.

Different Reactors

Temp	CC	Sel	Yield	=/-	CO2/CO	O2 Conv.	Time	GHSV	ECl	R	Ref.
700	19.5	55.5	11.0	2.5	0.8	35	135	714	0	A	29-138
700	18.9	59.7	11.4	2.1	0.9	34	135	714	0	C	29-152

Temperature gradients differ for catalyst beds of different length, and pressure drops this scale give only semiquantitative answers unless the same amounts of catalysts are used with similar process conditions and reactor configurations.

The selectivity was slightly better in the narrow reactor, as was expected from the smaller void volume after the catalyst bed, where lower conversion of C_2 products to carbon oxides after the catalyst bed would be expected. The reactor temperature gradients (see Figure 7 of the Second Quarterly Report and the Experimental section of this report) should result in a slightly lower overall temperature for the catalyst bed in Reactor C, since the narrow reactor requires the catalyst bed to be longer. The catalyst bed in 29-BKW-152 with Reactor C was 7.5 cm long. The bed in reaction 29-BKW-138 was 3 cm long. A more accurate comparison would be to compare catalyst in the narrow Reactor C with catalyst diluted with quartz to the same length catalyst bed, in the larger diameter Reactor A. This should result in a more similar temperature distribution across the catalyst bed, although void volumes after the catalyst bed are different, and this would be expected to affect results.

Reaction 30-BKW-9, with 1 g of catalyst diluted with 5 cc of 14/30 mesh quartz chips (3.2 cm catalyst bed length), may be compared with reaction 29-BKW-138 (3.0 cm bed length), where 5 grams of catalyst were run undiluted. Results show a higher selectivity, methane conversion, and yield for the larger amount of catalyst. This could result from slower deactivation for the larger amount of catalyst (more chloride present in the larger amount of catalyst for a longer period of time). Similar conclusions were reached when 30 g of catalyst were used in 29-BKW-119.

Different Catalyst Amounts

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	Ref.
700	19.5	55.5	11.0	2.5	0.8	9.9	5.0	135	714	0	29-138
700	16.4	34.0	5.5	2.3	0.7	10.0	4.7	255	714	0	30-9

Added Volatile Chloride to Retard Catalyst Deactivation

NaCl/α-alumina and BaCl2/α-alumina catalysts were observed to deactivate, and this was thought due in part to the loss of chloride from the catalyst, so catalysts were tested without and with addition of ethyl chloride in the feed gas. For these experiments, 140/200 mesh catalysts (10g) were diluted with 7 cc of quartz chips to prevent large pressure drops over the catalyst beds from the small particles. For both $BaCl_2$ (30-BKW-28, Figure 10) and NaCl (30-BKW-29, Figure 11) catalysts, a drop in rate was observed with time. Both reactions were oxygen limited. Addition of 500 ppm ethyl chloride in the feed gas resulted in increases in selectivity to C_2's, methane conversion, and yield to C_2's in each case. In neither case did the yield return to the original yield, and with the NaCl catalyst, yield, selectivity and methane conversion began dropping after an initial increase upon addition of ethyl chloride. Loss of chloride is one reason for catalyst deactivation. It was shown above that catalysts containing sodium and cesium lost these components during reaction.

Major process variables including methane to oxygen ratio, temperature, space velocity, and the amount of ethyl chloride in the feed gas were varied in experiment 30-BKW-36, which used a $BaCl_2/\alpha$-alumina catalyst. The selectivity, methane conversion, and yield varied as expected, with higher methane to oxygen ratios resulting in higher selectivities and lower methane conversions, and with selectivity increasing and methane conversion decreasing with an increase in space velocity. Increases in temperature resulted in higher methane conversions and lower selectivities. The ethyl chloride level in the feed gas was 500 ppm for the first fifty hours of the experiment, then it was dropped to 100 ppm. This resulted in a slight increase in methane conversion and yield to C_2's, with little change in the selectivity, as may be seen in Figure 12 and in Table 5. This indicates that 500 ppm ethyl chloride is not necessarily the optimum level for ethyl chloride under the process conditions used. In spite of the process changes, a 17% C_2 yield was obtained after 70 hours in reaction 30-BKW-36. The presence of ethyl chloride successfully retards catalyst deactivation..

Barium and sodium catalysts were tested starting with 100 ppm levels of ethyl chloride in the feed gas in experiments 30-BKW-44 and 45. The catalyst containing sodium deactivated more rapidly than the catalyst containing barium. This was one of the longest runs to date.

Lower levels of ethyl chloride were used in reaction 30-BKW-52, since results in 30-BKW-36 showed 100 ppm ethyl chloride to be better than 500 ppm ethyl chloride. Results from 50 ppm ethyl chloride showed this level to result in higher methane conversions and C_2 yields than 100 ppm ethyl chloride at 750 °C and 918 or 434 hr-1 space velocity. In the table below, all results are for reaction 30-BKW-52 in Reactor A at 750 °C. The methane conversion and selectivity were similar for ethyl chloride levels of 10 and 50 ppm, and at the 10 ppm level, the methane conversion dropped very slowly for over 80 hours. The C_2 yield was over 15% after over 160 hours of operation. Although the ethyl chloride level was not optimized, the presence of ethyl chloride clearly extended the lifetime of the catalyst.

Ethyl Chloride as Volatile Additive

CH4 C	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl
41.9	37.8	16.3	9.2	0.5	10.3	4.9	2415	434	100
44.8	39.5	17.6	8.8	0.7	10.5	5.1	4080	434	50
30.1	50.0	15.1	5.3	0.4	10.6	5.3	2640	918	100
32.8	49.6	16.4	5.2	0.6	10.3	5.2	3000	918	50
45.7	39.6	17.7	9.0	0.7	10.5	5.1	4170	434	50
43.8	40.0	17.7	9.0	0.8	10.3	5.2	4350	434	10
44.1	40.4	17.8	8.8	0.8	10.3	5.2	4440	434	10
37.1	38.4	15.0	7.1	0.9	10.0	5.0	9615	434	10

In reactions 30-BKW-53 (0.5% $BaCl_2$ on Norton 5551 α-alumina), 60 (5% $BaCl_2$ on Norton 5551 α-alumina), and 61 (5% $BaCl_2$ on Norton 5551 α-alumina), a variety of process conditions were explored, with 50 ppm of ethyl chloride in the feed gas. The catalyst for reaction 30-BKW-53 had lower levels of $BaCl_2$ than catalysts for the other two reactions, and although methane conversion was about the same with this catalyst as for the catalysts with higher levels of $BaCl_2$, selectivities were lower and ethylene to ethane ratios were higher. With 30-BKW-53, the barium chloride to alumina ratio is lower, and alumina might catalyze decomposition of barium chloride to release chlorine radicals into the gas phase, which can initiate conversion of C_2's to both ethylene and combustion products.

In reactions 30-BKW 60 and 61, C_2 yields comparable to better literature results were obtained, even after hours of catalyst operation. Alkaline earth chloride/metal oxide catalysts appear to exhibit superior C_2 yield/ethylene to ethane ratio/catalyst lifetime combinations than literature catalysts. Detailed results are presented in Table 5, and selected results are presented below.

High C_2 Yields with $BaCl_2$/α-Alumina/ECl

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	R	Ref.
750	43.8	39.0	17.1	12.0	0.7	10.4	5.0	75	357	0	A	30-53
750	43.1	48.8	21.0	9.2	0.3	10.2	4.9	25	878	50	D	30-60
800	44.5	47.0	20.8	8.4	0.4	10.8	5.2	1590	1463	50	D	30-60
800	25.8	62.1	16.0	2.8	0.5	10.5	5.1	2600	2341	50	D	30-60
750	40.3	48.8	19.7	7.2	0.4	10.2	4.9	65	878	50	C	30-61
775	45.8	41.7	19.0	12.5	0.6	10.8	5.2	1410	512	50	C	30-61
800	42.4	37.4	16.0	12.4	0.5	10.5	5.1	2560	585	50	C	30-61

In reaction 30-BKW-129 (Table 5), a 5% $CaCl_2$ on Norton 5551 α-alumina was found to exhibit C_2 yields, selectivities, and ethylene to ethane ratios similar to those of $BaCl_2$ on α-alumina catalysts. Ethylene to ethane ratios close to 20 were observed at the low space velocity of 878 hr^{-1} (750 °C).

Alkaline Earth/Alkali/Metal Oxide Catalysts

Alkaline earth/metal oxide catalysts with Na, K, Rb, and Cs compounds did not exhibit increased selectivities, activities, or ethylene to ethane ratios, when compared with alkaline earth/metal oxide catalysts without added alkali components. Reactions 30-BKW-100, 101, 106, 107, and 111 are summarized in Table 5

Alkaline Earth/Metal Oxide Catalysts -Other Anions

Low selectivities and yields to C_2's were obtained with phosphate and sulfate anions in place of chloride anions in catalysts of reactions 30-BKW-87 and 136 (Table 5), even in the presence of ethyl chloride in the feed gas. Other preparation methods for these catalysts might result in better catalysts. During the next two quarters, carbonate, nitrate, and other anions are planned to be explored for alkaline earth/metal oxide catalysts, with and without added volatile chloride.

Support Studies

A 1.41% $BaCl_2$ on Aldrich α-alumina catalyst of 100-140 mesh (29-BKW-133) was compared with the 1.41% $BaCl_2$ on Norton 5551 α-alumina catalyst of 100-140 mesh used in experiment 29-BKW-132. The catalyst on Norton 5551 α-alumina resulted in slightly higher activity and yield (Table 5 and below).

Different Supports

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	Ref.
700	26.7	48.8	13.1	3.3	1.0	10.0	5.2	125	682	0	29-132
700	23.6	52.7	12.5	5.4	0.5	10.0	5.2	80	682	0	29-133

Reactions 30-BKW-12 (1.4% $BaCl_2$ on Norton support 3232), 13 (1.4% $BaCl_2$ on Norton support 3235), and 22 (1.4% $BaCl_2$ on Norton support 5502) use different α-alumina supports than reaction 29-BKW-124 (1.4% $BaCl_2$ on Norton support 5551). Results show Norton supports 3232 and 3235 to result in inferior catalysts for methane coupling under conditions used. Norton support 5502 was interesting. Under comparable conditions, the catalyst on support 5502 showed higher selectivities and higher ethylene to ethane ratios than a catalyst on support 5551. Ethylene to ethane ratios were 7-9 at 700 °C and over 25 at 800 °C (see Table 5 for more information).

Different Supports

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	Ref.	Support
700	15.9	54.6	8.6	1.7	0.7	9.8	4.7	135	714	0	29-124	5551
700	27.7	0.8	0.2	0.7	4.2	10.0	4.8	90	370	0	30-12	3232
700	33.3	5.1	1.7	9.3	0.5	10.0	4.8	45	395	0	30-13	3235
700	29.6	52.1	15.2	8.6	0.3	10.5	5.0	45	638	0	30-22	5502

In reaction 30-BKW-37 ($BaCl_2$ on Norton support 5502 α-alumina), C_2 selectivity and C_2 yield are lower and the ethylene to ethane ratio is higher than in 30-BKW-36 (using Norton 5551 support) at the start of both reactions under the same conditions. Under similar process conditions, the ethylene to ethane ratio is higher for the catalyst on support 5502, with ratios of 20-25 observed. More information is presented in Table 5. Norton support 5551 has a lower surface area (0.25 m^2/g, BET method) and is less acidic (0.27 μmoles/g by irreversible ammonia absorption) than Norton support 5502 (0.75.m^2/g, 1.2 μmoles/g).

In reaction 30-BKW-93, with a $BaCl_2$ on Norton 5502 α-alumina catalyst, very high C_2 yields and ethylene to ethane ratios are observed using 50 ppm ethyl chloride, as shown in Figure 13. When the ethyl chloride level is dropped to 0, selectivity, methane conversion, ethylene to ethane ratio and yield all drop. Upon addition of 50 ppm ethyl chloride, the yield and ethylene to ethane ratio climb.

Reactions 30-BKW-86 (5% $BaCl_2$ on ZrO_2), 97 (5% $BaCl_2$ on ZnO), and 133 (5% $BaCl_2$ on Ga_2O_3), and 31-BKW-7 (5% $BaCl_2$ on Ga_2O_3) used non-alumina supports for catalysts. Selected results are presented below, and more complete results are presented in Table 6. The ethylene to ethane ratios are high on catalysts using ZrO_2 and Ga_2O_3 supports, as well as on those described above on alumina supports. Methane coupling on the $BaCl_2/Ga_2O_3$ catalysts compete with the better literature results, even after over 20 hours of operation, and the ethylene to ethane ratios remain high.

Non-Alumina Supports

Temp	CC	Sel	Yield	=/-	CO2/CO	CH4 in	O2 in	Time	GHSV	ECl	R	Ref.	Support
750	42.6	34.0	14.2	4.3	1.7	10.3	5.3	35	1200	0	D	30-86	ZrO_2
750	12.7	68.0	8.5	1.2	1.0	10.3	5.1	45	2000	50	D	30-97	ZnO
750	40.2	46.5	18.5	11.5	58.9	9.9	5.1	70	900	50	D	30-133	Ga_2O_3
750	42.6	49.0	20.5	7.3	183.5	9.9	5.1	275	900	50	D	30-133	Ga_2O_3
750	40.9	48.5	19.5	4.5	9.3	10.1	5.3	1125	1500	50	D	30-133	Ga_2O_3
750	34.9	47.8	16.6	3.8	4.9	10.3	5.2	1875	1500	50	C	31-7	Ga_2O_3
800	38.9	46.0	17.4	6.3	7.7	10.2	5.2	3030	1650	50	C	31-7	Ga_2O_3

In summary, supports are shown to have dramatic effects on methane coupling reactions using $BaCl_2$/metal oxide catalysts. Alkaline earth chloride/Norton 5551 α-alumina catalysts show higher ethylene to ethane ratios than literature catalysts such as Li/MgO, with comparable C_2 yields and C_2 selectivities. Similar catalysts on Norton support 5502, Ga_2O_3 and ZrO_2 show high ethylene to ethane ratios, whereas a catalyst on ZnO did not. Catalysts on Norton supports 3232 and 3235 were inactive and unselective. Concentration studies indicate an optimum loading of alkaline earth chloride, indicating a possible support/component interaction.

Metals in Activated States - Metal Molecular Sieve Catalysts

Metals in unusual oxidation states have been found to be stable in molecular sieves. Zeolites act as a solid matrix stabilizing odd electron states including Cu^+, Rh^{2+}, and

Co(0)[32]. Many atypical metal oxidation states were detected by esr because of unpaired electrons. These materials might show activity for abstracting hydrogen from methane to form the methyl radical necessary for coupling to C_2's. Ions in molecular sieves detected by esr include Pd(I), $4d^9$; Pd(III), $4d^7$; Co^{2+}, d^7; Ni^+, d^9; and Cr^{5+}, d^1[33]. Gallium promoted zeolites and crystalline galloaluminosilicates have been found[34-37] to efficiently convert alkanes to aromatics. In one of the patents published in this area[34], methane was converted to aromatics. It is thought that the gallium is in an environment in which it is particularly reactive for the activation of alkanes, since the conversion of methane selectively to aromatics can not be accomplished with gallium alone or with the sieve alone. Clearly, the environment in a zeolite is capable of supporting highly active states of metals. The zeolites in the reported patents have large pores. If small pore molecular sieves were substituted for the reported medium-pore materials, we may be able to effect the selective conversion of methane to light olefins including ethylene.

Other metal loaded molecular sieves have been reported to be highly active and selective in reactions involving hydrogen abstraction. A cesium-exchanged zeolite was found[38-43] to catalyze the alkylation of toluene with methanol to give styrene and ethylbenzene. It is likely that this reaction has proton abstraction as an essential step, followed by dehydrogenation of the alkylated product, ethyl benzene, to styrene. Similar catalysts prepared with smaller pore molecular sieves are of direct interest for methane coupling.

Molecular sieves with metals in the framework were of particular interest because of the possibility that metal ions locked into these structures might be stabilized in unusually active forms by being stabilized in unusual oxidation or coordination states[31]. Metals in molecular sieves have been shown by esr to contain highly active and less stable oxidation states. Some framework metal molecular sieves were therefore tested for methane coupling. Those of most interest contain metal ions which are components of methane coupling catalysts reported in the literature which exhibit high selectivities and activities to C_2's (e.g., manganese).

Framework metal molecular sieves were evaluated as catalysts for methane coupling. The materials are described in the Experimental Section. Both the conditions used and the results obtained from methane oxidation experiments with these materials are presented in Table 6. The catalytic materials were unselective, and some were surprisingly unreactive. Several of the sieves were examined by powder x-ray diffraction after use, and were found to have been unstable under reaction conditions, having lost crystallinity.

Silver Catalysts

One approach to avoid the heterogeneous/homogeneous mechanism in order to achieve higher C_2 selectivity/methane conversion combinations is to get away from the gas phase chemistry and make more of the reaction occur on the surface of the catalyst, at lower temperatures.

Catalysts were prepared containing silver, which is known to activate hydrocarbons unselectively at relatively low temperatures (compared to the typical temperatures of 700-950 °C used for methane coupling). Selective methane coupling activity is obtained in the presence of other catalyst components such as alkali and alkaline earth components and in the presence of chloride, despite the presence of the unselective metal component. The catalysts can be operated at relatively low temperature to effect methane coupling. Moreover, the use of the lower temperature reduces the homogeneous reaction rate in favor of the heterogeneous reactions.

C_2 yields as high as 10% were obtained at 650 °C for a low temperature catalyst containing silver, barium chloride, and α-alumina. No C_2 yields this high were known to have been reported in the literature at temperatures below 700 °C. Without the barium chloride, complete oxygen conversion occurs at temperatures of 300-500 °C, with methane converted only to carbon oxides. These results demonstrate the principle of enhanced surface reaction during methane coupling. Catalyst compositions and preparation procedures for silver catalysts used for methane coupling are presented in the Experimental Section and in Appendices D and E. Experimental conditions used and results are presented in Table 7.

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Tables and Figures showing the important experimental results are presented in Appendices B and C. In the Tables (Appendix B), reactant conversions are based on the molar amounts of reactants present at the inlet and outlet of the reactor. The product selectivities are based on the molar amount of carbon present in a particular product divided by the total molar amount of carbon present in all detected products as described in Appendix A.

Homogeneous Methane Oxidation

The extent of uncatalyzed homogeneous methane oxidation and the effects of experimental variables on the homogeneous oxidation were examined using a statistically designed set of 19 experiments. Experimental independent variables of interest were:

VARIABLE	RANGE	CENTER VALUE
T = Reactor temperature (°C)	(650 - 850)	750
P = Reactor pressure (psig)	(5 - 15)	10
M = Methane/oxygen (molar ratio)	(2 - 15)	8.5
F = Flow rate in reactor (cc/min)	(100 - 300)	200

The methane/oxygen mole ratio defined the reactant stream composition since only air (N_2/O_2 mole ratio = 3.8) and methane were mixed to form the reactant stream. For the composition range chosen the methane volume % varied from 28.6% to 75%. This range lies outside the explosive limits for methane/air mixtures at temperatures greater than 900 °C and atmospheric pressure. Separate experiments determined the void volume of the quartz bed which allowed a numerical value of the residence time to be determined. In the simple factorial design of experiments presented below, +1 means the maximum, -1 means the minimum, and 0 means the mean or center value of the defined range.

Sequence of experiments: (* - Gives the random order in which the experiments were performed.)

Experiment Number	T	P	M	F
1 (1)*	0	0	0	0
2 (16)	+1	+1	+1	+1
3 (5)	+1	+1	+1	-1
4 (3)	+1	+1	-1	+1
5 (9)	+1	+1	-1	-1
6 (11)	+1	-1	+1	+1
7 (8)	+1	-1	+1	-1
8 (2)	+1	-1	-1	+1
9 (15)	+1	-1	-1	-1
10 (10)	0	0	0	0
11 (6)	-1	+1	+1	+1
12 (18)	-1	+1	+1	-1
13 (12)	-1	+1	-1	+1
14 (13)	-1	+1	-1	-1
15 (17)	-1	-1	+1	+1
16 (14)	-1	-1	+1	-1
17 (7)	-1	-1	-1	+1
18 (4)	-1	-1	-1	-1
19 (19)	0	0	0	0

Experiments were carried out in random order with the exceptions that centerpoint values were used for the first, last, and middle experiments. A quartz reactor packed with 20 to 40 mesh washed quartz chips was used for all experiments. The reported temperatures are the values measured at the center of the tube furnace. The measured void volume in the heated region of the packed reactor was 25.1 cc. Individual experimental results are given in Tables 8-26, and a summary of all results is presented in Table 27.

High C_2 selectivities (51-59%) were obtainable; however, the high selectivities were observed only at low methane conversions (<5%). At higher methane conversions (>35%), the best C_2 selectivity observed was only 25%.

High ethylene to ethane ratios (4-10) were obtained for runs at high temperatures (850 °C) and long residence times (14-15 seconds). This was expected since these conditions favor the homogeneous conversion of ethane to ethylene by free radical chemistry.

The highest C_2 yield observed in the experimental set was 8.6%. This result is in agreement with a maximum C_{2+} yield of 9.3% reported by Wolf and Lane[25] for the homogeneous oxidation of methane. Higher C_2 yields have not been reported in the literature and it will be difficult, if not impossible, to obtain higher values from the homogeneous oxidation reaction alone.

Statistical analyses of the results were performed and regression models were developed. Many of the statistical models omit experimental variables, such as residence time and pressure, due to the fact that the extent of reaction went from almost no reaction at 650 °C to substantial reaction (complete O_2 conversion in many cases) at 850 °C, which caused the observed temperature effect to swamp the effects of variables of lesser importance. For this reason, models that omit experimental variables should be considered correct only if the omitted variables are assigned the values at the midpoint temperature (750 °C). For example, the equation for CH_4 conversion (C-conv) is correct for a pressure of 10 psig and a residence time of 9.3 seconds.

A summary of the models in exponential form follows.

Independent Variables: Centered variables obtained by subtracting the midpoints of the ranges

T^* = (Temperature in °C) - (750)
P^* = (Pressure in psig) - (10)
M^* = (Methane/oxygen molar ratio) - (8.3)
R^* = (Residence time in seconds) - (9.3)

Dependent Variables:

C-conv = CH_4 conversion in %
O-conv = O_2 conversion in %
C_2-sel = C_2 selectivity in %
C_3-sel = C_3 selectivity in %
C_2 yield = (CH_4 conversion X C_2 selectivity) in %
(=/-) = Ethylene/ethane molar ratio

Models:

$$\text{C-conv} = 2.52 \cdot e^{0.017T^*} \cdot e^{-0.1606M^*}$$

As expected, methane conversion increases exponentially with temperature and decreases with methane/oxygen ratio. The model is unbounded (no upper limit) since methane was the excess reagent in all experiments.

$$\text{O-conv} = \frac{100}{1 + 5.51 \cdot e^{-0.03246T^*}}$$

Oxygen conversion increases exponentially with temperature towards its upper limit (100%).

$$C_2\text{-sel} = \frac{100}{1 + 1.79 \cdot e^{-0.10338M^*} \cdot e^{0.07329R^*} \cdot e^{0.008M^*R^*}}$$

C_2 selectivity increases with methane/oxygen ratio and decreases with residence time. The reduction with residence time is due to the further reaction of the C_2 products. It is interesting that the model is not a function of temperature since C_2 selectivity increases with temperature in catalytic methane partial oxidation studies.

$$C_3\text{-sel} = 0.69 \cdot e^{0.01515T^*} \cdot e^{0.0009055T^*M^*}$$

$$C_2 \text{ yield} = 0.93 \cdot e^{0.01532T^*} \cdot e^{-0.077275M^*}$$

The C_2 yield is a function of temperature and methane/oxygen ratio similar to the model for methane conversion (C-conv).

$$(=/-) = 0.58 \cdot e^{0.01942T^*}$$

The temperature effect on the ethylene to ethane ratio is much greater than any of the other variables; thus, it masks their effects.

The study showed that the homogeneous gas phase oxidation of methane was too large to allow the separation of catalytic effects from gas phase effects at temperatures above 800 °C using the study's experimental conditions. For studies in this high temperature region, the residence times of reactants and products in the heated region must be lowered (less gas phase oxidation) by either increasing the reactant flow rate or by using reactors with smaller void volumes.

Since the models showed no sensitivities of dependent variables to pressure, the effect of reactor pressure on the extent of homogeneous reaction was further examined by running pressures of 5 psig and 15 psig at 750 °C and 800 °C (2:1 ratio of CH_4:O_2; reactor filled with 20 to 40 mesh quartz chips). The residence times were 7.2 seconds at 750 °C and 4.8 seconds at 800 °C. Residence times were chosen to give similar CH_4 conversions at 5 psig (CH_4 conversions approximately 13%) and were adjusted by changing flow rates. The experimental results are presented in Tables 28 and 29 and summarized in Table 30.

The results clearly show the expected trend that increasing the pressure results in a greater rate of the homogeneous reaction of methane. When the pressure was increased from 5 psig to 15 psig, the CH_4 conversion increased from 13% to 36% at both temperatures. The C_2 selectivity decreased with the increasing conversion while the ethylene to ethane ratio increased. These trends have been observed whether the increase in conversion is due to changes in pressure, flow rate, or temperature.

The pressure effect seems independent of temperature at 750 °C and 800 °C. Even though residence times were chosen to give equal CH_4 conversions at 5 psig, it is surprising how closely the CH_4 conversion and C_2 selectivity match for the two temperatures when the pressure increases from 5 psig to 15 psig. The C_2 selectivities were slightly larger for a given methane conversion at the higher temperature.

Experiments were carried out using unpacked reactors to study the effect of the quartz surface on the extent of the uncatalyzed reaction. For the study, experimental conditions were chosen to match those of three runs in the designed sequence

(Experiments 8, 14, and 19) except that the flow rates were increased to give the same residence times as the corresponding quartz packed reactor experiments. Experimental results for the empty reactors are presented in Table 31. A comparison of the empty reactor and quartz packed reactor results is given in Table 32.

The results indicate that the quartz surface inhibits the uncatalyzed reaction. At 850 °C the CH_4 conversion decreased from 43% to 35% and at 750 °C it decreased from 3.4% to 2.1% when a quartz packed reactor was used in place of an empty reactor. The very large effect seen at 650 °C was unexpected. The CH_4 conversion decreased from 30% with the empty reactor to 3.3% with the quartz-filled reactor. This result was checked in an experiment where results were first obtained using an empty reactor. The reactor was then opened, filled with quartz chips, and used to obtain additional experimental results (Table 33). The results agreed with those reported in Table 34 for 650 °C.

It is known that the homogeneous gas phase oxidation of methane proceeds by a complex chain branching free radical mechanism. The observed inhibition of the uncatalyzed reaction by the quartz surface could be explained by a surface reaction of a chain branching intermediate, such as $HO_2\cdot$ or H_2O_2, resulting in chain termination. The greater effect at lower temperatures (650 °C) could be due to more efficient surface chain termination or to more importance in the branching mechanism of the terminating species at the lower temperature relative to other reactions.

The effect of reversing the direction of reactant flow (flow up instead of down) for the empty reactor was examined to determine if the high conversion observed in the empty reactor was due to back-mixing of the gases in the reactor. The results obtained with the reverse flow (Table 34) agreed with the previous results (Table 32) showing that the results for the empty reactor were independent of the direction of reactant flow.

Perovskite Catalysts

A study of the abilities of complex and mixed metal oxides to oxidatively couple methane has been initiated this quarter. Perovskites, mixed metal oxides with an ABO_3 structure (A is large and B is small), were chosen as possible coupling catalysts due to their unique physical, chemical, and electrical properties. Perovskites behave as insulators (nonconductors), semiconductors, ionic conductors in which ions rather than electrons flow through the solid, metal-like conductors, and high temperature superconductors. In the perovskite structure (Figure 14), the A atom is surrounded by 12 oxygen ions and the B metal is surrounded by 6 oxygen ions. The sum of the ionic radii of the A and O ions must approximately equal the square root of two times the sum of the ionic radii of the B and O ions for the structure to be stable. The sum of the charges on A and B ions must equal +6. Perovskites are stable at high temperatures, have low surface areas, and can stabilize metal ions in unusual oxidation states. Complex perovskites ($[A_xA_y^{'}]BO_3$ or $A[B_xB_y^{'}]O_3$) can be formed when two different A or B atoms are present. If the A or B atoms have different oxidation states, lattice vacancies are induced. Also cation or anion-deficient perovskites (ABO_{3-x}) which contain lattice vacancies exist.

Tables 35-41 show results obtained for ABO_3 perovskites consisting of $LaMnO_3$, $LaFeO_3$, $BaFeO_3$, $BaPbO_3$, $SrPbO_3$, and $KNbO_3$. The materials were chosen such that A or B or both were changed in going from one catalyst to another. In most cases the A or B species were ones whose oxides have been reported in the literature as methane coupling catalysts. $BaPbO_3$ and $SrPbO_3$ were chosen due to literature reports of peroxide-like oxygen in the solid material[44]. This was of interest since sodium and barium peroxides have been reported to be good methane coupling materials at temperatures below 500 °C[45] . The changes in A and B for these catalysts are outlined in Table 42. None of the ABO_3 perovskites tested showed very promising results. Most showed very high reactivities (oxygen limited in many cases at 700 °C; 50 cc/min; 0.25 - 0.50g catalyst) but low C_2 selectivities (<15% at 700 °C). The best C_2 yields were seen with the $BaPbO_3$ catalyst (Table 39) which gave C_2 yields of 9-10% at 820 °C and GHSV's of 6,000 to 10,000 h^{-1}.

An example of the very high reactivity but low C_2 selectivity can be seen in Table 36. A 0.26g sample of $LaMnO_3$ gave complete oxygen conversion at 650 °C (flow rate of 233 cc/min) but only a 2% C_2 selectivity.

Tables 43 and 44 present the results obtained for $La_{0.65}Sr_{0.35}MnO_3$, a $(A_xA_y')BO_3$ type perovskite in which A and B were the same as those in $LaMnO_3$. This combination was chosen because of the high activity exhibited by the $LaMnO_3$ catalyst. Although the catalyst showed higher C_2 selectivities than the $LaMnO_3$ catalyst, the values are still very low (<30%) compared to reported literature catalysts. Additional experiments are planned to see if the C_2 selectivity can be substantially improved using other A' species.

Anion-deficient perovskites (ABO_{3-x}) were tested (Tables 45-47) to determine if the lattice vacancies would result in sites favorable for the formation of selective oxygen species. Table 45 ($KNbO_{3-x}$) gives results obtained with an anion-deficient form of the $KNbO_3$ catalyst (Table 41). The anion-deficient catalyst is much less active than the stoichiometric material (3.5% CH_4 conversion compared to 25% at 717 °C) but has higher C_2 selectivity (18% C_2 selectivity compared to <1%). However this trend is not observed when one compares the anion-deficient $LaMnO_{3-x}$ catalyst (Table 46) to its non-deficient counterpart ($LaMnO_3$; Table 35 and 36). In this case the anion-deficient material is just as active (both are O_2 limited at 700 °C), but less selective (<1% C_2 selectivity compared to 8-10%). From these results it is unclear as to whether anion vacancies facilitate the formation of active sites which favor C_2 formation.

An interesting result was obtained using a catalyst of the form $A(B_xB_y')O_3$. The results given in Table 48 for the $La[Rh_{0.5}Mn_{0.5}]O_3$ catalyst show that CO is the major product and that very high CH_4 conversions occur. A large H_2 peak was observed in the GC chromatographs but quantitative results were not obtained. However, using the assumptions that all reacted oxygen goes either to CO, CO_2, or H_2O and all reacted hydrogen goes to H_2 or H_2O, the percentages of reacted hydrogen converted to H_2 and H_2O could be calculated. Calculated results are given in Table 49. The calculations indicate that synthesis gas (CO and H_2) is the major product formed with this catalyst and the ratio of products agrees with an equilibrium for the reaction:

$$CO + H_2O \text{ -----> } CO_2 + H_2 .$$

Since alkali-doping has been reported to give improved C_2 selectivities, samples of the active $LaMnO_3$ catalyst were alkali-doped with K_2CO_3. The doping procedure resulted in mixtures of $LaMnO_3$ and K_2CO_3 in contrast to the work of Shamsi[46] in which alkali doping of $LaMnO_3$ was performed during the preparation of the perovskite and resulted in the formation of alkali material in the perovskite structure ($La_{0.9}Na_{0.1}MnO_3$). The results, shown in Table 50, were not improved when compared to results for the $LaMnO_3$ catalyst (Tables 35 and 36). The alkali-doped catalyst (10 wt % K_2CO_3/ $LaMnO_3$) is still very active (O_2 limited at 700 °C) with low C_2 selectivities (<5%). Future work will continue to study the effects of alkali-doping on the active perovskites.

Layered Perovskites Catalysts

A layered perovskite ($K_2La_2Ti_3O_{10}$) of unique crystal structure gave the "best" C_2 production of the complex metal oxides tested. Layered perovskites of the form $A_2Ln_2Ti_3O_{10}$ were first reported by Gopalakrishnan and Bhat[47] . The material was prepared with the objective of forming a Ruddlesden-Popper type layered oxide (general formula: $A_2[A_{n-1}B_nO_{3n+1}]$ where $[A_{n-1}B_nO_{3n+1}]$ perovskite type slabs of n octahedra in thickness are interleaved by A cations) capable of exhibiting ion exchange and intercalation behavior. Gopalakrishnan and Bhat synthesized the new series of layered perovskites of the general formula $A_2[Ln_2Ti_3O_{10}]$ (A=K,Rb; Ln=La,Nd,Sm,Gd,Dy). In this material three octahedrals of $[Ln_2Ti_3O_{10}]$ are separated by A cations (see Figure 15). Thus, in this material the perovskite layers are in intimate contact with an alkali ion dopant which is part of the crystalline materials. Such a structure assures all perovskite material is in contact with the alkali ion dopant and the loss of alkali ion dopant during reaction should be slower due to its positioning in the crystal lattice.

The materials exhibit ion exchange of the alkali metal in aqueous or molten salt media. Potassium ions of $K_2Ln_2Ti_3O_{10}$ are easily exchanged with Na^+ or Li^+ by treating with molten alkali-metal nitrates. Also, treatment with dilute acids results in the exchange of H^+ for K^+ ions.

In the temperature range of 770 to 820 °C, $K_2La_2Ti_3O_{10}$ gave C_2 selectivities of 31 to 38% and C_2 yields of 10 to 12% (Table 51) for over 100 hours. When larger sample sizes were used (Tables 52 and 53), C_2 yields of 14 to 15% were obtained over an 82 hour period (T = 800 °C; GHSV = 3600 h^{-1}). X-ray powder diffraction of the fresh and used catalyst showed $K_2La_2Ti_3O_{10}$ was the major crystalline phase present in the material.

The effects of changing the CH_4/O_2 ratio were measured for the $K_2La_2Ti_3O_{10}$ catalyst (Table 52). Figure 16 depicts the effects observed on the C_2 selectivity and C_2 yield at the different CH_4/O_2 ratios. As expected, higher CH_4/O_2 ratios resulted in higher C_2 selectivities but lower C_2 yields due to the decreased CH_4 conversions.

Attempts were made to improve the $K_2La_2Ti_3O_{10}$ catalyst by substituting other metals into its structure. Tables 54 to 56 present results obtained for three such materials ($K_2Sm_2Ti_3O_{10}$, $K_2Nd_2Ti_3O_{10}$, and $K_2La_2Mn_3O_{10}$). X-ray powder diffraction showed that $K_2Sm_2Ti_3O_{10}$ and $K_2Nd_2Ti_3O_{10}$ were formed; however, for the Mn preparation ($K_2La_2Mn_3O_{10}$) the major crystalline phase was $LaMnO_{3.15}$. These catalysts were all less selective than the $K_2La_2Ti_3O_{10}$ catalyst with C_2 yields <9%. Work in the next quarter will continue to look for ways to improve the selectivity and yield of the $K_2La_2Ti_3O_{10}$ catalyst. Possible ways include:

(1) use of other metals in the structure,
(2) alkali-doping of the material, and
(3) optimizing of reaction conditions.

SUMMARY:

BKW Laboratory

New alkali/metal oxide catalysts were explored, both to understand what is unique about alkali metal chloride/α-alumina catalysts, as well as to provide improved versions of those catalysts. Several alkali chloride/metal oxide catalysts show ethylene to ethane ratios from 10-25 with C_2 yields over 18%. It is concluded that alkali chloride/metal oxide catalysts deactivated too rapidly for them to be practical catalysts for methane coupling in a conventional manner. This was the case even when volatile chloride was added in the gas phase to replace any lost from the catalyst. Catalysts were shown to lose alkali metals rapidly.

Alkaline earth chloride/metal oxide catalysts were explored as less likely to lose metal components. These exhibit superior C_2 yield/ethylene to ethane ratio/catalyst lifetime combinations than literature catalysts, and show high C_2 yields after long periods of operation.

Metal molecular sieve catalysts tested were found to be unselective and unstable under reaction conditions. Some were surprisingly inactive.

Alkali chloride and alkaline earth chloride-doped silver catalysts are promising. A catalyst containing silver, barium chloride, and α-alumina exhibited C_2 yields as high as 10% at 650 °C. No C_2 yields this high were known to have been reported in the literature at temperatures below 700 °C.

KDC Laboratory

A statistical analysis of the designed set homogeneous gas phase results was performed. From the analysis, regression models were developed for the methane conversion, oxygen conversion, C_2 selectivity, C_3 selectivity, C_2 yield, and ethylene to ethane ratio.

Studies to measure the effect of total reactor pressure on the homogeneous gas phase reaction showed the expected trend (increasing the pressure resulted in a greater rate of homogeneous reaction). When the pressure was increased from 5 psig to 15 psig, the CH_4 conversion increased from 13% to 36% under the experimental conditions employed in the study. Results from the study also indicated that the product distribution for the gas phase reaction was not greatly affected by temperature in the interval 750 to 800 °C.

Experiments designed to measure the effect of the quartz surface on the homogeneous reaction showed that the quartz surface inhibited the uncatalyzed reaction. At 850 °C, the CH_4 conversion decreased from 43% to 35% ($CH_4/O_2 = 2.1$) and at 750 °C it decreased from 3.4% to 2.1% ($CH_4/O2 = 7.3$) when a quartz packed reactor was used in place of an empty reactor with equivalent residence times. An even larger effect was observed at 650 °C. This inhibition of the uncatalyzed reaction by the quartz surface could be explained by a surface reaction of some chain branching radical intermediate, such as $HO_2\cdot$, resulting in chain termination.

None of the ABO_3 perovskites tested this quarter showed very promising results. Most showed very high reactivities (oxygen limited in many cases at 700 °C; 50 cc/min; 0.25-0.50g catalyst) but low C_2 selectivities (<15% at 700 °C). Tests using anion-deficient perovskites (ABO_{3-x}) were inconclusive as to whether anion vacancies present in these materials facilitate the formation of active sites which favor C_2 formation.

A layered perovskite ($K_2La_2Ti_3O_{10}$) of unique crystal structure gave the "best" C_2 production of the complex metal oxides tested. In the temperature range of 770 to 820 °C, this catalyst gave C_2 selectivities of 31 to 38% and C_2 yields of 10 to 12% for over 100 hours ($CH_4/O_2 = 2.1$; GHSV = 3000 - 6000 h^{-1}). When larger sample sizes were used, C_2 yields of 14 to 15% were obtained over an 82 hour period (T = 800 °C; $CH_4/O_2 = 2.1$; GHSV = 3600 h^{-1}).

TASK 2: Process Conceptualization

INTRODUCTION:

This portion of the program covers all of the engineering studies. The intention is that engineering participation in economic evaluation, process conceptualization, and experimental design will speed up the development of a commercially attractive process.

The Comparison Case consists of the conversion of methane to synthesis gas followed by conversion of the synthesis gas to methanol. Methanol will be converted to liquid hydrocarbon fuels via olefins. All of the components of this technology have been demonstrated on a commercial or pilot scale. Case 1 will consist of the conversion of methane to ethylene. Case 2 will be the conversion of methane directly to C_2's and then to liquid hydrocarbon fuels. These two cases address the primary interests of UCC and DOE, respectively.

RESULTS AND DISCUSSION:

Comparison Case (Conventional Technology)

In order to establish a benchmark against which to compare emerging technologies for the direct conversion of methane to C_2's and C_2's to fuels, the economics of a Comparison Case process are being developed based on commercially demonstrated processes for the conversion of methane to synthesis gas, synthesis gas to methanol, and methanol to liquid fuels via olefins. This is illustrated in Figure 6 of the First Quarterly Report. Synthesis gas production will be accomplished by steam reforming of natural gas, and ICI's low pressure methanol process will be used to convert the synthesis gas to methanol. Heat and material balances have been completed for an integrated version of these two processes, as well as for a UCC process which will be used to convert the methanol to olefins.

The Mobil Olefins to Gasoline and Distillate (MOGD) process is currently under investigation for the final conversion of olefins to liquid fuels. Sufficient literature data has now been gathered to permit an analysis of this process. Initial efforts have been focused on developing a model which substantiates the various patent and literature claims. The model verification process is nearly complete. The overall process economics for the Comparison Case should be completed early next quarter.

Methane Coupling (Case 1)

Work has continued on the economic evaluation of a hypothetical process converting methane to ethylene and should be completed during the first year of the contract. An engineering model of the Methane Coupling System has been prepared. This model will allow heat and material balances to be generated easily and consistently for the system, based on projected reactor yields and other general process assumptions.

Heat and material balances form the basis for both investment and operating cost estimates, and being able to generate these easily and consistently will facilitate studying the sensitivity of the these key economic parameters to the independent process variables. This knowledge of the economic sensitivities will allow the laboratory program to be directed towards those aspects of the process that have the greatest economic impact.

An engineering model consists of a number of discrete unit operation "blocks" that are strung together using the process streams as the connecting members. Some blocks perform rigorous calculations to depict specific unit operations, while others perform artificial operations on the streams. These non-rigorous blocks are used when the details of the specific process operation are either not known or are irrelevant. In this way a whole process can be simulated before it is completely defined, while maintaining the modular flexibility that make revisions easy.

The Simplified Block Diagram and Material Balance

The Simplified Block Diagram for the process is shown in Figure 17, along with a summary of the Material Balance for Case 1 (Table 57) that was generated using the engineering model. The Material Balance is expressed in terms of thousands of pounds per hour for a unit producing one billion pounds per year of ethylene. The Methane Coupling engineering model consists of 40 blocks connected by 50 streams. The Simplified Block Diagram attached shows only the major streams and processing steps, with each "block" comprising one or more engineering blocks.

The Catalytic Reactor block is a non-rigorous representation of the conversion of a specified amount of raw material into products via a few simple stoichiometric equations. Reaction mechanisms and the effects of temperature and pressure on the reaction rates are not considered. An overall heat balance is performed, however, as the utilization of the heat released by this reaction has a significant impact on the overall process economics. For Case 1, the assumed operating conditions, conversion and selectivities are as follows:

* Methane-to-oxygen ratio = 9/1
* Pressure = 150 psig
* Temperature = 725 °C
* Oxygen purity = 97.5 mole %
* Selectivity = 47.3% ethylene

  38.1% ethane
  6.1% CO_2
  1.0% CO
  4.6% propylene
  2.8% propane
  0.2% butene

The feed to the Catalytic Reactor is a mixture of three process streams: the fresh methane feed (stream 1), the oxygen feed (stream 2), and the methane recycle (stream 3). Nearly all of the oxygen that is fed to the reactor is converted. But this corresponds to only a 22.4% conversion of methane per pass due to the high ratio of methane to oxygen in the feed. Therefore, unreacted methane is the major constituent in the reactor product (stream 4).

In the Quench step, a fixed temperature-pressure flash is performed which calculates rigorously the amount of water that will condense out of the reactor product stream when it is cooled to 45 °C (with cooling water). The remainder of water is assumed to be removed via a regenerable fixed-bed drying system. Stream 5 is the water removed via the combination of these two operations.

The Compression step is a rigorous calculation of the amount of power required to deliver the quenched reactor outlet stream to the pressure needed by the downstream processing blocks. In this case the pressure that is needed is set by the Cold Box, which operates at 530 psig. This operation would actually be carried out in three equal stages separated by intercoolers to limit the discharge temperature from each. For Case 1 the power required for this compression step is 27,000 HP per stage -- 81,000 HP total. Stream 6 is the discharge from the third stage.

The Acid Gas Removal step is a non-rigorous representation of an amine absorption system, similar to those used to sweeten natural gas. This is standard technology, and this process presents no unique requirements. Stream 7 is the carbon dioxide that is removed in this step.

The Cold Box and Expander steps are a rigorous treatment of the cryogenic distillation operations by which the unreacted methane is separated from the ethylene, ethane, and heavier products; and by which a purge stream is taken to remove inerts that enter the process via the raw materials. Cold Box designs are proprietary, but it can be revealed that the unit consists of a series of partial condensers feeding a distillation column in which ethylene, ethane, and heavier components are removed as the liquid bottoms product (stream 10), and in which a methane-rich stream is taken as the vapor overhead product. This vapor product is directed through a series of isentropic expanders in which the temperature and pressure of the mixture are progressively reduced, causing a portion of the material to condense at each stage. This condensed material is collected and returned to the column as reflux. The purge (stream 9) is let down to atmospheric pressure through its own dedicated expander to squeeze the maximum amount of organics from the inerts. Stream 3 is the methane recycle, which goes back to the reactor block.

The Ethylene Column block is a rigorous representation of the distillation column which produces refined (99.85%) ethylene (stream 11) from the crude product stream taken from the Cold Box (stream 10). For Case 1, this column is a 112 theoretical stage unit operating at an external reflux ratio of 4.5/1.

Finally, the Ethane Column block is a rigorous representation of the distillation column which produces ethane at a 98% purity (stream 13) from the Ethylene Column tails product (stream 12). For Case 1, this column is a 38 theoretical stage unit operating at an external reflux ratio of 0.64/1. Stream 14 is the remaining propylene, propane, and butene, which can either be sold as a mixture or further refined as individual products.

The Block Diagram and Material Balance information presented here for the Methane Coupling process is first-pass, not optimized. Future cases will have reactor operating conditions, conversions, and selectivities significantly different from those presented here. Not only the composition and quantities of the process streams will be different in these future cases, but also the way they are connected among the process blocks may be changed as well. Additional processing blocks may also be needed. For instance, if future cases involve adding a diluent to the reactor feed, then additional processing steps will be required to recover this diluent from the rest of the reactor products.

Methane to C_2's then Fuels (Case 2)

Case 2 will be the conversion of methane to C_2's then to liquid hydrocarbon fuels. Case 2 work will start after Case 1 and some of the sensitivity studies on Case 1 are completed, during the last nine months of the current contract. The first part of Case 2, methane coupling, is the same as Case 1. This will be integrated with the conversion of C_2's to liquid hydrocarbon fuels using Mobil's MOGD (Mobil Olefins to Gasoline and Distillate) process.

Support of Experimental Program

Modifications of the reactor were suggested to increase temperature uniformity in the catalyst bed and to reduce the reactor void volume to minimize the homogeneous (uncatalyzed) reaction. An analysis of gas phase homogeneous reaction kinetics shows that the methyl radical is important in converting ethane to ethylene.

SUMMARY:

Economics of a Comparison Case process are being developed so as to establish a baseline against which processes developed using methane coupling technology can be compared. It consists of conversion of methane to synthesis gas, synthesis gas to methanol, and methanol to liquid fuels via olefins. Work is nearly completed on this case.

An engineering model of the Methane Coupling System (Case 1, methane to ethylene) has been prepared. This model will allow heat and material balances to be generated easily and consistently for the system, based on projected reactor yields and other general process assumptions. Case 1 economics will be complete early in the next quarter.

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5. Research is currently being carried out in several countries including Canada, China, The Netherlands, France, Germany, England, Japan, United States, USSR, South Africa, and Australia.

6. Companies with patents in the area include Phillips Petroleum, Standard Oil, Atlantic Richfield, Idemitsu Kosan, Exxon, Akzo GmbH, W.R. Grace, Chevron, Johnson Matthey, and Amoco.

7. Research is currently being carried out at several academic sites including Texas A&M University (USA), Tokyo Institute of Technology (Japan), University of Twente (The Netherlands), Macquarie University (Australia), University of Mar del Plata (Argentina), and USSR Academy of Sciences (USSR).

8. Research is currently being carried out at governmental laboratories including Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Morgantown Energy Technology Center, and Sandia National Laboratory.

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VIII. APPENDICES

Appendix A. KEY TO TABLES AND TERMS

The following symbols are used in the key:

$n(i)_r$: relative molar amount of component "i" in the reactant stream (see Experimental Section).

$n(i)_p$: relative molar amount of component "i" in the product stream after correction for volume changes with nitrogen as an internal standard (see Experimental)

$f(i)$: number of carbon atoms per molecule of component "i".

Ref., #-KDC-X-#, or #-BKW-#	UCC notebook reference ID number.
Catalyst (Cat)	UCC code number for catalyst or chemical composition.
Weight (Wt)	Weight of catalyst sample (g).
Volume	Volume of catalyst before dilution with quartz beads (cc).
$CH_4/O_2/N_2$	Mole ratios of reactants in feed stream.
Flow (ccm)	Total reactant flow rate (cc/min at ambient conditions).
Temperature (Temp)	Temperature of the catalyst bed (°C).
Time	Time since reactant flow was started (hours or minutes indicated).
CH_4 Conv. (CH4 C or CC)	Mole % of methane reacted. $= \{[n(CH_4)_r - n(CH_4)_p] / n(CH_4)_r\} \text{ X } 100$
O_2 Conv. (O2 C)	Mole % of oxygen reacted. $= \{[n(O_2)_r - n(O_2)_p] / n(O_2)_r\} \text{ X } 100$
C Balance (C Bal)	Mole % carbon detected in the product stream compared to the reactant stream. $= \{[\Sigma f(i)n(i)_p] / n(CH_4)_r\} \text{ X } 100$; where the "Σ" is over all carbon containing components.
C_2 Selectivity (Sel)	Selectivity to ethane + ethylene expressed as a percent, based on methane reacted. $= \{2[n(C_2H_6)_p + n(C_2H_4)_p]\} / [\Sigma f(i)n(i)_p] \text{ X } 100$; where the "Σ" excludes CH_4

C_3 Selectivity	Selectivity to propane + propene expressed as a percent, based on methane reacted. $= \{3[n(C_3H_8)_p + n(C_3H_6)_p]\} / [\Sigma f(i)n(i)_p] \times 100$; where the "Σ" excludes CH_4.
C_2 Yield (or Yield)	Mole % of methane converted to C_2's, calculated as (CH_4 conversion) X (C_2 selectivity) / 100.
Ethylene/Ethane (=/-)	Mole ratio of ethylene to ethane in the product stream.
CO_2/CO	Mole ratio of carbon dioxide to carbon monoxide in the product stream.
GHSV	Gas hourly space velocity ($cc_{gas}\ cc_{cat}^{-1}\ h^{-1}$ at ambient temperature and room pressure).
ECl	Ethyl chloride in the feed gas in parts per million.
Reactor or R	The type of a reactor - A, B, C, D, E, or F.
R#	R#3 and R#4 refer to the two reactors in the BKW laboratory.

Appendix B. TABLES

Table 1. Control Studies, Uncatalyzed Reactions

Name	ECI	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	Reactor
29 BKW 139 R#4	0	700	50	1.64	9.25	0.15	6.62	0.32	1.25	2	9.928	4.963	100.15	90	A
29 BKW 139 R#4	0	700	50	0.82	9.75	0.08	5.38	0.28	1.1	2	9.928	4.963	100.63	180	A
29 BKW 139 R#4	0	800	50	7.93	24.78	1.99	21.04	1.47	0.17	2	9.928	4.963	101.1	270	A
29 BKW 139 R#4	0	800	50	9.46	27.54	2.62	22.51	1.65	0.12	2	9.928	4.963	100.68	465	A
29 BKW 139 R#4	0	800	50	10.04	27.89	2.82	23.66	1.74	0.11	2	9.928	4.963	100.72	555	A
29 BKW 139 R#4	0	800	50	11.26	28.17	3.17	20.1	1.85	0.1	2.13	9.902	4.643	99.99	690	A
29 BKW 139 R#4	0	800	50	12.52	28.68	3.59	26.44	2	0.09	2.03	10.085	4.969	99.94	1020	A
29 BKW 139 R#4	0	800	50	12.39	28.52	3.56	27.26	2.06	0.09	2.03	10.085	4.969	100.78	1200	A
29 BKW 139 R#4	0	800	50	13.05	28.94	3.79	28.18	2.12	0.09	2.03	10.085	4.969	100.45	1380	A
29 BKW 139 R#4	0	800	50	13.75	28.65	3.96	28.33	2.19	0.09	2.05	10.053	4.892	100.39	1620	A
29 BKW 139 R#4	0	800	50	13.79	28.32	3.95	29.89	2.25	0.09	2.05	10.053	4.892	101.22	1995	A
29 BKW 139 R#4	0	800	50	15.06	28.42	4.3	34.43	2.3	0.09	1.96	9.999	5.103	100.39	2280	A
29 BKW 139 R#4	0	800	50	15.7	28.75	4.51	29.8	2.33	0.09	2.12	10.196	4.803	99.84	2460	A
29 BKW 139 R#4	0	800	50	15	28.44	4.31	30.27	2.36	0.09	2.12	10.196	4.803	101.09	2640	A
29 BKW 139 R#4	0	800	50	15.26	28.71	4.42	30.93	2.37	0.09	2.12	10.196	4.803	100.9	2820	A
29 BKW 139 R#4	0	800	50	15.69	28.63	4.52	34.53	2.38	0.09	2.04	9.937	4.883	100.6	3060	A
29 BKW 139 R#4	0	800	50	18.18	28.76	5.14	34.98	2.46	0.09	2.04	9.937	4.883	98.33	3240	A
29 BKW 139 R#4	0	800	50	20.09	28.37	5.51	35.81	2.45	0.09	2.04	9.937	4.883	96.6	3435	A
29 BKW 139 R#4	0	800	50	16.3	28.83	4.75	36.22	2.47	0.09	1.98	9.843	4.978	101.12	3720	A
29 BKW 139 R#4	0	800	50	16.99	28.82	4.92	35	2.49	0.09	2.04	9.902	4.859	100.53	3900	A
29 BKW 139 R#4	0	800	50	17.04	28.93	4.96	35.24	2.49	0.09	2.04	9.902	4.859	100.56	4080	A
29 BKW 139 R#4	0	800	50	17.04	28.76	4.92	35.32	2.48	0.09	2.04	9.902	4.859	100.47	4260	A
30 BKW 49 R#4	0	750	50	6.76	26.25	1.73	9.2	0.63	0.07	2.02	9.951	4.935	97.47	195	A
30 BKW 49 R#4	0	750	50	4.39	26.35	1.15	11.16	0.68	0.07	1.95	10.022	5.147	99.82	330	A
30 BKW 49 R#4	0	750	50	2.55	26.27	0.68	10.58	0.67	0.06	1.95	10.022	5.147	101.57	510	A
30 BKW 49 R#4	0	750	50	4.4	26.33	1.15	8.31	0.66	0.06	2.04	10.071	4.941	99.59	690	A
30 BKW 49 R#4	0	750	50	3.64	26.52	0.97	7.71	0.64	0.06	2.04	10.071	4.941	100.37	870	A
30 BKW 49 R#4	0	750	50	2.69	26.38	0.72	7.18	0.63	0.06	2.04	10.071	4.941	101.28	1050	A
30 BKW 49 R#4	100	750	50	8.69	28.99	2.49	15.45	1.34	0.05	1.96	9.984	5.083	98.96	1230	A
30 BKW 49 R#4	100	750	50	10.71	29.58	3.1	17.91	1.51	0.05	1.96	9.984	5.083	97.87	1320	A
30 BKW 49 R#4	100	750	50	12.53	29.18	3.54	20.36	1.6	0.05	1.96	9.984	5.083	96.73	1410	A
30 BKW 79 R#3	0	750	50	1.79	36.56	0.66	6.05	0.27	0.1	1.9	10.087	5.302	99.97	50	D
30 BKW 79 R#3	0	750	50	2.05	38.84	0.79	5.78	0.27	0.07	1.9	10.087	5.302	99.59	135	D
30 BKW 79 R#3	0	775	50	4.19	40.52	1.67	8.04	0.4	0.05	1.9	10.087	5.302	98.53	225	D
30 BKW 79 R#3	0	800	50	6.63	41.22	2.68	12.05	0.65	0.03	1.9	10.087	5.302	98.22	315	D
30 BKW 79 R#3	0	750	50	4.12	43.73	1.75	6.54	0.27	0.04	1.9	10.087	5.302	97.28	400	D
30 BKW 79 R#3	50	750	50	2.15	41.79	0.89	0	0.54	0.03	2.05	10.351	5.058	99.41	540	D
30 BKW 79 R#3	50	750	50	0.93	42.25	0.4	-0.04	0.53	0.03	2.05	10.351	5.058	100.59	720	D
30 BKW 79 R#3	50	750	50	1.97	43.34	0.85	2.45	0.49	0.03	2.03	10.349	5.092	99.57	900	D
30 BKW 79 R#3	50	750	50	1.32	42.99	0.57	1.48	0.49	0.02	2.03	10.349	5.092	100.27	1080	D
30 BKW 79 R#3	50	750	50	0.24	43.56	0.1	0.95	0.47	0.02	2.03	10.349	5.092	101.34	1260	D

Table 1. Control Studies, Uncatalyzed Reactions (continued)

Name	ECl	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	Reactor
30 BKW 82 R#4	50	750	50	7.22	27.98	2	15.61	0.97	0.09	1.97	10.312	5.232	98.87	60	E
30 BKW 82 R#4	50	775	50	13.49	29.56	3.9	25.63	1.69	0.06	1.97	10.312	5.232	97.83	150	E
30 BKW 82 R#4	50	775	50	15.4	30.08	4.49	27.83	1.8	0.06	1.97	10.312	5.232	96.83	240	E
30 BKW 82 R#4	50	800	50	27.18	23.59	6.26	54.74	3.43	0.08	1.97	10.312	5.232	97.69	330	E
30 BKW 82 R#4	50	750	50	12.77	33.2	4.01	18.97	1.17	0.04	1.97	10.312	5.232	94.53	420	E
30 BKW 82 R#4	50	750	50	8.25	33.42	2.75	13.85	1.24	0.04	2	10.25	5.118	99.91	555	E
30 BKW 82 R#4	50	750	50	6.51	34.09	2.25	13.7	1.2	0.01	2	10.25	5.118	101.43	735	E
30 BKW 82 R#4	50	750	50	6.81	33.99	2.34	14.64	1.13	0.04	2	10.167	5.094	101.13	915	E
30 BKW 82 R#4	50	750	50	5.34	34.07	1.87	13.61	1.11	0.03	2	10.167	5.094	102.59	1095	E
30 BKW 82 R#4	50	750	50	3.79	34.37	1.36	12.48	1.12	0.03	2	10.167	5.094	104.17	1275	E
30 BKW 82 R#4	0	750	50	9.92	35.06	3.38	12.78	1.05	0.03	2.04	10.376	5.085	97.3	1455	E
30 BKW 82 R#4	100	750	50	12.14	35.06	4.06	13.93	1.07	0.04	2.04	10.376	5.085	95.27	1545	E
30 BKW 82 R#4	100	750	100	8.31	41.79	3.28	5.49	0.48	0.02	2.04	10.376	5.085	94.42	1590	E
30 BKW 82 R#4	100	800	160	10.38	39.5	3.91	8.71	0.73	0.22	2.04	10.376	5.085	95.25	1640	E

Table 2. Alkali/Metal Oxide Catalysts

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	+/-	CO2/CO	CH4/O2	CH4 In	O2 In	C Bal	Time	GHSV	C	ECI	R
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	100	30.1	48.7	15.0	56.3	6.7	0.21	1.9	9.4	4.9	102	85	233	C	0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	50	41.8	39.6	17.0	88.8	10.8	0.33	1.9	9.4	4.9	103	175	116	C	0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	50	43.4	39.2	17.1	89.6	10.6	0.37	2.0	9.6	4.8	101	310	116		0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	50	44.9	40.1	17.9	90.8	9.5	0.43	1.8	9.7	5.3	99	1585	116		0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	50	37.3	42.0	16.0	77.0	7.0	0.57	1.9	9.4	4.9	102	6805	116		0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	50	12.4	57.9	7.2	99.2	3.0	0.78	9.3	46.8	5.0	100	6955	116	C	0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	100	10.6	60.7	6.4	69.9	1.8	0.46	9.3	46.8	5.0	99	7225	233	C	0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	70	13.2	58.8	7.6	86.3	2.3	0.55	9.3	46.8	5.0	98	7315	163	C	0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	35	54.5	31.1	17.6	87.1	12.2	0.78	1.2	6.0	5.1	104	7450	81	C	0	A
29 BKW 99 R#3	30.0	NaCl,Al2O3,5551	700	35	55.9	31.0	17.6	86.3	12.5	0.76	1.2	6.0	5.1	102	7570	81		0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	80	11.9	58.2	6.9	19.7	1.5	0.17	1.9	9.7	5.1	99	45	1116	C	0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	24.5	46.4	11.5	48.3	4.8	0.25	1.9	9.6	5.2	101	180	349	C	0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	23.8	48.0	11.5	46.0	4.4	0.28	1.9	9.6	5.2	101	390	349		0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	24.5	48.2	11.8	46.4	4.2	0.29	1.8	9.7	5.3	100	615	349		0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	17.2	50.0	8.7	29.8	3.3	0.25	1.9	9.4	4.9	101	5295	349		0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	6.2	58.2	3.6	50.8	1.6	0.27	9.3	46.8	5.0	100	5445	349	C	0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	6.9	58.1	4.0	50.5	1.6	0.27	9.3	46.8	5.0	100	5535	349		0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	20.8	46.7	9.9	28.4	4.4	0.25	1.2	6.0	5.1	102	5940	349	C	0	A
29 BKW 101 R#4	5.0	NaCl,5551	700	25	20.4	46.9	9.7	24.9	3.9	0.23	1.2	5.9	4.9	101	6555	349		0	A
29 BKW 106 R#3	5.0	KCl,Al2O3,5551	700	25	20.9	45.0	9.3	39.5	3.6	0.21	2.0	9.9	5.1	99	90	366	C	0	A
29 BKW 106 R#3	5.0	KCl,Al2O3,5551	700	25	19.1	45.3	8.5	34.0	3.0	0.21	2.0	9.9	5.1	98	180	366		0	A
29 BKW 106 R#3	5.0	KCl,Al2O3,5551	700	25	18.3	45.0	8.0	30.7	2.6	0.22	2.0	9.9	5.1	97	270	366		0	A
29 BKW 106 R#3	5.0	KCl,Al2O3,5551	800	80	26.6	43.8	11.7	54.5	6.4	0.64	1.9	9.8	5.1	101	360	1171	C	0	A
29 BKW 106 R#3	5.0	KCl,Al2O3,5551	800	80	24.5	44.8	11.0	49.8	5.1	0.63	1.9	9.8	5.1	100	480	1171		0	A
29 BKW 106 R#3	5.0	KCl,Al2O3,5551	800	80	16.4	45.6	7.7	35.7	2.9	0.57	2.0	9.8	4.8	103	1155	1171		0	A
29 BKW 106 R#3	5.0	KCl,Al2O3,5551	800	10	28.0	31.5	8.6	69.5	5.3	1.66	2.0	9.9	5.0	98	1305	146	C	0	A
29 BKW 107 R#4	5.0	CsCl,Al2O3,5551,14/30	700	25	18.4	36.3	6.5	37.2	2.5	0.80	2.0	9.9	5.1	97	225	375		0	A
29 BKW 107 R#4	5.0	CsCl,Al2O3,5551,14/30	800	80	12.5	29.3	3.7	31.2	2.2	0.45	1.9	9.8	5.1	101	615	1200		0	A
29 BKW 107 R#4	5.0	CsCl,Al2O3,5551,14/30	800	80	8.3	29.4	2.5	22.5	1.6	0.43	2.0	9.8	4.8	103	1200	1200		0	A
29 BKW 107 R#4	5.0	CsCl,Al2O3,5551,14/30	800	10	29.1	16.5	4.8	87.5	6.7	2.68	2.0	9.9	5.0	99	1350	150	C	0	A
29 BKW 111 R#4	5.0	LiCl,Al2O3,5551	700	25	43.5	33.1	14.1	99.3	15.2	0.54	2.0	9.9	5.0	98	100	366	C	0	A
29 BKW 111 R#4	5.0	LiCl,Al2O3,5551	700	25	43.2	33.2	14.2	99.3	21.1	0.55	2.0	9.9	5.0	99	190	366		0	A
29 BKW 111 R#4	5.0	LiCl,Al2O3,5551	700	50	41.1	35.8	14.9	95.6	17.5	0.46	2.0	9.9	5.0	101	280	732	C	0	A
29 BKW 111 R#4	5.0	LiCl,Al2O3,5551	800	125	32.1	39.0	12.7	72.0	4.4	0.73	2.0	9.9	4.8	102	415	1829	C	0	A
29 BKW 111 R#4	5.0	LiCl,Al2O3,5551	800	125	19.9	34.8	7.1	47.6	1.9	0.70	2.0	9.9	4.8	102	625	1829		0	A
29 BKW 111 R#4	5.0	LiCl,Al2O3,5551	800	125	18.3	32.8	6.1	40.4	1.7	0.63	2.1	10.0	4.7	102	1210	1829		0	A
29 BKW 115 R#4	5.0	LiCl,Al2O3,5551	600	10	46.3	23.9	7.7	68.0	32.6	0.67	2.1	10.0	4.8	69	55	146	C	0	A
29 BKW 115 R#4	5.0	LiCl,Al2O3,5551	650	10	33.6	20.0	6.6	84.4	11.5	0.44	2.1	10.0	4.8	98	145	146		0	A
29 BKW 115 R#4	5.0	LiCl,Al2O3,5551	675	20	38.9	26.2	10.1	96.3	11.5	0.50	2.1	10.0	4.8	99	235	293	C	0	A
29 BKW 115 R#4	5.0	LiCl,Al2O3,5551	725	60	44.1	33.6	14.7	98.4	9.2	0.42	2.1	10.0	4.8	99	325	878	C	0	A
29 BKW 115 R#4	5.0	LiCl,Al2O3,5551	750	75	47.0	36.1	16.8	99.3	19.7	0.30	2.1	10.0	4.8	99	430	1098	C	0	A
29 BKW 115 R#4	5.0	LiCl,Al2O3,5551	750	75	39.7	34.2	13.9	91.8	15.1	0.42	2.0	10.2	5.1	102	565	1098		0	A
29 BKW 115 R#4	5.0	LiCl,Al2O3,5551	750	75	21.7	28.6	6.2	53.9	1.6	1.02	2.0	10.2	5.1	100	715	1098		0	A

Table 2. Alkali/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	±/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	700	40	43.6	37.0	16.5	97.7	15.1	0.24	1.9	10.2	5.3	102	75	93	C	0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	700	40	42.8	38.0	16.6	96.5	12.9	0.31	1.9	10.2	5.3	102	165	93		0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	700	40	41.8	38.2	16.5	95.7	11.7	0.35	1.9	10.2	5.3	103	255	93		0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	800	80	47.4	42.7	20.4	99.3	27.3	0.43	1.9	10.2	5.3	101	450	186	C	0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	800	80	48.0	43.2	20.7	99.2	25.2	0.46	2.0	10.2	5.1	100	585	186		0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	800	80	47.4	41.5	19.5	99.3	25.2	0.47	2.0	10.3	5.1	99	1515	186		0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	800	80	46.1	40.7	18.7	99.2	28.5	0.4[illegible]	2.0	10.1	5.0	99	1815	186		0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	800	100	46.9	37.7	17.3	99.2	33.0	0.42	2.0	10.1	5.0	98	1905	233	C	0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	800	120	45.8	35.7	16.0	99.2	24.4	0.40	2.0	10.1	5.0	98	1995	279	C	0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	800	25	45.4	36.6	15.6	99.2	43.6	1.15	2.0	10.1	5.0	94	2085	58	C	0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	700	40	25.4	42.6	10.3	45.0	4.7	0.34	2.0	10.1	5.0	96	2175	93	C	0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	700	40	25.8	42.5	10.4	44.7	4.5	0.35	2.0	10.1	5.0	95	2280	93		0	A
29 BKW 119 R#4	30.0	NaCl,Al2O3,5551	700	40	20.1	42.6	8.7	38.0	4.2	0.36	2.1	10.0	4.7	101	3105	93		0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	44.1	39.0	16.9	98.4	10.7	0.57	1.9	10.4	5.4	98	30	857	C	0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	43.6	37.3	16.0	99.2	12.1	0.48	1.9	10.4	5.4	98	210	857	C	0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	40.9	32.8	13.2	99.2	10.4	0.66	1.9	10.4	5.4	99	300	857		0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	37.2	27.9	10.4	99.2	7.2	0.91	1.9	10.4	5.4	100	390	857		0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	20.1	12.6	2.5	60.1	1.6	1.35	2.1	10.4	4.9	100	615	857		0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	15.4	7.4	1.2	45.9	1.0	0.96	2.1	10.4	4.9	101	4035	857		0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	29.9	23.3	7.7	98.7	8.8	0.57	1.8	9.9	5.6	111	4260	857	C	500	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	30.1	21.6	7.1	99.0	8.8	0.55	1.8	9.9	5.6	110	4350	857		500	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	24.9	13.6	3.5	75.8	4.8	0.38	2.1	10.6	5.0	104	5475	857		500	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	21.5	7.4	1.6	54.8	1.2	0.70	2.1	10.6	5.0	97	5610	857	C	0	A
30 BKW 29 R#4	10.0	NaCl,Al2O3,5552,140/200	750	80	21.7	6.9	1.4	52.6	1.1	0.69	2.1	10.6	5.0	96	5700	857		0	A
30 BKW 64 R#3	5.0	RbCl,Al2O3,5551,30/60	750	60	19.6	60.6	11.7	32.6	2.4	1.45	2.1	10.5	5.1	98	75	878	C	50	D
30 BKW 64 R#3	5.0	RbCl,Al2O3,5551,30/60	750	60	16.7	60.7	10.1	31.5	2.0	1.34	2.0	10.7	5.4	99	215	878		50	D
30 BKW 64 R#3	5.0	RbCl,Al2O3,5551,30/60	750	60	8.0	50.9	4.1	11.1	0.8	0.63	2.2	10.7	5.0	100	935	878		50	D
30 BKW 65 R#4	5.0	CsCl,Al2O3,5551,30/60	750	60	20.4	57.6	11.6	34.7	2.4	0.95	2.1	10.5	5.1	98	35	878	C	50	D
30 BKW 65 R#4	5.0	CsCl,Al2O3,5551,30/60	750	60	18.3	57.9	10.6	34.6	2.2	0.82	2.0	10.7	5.4	99	125	878		50	D
30 BKW 70 R#3	5.0	LiCl,Al2O3,5551,30/60	750	100	48.6	41.4	20.2	97.5	19.6	0.27	2.0	10.6	5.5	101	25	1463	C	50	D
30 BKW 70 R#3	5.0	LiCl,Al2O3,5551,30/60	750	100	32.2	43.9	14.2	65.1	3.1	0.45	2.0	10.6	5.5	100	115	1463		50	D
30 BKW 70 R#3	5.0	LiCl,Al2O3,5551,30/60	750	60	35.0	37.5	13.1	77.2	3.5	0.55	2.0	10.6	5.5	100	205	378	C	50	D
30 BKW 70 R#3	5.0	LiCl,Al2O3,5551,30/60	750	60	33.3	37.4	12.3	72.1	3.2	0.52	2.0	10.6	5.5	99	295	878		50	D
30 BKW 70 R#3	5.0	LiCl,Al2O3,5551,30/60	750	60	26.9	37.4	10.2	58.3	2.7	0.46	2.0	10.5	5.2	101	1195	878		50	D
30 BKW 71 R#4	5.0	KCl,Al2O3,5551,30/60	750	60	21.1	64.1	13.4	34.5	2.9	0.13	2.0	10.6	5.5	99	65	878	C	50	D
30 BKW 71 R#4	5.0	KCl,Al2O3,5551,30/60	750	60	19.2	65.2	12.4	30.8	2.4	0.13	2.0	10.6	5.5	98	160	878		50	D
30 BKW 73 R#3	5.0	KCl,Al2O3,5551,30/60	800	30	46.2	41.7	18.4	98.2	13.1	0.88	2.2	10.5	4.8	95	45	439	C	50	D
30 BKW 73 R#3	5.0	KCl,Al2O3,5551,30/60	800	60	35.7	48.1	16.9	68.5	5.7	0.66	2.2	10.5	4.8	98	140	878	C	50	D
30 BKW 73 R#3	5.0	KCl,Al2O3,5551,30/60	800	60	27.3	51.5	14.1	51.3	3.8	0.49	2.1	10.3	5.0	100	315	878		50	D
30 BKW 73 R#3	5.0	KCl,Al2O3,5551,30/60	800	60	9.7	43.6	4.3	17.5	1.4	0.20	2.2	10.6	4.9	102	1035	878		50	D
30 BKW 74 R#4	5.0	RbCl,Al2O3,5551,30/60	800	30	42.2	43.2	16.9	91.5	10.7	2.71	2.2	10.5	4.8	93	40	439	C	50	D
30 BKW 74 R#4	5.0	RbCl,Al2O3,5551,30/60	800	60	33.1	48.8	15.8	66.6	5.0	1.81	2.2	10.5	4.8	98	110	878	C	50	D
30 BKW 74 R#4	5.0	RbCl,Al2O3,5551,30/60	800	60	29.6	50.2	14.6	57.6	4.1	1.63	2.2	10.5	4.8	98	160	878		50	D

Table 2. Alkali/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 74 R#4	5.0	RbCl,Al2O3,5551,30/60	800	60	22.5	47.1	10.6	47.7	2.8	1.24	2.1	10.3	5.0	100	295	878		50	D
30 BKW 83 R#3	5.0	CsCl,Al2O3,5551,30/60	750	60	20.5	56.2	11.4	37.0	2.8	0.94	2.0	10.3	5.2	99	45	878	C	50	C
30 BKW 83 R#3	5.0	CsCl,Al2O3,5551,30/60	750	60	19.8	57.3	11.1	32.4	2.3	0.80	2.0	10.3	5.2	98	135	878		50	C
30 BKW 83 R#3	5.0	CsCl,Al2O3,5551,30/60	750	60	16.3	54.7	8.5	24.5	1.4	0.56	2.0	10.3	5.2	96	315	878		50	C
30 BKW 83 R#3	5.0	CsCl,Al2O3,5551,30/60	750	60	7.3	38.5	2.8	9.7	0.8	0.25	2.0	10.3	5.1	99	540	878		50	C
30 BKW 83 R#3	5.0	CsCl,Al2O3,5551,30/60	750	60	1.2	31.1	0.4	7.4	0.6	0.18	2.0	10.2	5.1	104	1260	878		50	C
30 BKW 83 R#3	5.0	CsCl,Al2O3,5551,30/60	750	60	4.5	25.1	1.1	4.2	0.4	0.27	2.0	10.4	5.1	98	1440	878	C	0	C
30 BKW 83 R#3	5.0	CsCl,Al2O3,5551,30/60	750	60	6.4	25.4	1.6	4.4	0.4	0.27	2.0	10.4	5.1	96	1530	878		0	C
30 BKW 118 R#	5.0	NaOH,5551,30/60	750	60	43.4	45.6	19.3	94.2	2.4	26.06	1.9	10.0	5.4	97	35	878	C	0	D
30 BKW 118 R#	5.0	NaOH,5551,30/60	750	60	17.7	34.8	5.9	34.4	1.0	0.96	1.9	10.0	5.4	97	125	878		0	D
30 BKW 118 R#	5.0	NaOH,5551,30/60	750	60	9.1	33.1	3.1	17.1	0.7	0.86	2.0	10.0	4.9	101	990	878		0	D
30 BKW 118 R#	5.0	NaOH,5551,30/60	750	60	12.0	55.2	6.6	13.3	1.1	0.34	2.1	10.1	4.7	100	1170	878	C	50	D
30 BKW 118 R#	5.0	NaOH,5551,30/60	750	60	13.2	58.0	7.6	14.5	1.3	0.28	2.1	10.1	4.7	99	1260	878		50	D
30 BKW 118 R#	5.0	NaOH,5551,30/60	750	60	12.2	60.1	7.3	18.0	1.2	0.28	2.0	10.2	5.0	100	2565	878		50	D
30 BKW 132 R#	5.0	NaCl,Ga2O3,30/60	750	60	39.2	45.7	17.7	96.8	15.5	16.92	1.9	9.9	5.1	99	35	900	C	50	D
30 BKW 132 R#	5.0	NaCl,Ga2O3,30/60	750	60	41.3	48.7	19.9	98.6	9.8	105.58	1.9	9.9	5.1	99	105	900		50	D
30 BKW 132 R#	5.0	NaCl,Ga2O3,30/60	750	60	42.5	49.7	20.7	98.2	8.5	111.34	1.9	9.9	5.1	98	230	900		50	D
30 BKW 132 R#	5.0	NaCl,Ga2O3,30/60	750	60	37.0	43.3	16.1	96.5	5.0	57.96	2.0	10.0	5.1	101	950	900		50	D
30 BKW 132 R#	5.0	NaCl,Ga2O3,30/60	750	100	[illegible]	47.9	17.9	89.7	4.2	13.69	1.9	10.1	5.3	99	1085	1500	C	50	D
30 BKW 132 R#	5.0	NaCl,Ga2O3,30/60	800	140	36.	39.1	14.2	97.6	4.2	85.94	1.9	10.1	5.3	99	1170	2100	C	50	D
30 BKW 134 R#	5.0	LiBO2,Al2O3,5502,30/60	700	60	7.0	58.3	4.0	12.3	0.6	0.26	1.9	10.1	5.3	97	30	783	C	50	D
30 BKW 134 R#	5.0	LiBO2,Al2O3,5502,30/60	700	60	6.5	60.7	3.8	11.4	0.6	0.20	1.9	10.1	5.3	98	65	783		50	D
30 BKW 134 R#	5.0	LiBO2,Al2O3,5502,30/60	750	60	11.4	59.3	6.6	19.1	1.4	0.12	1.9	10.1	5.3	98	125	783	C	50	D
30 BKW 134 R#	5.0	LiBO2,Al2O3,5502,30/60	750	50	10.8	59.6	6.4	18.8	1.4	0.11	1.9	10.1	5.3	98	200	652	C	50	D
30 BKW 134 R#	5.0	LiBO2,Al2O3,5502,30/60	750	50	9.2	59.6	5.4	9.8	1.2	0.10	2.0	10.1	5.0	99	335	652		50	D
30 BKW 134 R#	5.0	LiBO2,Al2O3,5502,30/60	750	50	5.8	59.1	3.5	8.8	1.0	0.08	2.0	10.0	5.0	101	1055	652		50	D

Appendix A and the Experimental Section describe Table headings and experimental procedures.
The C column shows a letter C whenever a process change was made. =/- is the ethylene to ethane molar ratio.

Table 3. Pure Components

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 23	5.0	NaCl,Pretzel "M" Salt	700	50	4.5	39.6	1.8	5.4	0.5	0.19	2.1	10.5	5.0	99	90	652	C	0	A
30 BKW 23	5.0	NaCl,Pretzel "M" Salt	700	50	4.8	40.8	1.9	5.2	0.5	0.16	2.1	10.5	5.0	98	180	652		0	A
30 BKW 23	5.0	NaCl,Pretzel "M" Salt	750	50	12.3	46.5	5.7	19.0	2.0	0.08	2.0	10.5	5.0	99	270	652	C	0	A
30 BKW 23	5.0	NaCl,Pretzel "M" Salt	800	25	33.0	26.5	8.8	75.6	9.1	0.12	2.0	10.5	5.0	101	360	326	C	0	A
30 BKW 23	5.0	NaCl,Pretzel "M" Salt	800	25	39.9	24.2	9.9	96.2	13.7	0.13	2.0	10.5	5.0	102	450	326		0	A
30 BKW 23	5.0	NaCl,Pretzel "M" Salt	800	25	34.2	25.0	8.7	83.7	11.5	0.12	1.9	10.4	5.4	102	1350	326		0	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	700	50	4.4	25.4	1.1	6.3	0.4	0.18	2.0	10.0	4.9	98	15	423	C	0	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	700	50	3.2	30.2	1.0	4.4	0.4	0.13	2.0	10.0	4.9	99	60	423		0	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	750	50	9.9	40.4	3.9	15.7	1.5	0.07	2.0	10.0	4.9	98	105	423	C	0	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	800	25	34.0	21.2	7.3	85.0	9.2	0.25	2.0	10.0	4.9	101	150	211	C	0	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	800	25	25.0	20.8	5.3	63.9	6.8	0.21	2.0	10.0	5.1	102	285	211		0	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	800	25	19.9	18.3	3.7	53.6	6.9	0.23	2.0	10.1	4.9	103	1005	211		100	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	800	25	22.0	17.9	4.0	54.6	6.3	0.21	2.0	10.0	5.1	101	1185	211	C	100	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	800	25	22.8	18.1	4.1	54.2	6.4	0.21	2.0	10.0	5.1	100	1275	211		100	A
30 BKW 48 R#3	5.0	NaCl,Alberger Coarse Flake Sal	800	25	23.6	18.2	4.3	54.1	6.4	0.20	2.0	10.0	5.1	99	1365	211		100	A
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	23.3	46.6	10.5	44.1	2.5	1.81	1.9	10.0	5.4	96	45	878	C	0	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	19.9	45.8	8.8	36.1	1.7	1.21	1.9	10.0	5.4	96	150	878		0	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	15.8	41.8	6.7	28.8	1.6	0.94	2.0	10.0	4.9	102	1005	878		0	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	19.5	48.5	9.4	32.8	2.4	1.16	2.1	10.1	4.7	99	1185	878	C	50	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	20.3	47.6	9.6	34.7	2.6	1.16	2.1	10.1	4.7	99	1275	878		50	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	21.3	48.4	10.3	39.3	2.5	0.68	2.0	10.3	5.1	100	3885	878		50	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	26.3	50.1	13.4	47.4	5.9	0.31	2.2	10.5	4.8	102	4060	878	C	500	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	25.8	49.8	13.1	45.7	5.8	0.24	2.2	10.5	4.8	102	4140	878		500	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	24.8	46.5	11.7	44.3	6.2	0.14	2.2	10.5	4.8	101	4325	878		500	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	20.1	49.4	9.9	36.8	2.8	0.27	1.9	10.4	5.4	100	4470	878	C	100	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	19.8	49.8	9.9	31.9	2.7	0.27	2.1	10.4	5.1	100	4605	878		100	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	15.5	46.2	7.2	24.1	2.4	0.17	2.1	10.4	4.9	101	8025	878		100	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	16.5	45.4	7.4	22.7	2.1	0.21	2.1	10.3	5.0	99	8340	878	C	50	C
30 BKW 119 R#	5.0	ZnCl2,5551,30/60	750	60	16.9	44.9	7.5	23.7	2.1	0.22	2.1	10.3	5.0	99	8435	878		50	C

Appendix A and the Experimental Section describe Table headings and experimental procedures.
The C column shows a letter C whenever a process change was made. =/- is the ethylene to ethane molar ratio.

Table 4. Melting Points

Chemical	Formula	Melting Point (°C)
Barium chloride	$BaCl_2$	963
Strontium chloride	$SrCl_2$	875
Lanthanum chloride	$LaCl_3$	860
Cerium chloride	$CeCl_3$	848
Sodium chloride	$NaCl$	801
Calcium chloride	$CaCl_2$	782
Potassium chloride	KCl	770
Rubidium chloride	$RbCl$	718
Cesium chloride	$CsCl$	645
Lithium chloride	$LiCl$	605
Zirconium chloride	$ZrCl_4$	437
Zinc Chloride	$ZnCl_2$	283

Table 5. Alkaline Earth/Metal Oxide Catalysts

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
29 BKW 110 R#3	5.0	BaCl2,Al2O3,5551	700	25	31.4	45.7	13.4	56.8	7.6	0.29	2.0	9.9	5.0	93	55	366	C	0	A
29 BKW 110 R#3	5.0	BaCl2,Al2O3,5551	700	25	26.4	48.0	12.4	51.7	5.7	0.46	2.0	9.9	5.0	98	145	366		0	A
29 BKW 110 R#3	5.0	BaCl2,Al2O3,5551	800	80	45.4	42.6	19.5	98.5	17.0	0.69	2.0	9.9	4.8	101	370	1171	C	0	A
29 BKW 110 R#3	5.0	BaCl2,Al2O3,5551	800	80	41.3	43.1	18.0	89.1	14.1	0.61	2.0	9.9	4.8	101	490	1171		0	A
29 BKW 110 R#3	5.0	BaCl2,Al2O3,5551	800	80	30.2	42.2	12.9	61.6	6.8	0.57	2.1	10.0	4.7	101	1165	1171		0	A
29 BKW 114 R#3	5.0	BaCl2,Al2O3,5551	700	10	42.4	30.8	12.1	87.9	14.5	0.22	2.1	10.0	4.8	92	110	146	C	0	A
29 BKW 114 R#3	5.0	BaCl2,Al2O3,5551	725	25	38.1	41.6	15.7	78.0	10.1	0.31	2.1	10.0	4.8	99	200	366	C	0	A
29 BKW 114 R#3	5.0	BaCl2,Al2O3,5551	750	25	42.5	36.5	15.4	93.4	13.8	0.39	2.1	10.0	4.8	99	290	366		0	A
29 BKW 114 R#3	5.0	BaCl2,Al2O3,5551	820	90	44.7	38.0	16.9	94.0	20.5	0.34	2.1	10.0	4.8	100	395	1317	C	0	A
29 BKW 114 R#3	5.0	BaCl2,Al2O3,5551	820	90	37.7	36.0	13.9	82.4	13.6	0.34	2.0	10.2	5.1	102	530	1317		0	A
29 BKW 114 R#3	5.0	BaCl2,Al2O3,5551	820	90	36.4	31.6	11.7	84.3	10.6	0.45	1.9	10.4	5.4	102	1040	1317		0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	700	50	41.4	37.4	15.7	93.3	18.2	0.25	1.9	10.2	5.3	102	30	122	C	0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	700	50	39.6	42.0	16.9	85.2	12.1	0.40	1.9	10.2	5.3	102	120	122		0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	700	40	39.8	39.2	16.1	90.9	11.4	0.47	1.9	10.2	5.3	103	210	98	C	0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	700	40	39.0	39.2	15.7	89.0	10.3	0.52	1.9	10.2	5.3	103	300	98		0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	800	80	45.5	39.3	18.1	99.3	20.3	0.63	2.0	10.2	5.1	101	540	195	C	0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	800	80	44.4	37.6	17.0	99.2	18.5	0.66	2.0	10.2	5.1	102	690	195		0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	800	80	43.1	37.0	15.6	99.2	13.7	2.25	2.0	10.1	5.0	98	4530	195		0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	700	40	32.7	25.6	8.5	85.6	4.6	1.87	2.0	10.1	5.0	102	4620	98	C	0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	700	40	32.8	28.8	9.2	77.4	4.4	1.78	2.0	10.1	5.0	97	4725	98		0	A
29 BKW 118 R#3	30.0	BaCl2,Al2O3,5551	700	40	28.8	28.8	8.5	74.4	4.2	1.89	2.1	10.0	4.7	102	5550	98		0	A
29 BKW 124 R#3	5.0	BaCl2,Al2O3,5551	700	50	18.0	56.3	10.1	26.3	2.4	0.44	2.1	9.8	4.7	100	45	714	C	0	A
29 BKW 124 R#3	5.0	BaCl2,Al2O3,5551	700	50	15.9	54.6	8.6	21.2	1.7	0.69	2.1	9.8	4.7	99	135	714		0	A
29 BKW 124 R#3	5.0	BaCl2,Al2O3,5551	700	25	23.0	44.5	10.4	46.4	2.9	0.78	2.1	9.8	4.7	101	225	357	C	0	A
29 BKW 124 R#3	5.0	BaCl2,Al2O3,5551	700	25	22.4	44.2	10.1	44.3	2.9	0.82	2.1	9.8	4.7	102	315	357		0	A
29 BKW 124 R#3	5.0	BaCl2,Al2O3,5551	800	80	42.6	39.2	17.3	93.2	11.9	0.47	2.1	9.8	4.7	104	420	1143	C	0	A
29 BKW 124 R#3	5.0	BaCl2,Al2O3,5551	800	80	38.6	37.7	14.9	83.5	10.3	0.46	2.1	9.9	4.7	102	555	1143		0	A
29 BKW 124 R#3	5.0	BaCl2,Al2O3,5551	800	80	32.7	32.0	10.5	75.7	6.3	0.70	2.0	10.2	5.1	101	1245	1143		0	A
29 BKW 125 R#4	5.0	BaCl2,Al2O3,5551	700	50	7.0	20.2	1.4	9.3	0.5	0.54	2.1	9.8	4.7	99	90	714	C	0	A
29 BKW 125 R#4	5.0	BaCl2,Al2O3,5551	700	50	5.1	17.3	0.9	8.0	0.7	0.56	2.1	9.8	4.7	100	180	714		0	A
29 BKW 125 R#4	5.0	BaCl2,Al2O3,5551	700	25	7.8	12.6	1.0	18.0	0.8	0.67	2.1	9.8	4.7	101	270	357	C	0	A
29 BKW 125 R#4	5.0	BaCl2,Al2O3,5551	700	25	7.5	12.1	0.9	16.4	0.7	0.66	2.1	9.8	4.7	101	360	357		0	A
29 BKW 125 R#4	5.0	BaCl2,Al2O3,5551	800	80	11.0	26.1	2.9	24.3	1.6	0.45	2.1	9.8	4.7	102	465	1143	C	0	A
29 BKW 125 R#4	5.0	BaCl2,Al2O3,5551	800	80	12.1	26.4	3.2	24.0	1.7	0.44	2.1	9.9	4.7	100	600	1143		0	A
29 BKW 128 R#3	5.0	BaCl2,Al2O3,5551	700	50	13.3	59.7	7.7	16.7	1.4	0.59	2.0	10.1	5.1	98	90	714	C	0	A
29 BKW 128 R#3	5.0	BaCl2,Al2O3,5551	700	50	13.3	58.5	7.6	16.4	1.3	0.73	2.0	10.1	5.1	97	180	714		0	A
29 BKW 128 R#3	5.0	BaCl2,Al2O3,5551	700	25	18.9	48.3	9.1	35.5	2.6	0.71	2.0	10.1	5.1	100	270	357	C	0	A
29 BKW 128 R#3	5.0	BaCl2,Al2O3,5551	700	25	18.4	47.9	8.8	34.8	2.5	0.75	2.0	10.1	5.1	100	360	357		0	A
29 BKW 128 R#3	5.0	BaCl2,Al2O3,5551	800	80	40.8	40.7	16.9	84.5	10.9	0.41	2.0	10.1	5.1	102	465	1143	C	0	A
29 BKW 128 R#3	5.0	BaCl2,Al2O3,5551	800	80	35.5	40.3	14.6	73.7	9.4	0.40	2.0	10.0	4.9	102	600	1143		0	A
29 BKW 128 R#3	5.0	BaCl2,Al2O3,5551	800	80	31.7	36.5	11.7	67.4	7.1	0.47	2.1	10.0	4.9	101	1290	1143		0	A
29 BKW 129 R#4	5.0	BaCl2,Al2O3,5551	700	50	21.2	55.8	11.7	32.8	3.9	0.32	2.0	10.1	5.1	99	45	714	C	0	A
29 BKW 129 R#4	5.0	BaCl2,Al2O3,5551	700	50	20.2	57.6	11.4	29.8	3.0	0.44	2.0	10.1	5.1	98	135	714		0	A

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
29 BKW 129 R#4	5.0	BaCl2,Al2O3,5551	700	25	27.7	46.5	12.8	52.8	5.2	0.53	2.0	10.1	5.1	99	225	357	C	0	A
29 BKW 129 R#4	5.0	BaCl2,Al2O3,5551	700	25	26.3	45.6	12.1	53.1	5.0	0.53	2.0	10.1	5.1	101	315	357		0	A
29 BKW 129 R#4	5.0	BaCl2,Al2O3,5551	800	80	37.3	36.1	13.7	82.9	9.2	0.46	2.0	10.1	5.1	102	405	1143	C	0	A
29 BKW 129 R#4	5.0	BaCl2,Al2O3,5551	800	80	28.8	31.0	9.1	67.6	4.2	0.71	2.0	10.1	5.1	101	510	1143		0	A
29 BKW 129 R#4	5.0	BaCl2,Al2O3,5551	800	80	22.7	24.4	5.6	55.3	3.0	0.82	2.1	10.0	4.9	101	1155	1143		0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	700	50	28.7	48.4	14.1	59.3	4.8	0.56	1.9	10.0	5.2	102	35	682	C	0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	700	50	26.7	48.8	13.1	54.3	3.3	1.01	1.9	10.0	5.2	100	125	682		0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	700	25	36.1	38.5	14.1	84.2	4.7	1.24	1.9	10.0	5.2	101	215	341	C	0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	700	25	36.4	37.8	13.8	84.3	4.7	1.23	1.9	10.0	5.2	100	305	341		0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	800	125	48.8	45.7	22.2	99.9	13.3	0.58	1.9	10.0	5.2	100	410	1705	C	0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	800	125	45.8	42.4	19.8	97.2	10.8	0.58	2.0	9.9	5.0	102	545	1705		0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	800	125	41.9	39.7	17.1	91.7	9.0	0.62	2.0	9.9	5.0	103	695	1705		0	A
29 BKW 132 R#3	5.0	BaCl2,Al2O3,5551	800	125	36.0	31.7	11.8	93.5	5.1	1.51	1.9	9.8	5.1	104	1235	1705		0	A
29 BKW 133 R#4	5.0	BaCl2,Al2O3,5551	700	50	23.6	52.7	12.5	45.8	5.4	0.45	1.9	10.0	5.2	101	80	682	C	0	A
29 BKW 133 R#4	5.0	BaCl2,Al2O3,5551	700	50	22.3	54.0	12.0	41.8	4.8	0.49	1.9	10.0	5.2	100	170	682		0	A
29 BKW 133 R#4	5.0	BaCl2,Al2O3,5551	700	25	30.8	42.7	13.2	65.3	10.5	0.43	1.9	10.0	5.2	100	260	341	C	0	A
29 BKW 133 R#4	5.0	BaCl2,Al2O3,5551	700	25	31.7	42.7	13.3	66.2	16.9	0.42	1.9	10.0	5.2	98	365	341		0	A
29 BKW 133 R#4	5.0	BaCl2,Al2O3,5551	800	125	35.6	40.5	14.4	74.8	15.7	0.36	1.9	10.0	5.2	100	455	1705	C	0	A
29 BKW 133 R#4	5.0	BaCl2,Al2O3,5551	800	125	29.1	23.8	7.1	80.5	2.6	2.01	2.0	9.9	5.0	102	590	1705		0	A
29 BKW 133 R#4	5.0	BaCl2,Al2O3,5551	800	125	24.6	16.5	4.2	77.9	2.2	2.77	1.9	9.8	5.1	103	1280	1705		0	A
29 BKW 138 R#3	5.0	BaCl2,Al2O3,5551	700	50	23.5	55.6	13.2	42.5	3.6	0.50	2.0	9.9	5.0	101	45	714	C	0	A
29 BKW 138 R#3	5.0	BaCl2,Al2O3,5551	700	50	19.5	55.5	11.0	35.4	2.5	0.75	2.0	9.9	5.0	101	135	714		0	A
29 BKW 138 R#3	5.0	BaCl2,Al2O3,5551	800	90	45.6	41.8	19.7	97.0	14.5	0.44	2.0	9.9	5.0	103	225	1286	C	0	A
29 BKW 138 R#3	5.0	BaCl2,Al2O3,5551	800	90	42.6	40.6	17.9	92.2	11.2	0.44	2.0	9.9	5.0	104	315	1286		0	A
29 BKW 138 R#3	5.0	BaCl2,Al2O3,5551	800	90	27.0	17.7	4.9	76.9	3.0	2.61	2.0	9.9	4.9	102	4215	1286		0	A
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	700	50	23.1	59.9	14.0	40.9	3.1	0.64	2.0	10.1	5.1	101	45	714	C	0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	700	50	18.9	59.7	11.4	33.9	2.1	0.87	2.0	10.1	5.1	101	135	714		0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	800	50	47.5	43.6	21.2	99.0	15.8	0.52	2.0	10.1	5.1	102	225	714	C	0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	800	50	47.2	42.3	20.4	99.1	13.6	0.53	2.0	10.1	5.1	102	315	714		0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	800	80	43.8	44.7	20.0	88.3	8.8	0.48	2.0	10.1	5.1	102	420	1143	C	0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	800	80	40.0	44.3	18.2	81.3	7.7	0.51	2.0	9.9	4.9	102	555	1143		0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	800	80	36.9	43.1	16.3	76.5	6.6	0.57	2.0	9.9	4.9	102	705	1143		0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	800	80	34.7	37.7	13.3	77.7	4.8	0.91	2.0	9.9	4.9	102	1395	1143		0	C
29 BKW 152 R#3	5.0	BaCl2,Al2O3,5551	800	50	38.9	34.2	13.6	93.4	6.7	1.14	2.0	9.9	4.9	102	1485	714	C	0	C
30 BKW 3 R#3	5.0	BaCl2,Al2O3,5551	700	50	21.8	39.4	8.6	43.7	4.2	0.36	2.0	9.9	4.9	100	30	714	C	0	A
30 BKW 3 R#3	5.0	BaCl2,Al2O3,5551	700	50	15.9	42.6	6.7	29.0	2.2	0.74	2.0	9.9	4.9	99	120	714		0	A
30 BKW 3 R#3	5.0	BaCl2,Al2O3,5551	800	60	44.6	30.8	13.9	98.8	19.4	0.37	2.0	9.9	4.9	101	210	857	C	0	A
30 BKW 3 R#3	5.0	BaCl2,Al2O3,5551	800	60	42.4	29.4	12.9	99.1	15.7	0.51	2.0	9.9	5.0	103	345	857		0	A
30 BKW 3 R#3	5.0	BaCl2,Al2O3,5551	800	60	34.7	24.8	9.0	89.9	6.5	0.78	2.0	9.9	4.9	104	1035	857		0	A
30 BKW 5 R#4	5.0	BaCl2,Al2O3,5551	700	50	20.8	41.0	8.5	40.8	3.5	0.52	2.0	9.9	4.9	99	75	698	C	0	A
30 BKW 5 R#4	5.0	BaCl2,Al2O3,5551	700	50	18.4	43.1	7.8	34.6	2.8	0.75	2.0	9.9	4.9	99	165	698		0	A
30 BKW 5 R#4	5.0	BaCl2,Al2O3,5551	800	60	44.7	30.7	13.8	99.1	19.5	0.43	2.0	9.9	4.9	100	255	837	C	0	A
30 BKW 5 R#4	5.0	BaCl2,Al2O3,5551	800	60	41.4	28.1	12.1	99.3	13.9	0.53	2.0	9.9	5.0	104	390	837		0	A

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 5 R#4	5.0	BaCl2,Al2O3,5551	800	60	34.4	24.2	8.7	91.1	7.1	0.78	2.0	9.9	4.9	104	1080	837		0	A
30 BKW 7 R#3	5.0	BaCl2,Al2O3,5551	700	150	7.4	50.1	3.7	8.2	0.8	0.61	2.1	10.0	4.7	99	30	2143	C	0	A
30 BKW 7 R#3	5.0	BaCl2,Al2O3,5551	700	150	6.7	53.5	3.6	6.1	0.7	1.08	2.1	10.0	4.7	100	120	2143		0	A
30 BKW 7 R#3	5.0	BaCl2,Al2O3,5551	700	50	16.2	43.0	7.0	27.5	2.2	1.02	2.1	10.0	4.7	100	210	714	C	0	A
30 BKW 7 R#3	5.0	BaCl2,Al2O3,5551	700	50	16.1	43.4	6.9	25.5	2.1	1.02	2.1	10.0	4.7	99	315	714		0	A
30 BKW 7 R#3	5.0	BaCl2,Al2O3,5551	800	125	42.1	36.2	15.5	87.9	10.8	0.39	2.1	10.0	4.7	101	405	1786	C	0	A
30 BKW 7 R#3	5.0	BaCl2,Al2O3,5551	800	125	39.0	37.5	14.6	78.2	7.7	0.46	2.1	10.0	4.7	100	495	1786		0	A
30 BKW 9 R#4	1.0	BaCl2,Al2O3,5551	700	30	10.5	44.7	4.7	16.3	1.4	0.41	2.1	10.0	4.7	99	75	2143	C	0	A
30 BKW 9 R#4	1.0	BaCl2,Al2O3,5551	700	30	8.2	42.6	3.5	11.2	0.9	0.66	2.1	10.0	4.7	99	165	2143		0	A
30 BKW 9 R#4	1.0	BaCl2,Al2O3,5551	700	10	16.4	34.0	5.5	32.5	2.3	0.66	2.1	10.0	4.7	100	255	714	C	0	A
30 BKW 9 R#4	1.0	BaCl2,Al2O3,5551	700	10	18.0	33.0	5.9	35.3	2.6	0.64	2.1	10.0	4.7	99	360	714		0	A
30 BKW 9 R#4	1.0	BaCl2,Al2O3,5551	800	25	39.4	23.0	9.1	94.5	15.9	0.33	2.1	10.0	4.7	101	450	1786	C	0	A
30 BKW 9 R#4	1.0	BaCl2,Al2O3,5551	800	25	38.0	21.0	8.0	91.0	12.2	0.37	2.1	10.0	4.7	100	540	1786		0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	50	27.7	0.8	0.2	99.3	0.7	4.16	2.1	10.0	4.8	102	90	370	C	0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	50	27.7	0.9	0.3	99.3	0.8	4.69	2.0	10.0	4.8	102	180	370		0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	80	28.4	0.5	0.1	99.3	0.0	3.89	2.0	10.0	4.8	101	270	592	C	0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	80	29.7	0.8	0.2	99.3	0.9	4.04	2.0	10.0	4.8	100	360	592		0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	125	29.1	0.8	0.2	99.3	0.8	3.30	2.0	10.0	4.8	101	450	925	C	0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	165	28.3	0.8	0.2	99.3	0.8	2.91	2.0	10.1	5.1	103	585	1221	C	0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	165	27.5	0.8	0.2	99.3	0.7	2.90	2.0	10.1	5.1	104	765	1221		0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	700	165	27.8	0.7	0.2	99.3	0.7	2.72	2.0	10.0	5.0	104	1305	1221		0	A
30 BKW 12	5.0	BaCl2,Al2O3,3232	600	165	17.2	-0.3	-0.1	56.5	0.0	2.11	2.0	10.2	4.9	100	1440	1221	C	0	A
30 BKW 13	5.0	BaCl2,Al2O3,3235	700	50	33.3	5.1	1.7	99.1	9.3	0.50	2.1	10.0	4.8	103	45	395	C	0	A
30 BKW 13	5.0	BaCl2,Al2O3,3235	700	50	29.3	5.9	1.8	88.6	8.4	0.81	2.0	10.0	4.8	104	135	395		0	A
30 BKW 13	5.0	BaCl2,Al2O3,3235	700	80	20.4	2.0	0.4	56.0	1.1	0.70	2.0	10.0	4.8	101	225	632	C	0	A
30 BKW 13	5.0	BaCl2,Al2O3,3235	700	80	19.9	1.6	0.3	52.1	0.8	0.78	2.0	10.0	4.8	100	315	632		0	A
30 BKW 13	5.0	BaCl2,Al2O3,3235	750	80	31.5	4.1	1.3	90.5	1.9	1.22	2.0	10.0	4.8	100	405	632	C	0	A
30 BKW 13	5.0	BaCl2,Al2O3,3235	750	80	29.8	3.5	1.1	89.2	1.5	1.34	2.0	10.0	4.8	101	495	632		0	A
30 BKW 13	5.0	BaCl2,Al2O3,3235	750	80	28.5	2.8	0.8	88.7	1.5	1.35	2.0	10.2	4.9	103	1350	632		0	A
30 BKW 22	5.0	BaCl2,Al2O3,5502,30/60	700	50	29.6	52.1	15.2	51.1	8.6	0.25	2.1	10.5	5.0	99	45	638	C	0	A
30 BKW 22	5.0	BaCl2,Al2O3,5502,30/60	700	50	29.6	53.6	15.6	50.8	7.2	0.33	2.1	10.5	5.0	99	140	638		0	A
30 BKW 22	5.0	BaCl2,Al2O3,5502,30/60	800	90	47.0	38.9	18.1	98.9	25.2	0.33	2.1	10.5	5.0	99	225	1148	C	0	A
30 BKW 22	5.0	BaCl2,Al2O3,5502,30/60	800	90	41.1	34.6	14.2	92.7	16.1	0.39	2.1	10.5	5.0	100	315	1148		0	A
30 BKW 22	5.0	BaCl2,Al2O3,5502,30/60	800	90	26.9	16.9	4.6	80.5	2.2	2.25	2.1	10.4	5.4	101	1305	1148		0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	43.6	37.6	15.9	96.3	9.0	1.08	1.9	10.4	5.4	97	75	857	C	0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	42.6	37.5	15.8	99.1	11.4	0.95	1.9	10.4	5.4	99	165	857	C	0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	39.3	31.3	12.3	99.2	5.8	1.36	1.9	10.4	5.4	100	255	857		0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	37.0	26.4	9.8	99.2	4.4	1.59	1.9	10.4	5.4	100	345	857		0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	34.0	18.3	6.3	99.1	3.1	1.87	2.1	10.4	4.9	101	570	857		0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	32.2	15.1	5.0	99.2	2.5	1.97	2.0	10.5	5.3	102	750	857		0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	28.1	5.0	1.4	95.7	1.2	4.97	2.1	10.4	4.9	101	3990	857		0	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	20.4	5.3	1.2	94.3	0.9	4.00	1.8	9.9	5.6	110	4215	857	C	500	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	35.2	29.1	11.3	98.9	8.2	0.47	1.8	9.9	5.6	111	4305	857		500	A

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	39.6	29.8	12.2	98.6	10.4	0.37	2.1	10.6	5.0	103	5565	857		500	A
30 BKW 28 R#3	10.0	BaCl2,Al2O3,5552,140/200	750	80	34.0	10.1	3.4	95.8	3.0	1.39	2.1	10.6	5.0	99	5655	857	C	0	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	80	40.1	45.0	18.4	79.9	12.9	0.16	2.0	10.4	5.3	102	75	1143	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	39.6	41.4	16.6	81.2	13.8	0.17	2.0	10.4	5.3	102	165	857	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	38.4	41.6	16.1	77.7	14.0	0.17	2.0	10.4	5.3	101	255	857		500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	37.5	41.6	15.8	75.7	13.9	0.16	2.0	10.4	5.3	101	345	857		500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	35.1	43.9	15.6	68.1	10.7	0.15	2.1	10.5	5.1	102	1200	857		500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	40	39.9	36.6	14.9	85.6	14.5	0.18	2.1	10.5	5.1	102	1245	571	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	40	40.0	36.6	14.9	85.8	14.4	0.18	2.1	10.5	5.1	102	1290	571		500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	40	38.0	41.6	16.0	76.4	12.5	0.17	2.1	10.5	5.1	101	1335	571	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	40	38.0	41.7	16.1	76.2	12.4	0.17	2.1	10.5	5.1	101	1380	571		500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	100	27.3	53.7	14.7	45.2	6.5	0.12	2.1	10.5	5.1	100	1425	1429	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	150	19.8	62.3	12.4	28.5	3.8	0.10	2.1	10.5	5.1	100	1470	2143	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	80	28.3	54.5	15.4	46.7	6.7	0.13	2.1	10.5	5.1	100	1515	1143	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	80	36.4	49.2	18.3	43.2	10.0	0.12	1.4	7.0	4.9	102	1605	1143	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	41.7	44.1	18.8	54.0	13.0	0.14	1.4	7.0	4.9	102	1650	857	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	46.0	40.7	19.4	54.3	16.2	0.13	1.2	5.7	4.9	103	1740	857	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	80	38.2	47.3	18.6	42.9	10.5	0.11	1.2	5.8	5.0	103	2640	1143	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	80	38.1	47.7	18.7	42.6	10.5	0.11	1.2	5.8	5.0	103	2685	1143		500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	775	80	52.9	35.3	19.7	66.0	20.0	0.15	1.2	5.8	5.0	105	2730	1143	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	775	120	47.0	41.6	20.5	56.3	14.3	0.14	1.2	5.8	5.0	105	2865	1714	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	100	35.1	50.1	18.2	39.0	9.0	0.11	1.2	5.8	5.0	104	2905	1429	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	775	160	40.0	47.8	19.9	45.3	10.5	0.12	1.2	5.8	5.0	104	2950	2286	C	500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	775	160	39.6	48.0	19.8	45.1	10.4	0.12	1.2	5.8	5.0	104	2995	2286		500	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	775	160	41.6	47.5	20.2	47.0	6.3	0.44	1.1	5.5	5.0	102	3080	2286	C	100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	775	160	41.9	46.9	20.1	46.8	6.3	0.46	1.1	5.5	5.0	102	3175	2286		100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	775	160	42.0	47.6	20.0	44.8	6.0	0.46	1.1	5.6	5.0	100	3940	2286		100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	800	160	60.2	33.4	20.8	76.9	13.3	0.44	1.1	5.6	4.9	103	4075	2286	C	100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	160	23.8	59.3	14.0	19.4	2.6	0.48	1.1	5.6	4.9	99	4120	2286	C	100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	80	37.9	47.1	17.9	39.0	5.4	0.46	1.1	5.6	4.9	100	4210	1143	C	100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	725	160	14.9	62.0	9.2	10.4	1.6	0.36	1.1	5.6	4.9	99	4250	2286	C	100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	725	40	36.3	42.6	15.5	39.8	5.4	0.45	1.1	5.6	4.9	100	4305	571	C	100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	48.0	35.8	17.4	58.6	8.2	0.45	1.1	5.6	4.9	101	4350	857	C	100	A
30 BKW 36 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	35.6	42.9	15.3	68.2	5.7	0.48	1.9	9.9	5.3	100	4485	857	C	100	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	80	40.0	36.0	14.8	88.1	23.9	0.16	2.0	10.4	5.3	103	30	1043	C	500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	70	42.3	33.7	14.5	94.9	17.8	0.17	2.0	10.4	5.3	102	120	913	C	500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	40.8	35.5	14.6	89.1	20.2	0.17	2.0	10.4	5.3	101	210	783		500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	41.1	34.0	14.1	91.1	19.7	0.17	2.0	10.4	5.3	101	300	783	C	500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	35.0	34.1	12.3	80.8	18.4	0.14	1.9	10.2	5.3	103	570	783		500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	29.4	32.3	9.9	69.4	14.8	0.12	2.0	10.4	5.1	104	1110	783		500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	44.8	23.1	10.9	64.5	24.7	0.11	1.2	5.7	4.9	105	1785	783	C	500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	43.1	23.0	10.4	61.9	23.8	0.11	1.2	5.7	4.9	105	2010	783		500	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	29.4	18.2	5.5	43.0	5.1	0.18	1.1	5.5	5.0	104	3135	783	C	100	A

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	29.0	17.8	5.3	42.2	5.0	0.18	1.1	5.5	5.0	103	3225	783		100	A
30 BKW 37 R#4	5.0	BaCl2,Al2O3,5502,60/100	750	60	28.9	17.3	5.1	38.7	4.7	0.18	1.1	5.6	5.0	101	3990	783		100	A
30 BKW 44 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	43.1	40.9	17.9	86.8	10.4	0.31	1.9	9.9	5.3	101	30	857	C	100	A
30 BKW 44 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	38.2	40.8	15.7	76.0	6.5	0.41	1.9	9.9	5.3	101	120	857		100	A
30 BKW 44 R#3	5.0	BaCl2,Al2O3,5551,60/100	750	60	26.7	44.7	12.2	50.6	4.5	0.38	1.9	9.5	5.1	102	3720	857		100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	50	45.5	40.4	18.5	99.0	18.5	0.42	2.1	10.4	5.0	100	35	361	C	0	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	50	44.6	40.3	17.9	99.1	12.3	0.71	2.1	10.4	5.0	100	120	361		0	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	43.8	40.5	17.9	98.2	9.6	0.78	2.1	10.3	4.9	101	255	434	C	0	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	43.2	40.1	17.6	98.0	8.7	0.82	2.1	10.3	4.9	101	435	434		0	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	42.8	38.9	16.7	96.5	7.8	0.79	2.0	10.3	5.2	100	1110	434		0	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	42.2	38.7	16.5	92.5	7.6	0.64	2.0	10.3	5.0	101	1290	434	C	100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	42.0	38.9	16.5	90.9	7.7	0.58	2.0	10.3	5.0	101	1380	434		100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	41.9	37.8	16.3	94.0	9.2	0.52	2.1	10.3	4.9	103	2415	434		100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	127	30.6	50.0	15.3	55.6	5.1	0.46	2.0	10.6	5.3	100	2550	918	C	100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	127	30.1	50.0	15.1	56.2	5.3	0.44	2.0	10.6	5.3	101	2640	918		100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	160	26.8	54.9	14.6	44.8	4.2	0.44	2.0	10.6	5.3	99	2730	1157	C	100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	160	28.2	54.8	15.1	46.1	4.3	0.44	2.0	10.6	5.3	98	2820	1157		100	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	127	32.8	49.6	16.4	61.3	5.2	0.57	2.0	10.3	5.2	101	3000	918	C	50	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	120	34.4	48.2	16.7	68.3	5.6	0.59	1.9	10.2	5.4	101	3135	867	C	50	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	120	34.5	47.6	16.7	69.7	5.6	0.60	1.9	10.2	5.4	101	3315	867		50	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	120	34.9	47.3	16.5	66.6	5.7	0.56	2.1	10.5	5.1	100	3990	867		50	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	44.8	39.5	17.6	97.5	8.8	0.68	2.1	10.5	5.1	100	4080	434	C	50	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	45.7	39.6	17.7	95.6	9.0	0.68	2.1	10.5	5.1	98	4170	434		50	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	43.8	40.0	17.7	96.1	9.0	0.76	2.0	10.3	5.2	101	4350	434	C	10	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	44.1	40.4	17.8	95.8	8.8	0.77	2.0	10.3	5.2	100	4440	434		10	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	37.1	38.4	15.0	90.4	7.1	0.90	2.0	10.0	5.0	105	9615	434		10	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	40.4	37.5	15.1	90.5	6.9	0.92	2.0	10.2	5.0	100	9750	434	C	0	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	41.5	38.0	15.5	91.8	7.1	1.04	2.0	10.2	5.0	98	9930	434		0	A
30 BKW 52 R#3	10.0	BaCl2,Al2O3,5551,60/100	750	60	38.6	38.6	15.1	90.3	6.9	0.91	2.0	10.2	5.0	102	10020	434	C	50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	50	43.8	39.0	17.1	99.1	12.0	0.69	2.1	10.4	5.0	100	75	357	C	0	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	43.3	38.6	16.7	99.2	8.5	0.89	2.1	10.4	5.0	100	165	429	C	0	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	42.0	37.4	15.8	99.1	7.2	1.03	2.1	10.3	4.9	101	300	429		0	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	38.0	29.2	11.2	97.4	5.0	1.12	2.0	10.3	5.2	101	1155	429		0	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	43.3	35.0	15.3	98.5	8.6	0.58	2.0	10.3	5.0	101	1335	429	C	100	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	43.5	35.3	15.5	98.2	9.1	0.55	2.0	10.3	5.0	101	1425	429		100	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	42.9	35.3	15.3	97.3	9.3	0.54	2.0	10.4	5.2	101	1740	429		100	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	42.7	36.5	15.8	95.3	9.0	0.51	2.0	10.6	5.3	101	2685	429		100	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	104	36.6	43.1	15.7	72.0	6.3	0.44	2.0	10.6	5.3	100	2775	743	C	100	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	104	37.9	42.7	15.9	73.9	6.4	0.45	2.0	10.5	5.3	98	2865	743		100	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	120	30.4	44.2	13.5	60.2	4.2	0.55	2.0	10.3	5.2	101	3045	857	C	50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	120	30.1	43.7	13.3	62.5	4.3	0.57	1.9	10.2	5.4	101	3180	857		50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	41.3	34.3	14.0	93.0	6.8	0.67	2.1	10.5	5.1	99	4125	429	C	50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	42.0	34.2	14.0	91.5	6.7	0.67	2.1	10.5	5.1	98	4215	429		50	A

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	+/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	37.5	30.9	11.7	91.0	5.2	0.88	2.0	10.3	5.2	101	4395	429	C	50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	37.7	30.0	11.3	91.1	5.0	0.91	2.0	10.3	5.2	100	4485	429		50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	27.8	21.9	6.5	80.4	4.0	0.81	2.0	10.0	5.0	106	9660	429		50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	31.5	20.0	6.3	82.7	3.4	1.16	2.0	10.2	5.0	100	9795	429	C	0	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	32.0	18.8	5.9	85.0	3.1	1.49	2.0	10.2	5.0	99	9885	429		0	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	30.6	18.8	5.8	85.1	3.0	1.54	2.0	10.2	5.0	100	9975	429	C	50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	32.5	25.3	8.5	82.0	5.5	0.49	2.0	10.2	5.0	103	10065	429		50	A
30 BKW 53 R#4	10.0	BaCl2,Al2O3,5551,60/100	750	60	32.8	25.9	8.7	82.0	5.5	0.48	2.0	10.2	5.0	103	10100	429		50	A
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	750	60	43.1	48.8	21.0	82.0	9.2	0.32	2.1	10.2	4.9	100	25	878	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	750	60	36.4	49.6	18.1	69.8	5.0	0.58	2.1	10.2	4.9	100	150	878		50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	750	60	33.1	48.2	16.1	63.9	4.8	0.66	2.1	10.5	4.9	101	870	878		50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	750	100	23.3	59.2	13.7	37.0	2.7	0.71	2.1	10.8	5.2	99	1005	1463	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	750	20	43.2	39.1	16.9	97.4	9.5	0.83	2.1	10.8	5.2	100	1095	293	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	775	60	45.7	42.8	19.5	94.9	9.3	0.57	2.1	10.8	5.2	100	1185	878	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	775	50	46.0	42.4	19.5	96.2	10.0	0.59	2.1	10.8	5.2	100	1275	732	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	775	35	45.9	41.8	19.1	97.7	11.6	0.63	2.1	10.8	5.2	99	1365	512	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	800	75	47.4	43.8	20.7	95.1	12.6	0.44	2.1	10.8	5.2	100	1465	1098	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	800	100	44.5	47.0	20.8	85.7	8.4	0.43	2.1	10.8	5.2	100	1590	1463	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	800	100	41.7	48.5	20.2	79.0	7.0	0.45	2.1	10.8	5.2	100	1770	1463		50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	800	100	33.2	52.9	17.5	59.3	4.6	0.47	2.1	10.5	5.1	100	2445	1463		50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	800	40	43.0	39.1	16.9	95.5	9.9	0.58	2.1	10.5	5.1	101	2520	585	C	50	D
30 BKW 60 R#3	5.0	BaCl2,Al2O3,5551,30/60	800	160	25.8	62.1	16.0	38.5	2.8	0.48	2.1	10.5	5.1	100	2600	2341	C	50	D
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	750	60	40.3	48.8	19.7	77.7	7.2	0.43	2.1	10.2	4.9	100	65	878	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	750	60	34.6	49.0	17.0	66.8	4.9	0.59	2.1	10.2	4.9	100	195	878		50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	750	60	31.8	46.8	15.0	62.3	5.0	0.65	2.1	10.5	4.9	101	915	878		50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	750	100	22.7	57.2	12.9	37.0	2.8	0.67	2.1	10.8	5.2	99	1050	1463	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	750	20	42.8	38.8	16.5	96.8	9.7	0.86	2.1	10.8	5.2	100	1140	293	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	775	60	45.2	42.2	19.1	95.3	9.8	0.58	2.1	10.8	5.2	100	1230	878	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	775	50	45.8	41.8	19.1	96.7	10.9	0.60	2.1	10.8	5.2	100	1320	732	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	775	35	45.8	41.7	19.0	97.7	12.5	0.64	2.1	10.8	5.2	99	1410	512	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	800	100	45.6	44.1	20.1	90.6	11.5	0.40	2.1	10.8	5.2	100	1505	1463	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	800	100	43.3	44.3	19.5	86.7	9.8	0.41	2.1	10.6	4.9	101	1635	1463		50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	800	100	34.7	44.8	15.9	69.7	6.7	0.38	2.1	10.8	5.2	102	2355	1463		50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	800	40	42.4	37.4	16.0	95.3	12.4	0.54	2.1	10.5	5.1	101	2560	585	C	50	C
30 BKW 61 R#4	5.0	BaCl2,Al2O3,5551,30/60	800	160	26.2	56.2	14.7	42.5	3.5	0.34	2.1	10.5	5.1	100	2645	2341	C	50	C
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	750	60	42.6	34.0	14.2	98.2	4.3	1.68	2.0	10.3	5.3	98	35	1200	C	0	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	750	100	40.8	35.9	14.7	97.8	2.8	2.41	2.0	10.3	5.3	101	245	2000	C	50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	750	100	39.9	35.4	14.3	97.5	2.9	2.19	2.0	10.3	5.3	102	425	2000		50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	750	100	38.5	34.8	13.8	95.4	3.0	1.75	2.0	10.3	5.1	103	6725	2000		50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	775	160	41.8	40.7	17.3	98.4	3.0	2.41	2.0	10.3	5.1	101	6875	3200	C	50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	775	160	41.7	41.0	17.4	98.5	2.9	2.54	2.0	10.3	5.1	101	6915	3200		50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	44.0	45.1	19.9	99.0	3.4	2.61	2.0	10.3	5.1	101	6995	3200	C	50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	44.9	44.5	20.0	99.0	3.5	2.71	2.0	10.3	5.1	100	7040	3200		50	D

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	46.0	44.7	20.1	99.0	3.5	2.76	2.0	10.3	5.1	98	7085	3200	C	0	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	46.6	44.1	20.0	99.0	3.5	2.68	2.0	10.3	5.1	97	7130	3200		0	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	43.5	41.9	18.3	99.0	3.1	3.33	1.9	9.9	5.1	101	7310	3200		0	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	37.1	32.0	12.0	99.0	1.7	5.29	1.9	9.9	5.2	101	7670	3200		0	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	37.6	30.5	11.5	99.0	1.7	5.02	2.1	9.9	4.8	100	8255	3200		0	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	41.3	35.4	14.7	98.7	2.7	2.73	2.0	10.2	5.1	100	8435	3200	C	50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	40.8	35.4	14.5	98.6	2.7	2.52	2.0	10.2	5.1	100	8525	3200		50	D
30 BKW 86 R#3	5.0	BaCl2,ZrO2,60/100	800	160	38.3	34.2	13.4	98.6	2.7	2.43	2.0	10.2	5.2	103	9470	3200		50	D
30 BKW 87 R#4	5.0	Ba3(PO4)2,Al2O3,5551,30/60	750	60	4.4	36.2	1.5	5.3	0.3	0.08	2.0	10.3	5.3	97	60	857	C	0	D
30 BKW 87 R#4	5.0	Ba3(PO4)2,Al2O3,5551,30/60	750	60	4.9	30.5	1.5	10.1	0.7	0.02	2.0	10.3	5.3	99	270	857	C	50	D
30 BKW 87 R#4	5.0	Ba3(PO4)2,Al2O3,5551,30/60	750	60	3.9	27.4	1.1	11.3	0.7	0.02	2.0	10.3	5.3	100	450	857		50	D
30 BKW 87 R#4	5.0	Ba3(PO4)2,Al2O3,5551,30/60	750	60	3.0	29.9	0.9	8.5	0.7	0.02	2.0	10.3	5.1	101	6750	857		50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	60	40.2	48.5	19.5	77.4	12.6	0.53	2.0	10.2	5.1	100	45	783	C	50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	60	44.4	48.3	21.3	88.9	12.4	0.83	2.0	10.2	5.1	99	135	783		50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	60	45.2	48.4	21.7	93.9	11.4	1.30	2.0	10.2	5.1	99	315	783		50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	60	44.6	48.6	21.6	94.3	10.9	1.52	2.1	10.1	4.9	100	450	783		50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	60	41.7	47.9	20.2	90.0	8.0	1.40	2.0	10.2	5.2	101	1170	783		50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	43.5	47.0	20.2	91.8	8.6	1.42	2.1	10.3	4.9	99	1260	652	C	50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	42.2	46.9	20.1	91.3	8.5	1.39	2.0	10.1	5.1	102	1305	652	C	0	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	43.0	46.5	20.1	91.3	8.4	1.46	2.0	10.1	5.1	100	1350	652		0	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	38.2	41.8	15.6	79.5	4.5	1.24	2.0	10.2	5.1	98	3110	652		0	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	32.6	30.6	10.1	75.9	3.3	0.94	2.0	10.1	5.0	101	5495	652		0	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	33.2	30.5	10.1	75.7	3.2	0.88	2.0	10.3	5.1	100	5810	652	C	50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	32.3	34.8	11.3	69.9	3.6	0.61	2.0	10.3	5.1	100	5900	652		50	D
30 BKW 93 R#4	5.0	BaCl2,Al2O3,5502,30/60	750	50	31.7	37.5	12.0	66.3	4.1	0.43	2.0	10.1	5.0	101	6575	652		50	D
30 BKW 97 R#3	5.0	BaCl2,ZnO,60/100	750	60	12.7	68.0	8.5	18.6	1.2	1.01	2.0	10.3	5.1	98	45	2000	C	50	D
30 BKW 97 R#3	5.0	BaCl2,ZnO,60/100	750	60	11.7	68.3	7.8	15.7	1.0	1.12	2.0	10.3	5.1	98	135	2000		50	D
30 BKW 97 R#3	5.0	BaCl2,ZnO,60/100	750	60	7.8	65.6	5.2	12.9	0.9	1.10	2.0	10.1	5.0	101	990	2000		50	D
30 BKW 100 R#3	5.0	RbCl,BaCl2,Al2O3,5551,30/60	750	60	38.2	47.6	17.7	72.6	9.9	0.96	2.0	10.1	5.0	97	85	900	C	0	D
30 BKW 100 R#3	5.0	RbCl,BaCl2,Al2O3,5551,30/60	750	60	36.5	48.8	17.2	68.5	8.2	1.15	2.0	10.1	5.0	97	175	900		0	D
30 BKW 100 R#3	5.0	RbCl,BaCl2,Al2O3,5551,30/60	750	60	32.2	51.2	16.3	59.1	4.2	0.99	2.0	10.1	5.1	99	1260	900		0	D
30 BKW 100 R#3	5.0	RbCl,BaCl2,Al2O3,5551,30/60	750	60	29.3	53.6	15.8	51.5	3.8	0.87	2.1	10.1	4.8	100	1345	900	C	50	D
30 BKW 100 R#3	5.0	RbCl,BaCl2,Al2O3,5551,30/60	750	60	29.0	53.1	15.5	51.9	4.0	0.83	2.1	10.1	4.8	101	1400	900		50	D
30 BKW 100 R#3	5.0	RbCl,BaCl2,Al2O3,5551,30/60	750	60	30.2	53.4	16.0	50.3	3.9	0.79	2.1	10.1	4.8	99	1480	900		50	D
30 BKW 101 R#4	5.0	CsCl,BaCl2,Al2O3,5551,30/60	750	60	40.8	43.2	17.2	83.4	12.0	1.03	2.0	10.1	5.0	98	45	900	C	0	D
30 BKW 101 R#4	5.0	CsCl,BaCl2,Al2O3,5551,30/60	750	60	40.5	43.2	17.0	84.9	8.9	1.62	2.0	10.1	5.0	97	135	900		0	D
30 BKW 101 R#4	5.0	CsCl,BaCl2,Al2O3,5551,30/60	750	60	40.3	46.3	18.0	79.3	6.3	1.59	2.0	10.1	5.0	96	315	900		0	D
30 BKW 101 R#4	5.0	CsCl,BaCl2,Al2O3,5551,30/60	750	60	39.6	45.7	17.9	81.6	6.2	1.50	1.8	9.8	5.4	99	450	900	C	0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	40.3	44.8	17.9	80.1	17.0	0.53	1.9	9.9	5.1	99	45	900	C	0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	42.4	47.6	20.0	85.5	12.4	1.18	1.9	9.9	5.1	99	130	900		0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	43.1	48.9	20.7	86.7	9.6	1.47	1.9	9.9	5.1	98	220	900		0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	41.8	48.5	20.2	85.8	8.3	1.40	2.0	9.8	5.0	100	670	900		0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	39.2	48.3	19.4	83.6	8.1	1.21	2.0	9.8	5.0	103	1030	900		0	D

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	39.3	51.0	20.0	75.7	6.9	1.12	2.0	9.8	4.9	100	1210	900	C	0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	39.0	51.5	20.0	74.1	6.6	1.11	2.0	9.8	4.9	99	1300	900		0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	38.7	51.4	19.8	73.3	6.5	1.09	2.0	9.8	4.9	99	1390	900		0	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	37.5	52.1	19.5	73.0	6.3	0.96	2.0	10.2	5.0	100	1480	900	C	50	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	50	37.4	52.3	19.5	71.7	6.1	0.94	2.0	10.2	5.0	100	1570	900		50	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	36.0	49.3	17.8	70.4	5.9	0.83	2.2	10.4	4.8	100	2470	900		50	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	33.4	53.8	17.9	62.0	5.0	0.77	2.1	10.3	5.0	99	2605	900	C	50	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	33.0	54.2	17.8	60.3	5.0	0.76	2.1	10.3	5.0	100	2695	900		50	D
30 BKW 106 R#3	5.0	NaCl,BaCl2,Al203,5551,30/60	750	60	33.1	54.6	17.9	58.9	4.8	0.75	2.1	10.3	5.0	99	2785	900		50	D
30 BKW 107 R#4	5.0	NaOH,BaCl2,Al203,5551,30/60	750	60	41.4	51.0	20.8	81.6	5.9	1.54	1.9	9.9	5.1	99	85	900	C	0	D
30 BKW 107 R#4	5.0	NaOH,BaCl2,Al203,5551,30/60	750	60	39.6	52.4	20.4	73.5	5.9	1.14	1.9	9.9	5.1	98	165	900		0	D
30 BKW 107 R#4	5.0	NaOH,BaCl2,Al203,5551,30/60	750	60	31.4	50.3	15.8	58.7	3.8	0.94	2.0	9.8	4.9	100	1345	900		0	D
30 BKW 107 R#4	5.0	NaOH,BaCl2,Al203,5551,30/60	750	60	30.0	55.5	16.6	53.8	3.9	0.75	2.0	10.2	5.0	100	1525	900	C	50	D
30 BKW 107 R#4	5.0	NaOH,BaCl2,Al203,5551,30/60	750	60	30.1	55.4	16.6	53.8	3.9	0.71	2.0	10.2	5.0	100	1615	900		50	D
30 BKW 107 R#4	5.0	NaOH,BaCl2,Al203,5551,30/60	750	60	27.8	53.4	14.7	46.4	3.3	0.41	2.1	10.3	5.0	99	2830	900		50	D
30 BKW 110 R#3	5.0	KH2PO4,BaCl2,5551,30/60	750	60	24.5	57.2	14.0	37.2	7.5	0.06	2.0	10.2	5.0	100	70	900	C	0	D
30 BKW 110 R#3	5.0	KH2PO4,BaCl2,5551,30/60	750	60	16.9	63.2	10.7	22.1	3.0	0.08	2.0	10.2	5.0	100	160	900		0	D
30 BKW 110 R#3	5.0	KH2PO4,BaCl2,5551,30/60	750	60	0.8	36.1	0.3	6.3	0.3	0.08	1.9	9.9	5.3	102	3605	900		0	D
30 BKW 110 R#3	5.0	KH2PO4,BaCl2,5551,30/60	750	60	2.4	41.2	1.0	8.5	0.5	0.06	1.9	10.3	5.4	101	3955	900	C	50	D
30 BKW 110 R#3	5.0	KH2PO4,BaCl2,5551,30/60	750	60	3.1	46.7	1.5	9.3	0.6	0.06	1.9	10.3	5.4	101	4030	900		50	D
30 BKW 110 R#3	5.0	KH2PO4,BaCl2,5551,30/60	750	60	4.3	56.0	2.5	9.9	0.8	0.06	2.0	10.2	5.2	102	5245	900		50	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	42.6	44.6	19.0	97.3	4.5	5.96	2.0	10.2	5.0	100	35	900	C	0	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	42.7	47.9	20.5	85.9	6.7	1.08	2.0	10.2	5.0	100	130	900		0	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	42.4	48.5	20.6	84.9	7.0	1.06	2.0	10.2	5.0	100	220	900		0	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	38.7	47.1	17.8	73.9	5.3	0.95	2.0	10.2	5.2	97	1300	900		0	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	34.2	43.3	14.9	70.8	4.2	0.90	2.0	10.2	5.1	101	1885	900		0	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	29.3	24.1	7.3	78.0	2.5	1.15	1.9	9.9	5.3	103	3965	900		0	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	26.4	29.7	8.0	62.6	2.4	0.60	1.9	10.3	5.4	102	4015	900	C	50	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	26.9	34.6	9.5	58.9	2.9	0.40	1.9	10.3	5.4	102	4105	900		50	D
30 BKW 111 R#4	5.0	KOH,BaCl2,5551,30/60	750	60	26.2	37.2	10.1	56.8	3.4	0.33	2.0	10.2	5.2	104	5320	900		50	D
30 BKW 129 R#4	5.0	CaCl2,6H2O,Al203,5551,30/60	750	60	45.4	35.6	16.1	98.7	18.3	1.12	2.0	10.1	5.2	100	40	878	C	50	D
30 BKW 129 R#4	5.0	CaCl2,6H2O,Al203,5551,30/60	750	60	44.4	35.3	16.0	98.9	19.7	0.93	2.0	10.1	5.2	102	75	878		50	D
30 BKW 129 R#4	5.0	CaCl2,6H2O,Al203,5551,30/60	750	100	44.0	40.6	18.4	89.1	16.9	0.48	2.0	10.1	5.2	103	120	1463	C	50	D
30 BKW 129 R#4	5.0	CaCl2,Al203,5551,30/60	750	100	24.0	44.4	10.6	40.9	2.4	0.39	2.0	10.1	5.1	100	1200	1463		50	D
30 BKW 129 R#4	5.0	CaCl2,6H2O,Al203,5551,30/60	750	100	24.3	57.0	14.0	36.6	2.9	0.38	2.0	10.1	5.2	101	215	1463		50	D
30 BKW 129 R#4	5.0	CaCl2,6H2O,Al203,5551,30/60	750	60	32.3	38.1	12.2	63.2	3.9	0.52	2.0	10.1	5.1	100	1295	878	C	50	D
30 BKW 129 R#4	5.0	CaCl2,6H2O,Al203,5551,30/60	750	60	32.8	37.4	12.2	64.0	3.9	0.54	2.0	10.1	5.1	99	1370	878		50	D
30 BKW 133 R#4	5.0	BaCl2,Ga2O3,30/60	750	60	40.2	46.5	18.5	98.5	11.5	58.85	1.9	9.9	5.1	99	70	900	C	50	D
30 BKW 133 R#4	5.0	BaCl2,Ga2O3,30/60	750	60	41.7	43.4	19.9	98.9	8.5	216.77	1.9	9.9	5.1	99	145	900		50	D
30 BKW 133 R#4	5.0	BaCl2,Ga2O3,30/60	750	60	42.6	49.0	20.5	98.9	7.3	193.51	1.9	9.9	5.1	98	275	900		50	D
30 BKW 133 R#4	5.0	BaCl2,Ga2O3,30/60	750	60	38.5	44.8	17.4	98.2	4.9	42.62	2.0	10.0	5.1	101	995	900		50	D
30 BKW 133 R#4	5.0	BaCl2,Ga2O3,30/60	750	100	40.9	48.5	19.5	93.9	4.5	9.27	1.9	10.1	5.3	98	1125	1500	C	50	D
30 BKW 133 R#4	5.0	BaCl2,Ga2O3,30/60	800	140	37.1	39.2	14.4	98.3	4.2	46.73	1.9	10.1	5.3	99	1205	2100	C	50	D

Table 5. Alkaline Earth/Metal Oxide Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 136 R#4	5.0	BaSO4,Al2O3,5502,30/60	750	60	10.1	43.8	4.4	18.8	1.1	0.32	1.9	10.1	5.3	98	35	783	C	50	D
30 BKW 136 R#4	5.0	BaSO4,Al2O3,5502,30/60	750	60	11.4	45.6	5.1	20.6	1.3	0.27	1.9	10.1	5.3	99	95	783		50	D
30 BKW 136 R#4	5.0	BaSO4,Al2O3,5502,30/60	750	50	11.0	45.6	4.9	20.0	1.3	0.25	1.9	10.1	5.3	99	185	652	C	50	D
30 BKW 136 R#4	5.0	BaSO4,Al2O3,5502,30/60	750	50	9.1	49.3	4.5	10.6	1.2	0.21	2.0	10.1	5.0	99	320	652		50	D
30 BKW 136 R#4	5.0	BaSO4,Al2O3,5502,30/60	750	50	6.6	50.8	3.4	10.0	1.1	0.16	2.0	10.0	5.0	101	1040	652		50	D
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	400	80	0.9	3.0	0.0	7.2	2.8	###	1.9	10.1	5.3	100	30	1091	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	600	60	12.3	2.3	0.3	49.0	3.0	9.90	1.9	10.1	5.3	100	35	900	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	600	60	8.5	3.7	0.3	31.2	2.5	10.10	1.9	10.1	5.3	99	100	900		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	650	60	12.1	16.7	2.0	41.5	1.3	5.92	1.9	10.1	5.3	100	170	900	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	650	60	12.7	14.0	1.8	45.4	1.2	4.85	1.9	10.1	5.3	100	245	900		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	700	60	22.4	30.4	6.8	68.0	2.4	11.71	1.9	10.1	5.3	100	310	900	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	700	60	23.9	30.0	7.2	72.2	2.3	12.67	1.9	10.1	5.3	99	375	900		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	700	60	25.2	35.6	9.0	69.8	2.1	6.77	2.1	10.2	4.8	101	1280	900		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	725	60	32.3	42.0	13.4	84.0	3.4	10.63	2.0	10.0	4.9	99	1415	900	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	725	60	32.9	42.3	13.8	85.3	3.5	10.80	2.0	10.0	4.9	99	1480	900		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	725	60	33.2	42.6	14.1	85.8	3.5	9.62	2.0	10.3	5.2	100	1685	900		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	725	100	29.0	46.1	13.4	68.9	2.7	3.88	2.0	10.3	5.2	100	1755	1500	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	725	100	28.7	46.1	13.3	68.7	2.6	3.62	2.0	10.3	5.2	100	1815	1500		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	750	100	34.9	47.8	16.6	82.0	3.8	4.86	2.0	10.3	5.2	100	1875	1500	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	750	80	36.0	45.9	16.4	86.4	4.0	5.91	2.0	10.3	5.2	99	2000	1200	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	750	80	34.5	45.5	15.7	84.7	3.7	5.41	2.0	10.3	5.2	100	2180	1200		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	750	80	32.5	44.9	14.5	80.0	3.3	4.83	2.0	10.2	5.2	99	2840	1200		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	775	100	36.1	46.4	16.5	85.5	4.5	5.46	2.0	10.2	5.2	98	2905	1500	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	775	100	35.8	46.4	16.3	85.1	4.5	5.47	2.0	10.2	5.2	98	2965	1500		50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	800	110	39.7	45.9	17.6	92.7	6.3	7.58	2.0	10.2	5.2	97	3000	1650	C	50	C
31 BKW 7 R#3	5.0	BaCl2,Ga2O3,60/100	800	110	38.9	46.0	17.4	92.7	6.3	7.70	2.0	10.2	5.2	97	3030	1650		50	C

* Appendix A and the Experimental Section describe Table headings and experimental procedures.
The C column shows a letter C whenever a process change was made. =/- is the ethylene to ethane molar ratio.

Inaccurate due to a small number, division by a small number, or not applicable.

Table 6. Molecular Sieve Catalysts

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	+/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
29 BKW 142 R#3	0.5	MnApso-5	700	50	20.9	3.1	0.7	69.1	0.8	0.99	2.1	9.6	4.6	103	45	5455	C	0	A
29 BKW 142 R#3	0.5	MnApso-5	700	50	19.6	2.8	0.6	64.8	0.7	0.89	2.1	9.6	4.6	103	195	5455		0	A
29 BKW 142 R#3	0.5	MnApso-5	700	50	18.6	3.3	0.6	60.4	0.5	0.69	2.1	10.1	4.8	102	1065	5455		0	A
29 BKW 143 R#4	0.5	CoApso-34	700	50	19.9	2.5	0.5	62.6	1.3	0.71	2.1	9.6	4.6	103	90	3000	C	0	A
29 BKW 143 R#4	0.5	CoApso-34	700	50	19.3	2.5	0.5	61.1	1.3	0.70	2.1	9.6	4.6	103	135	3000		0	A
29 BKW 143 R#4	0.5	CoApso-34	700	50	18.2	2.6	0.5	56.6	1.0	0.73	2.1	10.1	4.8	102	1110	3000		0	A
29 BKW 146 R#3	0.5	MnApso-34	700	50	26.3	5.5	1.5	85.1	2.1	0.48	2.1	10.1	4.8	104	30	3333	C	0	A
29 BKW 146 R#3	0.5	MnApso-34	700	50	26.8	3.3	0.9	83.4	1.0	0.56	2.1	10.1	4.8	102	120	3333		0	A
29 BKW 146 R#3	0.5	MnApso-34	700	50	24.0	3.1	0.8	80.2	1.0	0.59	1.9	10.2	5.3	103	1320	3333		0	A
29 BKW 147 R#4	0.5	MApo-34	700	50	3.1	15.5	0.5	4.7	0.3	0.54	2.1	10.1	4.8	99	75	4286	C	0	A
29 BKW 147 R#4	0.5	MApo-34	700	50	3.6	17.9	0.6	3.9	0.3	0.41	2.1	10.1	4.8	98	165	4286		0	A
29 BKW 147 R#4	0.5	MApo-34	800	50	10.8	27.5	3.0	23.2	1.7	0.11	2.1	10.1	4.8	100	450	4286	C	0	A
29 BKW 147 R#4	0.5	MApo-34	800	50	11.0	27.6	3.1	23.6	1.8	0.10	2.1	10.1	4.8	100	540	4286		0	A
29 BKW 147 R#4	0.5	MApo-34	800	50	12.1	28.5	3.5	30.4	2.0	0.09	1.9	10.2	5.3	101	1365	4286		0	A
29 BKW 151 R#4	0.5	CoAPO-34	700	50	6.2	22.7	1.5	27.6	2.4	0.73	2.0	10.1	5.1	108	30	3750	C	0	A
29 BKW 151 R#4	0.5	CoAPO-34	700	50	4.8	13.0	0.6	17.4	0.4	0.28	2.0	10.1	5.1	101	120	3750		0	A
29 BKW 151 R#4	0.5	CoAPO-34	800	50	19.0	22.5	4.3	47.0	2.7	0.15	2.0	10.1	5.1	101	405	3750	C	0	A
29 BKW 151 R#4	0.5	CoAPO-34	800	50	18.2	23.4	4.3	44.5	2.7	0.13	2.0	9.9	4.9	101	540	3750		0	A
29 BKW 151 R#4	0.5	CoAPO-34	800	20	24.8	17.9	4.5	63.9	3.6	0.17	2.0	9.9	4.9	102	1380	1500	C	0	A
30 BKW 66 R#3	0.5	AlPO4-5,powder	600	50	6.6	0.7	0.1	22.5	0.0	2.36	2.0	10.3	5.0	100	30	1875	C	0	C
30 BKW 66 R#3	0.5	AlPO4-5,powder	700	50	23.5	0.8	0.2	73.5	0.6	0.24	2.0	10.3	5.0	104	120	1875	C	0	C
30 BKW 66 R#3	0.5	AlPO4-5,powder	700	50	23.3	0.7	0.2	73.1	0.5	0.25	2.0	10.3	5.0	103	210	1875		0	C
30 BKW 66 R#3	0.5	AlPO4-5,powder	750	50	29.8	1.5	0.5	90.6	0.9	0.22	2.0	10.3	5.0	105	300	1875	C	0	C
30 BKW 66 R#3	0.5	AlPO4-5,powder	750	50	29.8	1.6	0.5	89.6	0.8	0.23	2.0	10.3	5.0	104	385	1875		0	C
30 BKW 66 R#3	0.5	AlPO4-5,powder	750	50	27.8	1.3	0.4	86.0	1.1	0.22	2.2	10.6	4.9	104	525	1875	C	50	C
30 BKW 6	0.5	AlPO4-5,powder	750	50	27.6	1.4	0.4	84.7	1.1	0.22	2.2	10.6	4.9	104	705	1875		50	C
30 BKW	0.5	AlPO4-5,powder	750	50	27.3	1.4	0.4	88.4	1.1	0.29	2.2	10.6	4.9	105	4125	1875		50	D
30 BKW 6	0.5	SAPO-5	600	50	2.3	2.3	0.1	8.8	0.0	11.39	2.0	10.3	5.0	100	75	5000	C	0	D
30 BKW 6	0.5	SAPO-5	700	50	14.4	0.6	0.1	58.3	0.1	35.11	2.0	10.3	5.0	100	165	5000	C	0	D
30 BKW [illegible] 4	0.5	SAPO-5	750	50	20.1	1.4	0.3	76.6	0.1	2.94	2.0	10.3	5.0	101	255	5000	C	0	D
30 BKW 67 R#4	0.5	SAPO-5	750	50	19.8	1.5	0.3	73.8	0.1	2.13	2.0	10.3	5.0	101	345	5000		0	D
30 BKW 67 R#4	0.5	SAPO-5	750	50	17.7	1.4	0.3	71.9	0.1	1.32	2.0	10.3	5.0	103	435	5000	C	50	D
30 BKW 67 R#4	0.5	SAPO-5	750	50	19.4	1.3	0.3	67.1	0.3	0.76	2.2	10.6	4.9	101	570	5000		50	D
30 BKW 67 R#4	0.5	SAPO-5	750	50	18.4	1.7	0.3	61.9	0.3	0.41	2.1	10.6	5.1	102	1110	5000		50	D
30 BKW 80 R#4	0.5	MAPO-36,powder	600	50	0.9	8.8	0.1	5.6	0.0	###	1.9	10.1	5.3	100	45	4286	C	0	C
30 BKW 90 R#4	0.5	MAPO-36,powder	600	50	1.3	8.8	0.1	5.3	0.0	###	1.9	10.1	5.3	99	135	4286		0	C
30 BKW 80 R#4	0.5	MAPO-36,powder	700	50	4.4	9.1	0.4	12.4	0.3	1.73	1.9	10.1	5.3	98	225	4286	C	0	C
30 BKW 80 R#4	0.5	MAPO-36,powder	750	50	7.3	15.1	1.1	17.5	0.4	0.49	1.9	10.1	5.3	98	315	4286	C	0	C
30 BKW 80 R#4	0.5	MAPO-36,powder	750	50	6.2	16.1	1.0	14.7	0.7	0.30	2.1	10.4	5.1	101	405	4286	C	50	C
30 BKW 80 R#4	0.5	MAPO-36,powder	750	50	7.0	16.6	1.2	14.6	0.7	0.22	2.1	10.4	5.1	100	540	4286		50	C
30 BKW 80 R#4	0.5	MAPO-36,powder	750	50	4.8	17.4	0.9	15.3	0.7	0.19	2.0	10.3	5.1	102	1260	4286		50	C
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	250	50	-1.3	3.5	0.0	0.8	-0.3	###	2.0	10.1	5.2	101	50	2000	C	0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	250	50	-0.6	25.1	-0.1	0.6	3.6	###	2.0	10.1	5.2	101	80	2000		0	D

Table 6. Molecular Sieve Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	295	50	-0.5	1.0	0.0	1.2	-0.5	###	2.0	10.1	5.2	101	125	2000	C	0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	295	50	-0.1	2.4	0.0	0.7	-0.4	###	2.0	10.1	5.2	100	165	2000		0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	500	50	0.2	3.0	0.0	1.3	-0.3	###	2.0	10.1	5.2	100	205	2000	C	0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	500	50	0.2	19.7	0.0	1.2	153.0	###	2.0	10.1	5.2	100	240	2000		0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	600	50	1.4	-0.4	0.0	5.0	0.8	###	2.0	10.1	5.2	99	315	2000	C	0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	600	50	0.6	1.7	0.0	3.7	3.5	###	2.0	10.1	5.2	100	350	2000		0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	700	50	2.7	11.1	0.3	9.4	0.2	1.68	2.0	10.1	5.2	99	500	2000	C	0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	700	50	2.2	11.6	0.3	8.7	0.2	1.63	2.0	10.1	5.2	100	680	2000		0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	700	50	2.6	13.8	0.4	4.1	0.2	0.72	2.0	10.1	5.0	99	3920	2000		0	D
30 BKW 95 R#3	0.5	Highly Acidic Molecular Sieve	700	50	3.5	11.1	0.4	8.6	0.6	0.97	2.0	10.3	5.1	99	4500	2000	C	50	D

* Appendix A and the Experimental Section describe Table headings and experimental procedures.
The C column shows a letter C whenever a process change was made. =/- is the ethylene to ethane molar ratio.
Inaccurate due to a small number, division by a small number, or not applicable.

Table 7. Silver Catalysts

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	+/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	500	60	24.5	-0.2	-0.1	99.1	0.0	###	2.0	10.2	5.0	100	35	818	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	500	60	24.9	-0.2	-0.1	99.1	0.0	###	2.0	10.2	5.0	99	70	818		50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	500	160	24.1	-0.3	-0.1	99.2	0.0	###	2.0	10.2	5.0	100	110	2182	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	500	160	24.4	-0.2	-0.1	99.2	0.0	###	2.0	10.2	5.0	100	145	2182		50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	160	6.5	-0.9	-0.1	23.4	0.0	###	2.0	10.2	5.0	99	185	2182	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	160	7.6	-0.9	-0.1	28.3	0.0	###	2.0	10.2	5.0	99	215	2182		50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	425	80	24.8	-0.3	-0.1	99.1	0.0	###	2.0	10.2	5.0	99	260	1091	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	425	120	25.0	-0.2	-0.1	98.9	0.0	###	2.0	10.2	5.0	99	305	1636	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	20.6	-0.3	-0.1	78.8	0.0	###	2.0	10.2	5.0	99	355	1091	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	19.1	-0.3	-0.1	82.3	0.0	###	1.9	10.1	5.3	101	485	1091		50	C
30 BKW 123 R#	5.0	Ag.Al203,5502,30/60	400	80	18.6	-0.3	-0.1	80.4	0.0	###	2.0	10.3	5.1	101	1205	1091		50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	6.7	-0.8	-0.1	30.4	0.0	###	2.2	10.5	4.8	101	1385	1091	C	500	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	5.2	-0.8	0.0	27.4	0.0	###	2.2	10.5	4.8	102	1470	1091		500	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	5.2	-0.9	-0.1	25.0	0.0	###	2.2	10.5	4.8	101	1630	1091		500	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	10.5	-0.7	-0.1	46.1	0.1	###	1.9	10.4	5.4	100	1790	1091	C	100	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	10.4	-0.5	-0.1	43.1	0.0	###	2.1	10.4	5.1	100	1925	1091		100	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	6.8	-0.9	-0.1	25.8	0.0	###	2.1	10.4	4.9	100	5165	1091		100	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	9.3	-0.7	-0.1	33.7	0.0	###	2.1	10.3	5.0	100	5660	1091	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	400	80	9.9	-0.7	-0.1	33.8	0.0	###	2.1	10.3	5.0	99	5750	1091		50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	600	80	24.4	-0.2	0.0	93.6	-0.2	###	2.1	10.3	5.0	99	5830	1091	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	700	80	31.5	19.6	6.0	98.9	1.0	43.15	2.1	10.3	5.0	98	5880	1091	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	700	80	30.0	13.2	3.9	98.9	0.4	91.97	2.1	10.3	5.0	98	5915	1091	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	700	25	30.5	17.5	5.3	98.9	3.2	27.59	2.0	10.1	5.2	99	6245	341	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	700	25	28.1	16.9	4.8	98.9	2.1	34.15	2.0	10.1	5.2	101	6425	341		50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	700	25	25.5	2.4	0.6	98.9	0.3	1630.80	2.0	10.1	5.1	100	7100	341			C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	700	160	25.6	1.6	0.4	99.0	0.2	1595.46	2.0	10.1	5.1	100	7190	2182	C	50	C
30 BKW 123 R#	5.0	Ag,Al203,5502,30/60	700	160	25.9	1.7	0.4	99.0	0.2	###	2.0	10.1	5.1	99	7280	2182		50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	400	80	0.9	3.0	0.0	7.2	2.8	###	1.9	10.1	5.3	100	30	1091	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	500	50	3.7	0.6	0.0	16.6	-3.3	###	1.9	10.1	5.3	100	110	682	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	500	50	5.0	0.6	0.0	15.7	-3.0	###	1.9	10.1	5.3	97	185	682		50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	600	50	7.2	2.7	0.2	28.3	0.9	###	1.9	10.1	5.3	99	270	682	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	600	50	6.5	4.8	0.3	24.8	0.8	###	1.9	10.1	5.3	99	335	682		50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	650	50	18.1	23.9	4.3	57.7	0.5	###	1.9	10.1	5.3	99	405	682	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	650	50	16.2	27.7	4.5	48.3	0.5	###	2.1	10.1	4.9	100	545	682		50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	650	50	13.8	30.2	4.2	46.5	0.5	###	2.0	10.1	5.1	102	1265	682		50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	675	50	25.5	34.0	8.6	73.0	0.8	971.96	2.0	10.2	5.0	99	1385	682	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	675	50	25.9	34.2	8.8	72.3	0.8	###	2.0	10.2	5.0	99	1455	682		50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	675	100	14.6	36.0	5.2	39.5	0.4	###	2.0	10.2	5.0	99	1530	1364	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	675	30	34.4	32.3	10.9	97.7	1.3	1010.11	2.0	10.2	5.0	98	1620	409	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	700	80	28.8	37.4	10.5	75.3	0.9	520.90	2.0	10.2	5.0	98	1710	1091	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	700	60	35.0	33.5	11.4	95.1	1.1	399.39	2.0	10.2	5.0	97	1790	818	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	700	60	35.5	31.5	10.8	98.2	1.1	673.14	2.0	10.2	5.0	97	1895	818		50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	700	60	28.8	22.9	6.7	99.0	0.7	572.87	2.1	10.1	4.9	102	7025	818		50	C

Table 7. Silver Catalysts (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	C	ECI	R
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	700	160	18.9	26.9	5.1	60.1	0.4	###	2.1	10.0	4.8	100	7160	2182	C	50	C
31 BKW 1 R#3	5.0	NaCl,Ag,Al2O3,5502,30/60	700	160	19.3	26.1	5.0	59.9	0.4	###	2.1	10.0	4.8	100	7250	2182		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	400	80	1.0	####	1.0	5.2	36.2	###	1.9	10.1	5.3	99	60	1091	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	500	50	3.6	45.6	1.6	7.7	192.8	###	1.9	10.1	5.3	97	150	682	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	500	50	2.5	33.2	0.8	8.9	37.4	###	1.9	10.1	5.3	98	225	682		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	600	50	12.2	20.7	2.5	39.0	0.3	###	1.9	10.1	5.3	99	305	682	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	600	50	11.9	21.8	2.6	38.6	0.3	###	1.9	10.1	5.3	99	365	682		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	650	50	32.1	32.1	9.9	84.9	0.8	###	1.9	10.1	5.3	96	440	682	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	650	50	29.5	30.6	9.0	87.6	0.8	2346.06	2.1	10.1	4.9	100	590	682		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	650	50	26.6	27.6	7.4	85.6	0.7	1155.29	2.0	10.1	5.1	101	1310	682		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	675	50	33.6	30.2	10.0	99.0	2.1	94.11	2.0	10.2	5.0	99	1420	682	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	675	30	34.3	29.9	10.1	99.0	5.1	78.56	2.0	10.2	5.0	98	1490	409	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	675	30	34.2	30.3	10.2	99.0	3.6	91.60	2.0	10.2	5.0	98	1565	409		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	675	100	27.5	31.7	8.6	77.6	0.7	298.82	2.0	10.2	5.0	98	1665	1364	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	700	130	33.6	27.2	8.9	98.4	1.3	129.31	2.0	10.2	5.0	98	1755	1773	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	700	140	32.4	22.0	6.9	99.0	1.0	385.15	2.0	10.2	5.0	97	1850	1909	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	700	140	28.0	14.7	4.1	99.0	0.5	###	1.9	10.1	5.2	100	2030	1909		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	700	140	24.0	8.3	2.0	98.9	0.3	###	2.1	10.1	4.9	103	7070	1909		50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	700	160	24.2	8.1	2.0	94.1	0.3	###	2.1	10.0	4.8	100	7205	2182	C	50	C
31 BKW 2 R#4	5.0	BaCl2,Ag,Al2O3,5502,30/60	700	160	24.0	8.7	2.1	90.9	0.3	###	2.1	10.0	4.8	100	7295	2182		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	400	50	0.4	0.8	0.0	7.4	-1.3	###	1.9	10.1	5.3	100	65	750	C	50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	500	50	2.0	0.4	0.0	12.8	-1.4	###	1.9	10.1	5.3	100	130	750	C	50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	500	50	1.5	-2.4	0.0	10.4	-0.6	###	1.9	10.1	5.3	100	200	750		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	600	50	4.9	4.4	0.2	23.8	1.3	###	1.9	10.1	5.3	100	280	750	C	50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	600	50	5.0	5.1	0.3	23.3	0.9	###	1.9	10.1	5.3	100	345	750		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	650	50	16.8	23.0	3.9	57.3	0.4	###	1.9	10.1	5.3	100	410	750	C	50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	650	50	15.8	24.1	3.8	54.6	0.4	###	1.9	10.1	5.3	100	470	750		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	650	50	12.4	25.8	3.2	39.7	0.4	###	2.1	10.2	4.8	101	1325	750		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	675	50	22.3	32.2	7.2	66.7	0.7	1228.98	2.0	10.0	4.9	100	1450	750	C	50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	675	50	22.2	32.4	7.2	65.6	0.7	5043.22	2.0	10.0	4.9	99	1525	750		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	675	50	22.1	32.4	7.2	65.7	0.7	###	2.0	10.3	5.2	100	1735	750		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	700	50	32.4	33.1	10.7	95.1	1.1	269.50	2.0	10.3	5.2	100	1795	750	C	50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	700	60	30.1	33.9	10.2	87.4	1.0	279.62	2.0	10.3	5.2	100	1855	900	C	50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	700	60	30.8	33.6	10.3	87.9	1.0	230.49	2.0	10.3	5.2	99	2055	900		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	700	60	32.3	29.7	9.5	96.8	0.9	332.50	2.0	10.2	5.2	99	2885	900		50	C
31 BKW 9 R#4	5.0	KCl,Ag,Al2O3,5502,30/60	700	80	28.5	31.1	8.8	84.5	0.7	224.64	2.0	10.2	5.2	99	2945	1200	C	50	C

•	Appendix A and the Experimental Section describe Table headings and experimental procedures. The C column shows a letter C whenever a process change was made. =/- is the ethylene to ethane molar ratio.
###	Inaccurate due to a small number, division by a small number, or not applicable.

Table 8. **Methane Coupling Activity of Quartz Packed Reactor [Experiment #1]**

CATALYST: * *
NOTEBOOK: 2-KDC-X-4

Weight (g): * *
Volume (cc): * *
Flow (cc/min): 100

$CH_4/O_2/N_2$: 8.36/1/3.73
GHSV (h 1): * *
Pressure (psig): 10

Temperature (°C)	750	750	750	750	750	750
Time (h)	1	2.5	5.5	8.5	11.5	14.5
CH_4 Conv., %	3.27	3.95	3.78	3.92	3.69	4.01
O_2 Conv., %	10.42	10.76	11.24	11.14	10.71	10.73
C Balance, %	98.36	97.66	97.85	97.70	97.91	97.60
C2 Selectivity, %	53.44	50.42	51.81	51.15	51.62	51.16
C3 Selectivity, %	1.28	2.42	1.51	2.32	1.53	1.53
C2 Yield, %	1.72	1.94	1.92	1.96	1.87	2.00
Ethylene/Ethane	0.55	0.45	0.45	0.45	0.44	0.46
CO_2/CO	0.06	0.07	0.08	0.08	0.08	0.09

**: Not applicable.

Table 9. Methane Coupling Activity of Quartz Packed Reactor [Experiment #2]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-36

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 164

CH4/O2/N2: 14.2/1/3.71 **GHSV (h 1):** * * **Pressure (psig):** 15

Temperature (°C)	850	850	850	850	850	850
Time (h)	1	4	6	8	10	12
CH4 Conv., %	4.56	4.50	4.56	4.31	4.41	4.16
O2 Conv., %	55.30	55.86	52.15	54.56	54.38	54.49
C Balance, %	101.17	101.17	101.17	101.40	101.28	101.48
C2 Selectivity, %	53.08	53.30	53.08	52.98	53.17	53.05
C3 Selectivity, %	7.27	7.33	7.27	7.26	7.19	7.26
C2 Yield, %	2.45	2.43	2.45	2.31	2.37	2.24
Ethylene/Ethane	2.13	2.12	2.13	2.12	2.09	2.11
CO2/CO	0.02	0.00	0.02	0.03	0.02	0.02

**: Not applicable.

Table 10. **Methane Coupling Activity of Quartz Packed Reactor [Experiment #3]**

CATALYST: * * **NOTEBOOK:** 2-KDC-X-12

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 56.9

CH4/O2/N2: 14.3/1/3.7 **GHSV (h 1):** * * **Pressure (psig):** 15

Temperature (°C)	850	850	850	850	850
Time (h)	1	2	3	4	5
CH4 Conv., %	8.24	7.78	7.60	7.66	7.83
O2 Conv., %	94.25	93.95	93.76	93.17	93.06
C Balance, %	99.76	100.39	100.60	100.55	100.35
C2 Selectivity, %	39.16	38.77	38.70	39.03	39.00
C3 Selectivity, %	7.31	7.33	7.30	7.25	7.25
C2 Yield, %	3.22	3.03	2.96	3.01	3.06
Ethylene/Ethane	6.56	6.31	6.23	5.93	5.87
CO2/CO	0.04	0.05	0.07	0.06	0.07

**: Not applicable.

Table 11. Methane Coupling Activity of Quartz Packed Reactor [Experiment #4]

CATALYST: * *		NOTEBOOK: 2-KDC-X-8			
Weight (g): * *	Volume (cc) * *		Flow (cc/min): 163		
CH4/O2/N2: 2.09/1/3.82	GHSV (h 1): * *		Pressure (psig): 15		
Temperature (°C)	850	850	850	850	850
Time (h)	1	4	7	10	13
CH4 Conv., %	38.07	39.01	38.97	38.48	34.51
O2 Conv., %	92.34	92.61	92.69	92.70	92.23
C Balance, %	96.91	96.08	96.12	97.63	103.61
C2 Selectivity, %	20.71	20.40	20.36	19.76	20.10
C3 Selectivity, %	1.16	1.15	1.14	1.11	1.14
C2 Yield, %	7.64	7.64	7.62	7.43	7.19
Ethylene/Ethane	4.84	4.86	4.83	4.81	4.83
CO2/CO	0.11	0.13	0.13	0.13	0.14

**: Not applicable.

Table 12. Methane Coupling Activity of Quartz Packed Reactor [Experiment #5]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-22

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 55.7

CH4/O2/N2: 2.03/1/3.83 **GHVS (h 1):** * * **Pressure (psig):** 15

Temperature (°C)	850	850	850	850	850	850
Time (h)	1	2	3	4	5	6
CH4 Conv., %	38.29	38.18	38.23	38.93	38.25	38.13
O2 Conv., %	94.36	94.38	94.41	94.39	94.42	94.40
C Balance, %	95.82	96.95	96.69	94.80	97.44	98.01
C2 Selectivity, %	15.86	15.37	15.34	15.91	15.10	14.86
C3 Selectivity, %	0.85	0.83	0.97	0.97	0.94	0.89
C2 Yield, %	5.82	5.69	5.67	5.87	5.63	5.55
Ethylene/Ethane	9.91	10.09	10.86	10.16	10.21	10.46
CO2/CO	0.09	0.12	0.12	0.12	0.15	0.16

**: Not applicable.

Table 13. Methane Coupling Activity of Quartz Packed Reactor [Experiment #6]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-26

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 108

CH4/O2/N2: 15.2/1/3.78 **GHSV (h 1):** * * **Pressure (psig):** 5

Temperature (°C)	850	850	850	850	850
Time (h)	1	2	3	4	6
CH4 Conv., %	2.35	4.11	2.27	3.13	3.06
O2 Conv., %	27.63	28.49	28.44	28.97	28.87
C Balance, %	100.84	99.09	101.02	100.11	100.23
C2 Selectivity, %	58.59	58.37	58.80	58.50	58.87
C3 Selectivity, %	5.88	6.15	6.14	6.10	6.13
C2 Yield, %	1.39	2.38	1.35	1.83	1.80
Ethylene/Ethane	1.35	1.37	1.36	1.39	1.36
CO2/CO	0.03	0.02	0.03	0.03	0.03

**: Not applicable.

Table 14. Methane Coupling Activity of Quartz Packed Reactor [Experiment #7]

CATALYST: **
NOTEBOOK: 2-KDC-X-20
Weight (g): **
Volume (cc): **
Flow (cc/min): 35.9
CH4/O2/N2: 14.6/1/3.71
GHSV (h 1): **
Pressure (psig): 5

Temperature (°C)	850	850	850	850	850
Time (h)	2	3	4	5	6
CH4 Conv., %	7.85	7.88	7.55	7.56	7.33
O2 Conv., %	84.02	81.95	83.30	83.08	82.19
C Balance, %	99.50	99.38	99.78	99.77	99.96
C2 Selectivity, %	41.52	42.14	41.78	41.86	42.29
C3 Selectivity, %	5.89	6.22	5.96	6.01	6.05
C2 Yield, %	3.24	3.30	3.15	3.16	3.10
Ethylene/Ethane	4.39	4.05	4.19	4.19	4.03
CO2/CO	0.05	0.05	0.05	0.05	0.06

**: Not applicable.

Table 15. Methane Coupling Activity of Quartz Packed Reactor
[Experiment #8]

CATALYST: * * NOTEBOOK: 2-KDC-X-6

Weight (g): * * Volume (cc): * * Flow (cc/min): 110

CH4/O2/N2: 2.09/1/3.82 GHSV (h 1): * * Pressure (psig): 5

Temperature (°C)	850	850	850	850	850
Time (h)	1	2	3	4	5
CH4 Conv., %	34.87	34.87	35.56	35.72	35.24
O2 Conv., %	79.72	80.61	81.09	81.43	81.63
C Balance, %	95.48	96.35	96.47	96.48	96.28
C2 Selectivity, %	26.67	25.85	25.20	24.95	25.37
C3 Selectivity, %	1.50	1.46	1.37	1.41	1.44
C2 Yield, %	8.88	8.68	8.64	8.60	8.61
Ethylene/Ethane	4.10	4.14	4.13	4.10	4.10
CO2/CO	0.03	0.03	0.09	0.10	0.04

**: Not applicable.

Table 16. Methane Coupling Activity of Quartz Packed Reactor [Experiment #9]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-35

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 36.1

CH4/O2/N2: 2.01/1/3.78 **GHSV (psig):** * * **Pressure (psig):** 5

Temperature (°C)	850	850	850
Time (h)	2	3	4
CH4 Conv., %	39.15	39.27	39.29
O2 Conv., %	93.74	93.41	93.49
C Balance, %	93.29	93.42	94.49
C2 Selectivity, %	16.32	16.54	16.11
C3 Selectivity, %	0.73	0.73	0.71
C2 Yield, %	5.96	6.07	5.98
Ethylene/Ethane	7.89	7.45	7.34
CO2/CO	0.01	0.01	0.04

**: Not applicable.

Table 17. Methane Coupling Activity of Quartz Packed Reactor [Experiment #10]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-24

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 100

CH4/O2/N2: 8.29/1/3.76 **GHSV (h 1):** * * **Pressure (psig):** 10

Temperature (°C)	750	750	750	750	750
Time (h)	1	2	3	5	7
CH4 Conv., %	1.10	1.37	1.14	1.15	1.00
O2 Conv., %	9.14	9.87	9.50	9.40	9.41
C Balance, %	100.29	100.06	100.30	100.31	100.44
C2 Selectivity, %	48.36	47.56	49.42	49.76	48.60
C3 Selectivity, %	1.41	1.41	1.25	1.70	1.45
C2 Yield, %	0.53	0.65	0.56	0.58	0.49
Ethylene/Ethane	0.41	0.40	0.40	0.40	0.40
CO2/CO	0.01	0.02	0.03	0.03	0.03

**: Not applicable.

Table 18. Methane Coupling Activity of Quartz Packed Reactor [Experiment #11]

CATALYST: ** **NOTEBOOK:** 2-KDC-X-16

Weight (g): ** **Volume (cc):** ** **Flow (cc/min):** 202

CH4/O2/N2: 14.3/1/3.7 **GHSV (h 1):** ** **Pressure (psig):** 15

Temperature (°C)	649	649	649	649
Time (h)	1	2	3	4
CH4 Conv., %	***	***	***	***
O2 Conv., %	1.77	1.84	1.36	0.91
C Balance, %	101.01	100.97	101.03	100.90
C2 Selectivity, %	***	***	***	***
C3 Selectivity, %	***	***	***	***
C2 Yield, %	***	***	***	***
Ethylene/Ethane	***	***	***	***
CO2/CO	***	***	***	***

**: Not applicable.
***: CH4 conversion too low for meaningful results.

Table 19. Methane Coupling Activity of Quartz Packed Reactor
[Experiment #12]

CATALYST: * *
NOTEBOOK: 2-KDC-X-40

Weight (g): * *
Volume (cc): * *
Flow (cc/min): 67.1

CH4/O2/N2: 14.6/1/3.72
GHSV (h 1): * *
Pressure (psig): 15

Temperature (°C)	649	649	649	649	649	649
Time (h)	1	3	6	8	10	12
CH4 Conv., %	0.78	0.81	0.60	0.83	0.65	0.90
O2 Conv., %	3.88	3.63	3.37	2.14	4.40	2.12
C Balance, %	99.53	99.49	99.69	99.45	99.64	99.38
C2 Selectivity, %	30.05	30.15	30.85	31.52	28.70	30.98
C3 Selectivity, %	0.00	0.00	0.00	0.00	0.00	0.00
C2 Yield, %	0.23	0.24	0.19	0.26	0.19	0.28
Ethylene/Ethane	0.07	0.06	0.06	0.07	0.06	0.07
CO2/CO	0.05	0.04	0.08	0.02	0.05	0.03

**: Not applicable.

Table 20. Methane Coupling Activity of Quartz Packed Reactor [Experiment #13]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-28

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 201

CH4/O2/N2: 2.05/1/3.83 **GHSV (h 1):** * * **Pressure (psig):** 15

Temperature (°C)	649	649	649	649
Time (h)	1	5	7	9
CH4 Conv., %	0.84	1.45	0.73	1.02
O2 Conv., %	* * *	* * *	* * *	* * *
C Balance, %	99.55	98.78	99.62	99.31
C2 Selectivity, %	17.47	31.98	21.45	16.29
C3 Selectivity, %	0.00	0.00	0.00	0.00
C2 Yield, %	0.15	0.46	0.16	0.17
Ethylene/Ethane	0.02	0.05	0.03	0.03
CO2/CO	* * * *	* * * *	* * * *	* * * *

**: Not applicable.
***: O2 conversion too low for meaningful results.
****: CO2 amount too low for meaningful results.

Table 21. Methane Coupling Activity of Quartz Packed Reactor [Experiment #14]

CATALYST: * *	NOTEBOOK: 2-KDC-X-30				
Weight (g): * *	Volume (cc): * *		Flow (cc/min): 67.1		
CH4/O2/N2: 2.06/1/3.84	GHSV (h 1): * *		Pressure (psig): 15		
Temperature (°C)	649	649	649	649	649
Time (h)	1	2	3	4	5
CH4 Conv., %	2.46	3.07	3.01	3.30	3.23
O2 Conv., %	0.72	1.67	1.77	1.89	1.86
C Balance, %	98.80	98.37	98.63	98.36	98.56
C2 Selectivity, %	20.24	20.04	20.69	21.74	22.98
C3 Selectivity, %	0.52	0.00	0.45	0.89	0.82
C2 Yield, %	0.49	0.61	0.62	0.71	0.73
Ethylene/Ethane	0.12	0.13	0.13	0.15	0.16
CO2/CO	* * *	* * *	* * *	* * *	* * *

**: Not applicable.
***: CO2 amount too low for meaningful results.

Table 22. Methane Coupling Activity of Quartz Packed Reactor [Experiment #15]

CATALYST: ** **NOTEBOOK:** 2-KDC-X-38

Weight (g): ** **Volume (cc):** ** **Flow(cc/min):** 133

$CH_4/O_2/N_2$: 14.6/1/3.72 **GHSV (h 1):** ** **Pressure:** 5 psig

Temperature (°C)	649	649	649	649
Time (h)	1	2	3	4
CH_4 Conv., %	***	***	***	***
O_2 Conv., %	0.33	0.48	0.29	0.53
C Balance, %	100.56	100.41	100.37	100.20
C_2 Selectivity, %	***	***	***	***
C_3 Selectivity, %	***	***	***	***
C_2 Yield, %	***	***	***	***
Ethylene/Ethane	***	***	***	***
CO_2/CO	***	***	***	***

**: Not applicable.
***: CH_4 conversion too low for meaningful results.

Table 23. Methane Coupling Activity of Quartz Packed Reactor [Experiment #16]

CATALYST: ** **NOTEBOOK:** 2-KDC-X-32

Weight (g): ** **Volume (cc):** ** **Flow (cc/min):** 43.5

CH4/O2/N2: 14.7/1/3.74 **GHSV (h 1):** ** **Pressure (psig):** 5

Temperature (°C)	649	649	649	649	649	649
Time (h)	1	4	6	8	10	12
CH4 Conv., %	***	***	***	***	***	***
O2 Conv., %	2.87	2.74	2.70	2.70	2.60	2.73
C Balance, %	99.71	100.17	99.93	100.30	100.34	100.30
C2 Selectivity, %	***	***	***	***	***	***
C3 Selectivity, %	***	***	***	***	***	***
C2 Yield, %	***	***	***	***	***	***
Ethylene/Ethane	***	***	***	***	***	***
CO2/CO	***	***	***	***	***	***

**: Not applicable.
***: CH4 conversion too low for meaningful results.

Table 24. Methane Coupling Activity of Quartz Packed Reactor [Experiment #17]

CATALYST: * *
NOTEBOOK: 2-KDC-X-18

Weight (g): * *
Volume (cc): * *
Flow (cc/min): 133

CH4/O2/N2 : 2.0/1/3.78
GHSV (h 1): * *
Pressure (psig): 5

Temperature (°C)	649	649	649	649
Time (h)	2	3	4	6
CH4 Conv., %	1.48	1.13	0.90	1.05
O2 Conv., %	1.43	2.18	0.69	0.40
C Balance, %	98.76	99.05	99.27	99.10
C2 Selectivity, %	15.33	19.27	23.56	22.61
C3 Selectivity, %	0.00	0.00	0.00	0.00
C2 Yield, %	0.22	0.22	0.21	0.24
Ethylene/Ethane	0.00	0.00	0.02	0.00
CO2/CO	***	***	***	***

**: Not applicable.
***: CO2 amount too low for meaningful results.

Table 25. Methane Coupling Activity of Quartz Packed Reactor [Experiment #18]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-10

Weight (g): * * **Volume (cc):** * * **Flow (cc/min):** 43.8

CH4/O2/N2: 2.00/1/3.83 **GHSV (h 1):** * * **Pressure (psig):** 5

Temperature (°C)	650	650	650	650
Time (h)	1	2	3	4
CH4 Conv., %	0.42	0.55	0.72	0.76
O2 Conv., %	* * *	* * *	* * *	* * *
C Balance, %	100.40	100.25	100.10	100.17
C2 Selectivity, %	24.94	23.81	24.73	23.95
C3 Selectivity, %	0.00	0.00	0.00	0.00
C2 Yield, %	0.11	0.13	0.18	0.18
Ethylene/Ethane	0.06	0.06	0.05	0.05
CO2/CO	0.23	0.20	0.24	0.22

**: Not applicable.
***: O2 conversion too low for meaningful results.

Table 26. Methane Coupling Activity of Quartz Packed Reactor [Experiment #19]

CATALYST: * *

NOTEBOOK: 2-KDC-X-42

Weight (g): * *

Volume (cc): * *

Flow (cc/min): 100

CH4/O2/N2: 8.14/1/3.71

GHSV (h 1): * *

Pressure (psig): 10

Temperature (°C)	749	749	749
Time (h)	1	3	4
CH4 Conv., %	1.90	1.92	2.19
O2 Conv., %	11.68	10.76	11.14
C Balance, %	99.95	99.86	99.61
C2 Selectivity, %	53.72	53.98	53.37
C3 Selectivity, %	2.52	2.36	2.20
C2 Yield, %	1.02	1.03	1.16
Ethylene/Ethane	0.48	0.46	0.46
CO2/CO	0.01	0.00	0.00

**: Not applicable.

Table 27. Summary of Experimental Variables for Homogeneous Gas Phase Experiments

Experiment #	T (C)	P (psig)	CH4/O2 Ratio (mole/mole)	FR* (cc/min)	FR(reactor)** (cc/min)	Residence Time*** (sec)
1	750	10	8.36/1	100	208	7.25
2	850	15	14.3/1	164	311	4.84
3	850	15	14.3/1	56.9	108	14.0
4	850	15	2.09/1	163	309	4.87
5	850	15	2.03/1	55.7	106	14.3
6	850	5	15.2/1	108	309	4.88
7	850	5	14.7/1	35.9	103	14.7
8	850	5	2.09/1	110	315	4.79
9	850	5	2.01/1	36.1	103	14.6
10	750	10	8.29/1	100	208	7.25
11	649	15	14.3/1	202	315	4.79
12	649	15	14.6/1	67.1	105	14.4
13	649	15	2.05/1	201	313	4.81
14	649	15	2.06/1	67.1	105	14.4
15	649	5	14.6/1	133	312	4.82
16	649	5	14.7/1	43.5	102	14.7
17	649	5	2.00/1	133	312	4.82
18	650	5	2.00/1	43.8	103	14.6
19	749	10	8.14/1	100	208	7.25

*: Ambient conditions.

**: FR(reactor)= FR x (14.7/(P+14.7)) x ((T+273)/293)

***: Residence Time = [Void Volume/FR(reactor)] x 60; where, the void volume of the quartz bed is 25.1cc

Table 27. Summary of Experimental Results for Homogeneous Gas Phase Experiments (Continued)

Experiment #	CH4 Conv. (%)	O2 Conv. (%)	C2 Sele. (%)	C3 Sele. (%)	C2 Yield (%)	Ethylene/Ethane (mole/mole)	CO2/CO (mole/mole)	C Balance (%)
1	3.9	10.9	51.2	1.9	1.9	0.5	0.08	97.7
2	4.4	54.3	53.1	7.3	2.4	2.1	0.02	101.3
3	7.7	93.5	38.9	7.3	3.0	6.1	0.06	100.3
4	37.7	92.6	20.2	1.1	7.5	4.8	0.13	96.7
5	38.3	94.4	15.3	0.9	5.7	10.4	0.13	96.6
6	3.1	28.7	58.6	6.1	1.8	1.4	0.03	100.3
7	7.6	82.9	41.9	6.0	3.2	4.2	0.05	99.7
8	35.4	81.2	25.3	1.4	8.6	4.1	0.06	96.4
9	39.3	93.5	16.3	0.7	6.0	7.4	0.03	93.7
10	1.2	9.5	48.9	1.5	0.6	0.4	0.03	100.3
11	* *	1.4	* *	* *	* *	* *	* *	101.0
12	0.8	2.5	30.4	0.0	0.2	0.1	0.04	99.5
13	1.1	* * *	23.2	0.0	0.3	0.0	* * * *	99.6
14	3.3	1.9	21.8	0.5	0.7	0.2	* * * *	98.5
15	* *	0.4	* *	* *	* *	* *	* *	100.4
16	* *	2.7	* *	* *	* *	* *	* *	100.1
17	1.3	1.1	19.8	0.0	0.3	0.0	* * * *	98.9
18	0.7	* * *	27.2	0.0	0.2	0.2	0.22	100.2
19	2.1	11.0	53.7	2.3	1.1	0.5	0	99.8

**: CH4 conversion too low for meaningful results.
***: O2 conversion too low for meaningful results.
****: CO2 amount too low for meaningful results.

Table 28. Homogeneous Gas Phase Reaction - Pressure Effect at 750 °C
[Quartz Packed Reactor]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-84

Weight (g): * * **Volume (cc):** * *

CH4/O2/N2: 2.02/1/3.85 **Pressure (psig):** 5

Temperature (°C)	750	750	750	750	750	750	750
Flow (cc/min)	80	80	80	80	80	80	80
GHSV (h 1)	* *	* *	* *	* *	* *	* *	* *
Time (h)	1	3	5	7	9	11	15
CH4 Conv., %	12.47	12.36	13.79	12.96	13.05	12.69	13.09
O2 Conv., %	24.29	24.99	26.65	25.08	26.20	26.04	26.74
C Balance, %	100.02	100.38	99.31	100.19	100.08	100.41	100.47
C2 Selectivity, %	35.52	35.61	35.23	35.32	35.26	35.46	34.90
C3 Selectivity, %	1.90	2.09	1.88	1.90	1.90	1.93	1.90
C2 Yield, %	4.43	4.42	4.82	4.58	4.60	4.52	4.59
Ethylene/Ethane	1.22	1.23	1.28	1.27	1.27	1.26	1.29
CO2/CO	0.07	0.07	0.07	0.07	0.07	0.07	0.07

**: Not applicable.

Table 28. Homogeneous Gas Phase Reaction - Pressure Effect at 750 °C (Continued) [Quartz Packed Reactor]

CATALYST: ** NOTEBOOK: 2-KDC-X-84

Weight (g): ** Volume (cc): **

CH4/O2/N2: 2.02/1/3.85 Pressure (psig): 15

Temperature (°C)	750	750	750	750	750	750	750
Flow (cc/min)	120	120	120	120	120	120	120
GHSV (h 1)	**	**	**	**	**	**	**
Time (h)	17	18	19	20	21	22	23
CH4 Conv., %	35.66	35.25	35.35	35.39	36.36	35.69	35.94
O2 Conv., %	87.34	87.84	88.19	88.38	88.67	88.90	87.65
C Balance, %	96.93	98.97	99.04	99.18	96.86	98.94	96.89
C2 Selectivity, %	21.10	20.01	19.92	19.84	20.58	19.69	20.76
C3 Selectivity, %	1.56	1.48	1.48	1.71	1.51	1.49	1.06
C2 Yield, %	7.29	6.98	6.98	6.96	7.25	6.95	7.23
Ethylene/Ethane	2.78	2.79	2.79	2.79	2.79	2.80	2.78
CO2/CO	0.23	0.21	0.21	0.22	0.23	0.22	0.22

**: Not applicable.

Table 29. Homogeneous Gas Phase Reaction - Pressure Effect at 800 ° [Quartz Packed Reactor]

CATALYST: * *		NOTEBOOK: 2-KDC-X-80	
Weight (g): * *		Volume (cc): * *	
CH4/O2/N2: 2.02/1/3.85		Pressure (psig): 5	
Temperature (°C)	799	799	799
Flow (cc/min)	114	114	114
GHSV (h 1)	* *	* *	* *
Time (h)	3	4	5
CH4 Conv., %	12.98	13.12	13.80
O2 Conv., %	25.79	25.60	26.22
C Balance, %	100.48	100.62	100.35
C2 Selectivity, %	37.63	37.19	37.21
C3 Selectivity, %	2.11	2.01	2.04
C2 Yield, %	4.91	4.91	5.15
Ethylene/Ethane	1.48	1.52	1.55
CO2/CO	0.10	0.10	0.10

**: Not applicable.

Table 29. Homogeneous Gas Phase Reaction - Pressure Effect at 800 °C (Continued) [Quartz Packed Reactor]

CATALYST: * * **NOTEBOOK:** 2-KDC-X-80

Weight (g): * * **Volume (cc):** * *

CH4/O2/N2: 2.02/1/3.85 **Pressure (psig):** 10

Temperature (°C)	799	799	799	799	799	799	799
Flow (cc/min)	143	143	143	143	143	143	143
GHSV (h 1)	* *	* *	* *	* *	* *	* *	* *
Time (h)	6	8	10	12	14	16	18
CH4 Conv., %	24.89	26.79	27.55	28.21	28.96	28.97	29.37
O2 Conv., %	51.56	55.96	60.22	61.59	62.44	62.98	63.95
C Balance, %	98.33	97.92	99.79	99.48	97.90	98.18	98.02
C2 Selectivity, %	30.77	30.29	27.91	27.77	28.57	28.51	28.30
C3 Selectivity, %	1.76	1.80	1.69	1.65	1.70	1.68	1.68
C2 Yield, %	7.53	7.95	7.68	7.79	8.10	8.11	8.15
Ethylene/Ethane	2.44	2.52	2.62	2.64	2.70	2.66	2.66
CO2/CO	0.14	0.15	0.14	0.14	0.15	0.15	0.16

**: Not applicable.

Table 29. **Homogeneous Gas Phase Reaction - Pressure Effect at 800 °C (Continued)**
[Quartz Packed Reactor]

CATALYST: * *
NOTEBOOK: 2-KDC-X-80

Weight (g): * *
Volume (cc): * *

CH4/O2/N2: 2.01/1/3.85
Pressure (psig): 15

Temperature (°C)	799	799	799	799	799	799	799
Flow (cc/min)	171	171	171	171	171	171	171
GHSV (h 1)	* *	* *	* *	* *	* *	* *	* *
Time (h)	23	24	25	26	27	28	29
CH4 Conv., %	35.37	35.72	35.75	35.97	36.05	36.17	36.15
O2 Conv., %	83.26	83.53	83.89	83.93	84.13	84.34	84.37
C Balance, %	97.78	97.31	97.55	97.16	97.17	97.03	97.10
C2 Selectivity, %	23.59	23.36	23.33	23.08	23.13	23.06	23.01
C3 Selectivity, %	1.53	1.52	1.51	1.49	1.50	1.50	1.50
C2 Yield, %	8.16	8.12	8.14	8.07	8.10	8.09	8.08
Ethylene/Ethane	3.14	3.15	3.15	3.15	3.14	3.15	3.14
CO2/CO	0.19	0.19	0.19	0.19	0.19	0.19	0.19

**: Not applicable.

Table 30. Effect of Pressure on the Homogeneous Gas Phase Oxidation of Methane in Quartz Filled Reactors

Temperature (°C)	750	750	799	799	799
Pressure (psig)	5	15	5	10	15
CH4/O2 (mole/mole)	2.0/1	2.0/1	2.0/1	2.0/1	2.0/1
Residence Time (sec)	7.2	7.3	4.8	4.8	4.9
CH4 Conv., %	12.9	35.7	13.3	28.6	35.9
O2 Conv., %	25.7	88.1	25.9	62.2	83.9
C2 Sele., %	35.3	20.3	37.3	28.2	23.2
C3 Sele., %	1.9	1.5	2	1.7	1.5
C2 Yield, %	4.6	7.1	5	8	8.1
=/- (mole/mole)*	1.3	2.8	1.5	2.7	3.1
CO2/CO (mole/mole)	0.07	0.22	0.1	0.15	0.19

*: =/- represents ethylene/ethane.

Table 31. Homogeneous Gas Phase Reaction - Empty Reactor

CATALYST: * *		**NOTEBOOK:**	2-KDC-X-62
Weight (g): * *		**Volume (cc):**	* *
CH4/O2/N2: 8.23/1/3.78		**Pressure (psig):**	10
Temperature (°C)	750	750	750
Flow (cc/min)	207	207	207
GHSV (h 1)	* *	* *	* *
Time (h)	3	4	5
CH4 Conv., %	3.32	3.11	3.79
O2 Conv., %	26.10	25.78	26.62
C Balance, %	100.98	101.04	100.34
C2 Selectivity, %	52.73	53.57	53.05
C3 Selectivity, %	3.30	3.44	3.28
C2 Yield, %	1.77	1.69	2.02
Ethylene/Ethane	0.82	0.79	0.79
CO2/CO	0.03	0.03	0.03

**: Not applicable.

Table 31. Homogeneous Gas Phase Reaction - Empty Reactor (Continued)

CATALYST: * * **NOTEBOOK:** 2-KDC-X-64

Weight (g): * * Volume (cc): * *

CH4/O2/N2: 2.08/1/3.95 Pressure (psig): 15

Temperature (°C)	650	650	650	650	650	650	650
Flow (cc/min)	139	139	139	139	139	139	139
GHSV (h 1)	* *	* *	* *	* *	* *	* *	* *
Time (h)	6	7	10	12	14	16	18
CH4 Conv., %	30.90	31.18	30.22	30.15	29.68	29.43	30.12
O2 Conv., %	73.93	72.75	72.52	70.83	70.72	70.59	70.78
C Balance, %	95.60	95.15	96.95	95.33	95.88	97.03	95.30
C2 Selectivity, %	19.74	19.63	19.07	20.16	20.03	19.26	20.15
C3 Selectivity, %	1.65	1.65	1.54	1.71	1.70	1.64	1.71
C2 Yield, %	5.83	5.82	5.59	5.79	5.70	5.50	5.78
Ethylene/Ethane	2.00	2.00	1.99	1.97	1.97	1.97	1.97
CO2/CO	0.19	0.19	0.18	0.18	0.12	0.17	0.18

**: Not applicable.

Table 31. Homogeneous Gas Phase Reaction - Empty Reactor (Continued)

CATALYST: * * NOTEBOOK: 2-KDC-X-66

Weight (g): * * Volume (cc): * *

CH4/O2/N2: 2.1/1/3.86 Pressure (psig): 5

Temperature (°C)	850	850	850	850
Flow (cc/min)	228	228	228	228
GHSV (h 1)	* *	* *	* *	* *
Time (h)	25	26	27	28
CH4 Conv., %	42.77	42.44	43.22	42.90
O2 Conv., %	93.29	93.21	93.24	93.25
C Balance, %	94.72	95.28	94.03	94.46
C2 Selectivity, %	16.18	16.34	16.38	16.39
C3 Selectivity, %	0.62	0.61	0.60	0.57
C2 Yield, %	6.55	6.61	6.66	6.64
Ethylene/Ethane	4.85	4.84	4.83	4.84
CO2/CO	0.17	0.17	0.17	0.17

**: Not applicable.

Table 32. Comparison of Homogeneous Gas Phase Oxidation of Methane in Empty and Quartz Filled Reactors

	EMPTY	FILLED	EMPTY	FILLED	EMPTY	FILLED
Temperature (°C)	850	850	750	749	650	649
Pressure (psig)	5	5	10	10	15	15
CH4/O2 (mole/mole)	2.1/1	2.1/1	8.2/1	8.1/1	2.1/1	2.1/1
Residence Time (sec)	4.8	4.8	7.26	7.25	14.4	14.4
CH4 Conv., %	42.8	35.4	3.4	2.1	30.2	3.3
O2 Conv., %	93.2	81.1	26.6	10.9	71.7	1.9
C2 Sele., %	16.3	25.3	53.1	53.7	19.7	21.8
C3 Sele., %	0.6	1.4	3.3	2.3	1.6	0.5
C2 Yield, %	6.6	8.6	1.8	1.1	5.7	0.7
=/- (mole/mole)*	4.8	4.1	0.8	0.5	2	0.15
CO2/CO (mole/mole)	0.17	0.07	0.03	0	0.17	0

*: =/- represents ethylene/ethane.

Table 33. Homogeneous Gas Phase Reaction - Empty vs Quartz Packed Reactor*

CATALYST: * * **NOTEBOOK:** 2-KDC-X-87

Weight (g): * * **Volume (cc):** * *

CH4/O2/N2: 2.07/1/3.84 **Pressure (psig):** 15

	EMPTY			QUARTZ PACKED		
Temperature (°C)	650	650	650	650	650	650
Flow (cc/min)	139	139	139	68	68	68
GHSV (h 1)	* *	* *	* *	* *	* *	* *
Time (h)	1	2.15	2.75	4.75	5.15	6
CH4 Conv., %	29.37	29.70	30.26	0.52	1.22	0.08
O2 Conv., %	70.57	71.81	72.88	1.38	1.45	1.32
C Balance, %	101.15	101.25	101.05	100.15	99.53	100.80
C2 Selectivity, %	17.59	17.49	17.36	17.96	16.39	17.42
C3 Selectivity, %	1.32	1.30	1.30	0.00	0.00	0.00
C2 Yield, %	5.22	5.26	5.31	0.09	0.20	-0.01
Ethylene/Ethane	1.95	1.95	1.97	0.07	0.07	0.06
CO2/CO	0.17	0.17	0.17	0.25	0.24	0.25

*: Flow rates adjusted to give the same residence times.
**: Not applicable.

Table 34. **Homogeneous Gas Phase Reaction - Empty Reactor with Inverted Flow**

CATALYST: * * **NOTEBOOK:** 2-KDC-X-73

Weight (g): * * **Volume (cc):** * *

CH4/O2/N2: 2.05/1/3.89 **Pressure (psig):** 15

Temperature (°C)	650	650	650	650	650
Flow (cc/min)	139	139	139	139	139
GHSV (h 1)	* *	* *	* *	* *	* *
Time (h)	2	3	4	5	6
CH4 Conv., %	29.67	30.22	30.26	30.21	30.12
O2 Conv., %	70.94	73.12	73.69	73.72	70.78
C Balance, %	96.63	96.49	96.64	97.72	95.30
C2 Selectivity, %	19.51	19.34	19.37	18.45	20.15
C3 Selectivity, %	1.40	1.44	1.46	1.40	1.71
C2 Yield, %	5.59	5.64	5.67	5.45	5.78
Ethylene/Ethane	1.73	1.73	1.73	1.74	1.97
CO2/C0	0.18	0.18	0.18	0.17	0.18

**: Not applicable.

Table 35. Methane Coupling Activity of LaMnO3
[Run 1]

CATALYST: LaMnO3

NOTEBOOK: 3-KDC-X-5

Weight (g): 1.009

Volume (cc): 1.5

CH4/O2/N2: 2.02/1/3.96

Pressure (psig): 5 at 50 cc/min; 10 at 100 cc/min

Temperature (°C)	702	702	702	702	702	702	702	750
Flow (cc/min)	50	50	100	100	100	100	100	150
GHSV (h 1)	2000	2000	4000	4000	4000	4000	4000	6000
Time (h)	1	3	5	7	9	11	16	19
CH4 Conv., %	23.72	23.66	25.77	25.69	25.85	25.72	25.65	22.19
O2 Conv., %	94.25	94.33	94.34	94.49	94.53	94.48	94.50	94.49
C Balance, %	99.00	101.08	101.42	96.12	94.92	89.76	87.65	105.83
C2 Selectivity, %	4.73	5.10	14.56	18.75	20.18	27.45	33.85	17.65
C3 Selectivity, %	0.05	0.06	0.39	0.55	0.60	0.83	1.08	0.29
C2 Yield, %	1.11	1.22	3.81	4.63	4.95	6.34	7.61	4.14
Ethylene/Ethane	0.30	0.28	0.50	0.47	0.47	0.47	0.48	0.89
CO2/CO	67.50	66.03	65.73	43.33	56.79	31.66	21.66	35.12

Table 35. Methane Coupling Activity of LaMnO3 (Continued) [Run 1]

CATALYST: LaMnO3 **NOTEBOOK:** 3-KDC-X-5

Weight (g): 1.009 **Volume (cc):** 1.5

CH4/O2/N2: 2.02/1/3.96 **Pressure (psig):** 10 at 150 cc/min; 11.5 at 200 cc/min

Temperature (°C)	750	750	750	750	800	800	800
Flow (cc/min)	150	200	200	200	200	200	200
GHSV (h 1)	6000	8000	8000	8000	8000	8000	8000
Time (h)	21	23	24	25	26	28	30
CH4 Conv., %	22.10	21.99	21.90	22.01	21.84	21.12	20.74
O2 Conv., %	94.30	94.46	94.44	94.43	94.43	94.27	94.20
C Balance, %	107.18	106.67	106.60	106.57	106.26	104.02	98.78
C2 Selectivity, %	15.73	15.33	15.18	15.26	10.74	12.20	16.62
C3 Selectivity, %	0.27	0.23	0.23	0.23	0.13	0.16	0.23
C2 Yield, %	3.73	3.60	3.54	3.58	2.49	2.68	3.41
Ethylene/Ethane	0.88	0.92	0.88	0.86	1.24	1.08	1.09
CO2/CO	36.42	26.37	26.50	27.07	14.43	12.72	8.79

Table 36. Methane Coupling Activity of LaMnO3
[Run 2]

CATALYST: LaMnO3 **NOTEBOOK:** 3-KDC-X-13

Weight (g): 0.255 **Volume (cc):** 0.5

CH4/O2/N2: 2.04/1/3.81 **Pressure (psig):** 5

Temperature (°C)	699	699	699	699	699	699	699	699
Flow (cc/min)	150	200	200	200	200	200	200	200
GHSV (h 1)	18000	24000	24000	24000	24000	24000	24000	24000
Time (h)	1	2	3	4	8	12	16	20
CH4 Conv., %	23.75	25.27	25.78	26.19	26.00	25.80	25.24	25.33
O2 Conv., %	94.69	94.76	94.73	94.73	94.73	94.73	94.72	94.76
C Balance, %	100.80	100.43	100.42	100.46	100.28	100.43	100.74	100.62
C2 Selectivity, %	4.39	9.69	10.55	12.00	11.81	11.54	11.36	10.77
C3 Selectivity, %	0.00	0.22	0.27	0.33	0.33	0.32	0.31	0.29
C2 Yield, %	1.05	2.46	2.73	3.16	3.08	2.99	2.89	2.74
Ethylene/Ethane	0.23	0.31	0.31	0.33	0.32	0.31	0.32	0.31
CO2/CO	111.17	87.32	86.98	83.35	81.92	81.92	82.12	65.57

Table 36. **Methane Coupling Activity of LaMnO3 (Continued)**
[Run 2]

CATALYST: LaMnO3 **NOTEBOOK:** 3-KDC-X-13

Weight (g): 0.255 **Volume (cc):** 0.5

CH4/O2/N2: 2.04/1/3.81 **Pressure (psig):** 5

Temperature (°C)	650	650	600	400	300	500
Flow (cc/min)	233	233	233	233	233	233
GHSV (h 1)	27960	27960	27960	27960	27960	27960
Time (h)	22.5	23	24	25	26	27
CH4 Conv., %	23.08	22.89	11.58	**	**	**
O2 Conv., %	94.67	94.60	47.07	0.82	0.44	4.76
C Balance, %	101.17	100.99	106.16	99.60	99.63	99.50
C2 Selectivity, %	2.22	1.57	0.34	**	**	**
C3 Selectivity, %	0.00	0.00	0.00	**	**	**
C2 Yield, %	0.52	0.36	0.05	**	**	**
Ethylene/Ethane	0.06	0.03	0.09	**	**	**
CO2/CO	105.16	456.53	2.00	**	**	**

**: CH4 conversion too low for meaningful results.

Table 37. **Methane Coupling Activity of LaFeO3**

CATALYST: LaFeO3　　**NOTEBOOK:** 3-KDC-X-47

Weight (g): 0.254　　**Volume (cc):** 0.5

CH4/O2/N2: 2.03/1/3.76　　**Pressure (psig):** 5

Temperature (°C)	705	705	719	719	719	764	764	764
Flow (cc/min)	50	50	100	100	100	150	150	150
GHSV (h 1)	6000	6000	12000	12000	12000	18000	18000	18000
Time (h)	0.5	1	2	3.5	4	7	10	14
CH4 Conv., %	28.61	27.56	26.70	25.69	26.31	30.68	28.69	29.32
O2 Conv., %	94.61	94.65	92.88	92.73	92.60	94.03	93.36	93.42
C Balance, %	98.61	99.88	100.32	101.54	100.35	101.65	101.55	100.86
C2 Selectivity, %	12.65	12.55	14.46	14.19	13.94	23.52	22.90	22.44
C3 Selectivity, %	0.45	0.43	0.52	0.50	0.47	1.28	1.17	1.11
C2 Yield, %	3.57	3.45	3.87	3.70	3.68	7.33	6.67	6.64
Ethylene/Ethane	0.10	0.09	0.17	0.17	0.16	0.65	0.63	0.66
CO2/CO	13.81	17.45	22.90	23.33	23.69	4.41	5.51	5.35

Table 37. Methane Coupling Activity of LaFeO3 (Continued)

CATALYST: LaFeO3 **NOTEBOOK:** 3-KDC-X-47

Weight (g): 0.254 **Volume (cc):** 0.5

CH4/O2/N2: 2.03/1/13.76 **Pressure (psig):** 5

Temperature (°C)	764	757	803	803	803	803	803	803
Flow (cc/min)	150	150	150	150	150	250	250	250
GHSV (h 1)	18000	18000	18000	18000	18000	30000	30000	30000
Time (h)	18	22	25	26	27	28	29	30
CH4 Conv., %	29.68	29.78	33.05	32.28	31.95	32.15	32.40	32.47
O2 Conv., %	93.29	93.23	94.59	94.59	94.66	94.60	94.78	94.62
C Balance, %	100.65	100.52	99.63	100.56	100.12	100.30	99.74	99.44
C2 Selectivity, %	22.23	21.56	21.55	22.86	21.40	21.84	20.58	19.88
C3 Selectivity, %	1.07	1.00	0.87	0.89	0.81	0.69	0.71	0.70
C2 Yield, %	6.64	6.45	7.10	7.42	6.85	7.04	6.65	6.42
Ethylene/Ethane	0.71	0.73	1.07	1.01	0.95	0.89	0.91	0.87
CO2/CO	4.85	4.51	3.98	4.07	4.07	4.06	4.07	4.24

Table 38. Methane Coupling Activity of BaFeO3

CATALYST: BaFeO3 **NOTEBOOK:** 3-KDC-X-75

Weight (g): 0.501 **Volume (cc):** 0.5

CH4/O2/N2: 2.09/1/3.88 **Pressure (psig):** 5

Temperature (°C)	700	700	700	700	751	751	751	751
Flow (cc/min)	50	50	50	50	100	100	100	100
GHSV (h 1)	6000	6000	6000	6000	12000	12000	12000	12000
Time (h)	2	3	4	5	6	9	13	15
CH4 Conv., %	20.83	20.89	21.83	22.44	25.82	25.10	23.37	22.57
O2 Conv., %	73.00	74.71	75.56	78.64	86.80	84.03	79.50	78.22
C Balance, %	101.12	102.04	100.91	101.46	101.51	101.24	101.09	101.05
C2 Selectivity, %	13.05	13.97	14.88	14.68	20.69	20.23	18.52	17.23
C3 Selectivity, %	0.28	0.30	0.35	0.36	0.71	0.66	0.52	0.44
C2 Yield, %	2.75	2.98	3.28	3.34	5.42	5.14	4.37	3.93
Ethylene/Ethane	0.54	0.60	0.64	0.65	0.89	0.83	0.74	0.68
CO2/CO	83.45	27.17	123.45	50.93	84.09	130.04	148.50	172.93

Table 38. Methane Coupling Activity of BaFeO3 (Continued)

CATALYST: BaFeO3 NOTEBOOK: 3-KDC-X-75
Weight (g): 0.501 Volume (cc): 0.5
CH4/O2/N2: 2.09/1/3.88 Pressure (psig): 5

Temperature (°C)	745	800	800	800	800	800	800	800
Flow (cc/min)	100	150	150	150	150	100	100	100
GHSV (h 1)	12000	18000	18000	18000	18000	12000	12000	12000
Time (h)	19	22	23	24	25	26	27	28
CH4 Conv., %	21.21	28.25	28.01	27.76	27.23	28.50	28.46	28.61
O2 Conv., %	74.63	93.38	92.24	91.76	90.24	94.55	94.55	94.51
C Balance, %	101.22	101.36	101.40	101.44	101.29	101.34	101.60	101.59
C2 Selectivity, %	16.59	23.56	23.32	23.16	22.76	22.45	22.48	21.84
C3 Selectivity, %	0.39	0.90	0.88	0.87	0.85	0.81	0.88	0.86
C2 Yield, %	3.56	6.75	6.62	6.52	6.28	6.48	6.50	6.35
Ethylene/Ethane	0.65	1.06	1.04	1.03	1.01	1.06	1.11	1.11
CO2/CO	180.26	149.26	140.75	189.29	129.49	163.56	169.93	72.58

Table 39. Methane Coupling Activity of $BaPbO_3$

CATALYST: $BaPbO_3$ **NOTEBOOK:** 2-KDC-X-44

Weight (g): 1.005 **Volume (cc):** 1

$CH_4/O_2/N_2$: 1.82/1/22.56 **Pressure (psig):** 5

Temperature (°C)	800	800	750	750	750	750	800	800
Flow (cc/min)	50.3	50.3	50.5	50.5	50.5	50.5	100	100
GHSV (h 1)	3018	3018	3030	3030	3030	3030	6000	6000
Time (h)	1	2	6	9	13	17	21	22
CH_4 Conv., %	33.77	35.24	22.05	22.55	22.17	21.53	27.24	27.01
O_2 Conv., %	94.52	94.68	70.87	69.58	69.88	68.68	82.61	95.12
C Balance, %	98.17	104.72	100.19	100.70	106.20	109.02	107.31	109.08
C_2 Selectivity, %	37.18	27.35	28.53	26.76	22.12	20.36	26.36	25.28
C_3 Selectivity, %	3.00	2.69	1.99	2.02	1.50	1.36	2.03	1.92
C_2 Yield, %	12.33	10.09	6.30	6.08	5.21	4.78	7.71	7.45
Ethylene/Ethane	3.39	4.01	1.50	1.43	1.47	1.42	2.16	2.14
CO_2/CO	31.04	81.44	16.16	19.25	23.83	25.82	16.12	17.04

Table 39. Methane Coupling Activity of BaPbO3 (Continued)

CATALYST: BaPbO3 **NOTEBOOK:** 2-KDC-X-44

Weight (g): 1.005 **Volume (cc):** 1

CH4/O2/N2 : 1.82/1/22.56 **Pressure (psig):** 5

Temperature (°C)	800	820	820	820	820	820	820	820
Flow (cc/min)	100	100	100	150	150	175	175	175
GHSV (h 1)	6000	6000	6000	9000	9000	10500	10500	10500
Time (h)	23	24	25	26	28	34	36	42
CH4 Conv., %	26.77	31.47	31.25	27.61	28.71	26.57	26.77	26.20
O2 Conv., %	81.02	93.52	93.09	82.38	83.09	74.02	74.11	73.67
C Balance, %	108.37	107.26	106.63	102.41	97.79	98.36	103.30	107.52
C2 Selectivity, %	25.66	27.30	28.05	32.87	37.18	37.59	31.28	27.84
C3 Selectivity, %	1.94	2.14	2.19	2.47	2.82	2.64	2.22	1.93
C2 Yield, %	7.44	9.21	9.35	9.29	10.44	9.82	8.65	7.84
Ethylene/Ethane	2.13	2.99	3.03	2.32	2.45	2.04	2.04	2.05
CO2/CO	16.20	19.15	18.28	10.46	8.07	7.34	9.89	10.62

Table 40. Methane Coupling Activity of SrPbO3

CATALYST: SrPbO3 **NOTEBOOK:** 2-KDC-X-50

Weight (g): 1.027 **Volume (cc):** 0.5

CH4/O2/N2 : 1.82/1/22.56 **Pressure (psig):** 3

Temperature (°C)	750	750	800	800	800	800	800	800
Flow (cc/min)	50	50	50	50	100	100	100	100
GHSV (h 1)	6000	6000	6000	6000	12000	12000	12000	12000
Time (h)	1	2	3	4	6	10	14	18
CH4 Conv., %	9.81	8.65	28.64	27.74	16.19	15.85	14.00	12.57
O2 Conv., %	33.24	32.92	94.12	90.42	46.37	44.43	41.23	39.28
C Balance, %	96.92	98.22	101.26	104.13	101.57	104.10	105.66	106.40
C2 Selectivity, %	22.50	19.80	23.02	21.38	25.44	22.27	22.18	22.33
C3 Selectivity, %	0.59	0.44	1.67	1.80	1.50	1.33	1.18	1.30
C2 Yield, %	2.14	1.68	6.68	6.18	4.18	3.67	3.28	2.99
Ethylene/Ethane	0.57	0.44	2.20	2.76	1.30	1.24	1.18	1.13
CO2/CO	8.78	9.75	51.78	17.26	7.79	8.95	8.42	7.56

Table 41. Methane Coupling Activity of KNbO3

CATALYST: KNbO3 **NOTEBOOK:** 3-KDC-X-37

Weight (g): 0.254 **Volume (cc):** 0.5

CH4/O2/N2: 2.08/1/3.84 **Pressure (psig):** 5

Temperature (°C)	702	702	717	811	826
Flow (cc/min)	50	50	100	100	150
GHSV (h 1)	6000	6000	12000	12000	18000
Time (h)	2	3	4	5	6
CH4 Conv., %	27.30	26.40	24.88	28.06	26.51
O2 Conv., %	94.59	94.64	92.42	94.31	91.30
C Balance, %	99.93	99.78	100.04	99.53	99.88
C2 Selectivity, %	0.61	0.67	0.78	2.85	3.99
C3 Selectivity, %	0.00	0.00	0.00	0.01	0.00
C2 Yield, %	0.17	0.18	0.19	0.80	1.06
Ethylene/Ethane	0.00	0.00	0.01	0.17	0.23
CO2/CO	4.23	5.18	5.15	3.14	3.55

Table 42. **Changes in the ABO_3 Perovskite Structure for Catalysts Tested**

Catalyst	Changes in A or B
LaMnO3	$A(1)B(1)O_3$
LaFeO3	$A(1)B(2)O_3$
BaFeO3	$A(2)B(2)O_3$
BaPbO3	$A(2)B(3)O_3$
SrPbO3	$A(3)B(3)O_3$
KNbO3	$A(4)B(4)O_3$

Table 43. Methane Coupling Activity of La0.65Sr0.35MnO3
[Run 1]

CATALYST: La0.65Sr0.35MnO3 **NOTEBOOK:** 3-KDC-X-17

Weight (g): 0.256 **Volume (cc):** 0.5

CH4/O2/N2: 2.03/1/3.82 **Pressure (psig):** 5

Temperature (°C)	703	703	703	703	703	773	773	773
Flow (cc/min)	200	200	200	200	200	200	200	200
GHSV (h 1)	24000	24000	24000	24000	24000	24000	24000	24000
Time (h)	1	2	6	10	14	20	21	21.5
CH4 Conv., %	22.46	21.46	20.35	20.08	19.27	30.19	30.08	30.64
O2 Conv., %	82.62	78.45	74.57	73.81	71.64	94.68	94.71	94.79
C Balance, %	101.49	101.18	101.60	101.46	101.78	102.07	101.06	100.47
C2 Selectivity, %	10.07	9.03	8.52	8.58	8.31	24.45	23.28	23.03
C3 Selectivity, %	0.38	0.16	0.12	0.13	0.08	1.33	1.27	1.23
C2 Yield, %	2.29	1.96	1.76	1.75	1.63	7.54	7.08	7.09
Ethylene/Ethane	0.26	0.26	0.29	0.29	0.30	0.76	0.74	0.74
CO2/CO	20.63	17.86	14.54	15.92	15.20	17.21	21.55	21.22

Table 43. Methane Coupling Activity of La0.65Sr0.35MnO3(Continued) [Run 1]

CATALYST: La0.65Sr0.35MnO3 **NOTEBOOK:** 3-KDC-X-17

Weight (g): 0.255 **Volume (cc):** 0.5

CH4/O2/N2: 2.05/1/3.83 **Pressure (psig):** 5

Temperature (°C)	802	802	802	802	750	750	750	750
Flow (cc/min)	245	245	245	245	245	245	245	245
GHSV (h 1)	29400	29400	29400	29400	29400	29400	29400	29400
Time (h)	22.5	23.5	24	25	28.5	30	34	38
CH4 Conv., %	32.11	32.39	31.64	31.90	27.85	27.65	27.74	27.73
O2 Conv., %	94.59	94.65	94.66	94.68	94.01	94.14	94.10	94.01
C Balance, %	100.78	100.33	100.45	100.53	100.21	100.19	100.17	100.25
C2 Selectivity, %	27.15	26.84	26.72	26.58	16.12	16.23	16.61	16.87
C3 Selectivity, %	1.46	1.48	1.44	1.43	0.74	0.74	0.76	0.78
C2 Yield, %	8.79	8.72	8.49	8.52	4.50	4.50	4.62	4.69
Ethylene/Ethane	0.83	0.82	0.81	0.80	0.28	0.30	0.33	0.35
CO2/CO	20.26	19.34	20.37	20.56	17.33	16.41	15.80	15.55

Table 44. **Methane Coupling Activity of La0.65Sr0.35MnO3**
[Run 2]

CATALYST: La0.65Sr0.35MnO3 **NOTEBOOK:** 3-KDC-X-24

Weight (g): 0.102 **Volume (cc):** 0.5

CH4/O2/N2: 2.04/1/3.83 **Pressure (psig):** 5

Temperature (°C)	677	677	701	701	770	770	770	770
Flow (cc/min)	100	100	100	100	150	150	150	150
GHSV (h 1)	12000	12000	12000	12000	18000	18000	18000	18000
Time (h)	1	1.5	2.25	3	5	7	9	11
CH4 Conv., %	20.45	20.68	23.06	23.51	28.10	27.01	26.77	26.60
O2 Conv., %	65.52	65.48	75.47	75.87	85.38	85.12	84.93	84.78
C Balance, %	100.43	100.02	100.93	100.14	100.57	100.72	100.68	100.68
C2 Selectivity, %	11.44	10.95	13.69	12.87	23.63	22.21	21.54	21.28
C3 Selectivity, %	0.39	0.34	0.53	0.00	1.14	1.01	0.95	0.93
C2 Yield, %	2.35	2.27	3.19	3.03	6.68	6.04	5.81	5.70
Ethylene/Ethane	0.52	0.49	0.56	0.54	0.88	0.85	0.83	0.82
CO2/CO	13.84	14.87	17.88	17.87	19.21	21.15	21.72	22.29

Table 44. Methane Coupling Activity of La0.65Sr0.35MnO3 (Continued) [Run 2]

CATALYST: La0.65Sr0.35MnO3 **NOTEBOOK:** 3-KDC-X-24

Weight (g): 0.102 **Volume (cc):** 0.5

CH4/O2/N2: 2.04/1/3.83 **Pressure (psig):** 5

Temperature (°C)	770	770	770	800	800	815	825	825
Flow (cc/min)	150	150	150	250	250	250	250	200
GHSV (h 1)	18000	18000	18000	30000	30000	30000	30000	24000
Time (h)	15	17	19	21.5	22	23	25	27
CH4 Conv., %	26.39	26.28	26.33	27.88	28.59	28.74	28.76	27.93
O2 Conv., %	84.77	84.80	84.76	83.55	83.22	84.86	85.50	84.85
C Balance, %	100.85	100.94	100.80	100.38	100.25	100.81	100.62	100.38
C2 Selectivity, %	21.03	20.93	20.85	27.52	28.11	28.37	27.89	24.92
C3 Selectivity, %	0.91	0.91	0.90	1.17	1.25	1.23	1.15	1.00
C2 Yield, %	5.60	5.55	5.53	7.70	8.06	8.22	8.07	6.99
Ethylene/Ethane	0.81	0.80	0.79	0.90	0.97	1.01	1.01	0.87
CO2/CO	22.45	21.84	21.66	18.78	19.30	19.84	19.14	19.91

Table 44. **Methane Coupling Activity of La0.65Sr0.35MnO3 (Continued)**
[Run 2]

CATALYST: La0.65Sr0.35MnO3 **NOTEBOOK:** 3-KDC-X-24

Weight (g): 0.102 **Volume (cc):** 0.5

CH4/O2/N2: 4.8/1/3.8 **Pressure (psig):** 2.5

Temperature (°C)	700	700	700	700	700	700
Flow (cc/min)	100	100	100	100	100	100
GHSV (h 1)	12000	12000	12000	12000	12000	12000
Time (h)	29	31	33	37	57	61
CH4 Conv., %	5.91	5.27	5.00	4.63	4.84	4.78
O2 Conv., %	71.91	67.60	68.19	71.55	71.33	68.76
C Balance, %	104.03	104.55	104.87	105.43	105.25	105.48
C2 Selectivity, %	21.41	21.20	21.47	22.06	22.45	22.11
C3 Selectivity, %	0.83	0.82	0.69	0.72	0.75	0.94
C2 Yield, %	1.32	1.17	1.13	1.08	1.14	1.12
Ethylene/Ethane	0.17	0.17	0.17	0.18	0.19	0.19
CO2/CO	8.79	8.19	8.18	8.12	8.28	8.05

Table 45. Methane Coupling Activity of KNbO3-x

CATALYST: KNbO3-x

NOTEBOOK: 3-KDC-X-41

Weight (g): 0.23

Volume (cc): 0.5

CH4/O2/N2: 1.98/1/3.88

Pressure (psig): 5

Temperature (°C)	724	724	724	724	724	749	749
Flow (cc/min)	50	50	50	50	50	50	50
GHVS(h 1)	6000	6000	6000	6000	6000	6000	6000
Time (h)	2	4	6	8	12	17	18
CH4 Conv., %	3.28	3.47	3.49	3.58	3.48	6.08	5.90
O2 Conv., %	7.40	7.03	7.49	7.22	7.53	13.25	13.41
C Balance, %	99.61	99.46	99.50	99.39	99.55	99.49	99.76
C2 Selectivity, %	18.43	18.43	18.37	18.54	18.31	23.49	23.90
C3 Selectivity, %	0.22	0.21	0.24	0.22	0.24	0.71	0.81
C2 Yield, %	0.60	0.64	0.64	0.66	0.63	1.42	1.41
Ethylene/Ethane	0.30	0.31	0.31	0.32	0.32	0.68	0.68
CO2/CO	0.50	0.46	0.43	0.43	0.41	0.34	0.34

Table 45. Methane Coupling Activity of KNbO3-x (Continued)

CATALYST: KNbO3-x **NOTEBOOK:** 3-KDC-X-41

Weight (g): 0.23 **Volume (cc):** 0.5

CH4/O2/N2: 1.98/1/3.88 **Pressure (psig):** 5

Temperature (°C)	749	749	800	800	800	800	800
Flow (cc/min)	50	50	50	50	50	50	50
GHSV (h 1)	6000	6000	6000	6000	6000	6000	6000
Time (h)	19	20	23	25	27	29	31
CH4 Conv., %	6.05	5.83	20.18	20.71	21.26	21.48	21.72
O2 Conv., %	13.80	13.74	48.41	49.88	51.64	52.54	53.57
C Balance, %	99.75	100.02	100.53	100.20	100.38	100.58	100.67
C2 Selectivity, %	23.83	23.93	25.90	26.49	26.51	26.54	26.49
C3 Selectivity, %	0.75	0.77	1.84	0.10	0.11	0.11	0.12
C2 Yield, %	1.44	1.40	5.25	5.50	5.66	5.73	5.79
Ethylene/Ethane	0.70	0.71	2.48	2.49	2.52	2.52	2.52
CO2/CO	0.33	0.34	0.36	0.35	0.34	0.33	0.34

Table 46. Methane Coupling Activity of LaMnO3-x

CATALYST: LaMnO3-x

NOTEBOOK: 3-KDC-X-9

Weight (g): 0.519

Volume (cc): 1.3

CH4/O2/N2: 2.11/1/3.84

Pressure (psig): 5

Temperature (°C)	704	704	704	704	704	750	750	750
Flow (cc/min)	100	100	100	100	100	150	200	200
GHSV (h 1)	4615	4615	4615	4615	4615	6923	9231	9231
Time (h)	1	2	4	8	14	16	20	21
CH4 Conv., %	23.57	23.93	22.84	22.19	22.15	25.46	28.31	28.71
O2 Conv., %	94.73	94.47	94.66	94.67	94.67	94.53	94.57	94.62
C Balance, %	99.26	97.41	90.04	85.65	85.81	93.19	94.53	95.40
C2 Selectivity, %	0.75	0.74	1.18	0.00	0.00	2.06	2.65	2.65
C3 Selectivity, %	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C2 Yield, %	0.17	0.17	0.24	0.00	0.00	0.49	0.71	0.73
Ethylene/Ethane	0.00	0.00	0.04	**	**	0.13	0.09	0.10
CO2/CO	78.37	77.66	46.49	27.68	29.04	36.14	40.77	39.34

**: No C2's detected.

Table 46. Methane Coupling Activity of LaMnO3-x (Continued)

CATALYST: LaMnO3-x **NOTEBOOK:** 3-KDC-X-9

Weight (g): 0.519 **Volume (cc):** 1.3

CH4/O2/N2: 2.07/1/3.84 **Pressure (psig):** 5

Temperature (°C)	750	800	800	800	800	800	800
Flow (cc/min)	200	250	250	250	250	250	250
GHSV (h 1)	9231	11538	11538	11538	11538	11538	11538
Time (h)	22	25	27	29	31	33	35
CH4 Conv., %	28.70	31.35	31.50	31.56	30.57	31.79	31.82
O2 Conv., %	94.59	94.66	94.68	94.63	94.64	94.64	94.64
C Balance, %	97.27	96.59	96.75	96.79	97.75	96.53	96.49
C2 Selectivity, %	2.72	9.19	9.59	9.75	9.67	9.43	9.42
C3 Selectivity, %	0.00	0.10	0.12	0.13	0.14	0.14	0.13
C2 Yield, %	0.76	2.78	2.92	2.98	2.89	2.89	2.89
Ethylene/Ethane	0.09	0.38	0.29	0.25	0.20	0.18	0.16
CO2/CO	42.20	11.85	10.92	10.33	9.47	9.15	8.90

Table 47. **Methane Coupling Activity of BaTiO3-x**

CATALYST: BaTiO3-x **NOTEBOOK:** 3-KDC-X-33

Weight (g): 0.251 **Volume (cc):** 0.5

CH4/O2/N2: 2.06/1/3.84 **Pressure (psig):** 5

Temperature (°C)	699	699	750	750	750	750	750	850
Flow (cc/min)	50	50	50	50	50	50	50	50
GHSV (h 1)	6000	6000	6000	6000	6000	6000	6000	6000
Time (h)	1	2.5	3	5	9	13	17	23
CH4 Conv., %	8.22	9.56	16.61	14.54	13.68	11.94	10.38	28.45
O2 Conv., %	22.41	24.82	49.05	44.32	40.91	36.36	33.28	94.55
C Balance, %	99.25	97.53	99.52	100.23	100.35	100.86	101.54	99.79
C2 Selectivity, %	8.94	6.46	17.14	17.16	17.55	17.88	18.28	15.68
C3 Selectivity, %	0.00	0.04	0.70	0.70	0.65	0.63	0.62	1.63
C2 Yield, %	0.73	0.60	2.83	2.50	2.41	2.15	1.93	4.45
Ethylene/Ethane	0.57	0.25	1.08	1.00	0.96	0.87	0.82	3.26
CO2/CO	7.81	8.09	6.60	5.20	4.09	3.20	2.89	4.68

Table 47. Methane Coupling Activity of BaTiO3-x (Continued)

CATALYST: BaTiO3-x **NOTEBOOK:** 3-KDC-X-33

Weight (g): 0.251 **Volume (cc):** 0.5

CH4/O2/N2: 2.1/1/3.86 **Pressure (psig):** 5

Temperature (°C)	850	850	850	850	850	850	850	850
Flow (cc/min)	150	250	250	250	250	250	250	250
GHSV (h 1)	18000	30000	30000	30000	30000	30000	30000	30000
Time (h)	25	27	28	30	34	38	42	44
CH4 Conv., %	24.78	21.74	18.58	19.73	19.71	19.00	18.34	18.15
O2 Conv., %	67.85	50.83	40.50	44.80	43.99	42.57	42.15	41.22
C Balance, %	99.08	98.48	98.28	98.76	98.56	98.87	99.25	99.06
C2 Selectivity, %	25.28	30.25	32.12	31.31	31.60	32.23	33.18	33.41
C3 Selectivity, %	1.64	1.71	1.79	1.87	1.61	1.63	0.15	0.15
C2 Yield, %	6.21	6.47	5.86	6.10	6.14	6.05	6.04	6.01
Ethylene/Ethane	2.34	1.93	1.49	1.68	1.66	1.62	1.64	1.60
CO2/CO	2.77	1.65	1.78	1.72	1.54	1.46	1.38	1.36

Table 48. **Methane Coupling Activity of La[Rh(0.5)Mn(0.5)]O3**

CATALYST: La[Rh(0.5)Mn(0.5)]O3 **NOTEBOOK:** 3-KDC-X-27

Weight (g): 0.229 **Volume (cc):** 0.5

CH4/O2/N2: 4.8/1/3.8 **Pressure (psig):** 5

Temperature (°C)	698	698	700	700	800	800	800	800
Flow (cc/min)	50	100	150	150	250	250	250	250
GHSV (h 1)	6000	12000	18000	18000	30000	30000	30000	30000
Time (h)	1	2	3	3.5	5	6	8	10
CH4 Conv., %	62.40	56.09	53.24	48.78	72.30	78.21	79.42	79.45
O2 Conv., %	94.93	94.55	94.54	94.74	94.65	94.58	93.85	93.88
C Balance, %	96.58	97.30	96.83	98.49	99.63	92.68	94.71	94.89
C2 Selectivity, %	0.16	0.21	0.20	0.20	0.88	0.13	0.07	0.07
C3 Selectivity, %	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C2 Yield, %	0.10	0.11	0.10	0.09	0.63	0.09	0.05	0.05
Ethylene/Ethane	0.00	0.00	-0.02	-0.02	3.43	0.04	0.09	0.09
CO2/CO	0.31	0.44	0.53	0.65	0.13	0.10	0.08	0.08

Table 48. **Methane Coupling Activity of La[Rh(0.5)Mn(0.5)]O3**
(Continued)

CATALYST: La[Rh(0.5)Mn(0.5)]O3 **NOTEBOOK:** 3-KDC-X-27

Weight (g): 0.229 **Volume (cc):** 0.5

CH4/O2/N2: 2.06/1/3.83 **Pressure (psig):** 5

Temperature (°C)	800	800	800	750	750	750
Flow (cc/min)	250	250	250	250	250	250
GHSV (h 1)	30000	30000	30000	30000	30000	30000
Time (h)	12	14	18	21	22	23
CH4 Conv., %	79.07	78.83	78.42	67.47	68.42	68.88
O2 Conv., %	93.95	93.93	93.92	94.11	94.49	94.47
C Balance, %	95.13	95.34	95.47	95.34	95.92	95.88
C2 Selectivity, %	0.07	0.07	0.07	0.07	0.07	0.07
C3 Selectivity, %	0.00	0.00	0.00	0.00	0.00	0.00
C2 Yield, %	0.05	0.05	0.05	0.05	0.04	0.04
Ethylene/Ethane	0.09	0.10	0.08	0.01	-0.01	-0.01
CO2/CO	0.08	0.08	0.08	0.20	0.19	0.18

Table 49. Calculated Percentages of Hydrogen Converted to H_2 and H_2O for La[Rh(0.5)Mn(0.5)]O3 Catalyst

	Experimental Results		
CH_4/O_2 Mole Ratio	2.0/1	2.0/1	2.0/1
Temperature (°C)	700	750	800
CH_4 Conv., %	55.1	68.3	78.9
O_2 Conv., %	94.7	94.4	94
C Balance, %	97.3	95.7	94.7
C_2H_4 Selectivity, %	0	0	0.01
C_2H_6 Selectivity, %	0.19	0.07	0.07
CO Selectivity, %	67.9	84.1	92.3
CO_2 Selectivity, %	31.9	15.9	7.6

	Calculated Results		
%H as H_2	80.6	88.3	92.2
%H as H_2O	19.4	11.7	7.8
$[CO_2]\ [H_2]\ /\ [CO]\ [H_2O]$	1.95	1.43	0.97

Table 50. Methane Coupling Activity of 10 wt% K2CO3/LaMnO3

CATALYST: 10 wt% K2CO3/LaMnO3 **NOTEBOOK:** 3-KDC-X-61

Weight (g): 0.259 **Volume (cc):** 0.5

CH4/O2/N2: 2.06/1/3.79 **Pressure (psig):** 5

Temperature (°C)	700	700	700	700	753	753	753	753
Flow (cc/min)	50	100	100	100	100	100	100	100
GHVS (h 1)	6000	12000	12000	12000	12000	12000	12000	12000
Time (h)	1	2	3	4	5	9	13	17
CH4 Conv., %	23.82	23.99	23.83	24.08	25.03	24.72	24.80	24.68
O2 Conv., %	94.43	94.59	94.22	94.04	94.57	94.63	94.64	94.68
C Balance, %	99.31	99.39	99.79	99.54	99.40	99.46	99.40	99.56
C2 Selectivity, %	2.95	3.16	3.47	3.74	5.98	7.10	7.37	7.99
C3 Selectivity, %	0.01	0.02	0.02	0.03	0.06	0.09	0.10	0.12
C2 Yield, %	0.70	0.75	0.83	0.90	1.49	1.75	1.82	1.96
Ethylene/Ethane	0.20	0.18	0.13	0.14	0.33	0.33	0.32	0.32
CO2/CO	194.40	152.08	174.15	221.17	78.10	56.51	54.54	60.91

Table 50. Methane Coupling Activity of 10 wt% K2CO3/LaMnO3 (Continued)

CATALYST: 10 wt% K2CO3/LaMnO3 **NOTEBOOK:** 3-KDC-X-61

Weight (g): 0.259 **Volume (cc):** 0.5

CH4/O2/N2: 2.06/1/3.79 **Pressure (psig):** 5

Temperature (°C)	803	803	803	803	803	803	803	803
Flow (cc/min)	200	200	200	200	200	200	200	200
GHVS (h 1)	24000	24000	24000	24000	24000	24000	24000	24000
Time (h)	19	24	26	29	33	35	37	39
CH4 Conv., %	26.42	26.73	26.63	26.94	27.36	27.30	27.54	27.28
O2 Conv., %	94.59	94.57	94.57	94.65	94.64	94.61	94.61	94.63
C Balance, %	99.73	99.57	99.88	99.75	99.35	99.43	99.29	99.52
C2 Selectivity, %	14.51	14.90	15.07	15.20	15.45	15.64	16.81	16.40
C3 Selectivity, %	0.29	0.30	0.32	0.37	0.38	0.38	0.40	0.38
C2 Yield, %	3.82	3.97	4.01	4.09	4.20	4.25	4.60	4.45
Ethylene/Ethane	0.56	0.57	0.56	0.56	0.56	0.55	0.61	0.58
CO2/CO	40.68	40.87	40.43	38.72	40.16	39.73	41.04	36.29

Table 51. Methane Coupling Activity of $K_2La_2Ti_3O_{10}$
[Run 1]

CATALYST: $K_2La_2Ti_3O_{10}$ **NOTEBOOK:** 3-KDC-X-53

Weight (g): 1.008 **Volume (cc):** 1

$CH_4/O_2/N_2$: 2.04/1/3.79 **Pressure (psig):** 5

Temperature (°C)	722	722	722	722	750	750	770	770
Flow (cc/min)	50	50	50	50	50	50	50	50
GHSV (h 1)	3000	3000	3000	3000	3000	3000	3000	3000
Time (h)	2	5	9	13	16	20	22	24
CH_4 Conv., %	31.15	30.37	30.03	29.35	32.67	32.48	33.92	33.61
O_2 Conv., %	88.16	86.23	85.40	84.12	89.80	89.75	92.05	92.06
C Balance, %	100.25	100.07	99.94	100.00	100.01	100.11	100.51	100.90
C_2 Selectivity, %	24.55	23.94	23.08	22.05	27.89	27.99	30.67	30.66
C_3 Selectivity, %	1.43	1.25	1.15	1.04	1.43	1.42	1.51	1.85
C_2 Yield, %	7.67	7.27	6.93	6.47	9.11	9.10	10.46	10.40
Ethylene/Ethane	1.08	1.08	1.08	1.07	1.40	1.43	1.62	1.62
CO_2/CO	5.02	4.64	4.54	4.33	5.03	4.84	5.29	5.37

Table 51. Methane Coupling Activity of K2La2Ti3O10 (Continued) [Run 1]

CATALYST: K2La2Ti3O10
NOTEBOOK: 3-KDC-X-53
Weight (g): 1.008
Volume (cc): 1
CH4/O2/N2: 2.04/1/3.79
Pressure (psig): 5

Temperature (°C)	800	800	800	800	800	800	800	800
Flow (cc/min)	50	50	50	50	50	50	50	50
GHSV (h 1)	3000	3000	3000	3000	3000	3000	3000	3000
Time (h)	25	28	36	48	54	64	76	84
CH4 Conv., %	35.45	34.95	34.84	34.99	34.44	34.18	33.67	33.84
O2 Conv., %	94.14	93.88	93.56	93.38	92.59	92.06	91.07	90.98
C Balance, %	100.12	99.73	99.59	99.78	99.39	99.43	99.54	99.65
C2 Selectivity, %	33.89	33.66	33.19	32.82	32.58	32.12	31.47	31.00
C3 Selectivity, %	1.47	1.52	1.52	1.51	1.51	1.50	1.50	1.48
C2 Yield, %	12.03	11.73	11.51	11.46	11.15	10.92	10.55	10.45
Ethylene/Ethane	1.87	1.90	1.95	1.99	2.01	2.04	2.07	2.08
CO2/CO	5.89	5.76	5.52	5.31	5.08	4.86	4.50	4.48

Table 51. **Methane Coupling Activity of K2La2Ti3O10 (Continued)**
[Run 1]

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 3-KDC-X-53

Weight (g): 1.008 **Volume (cc):** 1

CH4/O2/N2: 2.05/1/3.79 **Pressure (psig):** 5

Temperature (°C)	800	800	811	811	814	814	824	824
Flow (cc/min)	40	40	100	100	150	150	200	200
GHSV (h 1)	2400	2400	6000	6000	9000	9000	12000	12000
Time (h)	85	86	87.5	88	89	90	91	92
CH4 Conv., %	33.62	33.22	35.09	31.11	29.75	29.33	26.88	26.77
O2 Conv., %	92.21	92.47	81.82	81.80	73.90	73.55	64.73	64.02
C Balance, %	100.10	100.84	96.40	100.91	100.17	100.55	100.33	100 23
C2 Selectivity, %	30.85	30.70	33.26	32.77	34.92	34.86	36.76	36.60
C3 Selectivity, %	1.44	1.78	1.65	1.64	1.70	1.71	1.78	1.78
C2 Yield, %	10.38	10.28	11.25	10.29	10.41	10.28	9.92	9.82
Ethylene/Ethane	2.14	2.16	1.74	1.74	1.52	1.52	1.30	1.28
CO2/CO	4.84	4.83	3.55	3.16	2.79	2.64	2.50	2.55

Table 51. **Methane Coupling Activity of K2La2Ti3O10 (Continued)**
[Run 1]

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 3-KDC-X-53

Weight (g): 1.008 **Volume (cc):** 1

CH4/O2/N2: 2.05/1/3.79 **Pressure (psig):** 5

Temperature (°C)	820	820	820	820	820	820	820
Flow (cc/min)	100	100	100	100	100	100	100
GHSV (h 1)	6000	6000	6000	6000	6000	6000	6000
Time (h)	94	96	97.5	98	99	100	101
CH4 Conv., %	32.21	31.35	31.46	30.90	30.72	30.25	29.99
O2 Conv., %	81.76	81.35	81.10	80.53	80.06	79.60	79.31
C Balance, %	99.24	100.25	99.88	100.34	100.13	100.29	101.02
C2 Selectivity, %	33.76	33.83	34.00	33.55	33.69	33.89	33.26
C3 Selectivity, %	1.68	1.64	1.66	1.63	1.64	1.65	1.61
C2 Yield, %	10.79	10.63	10.68	10.40	10.36	10.28	10.08
Ethylene/Ethane	1.80	1.81	1.82	1.81	1.79	1.78	1.78
CO2/CO	3.38	3.04	3.03	2.90	2.96	2.80	2.78

Table 52. **Methane Coupling Activity of K2La2Ti3O10**
[Run 2]

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 3-KDC-X-69

Weight (g): 4.005 **Volume (cc):** 3.3

CH4/O2/N2: 2.06/1/3.79 **Pressure (psig):** 7

Temperature (°C)	803	803	803	803	803	803	803	803
Flow (cc/min)	200	200	200	200	200	200	200	200
GHSV (h 1)	3636	3636	3636	3636	3636	3636	3636	3636
Time (h)	1.5	4	6	10	14	18	22	26
CH4 Conv., %	37.63	37.09	36.77	36.54	36.39	36.27	36.43	36.46
O2 Conv., %	94.74	94.60	94.82	94.74	94.82	94.75	94.77	94.83
C Balance, %	99.88	99.66	100.01	100.16	100.12	100.30	100.04	99.97
C2 Selectivity, %	39.12	39.11	39.10	39.01	39.04	38.81	38.61	37.97
C3 Selectivity, %	1.02	1.07	1.09	1.11	1.10	1.10	1.10	1.10
C2 Yield, %	14.70	14.46	14.38	14.28	14.22	14.12	14.07	13.84
Ethylene/Ethane	1.61	1.57	1.55	1.55	1.55	1.55	1.54	1.57
CO2/CO	7.76	7.46	7.52	7.41	7.31	7.27	7.20	7.32

Table 52. Methane Coupling Activity of K2La2Ti3O10 (Continued) [Run 2]

CATALYST: K2La2Ti3O10 NOTEBOOK: 3-KDC-X-69

Weight (g): 4.005 Volume (cc): 3.3

CH4/O2/N2: 2.06/1/3.79 Pressure (psig): 7

Temperature (°C)	803	803	803	803	856	856	799
Flow (cc/min)	200	200	200	200	240	240	200
GHSV (h 1)	3636	3636	3636	3636	4364	4364	3636
Time (h)	62	70	78	82	84	84.5	85.5
CH4 Conv., %	37.08	36.54	36.48	36.09	35.89	36.10	36.35
O2 Conv., %	94.62	94.79	94.82	94.74	94.61	94.65	94.61
C Balance, %	99.64	100.16	99.62	99.88	99.89	99.86	100.29
C2 Selectivity, %	38.77	39.01	38.30	38.50	36.77	36.43	38.17
C3 Selectivity, %	1.08	1.11	1.06	1.06	0.91	0.91	1.05
C2 Yield, %	14.33	14.28	13.92	13.88	13.18	13.13	13.92
Ethylene/Ethane	1.57	1.55	1.53	1.53	2.11	2.09	1.52
CO2/CO	7.43	7.41	6.84	6.98	5.50	5.60	6.96

Table 52. Methane Coupling Activity of K2La2Ti3O10 (Continued)
[Run 2]

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 3-KDC-X-69

Weight (g): 4.005 **Volume (cc):** 3.3

CH4/O2/N2: 3.65/1/3.81 **Pressure (psig):** 7 **CH4/O2/N2:** 6.99/1/3.76

Temperature (°C)	799	799	799	803	803	803	803	803
Flow (cc/min)	200	200	200	200	200	200	200	200
GHSV (h 1)	3636	3636	3636	3636	3636	3636	3636	3636
Time (h)	89	90	91	93	94	97	99	105
CH4 Conv., %	18.72	19.01	19.26	12.50	12.63	11.86	11.70	11.21
O2 Conv., %	94.63	94.64	94.77	94.76	94.65	93.65	93.61	93.59
C Balance, %	106.17	105.99	105.72	102.97	102.93	103.40	103.63	103.91
C2 Selectivity, %	49.63	49.23	49.24	58.45	57.67	59.01	59.04	59.10
C3 Selectivity, %	1.84	1.80	1.85	2.36	2.35	2.40	2.40	2.42
C2 Yield, %	9.86	9.92	10.03	7.52	7.50	7.23	7.16	6.88
Ethylene/Ethane	1.06	1.08	1.06	0.85	0.86	0.85	0.85	0.84
CO2/CO	5.23	5.01	5.17	4.09	3.53	4.00	3.81	3.88

Table 53. **Methane Coupling Activity of K2La2Ti3O10**
[Run 3]

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 3-KDC-X-93

Weight (g): 4.013 **Volume (cc):** 4

CH4/O2/N2: 2.04/1/3.81 **Pressure (psig):** 7

Temperature (°C)	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200
GHSV (h 1)	3000	3000	3000	3000	3000	3000	3000
Time (h)	1	4	12	20	28	36	44
CH4 Conv., %	38.86	38.34	37.67	36.95	37.48	36.53	36.66
O2 Conv., %	94.26	93.27	94.66	94.69	94.73	94.70	94.65
C Balance, %	101.21	100.90	100.79	101.77	100.76	101.94	101.40
C2 Selectivity, %	42.07	40.73	40.45	40.11	38.82	38.38	37.33
C3 Selectivity, %	1.66	1.77	1.71	1.66	1.59	1.56	1.49
C2 Yield, %	16.55	15.76	15.44	15.08	14.66	14.29	13.88
Ethylene/Ethane	1.84	1.81	1.81	1.82	1.88	1.90	1.92
CO2/CO	8.20	6.65	6.40	5.85	5.72	5.56	5.32

Table 54. Methane Coupling Activity of K2Sm2Ti3O10

CATALYST: K2Sm2Ti3O10 **NOTEBOOK:** 3-KDC-X-96

Weight (g): 1.03 **Volume (cc):** 0.6

CH4/O2/N2: 2.07/1/3.79 **Pressure (psig):** 5

Temperature (°C)	700	700	700	700	700	750	750	750
Flow (cc/min)	50	50	50	50	50	50	50	50
GHSV (h 1)	5000	5000	5000	5000	5000	5000	5000	5000
Time (h)	1	2	3	11	13	16	18	20
CH4 Conv., %	11.82	9.17	7.80	7.32	6.97	14.88	14.58	14.68
O2 Conv., %	31.41	24.18	20.75	20.22	21.13	40.26	38.16	37.68
C Balance, %	99.24	99.80	100.32	100.15	100.39	100.04	99.80	99.84
C2 Selectivity, %	8.19	7.47	5.94	4.78	4.73	15.60	16.34	16.89
C3 Selectivity, %	0.23	0.09	0.07	0.05	0.05	0.54	0.61	0.77
C2 Yield, %	0.96	0.68	0.46	0.35	0.33	2.32	2.38	2.48
Ethylene/Ethane	0.60	0.52	0.48	0.49	0.49	0.98	1.03	1.09
CO2/CO	4.11	2.61	2.06	1.75	1.69	1.97	1.67	1.54

Table 54. **Methane Coupling Activity of K2Sm2Ti3O10 (Continued)**

CATALYST: K2Sm2Ti3O10
NOTEBOOK: 3-KDC-X-96

Weight (g): 1.03
Volume (cc): 0.6

CH4/O2/N2: 2.06/1/3.81
Pressure (psig): 5

Temperature (°C)	750	801	801	801	801	900	900	800	801
Flow (cc/min)	50	50	50	50	50	50	50	50	50
GHSV (h 1)	5000	5000	5000	5000	5000	5000	5000	5000	5000
Time (h)	23	24	27	31	35	37	40	41	43
CH4 Conv., %	14.76	25.26	24.77	23.98	23.40	32.08	32.54	24.35	24.00
O2 Conv., %	36.60	70.29	66.46	64.30	62.65	94.51	95.02	76.77	72.76
C Balance, %	99.60	99.95	99.88	99.66	99.88	99.61	99.52	100.17	100.29
C2 Selectivity, %	17.22	23.01	23.56	23.32	23.19	15.88	14.90	17.80	18.95
C3 Selectivity, %	0.79	1.67	1.91	1.68	1.66	1.73	1.67	1.18	1.32
C2 Yield, %	2.53	5.81	5.83	5.57	5.42	5.08	4.83	4.34	4.56
Ethylene/Ethane	1.14	3.11	3.34	3.17	3.12	21.57	21.69	2.08	2.43
CO2/CO	1.39	2.29	1.83	1.69	1.51	2.54	1.62	4.92	3.49

Table 54. Methane Coupling Activity of K2Sm2Ti3O10 (Continued)

CATALYST: K2Sm2Ti3O10 **NOTEBOOK:** 3-KDC-X-96

Weight (g): 1.03 **Volume (cc):** 0.6

CH4/O2/N2: 2.07/1/3.79 **Pressure (psig):** 5

Temperature (°C)	818	818	818	818	818	818	818	818
Flow (cc/min)	50	50	50	50	100	100	150	150
GHSV (h 1)	5000	5000	5000	5000	10000	10000	15000	15000
Time (h)	46	51	55	59	60	62	63	64
CH4 Conv., %	26.60	25.04	25.22	25.18	17.71	17.05	13.06	13.16
O2 Conv., %	90.47	80.37	77.04	76.03	38.73	38.34	26.41	26.30
C Balance, %	100.08	100.20	99.76	100.23	99.05	99.73	99.43	99.14
C2 Selectivity, %	15.02	16.15	19.71	19.92	25.49	25.62	28.00	28.39
C3 Selectivity, %	1.13	1.28	1.69	1.77	1.55	1.75	2.65	1.44
C2 Yield, %	4.00	4.05	4.96	5.03	4.47	4.36	3.64	3.70
Ethylene/Ethane	1.95	2.19	3.12	3.17	2.06	2.06	1.41	1.42
CO2/CO	12.71	6.39	3.80	3.42	0.67	0.64	0.54	0.54

Table 55. **Methane Coupling Activity of K2Nd2Ti3O10**

CATALYST: K2Nd2Ti3O10 **NOTEBOOK:** 3-KDC-X-89

Weight (g): 1.013 **Volume (cc):** 0.8

CH4/O2/N2: 2.04/1/3.80 **Pressure (psig):** 5

Temperature (°C)	700	700	750	750	750	750	800	800	800
Flow (cc/min)	50	50	50	50	50	50	50	50	50
GHSV (h 1)	3750	3750	3750	3750	3750	3750	3750	3750	3750
Time (h)	1	2	3	5	9	17	18	20	22
CH4 Conv., %	10.14	9.67	17.12	16.72	15.69	14.24	25.51	25.76	25.40
O2 Conv., %	30.07	26.97	50.10	47.96	42.92	37.55	77.65	80.29	81.63
C Balance, %	101.05	100.36	101.43	101.41	101.32	101.22	101.95	101.64	101.37
C2 Selectivity, %	12.02	8.95	20.68	20.16	20.60	21.53	24.20	22.96	21.73
C3 Selectivity, %	0.12	0.10	0.61	0.69	0.74	0.81	1.51	1.42	1.32
C2 Yield, %	1.23	0.87	3.59	3.42	3.27	3.10	6.29	6.01	5.60
Ethylene/Ethane	0.62	0.64	1.41	1.39	1.43	1.38	2.[illegible]5	1.99	1.82
CO2/CO	3.89	3.34	3.35	2.90	1.89	1.29	2.81	3.61	4.24

Table 56. **Methane Coupling Activity of K2La2Mn3O10**

CATALYST: K2La2Mn3O10 **NOTEBOOK:** 3-KDC-X-79

Weight (g): 1.004 **Volume (cc):** 1

CH4/O2/N2: 2.05/1/3.81 **Pressure (psig):** 5

Temperature (°C)	700	700	700	700	749	749	749	802
Flow (cc/min)	50	50	50	50	50	50	50	50
GHSV (h 1)	3000	3000	3000	3000	3000	3000	3000	3000
Time (h)	2	4	8	14	17	20	23	24
CH4 Conv., %	22.93	22.77	22.09	20.55	25.74	25.72	25.89	27.81
O2 Conv., %	94.56	94.01	89.78	81.73	93.13	92.04	91.16	94.71
C Balance, %	100.92	101.39	100.99	100.84	101.29	101.04	101.00	100.97
C2 Selectivity, %	1.03	1.78	3.24	4.44	14.19	15.97	16.86	17.03
C3 Selectivity, %	0.00	0.01	0.04	0.04	0.45	0.51	0.57	0.52
C2 Yield, %	0.24	0.41	0.72	0.92	3.70	4.15	4.41	4.78
Ethylene/Ethane	0.23	0.22	0.24	0.29	0.59	0.67	0.70	1.01
CO2/CO	**	**	**	157.59	89.28	85.48	80.18	39.09

**: No CO detected.

Table 56. Methane Coupling Activity of K2La2Mn3O10 (Continued)

CATALYST: K2La2Mn3O10 NOTEBOOK: 3-KDC-X-79

Weight (g): 1.004 Volume (cc): 1

CH4/O2/N2: 2.05/1/3.81 Pressure (psig): 5

Temperature (°C)	802	801	801	801	801	798	798	798
Flow (cc/min)	50	100	100	100	100	50	50	75
GHSV (h 1)	3000	6000	6000	6000	6000	3000	3000	4500
Time (h)	25	26	30	34	40	44	46	47
CH4 Conv., %	28.44	26.59	26.57	26.20	24.42	30.15	30.81	29.16
O2 Conv., %	94.55	91.88	86.13	81.94	76.78	94.42	94.54	88.91
C Balance, %	100.75	101.88	100.81	100.96	101.65	101.54	101.01	100.71
C2 Selectivity, %	18.22	18.86	23.11	25.32	27.46	27.21	27.15	26.65
C3 Selectivity, %	0.51	0.60	0.88	1.10	1.25	1.42	1.47	1.35
C2 Yield, %	5.22	5.11	6.19	6.70	6.82	8.33	8.45	7.83
Ethylene/Ethane	1.03	0.83	0.92	0.98	1.05	1.43	1.46	1.30
CO2/CO	32.85	64.43	34.28	18.73	12.64	26.62	25.05	15.58

Table 56. **Methane Coupling Activity of $K_2La_2Mn_3O_{10}$ (Continued)**

CATALYST: $K_2La_2Mn_3O_{10}$

NOTEBOOK: 3-KDC-X-79

Weight (g): 1.004

Volume (cc): 1

$CH_4/O_2/N_2$: 2.05/1/3.81

Pressure (psig): 5

Temperature (°C)	798	798	821	821	821	821	700	700
Flow (cc/min)	75	75	100	100	100	100	50	50
GHSV (h 1)	4500	4500	6000	6000	6000	6000	3000	3000
Time (h)	49	50	52	55	59	64	68	68.5
CH_4 Conv., %	28.82	28.72	29.81	29.16	28.85	28.35	17.23	17.46
O_2 Conv., %	88.16	88.01	87.32	86.69	86.00	85.46	66.39	64.94
C Balance, %	101.22	101.58	101.03	101.01	101.00	101.38	100.65	100.36
C2 Selectivity, %	27.59	27.41	29.62	29.31	29.23	29.37	5.14	5.10
C3 Selectivity, %	1.42	1.43	1.62	1.56	1.54	1.57	0.05	0.06
C2 Yield, %	8.05	8.00	8.92	8.63	8.52	8.44	0.89	0.89
Ethylene/Ethane	1.29	1.30	1.44	1.40	1.37	1.38	0.33	0.34
CO_2/CO	12.89	11.94	8.90	8.87	8.03	7.36	41.90	35.10

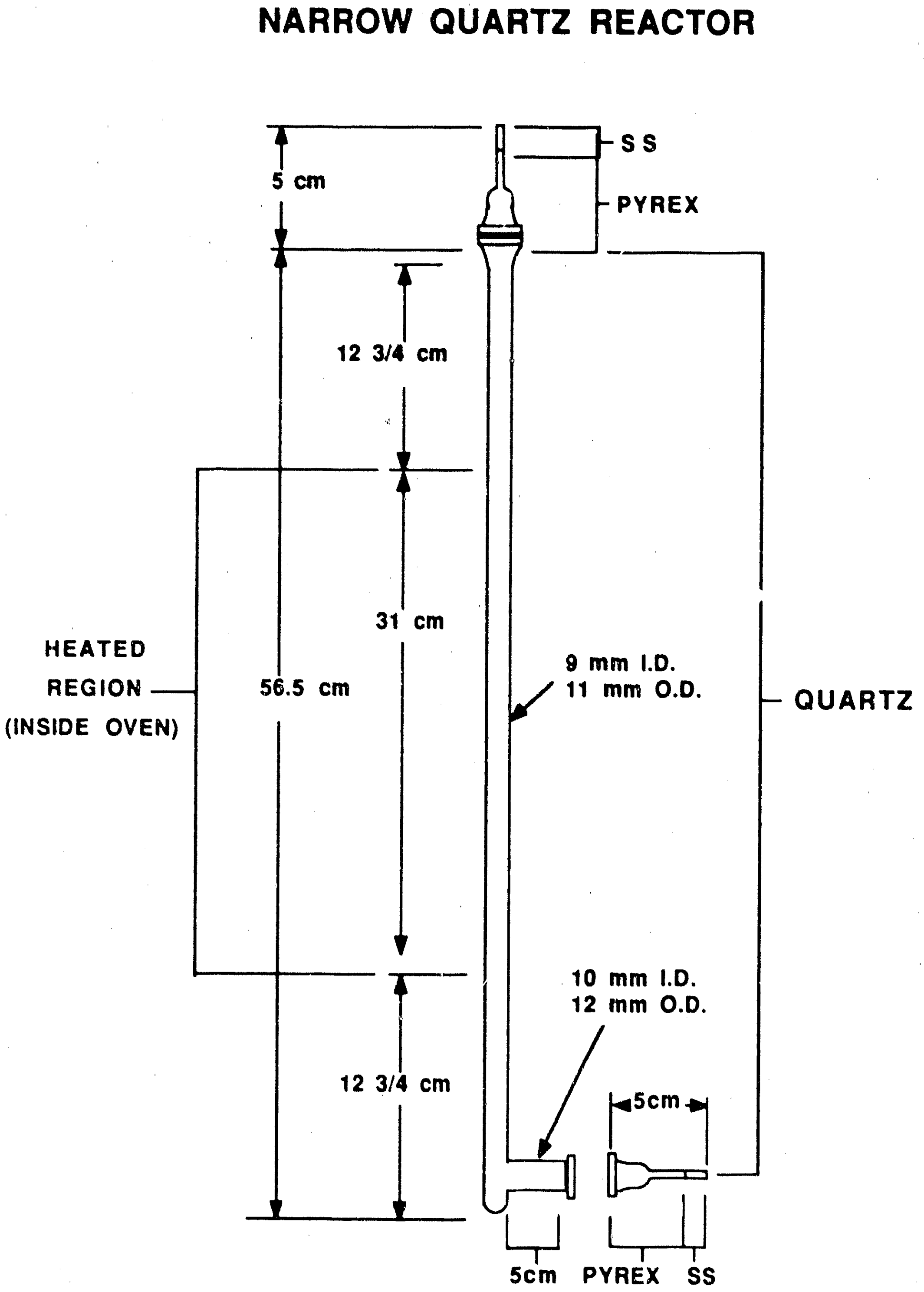
Table 57. Methane Coupling Material Balance - Case 1

Stream	**1**	**2**	**3**	**4**	**5**	**6**	**7**
	CH4 Feed	O2 Feed	CH4 Recycle	Rx Product	Quench Water	Comp Dischg	CO2 Purge
N2	2.6	6.5	80.6	89.7		89.7	
O2		285.8	0.8	0.9		0.9	
CO			0.8	0.9		0.9	
CO2	1.1			51.1		51.1	51.1
CH4	371.6		922.2	1003.7		1003.7	
C2H4			12.5	133.5		133.5	
C2H6	3.7		1.8	110.0		110.0	
C3H6				11.7		11.7	
C3H8				7.4		7.4	
C4H8				0.5		0.5	
H2O				280.7	280.7		
Total	**379.0**	**292.3**	**1018.7**	**1690.1**	**280.7**	**1409.4**	**51.1**

Stream	**8**	**9**	**10**	**11**	**12**	**13**	**14**
	Cold Box Feed	Inert Purge	C2H4 RC Feed	C2H4 RC Make	C2H4 RC Tails	C2H6 RC Make	C2H6 RC Tails
N2	89.7	9.1					
O2	0.9	0.1					
CO	0.9	0.1					
CO2							
CH4	1003.7	81.4					
C2H4	133.5	0.1	120.9	119.8	1.1	1.1	
C2H6	110.0		108.1	0.1	108.0	107.8	0.2
C3H6	11.7		11.7		11.7	1.3	10.4
C3H8	7.4		7.4		7.4	0.1	7.3
C4H8	0.5		0.5		0.5		0.5
H2O							
Total	**1358.3**	**90.8**	**248.6**	**119.9**	**128.7**	**110.3**	**18.4**

Appendix C. FIGURES

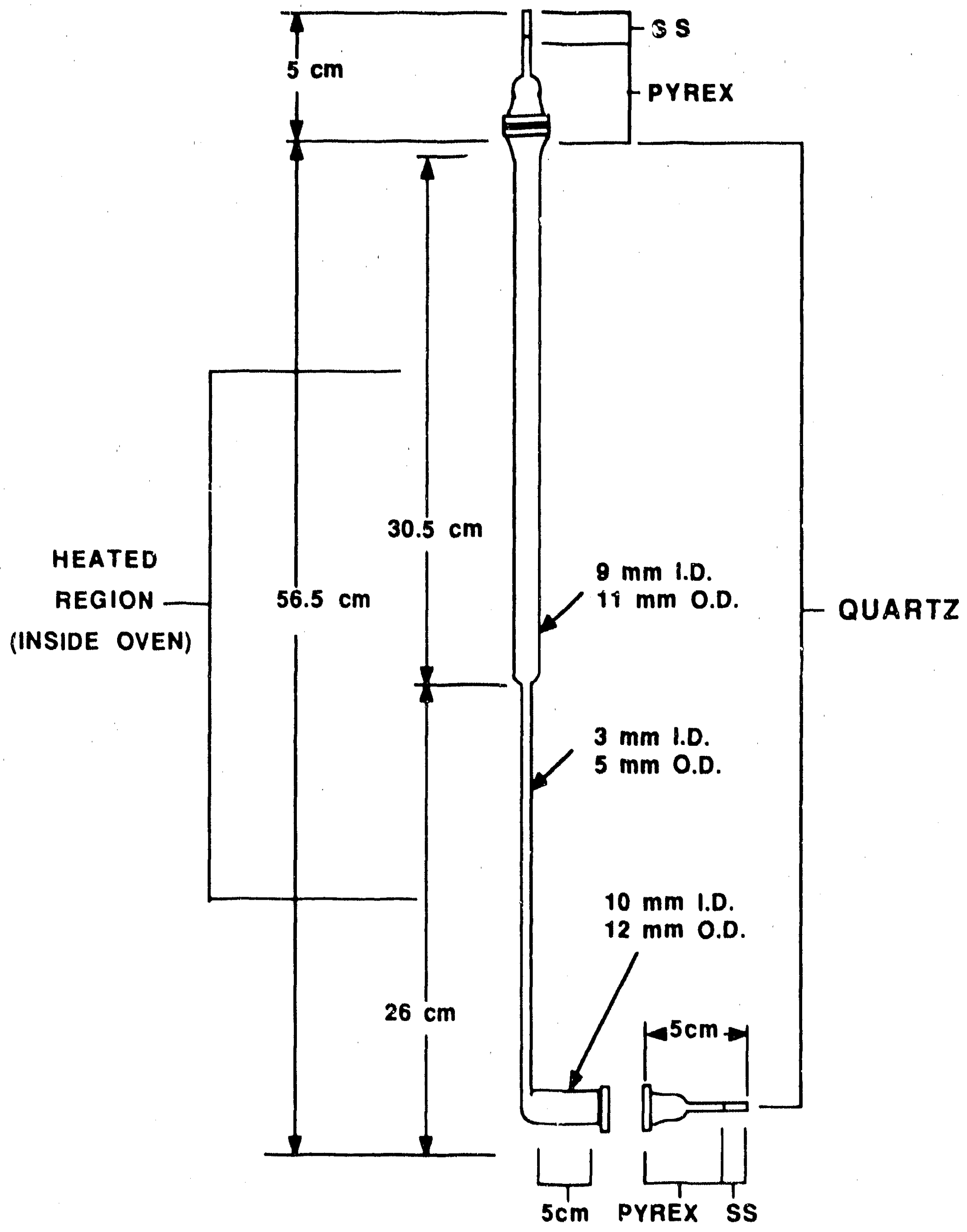
Figure 2. Reactor C



ALL O-RING CONNECTIONS
Not to scale

Figure 3. Reactor D

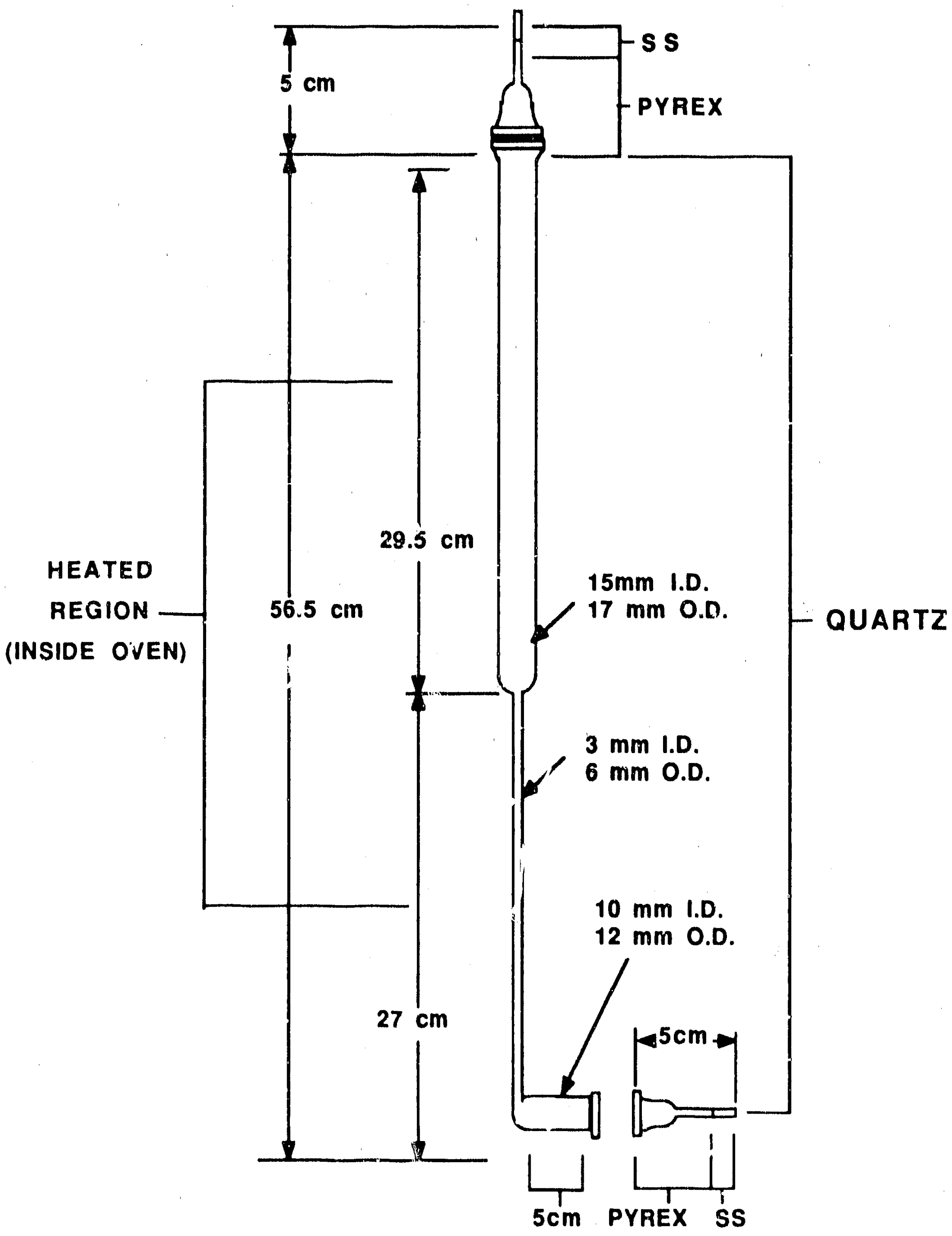
NARROW TO CAPILLARY QUARTZ REACTOR



ALL O-RING CONNECTIONS
Not to scale

Figure 4. Reactor E

FAT TO CAPILLARY QUARTZ REACTOR



ALL O-RING CONNECTIONS
Not to scale

Figure 5. Uncatalyzed Selectivities

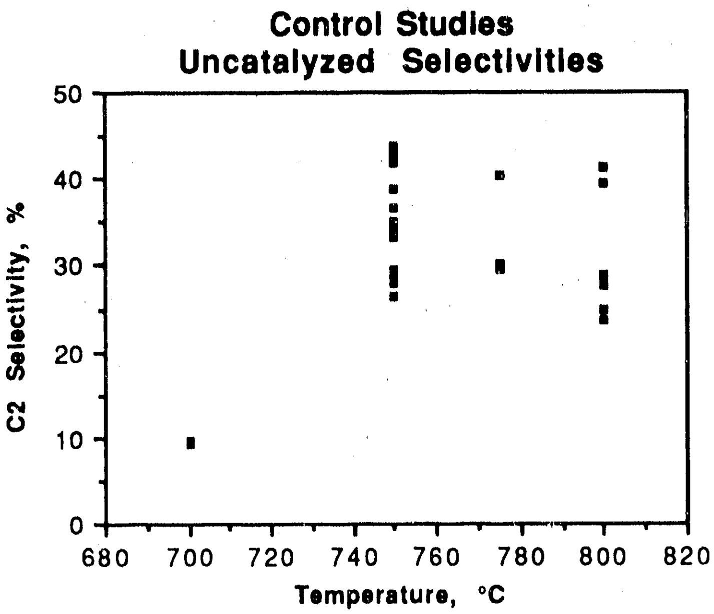


Figure 6. Control Studies, Uncatalyzed Methane Conversion

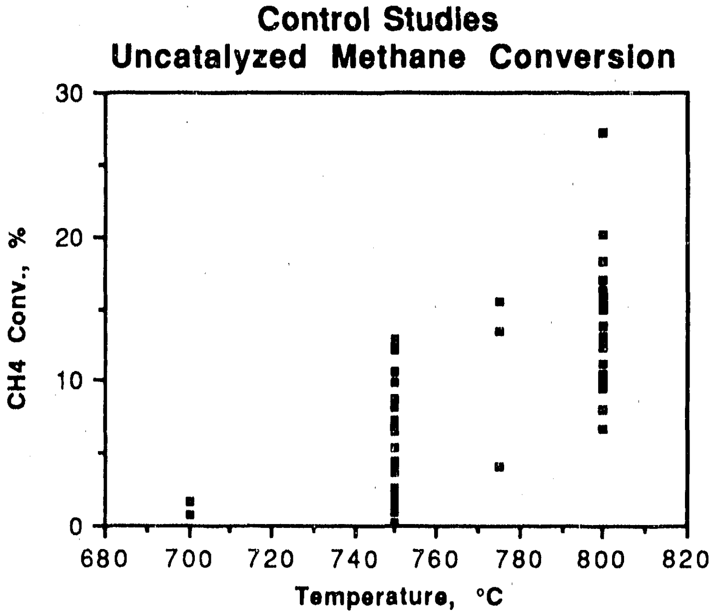


Figure 7. Effect of ECl on C2H4/C2H6 Ratio, 30-BKW-49

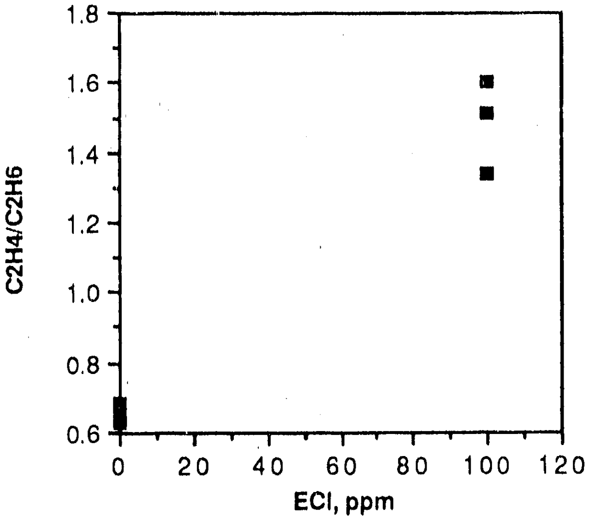


Figure 8. Effect of ECl on Selectivity 30-BKW-49

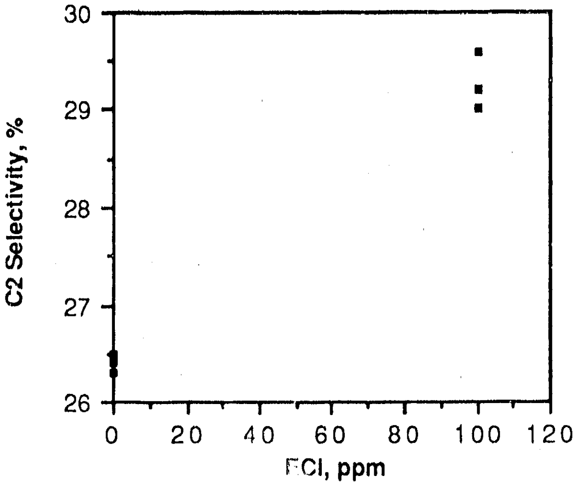


Figure 9. Effect of ECl on Methane Conversion, 30-BKW-49

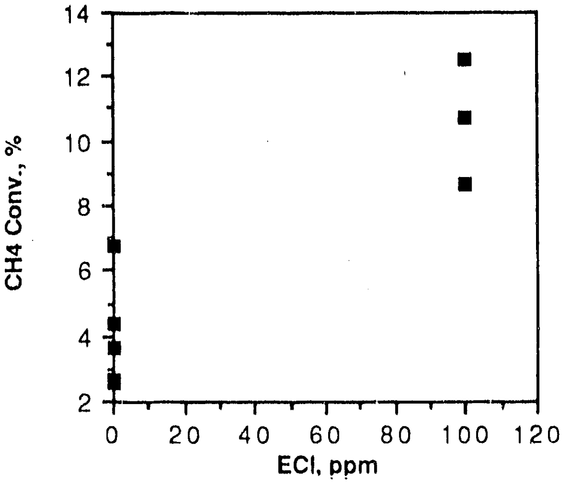


Figure 10. **Addition of Ethyl Chloride in the Feed Gas to a BaCl2/Al2O3 Methane Coupling Catalyst**

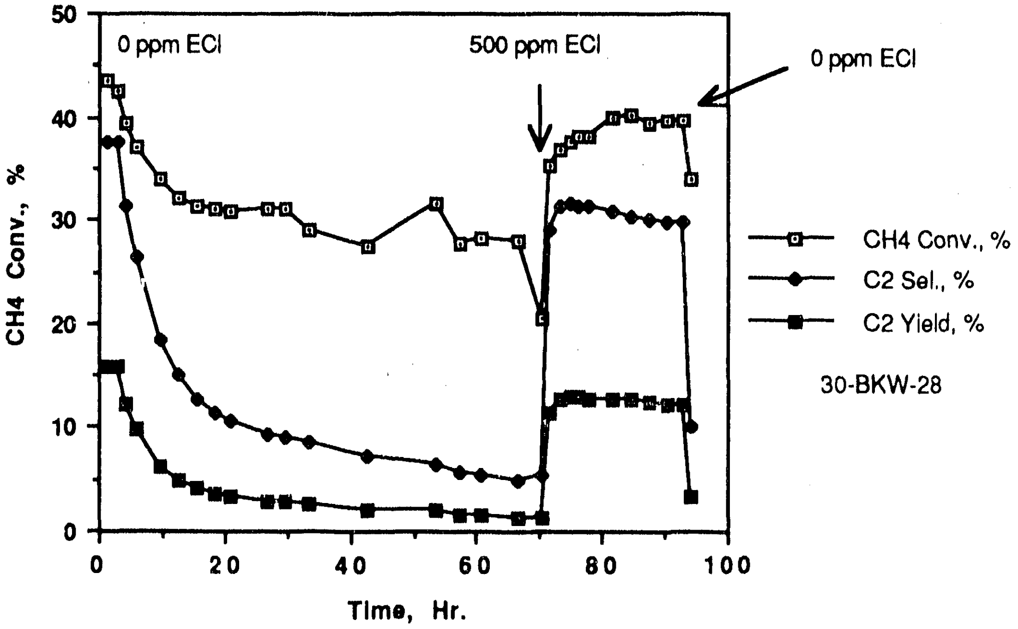


Figure 11. **Addition of Ethyl Chloride in the Feed Gas to a NaCl/Al2O3 Methane Coupling Catalyst**

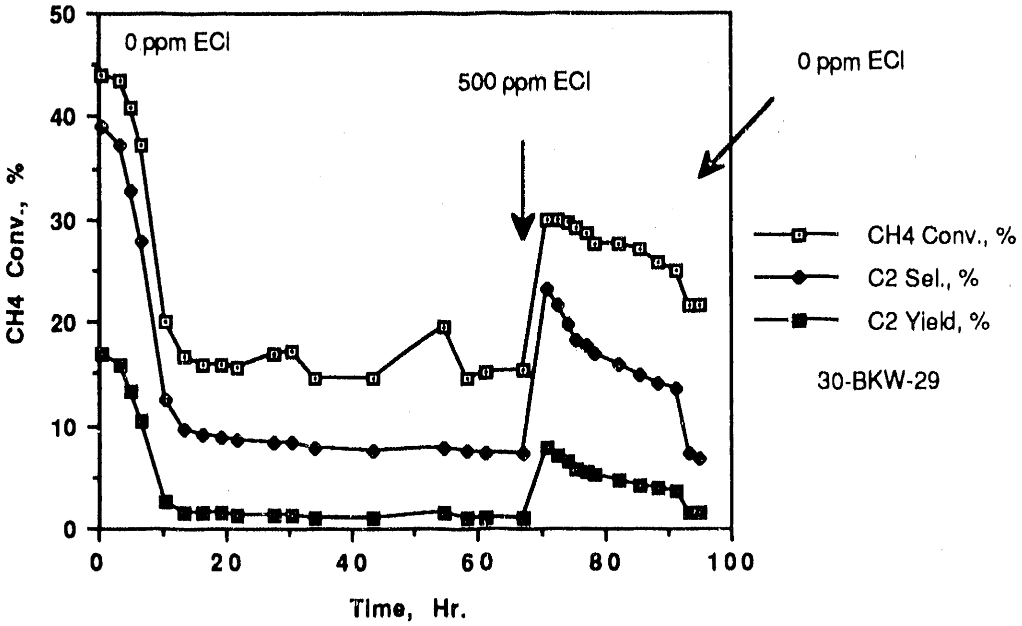


Figure 12. Effect of Ethyl Chloride on Methane Coupling with a $BaCl_2/\alpha\text{-}Al_2O_3$ Catalyst

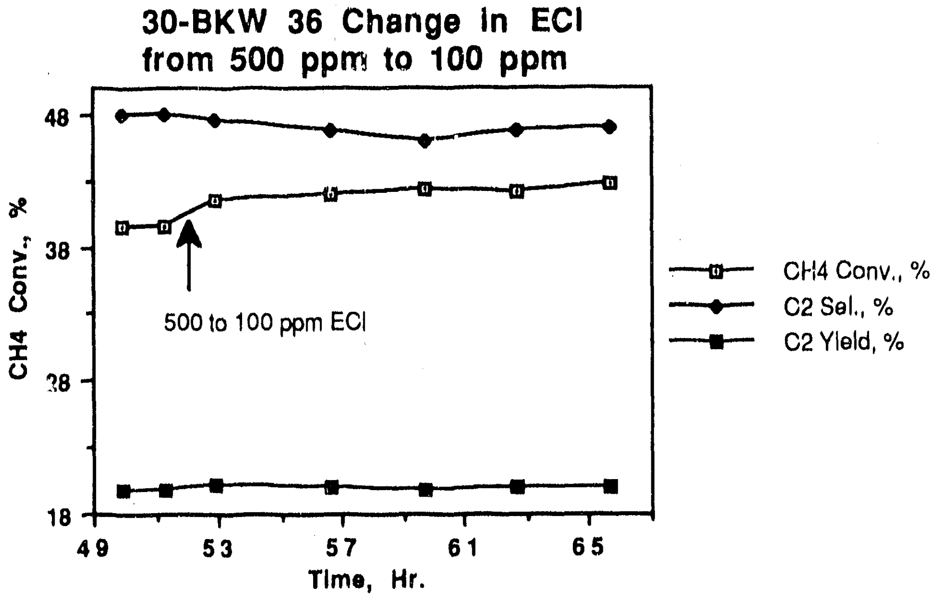


Figure 13. High C2 Yields with Lower ECl Levels

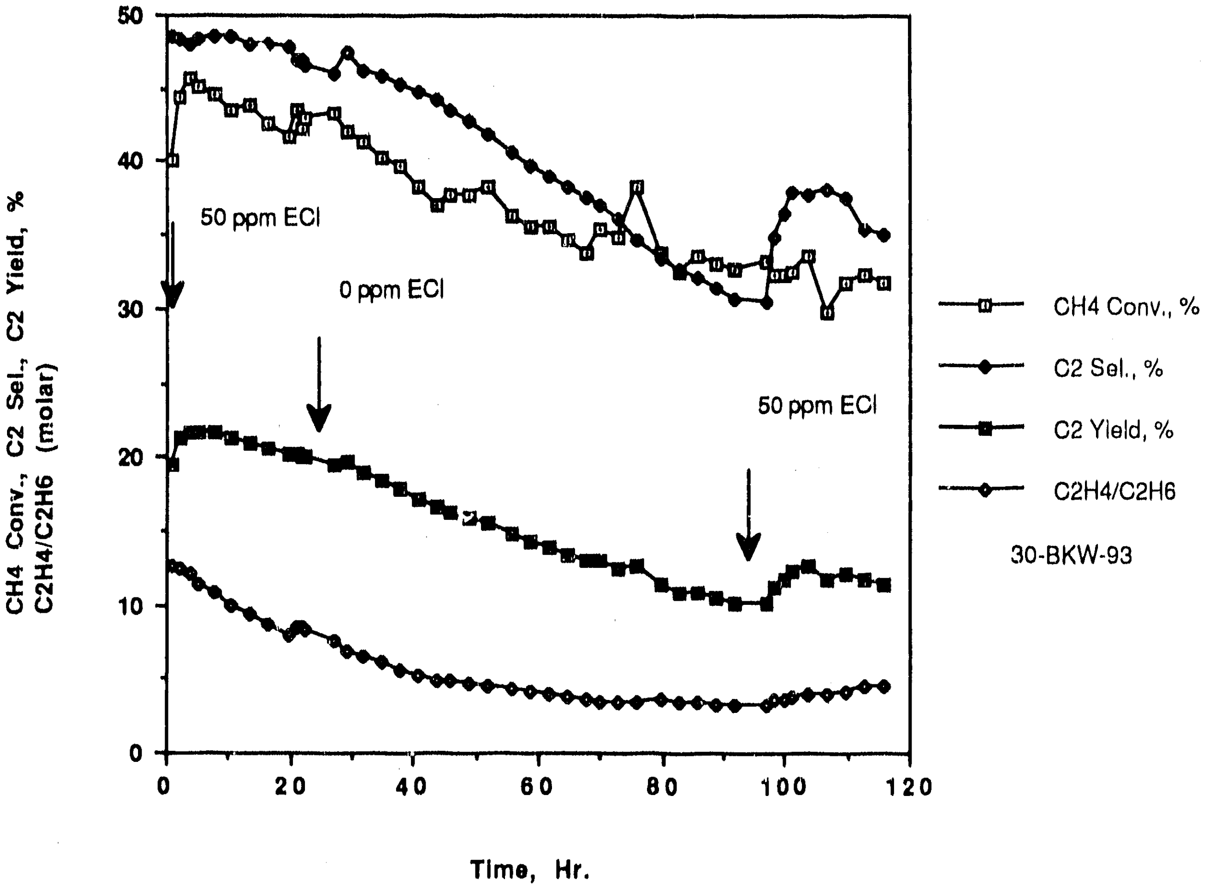


Figure 14. ABO_3 Perovskite Structure

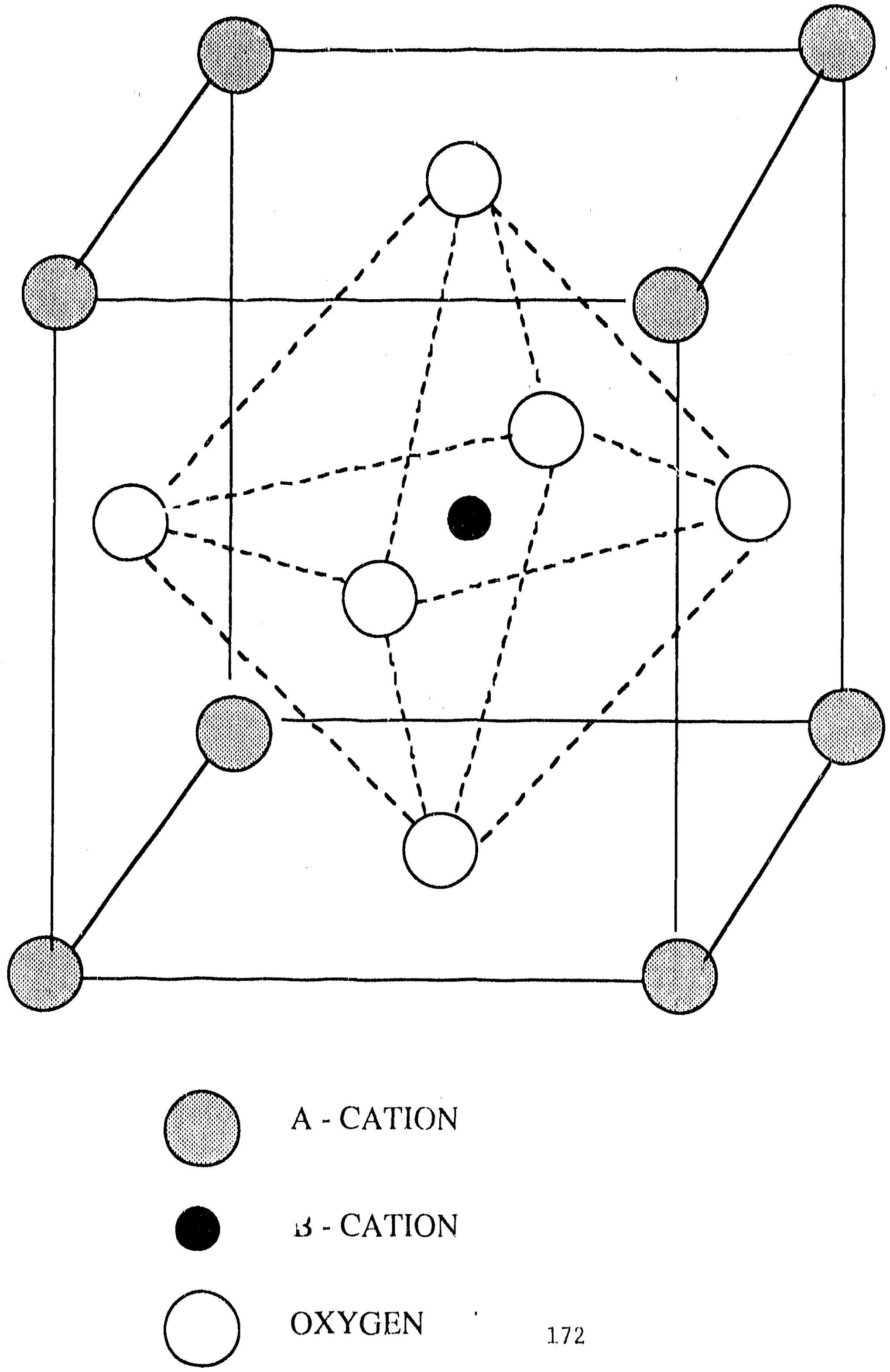


Figure 15. **Structure of $K_2La_2Ti_3O_{10}$ Layered Perovskite**

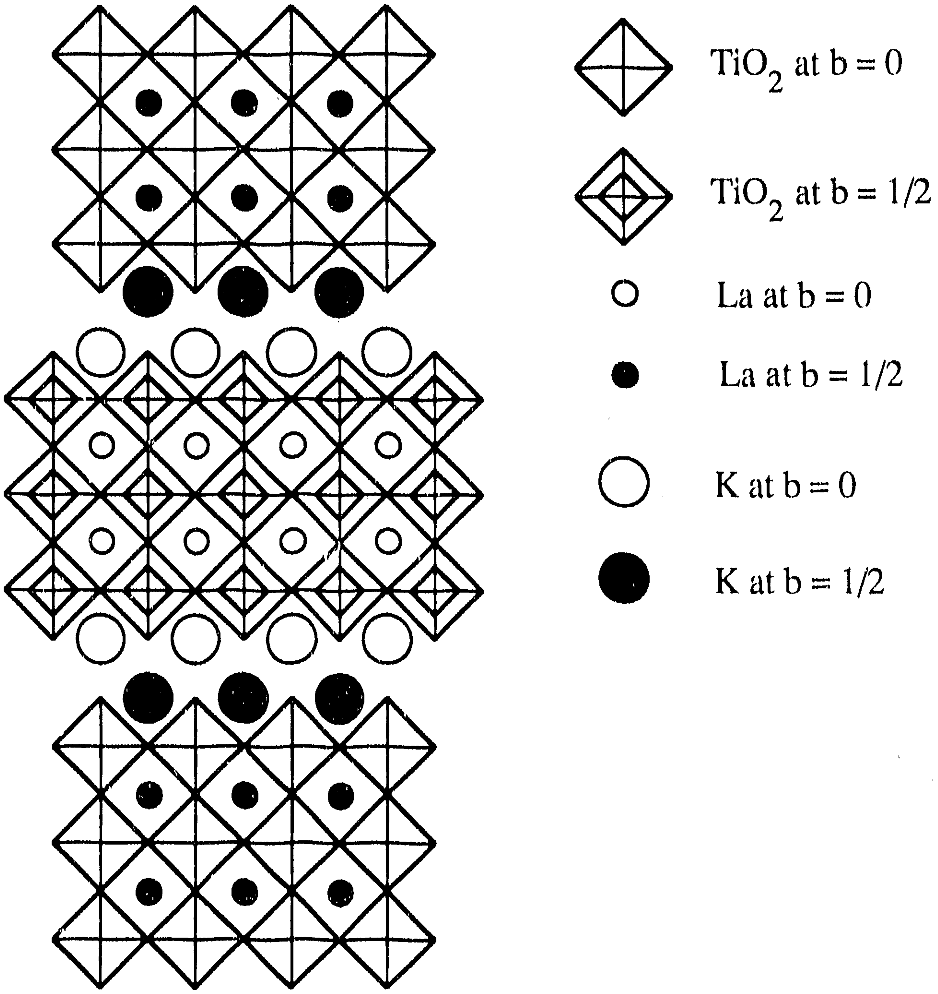


Figure 16. **Effect of CH4/O2 Ratio**

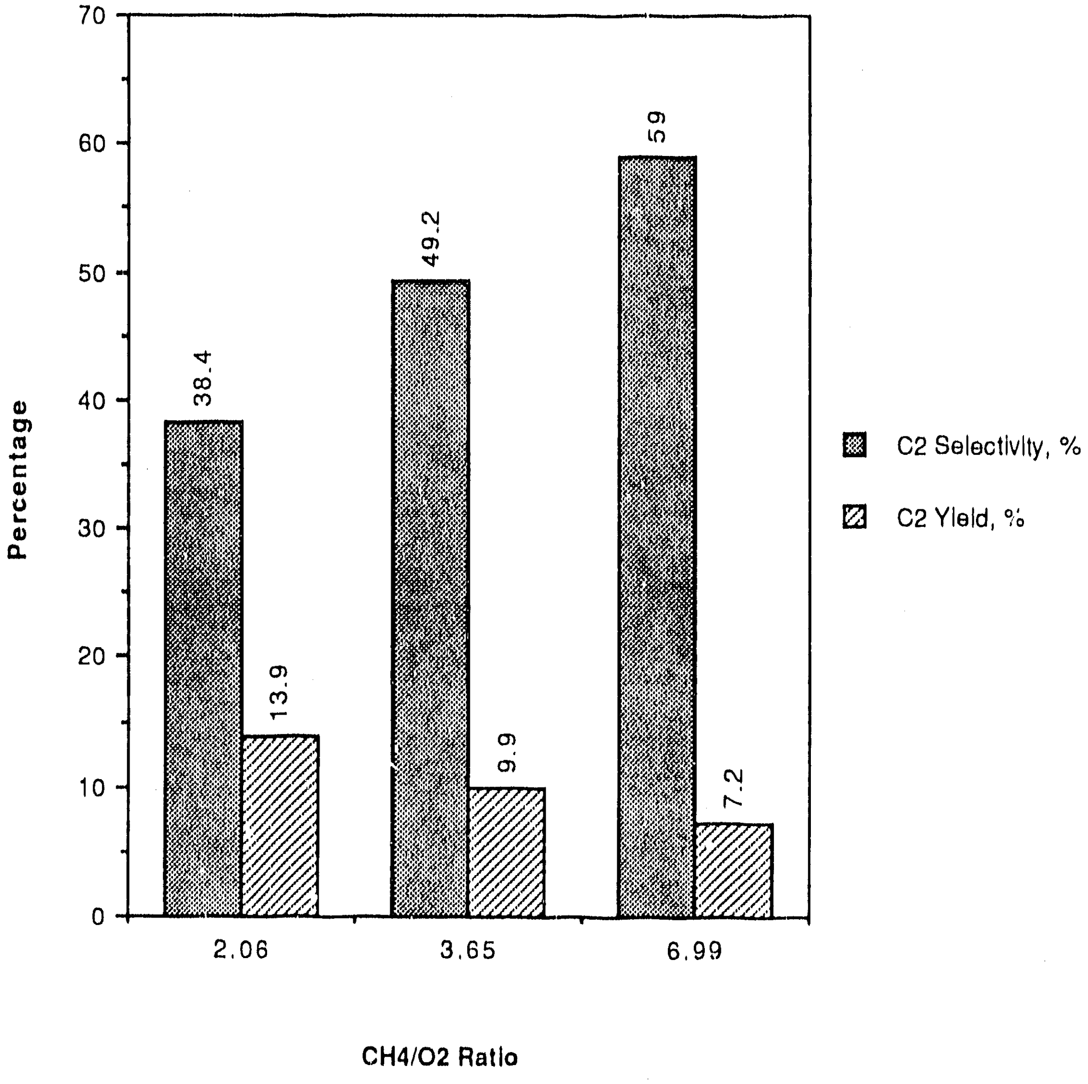
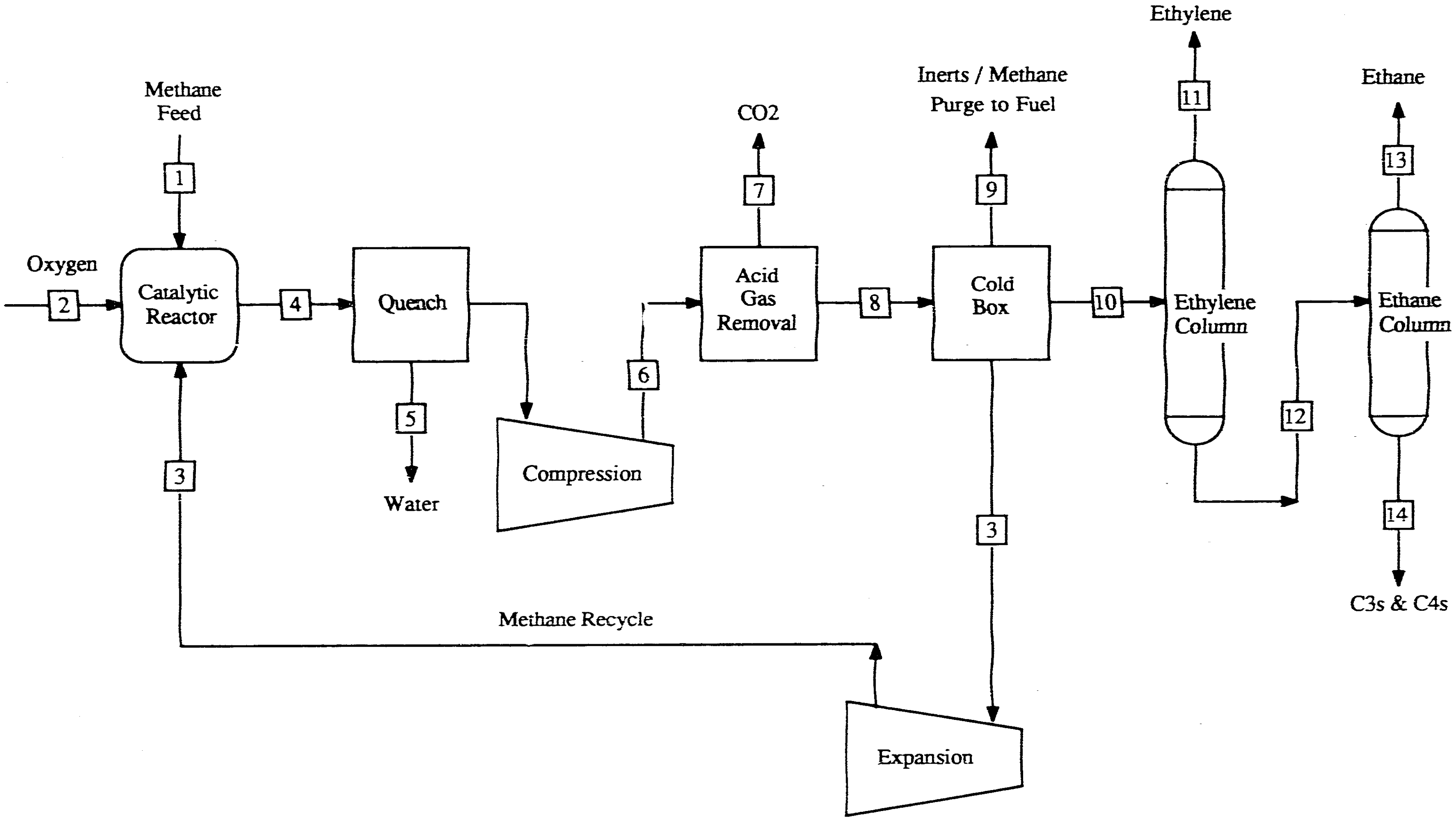


Figure 17. <u>Methane Coupling Process Simplified Block Diagram</u>



July 8, 1988
JLMatherne

Appendix D. CATALYST COMPOSITIONS AND PREPARATIONS

Ref. Run(Reactor #)	Catalyst	Wt. % Components	Moles/g Support	g/cc Catalyst	Mesh Prepared	Reference of Preparation	Date Run	Wt. % Metals	Preparati Procedur	g Support or * g Cat.
29-BKW-106(R#3)	KCl / Al2O3, Norton SA 5551	4.85	0.000684	1.16	14/30	29-BKW-77B	4/5/88	2.67	A	10
29-BKW-110(R#3)	BaCl2 / Al2O3, Norton SA 5551	12.43	0.000682	1.16	14/30	29-BKW-77C	4/6/88	9.36	A#1	10
29-BKW-114(R#3)	BaCl2 / Al2O3, Norton SA 5551	12.43	0.000682	1.16	14/30	29-BKW-77C	4/7/88	9.36	A#1	10
29-BKW-107(R#4)	CsCl / Al2O3, Norton SA 5551	7.06	0.000451	1.16	14/30	29-BKW-77D	4/5/88	[illegible]	A	10
29-BKW-111(R#4)	LiCl / Al2O3, Norton SA 5551	2.82	0.000683	1.16	14/30	29-BKW-77E	4/6/88	0.47	A	10
29-BKW-115(R#4)	LiCl / Al2O3, Norton SA 5551	2.82	0.000683	1.16	14/30	29-BKW-77E	4/7/88	0.47	A	10
29-BKW-99(R#3)	NaCl / Al2O3, Norton SA 5551	3.85	0.000683	1.16	14/30	29-BKW-98A	3/30/88	1.57	A	30
29-BKW-101(R#4)	NaCl / Al2O3, Norton SA 5551	13.79	0.00274	1.16	14/30	29-BKW-98B	3/31/88	6.29	A	10
29-BKW-119(R#4)	NaCl / Al2O3, Norton SA 5551	3.85	0.000683	1.16	14/30	29-BKW-120A	4/8/88	1.57	A	30
29-BKW-118(R#3)	BaCl2 / Al2O3, Norton SA 5551	12.43	0.000683	1.16	14/30	29-BKW-120B	4/8/88	9.36	A#1	30
29-BKW-128(R#3)	BaCl2 / Al2O3, Norton SA5551	12.43	0.000682	1.16	14/30	29-BKW-121A	4/13/88	9.36	A#1	10
29-BKW-124(R#3)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	14/30	29-BKW-121B	4/12/88	0.94	A	10
29-BKW-129(R#4)	BaCl2 / Al2O3, Norton SA5551	0.145	0.00000696	1.16	14/30	29-BKW-121C	4/13/88	0.095	A	10
29-BKW-125(R#4)	BaCl2 / Al2O3, Norton SA5551	0.019	0.00000091	1.16	14/30	29-BKW-121D	4/12/88	0.0125	A	10
29-BKW-132(R#3)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	100/140	29-BKW-131A	4/14/88	[illegible]	A	5
29-BKW-133(R#4)	BaCl2 / Al2O3, Aldrich	1.44	0.00007	1.16	100/140	29-BKW-131B	4/14/88	0.96	A	5
29-BKW-138(R#3)	BaCl2/ Al2O3, Norton SA5551	1.41	0.0000686	1.16	30/60	29-BKW-131C	4/15/88	0.94	A	10
29-BKW-152(R#3)	BaCl2/ Al2O3, Norton SA5551	1.41	0.0000686	1.16	30/60	29-BKW-131C	4/20/88	0.94	A	10
30-BKW-3(R#3)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	30/60	29-BKW-150A	4/21/88	0.94	A	10
30-BKW-7(R#3)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	30/60	29-BKW-150B	4/22/88	0.94	A	10
30-BKW-9(R#4)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	30/60	29-BKW-150B	4/22/88	0.94	A	10
30-BKW-5(R#4)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	60/100	29-BKW-150C	4/21/88	0.94	A	10
30-BKW-36(R#3)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	60/100	29-BKW-150C	5/3/88	0.94	A	10
30-BKW-28(R#3)	BaCl2 / Al2O3, Norton SA5551	1.41	0.0000686	1.16	140/200	29-BKW-150D	4/29/88	0.94	A	10
30-BKW-29(R#4)	NaCl / Al2O3, Norton SA5551	0.4	0.0000686	1.16	140/200	29-BKW-150E	4/29/88	0.158	A	10
29-BKW-142(R#3)	MnAPSO - 5			0.91	powder	003-55-1-2C,SWK	4/18/88			
29 BKW-143(R#4)	CoAPSO - 34			0.5	powder	100058-5,SWK	4/18/88			
29-BKW-146(R#3)	MnAPSO - 34			0.56	powder	0024-61-1-3,SWK	4/19/88			
29-BKW-147(R#4)	MAPO - 34			0.71	powder	9688-68,SWK	4/19/88			
29-BKW-151(R#4)	[illegible] - 34			0.625	powder	9940-81,SWK	4/20/88			
30-BKW-12(R#3)	[illegible]2O3, Norton SA3232	1.41	0.0000686	0.62	30/60	30-BKW-11A	4/27/88	0.94	A	10
30-BKW-13(R#4)	[illegible]O3, Norton SA3235	1.41	0.0000686	0.66	30/60	30-BKW-11B	4/27/88	0.94	A	10
30-BKW-22(R#3)	BaCl2 / Al2O3, Norton SA5502	1.41	0.0000686	1.08	30/60	30-BKW-11C	4/28/88	0.94	A	10
30-BKW-48(R#3)	Alberger Coarse Flake Salt (NaCl)	100		0.7		30-BKW-19	5/9/88			
30-BKW-23(R#4)	Pretzel "M" Salt (NaCl)	100		1.09		30-BKW-20	4/28/88			
30-BKW-37(R#4)	BaCl2 / Al2O3, Norton SA5502	1.41	0.0000686	1.08	60/100	30-BKW-34A	5/3/88	0.94	A	5
30-BKW-45(R#4)	NaCl / Al2O3, Norton SA5551	0.4	0.0000683	1.16	60/100	30-BKW-34B	5/6/88	0.158	A	5
30-BKW-44(R#3)	BaCl2 / Al2O3, Norton SA5551	0.146	0.000007	1.16	60/100	30-BKW-34C	5/6/88	0.096	A	5
30-BKW-53(R#4)	BaCl2 / Al2O3, Norton SA5551	0.507	0.0000245	1.16	60/100	30-BKW-34E	5/10/88	0.337	A	10
30-BKW-52(R#3)	BaCl2 / Al2O3, Norton SA5551	5.033	0.00025	1.16	60/100	30-BKW-34F	5/10/88	3.5	A	10
30-BKW-60(R#3)	BaCl2 / Al2O3, Norton SA5551	5.033	0.00025	1.16	30/60	30-BKW-34H	5/17/88	3.5	A	10

Appendix D. CATALYST COMPOSITIONS AND PREPARATIONS

Ref. Run(Reactor #)	Catalyst	Wt. % Components	Moles/g Support	g/cc Catalyst	Mesh Prepare	Reference of Preparation	Date Run	Wt. % Metals	Preparati Procedu	g Support or * g Cat.
30-BKW-61(R#4)	BaCl2 / Al2O3, Norton SA5551	5.033	0.00025	1.16	30/60	30-BKW-34H	5/17/88	3.5	A	10
30-BKW-65(R#4)	CsCl / Al2O3, Norton SA5551	4.04	0.00025	1.16	30/60	30-BKW-34I	5/19/88	3.32	A	10
30-BKW-83(R#3)	CsCl / Al2O3, Norton SA5551	4.04	0.00025	1.16	30/60	30-BKW-34I	5/26/88	3.32	A	10
30-BKW-64(R#3)	RbCl / Al2O3, Norton SA5551	2.934	0.00025	1.16	30/60	30-BKW-34J	5/19/88	2.13	A	10
30-BKW-74(R#4)	RbCl / Al2O3, Norton SA5551	2.934	0.00025	1.16	30/60	30-BKW-34J	5/24/88	2.13	A	10
30-BKW-66(R#3)	AlPO4 - 5			0.31	powder	SWK	5/20/88		A	
30-BKW-67(R#4)	SAPO - 5			0.83	powder	SWK	5/20/88		A	
30-BKW-70(R#3)	LiCl / Al2O3, Norton SA5551	1.05	0.00025	1.16	30/60	30-BKW-68A	5/23/88	0.172	A	10
30-BKW-71(R#4)	KCl / Al2O3, Norton SA5551	1.831	0.00025	1.16	30/60	30-BKW-68B	5/23/88	0.978	A	10
30-BKW-73(R#3)	KCl / Al2O3, Norton SA5551	1.831	0.00025	1.16	30/60	30-BKW-68B	5/24/88	0.978	A	10
30-BKW-93(R#4)	BaCl2 / Al2O3, Norton SA5502	5.033	0.000254	1.08	30/60	30-BKW-68D	6/2/88	3.5	A	5
30-BKW-97(R#3)	BaCl2 / ZnO	5.033	0.00025	2.78	60/100	30-BKW-68E	6/6/88	3.5	A	10
30-BKW-80(R#4)	MAPO - 36			0.71	powder	10232-20,SWK	5/25/88		A	
30-BKW-86(R#3)	BaCl2 / ZrO2	5.033	0.00025	1.67	60/100	30-BKW-81A	5/27/88	3.5	A	10
30-BKW-87(R#4)	Ba3(PO4)2	2.15	0.0000366	1.19	30/60	30-BKW-81B	5/27/88	1.5	A#2	5
30-BKW-95(R#3)	B(otf)3 / LZ10	7		0.33	powder	12957-19-3,SWK	6/3/88			
30-BKW-100(R#3)	RbCl, BaCl2 / Al2O3, Norton SA5551	3.0689,5.033	262,0.000255	1.16	30/60	30-BKW-98A	6/7/88	2.24,3.32	A	5
30-BKW-101(R#4)	CsCl, BaCl2 / Al2O3, Norton SA5551	4.2237,5.033	262,0.000255	1.16	30/60	30-BKW-98B	6/7/88	3.48,3.32	A	5
30-BKW-106(R#3)	NaCl, BaCl2 / Al2O3, Norton SA5551	1.5089,5.033	262,0.000255	1.16	30/60	30-BKW-98C	6/8/88	0.602,3.32	A	5
30-BKW-107(R#4)	NaOH, BaCl2 / Al2O3, Norton SA5551	1.037,5.033	268,0.000255	1.16	30/60	30-BKW-98D	6/8/88	0.602,3.32	A	5
30-BKW-111(R#4)	KOH, BaCl2 / Al2O3, Norton SA5551	1.439,5.033	0026,0.00025	1.16	30/60	30-BKW-98F	6/10/88	1.015,3.5	A	5
30-BKW-110(R#3)	KH2PO4, BaCl2 / Al2O3, Norton SA5551	3.419,5.033	0026,0.00025	1.16	30/60	30-BKW-98G	6/10/88	1.015,3.5	A	5
30-BKW-118(R#3)	NaOH / Al2O3, Norton SA5551	1.037	0.00026	1.16	30/60	30-BKW-98H	6/14/88	0.606	A	5
30-BKW-119(R#4)	ZnCl2 / Al2O3, Norton SA5551	3.419	0.00026	1.16	30/60	30-BKW-98I	6/14/88	1.7	A	5
30-BKW-123(R#3)	Ag / Al2O3, Norton SA5502	9.13		1.14	cylindrical	30-BKW-115	6/16/88	10.05	C	300
31-BKW-9(R#4)	KCl, Ag / Al2O3, Norton SA5502	1.96,9.13	0.000268	1.08	30/60	30-BKW-122A	6/29/88	1.17,10.05	C(*) + A	(*5 g 30-BKW-115)
31-BKW-16(R#3)	LiCl, Ag / Al2O3, Norton SA5502	1.125,9.13	0.000268	1.08	30/60	30-BKW-122B	7/5/88	0.207,10.05	C(*) + A	(*5 g 30-BKW-115)
31-BKW-2(R#4)	BaCl2, Ag / Al2O3, Norton SA5502	5.285,9.13	0.000268	1.08	30/60	30-BKW-122C	6/23/88	4.08,10.05	C(*) + A	(*5 g 30-BKW-115)
31-BKW-1(R#3)	NaCl, Ag / Al2O3, Norton SA5502	1.5438,9.13	0.000268	1.08	30/60	30-BKW-122D	6/23/88	0.686,10.05	C(*) + A	(*5 g 30-BKW-115)
31-BKW-17(R#4)	CsCl, Ag / Al2O3, Norton SA5502	4.319,9.13	0.000268	1.08	30/60	30-BKW-122E	7/15/88	3.96,10.05	C(*) + A	(*5 g 30-BKW-115)
30-BKW-129(R#4)	CaCl2.6H2O / Al2O3, Norton SA5551	5.267	0.000254	1.16	30/60	30-BKW-125A	6/20/88	1.016	A	5
30-BKW-133(R#4)	BaCl2 / Ga2O3	5.033	0.000254	1.25	30/60	30-BKW-125B	6/21/88	3.5	A	5
30-BKW-132(R#3)	NaCl / Ga2O3	1.466	0.000254	1.25	30/60	30-BKW-125C	6/21/88	0.585	A	5
30-BKW-136(R#4)	BaSO4 / Al2O3, Norton SA5502	5.607	0.000254	1.08	30/60	30-BKW-125D	6/22/88	3.5	B	5
30-BKW-134(R#3)	LiBO2 / Al2O3, Norton SA5502	1.244	0.000254	1.08	30/60	30-BKW-125E	6/22/88	0.172	B#1	5
30-BKW-135(R#4)	Li2B4O7 / Al2O3, Norton SA5502	4.123	0.000254	1.08	30/60	30-BKW-125F	6/22/88	0.353	B#1	5
31-BKW-7(R#3)	BaCl2 / Ga2O3	5.033	0.000254	1.25	60/100	30-BKW-125I	6/29/88	3.5	A	5

A.) The loading of the catalyst is expressed as wt.% metal against 100 wt.% support (e.g. Al2O3, Ga2O3).

B.) Mesh size shown refers to the mesh size of the catalyst when prepared and is not necessarily that which was run.

C.) Refer to the Experimental Section and appropriate Appendices for descriptions of preparation procedures in the Catalyst Preparation column.

E.) Grams/cc shown refers to the measured grams/cc of catalyst at the beginning of each run and after catalyst preparation.

Appendix E. CATALYST PREPARATION PROCEDURES FOR BKW LABORATORY

Procedure A

In Procedure A, supported catalysts are prepared using the incipient wetness technique. In this procedure, the amounts of components required to give the desired loading are dissolved in a quantity of deionized, distilled water necessary to just fill the pores of the support. The solution is then added to the support particles. In some cases, if the dopants are not easily soluble, suspensions of the components are added to the support. The resulting material is dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa for 1 to 50 hours (usually 18-20 hours). The dried catalysts are either tested without further treatment or first calcined in air. Metal or inorganic compound loadings are expressed as weight percent based on 100 weight percent of the support.

Procedure A#1 is the same as Procedure A except that two impregnations are used, each with half of the inorganic compound added to the catalyst. Samples are heated for 1 hour at 130 °C between impregnations.

Procedure A#2 is the same as Procedure A except that a phosphoric acid solution or suspension of the metal salt is used in place of water.

Procedure B

In Procedure B, supported catalysts were prepared by adding the proper amount of component(s) to a mixture of water which was stirred with the support, while heating in a glass container on a hotplate for 2 to 3 hours (or until almost no water left), to distribute the material in and on the support. If the dopants were not easily soluble, they were finely ground first. Deionized, distilled water was used (50 mL unless stated otherwise). The resulting material was dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa for 1 to 50 hours (usually 18-20 hours). The dried catalysts were then calcined in air. Metal or inorganic compound loadings are expressed as weight percent based on the weight of the support.

Procedure B#1 is the same as Procedure B except 30 mL of deionized, distilled water were used.

Procedure C

Silver/lactic acid solution preparation method (see Experimental Section).

END

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