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DIRECT CONVERSION OF METHANE TO C_2's AND LIQUID FUELS

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By Barbara Knight Warren; Kenneth D. Campbell; J. L. Matherne

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Union Carbide Chemical and Plastics Company Inc.
South Charleston Technical Center
South Charleston, West Virginia 25303

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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

Research on promoted metal oxide catalysts has continued with the study of alkaline earth/metal oxide halide catalysts. A barium bromide/alumina catalyst was comparable in methane conversion and selectivity to C_2's to barium chloride/alumina catalysts. The effects of varying methane to oxygen feed ratios were explored for one of the best alkaline earth catalysts and one of the best literature catalysts (Li/MgO). The Li/MgO catalyst deactivates faster at 700 °C than the alkaline earth catalyst does at 750 °C. With 81% methane and 4.3% oxygen in the feed gas, a selectivity of 76% to C_2's was observed at 18% methane conversion (oxygen limited) over the alkaline earth catalyst. A significant decrease in the selectivity to C_2's is observed upon addition of ethane to the feed gas (feed gas methane/ethane ratio of 3). This observation demonstrates that a significant amount of ethane should not be recycled during methane oxidation over these types of catalysts under process conditions used. Methane oxidation over barium carbonate alone results in high enough selectivities and methane conversions to suggest an oxidized barium species may be responsible for methane oxidation on barium/metal oxide catalysts.

Methane coupling studies have continued using layered perovskite catalysts in the cofeed mode and double perovskite catalysts in the sequential mode. Physical mixtures of the phases used to make $K_2La_2TiO_3O_{10}$ were observed to be as active and selective for methane coupling as the layered perovskite itself in the cofeed mode. Oxide solid solutions of praseodymium and cerium have been prepared for testing as methane coupling catalysts.

Addition of sodium to the double perovskite $LaCaMnCoO_6$ resulted in a catalyst with improved selectivity over the one without sodium. This Na-doped layered perovskite exhibits a loss of selectivity and conversion with time on-stream in the sequential mode of operation. This behavior differs from that of the $Mn/Na_4P_2O_7/SiO_2$ ARCO catalyst and other literature catalysts, which exhibit increases in selectivity to C_2's as catalyst activity falls.

A reactor system containing two reactors is under construction. These reactors will be used to study different feed diluents, including steam. One reactor will be used to study the effects of pressure on the reaction.

Process economics were explored for a hypothetical methane coupling scheme employing a feed mixture of 7/2/1 nitrogen/methane/oxygen. An absorber/stripper separation system was considered because its relatively low operating pressure minimizes

the load on the compression system. However, the huge solvent cycle flow rates and refrigeration loads indicate that this separation system is impractical for the methane coupling application.

The total fixed investment for a unit producing one billion pounds per year of ethylene using the process scheme used for Case 1[4] is $343MM at an ethylene/ethane production ratio of 1 [24% return on investment (ROI)] and $453MM at a production ratio of 10 (33% ROI).

Economic evaluations of the first two of a series of cases based on extrapolations of Union Carbide methane coupling results have been completed. The process schemes used are considered more realistic, achievable, and generally applicable to future methane coupling results than those used for the original Case 1[4].

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 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, methane coupling research on promoted metal oxide catalysts has continued with the study of alkaline earth/metal oxide catalysts. Bromide was studied in place of chloride for alkaline earth/halide/metal oxide catalysts. The effects of varying the methane to oxygen feed ratios were compared for one of the best alkaline earth catalysts and one of the best literature catalysts (Li/MgO). Research on catalysts designed to contain activated metals and other novel catalysts and process ideas has continued with tests of complex and mixed metal oxides of particular structures, including layered perovskites (in the cofeed mode), double perovskites (in the sequential mode), and the study of solid oxide solutions containing praseodymium and cerium. A reactor system containing two reactors is under construction. These reactors will be used to study different feed diluents, including steam. One reactor will be used to study the effects of pressure on the reaction.

During the last few months of the contract, the methane to C_2's step will be integrated with C_2's to fuels step. In addition, the use of a synthetic feed similar in composition to a typical processed natural gas mixture 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 was completed to provide process performance targets (the minimum productivity and selectivity necessary) which any new catalyst must meet to be economically attractive. The economic evaluation of a hypothetical methane to ethylene case (Case 1) was reported last quarter. Sensitivity studies of process variables on Case 1 are continuing. Results from process configuration studies and economic sensitivity analyses shall be used to establish catalyst performance targets such as desirable ranges for conversions, selectivities, pressures, and temperatures. Economic evaluation of the conversion of methane to C_2's then conversion of the C_2's to liquid fuels (Case 2) will identify promising process configurations, define catalyst performance criteria, and provide information to assist in designing catalysts and test reactors.

During the last year of Task 2, catalysts or systems identified in Task 1 as having the most potential shall be evaluated. 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 eighth quarter of the two-year contract.

During the first 15 months of the contract, the catalyst design, preparation, testing, and performance evaluation work under Task 1 was 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 and site services (maintenance) personnel. During the last 9 months of the contract, the catalyst design, preparation, testing and evaluation work was planned to be conducted by 1.3 full-time catalyst chemists and 1.5 full-time laboratory technicians. A third catalyst chemist and a third laboratory technician have joined the project and are pursuing process research on methane coupling.

Three engineers are involved in Task 2. Two of these are concerned mainly with process conceptualization, process integration, economic guidance, and input into the laboratory program on hydrocarbons, separations, equipment, and thermodynamics. The third is concerned with engineering assistance in the design of catalysts and reactor configurations, and in catalyst testing and interpretation of results. Thirteen man months of engineering support were planned for the duration of the contract. This includes economic evaluation of the most promising catalysts, continued support for catalyst testing, and assistance in writing the final report.

IV. ORGANIZATION

Union Carbide's 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. During the initial portion of the contract, this group was part of the Engineering, Manufacturing and Technology Services Division.

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

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.

Research on promoted metal oxide catalysts has continued with the study of alkaline earth/metal oxide halide catalysts. A barium bromide/alumina catalyst was comparable in methane conversion and selectivity to C_2's to barium chloride/alumina catalysts. The effects of varying methane to oxygen feed ratios were explored for one of the best alkaline earth catalysts and one of the best literature catalysts (Li/MgO). The Li/MgO catalyst deactivates faster at 700 °C than the alkaline earth catalyst does at 750 °C. With 81% methane and 4.3% oxygen in the feed gas, a selectivity of 76% to C_2's was observed at 18% methane conversion (oxygen limited) over the alkaline earth catalyst. A significant decrease in the selectivity to C_2's is observed upon addition of ethane to the feed gas (feed gas methane/ethane ratio of 3). This observation demonstrates that a significant amount of ethane should not be recycled during methane oxidation over these types of catalysts under process conditions used. Methane oxidation over barium carbonate alone results in high enough selectivities and methane conversions to suggest an oxidized barium species may be responsible for methane oxidation on barium/metal oxide catalysts.

Methane coupling studies have continued using layered perovskites in the cofeed mode and double perovskites in the sequential mode. The $Mn/Na_4P_2O_7/SiO_2$ ARCO catalyst exhibits a different activity pattern than a Na-doped layered perovskite containing La, Ca, Mn, and Co. Oxide solid solutions of praseodymium and cerium have been prepared for use as methane coupling catalysts.

A reactor system containing two reactors is under construction. These reactors will be used to study different feed diluents, including steam. One reactor will be used to study the effects of pressure on the reaction.

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.

The Comparison Case consists of conversion of methane to synthesis gas, synthesis gas to methanol, and methanol to liquid fuels via olefins. The economic evaluations of the Comparison Case and of Case 1 (a hypothetical methane to ethylene case) were reported last quarter. Process economics were explored for a hypothetical methane coupling scheme employing a feed mixture of 7/2/1 nitrogen/methane/oxygen. An absorber/stripper separation system was considered because its relatively low operating pressure, which minimizes the load on the compression system. However, the huge solvent cycle flow rates and refrigeration loads indicate that this separation system is impractical for the methane coupling application.

The total fixed investment for a unit producing one billion pounds per year of ethylene using the process scheme used for Case 1[4] is $343MM at an ethylene/ethane production ratio of 1 [24% return on investment (ROI)] and $453MM at a production ratio of 10 (33% ROI).

Economic evaluations of the first two of a series of cases based on extrapolations of Union Carbide results have been completed. The process schemes used are considered more realistic, achievable, and generally applicable to future methane coupling results than those used for the original Case 1.[4] 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. Work to support the experimental program has continued through regular meetings and follow-up work of the chemists and engineers in which experimental problems and possibilities are explored.

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 designed to possess metals in unusual oxidation states or energies, and new catalyst and process concepts.

In the next quarters, the plan for Task 2 is to explore additional cases for direct coupling of methane to C_2's, including actual laboratory results, and to explore additional economic sensitivity studies. The economics of Case 2, the conversion of methane to C_2's by oxidative methane coupling followed by the conversion of the C_2's to liquid hydrocarbon fuels, will be studied. Support of the experimental program will continue through regular meetings of engineers and chemists.

VII. TECHNICAL AND EXPERIMENTAL RESULTS

By B. K. Warren, K. D. Campbell, and J. L. Matherne

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VII. TECHNICAL AND EXPERIMENTAL RESULTS

TASK 1: Catalyst Design and Testing

INTRODUCTION:

Background

The mechanism proposed for the catalytic oxidative coupling of methane[5-13] over metal oxides studied was discussed in previous Quarterly Reports and will be reviewed briefly here. It 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 reviewed 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[14]. Others[15,16] have proposed a yield barrier closer to 30%. 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.

Literature reports contain no data which indicates that the catalysts studied give stable, long-term performance. Rapid deactivation is shown in most cases. Recently, one catalyst was reported to run for over 100 hours with about a 14% C_2 yield[17], but this yield is considered low, since there are many literature yields in the 18% yield range. A few metal oxide catalysts which are less volatile (e.g., Sm_2O_3)[18] 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.

The use of halides either as ingredients in methane coupling catalysts or as feed gas additives during the coupling process has become a topic of interest in recent literature. The literature and patent data relevant to halide addition, along with the conclusions presented by these sources, are summarized in Appendix G of the Fifth Quarterly Report[4].

The reasoning for the use of halides is described in the Third[19], Fourth [20], and Fifth[4] Quarterly Reports. In these reports, stable catalyst systems were reported which exhibit high ethylene to ethane product ratios in the presence of optimum levels of added volatile chloride. Halide addition was shown[4,20] to increase C_2 selectivity and C_2 yield through increases in the rates to C_2 products and a decrease in the rate to CO_2. Reported literature results with high ethylene to ethane product ratios are transient results (see Appendix G of the Fifth Quarterly Report[4]).

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. Catalysts which might provide high (greater than 1) ethylene to ethane product ratios were of particular interest. Studies began with the exploration of a very simple NaCl on α-alumina catalyst (First[21] and Second[22] Quarterly Reports) and proceeded in the following Quarterly Reports[4,19,20] to alkaline earth chloride/metal oxide catalysts, which were shown to be less likely to contain volatile catalyst components than alkali chlorides/metal oxide catalysts. These alkaline earth chloride/metal oxide catalysts were shown[4,19,20,22,23] to exhibit superior combinations of C_2 yields (18-24%), ethylene to ethane product ratios (2-10), and catalyst lifetimes (hundreds of hours) compared to literature catalysts.

Exploration of alkaline earth/metal oxide catalysts and other metal/metal oxide catalysts continued, both to understand what is unique about alkaline earth chloride/metal oxide catalysts, as well as to provide improved versions of these catalysts. Studies last quarter[4] emphasized studies of catalyst stability, the determination of which catalyst components are necessary for the high ethylene to ethane product ratios, non-chloride anions, and the possibility of using non-group IA or IIA metals.

In methane coupling reactions in the cofeed mode, alkaline earth carbonate/metal oxide catalysts were found to exhibit longer periods of stable performance at higher methane conversions than similar alkaline earth chloride catalysts under comparable conditions[4]. Higher ethylene to ethane product ratios result from alkaline earth carbonate catalysts prepared with titanium oxide or gallium oxide than from similar catalysts prepared with alumina.

It was concluded[4] that Union Carbide has developed catalysts which are comparable in selectivity, activity, and C_2 yield to the better literature catalysts, but the Union Carbide catalysts exhibit higher ethylene to ethane product ratios and longer catalyst lifetimes than have been previously reported. As an example, after over 350 hours of methane coupling with a 5 weight percent barium carbonate on titanium dioxide catalyst (with ethyl chloride in the feed gas), a C_2 yield of 22%, a C_2 selectivity of 58%, and an ethylene to ethane product ratio of 8 are obtained[4].

Ethane was of interest as an additive to methane coupling reactions, because it is a major product of the reaction, and some ethane might need to be recycled in a methane coupling process. The possibility of using a methane coupling catalyst to convert ethane to ethylene (perhaps at lower temperatures) is also of interest.

The layered perovskite, $K_2La_2Ti_3O_{10}$, identified in the Third Quarterly Report[19] as a good methane coupling catalyst was further studied. Studies examined the effects of adding alkali dopants and substituting other lanthanides in the structure. Also, the methane coupling abilities of components used to prepare the perovskite and physical mixtures of the components were measured.

Effects of changing the partial pressures of the reactants by adding more diluent gas were observed and the importance of crystalline phases in methane coupling catalysts was studied using lithium metasilicate and lithium orthosilicate.

Sequential methane coupling studies were initiated last quarter[4]. In continued studies, a Mn/$Na_4P_2O_7$/silica literature catalyst[24] was examined to compare its performance with a Na_2CO_3/$LaCaMnCoO_6$ catalyst. The effects of using K_2CO_3 instead of Na_2CO_3 as dopant were also examined.

Oxygen carriers consisting of oxide solid solutions of praseodymium and cerium were tested as methane coupling catalysts in the cofeed mode.

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 is done in the KDC laboratory. Codes including BKW indicate that work is done in the BKW laboratory. The laboratory reactor systems are illustrated in Figure 1 of the Second Quarterly Report[22] and in Figure 4 of the Fourth Quarterly Report[20], 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[22].

Linde oxygen, nitrogen, air, and ultra high-purity methane are 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.

The reactor systems 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. Reactions coded with BKW are run at about 11 psig (176 kPa). Reactions coded with KDC are usually run at 5 psig (135 kPa).

In both laboratories, the gas mixtures entering and exiting the reactor system are analyzed by gas chromatographic methods (vpc) using Hewlett-Packard Model HP-5880A gas chromatographs equipped with thermal conductivity detectors. Ultrapure helium is used for vpc analyses. Calibrations are done in the HP ESTD mode using calibration gases (Tables 5 and 9 of the Second Quarterly Report[22]) prepared by Union Carbide's Automated Analytical Services group. Injections of calibration gases, product streams, and reactant streams are 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[22]. In both laboratories, the components analyzed include methane, oxygen, nitrogen, ethane, ethylene, propane, propene, carbon monoxide, and carbon dioxide. Analyses for C_4's is not necessarily carried out unless there are large amounts of C_3's. Carbon balance calculations indicate that other hydrocarbon products and oxygenates are not present in significant quantities; thus, analyses of heavier hydrocarbons and oxygenates are 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 are used as read from the vpc. The numbers as read from the vpc for product components are 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 are used.

Pore size distributions were measured by the BET method with a Micromeritics ASAP-2400 instrument. Analyses of percentages of various elements were accomplished by ICP.

BKW Laboratory

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

Catalyst compositions are described in Appendix D. For those catalysts prepared from adding components, these are generally high purity (99.99+) components added by Procedure A, Procedure B, or a variation on Procedure B, described in Appendix E. 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). Most dried catalysts are tested without further treatment. A few are 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 hot plate 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).

BaCO3 tested was obtained from AESAR, 99.99+% and prepared by Procedure P of Appendix E.

Catalysts derived from hydrotalcites were prepared as described in Procedure R of Appendix E.

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.

All experiments this quarter in the BKW laboratory are done in the cofeed mode where methane and oxygen are simultaneously fed. In all cases, 10% methane and 5% oxygen are fed. The balance gas is nitrogen, and in some cases, ethyl chloride is fed in parts per million (from a mixed gas with methane). 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) are 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 a high temperature ceramic fiber insulation, and a helically coiled alloy heating element. The furnaces are equipped with a chromel-alumel (type K) thermocouple (centrally positioned within the heated region) which is 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 are 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, are used in parallel for each reactor so that one cold trap can be removed and sampled while the other one is collecting product. These traps are located after the reactor outlet (after the low flow switches) and before the reactor back pressure regulator. Another trap is present in the line after the back pressure regulator. This third trap is not cooled.

Compounds which are not trapped are 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 are used for the analyses. Details of the analytical procedures may be found in the Experimental Section, Tables, and Figures of the Second Quarterly Report [22]. Feed streams are periodically analyzed before, during, and after runs. Analyses of trapped liquids by gc-ms indicate only water. The water is acidic (<pH 3) by litmus paper. By ir, traces of carbonyls are 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 are calibrated in place. Quartz tubing used in the construction of reactors is obtained from National Scientific Company.

The only reactor used in the BKW laboratory this quarter was shown in Figure 3 of the Third Quarterly Report[19], and described in the Experimental Section of the Third[19] (and Fourth[20] and Fifth[4]) Quarterly Reports. Reactor D is operated vertically as shown for another reactor in Figure 5 of the Second Quarterly Report[22]. 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. There is a significant temperature drop from the catalyst bed to the bottom of the reactor.

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

The reactors are filled with washed quartz chips above and below the catalyst bed. Tubing of 0.3 cm i. d. in Reactor D is not filled with quartz. Quartz wool is used to separate quartz chips from the catalyst bed and to hold quartz chips in the reactor. Undiluted catalysts of varying mesh sizes are used except in cases where the catalyst is only available as a fine powder. In these cases, it is diluted with quartz chips.

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

KDC Laboratory

Substances tested for catalytic methane coupling activities this quarter included mixed and complex metal oxides, supported metal oxides, Pr-Ce oxides solid solutions, and literature catalysts.

Mixed and complex metal oxide catalysts, such as $A_2Ln_2Ti_3O_{10}$ layered perovskites, were prepared using a high temperature migration technique. The double perovskite, $LaCaMnCoO_6$, was prepared using a "liquid mix - citrate" technique.

In the high temperature migration technique[25], 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 6 to 24 hours depending on the oxide being prepared. 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.

In the liquid mix - citrate procedure used to prepare $LaCaMnCoO_6$[26], mixtures of $La(NO_3)_3$, $Co(NO_3)_2$, $MnCO_3$, and $CaCO_3$ having the correct stoichiometric ratios of metals were ground to fine powders and dissolved in saturated citric acid solution. Ethylene glycol was added to the citric solution (3%, v/v) and the solution was evaporated with constant stirring until a thick black syrup remained. This material was heated in air at 450 °C for 16 h to eliminate the organic material, then calcined in air at 550 °C (16 h) and 1000 °C (8 h). The resulting material was a homogeneous, dark powder.

Literature catalysts reported by Union Carbide as oxygen carriers[27], Pr-Ce oxides solid solution and Ag-Pr-Ce oxides solid solution, were prepared using a coprecipitation method. In the method, two aqueous solutions were used. Solution one consisted of nitrates of praseodymium, cerium, and silver (if desired) in amounts needed to give the desired composition. Solution two contained ammonium carbonate in an amount sufficient to precipitate all the metals as carbonates. Solution one was then added dropwise to solution two with continuous stirring. The precipitate was separated by filtration and washed with deionized water. The solid was then dried in a vacuum oven at 110-130 °C and calcined at 750 °C for 2 hours.

Alkali doping of the layered perovskites, double perovskite, and Pr-Ce oxide solid solutions was performed using a slurry technique. In the slurry technique, the required amounts of constituents needed to give the desired composition were added to 100-150 cc of distilled water. The mixture was evaporated with constant stirring until a thick slurry (paste) resulted. The paste was then dried in a vacuum oven at 110-130 °C. The alkali doped layered perovskites and double perovskite were calcined before testing at 800 °C for 12-24 hours. The alkali doped Pr-Ce oxide solid solutions were calcined before testing at 800 °C for 2 hours.

Physical mixtures of K_2CO_3 - La_2O_3 and K_2CO_3 - La_2O_3 - TiO_2 were prepared using the slurry technique without the calcination step.

Barium and strontium doped MgO were prepared by the slurry technique using a methanol/water mixture (11:1 volumetric ratio) as the dissolving media. Ion exchanging of Ba and Sr on MgO was carried out using the same solvent. In the ion-exchange process, the MgO was mixed with the methanol/water solution containing the Ba or Sr for 2 hours and then filtered and washed with methanol. Materials were dried in a vacuum oven at 100-130 °C and calcined at 800 °C for 12-18 hours.

A literature catalyst reported by ARCO[24], $Mn/Na_4P_2O_7$/silica, was prepared using an incipient wetness technique. In the incipient wetness procedure, the amounts of manganese acetate, $Mn(C_2H_3O_2)_2$, and sodium pyrophosphate, $Na_4P_2O_7$, required to give the desired metal and phosphorus loadings was dissolved in a quantity of distilled water necessary to just wet the silica (fill the void volume of the support). The silica was then added to the solution and thoroughly mixed to insure even wetting. The resulting material was dried in a vacuum oven at 110-130 °C overnight and then calcined at 800 °C for 16 hours.

Quartz reactors were used for all of the work this quarter in the KDC laboratory. These include Reactor A (Figure 5 of the Second Quarterly Report[22]), Reactor B (described in the Experimental Section of the Third Quarterly Report[19]), Reactor F (Figure 5 of the Fourth Quarterly Report[20]), Reactor G (Figure C1 of the Fifth Quarterly Report[4]), and Reactor H (Figure C2 of the Fifth Quarterly Report[4]). Reactors A, B, and F were used in the cofeed mode studies. Reactors G and H were used for sequential mode (pulse) studies.

Reactor B was used for most of the cofeed studies carried out in the KDC laboratory this quarter. It was constructed of 1.5 cm i.d. quartz tubing (1.7 cm o.d.) with a thermocouple well positioned along the center of the reactor of 3 mm i.d. quartz tubing (0.5 cm o.d.) enlarging to 1.3 cm o.d. at the outlet end (26.7 cm) of the thermocouple well. All quartz tubing used in the construction of the reactor was obtained from National Scientific Company. The thermocouple well extends through the catalyst bed (into the preheater region) which allows the temperatures of the preheater, catalyst bed and post-catalyst region to be monitored. The reactor had a length of 55.9 cm and the thermocouple well extended 33.0 cm into the reactor. The ends of the reactor are made up of quartz "O"-ring joints (1.5 cm i.d. at inlet ; 0.9 cm i.d. at outlet) which allows easy placement of the reactor in the system. The joints were connected using FETFE "O"-rings obtained from Ace Glass Incorporated. The "O"-ring joints were supplied by Quartz Scientific Inc.

The 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 either a solid 1.3 cm o.d. quartz rod with 20 to 40 mesh washed quartz chips around the outside or 20 to 40 mesh washed quartz chips (preheater region).

Other cofeed 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 - 5.00 grams of catalyst. For some experiments the catalyst was 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.

In cofeed studies, charged reactors were flushed with nitrogen during heating. The reactor temperature was raised to 450-500 °C and the catalyst was usually 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 timed 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.

Reaction conditions used for catalytic cofeed runs included:

temperature	200 - 850 °C
reactant flow rate	25 - 250 cc/min
weight of catalyst	0.25 - 30.00 grams
methane	5 - 90 molar%
methane/oxygen molar ratio	1.1 - 10
water	0 %
nitrogen	balance

Sequential mode studies were performed using one of the KDC reactor units modified such that product gases exiting the reactor could be collected in gas bags. In a typical sequential experiment, Reactor G or H was charged with catalyst by adding quartz wool, catalyst, quartz wool, and 20 to 40 mesh washed quartz chips (preheater region).

Reaction conditions used for catalytic sequential runs included:

temperature	700 - 900 °C
conditioning air flow rate	100 - 250 cc/min
conditioning time	1 - 2 hours
methane flow rate	50 - 150 cc/min
weight of catalyst	2 - 20 grams
product collection times	0 - 3 min 0 - 2, 2 - 5, and 5 - 10 min

Charged reactors were flushed with air while the reactor temperature was raised to the desired value. Then, the catalyst was conditioned with flowing air (100-250 cc/min) for 1-2 hours. After conditioning the air flow was stopped and the reactor was flushed with nitrogen. Nitrogen flow was stopped, methane flow was initiated, and samples of gaseous product were collected immediately after exiting the reactor using gas sampling bags. The product samples were obtained during timed intervals. The reactor was then flushed with nitrogen, the reactor temperature was set to the desired value, the catalyst was conditioned with air, and the process was repeated. Collected samples were analyzed using the same GC analysis employed for the cofeed studies. After the experiment, the reactor was flushed with nitrogen while cooling. The reactor was cleaned between experiments by thoroughly rinsing with acid followed by distilled water.

In the KDC laboratory, oxygen conversions show a maximum of 95 to 96% due to the presence of argon in the feed air. The argon and oxygen components are not separated in the GC separation scheme. Carbon balance calculations indicate that other hydrocarbon products are not present in significant quantities; thus, analyses for heavier hydrocarbons and oxygenates are not performed during these screening experiments.

RESULTS AND DISCUSSION:

BKW Laboratory

Alkaline Earth Catalysts on Non-Alumina Supports

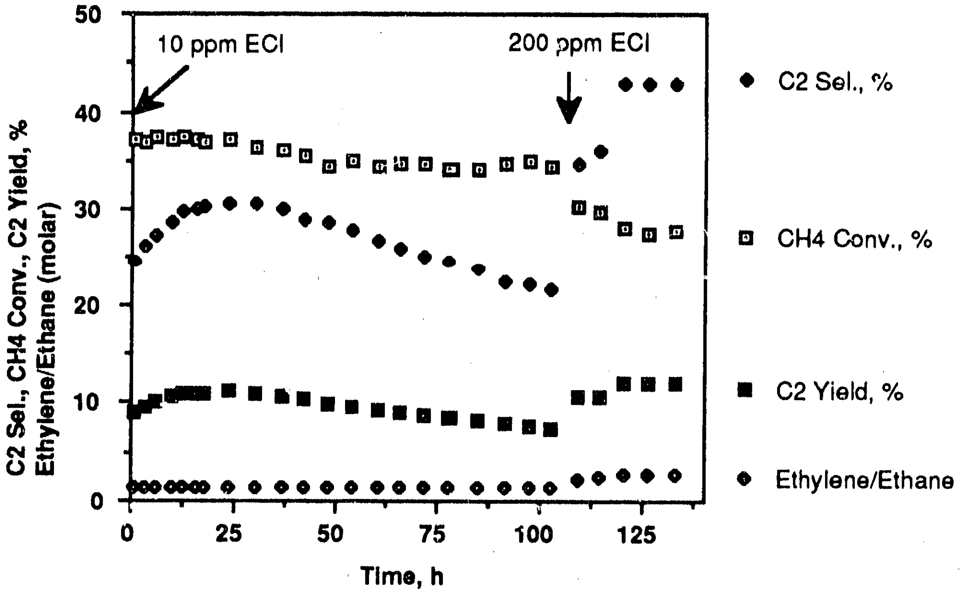
In the Fourth[20] and Fifth[4] Quarterly Reports, catalysts were described which produce high ethylene to ethane ratios during methane oxidation, and which are stable in the presence of an optimum amount of added volatile chloride (which depends upon the catalyst and the process conditions). High ethylene to ethane ratios were not obtained under conditions used with catalysts prepared using basic supports, such as MgO. For high C_2 yields, catalysts prepared with the more acidic supports required more volatile chloride than catalysts prepared with less acidic types of α-alumina (see the Fourth Quarterly Report[20]). Since catalysts with acidic supports exhibited higher ethylene to ethane product ratios, catalysts prepared with other, more acidic supports were of interest. Results from three of these are presented in Table B1 of Appendix B.

Catalysts prepared from barium chloride and silica and barium carbonate alone were prepared and tested as reported in the Fifth Quarterly Report[4]. Yields to C_2's were very low with these catalysts, but ethyl chloride in the feed gas was not present in concentrations higher than 10 ppm. The initial C_2 yield (after 30 minutes of reaction) for reaction 32-BKW-110 ($BaCl_2/SiO_2$, Table B3 of the Fifth Quarterly Report[4]) was 11.3%, with a C_2 selectivity of 27%. The selectivity dropped to 6% and the C_2 yield dropped to 1.7% after 5 1/2 hours on-stream. It was thought that yields might be higher if higher levels of ethyl chloride were added to the feed gas, since a $BaCO_3/TiO_2$ catalyst exhibited C_2 yields of 18-22% with 250 and 500 ppm ethyl chloride (see Table B2 and Figure C17 of the Fifth Quarterly Report[4]). The used catalyst from reaction 32-BKW-110 ($BaCl_2/SiO_2$, Table B3 of the Fifth Quarterly Report[4]) was retested with 200 ppm ethyl chloride in the feed gas. A selectivity to C_2's over 14% was not observed, and although the initial C_2 yield was 5%, it dropped to 0.5% after 90 hours of reaction (750 °C, 2217 h^{-1} GHSV).

Gamma-alumina was also used for the preparation of one catalyst. Barium carbonate, rather than barium chloride was used. At 650 °C and a space velocity of 6000 h^{-1}, carbon dioxide and carbon monoxide were the only significant products observed. Levels of both 10 and 200 ppm ethyl chloride were used in the feed gas (see Table B1 of Appendix B).

It was reported that initial ethylene to ethane ratios of 4 ($BaCl_2/ZrO_2$, 30-BKW-86, Table 5 of the Third Quarterly Report[19]) and 15 ($CaCl_2/ZrO_2$, 31-BKW-21, Table 9 of the Fourth Quarterly Report[20]) could be obtained at 750 °C and space velocities of 1000-1200 h^{-1} with alkaline earth/ZrO_2 catalysts. Ethyl chloride levels of greater than 50 ppm were not used to test these catalysts. Although chloride catalysts showed initially high ethylene to ethane ratios, catalysts prepared from both alkaline earth carbonates and alkaline earth chlorides on the same support, showed similar ethylene to ethane ratios after they had been run until results were constant. Catalysts prepared from carbonates generally exhibited higher lined-out activities, under similar conditions (see the Fourth[20] and Fifth Quarterly Reports[4]). A $BaCO_3/ZrO_2$ catalyst was tested with 10 and 200 ppm ethyl chloride at 750 °C and 5053 h^{-1} GHSV. Ethylene to ethane ratios over 3 were not observed. After over 120 hours of reaction (over 30 with 200 ppm ethyl chloride), the C_2 yield was 12% with a C_2 selectivity of 42%. Figure 2 shows that the C_2 selectivity and C_2 yield are relatively stable with 200 ppm ethyl chloride in the feed gas, and higher levels of chloride could result in increased selectivity and C_2 yields.

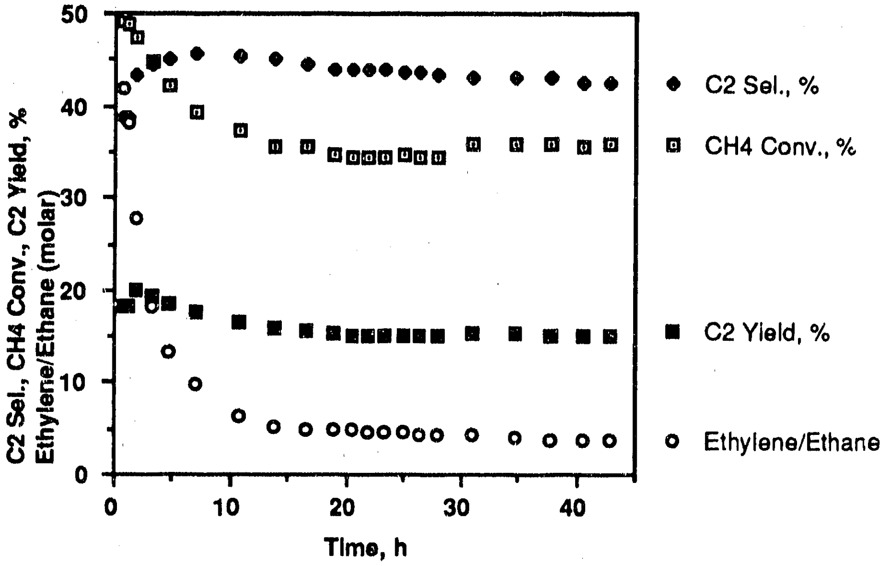
Figure 2. **$BaCO_3/ZrO_2$, 32-BKW-128**



Non-Chloride Halides

Methane coupling results with bromide or fluoride, rather than chloride as catalyst component and/or volatile halide additive, are summarized in Table B2 of Appendix B. Figure 3 shows the results of methane oxidation with a $BaBr_2/Al_2O_3$ catalyst at 750 °C and a space velocity of 2087 $h^{-1.}$ The first two data points on Figure 3 were with a space velocity of $1043h^{-1}$ where the reaction was oxygen limited.

Figure 3. $BaBr_2/Al_2O_3$, 32-BKW-122



The C_2 yield and C_2 selectivity line out to fairly constant values, where they remain for over 30 hours. These results may be compared with those presented in Figure 12 of the Fourth Quarterly Report[20], where a $BaCl_2/Al_2O_3$ catalyst using the same support is tested (also without added volatile halide and at 750 °C, but at a much lower space velocity). For the $BaBr_2/Al_2O_3$ catalyst, the initial ethylene to ethane ratios are among the highest observed (see Table B2 of Appendix B). The lined-out ethylene to ethane product ratios for the space velocity and temperature used are higher than those typically observed for barium catalysts on most alumina supports, with or without added volatile chloride (e.g., see 32-BKW-63 in Table B1 of the Fifth Quarterly Report[4]).

The maximum C_2 selectivity observed was 23% and the maximum C_2 yield observed was 8.5% for a BaF_2/Al_2O_3 catalyst at 750 °C and 1067 GHSV (Table B2 of Appendix B, either 0 or 10 ppm ethyl chloride), indicating that alkaline earth fluoride catalysts are inferior to chloride and bromide catalysts for methane coupling.

Ethyl bromide (EBr) was used in the feed gas in reactions 32-BKW-66, ($BaCl_2/Al_2O_3$ catalyst) and 32-BKW-67 ($BaCO_3/Al_2O_3$ catalyst). Both catalysts were tested at 750 °C with space velocities of slightly over 2000 h^{-1} (Table B2 of Appendix B). Results are shown in Figures 4 and 5.

Figure 4. $BaCl_2/Al_2O_3$, 33-BKW-66

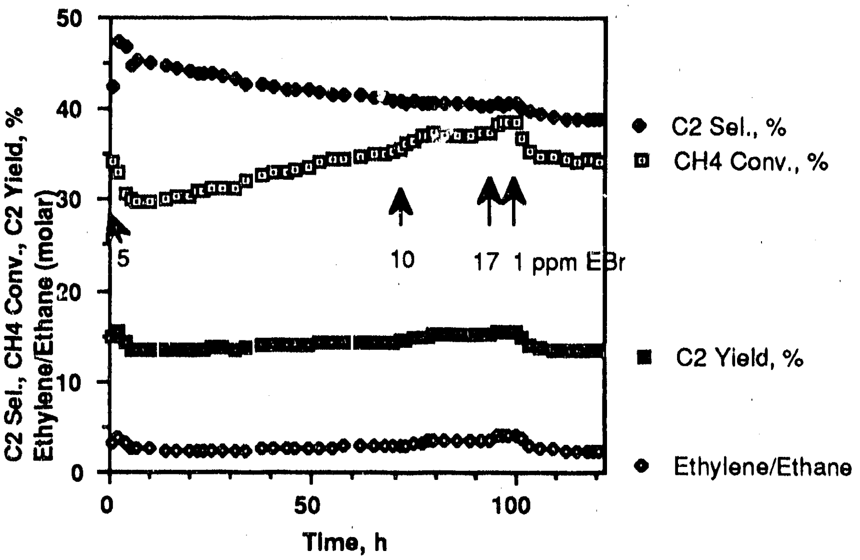
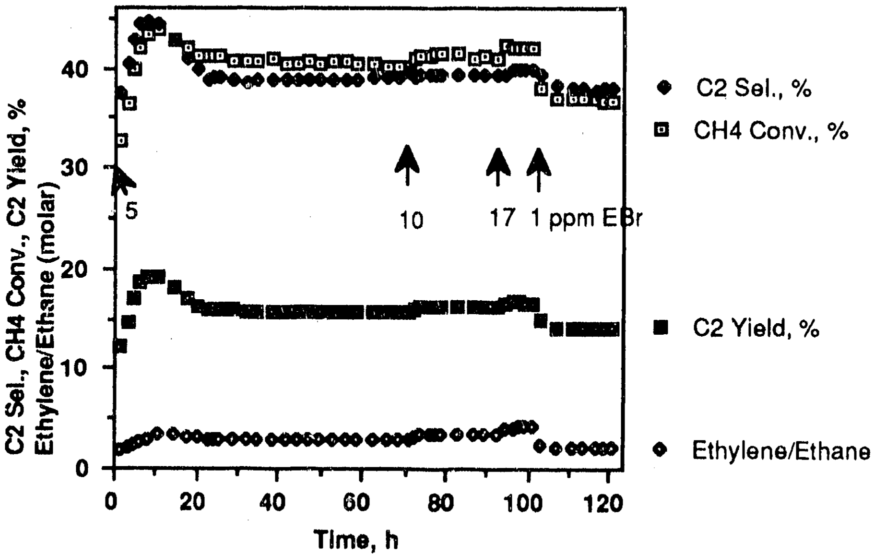


Figure 5. $BaCO_3/Al_2O_3$, 33-BKW-67



Four different, low levels of ethyl bromide were used, and catalyst performance did not change much when the ethyl bromide level was changed. The carbonate catalyst was observed to undergo a period of activation. The maximum C_2 selectivity, C_2 yield, methane conversion, and ethylene to ethane product ratio were observed after 10 hours. The performance of both catalysts then lined out with similar C_2 selectivities, C_2 yields, methane conversions, and ethylene to ethane ratios.

Comparative Examples

Table B3 of Appendix B presents results from comparative examples with one of the best reported literature catalysts[5-8,10]. Two Li/MgO catalysts were prepared using Li_2CO_3. The catalyst used for reaction 32-BKW-135 was the same as the one used for 32-BKW-134, except that the catalyst for 32-BKW-135 was heated at 850 °C in air for 2 hours, and the catalyst for 32-BKW-134 was heated in air for 600 °C for 12 hours. The surface area of the catalyst heated at 850 °C was 1.6 m^2/g before reaction, whereas the surface area of the catalyst for 32-BKW-134, heated only to 600 °C was 32.7 m^2/g. After reaction, the catalyst used in reaction 32-BKW-134 had a surface area of 0.98 m^2/g, and the catalyst used for reaction 32-BKW-135 had a surface area of 1.18 m^2/g. The rate of methane conversion in the catalyst with the higher surface area, for 32-BKW-134, was higher initially but it dropped to a level comparable to that of the catalyst in 32-BKW-135 after a few hours (see Figures 6 and 7 below).

Although the pattern of reactivity for both catalysts with process changes was similar (see Figures 5 and 6, and see Table B1 of Appendix B for process changes in these two figures), the catalyst for reaction 32-BKW-135 was slightly more selective in forming C_2's, and it deactivated at a slightly lower rate after the first few hours of reaction. One gram of catalyst was tested in both cases, but the catalyst heated at 850 °C was twice as dense, therefore, although the same flow rates are used in experiments, the space velocities in 32-BKW-135 are twice those in 32-BKW-134.

Figure 6. Li_2CO_3/MgO, 32-BKW-134

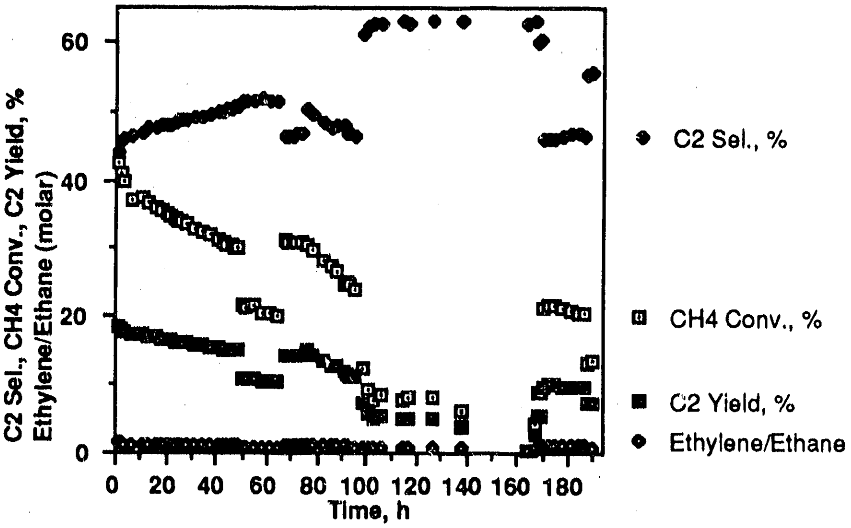
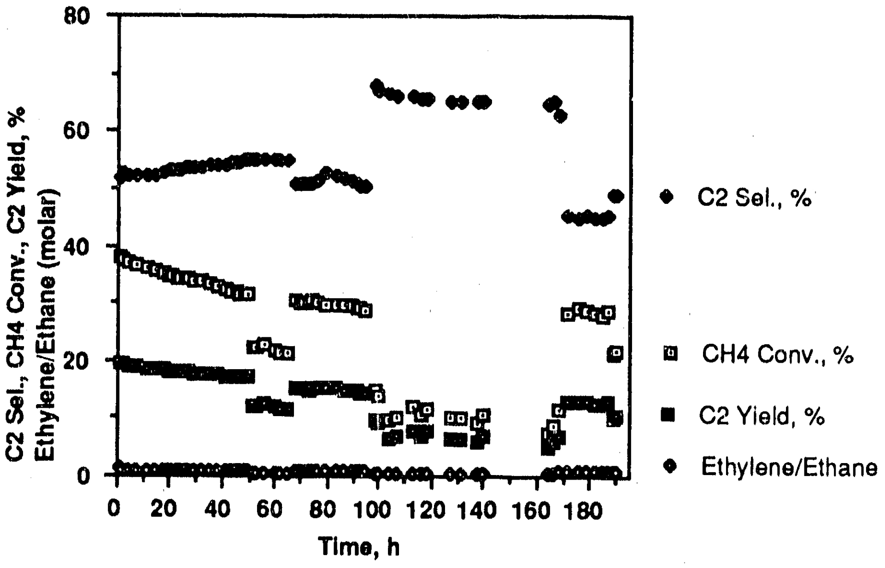


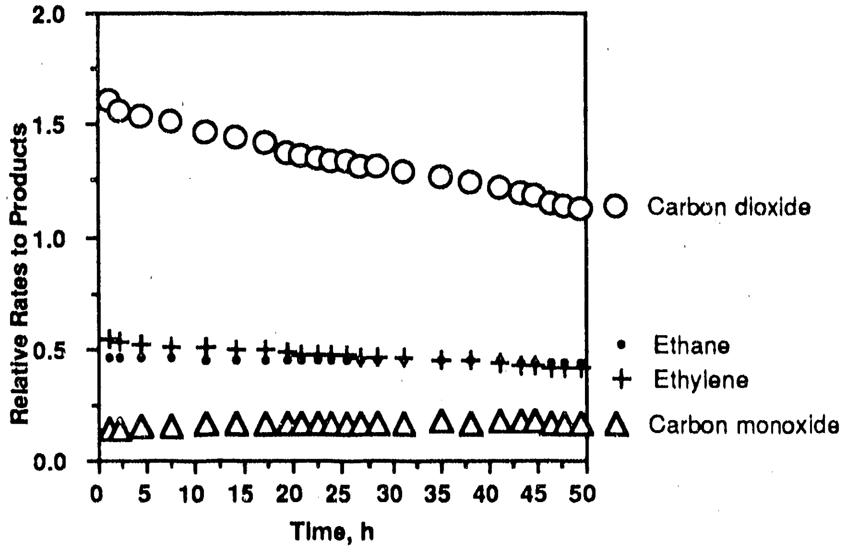
Figure 7. Li_2CO_3/MgO, 32-BKW-135



Methane conversion in Figure 7 is observed to drop rapidly during the first fifty hours of reaction, mainly due to a drop in the rate to CO_2. The C_2 yield drops 12% during this time period, predominately due to the drop in rate to ethylene, as shown in

Figure 8. The rate to ethane remains fairly constant during the first fifty hours of this reaction. The rate to CO rises slightly.

Figure 8. Li_2CO_3/MgO, 32-BKW-135



The addition of 10 ppm of ethyl chloride to reaction 32-BKW-135 at 74.1 h (4445 m) resulted in no significant changes in methane conversion, C_2 selectivity, C_2 yield, or the ethylene to ethane product ratio (Table B3 of Appendix B). In reaction 31-BKW-87 (Table 10 of the Fourth Quarterly Report[20]), addition of 500 ppm ethyl chloride to a LiCl/MgO catalyst resulted in a significant drop in methane conversion (26 to 11%) which rose upon removal of ethyl chloride from the feed gas (to 20%). This indicates that ethyl chloride in the feed gas may be absent under optimum conditions for a Li/MgO catalyst, whereas it is required for optimum catalyst performance in the alkaline earth/acidic metal oxide catalysts.

Both $LiCO_3$/MgO catalysts lost lithium during the reaction. The catalyst for reaction 32-BKW-134 had 2.5% lithium prior to reaction, and 1.1% lithium after reaction. The catalyst for 32-BKW-135 had 2.2% lithium before reaction and 1.6% lithium after reaction. In contrast, the catalyst used for the long reaction 33-BKW-74 (Table B4 of Appendix B) did not lose a significant amount of barium in the reaction, even though the reaction was conducted at higher temperatures. It contained 3.1% barium before and after reaction.

Although optimum conditions for the Li/MgO catalysts are not the same as those for the alkaline earth/metal oxide/Cl catalysts, (Li/MgO catalysts lose lithium rapidly at temperatures above 720 °C and require no added chloride), Table 1 below shows for different methane to oxygen ratios that a Li/MgO (33-BKW-135, Table B3 of Appendix B) catalyst is more active than barium/α-alumina catalysts 33-BKW-7 and 33-BKW-74 (Table B4 of Appendix B), but selectivities and activities for the two types of catalysts are similar, with similar maximum C_2 yields.

Table 1. Different Methane to Oxygen Ratios for $BaCO_3/Al_2O_3$ and Li/MgO Catalysts

Name	Catalyst	Temp	CH4 C	Sel	Yield	=/-	CH4/O2	CH4 in	O2 in	Time, h	GHSV	ECl
32-135	Li/MgO	720	37.91	51.8	19.31	1.18	1.98	9.509	4.8	1	9600	0
32-135	Li/MgO	700	30.5	51.1	15.4	1.0	2.0	9.5	4.8	68	4800	0
33-7	Ba/Al_2O_3	750	45.2	43.4	19.4	3.1	2.0	9.4	4.8	289	1667	50
32-135	Li/MgO	700	21.5	49.1	10.5	0.7	2.2	10.1	4.6	190	4800	0
33-74	Ba/Al_2O_3	750	43.0	46.4	19.7	3.1	2.0	10.1	5.0	291	1116	4
33-74	Ba/Al_2O_3	750	39.5	42.8	16.9	3.6	2.1	20.6	9.6	359	1088	30
32-135	Li/MgO	700	28.9	45.1	12.9	1.1	2.1	19.6	9.3	175	4800	0
33-7	Ba/Al_2O_3	750	43.8	41.8	18.1	3.9	2.2	19.2	8.9	286	1667	50
32-135	Li/MgO	700	15.0	67.8	9.8	0.6	9.2	78.8	8.6	98	7200	0
33-74	Ba/Al_2O_3	750	11.0	70.9	7.5	0.8	8.1	79.6	9.9	410	2233	47
33-7	Ba/Al_2O_3	750	9.8	76.4	7.5	1.2	18.5	81.1	4.4	138	1667	17

The major difference in the alkaline earth/non-basic metal oxide/chloride catalysts and the Li/MgO catalysts is that the Li/MgO catalyst irreversibly deactivates by the loss of Li, whereas the alkaline earth catalysts do not lose alkaline earth metals (see 33-BKW-74 below, and see previous Quarterly Reports.

Alkaline Earth/Alpha-Alumina Catalysts

$BaCO_3/Al_2O_3$ catalysts with high (30%, 33-BKW-1) and low (5%, 33-BKW-2) concentrations of barium carbonate were prepared using Norton 5402 α-alumina support. In the presence of 10, 50, or 0 ppm ethyl chloride, the performance of these catalysts was to be compared with that of catalysts made using Norton 5451 alumina (see discussion of reactions 33-BKW-6 and 7 below, and Table B4 of Appendix B). The 5402 support has more acidity per weight and per surface area than the 5451 support (see Table 4 of the

Fourth Quarterly Report[20]). Results from tests with these two catalysts are shown in Table B4 of Appendix B and in Figures C1 and C2 of Appendix C. The performance of the catalyst containing 30% barium carbonate, although inferior to catalysts on Norton 5451 under similar conditions, was better (12% C_2 yield and 32% C_2 selectivity) than the catalyst containing only 5% barium carbonate (7% C_2 yield and 21% C_2 selectivity).

ECl Level Effects with Different Alkaline Earth Concentrations

Figures 9 and 10 below and Figure C3 of Appendix C display methane coupling reactions which use catalysts with 5% (33-BKW-6) and 30% (33-BKW-7) barium carbonate, respectively, on Norton support 5451. Figures 9 and 10 below display the first 140 hours of reaction with these two catalysts.

Figure 9. $BaCO_3/Al_2O_3$, 33-BKW-6

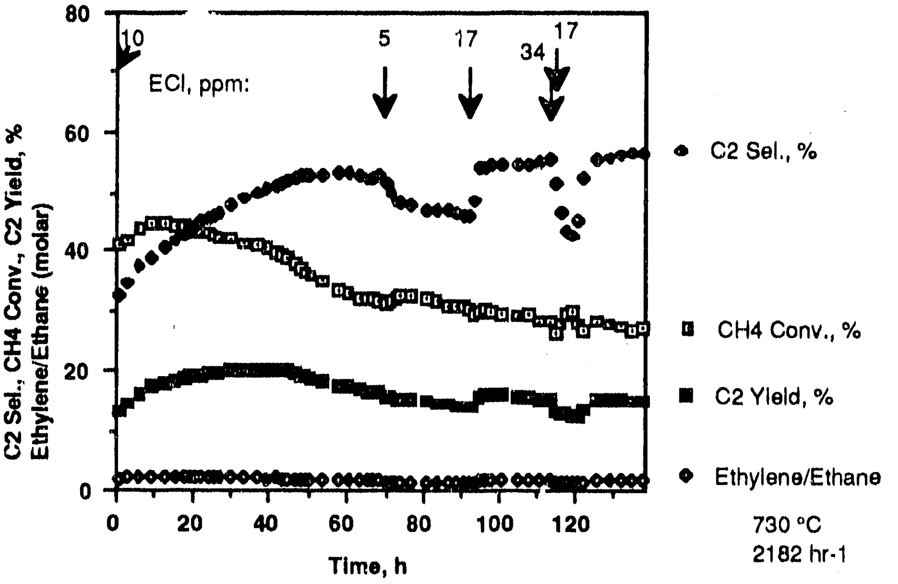
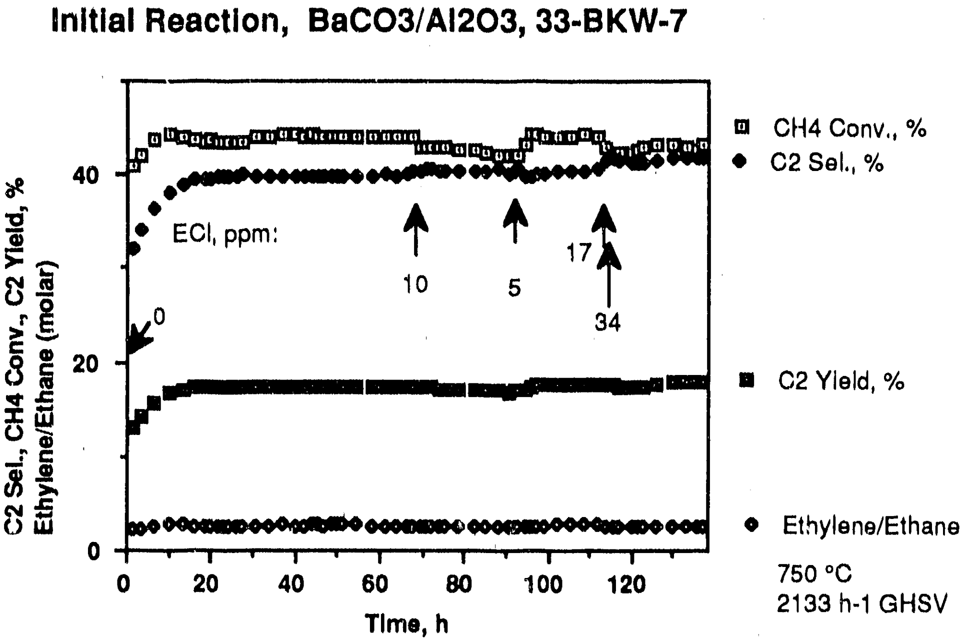


Figure 10. $BaCO_3/Al_2O_3$, 33-BKW-7

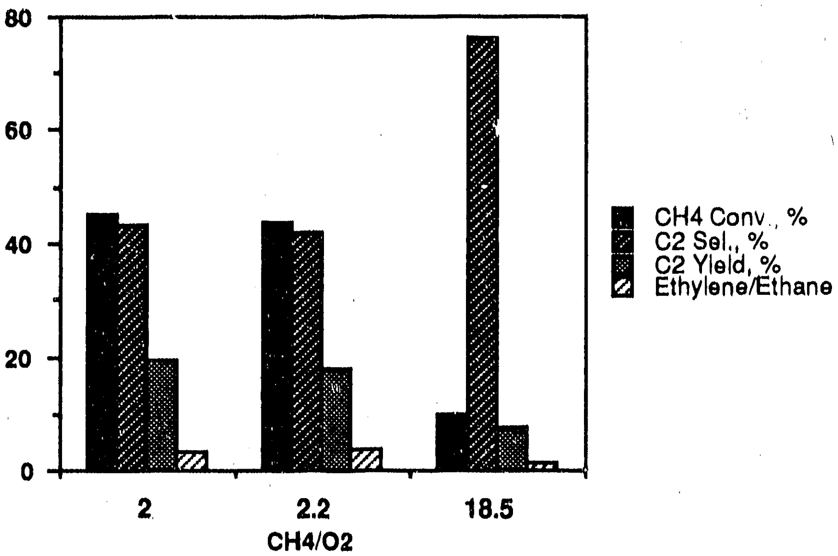


After an initial period of activation for both of these catalysts, the methane conversion continued to drop for the catalyst containing only 5% barium carbonate with several levels of ethyl chloride (10, 5, 34, and 17 ppm). For both catalysts, C_2 selectivity and C_2 yield were superior to results from the catalysts on the more acidic support used in reactions 33-BKW-1 and 2. The selectivity was very sensitive to changes in the ethyl chloride level for the catalyst made with 5% barium carbonate, whereas the selectivity was relatively insensitive to ethyl chloride level (as may be seen in Figures 9 and 10) for the catalyst made with 30% barium carbonate.

Methane to Oxygen Ratios

Figure 11 (33-BKW-7, Table B4 of Appendix B) shows that methane conversion, C_2 selectivity, C_2 yield, and the ethylene to ethane product ratio at 750 °C and 1667 h^{-1} GHSV are affected strongly by the methane to oxygen ratio in the feed gas, but only slightly by the concentrations of the feed gases at a given ratio, for the particular process conditions explored. The methane concentration was 5% for the methane to oxygen ratio of 2, and it was 10% for the methane to oxygen ratio of 2.2 in Figure 11.

Figure 11. $BaCO_3/Al_2O_3$, 33-BKW-7



Methane coupling was conducted in reaction 33-BKW-7 for over 400 hours. Table 2 below shows that at conditions identical to those used during the earlier portion of the reaction, results after 400 hours were almost the same as those immediately after activation (C_2 selectivity and C_2 yield were actually higher after 405 hours than they were at 13 or 96 hours). The temperature was 750 °C and the space velocity was 2133 h^{-1} for these examples. The catalyst was undergoing activation for the first 13 hours on-stream. Between 96 and 405 hours, the catalyst was tested at many methane to oxygen ratios, space velocities, and temperatures.

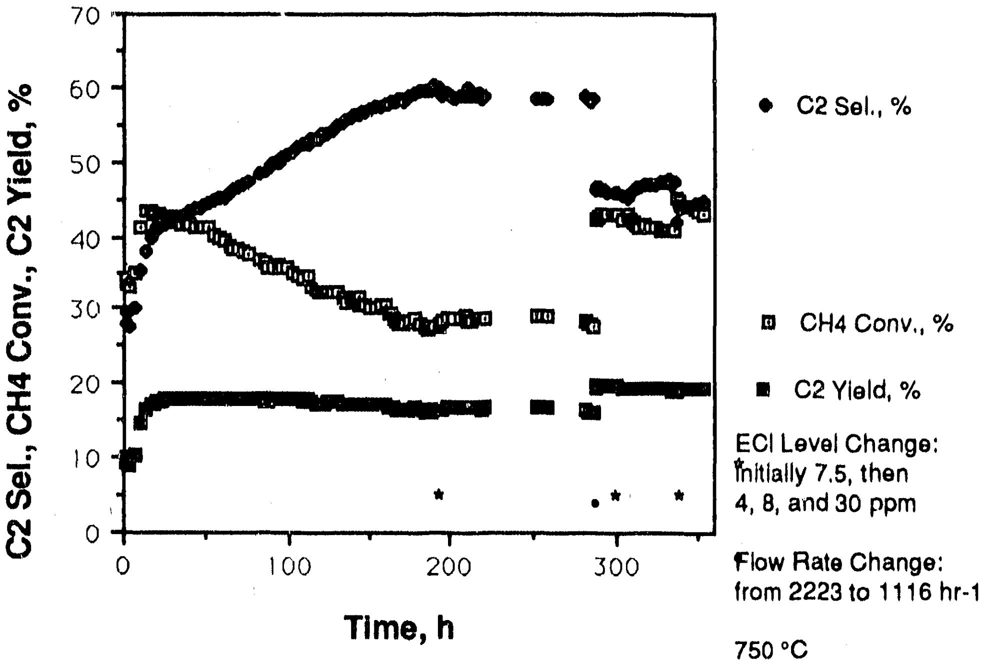
Table 2. Stability of a $BaCO_3/Al_2O_3$ Catalyst, 33-BKW-7

CH4 C	Sel	Yield	=/-	CO2/CO	Time, h	ECl
44.0	39.0	17.1	2.7	3.1	13	10
44.2	39.9	17.4	2.6	3.0	96	17
37.3	47.6	17.6	2.0	2.3	405	17

A C_2 yield of over 20% was obtained in reaction 33-BKW-6. The C_2 yield then dropped (see Figure 9 above). A change in the ethyl chloride level from 10 to 5 ppm did not result in an improvement in catalyst performance. Ethyl chloride levels higher than 10 ppm also resulted in poor catalyst performance. It was thought that this 5% barium carbonate on alumina catalyst might be extremely sensitive to changes in ethyl chloride, and that 5 ppm ethyl chloride might have been lower than the optimum amount of ECl, whereas 10 ppm of ethyl chloride might have been too much.

Figure 12 below shows that an intermediate level of ethyl chloride (7.5 ppm) was used in reaction 33-BKW-74, at 750 °C and 2233 h^{-1} GHSV. The C_2 yield remained between 16 and 18% for over 190 hours, at which time, the ethyl chloride level was adjusted to 4 ppm. The C_2 yield remained between 16 and 18% an additional 95 hours. Upon changing the space velocity to 1116 h^{-1}, the C_2 yield rose to above 19% and remained there for 70 hours, at which time a lowering of the space velocity coupled with an increase in the ethyl chloride level to 40 ppm resulted in a decrease in methane conversion and selectivity to C_2's. ICP analyses of fresh and used catalysts for this reaction showed 3.1% barium in each catalyst, indicating no loss of barium during the methane coupling reaction.

Figure 12. $BaCO_3/Al_2O_3$, 33-BKW-74



ECl Level Change: Initially 7.5, then 4, 8, and 30 ppm

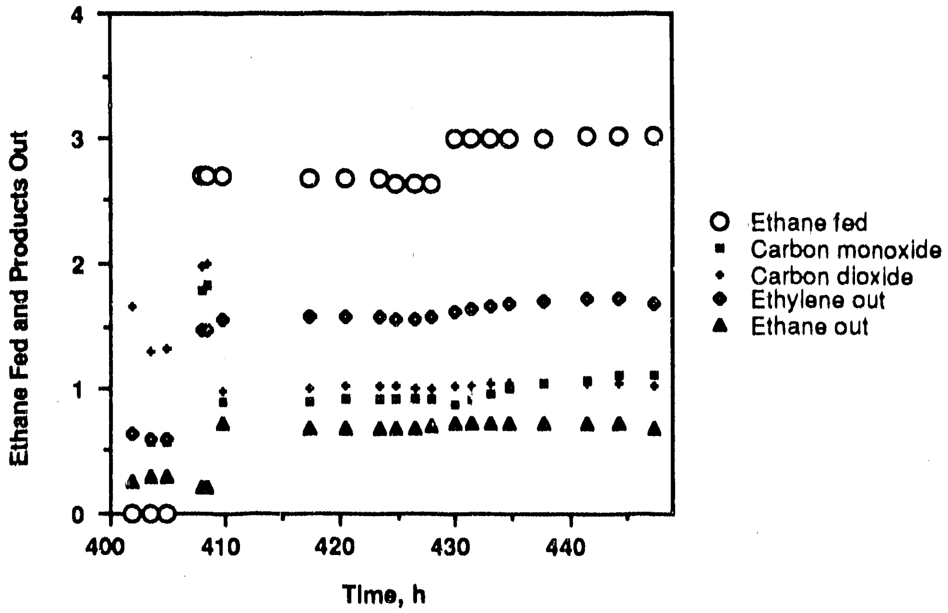
Flow Rate Change: from 2223 to 1116 hr-1

750 °C

Added Ethane

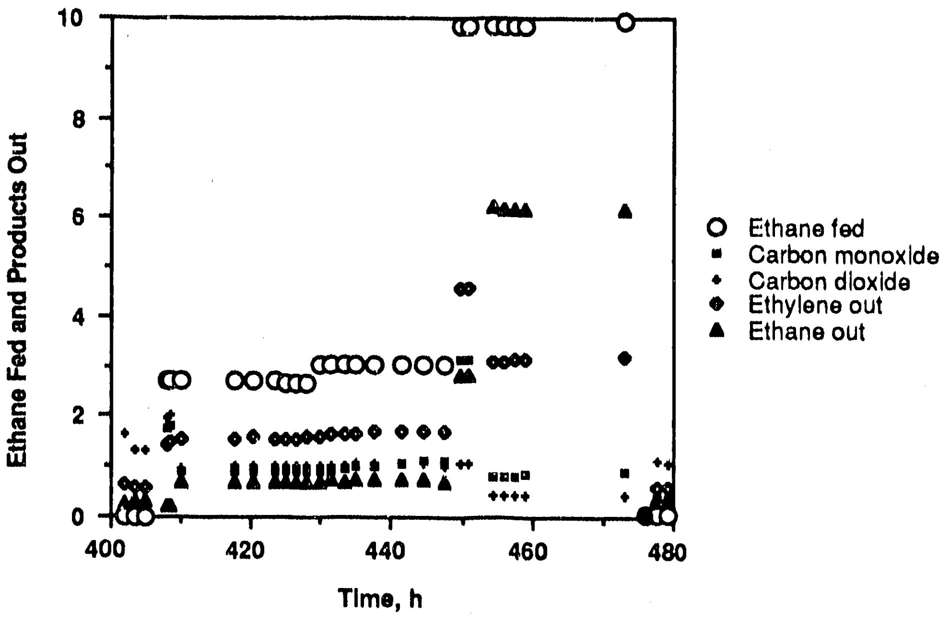
After the time period displayed in Figure 12 for reaction 33-BKW-7, ethane was tested as a feed component in the methane coupling reaction. It is likely that some ethane would be recycled in a methane coupling process, since it is a major product of methane coupling. Therefore, different levels of ethane were added to the methane coupling reaction. Results are displayed below in Figures 13 and 14.

Figure 13. Added Ethane, $BaCO_3/Al_2O_3$, 33-BKW-7



When ethane is added at the level of 2.7%, the amount of ethane leaving the reactor is less than that added to the reactor. The ethylene amount is higher than without added ethane, as are the amounts of carbon dioxide and carbon monoxide. At a higher level of added ethane, the carbon dioxide to carbon monoxide ratio drops by an increase in the rate to CO, so that more CO is produced than is CO_2. Figure 14 shows that when 10% ethane is fed, 3% ethylene is produced in the product mixture. CO and CO_2 are produced to a smaller extent. Since much of the ethane would burn if it were recycled, most of the ethane should be removed from a methane oxidation recycle stream.

Figure 14. Added Ethane, $BaCO_3/Al_2O_3$, 33-BKW-7



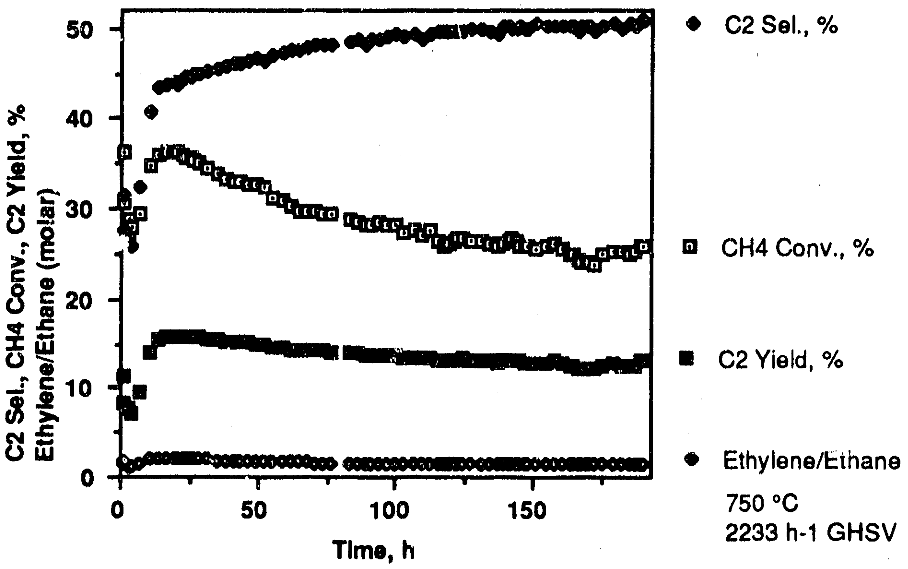
Other Anions

Table B4 of Appendix B presents a summary of methane coupling results for a barium nitrate on α–alumina catalyst in reaction 33-BKW-49. The Fifth Quarterly Report[4] describes expectations and reasons for using non-halide anions in preparation of the alkaline earth/non-basic metal oxide catalysts. Selectivity and activity are low without added ethyl chloride. Ethyl chloride levels of 0, 10, 2, then 200 ppm were used. The 10 ppm level of ethyl chloride was too low to sustain good activities and C_2 selectivities, but with 200 ppm ethyl chloride, C_2 yields as high as 16.3% and C_2 selectivities as high as 69% were observed. The increase in C_2 selectivity coupled with a decrease in C_2 yield and methane conversion indicate that optimum catalyst performance would be found at levels of ethyl chloride between 10 and 200 ppm. The purpose of this experiment was to determine if similar patterns of catalyst performance would result over catalysts prepared from metal nitrates, metal carbonates, and metal halides. The results indicate that the metal salt used has little impact on catalyst performance.

Pure Components

Results of methane coupling with pure components is presented in Table B5 of Appendix B. The oxidation of methane over gamma-alumina at 650 °C is oxygen limited, and carbon dioxide is the major product, while carbon monoxide is the only significant minor product. Pure barium carbonate was surprisingly effective for methane coupling at 750 °C, a space velocity of 2233 h^{-1}, and with 7.5 ppm ethyl chloride in the feed gas (Table B5 of Appendix B, and Figure 15 below). A peak C_2 yield of 15.7% was obtained at a C_2 selectivity of 43.8%. This indicates that a barium species is likely to be the active component for oxidizing methane in barium/metal oxide catalysts. The barium carbonate, 99.997%, had a surface area of 0.59 m^2/g prior to reaction and 0.26 m^2/g after reaction.

Figure 15. $BaCO_3$, 33-BKW-75



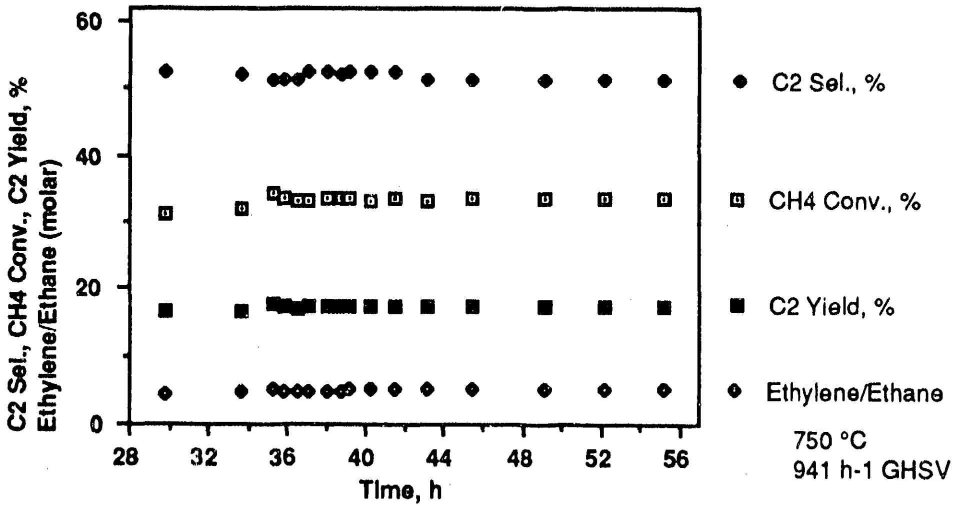
Barium Chloride on Other Supports

Catalysts were prepared on four additional α-alumina supports and tested for methane coupling activity and selectivity (Table B6 of Appendix B). Barium chloride was used as the source of alkaline earth, since high initial C_2 yields and C_2 selectivities with the chloride anion gave an indication of whether the catalyst would be good for methanc coupling at optimum ethyl chloride levels, whereas, if the wrong ethyl chloride level were chosen, catalyst testing results would not indicate whether a possibly superior catalyst could be prepared from a particular support. Catalysts were tested at three levels of added ethyl chloride, 0, 10, and 200 ppm. The supports used to prepare catalysts for these four reactions, 33-BKW-54, 55, 62, and 63, had surface areas of 0.19 (Norton 8855001, type 6596), 1.42 (Norton 8855011), 0.49 (Norton 8855002), and 0.12 m^2/g (Norton 8855003, type 5452), respectively.

A high C_2 selectivity was seen at low methane conversions for the catalyst in reaction 33-BKW-54. The initial C_2 yield was over 25%. This catalyst responded to an increase in added ethyl chloride from 10 to 200 ppm in the feed gas by a rise in selectivity, C_2 yield, methane conversion, and ethylene to ethane product ratio. The final C_2 yield, however, was only 5%, due to the low methane conversion. Although initial C_2 selectivity was not as high for the catalyst in reaction 33-BKW-55, activity did not drop as sharply as it did for the catalyst in reaction 33-BKW-54. The final C_2 yield with 200 ppm ethyl chloride was only 3%.

Methane coupling with the catalyst in reaction 33-BKW-62 resulted in methane conversions of 29-34%, C_2 selectivities of 51-53%, and C_2 yields of 15-18%, with ethylene to ethane product ratios of 3-5, with 200 ppm ethyl chloride in the feed gas. Figure 16 shows the stability of catalyst performance from this reaction for the period during which 200 ppm ethyl chloride was used.

Figure 16. $BaCO_3/Al_2O_3$, 33-BKW-62



Methane coupling in reaction 33-BKW-63 also shows stable catalyst behavior with 200 ppm ethyl chloride in the gas feed, but the C_2 yield and C_2 selectivity (Table B6 of Appendix B) are not as good as those for the reaction shown in Figure 16.

Hydrotalcite Catalysts

Hydrotalcites are interesting layered, basic inorganic materials containing magnesium and aluminum cations, and hydroxide and carbonate anions, usually also containing water. It was thought that these materials would be a good starting material for catalysts and supports. The elemental composition of the materials used was:

$$Mg_6Al_2(OH)_{16}(CO_3^{=})\cdot{\sim}4H_2O.$$

The Mg/Al ratio of the bulk compounds is approximately 3. The surface composition of the hydrotalcites is described in Appendix E.

A uniform and pure MgAl oxide was of interest, since different supports have been observed to produce catalysts with widely different methane coupling abilities, and because this material might be a precursor to materials with finely dispersed metal ions. Three samples of hydrotalcites were heated at 450 °C for 18 hours in air, heated at 850 °C for 4 hours in air, then tested for methane coupling activity (33-BKW-33, 34, and 39, Table 7 of Appendix B). Upon heating these materials at 450 °C, they lose carbon dioxide to produce $Mg_6Al_2O_8(OH)_2$. Further heating results in $Mg_6Al_2O_4$ (spinel). The resulting materials were highly active but unselective for the conversion of methane to C_2's.

Three samples of hydrotalcites which had been heated to only 450 °C were doped with $BaCO_3$, then heated at 850 °C for 4 hours. These were also tested for methane coupling activity (33-BKW-42, 43, and 48, Table 7 of Appendix B), and were also found to be highly active but unselective for the conversion of methane to C_2's.

KDC Laboratory

Tables and Figures showing the important experimental results are presented in Appendices B and C. In the Tables (Appendix B), all results are for the cofeed mode (simultaneous feeding of methane and oxygen) unless indicated as sequential mode (sequential additions of methane, nitrogen, and oxygen). For the cofeed runs, reactant conversions are based on the molar amounts of reactants present at the inlet and outlet of the reactor. In the sequential runs, reactant conversions are based on the molar amount of reactant and the total molar amount of carbon present in the product stream. Carbon balances were not obtained for the sequential runs. For both cofeed and sequential, 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. Appendix A contains the keys to the Tables.

Layered Perovskites

Additional studies were carried out on the layered perovskite ($K_2La_2Ti_3O_{10}$) identified in the Third Quarterly Report[19] as a good coupling catalyst. Layered perovskites of the form $A_2Ln_2Ti_3O_{10}$ were first reported by J. Gopalakrishnan and V. Bhat[24]. 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 these materials three octahedrals of $[Ln_2Ti_3O_{10}]$ are separated by A cations (Figure 15 of the Third Quarterly Report[19]). Thus, 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.

Results obtained for the $K_2La_2Ti_3O_{10}$ catalyst using a $CH_4/O_2/N_2$ ratio of 2/1/18 are shown in Table B8 of Appendix B. Catalysts were prepared and tested to determine if alkali doping of the $K_2La_2Ti_3O_{10}$ layered perovskite would improve the catalytic performance. Tests were run using Na_2CO_3 (Table B9 of Appendix B), K_2CO_3 (Table B10 of Appendix B), and Li_2CO_3 (Table B11 of Appendix B) as dopants. Table B12 of Appendix B gives a comparison of the effects of the alkali doping on the catalytic results. The alkali dopings had little effect on the C_2 selectivities (C_2 selectivity ranges from 38-

41%) but did result in decreased activity especially for the Na and Li dopants. These results were expected since the layered structure has alkali ions (K^+) associated in the structure with the active lanthanide species. Additional alkali doping should not affect the C_2 selectivity since the lanthanide species already have alkali ions in close proximity and would decrease activity due to the coating of the active surface with the alkali dopant.

Studies were performed to measure the methane coupling abilities of the components used in the preparation of the $K_2La_2Ti_3O_{10}$ layered perovskites. Materials tested include K_2CO_3 (Table B13 of Appendix B), TiO_2 (Table B14 of Appendix B), La_2O_3 (Table B15 of Appendix B), K_2CO_3-La_2O_3 mixture (Table B16 of Appendix B), and K_2CO_3-La_2O_3-TiO_2 (Table B17 of Appendix B). A comparison of the results is given in Table B18 of Appendix B. The K_2CO_3-La_2O_3 and K_2CO_3-La_2O_3-TiO_2 mixtures had metal molar ratios the same as $K_2La_2Ti_3O_{10}$ (1:1 and 2:2:3).

The $K_2CO_3/La_2O_3/TiO_2$ and K_2CO_3/La_2O_3 mixtures gave similar results when equal amounts of K_2CO_3/La_2O_3 were tested (2.6g of K_2CO_3/La_2O_3 and 4.0g of $K_2CO_3/La_2O_3/TiO_2$). Methane conversions of 34% and C_2 selectivities of 40-42% at 800 °C for both materials indicate that TiO_2 is not involved in the coupling process.

The La_2O_3, $K_2La_2Ti_3O_{10}$, K_2CO_3/La_2O_3, and $K_2CO_3/La_2O_3/TiO_2$ catalysts gave similar results under the experimental conditions used. Methane conversions of 34-38% and C_2 selectivities of 39-42% were obtained for all materials at 800 °C. The similarity of the results is partially due to the fact that all of these catalysts were oxygen limited under the experimental conditions.

The TiO_2 was more active (oxygen limited) than the K_2CO_3 (oxygen conversion of 80%) at 800 °C but the TiO_2 was unselective (C_2 selectivity of 16%) compared to the K_2CO_3 (C_2 selectivity of 31%).

Concurrent experiments were carried out on $K_2La_2Ti_3O_{10}$ and K_2CO_3/La_2O_3 using the same experimental conditions and the same number of moles of K and La (2.0g of $K_2La_2Ti_3O_{10}$ and 1.4g of K_2CO_3/La_2O_3) for a direct comparison of the materials. Results are presented in Table B19 of Appendix B ($K_2La_2Ti_3O_{10}$) and Table B20 of Appendix B (K_2CO_3/La_2O_3). The results are similar with the K_2CO_3/La_2O_3 mixture being more active and slightly more selective than the $K_2La_2Ti_3O_{10}$. The experiments were not performed over a long enough time period to determine if the layered perovskite structure would enhance the long term retention of the alkali resulting in greater catalyst stability. Powder x-ray analysis of the used $K_2La_2Ti_3O_{10}$ identified the major crystalline phase as the $K_2La_2Ti_3O_{10}$ layered perovskite.

The effects of changing the amount of diluent in the feed stream (changing the partial pressures of the reactants) were measured for the $K_2Pr_2Ti_3O_{10}$ (Table B21 of Appendix B) and $K_2Ce_2Ti_3O_{10}$ (Table B22 of Appendix B) layered perovskites reported in the Fifth Quarterly Report[4]. In the experiment, the feedstream composition of $CH_4/O_2/N_2$ was changed from 2/1/3.8 to 2.1/1/18. This resulted in a change of the partial pressures of CH_4/O_2 from 5.8 psia/2.9 psia to 2.0 psia/0.94 psia. The lowering of the partial pressures by increasing the diluent resulted in a slight decrease in the methane conversion but a significant increase in the C_2 selectivity. For $K_2Pr_2Ti_3O_{10}$ the CH_4 conversion decreased from 23.7% to 22.0% while the C_2 selectivity increased from 29% to 37%. For $K_2Ce_2Ti_3O_{10}$, the CH_4 conversion decreased from 28.9% to 27.4% while the C_2 selectivity increased from 33% to 41%. Since it is impossible to separate the contribution of the gas phase homogeneous reaction from the heterogeneous reaction, it is unclear if the effects noted are due to changes in the catalytic heterogeneous reaction. However, the results show that the amount of diluent does affect the overall results.

Attempts were made to improve the catalytic performance of $K_2La_2Ti_3O_{10}$ by substituting other lanthanides (Tb, Lu, or Er) into its structure. Powder x-ray diffraction patterns of the materials formed using Tb_4O_7, Lu_2O_3, and Er_2O_3 did not show patterns characteristic of the layered perovskites. This was expected since the radii of the later lanthanides is probably not large enough to stabilize the $Ln_2Ti_3O_{10}$ perovskite layers. The multiple oxidation states of Tb is considered the reason it did not form the crystalline structure. The main crystalline phases observed were the lanthanide oxides used in the preparations. Tables B23-B25 of Appendix B give the catalytic results obtained with these materials.

Table B26 of Appendix B presents a summary of results obtained at 800 °C for all the layered materials tested since the Third Quarterly Report[19]. The highest C_2 selectivities were obtained with $K_2La_2Ti_3O_{10}$ (41%), K_2CO_3-Tb_4O_7-TiO_2 (46%), K_2CO_3-Er_2O_3-TiO_2 (42%), K_2CO_3-Lu_2O_3-TiO_2 (39%), and $K_2Pr_2Ti_3O_{10}$ (40%). None of the substitutions in the original $K_2La_2Ti_3O_{10}$ catalyst resulted in significantly improved selectivity or activity.

Crystalline Phases

The importance of crystalline phases was seen in studies using lithium metasilicate, Li_2SiO_3, (Table B27 of Appendix B) and lithium orthosilicate, Li_4SiO_4, (Tables B28 and B29 of Appendix B). At 700 °C ($CH_4/O_2/N_2$ = 2.1/1/3.8; GHSV = 1700 h^{-1}), the orthosilicate was initially moderately active (CH_4 conversion = 14%) with good selectivity (C_2 selectivity = 55%) compared to the metasilicate (CH_4 conversion = 9.6%; C_2 selectivity = 11%). Deactivation occurred with the lithium orthosilicate. Also, lithium orthosilicate heated to 800 °C gave results similar to the lithium metasilicate. The deactivation and similar results were thought due to the conversion of the ortho into the meta form; however, x-ray analyses of the used materials showed no changes in the crystal phases. Future studies will determine if the ortho phase of sodium silicate is also selective compared to the meta phase.

Alkaline Earth/MgO Catalysts

Catalysts were prepared and tested to determine if Ba or Sr ion-exchanged MgO or very low loadings of Ba and Sr on MgO would result in a selective methane coupling system. The goal of the low dopant levels and ion-exchanging was to obtain powdered MgO materials having monolayer amounts of Ba or Sr species segregated upon the surface[28]. It was thought that such a monolayer arrangement would result in good methane coupling surfaces. Results are presented for the undoped MgO used in the experiments (Table B30 of Appendix B), 0.65 wt% $Ba(NO_3)_2/MgO$ (Table B31 of Appendix B), ion-exchanged Ba^{2+}/MgO (Table B32 of Appendix B), 0.53 wt% $Sr(NO_3)_2/MgO$ (Table B33 of Appendix B), and ion-exchanged Sr^{2+}/MgO (Table B34 of Appendix B). None of the materials tested gave C_2 yields above 9%. Addition of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ to MgO increased the activity at 700 °C and 750 °C but gave much lower C_2 selectivities. At 800 °C the differences were not as great. Results obtained with the ion-exchanged Ba^{2+}/MgO catalyst were not as good as those with the $Ba(NO_3)_2/MgO$ catalyst. For Sr, the ion-exchanged catalyst gave the better results.

Methane Coupling in the Sequential Mode

Since the pioneering work at Union Carbide[29] almost all of the literature studies dealing with the oxidative coupling of methane have utilized the concurrent feed of methane and oxygen. The main exceptions are the numerous works reported by Atlantic Richfield Company (ARCO) which uses a sequential or pulse flow of reactants as initially reported by Union Carbide[29]. In the sequential technique, the catalyst is first oxidized by the passage of air or oxygen over the catalyst. The system is then flushed with an inert gas and methane is passed over the catalysts. The sequence can then be repeated. In the ARCO work, manganese-silica catalysts[30] were reported to give the best C_2 yields. The effects of alkali or alkaline doping of the manganese-silica catalysts[31] were studied. Alkali- and alkaline-doping, especially Na, increased the yields of higher hydrocarbons. A 15% Mn - 5% $Na_4P_2O_7$ - silica catalyst repeatedly gave 17% yields of higher hydrocarbons for 2 minutes at 850 °C. The beneficial effect of sodium addition was thought to be due to increased surface basicity, reduction of surface area, and a specific sodium-manganese interaction.

Most of the work reported by ARCO used transition metal oxides supported on silica. Only in a few cases were dopants added to the catalysts, such as the studies on Mn/silica, CeO_2, and Pr_6O_{11}. In a recent article, Otsuka[32] proposed that the active species in a Li/NiO coupling catalyst was the complex oxide $LiNiO_2$. The oxidative coupling of methane was thought to proceed through the following redox cycle:

$$2LiNiO_2 + 2CH_4 = Li_2O + 2NiO + C_2H_6 + H_2O$$

$$Li_2O + 2NiO + 1/2O_2 = 2LiNiO_2$$

If such a cycle is occurring, this catalyst should give even better coupling results when studied using the sequential technique. Also, if this is the active species for Li/NiO it is possible that other alkali-doped coupling catalysts react by similar mechanisms; thus, they too should give good results using the sequential technique.

In order to carry out sequential studies, one of the reactor units was modified such that the product stream could be collected in gas sampling bags directly after exiting the reactor. Product samples were collected during timed intervals and analyzed using the same analytical GC procedure employed in the cofeed studies.

In order to check the system and also to have a base case for comparing results, an ARCO literature catalyst ($Mn/Na_4P_2O_7$/silica) was tested in both the cofeed (Table B35 of Appendix B) and sequential (Table B36 of Appendix B) modes.

The $Mn/Na_4P_2O_7$/silica catalyst was active in the cofeed (Table B35 of Appendix B) mode (oxygen limited at 800 °C and GHSV of 612 h^{-1}) with moderate C_2 selectivities (34-35%). Results obtained in the sequential mode (Table B36 of Appendix B) showed the system was operating correctly. The conversion decreased and C_2 selectivities increased with time during a run which agrees with the trends reported for all literature catalysts.

Double Perovskites

A double perovskite, $LaCaMnCoO_6$, was tested during the Fourth Quarter as a coupling catalyst due to its unique structure and redox properties. Synthesis of

$LaCaMnCoO_6$ was first reported in 1988[26]. The material is an ordered perovskite showing multiple occupation of both A (La and Ca) and B (Mn and Co) sublattice sites. X-ray diffraction patterns suggested the crystalline material possessed some ordered domains, while in other areas the cations were distributed at random. For the ordered domains, the most probable structural model is an ABO_3 perovskite-type structure in which Mn^{4+} and Co^{3+} ions occupied B positions in adjacent ABO_3 units while La^{3+} and Ca^{2+} ions alternate in the A positions. The material has a unique redox property in that two ions in the structure undergo reduction.

$$LaCaMn^{4+}Co^{3+}O_6 + H_2 \longrightarrow LaCaMn^{3+}Co^{2+}O_5 + H_2O$$

This makes the material of interest as a methane coupling catalyst for sequential studies as well as cofeed studies.

The $LaCaMnCoO_6$ catalyst was active (Fourth Quarterly Report[20]) in the cofeed mode (O_2 limited at 700 °C) but gave very low C_2 selectivities (<3%). In the sequential mode (Fifth Quarterly Report[4]), this material gave low C_2 selectivities (<6%) over a temperature range of 700 to 900 °C, but the CH_4 conversions were greater than those obtained using $Mn/Na_4P_2O_7$/silica.

Sodium doping (Na_2CO_3) of $LaCaMnCoO_6$ drastically changed its catalytic properties. $LaCaMnCoO_6$ gave very low C_2 selectivities in cofeed studies (< 3%); but, Na doped $LaCaMnCoO_6$ (Table B37 of Appendix B) gave moderate C_2 selectivities (34-38%) at 800 °C.

Comparison studies on $Mn/Na_4P_2O_7$/silica (Table B36 of Appendix B) and $Na_2CO_3/LaCaMnCoO_6$ (Tables B38 and B39 of Appendix B) were performed in the sequential mode. The $Mn/Na_4P_2O_7$/silica catalyst showed greater initial activity, faster deactivation, and lower initial C_2 selectivity. For example, at 850 °C and 150 ccm of CH_4, the $Mn/Na_4P_2O_7$/silica catalyst gave CH_4 conversions/C_2 selectivities of 26.5%/44.7% and 5.5%/69.5% for collection times of 0 to 2 and 2 to 5 minutes. For the same conditions and time intervals, the $Na_2CO_3/LaCaMnCoO_6$ gave 11.3%/77% and 10%/65%. A major difference between the catalysts is that the $Na_2CO_3/LaCaMnCoO_6$ shows the highest C_2 selectivity at the start of the reduction where the CH_4 conversion is greatest. This behavior is not reported for any literature catalyst.

Comparison studies on K_2CO_3 (Table B40 of Appendix B) and Na_2CO_3 (Tables B38 and B39 of Appendix B) doped $LaCaMnCoO_6$ were performed in the sequential mode. K_2CO_3 doping resulted in lower activity and lower C_2 selectivity. For example, at 800 °C and 150 ccm of CH_4, the K_2CO_3 doped catalyst gave CH_4 conversions/C_2 selectivities of 4.7%/83% and 3.2%/54% for collection times of 0 to 2 and 2 to 5 minutes.

For the same conditions and time intervals, the Na_2CO_3 doped catalyst gave CH_4 conversions/C_2 selectivities of 7.3%/91% and 5.4%/85%.

Pr/Ce Oxygen Carriers

Union Carbide patented oxygen carriers[27] consisting of oxide solid solutions of praseodymium and cerium were prepared for testing as methane coupling catalysts in the cofeed and sequential modes. These materials were of interest due to their usefulness as oxygen carriers in a reversible cyclic oxidation-reduction process for separating oxygen from air.

Materials tested in the cofeed mode included Pr-Ce oxides (Table B41 of Appendix B), Na doped Pr-Ce oxides (Table B42 of Appendix B), Ag-Pr-Ce oxides (Table B43 of Appendix B), and Na doped Ag-Pr-Ce oxides (Table B44 of Appendix B). Both undoped materials had high activities (O_2 limited at 600 °C; GHSV = 1200-1300 h^{-1}; $CH_4/O_2/N_2$ = 2/1/3.8) but low C_2 selectivities (<20%) in the temperature range of 550 to 750 °C. Na-doping (Na_2CO_3) of the catalysts (Tables B29 and B31 of Appendix B) resulted in decreased activities but greatly enhanced C_2 selectivities. For example, CH_4 conversions of 32-34% with C_2 selectivities of 44-46% were obtained at 700-750 °C (GHSV = 1250-1300 h-1; $CH_4/O_2/N_2$ = 2/1/3.8).

SUMMARY:

BKW Laboratory

Research on promoted metal oxide catalysts has continued with the study of alkaline earth/metal oxide halide catalysts. A barium bromide/alumina catalyst was comparable in methane conversion and selectivity to C_2's to barium chloride/alumina catalysts. The effects of varying methane to oxygen feed ratios were explored for one of the best alkaline earth catalysts and one of the best literature catalysts (Li/MgO). The Li/MgO catalyst deactivates faster at 700 °C than the alkaline earth catalyst does at 750 °C. With 81% methane and 4.3% oxygen in the feed gas, a selectivity of 76% to C_2's was observed at 18% methane conversion (oxygen limited) over the alkaline earth catalyst. A significant decrease in the selectivity to C_2's is observed upon addition of ethane to the feed gas (feed gas methane/ethane ratio of 3). This observation demonstrates that a significant amount of ethane should not be recycled during methane oxidation over these types of catalysts under process conditions used. Methane oxidation over barium carbonate alone results in high enough selectivities and methane conversions to suggest an oxidized barium species may be responsible for methane oxidation on barium/metal oxide catalysts.

KDC Laboratory

Studies were continued on the layered perovskite ($K_2La_2Ti_3O_{10}$) catalysts. The addition of alkali dopants had little effect on the C_2 selectivities (C_2 selectivity ranged from 38-41%) but did result in decreased activity especially for the Na and Li dopants. Experiments performed to measure the methane coupling abilities of the components used in the preparation of the $K_2La_2Ti_3O_{10}$ layered perovskites showed that La_2O_3, $K_2La_2Ti_3O_{10}$, K_2CO_3/La_2O_3, and $K_2CO_3/La_2O_3/TiO_2$ catalysts gave similar results under the experimental conditions used. Methane conversions of 34-38% and C_2 selectivities of 39-42% were obtained for all materials at 800 °C. The similarities in results was partially due to the fact that all of these catalysts were oxygen limited under the experimental conditions.

The lowering of the partial pressures of methane and oxygen by increasing the diluent resulted in a slight decrease in the methane conversion but a significant increase in the C_2 selectivity over two layered perovskites.

The importance of crystalline phases was seen in studies using lithium metasilicate, Li_2SiO_3, and lithium orthosilicate, Li_4SiO_4. The orthosilicate was initially more active with much higher C_2 selectivity compared to the metasilicate.

Sodium doping (Na_2CO_3) of $LaCaMnCoO_6$ drastically changed its catalytic properties. $LaCaMnCoO_6$ gave very low C_2 selectivities in cofeed studies; but, Na doped $LaCaMnCoO_6$ gave moderate C_2 selectivities at 800 °C.

In the sequential mode, a $Mn/Na_4P_2O_7$/silica literature catalyst showed greater initial activity, faster deactivation, and lower initial C_2 selectivity than the $Na_2CO_3/LaCaMnCoO_6$ catalyst. A major difference between the catalysts was that the $Na_2CO_3/LaCaMnCoO_6$ shows the highest C_2 selectivity at the start of a run where the CH_4 conversion is greatest. This behavior is not reported for any literature catalyst. K_2CO_3 doping of $LaCaMnCoO_6$ resulted in lower activity and lower C_2 selectivity than Na_2CO_3.

Oxygen carriers consisting of oxide solid solutions of praseodymium and cerium were tested in the cofeed mode. Undoped materials had high activities but low C_2 selectivities. Na-doping (Na_2CO_3) of the catalysts resulted in decreased activities but greatly enhanced C_2 selectivities.

TASK 2: Process Conceptualization

INTRODUCTION:

This portion of the program covers all of the engineering studies. The belief 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 Union Carbide and DOE, respectively.

RESULTS AND DISCUSSION:

Methane Coupling (Case 1)

The economic evaluation of a hypothetical process for converting methane to ethylene was previously reported (Case 1, see the Process Conceptualization section, Figure 17 and Table 57 of the Third Quarterly Report[19], the Process Conceptualization Section of the Fourth Quarterly Report[20], and the Fifth Quarterly Report[4]. The results of the economic evaluation of Methane Coupling Case 1 indicated[4] that a commercial-scale unit could produce ethylene at a variable cost of $0.0588 per pound. The ISBL (inside battery limits) investment for this 1.0 billion pound per year unit would be $311MM. This resulted in a Return on Investment of 24 percent (after tax).

As the reactor temperature increases within the range of 625-825 °C, so does the ISBL investment, due to the higher cost of construction for the reactor vessel at higher temperatures. Therefore, all things being equal, the economics favor a lower reactor operating temperature. As the reactor operating pressure increases within the range of 80-240 psig, the variable cost per pound of ethylene decreases. This is due entirely to the lower compression costs that higher reactor operating pressure affords. Therefore, all things being equal, the economics favor a higher reactor operating pressure.

Within Task 2, sensitivity studies have continued around Case 1, a first-pass economic analysis of a hypothetical process for oxidatively coupling methane to form heavier hydrocarbons, predominantly ethylene and ethane. These sensitivity studies have explored the impact on the process economics of the reactor diluent, and of the relative proportions in which ethylene and ethane are formed.

Also within Task 2, a series of studies has been initiated based on mild extrapolations of actual Union Carbide laboratory results from the most promising catalysts discovered to date.

Sensitivity Studies Around Case 1

Nitrogen Diluent and Absorber/Stripper Separation

Case 1 used no diluent, and therefore, a methane/oxygen ratio of 9/1 was required to stay out of the explosive region. This high ratio limits the methane conversion to about 22 percent. Adding a diluent allows the methane/oxygen ratio to be lowered safely, and allows the methane conversion per pass to be increased.

Specifically, a case has been evaluated which employs a feed mixture which is 7/2/1 nitrogen/methane/oxygen. In addition to the higher methane conversion mentioned above, using nitrogen as the diluent provides the added benefit of allowing raw air to be fed to the process versus oxygen, eliminating the investment and operating expense of the air separation unit. The nitrogen that enters the process in this way must be purged out by separating it from the nitrogen/methane recycle. An absorber/stripper arrangement has been evaluated for this nitrogen/methane separation.

Figure C4 of Appendix C is a simplified block diagram of this hypothetical process. Table B45 of Appendix B contains the corresponding material balance for a unit producing one billion pounds per year of ethylene via this process. Air, fresh methane and recycle methane/nitrogen are fed to the catalytic reactor so that a 7/2/1 (molar) nitrogen/methane/oxygen feed mix is achieved. It was assumed that about 48% of the methane is converted, about 57% to C_2's, for an overall yield to C_2's of about 27%. The ratio of ethylene to ethane was assumed to be 6.5/1. The assumed reactor conditions are 725°C and 150 psig. Results from 33-BKW-7 and 33-BKW-74 (Table B4 of Appendix B) were considered in generating this hypothetical case.

Following reactor product cooling and quench steps to remove most of the water of reaction, the reactor product gas enters a single-stage compression step followed by a combination acid gas removal and molecular sieve dryer system.

The main attraction of the absorber/stripper separation system is its relatively low operating pressure (200 psig), which minimizes the load on the compression system (43,000 HP in this case). However, the required solvent flow rate for the absorber/stripper system is 30 million pounds per hour, and the refrigeration load on the solvent recycle cooler is 670,000 HP! Increasing the absorber stripper pressure to 500 psig cuts the solvent flow rate to 12 million pounds per hour, and the refrigeration load on the solvent recycle cooler to 270,000 HP, but the compression system load increases to 144,000 HP. This is better overall than the low pressure version, but still no bargain. Either way, the huge solvent cycle flow rates and refrigeration loads indicate that this separation scheme is totally impractical for this application.

Ethylene/Ethane Production Ratio

Also, in Case 1 it was assumed that ethylene and ethane would be produced in approximately equal amounts. Reducing the amount of ethane produced relative to ethylene would cause the investment for a given amount of ethylene capacity to be reduced.

Specifically, a case has been evaluated which is identical to the Case 1, except that the ethylene to ethane production ratio is 10 versus 1. Figure C5 of Appendix C is a simplified block diagram of the Case 1 Oxidative Coupling Process. Table B46 of Appendix B contains the corresponding material for a unit producing one billion pounds per year of ethylene via this process at an ethylene production ratio of 10.

Table B47 of Appendix B presents the economic sensitivity of Case 1 to the ethylene to ethane production ratio.

As expected, the Total Fixed Investment for a unit producing one billion pounds per year of ethylene is much lower at the higher production ratio: $343MM versus $453MM in Case 1. Also as expected, the variable cost per pound of ethylene is higher at the higher production ratio due the the reduced co-product credits that result. Once the fixed costs are included, however, the total cash cost for the two cases are identical. Correspondingly, the Return on Investment increases with the ethylene to ethane production ratio from 24% at 1 to 33% at 10. Therefore, the economics of the methane oxidative coupling process exhibit a significant sensitivity to the ethylene to ethane production ratio. The net magnitude of this sensitivity is dependent, however, on the cost of the process changes necessary to bring about such a production ratio change, which have been neglected for this analysis.

Cases Based on Actual Union Carbide Laboratory Results

The first two of a series of economic cases based on extrapolations from actual Union Carbide catalyst testing results have been completed. These extrapolations represent what might be achievable from a fully optimized catalyst system based on results from the catalyst screening program currently in progress. The assumed performance parameters and the results of the economic analysis for the first two of these cases are summarized below:

Case	A1.2a	A1.2b
Feed diluent	methane	methane
Oxygen concentration in Rx feed, %	11.2	5.2
Methane/oxygen, molar ratio	7.3	17.3
Methane conversion, %	18.4	9.9
Selectivity to C_2's, %	76.7	87.1
C_2 yield, %	14.1	8.6
Reactor pressure, psig	50	50
Ethylene/ethane production ratio, molar	3	3
Total Fixed Investment, $MM	471	599
Cash Cost, $/lb ethylene	0.127	0.154

Although there is no added diluent other than methane, the actual contents of the stream into the reactor 2-3 mole% hydrogen (from the cracking reactor), 3.6 mole% nitrogen (introduced with oxygen), 0.7% CO, 0.1% ethylene, and 0.1% ethane for case A1.2a. The benefits of the higher selectivity in Case A1.2a versus A1.2b are overwhelmed by the negative impact of the lower conversion. Table B48 of Appendix B contains the details of the economic analysis of these two cases.

Figure C6 of Appendix C is a simplified block diagram of the process scheme used for these cases. Tables B49 and B50 of Appendix B contain the corresponding material balances for Cases A1.2a and A1.2b, respectively. Oxygen plus fresh recycle methane is fed to the Catalytic Oxidative Coupling Reaction System, which is assumed to be of a fluidized-bed design. The reactor product is quenched to stop the reaction and to remove water. The product mixture is then compressed and treated in a combination acid gas removal and molecular sieve dryer system. The dried gas then enters a combination cold box and methane column system, in which the product C_2's and heavier components are separated from the unreacted methane. The methane is recycled to the Reaction System after a purge has been taken to remove any inerts that may have entered the system via the raw materials. The C_2 and heavier products enter a de-ethanizer column which removes the C_3 and heavier products from the C_2's. The C_2's are then split in an ethylene column. The purified ethylene product is suitable for either commercial sales or downstream processing.

The ethane that is recovered from the base of the ethylene column is recycled to a steam cracking furnace and converted to ethylene and other light hydrocarbons. The cracked gas is quenched and then combined with the product from the Oxidative Coupling Reactor in the compression system.

This process configuration and the set of assumptions used in Cases Al.2a and Al.2b are felt to be more realistic, achievable, and generally applicable than those used for the original Case 1, and therefore will form a better center-point for sensitivity studies. For instance, the reactor pressure of 50 psig in these cases is much closer to the actual experimental conditions than that which was used in the original Case 1 (150 psig). Also, the economics of these cases includes facilities to utilize the ethane that is co-produced in the Oxidative Coupling Reactor, as opposed to the original Case 1 which relied on an outside consumer buying this material.

The result obtained after 8300 minutes of time on-stream of reaction 33-BKW-7 (Table B4 of Appendix B) was used as the basis for Case Al.2a. At this time analyses indicated a C_2 selectivity of 76.39%, a methane conversion of 9.84%, an oxygen conversion of 99.6%, and an ethylene to ethane product ratio of 1.24. The space velocity was 1667 h^{-1} and the temperature was 750 °C, with the reactor pressure 11 psig (1.76 kPa). The oxygen fed was 4.83%, with 89.2% nitrogen fed and 5.55% nitrogen fed. Products (relative moles) were:

CH_4	80.52
CO	0.269
CO_2	1.28
C_2H_4	1.90
C_2H_6	1.54
C_3H_6	0.13
C_3H_8	0.05

It was assumed that if the feed oxygen level were doubled, at 100% oxygen conversion, the methane conversion would double. It was assumed that the pressure could be changed to 50 psig (438 kPa).

A decrease in the methane to oxygen feed ratio would result in a decrease in selectivity, but the space velocity would be raised from 1667 to 3400 h^{-1} to counteract this. The ethyl chloride level in the feed gas was assumed to be 50 ppm rather than the 17 ppm of the example, since better results were obtained with high methane levels using 50 ppm in reaction 33-BKW-7. The C_2H_4/C_2H_6 product ratio was assumed to be 3, rather than 1.2, since a higher ECl level was assumed. These assumptions are considered justified for optimized future catalysts and process conditions. This series of case studies will include evaluations of two or more combinations of methane conversion/selectivity on each of the four diluents that will be considered:

- methane - high methane/oxygen (complete)
- nitrogen - methane/oxygen = 2/1 (in progress)
- steam - methane/oxygen = 2/1 (in progress)
- none - sequential operation

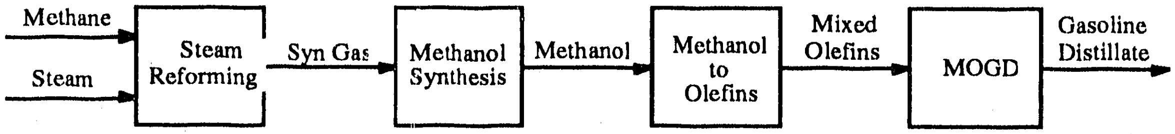
Methane to C_2's then Fuels (Case 2)

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 few months of the 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.

Comparison Case (Conventional Technology)

In order to establish a benchmark against which to compare emerging technology for the direct conversion of methane to ethylene and liquid fuels, a Comparison Case was developed based upon existing technologies which have been demonstrated to be feasible or have already been commercialized for the conversion of methane to syn-gas, syn-gas to methanol and methanol to liquid fuels. This is illustrated in Figure 17 below.

Figure 17. Methane Coupling Comparison Case Block Diagram



Synthesis gas production is accomplished by steam reforming of natural gas, and ICI's low pressure methanol process is used to convert the the synthesis gas to methanol. A UOP[32] process is used to convert the methanol to olefins, and the Mobil Olefins to Gasoline and Distillate (MOGD) process is used for the final conversion of olefins to liquid fuels. An analysis of this process was reported last quarter[4].

For the Comparison Case, the total fixed investment is $455MM and a sales price of $1.71/gallon of gasoline and distillate products will be required in order to generate a ten percent after tax return on investment based upon a natural gas cost of $1.65/MMBTU. Existing technology for the conversion of methane to liquid fuels is not competitive with the current oil based route in the present pricing environment. The impact of methane cost on the required sales cost of gasoline and distillate for the Comparison Case and the Hypothetical Case were reviewed[4]. The Comparison Case will be compared with results from Case 2, the conversion of methane to fuels through intermediate light gases rich in C_2's (Case 1 integrated with Mobil Olefins to Gasoline and Distillate, not yet done).

Support of Experimental Program

Support of the experimental program has continued through regular meetings of the chemists and engineers with discussions of the laboratory results, the proposed process configurations, results of heat and material balances, and preliminary economics.

SUMMARY:

A methane coupling case was explored which employs a feed mixture which is 7/2/1 nitrogen/methane/oxygen.

An absorber/stripper separation system was explored for the potential advantage of its relatively low operating pressure, which minimizes the load on the compression system. Huge solvent cycle flow rates and refrigeration loads indicate that this separation system is impractical for the methane coupling application.

The total fixed investment for a unit producing one billion pounds per year of ethylene is \$343MM at an ethylene/ethane production ratio of (24% ROI) and \$453MM at a production ratio of 110 (33% ROI). The economics of the methane coupling process exhibit a significant sensitivity to the ethylene to ethane product ratio.

Economic evaluations for the first two of a series of cases based on extrapolations of Union Carbide results have been completed. The hypothetical process schemes for these two cases are considered more realistic, achievable, and generally applicable to future methane coupling results than those used for the original Case 1[4].

Both schemes have very high selectivities to C_2's and use no diluent other than methane. The case with the best results (lower selectivity and higher methane conversion) requires a \$471MM total fixed investment and is based on a transient laboratory results of 76% selectivity to C_2's with 18% methane conversion.

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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-#	Union Carbide notebook reference ID number.
Catalyst (Cat)	Union Carbide 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 (minutes, unless hours indicated).
CH_4 Conv. (CH4 C or CC)	Mole % of methane reacted. $= \{[n(CH_4)_r - n(CH_4)_p]/n(CH_4)_r\} \times 100$
O_2 Conv. (O2 C)	Mole % of oxygen reacted. $= \{[n(O_2)_r - n(O_2)_p]/n(O_2)_r\} \times 100$
C Balance (C Bal)	Mole % carbon detected in the product stream compared to the reactant stream. $= \{[\Sigma f(i)n(i)_p]/n(CH_4)_r\} \times 100$; 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. $= \{2[n(C_2H_6)_p + n(C_2H_4)_p]\}/[\Sigma f(i)n(i)_p] \times 100$; 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, F, G, or H.
R#	R#3 and R#4 refer to the two reactors in the BKW laboratory.
Activity	Methane conversion.

Appendix B. TABLES

Table B1. Other Supports

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
32 BKW 120 R#4	2.0	BaCl2,SiO2,60/100	750	160	35.7	14.0	5.0	98	2.8	1.2	2.0	9.4	4.6	100	30	2217	200
32 BKW 120 R#4	2.0	BaCl2,SiO2,60/100	730	160	34.0	13.0	4.4	92	2.9	1.1	2.0	9.4	4.6	100	130	2217	200
32 BKW 120 R#4	2.0	BaCl2,SiO2,60/100	730	160	10.3	5.2	0.5	27	1.9	0.2	2.0	9.3	4.7	100	5470	2217	200
32 BKW 120 R#4	2.0	BaCl2,SiO2,60/100	730	160	10.3	5.3	0.5	27	1.9	0.2	2.0	9.3	4.7	100	5540	2217	200
32 BKW 128 R#3	5.0	BaCO3,ZrO2,60/100	750	160	37.1	24.7	9.1	96	1.3	5.4	2.0	9.3	4.6	99	45	5053	10
32 BKW 128 R#3	5.0	BaCO3,ZrO2,60/100	750	160	36.9	26.1	9.6	94	1.3	4.8	2.0	9.3	4.6	99	185	5053	10
32 BKW 128 R#3	5.0	BaCO3,ZrO2,60/100	750	160	37.1	30.6	11.2	88	1.4	4.1	2.0	9.6	4.8	98	1445	5053	10
32 BKW 128 R#3	5.0	BaCO3,ZrO2,60/100	750	160	34.0	23.9	8.1	84	1.4	2.4	2.0	9.8	5.0	99	5090	5053	10
32 BKW 128 R#3	5.0	BaCO3,ZrO2,60/100	750	160	34.8	22.5	7.8	83	1.4	2.3	2.0	9.5	4.9	99	5450	5053	200
32 BKW 128 R#3	5.0	BaCO3,ZrO2,60/100	750	160	35.0	22.2	7.6	83	1.4	2.2	2.0	9.5	4.9	99	5810	5053	200
32 BKW 128 R#3	5.0	BaCO3,ZrO2,60/100	750	160	28.1	42.8	12.0	48	2.7	0.4	1.9	9.5	5.0	100	7205	5053	200
32 BKW 129 R#4	1.0	BaCO3,Gamma Al2O3,6573,60/10	650	160	31.2	0.0	0.0	81	####	1.0	2.0	9.3	4.6	102	75	6000	10
32 BKW 129 R#4	1.0	BaCO3,Gamma Al2O3,6573,60/10	650	160	30.5	####	0.0	79	####	0.9	2.0	9.3	4.6	102	165	6000	10
32 BKW 129 R#4	1.0	BaCO3,Gamma Al2O3,6573,60/10	650	160	29.9	0.0	0.0	75	####	0.8	2.0	9.6	4.8	102	570	6000	10
32 BKW 129 R#4	1.0	BaCO3,Gamma Al2O3,6573,60/10	650	160	30.3	0.0	0.0	77	####	0.9	2.0	9.8	5.0	101	5070	6000	10
32 BKW 129 R#4	1.0	BaCO3,Gamma Al2O3,6573,60/10	650	160	31.1	####	0.0	75	####	0.9	2.0	9.5	4.9	101	5430	6000	200
32 BKW 129 R#4	1.0	BaCO3,Gamma Al2O3,6573,60/10	650	160	31.5	0.0	0.0	75	####	0.9	2.0	9.5	4.9	100	5790	6000	200
32 BKW 129 R#4	1.0	BaCO3,Gamma Al2O3,6573,60/10	650	160	26.8	0.5	0.1	61	####	0.5	2.0	9.5	4.8	102	7545	6000	200

Appendix A and the Experimental Section describe Table headings and experimental procedures.
Inaccurate due to a small number or division by a small number.
Reactor D was used for all Experiments.

Table B2. Non-Chloride Halides

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECl	EBr*
32 BKW 122 R#3	5.0	BaBr2.2H2O,Al2O3,5451,60/100	750	80	49.2	38.6	18.3	98	41.9	0.4	2.0	9.4	4.7	96	40	1043	0	
32 BKW 122 R#3	5.0	BaBr2.2H2O,Al2O3,5451,60/100	750	80	48.8	38.9	18.3	98	38.1	0.6	2.0	9.4	4.7	96	75	1043	0	
32 BKW 122 R#3	5.0	BaBr2.2H2O,Al2O3,5451,60/100	750	160	47.5	43.4	19.9	91	27.8	0.6	2.0	9.4	4.7	96	115	2087	0	
32 BKW 122 R#3	5.0	BaBr2.2H2O,Al2O3,5451,60/100	750	160	44.8	44.6	19.4	85	18.2	0.9	2.0	9.4	4.7	97	190	2087	0	
33 BKW 38 R#3	5.0	BaF2,Al2O3,5451,60/100	750	80	17.3	23.2	4.0	42	0.9	1.5	2.0	10.5	5.2	101	60	1067	0	
33 BKW 38 R#3	5.0	BaF2,Al2O3,5451,60/100	750	80	21.7	19.6	4.3	54	1.1	1.9	2.0	10.5	5.2	100	140	1067	0	
33 BKW 38 R#3	5.0	BaF2,Al2O3,5451,60/100	750	80	36.4	23.3	8.5	96	1.9	5.6	2.1	10.6	5.1	100	965	1067	0	
33 BKW 38 R#3	5.0	BaF2,Al2O3,5451,60/100	750	80	36.7	23.1	8.4	97	2.0	5.7	2.0	10.5	5.2	100	1550	1067	0	
33 BKW 38 R#3	5.0	BaF2,Al2O3,5451,60/100	750	80	36.5	22.5	8.2	97	2.2	5.8	2.0	10.4	5.2	100	1640	1067	10	
33 BKW 38 R#3	5.0	BaF2,Al2O3,5451,60/100	750	80	36.6	22.9	8.4	97	2.1	5.8	2.0	10.4	5.2	100	1730	1067	10	
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	34.3	42.4	14.8	66	3.4	1.3	2.0	10.2	5.2	102	35	2182	5	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	33.0	47.4	15.6	60	3.9	1.2	2.0	10.2	5.2	100	110	2182	5	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	35.7	41.0	14.5	70	2.9	1.5	2.0	10.5	5.1	99	4285	2182	5	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	36.2	40.5	14.7	70	3.1	1.4	1.9	9.9	5.2	100	4375	2182	10	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	36.7	40.8	14.9	71	3.3	1.4	1.9	9.9	5.2	100	4510	2182	10	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	37.3	40.5	15.1	72	3.5	1.4	1.9	9.8	5.1	100	5320	2182	10	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	37.4	40.3	15.1	73	3.6	1.4	1.9	9.9	5.2	100	5625	2182	10	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	36.4	40.7	15.5	74	4.0	1.3	1.9	10.0	5.1	99	5725	2182	17	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	38.5	40.3	15.5	73	4.1	1.3	1.9	10.0	5.1	100	5815	2182	17	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	38.6	40.6	15.6	74	4.2	1.3	1.9	10.0	5.1	99	5995	2182	17	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	37.0	40.0	14.9	74	3.8	1.4	2.0	10.2	5.1	101	6105	2182	1	EBr
33 BKW 66 R#3	4.9	BaBr2,Al2O3,5451,60/100	750	160	35.5	39.8	14.1	72	3.0	1.5	2.0	10.2	5.1	100	6220	2182	1	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	32.8	37.4	12.3	73	1.8	3.2	2.0	10.2	5.2	100	70	2233	5	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	36.4	40.4	14.7	78	2.1	2.8	2.0	10.2	5.2	100	190	2233	5	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	43.9	44.3	19.2	91	3.5	2.7	2.0	10.2	5.2	98	640	2233	5	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.0	39.6	15.7	83	2.8	1.7	2.0	10.5	5.1	99	4240	2233	5	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.9	39.2	16.1	83	3.2	1.6	1.9	9.9	5.2	100	4330	2233	10	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	41.3	39.4	16.2	83	3.4	1.6	1.9	9.9	5.2	100	4420	2233	10	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	41.3	39.5	16.3	83	3.4	1.6	1.9	9.9	5.2	100	4555	2233	10	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.9	39.4	16.2	82	3.5	1.5	1.9	9.8	5.1	100	5545	2233	10	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.3	39.4	16.5	83	4.1	1.5	1.9	10.0	5.1	99	5680	2233	17	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.0	39.8	16.6	83	4.1	1.5	1.9	10.0	5.1	99	5770	2233	17	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.0	39.8	16.6	83	4.1	1.5	1.9	10.0	5.1	99	6040	2233	17	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	37.9	39.3	14.9	79	2.5	1.7	2.0	10.2	5.1	100	6175	2233	1	EBr
33 BKW 67 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	37.0	38.3	14.2	78	2.1	1.8	2.0	10.2	5.1	100	6400	2233	1	EBr

Appendix A and the Experimental Section describe Table headings and experimental procedures.

Inaccurate due to a small number or division by a small number.

EBR* indicates whether ethyl bromide was used instead of ethyl chloride. The concentration used is indicated in the ECl column, as for ECl.

Reactor D was used for all experiments.

Table B3. Comparative Examples

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECl
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	720	160	42.7	44.1	18.5	92	1.6	8.7	2.0	9.5	4.8	98	35	4800	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	720	160	40.9	45.8	18.3	85	1.4	8.7	2.0	9.5	4.8	98	110	4800	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	720	160	30.2	50.6	15.0	56	1.0	5.2	1.9	9.6	4.9	98	2915	4800	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	160	21.7	51.6	11.0	38	0.7	4.3	1.9	9.6	4.9	98	3005	4800	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	160	21.3	51.6	10.8	38	0.7	4.3	1.9	9.6	4.9	99	3095	4800	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	160	20.2	51.6	10.4	33	0.7	4.2	2.0	9.6	4.8	100	3860	4800	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	31.2	46.6	14.3	61	1.1	6.3	2.0	9.5	4.8	99	4055	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	31.0	46.5	14.2	61	1.1	6.3	2.0	9.5	4.8	99	4145	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	30.9	46.6	14.2	60	1.1	6.3	2.0	9.5	4.8	99	4415	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	30.6	50.4	15.2	59	1.2	6.4	2.0	9.7	4.9	99	4580	2400	10
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	29.6	49.6	14.5	56	1.2	5.8	2.0	9.7	4.9	99	4715	2400	10
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	26.8	48.0	12.7	49	1.1	3.7	2.0	9.7	4.9	98	5300	2400	10
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	24.7	47.9	11.8	48	1.1	3.5	2.0	9.6	4.9	100	5435	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	25.0	46.9	11.6	46	1.0	3.3	2.0	9.6	4.9	99	5545	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	24.0	46.5	11.0	44	0.9	3.1	2.0	9.6	4.9	99	5705	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	120	12.4	61.2	7.3	58	0.7	2.2	9.2	78.8	8.6	97	5930	3600	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	120	9.4	62.4	5.8	57	0.7	2.2	9.2	78.8	8.6	100	6020	3600	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	120	6.1	62.9	3.9	48	0.6	1.9	9.2	77.4	8.4	102	8315	3600	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	120	0.3	62.9	0.2	35	0.5	1.6	9.2	77.0	8.3	107	9845	3600	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	120	4.3	63.1	2.8	37	0.5	1.6	9.2	77.0	8.3	102	10005	3600	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	65	8.9	60.1	5.4	60	0.8	1.9	9.2	77.1	8.4	100	10070	1950	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	65	9.0	60.3	5.4	60	0.8	1.9	9.2	77.1	8.4	100	10160	1950	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	21.4	45.9	9.8	43	1.1	2.6	2.1	19.6	9.3	100	10250	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	21.6	46.1	9.9	43	1.1	2.6	2.1	19.6	9.3	100	10340	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	20.7	46.5	9.6	40	1.0	2.5	2.1	19.3	9.2	99	11175	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	13.2	55.4	7.3	23	0.6	1.9	2.2	10.1	4.6	101	11285	2400	0
32 BKW 134 R#3	1.0	Li2CO3,MgO,60/100	700	80	13.5	55.9	7.5	23	0.6	1.8	2.2	10.1	4.6	100	11350	2400	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	720	160	37.9	51.8	19.3	73	1.2	11.5	2.0	9.5	4.8	98	65	9600	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	720	160	37.3	52.6	19.2	71	1.2	10.9	2.0	9.5	4.8	98	140	9600	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	720	160	31.4	55.0	17.0	56	1.0	6.6	1.9	9.6	4.9	98	2960	9600	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	160	22.4	55.3	12.2	38	0.6	5.5	1.9	9.6	4.9	98	3050	9600	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	160	22.0	55.2	12.1	39	0.6	5.6	1.9	9.6	4.9	99	3140	9600	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	160	22.7	55.1	12.3	37	0.6	5.5	2.0	9.8	4.9	98	3320	9600	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	160	21.2	55.1	11.6	36	0.6	5.5	2.0	9.6	4.8	100	3905	9600	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	30.5	51.1	15.4	58	1.0	8.7	2.0	9.5	4.8	99	4085	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	30.2	50.8	15.1	57	1.0	8.5	2.0	9.5	4.8	99	4175	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	29.9	51.0	15.0	56	1.0	8.4	2.0	9.5	4.8	99	4355	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	30.4	51.0	15.1	56	0.9	8.2	2.0	9.7	4.9	98	4445	4800	10
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	30.1	51.4	15.3	56	1.0	8.4	2.0	9.7	4.9	99	4535	4800	10
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	29.8	52.7	15.4	56	0.9	9.3	2.0	9.7	4.9	98	4760	4800	10
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	29.5	51.3	14.9	55	0.9	7.9	2.0	9.7	4.9	98	5345	4600	10
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	29.0	51.0	14.6	55	0.9	7.6	2.0	9.6	4.9	98	5495	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	29.2	50.5	14.5	55	0.9	7.5	2.0	9.6	4.9	99	5570	4800	0

Table B3. Comparative Examples (continued)

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	28.7	50.2	14.2	54	0.9	7.1	2.0	9.6	4.9	99	5660	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	120	15.0	67.8	9.8	74	0.6	5.3	9.2	78.8	8.6	96	5885	7200	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	120	14.1	67.1	9.2	73	0.6	4.9	9.2	78.8	8.6	97	5975	7200	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	120	10.8	65.1	7.0	65	0.6	3.7	9.2	77.4	8.4	100	8405	7200	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	120	7.3	64.7	4.9	64	0.6	3.7	9.2	77.0	8.3	104	9875	7200	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	120	8.7	65.2	5.8	64	0.5	3.6	9.2	77.0	8.3	102	9975	7200	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	65	11.3	63.0	7.2	78	0.8	4.7	9.2	77.1	8.4	100	10110	3900	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	28.4	45.1	12.8	62	1.1	6.3	2.1	19.6	9.3	100	10295	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	28.9	45.1	12.9	62	1.1	6.2	2.1	19.6	9.3	99	10520	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	28.8	45.2	12.8	61	1.1	6.0	2.1	19.3	9.2	99	11210	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	21.1	48.8	10.3	43	0.7	4.1	2.2	10.1	4.6	100	11330	4800	0
32 BKW 135 R#4	1.0	Li2CO3,MgO,60/100	700	80	21.5	49.1	10.5	43	0.7	4.2	2.2	10.1	4.6	100	11405	4800	0

Appendix A and the Experimental Section describe Table headings and experimental procedures.
Reactor D was used for all experiments.

Table B4. Alkaline Earth/Alpha Alumina Catalysts

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	+/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	31.6	20.6	6.5	82	1.4	4.7	2.0	9.7	4.9	99	55	2182	10
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	31.4	21.1	6.6	80	1.4	3.7	2.0	9.7	4.9	99	125	2182	10
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	17.5	18.0	3.2	38	0.7	0.7	2.0	9.6	4.9	101	2425	2182	10
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	17.9	14.1	2.6	43	0.6	0.9	2.0	9.6	4.8	101	2650	2182	50
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	18.2	13.3	2.4	43	0.6	1.0	2.0	9.6	4.8	101	2710	2182	50
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	18.1	11.6	2.1	42	0.6	0.9	2.0	9.8	4.9	100	3865	2182	50
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	18.1	10.3	1.9	43	0.6	1.0	2.1	10.0	4.8	100	4075	2182	0
33 BKW 1 R#3	5.0	BaCO3,Al2O3,5402,60/100	750	160	18.3	9.3	1.7	44	0.6	1.2	2.1	10.0	4.8	100	4170	2182	0
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	35.5	22.0	7.7	95	1.4	7.5	2.0	9.7	4.9	99	85	2286	10
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	36.1	22.4	8.0	95	1.6	6.7	2.0	9.7	4.9	99	150	2286	10
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	37.6	29.9	11.2	88	2.0	3.7	2.0	9.6	4.9	99	2470	2286	10
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	37.2	30.5	11.3	89	2.0	3.7	2.0	9.6	4.8	100	2620	2286	50
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	37.4	30.9	11.5	89	2.0	3.8	2.0	9.6	4.8	100	2680	2286	50
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	39.1	31.9	12.3	92	2.2	3.8	2.0	9.7	4.9	99	3730	2286	50
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	39.2	31.8	12.3	92	2.2	3.8	2.0	9.7	4.9	99	3910	2286	50
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	38.8	32.2	12.4	92	2.2	3.8	2.1	10.0	4.8	99	4045	2286	0
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	38.7	32.2	12.4	92	2.2	3.8	2.1	10.0	4.8	99	4105	2286	0
33 BKW 2 R#4	5.0	BaCO3,Al2O3,5402,60/100	750	160	38.8	32.4	12.5	92	2.2	3.8	2.1	10.0	4.8	99	4225	2286	0
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	41.1	32.7	13.4	98	2.1	5.7	2.0	9.6	4.9	100	50	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.0	34.9	14.5	96	2.4	4.7	2.0	9.6	4.9	99	[illegible]	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.5	50.9	20.2	73	2.3	2.4	2.0	9.6	4.8	98	2365	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	31.9	52.7	16.7	53	1.9	1.4	2.0	9.5	4.8	99	4120	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	31.4	51.4	16.1	56	1.9	1.4	2.0	9.7	4.8	100	4210	2182	5
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	32.0	49.9	15.9	57	1.8	1.5	2.0	9.7	4.8	100	4285	2182	5
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	30.6	46.2	14.1	55	1.7	1.4	2.1	9.8	4.7	100	5530	2182	5
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	29.7	48.5	14.4	50	1.7	1.4	2.0	9.4	4.8	100	5620	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	30.0	53.8	16.0	49	2.0	1.2	2.0	9.4	4.8	99	5705	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	30.8	54.1	16.4	49	2.0	1.2	2.0	9.4	4.8	99	5800	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	28.3	55.2	15.5	44	1.9	1.1	2.0	9.3	4.8	99	6790	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	26.4	51.4	13.6	44	1.7	1.1	2.1	9.5	4.6	100	6875	2182	34
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	28.1	46.6	13.1	52	1.6	1.2	2.1	9.5	4.6	100	6960	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	29.8	43.4	12.9	56	1.7	1.4	2.1	9.5	4.6	100	7060	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	28.2	55.8	15.7	44	2.1	1.0	2.1	9.7	4.7	100	7735	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	27.2	56.5	15.3	45	2.0	1.0	2.0	9.7	4.8	99	8230	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	8.4	73.2	6.2	90	1.3	1.0	18.5	81.1	4.4	100	8320	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	7.9	72.1	5.7	79	1.2	0.9	18.3	81.3	4.4	100	9850	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	650	125	0.8	54.8	0.5	12	0.2	3.7	18.3	81.3	4.4	100	9940	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	125	2.5	72.5	1.8	29	0.4	1.6	18.3	81.3	4.4	100	10010	1705	17

Table B4. Alkaline Earth/Alpha Alumina 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	ECI
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	125	2.5	70.1	1.7	29	0.4	1.6	18.3	81.3	4.4	100	10065	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	125	3.8	60.7	2.3	24	0.5	1.2	8.8	79.8	9.1	100	10125	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	125	3.9	58.0	2.3	18	0.4	1.0	8.7	77.3	8.9	99	13855	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	9.1	61.9	5.7	62	1.5	0.7	8.7	77.3	8.9	102	13990	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	12.1	62.0	7.5	70	1.5	0.8	8.7	77.3	8.9	100	14080	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	11.0	61.8	6.8	68	1.5	0.8	8.7	77.3	8.9	101	14145	1705	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	13.0	61.5	8.1	79	1.8	0.8	8.8	78.7	8.9	101	14390	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	12.8	62.2	8.0	76	1.7	0.8	8.8	78.7	8.9	101	14485	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	13.3	63.4	8.4	72	1.6	0.7	8.8	78.7	8.9	99	14575	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	9.8	63.2	6.2	55	1.4	0.6	8.8	77.4	8.8	100	15790	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	25.8	51.4	13.1	44	2.7	0.6	2.2	19.3	8.9	99	15970	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	24.6	51.9	12.6	41	2.5	0.5	2.2	19.3	8.9	99	16150	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	20.6	53.8	11.0	33	2.1	0.5	2.2	19.2	8.9	99	17125	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	20.5	62.0	12.6	27	1.9	0.5	2.0	9.4	4.8	99	17245	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	125	20.3	62.0	12.5	27	1.9	0.5	2.0	9.4	4.8	99	17305	1705	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	16.4	65.3	10.6	20	1.4	0.5	2.0	9.4	4.8	100	17395	2182	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	16.0	65.7	10.5	20	1.4	0.5	2.0	9.4	4.8	100	17575	2182	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	14.1	66.2	9.4	18	1.3	0.5	1.9	9.3	4.8	100	18295	2182	50
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	13.6	64.1	8.7	17	1.1	0.6	2.0	9.5	4.8	100	18385	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	14.2	63.7	9.0	17	1.0	0.6	2.0	9.5	4.8	99	18490	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	14.7	63.5	9.2	18	1.0	0.7	2.0	9.5	4.8	99	18760	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	13.3	62.9	8.4	17	1.0	0.7	2.0	9.3	4.7	100	19750	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	100	20.1	56.7	11.3	28	1.6	0.7	2.0	9.3	4.7	100	19840	1364	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	100	20.1	56.6	11.3	28	1.6	0.7	2.0	9.3	4.7	100	19930	1364	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	100	20.3	56.6	11.4	29	1.6	0.7	2.0	9.4	4.8	99	20695	1364	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	100	19.6	55.5	10.8	28	1.6	0.7	2.0	9.2	4.7	100	24070	1364	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	13.5	61.7	8.3	16	1.0	0.7	2.0	9.2	4.7	99	24160	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	13.5	62.2	8.4	17	1.0	0.7	2.0	9.2	4.7	99	24250	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	18.1	####	####	95	####	0.2	1.6	7.3	4.7	103	24565	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	18.0	####	####	96	####	0.2	1.6	7.3	4.7	104	24655	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	18.1	####	####	98	####	0.3	1.6	7.4	4.7	105	25015	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	19.0	####	####	98	####	0.3	1.6	7.4	4.7	104	25375	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	14.5	####	####	72	####	0.2	1.6	7.3	4.6	102	25555	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	14.4	####	####	72	####	0.2	1.6	7.3	4.6	103	25645	2182	17
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	14.0	####	####	66	####	0.1	1.6	8.3	5.1	96	25765	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	13.8	####	####	67	####	0.1	1.6	8.3	5.1	97	25845	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	12.5	####	####	72	####	0.1	1.7	8.3	5.0	105	26635	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	13.5	####	####	71	####	0.1	1.7	8.3	5.0	102	26815	2182	200

Table B4. Alkaline Earth/Alpha Alumina 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	ECI
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	75.9	62.7	85.6	99	####	0.1	1.7	8.3	5.0	180	26950	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	76.3	63.4	86.0	99	####	0.1	1.7	8.3	5.0	178	27030	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	700	160	76.4	63.2	85.6	99	####	0.1	1.7	8.3	5.0	177	27105	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	650	160	####	####	####	98	####	0.1	0.2	0.9	5.0	114	27185	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	650	160	####	####	####	98	####	0.1	0.2	0.9	5.0	116	27330	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	650	160	####	####	####	98	####	0.1	0.2	0.9	5.1	110	28370	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	650	160	1.7	52.5	0.9	1	####	0.2	2.0	10.3	5.1	99	28545	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	10.6	62.1	6.6	12	1.9	0.2	2.0	10.3	5.1	100	28635	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	11.7	62.0	7.2	13	2.0	0.3	2.0	10.3	5.1	99	28715	2182	200
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	11.2	68.8	7.7	13	1.2	0.4	2.0	10.3	5.1	100	28845	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	12.8	68.6	8.8	16	1.2	0.5	2.0	10.3	5.1	100	28950	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	12.0	63.5	7.6	15	1.0	0.7	2.0	10.5	5.1	99	29850	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	13.5	62.2	8.3	16	1.1	0.7	2.0	10.3	5.2	99	30270	2182	10
33 BKW 6 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	13.8	59.0	8.1	18	1.0	0.7	2.0	10.3	5.2	99	30795	2182	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.9	32.1	13.2	99	2.1	7.3	2.0	9.6	4.9	101	80	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.0	34.0	14.2	99	2.4	6.8	2.0	9.6	4.9	99	205	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	43.9	40.2	17.4	92	2.6	2.9	2.0	9.5	4.8	99	4075	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.8	40.4	17.3	92	2.6	2.9	2.0	9.7	4.8	100	4165	2133	5
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	43.0	40.6	17.3	92	2.6	2.9	2.0	9.7	4.8	99	4255	2133	5
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.2	40.6	17.0	90	2.5	3.0	2.1	9.8	4.7	99	5575	2133	5
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	43.3	39.9	17.1	90	2.6	3.0	2.0	9.4	4.8	99	5665	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	44.2	39.9	17.4	91	2.6	3.0	2.0	9.4	4.8	98	5755	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	44.4	40.4	17.7	91	2.8	2.9	2.0	9.3	4.8	99	6520	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	44.0	40.5	17.7	91	2.7	2.9	2.0	9.3	4.8	99	6700	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	43.0	41.5	17.7	91	2.6	2.8	2.1	9.5	4.6	99	6835	2133	34
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.0	41.8	17.5	90	2.6	2.8	2.1	9.5	4.6	100	6920	2133	34
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.4	41.5	17.4	90	2.6	2.8	2.1	9.5	4.6	99	7000	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.4	41.2	17.2	90	2.5	2.8	2.0	9.7	4.8	99	7190	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	43.2	41.8	17.8	90	2.7	2.8	2.0	9.7	4.8	99	8210	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	125	9.8	76.4	7.5	100	1.2	4.7	18.5	81.1	4.4	100	8300	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	125	9.8	76.1	7.5	100	1.3	4.7	18.5	81.1	4.4	100	8370	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	725	125	9.2	73.2	6.7	97	1.2	3.1	18.5	81.1	4.4	100	8485	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	725	125	9.1	74.1	6.7	97	1.2	3.1	18.5	81.1	4.4	100	8515	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	8.4	72.7	6.1	89	1.0	2.8	18.5	81.1	4.4	100	8615	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	8.3	72.6	6.0	87	1.0	3.0	18.3	81.3	4.4	100	9840	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	650	125	1.9	53.8	1.0	27	0.2	2.8	18.3	81.3	4.4	100	9975	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	670	125	3.3	62.1	2.1	40	0.3	2.7	18.3	81.3	4.4	100	10040	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	670	125	3.2	61.7	2.0	40	0.3	2.8	18.3	81.3	4.4	100	10095	1667	17

Table B4. Alkaline Earth/Alpha Alumina 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	ECI
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	670	125	4.1	47.2	2.0	29	0.4	2.2	8.8	79.8	9.1	100	10165	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	670	125	4.7	47.6	2.2	27	0.4	2.0	8.7	77.3	8.9	99	13900	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	125	16.3	64.8	10.6	99	2.2	3.7	8.7	77.3	8.9	100	14035	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	11.3	60.6	6.9	71	1.2	2.3	8.7	77.3	8.9	100	14115	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	12.0	60.3	7.2	70	1.2	2.2	8.7	77.3	8.9	99	14210	1667	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	11.7	61.5	7.2	69	1.2	2.3	8.8	78.7	8.9	100	14420	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	11.6	61.7	7.1	66	1.1	2.2	8.8	78.7	8.9	99	14530	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	10.4	61.9	6.4	61	1.1	2.1	8.8	77.4	8.8	100	15835	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	23.9	46.4	11.1	46	1.6	2.2	2.2	19.3	8.9	100	15925	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	24.5	46.3	11.3	46	1.6	2.2	2.2	19.3	8.9	99	16015	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	710	125	24.1	46.5	11.1	45	1.5	2.2	2.2	19.2	8.9	99	17095	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	125	43.8	41.8	18.1	96	3.9	3.0	2.2	19.2	8.9	99	17170	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	125	43.6	41.6	17.9	95	3.9	2.9	2.2	19.2	8.9	99	17200	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	125	45.2	43.2	19.3	89	3.1	3.1	2.0	9.4	4.8	99	17275	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	125	45.2	43.4	19.4	89	3.1	3.1	2.0	9.4	4.8	99	17330	1667	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.5	45.9	19.3	80	2.6	2.8	2.0	9.4	4.8	99	17455	2133	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	42.2	45.8	19.2	79	2.5	2.7	2.0	9.4	4.8	99	17635	2133	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	41.2	46.0	18.8	76	2.4	2.5	2.0	9.5	4.8	99	18220	2133	50
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.4	46.0	18.6	76	2.3	2.5	1.9	9.3	4.8	100	18355	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.5	46.1	18.6	76	2.3	2.5	1.9	9.3	4.8	100	18445	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	40.3	46.3	18.6	75	2.3	2.5	1.9	9.3	4.8	100	18535	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	39.6	46.5	18.3	73	2.2	2.4	2.0	9.5	4.8	99	19660	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	100	44.5	42.1	18.6	90	2.9	2.8	2.0	9.3	4.7	99	19795	1333	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	100	44.6	41.9	18.5	89	2.9	2.8	2.0	9.3	4.7	99	19885	1333	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	100	42.7	42.9	18.2	83	2.6	2.6	2.0	9.2	4.7	99	24115	1333	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	36.9	47.7	17.5	66	1.9	2.3	2.0	9.2	4.7	99	24205	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	37.3	47.6	17.6	66	2.0	2.3	2.0	9.2	4.7	99	24295	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	16.6	####	####	97	-0.5	1.1	1.6	7.3	4.7	100	24475	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	16.7	####	####	97	-0.5	1.1	1.6	7.3	4.7	100	24505	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	10.5	####	####	56	-0.7	1.1	1.6	7.3	4.7	99	24595	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	10.8	####	####	57	-0.7	1.1	1.6	7.4	4.7	99	25045	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	11.3	####	####	56	-0.7	1.1	1.6	7.3	4.6	98	25680	2133	17
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	12.2	####	####	57	-0.7	1.1	1.6	8.3	5.1	94	25800	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	11.7	####	####	58	-0.7	1.1	1.6	8.3	5.1	96	25890	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	10.3	####	####	60	-0.7	0.9	1.7	8.3	5.0	101	26665	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	11.5	####	####	60	-0.7	0.9	1.7	8.3	5.0	98	26845	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	####	####	####	99	-0.6	0.3	0.2	0.9	5.0	125	26995	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	700	160	####	####	####	99	-0.6	0.3	0.2	0.9	5.0	109	27065	2133	200

Table B4. Alkaline Earth/Alpha Alumina 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	ECI
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	650	160	####	####	####	47	-0.8	0.5	0.2	0.9	5.0	100	27265	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	650	160	####	####	####	47	-0.8	0.5	0.2	0.9	5.0	99	27355	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	650	160	####	####	####	50	-0.8	0.4	0.2	0.9	5.1	96	28380	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	650	160	3.7	27.4	1.0	6	3.1	2.5	2.0	10.3	5.1	100	28560	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	32.1	52.5	16.7	53	1.9	3.0	2.0	10.3	5.1	99	28665	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	31.5	52.7	16.4	52	1.9	2.9	2.0	10.3	5.1	99	28745	2133	200
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	31.5	55.0	17.2	52	1.6	2.9	2.0	10.3	5.1	99	28900	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	31.5	54.9	17.2	52	1.6	2.9	2.0	10.3	5.1	100	28990	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	32.4	55.3	17.7	53	1.7	2.8	2.0	10.4	5.2	99	29170	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	31.0	56.5	17.2	49	1.6	2.8	2.0	10.5	5.1	99	29890	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	30.5	56.7	17.0	48	1.5	2.4	2.0	10.3	5.2	98	30235	2133	10
33 BKW 7 R#4	5.0	BaCO3,Al2O3,5451,60/100	750	160	30.4	56.7	17.0	47	1.6	2.4	2.0	10.3	5.2	99	30835	2133	10
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	17.5	13.8	2.4	45	0.6	2.3	2.0	10.4	5.2	100	105	2133	0
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	17.1	13.2	2.3	44	0.6	2.1	2.0	10.4	5.2	100	330	2133	0
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	16.2	9.1	1.5	43	0.6	1.9	2.0	10.4	5.3	101	3795	2133	0
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	26.6	52.0	14.2	42	3.0	0.4	2.0	10.4	5.1	102	3930	2133	10
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	19.0	50.5	9.8	28	1.7	0.5	2.0	10.4	5.1	102	4020	2133	10
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	17.7	47.8	8.5	28	1.5	0.5	2.0	10.4	5.1	101	4110	2133	10
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	14.6	38.6	5.7	25	1.0	0.6	2.0	10.3	5.1	101	4300	2133	2
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	13.9	35.6	5.0	24	1.0	0.6	2.0	10.3	5.1	101	4380	2133	2
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	9.4	19.6	1.9	18	0.5	0.6	2.0	10.3	5.1	102	5820	2133	2
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	12.4	27.5	3.4	22	0.8	0.5	2.0	10.4	5.2	100	5910	2133	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	12.8	28.4	3.7	22	0.8	0.5	2.0	10.4	5.2	100	6000	2133	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	27.5	57.5	16.0	39	3.3	0.3	2.0	10.3	5.2	101	6405	2133	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	26.8	57.5	15.4	37	3.2	0.3	2.0	10.4	5.2	100	6900	2133	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	33.2	48.8	16.3	52	4.6	0.3	2.0	10.4	5.2	101	6935	2133	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	160	33.3	49.6	16.5	52	4.5	0.3	2.0	10.4	5.2	100	6965	2133	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	225	25.2	56.5	14.2	35	3.0	0.3	2.0	10.4	5.2	100	7010	3000	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	225	24.8	56.8	14.1	34	2.9	0.3	2.0	10.4	5.2	100	7050	3000	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	225	19.6	64.1	12.5	24	2.1	0.3	2.0	10.4	5.2	100	7125	3000	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	225	19.2	65.1	12.4	23	2.0	0.3	2.0	10.4	5.2	99	7215	3000	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	225	13.2	69.1	9.1	14	1.4	0.2	2.0	10.4	5.2	100	8340	3000	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	80	32.1	51.0	16.4	48	4.6	0.2	2.0	10.4	5.2	100	8415	1067	200
33 BKW 49 R#4	5.0	Ba(NO3)2,Al2O3,5451,60/100	750	80	31.5	51.4	16.3	47	4.6	0.3	2.0	10.4	5.2	100	8445	1067	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	34.6	29.5	10.1	83	1.5	4.9	2.0	10.2	5.1	99	55	2233	7.5
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	33.4	28.1	9.3	81	1.4	4.8	2.0	10.2	5.1	99	120	2233	7.5
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	36.1	50.8	18.0	62	1.8	2.0	2.0	10.2	5.1	98	5965	2233	7.5
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	27.8	60.3	16.4	40	1.6	1.7	2.1	10.3	5.0	98	11440	2233	7.5

Table B4. Alkaline Earth/Alpha Alumina 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	ECI
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	27.5	60.1	16.4	42	1.6	1.7	2.0	10.2	5.2	99	11545	2233	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	27.9	59.6	16.5	43	1.6	1.7	2.0	10.2	5.2	100	11635	2233	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	29.1	59.0	17.0	45	1.6	1.8	2.0	10.2	5.2	99	12490	2233	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	27.7	58.7	16.2	45	1.6	1.9	2.0	10.2	5.1	100	17115	2233	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	42.2	46.5	19.5	80	3.1	1.9	2.0	10.1	5.0	99	17195	1116	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	42.3	46.6	19.6	81	3.1	1.9	2.0	10.1	5.0	99	17270	1116	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	43.0	46.4	19.7	82	3.1	2.0	2.0	10.1	5.0	99	17440	1116	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	43.2	45.4	19.4	84	2.9	2.3	2.0	10.2	5.1	99	18470	1116	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	42.3	46.1	19.4	83	2.9	2.2	2.0	10.1	5.1	100	18565	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.9	46.2	19.3	82	2.9	2.2	2.0	10.1	5.1	100	18640	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.7	46.5	19.4	81	2.9	2.1	2.0	10.1	5.1	100	18745	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.3	46.6	19.3	80	2.9	2.0	2.0	10.1	5.1	100	18835	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.6	47.0	19.4	79	2.9	1.9	2.0	10.2	5.1	99	19015	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.5	47.0	19.3	79	3.0	1.9	2.0	10.2	5.1	99	19240	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.2	47.1	19.3	78	3.0	1.9	2.0	10.2	5.1	100	19420	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	40.8	47.3	19.3	77	3.0	1.8	2.0	10.2	5.1	100	19600	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	40.9	47.6	19.3	77	2.9	1.8	2.0	10.3	5.1	99	19735	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.0	47.2	19.3	78	3.0	1.8	2.0	10.3	5.1	99	19825	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	40.8	47.8	19.3	77	3.0	1.8	2.0	10.3	5.1	99	19915	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	41.0	47.3	19.3	77	2.9	1.8	2.0	10.3	5.1	99	20090	1116	8
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	45.2	42.0	19.1	89	3.6	1.9	2.0	10.2	5.1	101	20185	837	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	44.8	43.9	19.5	88	3.6	1.8	2.0	10.2	5.1	99	20275	837	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	43.0	44.6	19.2	80	3.8	1.1	2.0	10.3	5.1	100	21220	837	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	42.8	38.9	16.7	91	4.3	1.1	2.1	20.6	9.6	100	21400	837	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	78	39.5	42.3	16.7	80	3.6	1.2	2.1	20.6	9.6	100	21460	1088	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	78	39.5	42.8	16.9	81	3.6	1.2	2.1	20.6	9.6	100	21520	1088	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	75	28.1	50.8	14.2	92	2.9	1.3	3.9	38.8	9.8	99	21555	1047	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	75	28.3	50.1	14.1	94	2.9	1.4	3.9	38.8	9.8	100	21625	1047	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	75	28.5	50.2	14.2	95	2.9	1.4	3.9	38.8	9.8	99	21715	1047	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	75	27.7	50.4	13.9	93	2.8	1.5	3.9	38.7	9.9	100	22480	1047	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	51.3	33.3	17.3	62	4.2	1.5	1.1	10.5	9.5	101	22615	1116	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	80	50.5	34.0	17.4	61	4.2	1.4	1.1	10.5	9.5	101	22695	1116	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	57.6	28.9	16.9	75	5.2	1.5	1.1	10.5	9.5	102	22740	837	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	57.7	28.8	16.9	75	5.2	1.5	1.1	10.5	9.5	102	22740	837	30
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	16.7	58.4	9.7	98	2.2	1.5	8.5	79.9	9.4	100	22815	837	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	60	16.7	58.8	9.7	98	2.2	1.4	8.5	79.9	9.4	99	22905	837	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	100	14.3	61.9	8.9	82	1.6	1.2	8.0	79.2	9.9	100	22970	1395	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	100	14.5	63.4	9.1	81	1.6	1.2	8.0	79.2	9.9	99	23000	1395	47

Table B4. Alkaline Earth/Alpha Alumina 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	ECl
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	10.6	69.7	7.3	48	1.0	1.3	8.0	79.2	9.9	99	23085	2233	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	9.4	69.8	6.6	46	1.0	1.2	8.0	79.2	9.9	99	23175	2233	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	11.0	70.9	7.5	39	0.8	1.1	8.1	79.6	9.9	96	24570	2233	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	7.2	71.3	5.1	34	0.7	1.1	8.0	80.1	10.0	100	25470	2233	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	6.4	70.8	4.6	35	0.8	1.1	8.0	80.0	10.0	101	27000	2233	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	8.5	72.6	6.1	36	0.7	1.3	8.0	80.0	10.0	98	27075	2233	47
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	6.4	70.8	4.5	27	0.6	0.9	8.0	80.0	10.0	99	27180	2233	100
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	7.0	71.6	4.9	26	0.6	0.7	8.0	80.0	10.0	98	27270	2233	100
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	8.1	71.5	5.6	26	0.6	0.7	8.0	80.0	10.0	97	27360	2233	100
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	####	72.3	####	14	0.5	0.7	8.0	79.8	10.0	107	28295	2233	100
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	####	70.4	####	12	0.5	0.4	8.0	79.7	10.0	105	28395	2233	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	####	70.6	####	12	0.5	0.4	8.0	79.7	10.0	105	28485	2233	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	1.5	71.3	1.1	14	0.5	0.3	8.0	79.7	10.0	102	28575	2233	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	10.9	65.2	7.2	11	1.2	0.2	2.0	10.1	5.1	101	28710	2233	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	11.0	64.4	7.2	11	1.1	0.1	2.0	10.1	5.1	100	28800	2233	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	11.1	66.1	7.3	11	1.1	0.1	2.0	10.1	5.1	100	28890	2233	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	8.4	71.0	6.0	9	1.0	0.1	2.0	10.1	5.1	100	29655	2233	200
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	9.6	70.1	6.7	10	0.7	0.4	2.0	10.1	5.1	99	29790	2233	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	10.4	70.3	7.2	12	0.8	0.5	2.0	10.1	5.1	99	29875	2233	4
33 BKW 74 R#3	5.0	BaCO3,Al2O3,5451,60/100	750	160	13.7	68.8	9.3	14	0.9	0.9	1.9	9.9	5.1	99	31230	2233	4

Appendix A and the Experimental Section describe Table headings and experimental procedures.

Inaccurate due to a small number or division by a small number.

EBR* indicates whether ethyl bromide was used instead of ethyl chloride. The concentration used is indicated in the ECl column, as for ECl.

Reactor D was used for all experiments.

Table B5. Pure Compounds

Name	Wt	Catalyst	Temp	Ccm	CH_4 C	Sel	Yield	O_2 C	=/-	CO_2/CO	CH_4/O_2	CH_4 in	O_2 in	C Bal	Time	GHSV	ECI
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	750	160	36.5	####	####	98	0.0	1.4	2.0	9.4	4.7	101	145	2133	0
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	700	160	35.9	0.3	0.1	98	0.2	1.2	2.0	9.4	4.7	101	235	2133	0
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	700	160	35.6	0.4	0.1	98	0.2	1.2	2.0	9.5	4.7	101	460	2133	0
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	700	160	35.2	0.4	0.1	98	0.1	1.2	2.1	9.6	4.6	102	1045	2133	0
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	650	160	33.1	0.1	0.0	98	1.2	0.9	2.1	9.5	4.6	104	1180	2133	0
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	650	160	32.9	4.6	1.6	98	0.0	0.9	2.1	9.5	4.6	105	1270	2133	0
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	600	160	27.9	####	####	90	0.0	0.8	2.1	9.5	4.6	104	1540	2133	0
32 BKW 123 R#4	2.5	Gamma Al_2O_3,6573,60/100	600	160	27.8	####	####	89	0.0	0.8	2.1	9.5	4.6	104	1630	2133	0
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	36.2	31.6	11.3	88	1.7	7.0	2.0	10.2	5.1	99	30	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	28.0	25.8	7.2	69	1.2	5.9	2.0	10.2	5.1	99	255	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	29.5	32.4	9.5	67	1.6	5.2	2.0	10.2	5.1	99	430	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	36.0	43.3	15.4	68	2.1	2.4	2.0	10.2	5.2	99	835	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	36.3	43.8	15.7	68	2.1	2.1	2.0	10.2	5.2	99	1015	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	35.7	44.5	15.8	65	2.0	2.1	2.0	10.2	5.1	99	1420	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	30.3	47.6	14.4	52	1.7	1.9	2.0	10.1	5.1	100	3715	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	27.5	49.4	13.5	45	1.5	1.8	2.0	10.2	5.1	99	6415	2233	7.5
33 BKW 75 R#4	5.0	$BaCO_3$,40/100	750	160	25.9	50.7	12.9	39	1.4	1.7	2.1	10.3	5.0	99	11410	2233	7.5

Appendix A and the Experimental Section describe Table headings and experimental procedures.

Inaccurate due to a small number or division by a small number.

Reactor D was used for all experiments.

Table B6. BaCl2/Other Supports

Name	Wt	Catalyst	Temp	Ccm	CH4 C	S%	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
33 BKW 54 R#3	5.0	BaCl2,Al2O3,8855001,18/60	750	160	41.5	62.1	25.3	61	5.5	0.7	2.1	10.6	5.1	98	35	2341	0
33 BKW 54 R#3	5.0	BaCl2,Al2O3,8855001,18/60	750	160	31.4	69.1	21.3	40	3.2	0.8	2.1	10.6	5.1	98	90	2341	0
33 BKW 54 R#3	5.0	BaCl2,Al2O3,8855001,18/60	750	160	20.0	73.0	14.5	22	1.7	0.9	2.0	10.4	5.1	99	215	2341	10
33 BKW 54 R#3	5.0	BaCl2,Al2O3,8855001,18/60	750	160	13.3	73.0	9.6	14	1.0	0.9	2.0	10.4	5.1	99	350	2341	10
33 BKW 54 R#3	5.0	BaCl2,Al2O3,8855001,18/60	750	160	8.0	66.5	5.3	10	0.6	0.7	2.0	10.4	5.2	99	5255	2341	10
33 BKW 54 R#3	5.0	BaCl2,Al2O3,8855001,18/60	750	160	6.9	66.1	4.6	8	0.6	0.7	2.0	10.3	5.2	100	5390	2341	200
33 BKW 54 R#3	5.0	BaCl2,Al2O3,8855001,18/60	750	160	7.0	66.0	4.6	9	0.6	0.7	2.0	10.3	5.2	100	5480	2341	200
33 BKW 55 R#4	5.0	BaCl2,Al2O3,8855011,14/70	750	160	46.1	34.9	16.4	98	6.2	1.1	2.1	10.6	5.1	102	65	1959	0
33 BKW 55 R#4	5.0	BaCl2,Al2O3,8855011,14/70	725	160	41.6	29.9	12.6	96	3.3	1.7	2.0	10.4	5.1	101	170	1959	10
33 BKW 55 R#4	5.0	BaCl2,Al2O3,8855011,14/70	725	160	40.5	30.5	12.5	90	2.8	1.6	2.0	10.4	5.1	101	395	1959	10
33 BKW 55 R#4	5.0	BaCl2,Al2O3,8855011,14/70	725	160	31.0	11.7	3.7	78	1.1	1.2	2.0	10.4	5.2	102	5300	1959	10
33 BKW 55 R#4	5.0	BaCl2,Al2O3,8855011,14/70	725	160	29.5	11.3	3.5	76	1.1	1.2	2.0	10.3	5.2	103	5420	1959	200
33 BKW 55 R#4	5.0	BaCl2,Al2O3,8855011,14/70	725	160	29.6	11.3	3.4	75	1.1	1.2	2.0	10.3	5.2	103	5525	1959	200
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	160	22.2	63.0	13.9	30	2.2	0.5	2.0	10.4	5.2	100	30	1882	10
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	80	29.8	53.2	15.6	45	3.2	0.5	2.0	10.0	5.1	98	1225	941	10
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	80	29.8	51.3	15.2	45	3.1	0.6	2.0	10.1	5.1	99	1520	941	0
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	80	29.0	51.9	15.0	45	3.1	0.5	1.9	9.9	5.1	100	1610	941	200
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	80	31.4	52.7	16.6	46	4.3	0.3	1.9	9.9	5.1	100	1790	941	200
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	80	31.8	52.3	16.8	47	4.6	0.2	1.9	9.9	5.2	101	2015	941	200
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	80	34.4	51.3	17.7	52	5.0	0.2	1.9	10.0	5.2	100	2115	941	200
33 BKW 62 R#3	5.0	BaCl2,Al2O3,8855002,18/60	750	80	33.5	51.4	17.3	51	4.9	0.2	1.9	10.0	5.2	101	2150	941	200
33 BKW 63 R#4	5.0	BaCl2,Al2O3,8855003,14/50	750	160	54.5	52.1	27.8	98	10.2	1.3	2.0	10.4	5.2	98	60	2133	10
33 BKW 63 R#4	5.0	BaCl2,Al2O3,8855003,14/50	750	180	32.6	25.9	8.6	67	1.8	0.8	2.0	10.0	5.1	101	1185	2400	10
33 BKW 63 R#4	5.0	BaCl2,Al2O3,8855003,14/50	750	180	32.6	25.3	8.3	67	1.7	0.8	2.0	10.0	5.1	101	1280	2400	10
33 BKW 63 R#4	5.0	BaCl2,Al2O3,8855003,14/50	750	180	32.2	23.9	7.8	70	1.5	0.9	2.0	10.1	5.1	101	1475	2400	0
33 BKW 63 R#4	5.0	BaCl2,Al2O3,8855003,14/50	750	180	31.6	23.3	7.5	69	1.5	0.9	1.9	9.9	5.1	102	1565	2400	200
33 BKW 63 R#4	5.0	BaCl2,Al2O3,8855003,14/50	750	180	28.5	31.0	9.1	50	2.3	0.2	1.9	9.9	5.1	103	1655	2400	200

Appendix A and the Experimental Section describe Table headings and experimental procedures.
Reactor D was used for all experiments.

Table B7. Hydrotalcite Catalysts

Name	Wt	Catalyst	Temp	Ccm	CH4 C	Sel	Yield	O2 C	=/-	CO2/CO	CH4/O2	CH4 in	O2 in	C Bal	Time	GHSV	ECI
33 BKW 33 R#3	1.5	MgAlOH,60/100	750	160	36.7	3.7	1.4	98	1.4	1.5	2.0	10.2	5.1	102	50	2341	0
33 BKW 33 R#3	1.5	MgAlOH,60/100	750	160	36.7	-0.1	0.0	97	0.0	1.5	2.0	10.2	5.1	101	120	2341	0
33 BKW 33 R#3	1.5	MgAlOH,60/100	700	160	26.7	0.4	0.1	62	0.9	0.9	2.0	10.2	5.1	102	210	2341	0
33 BKW 33 R#3	1.5	MgAlOH,60/100	700	160	26.3	0.3	0.1	63	0.0	0.9	2.0	10.1	5.1	102	390	2341	0
33 BKW 33 R#3	1.5	MgAlOH,60/100	700	160	26.2	0.6	0.2	62	0.6	0.9	2.0	10.1	5.1	103	795	2341	0
33 BKW 33 R#3	1.5	MgAlOH,60/100	700	160	25.7	0.5	0.1	61	0.7	0.9	2.0	10.2	5.0	103	1290	2341	0
33 BKW 33 R#3	1.5	MgAlOH,60/100	700	160	26.4	0.6	0.2	62	0.6	0.9	2.0	10.3	5.1	102	1380	2341	10
33 BKW 33 R#3	1.5	MgAlOH,60/100	700	160	26.6	0.6	0.2	62	0.6	0.9	2.0	10.3	5.1	102	1470	2341	10
33 BKW 34 R#4	1.5	MgAlOH,60/100	750	160	35.8	5.6	2.0	99	1.3	2.3	2.0	10.2	5.1	101	95	2341	0
33 BKW 34 R#4	1.5	MgAlOH,60/100	700	160	32.0	1.9	0.6	99	0.6	7.2	2.0	10.2	5.1	99	185	2341	0
33 BKW 34 R#4	1.5	MgAlOH,60/100	700	160	32.3	1.8	0.6	99	0.6	6.6	2.0	10.2	5.1	99	275	2341	0
33 BKW 34 R#4	1.5	MgAlOH,60/100	700	160	33.1	1.5	0.5	98	0.5	4.2	2.0	10.1	5.1	101	1040	2341	0
33 BKW 34 R#4	1.5	MgAlOH,60/100	650	160	21.6	0.1	0.0	68	0.0	14.4	2.0	10.2	5.0	100	1175	2341	0
33 BKW 34 R#4	1.5	MgAlOH,60/100	650	160	21.8	0.1	0.0	68	0.0	10.8	2.0	10.2	5.0	100	1265	2341	0
33 BKW 34 R#4	1.5	MgAlOH,60/100	650	160	24.1	0.3	0.1	67	0.5	9.8	2.0	10.3	5.1	98	1355	2341	10
33 BKW 34 R#4	1.5	MgAlOH,60/100	650	160	22.2	0.3	0.1	67	0.6	9.3	2.0	10.3	5.1	99	1425	2341	10
33 BKW 39 R#4	1.5	MgAlOH,60/100	750	160	35.8	3.2	1.2	93	1.3	1.3	2.0	10.5	5.2	103	200	2341	0
33 BKW 39 R#4	1.5	MgAlOH,60/100	750	160	36.0	3.2	1.2	93	1.3	1.3	2.0	10.5	5.2	103	290	2341	0
33 BKW 39 R#4	1.5	MgAlOH,60/100	750	160	35.4	3.4	1.2	92	1.2	1.3	2.0	10.6	5.2	103	605	2341	0
33 BKW 39 R#4	1.5	MgAlOH,60/100	750	160	34.8	3.5	1.2	90	1.3	1.3	2.0	10.5	5.2	103	1565	2341	0
33 BKW 39 R#4	1.5	MgAlOH,60/100	750	160	35.0	3.2	1.1	90	1.5	1.3	2.0	10.4	5.2	103	1685	2341	10
33 BKW 39 R#4	1.5	MgAlOH,60/100	750	160	36.1	3.0	1.1	90	1.7	1.3	2.0	10.4	5.2	102	1775	2341	10
33 BKW 39 R#4	1.5	MgAlOH,60/100	750	160	35.0	3.6	1.3	89	1.4	1.2	2.0	10.4	5.2	104	2270	2341	10
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	750	160	34.7	5.8	2.0	99	1.4	2.4	2.0	10.3	5.2	102	40	2400	0
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	33.0	1.7	0.6	92	0.9	2.0	2.0	10.3	5.2	102	100	2400	0
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	33.1	1.7	0.6	91	0.9	2.0	2.0	10.3	5.2	102	210	2400	0
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	32.5	1.4	0.5	89	0.9	1.9	2.0	10.4	5.2	102	1290	2400	0
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	33.4	1.6	0.5	87	1.2	1.8	2.0	10.4	5.2	101	1470	2400	10
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	33.6	2.0	0.7	86	1.3	1.6	2.0	10.4	5.2	102	1650	2400	10
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	34.2	2.8	1.0	87	1.1	1.1	2.0	10.3	5.2	103	2640	2400	10
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	34.2	2.7	1.0	87	1.2	1.1	2.0	10.3	5.2	104	3090	2400	200
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	36.9	8.8	3.5	86	2.7	0.6	2.0	10.3	5.2	106	3270	2400	200
33 BKW 42 R#3	1.5	BaCO3,MgAlOH,60/100	725	160	38.8	11.2	4.6	90	2.8	0.6	2.0	10.2	5.2	106	170	2400	200
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	750	160	34.9	4.2	1.5	99	1.3	2.2	2.0	10.3	5.2	102	75	2400	0
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	33.2	1.5	0.5	91	0.8	1.9	2.0	10.3	5.2	102	130	2400	0
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	33.1	1.4	0.5	90	0.8	1.8	2.0	10.3	5.2	102	255	2400	0
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	32.3	1.1	0.4	86	0.9	1.7	2.0	10.4	5.2	102	1330	2400	0
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	33.4	1.4	0.5	85	1.2	1.6	2.0	10.4	5.2	101	1515	2400	10
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	33.2	1.7	0.6	85	1.3	1.5	2.0	10.4	5.2	102	1695	2400	10
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	34.2	2.4	0.9	86	1.1	1.1	2.0	10.3	5.2	103	2595	2400	10
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	35.1	4.5	1.7	86	2.1	1.0	2.0	10.3	5.2	104	3135	2400	200
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	37.1	8.2	3.2	87	2.7	0.6	2.0	10.3	5.2	106	3315	2400	200
33 BKW 43 R#4	1.5	BaCO3,MgAlOH,60/100	725	160	38.2	9.7	4.0	89	2.8	0.5	2.0	10.2	5.2	106	4125	2400	200

Table B7. Hydrotalcite 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	ECI
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	30.3	3.3	1.0	99	0.6	11.1	2.0	10.4	5.2	99	30	2400	0
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	29.4	1.9	0.6	99	0.5	12.4	2.0	10.4	5.2	100	150	2400	0
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	27.9	0.2	0.1	86	0.0	5.5	2.0	10.4	5.3	101	3750	2400	0
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	31.8	0.7	0.2	85	1.0	5.5	2.0	10.4	5.1	97	3885	2400	10
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	30.4	1.9	0.6	91	0.9	3.4	2.0	10.4	5.1	103	3970	2400	10
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	33.3	1.8	0.6	93	0.6	1.9	2.0	10.4	5.1	103	4065	2400	10
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	33.8	1.6	0.6	94	0.5	1.6	2.0	10.4	5.1	103	4140	2400	10
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	33.2	1.1	0.4	89	0.5	1.3	2.0	10.3	5.1	104	4335	2400	2
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	32.9	0.8	0.3	86	0.4	1.2	2.0	10.3	5.1	103	4425	2400	2
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	25.8	0.3	0.1	66	0.6	1.0	2.0	10.3	5.1	104	5685	2400	2
33 BKW 48 R#5	1.5	BaCO3,MgAlOH,60/100	675	160	26.7	0.3	0.1	65	0.6	1.0	2.0	10.4	5.2	103	5955	2400	200
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	27.0	0.4	0.1	64	0.6	0.9	2.0	10.4	5.2	103	6135	2400	200
33 BKW 48 R#3	1.5	BaCO3,MgAlOH,60/100	675	160	32.5	3.1	1.1	74	1.6	0.4	2.0	10.3	5.2	107	6720	2400	200

Appendix A and the Experimental Section describe Table headings and experimental procedures.
Reactor D was used for all experiments.

Table B8. Methane Coupling Activity of K2La2Ti3O10

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 6-KDC-X-90

Weight (g): 4.098 **Volume (cc):** 3.8

CH4/O2/N2: 2.02/1/18 **Pressure (psig):** 5

Temperature (°C)	801	801	801	801	801	801	801	801	801	801
Flow (cc/min)	200	200	200	200	200	100	100	100	100	100
GHSV (h-1)	3158	3158	3158	3158	3158	1579	1579	1579	1579	1579
Time (h)	1	3	7	11	17	21	23	29	35	41
CH4 Conv., %	29.25	27.31	26.89	26.80	26.43	32.50	32.38	32.62	32.21	32.11
O2 Conv., %	80.00	75.35	73.11	71.96	70.94	88.17	88.01	91.62	91.63	91.61
C Balance, %	101.44	101.82	101.45	100.79	101.01	100.02	100.07	101.19	101.80	101.74
C2 Selectivity, %	38.34	38.21	37.85	37.56	37.52	36.91	37.18	37.21	37.19	37.10
C3 Selectivity, %	1.98	1.83	1.83	1.77	1.79	2.27	1.95	1.94	1.98	1.98
C2 Yield, %	11.38	10.62	10.33	10.15	10.02	12.00	12.05	12.28	12.19	12.12
Ethylene/Ethane	1.33	1.28	1.29	1.31	1.33	1.74	1.73	1.80	1.81	1.83
CO2/CO	17.01	15.32	14.43	13.87	13.09	17.34	17.38	20.86	20.64	20.12

Table *B9. Methane Coupling Activity of 20 wt% Na2CO3/ K2La2Ti3O10*

CATALYST: 20 wt% Na2CO3/ K2La2Ti3O10 **NOTEBOOK:** 7-KDC-X-92

Weight (g): 4.001 **Volume (cc):** 4.2

CH4/O2/N2: 2.02/1/3.81 **Pressure (psig):** 5

Temperature (°C)	801	801	801	801	801	801	801	801	801	801
Flow (cc/min)	200	200	200	200	200	150	150	150	150	150
GHSV (h-1)	2857	2857	2857	2857	2857	2142	2142	2142	2142	2142
Time (h)	1	3	7	11	17	21	23	31	37	41
CH4 Conv., %	24.54	24.57	25.00	24.40	23.45	31.89	31.95	30.97	30.42	29.87
O2 Conv., %	73.44	73.41	68.79	65.75	62.07	92.13	91.32	90.31	89.27	87.92
C Balance, %	102.77	103.82	101.57	101.42	101.45	102.13	101.82	102.07	102.18	101.93
C2 Selectivity, %	35.51	37.58	39.15	40.48	41.33	35.97	36.69	36.15	35.83	35.49
C3 Selectivity, %	0.42	1.51	1.78	1.96	2.02	1.68	1.73	1.54	1.43	1.43
C2 Yield, %	8.96	9.58	9.94	10.02	9.83	11.72	11.93	11.43	11.14	10.81
Ethylene/Ethane	0.95	1.15	1.21	1.23	1.21	1.55	1.59	1.54	1.48	1.44
CO2/CO	38.10	22.97	25.92	26.48	26.28	7.47	8.48	8.60	9.10	10.18

Table B10. Methane Coupling Activity of 36 wt% K_2CO_3/ $K_2La_2Ti_3O_{10}$

CATALYST: 36 wt% K_2CO_3/ $K_2La_2Ti_3O_{10}$ **NOTEBOOK:** 6-KDC-X-98

Weight (g): 4.035 **Volume (cc):** 3.8

$CH_4/O_2/N_2$: 2.02/1/3.79 **Pressure (psig):** 5

Temperature (°C)	801	801	801	801	801	801	801
Flow (cc/min)	200	200	200	250	250	250	250
GHSV (h^{-1})	3158	3158	3158	3947	3947	3947	3947
Time (h)	1	3	5	7	11	17	21
CH_4 Conv., %	33.88	33.10	33.20	28.78	28.32	27.33	27.22
O_2 Conv., %	94.49	94.25	94.68	91.15	85.93	84.10	83.68
C Balance, %	100.63	101.27	100.84	101.40	100.66	101.39	101.43
C2 Selectivity, %	39.17	38.71	37.72	30.11	30.76	31.37	31.58
C3 Selectivity, %	1.55	1.54	1.44	0.66	0.78	0.89	0.92
C2 Yield, %	13.36	12.98	12.63	8.79	8.77	8.69	8.72
Ethylene/Ethane	1.87	1.84	1.96	1.09	1.16	1.22	1.24
CO_2/CO	23.38	20.53	38.84	20.34	17.18	14.18	13.50

Table B11. Methane Coupling Activity of 40 wt% Li2CO3/ K2La2Ti3O10

CATALYST: 40 wt% Li2CO3/ K2La2Ti3O10 **NOTEBOOK:** 7-KLC-X-95

Weight (g): 4.035 **Volume (cc):** 3.65

CH4/O2/N2: 2.02/1/3.79 **Pressure (psig):** 5

Temperature (°C)	801	801	801	801	801	801	801	801	801	801
Flow (cc/min)	200	200	200	200	200	200	100	100	100	100
GHSV (h-1)	3288	3288	3288	3288	3288	3288	1644	1644	1644	1644
Time (h)	1	3	9	13	19	23	25	27	33	37
CH4 Conv., %	22.46	24.88	25.58	24.57	22.07	21.36	31.08	30.97	29.69	28.96
O2 Conv., %	58.93	65.69	66.18	63.89	57.07	54.56	87.10	85.84	82.09	79.85
C Balance, %	104.17	101.77	101.12	101.04	101.86	101.07	101.21	100.98	100.97	101.06
C2 Selectivity, %	38.17	38.45	38.54	38.66	39.86	40.06	35.47	35.28	35.09	34.91
C3 Selectivity, %	1.98	2.42	2.48	2.13	2.31	2.25	2.79	2.79	2.71	2.71
C2 [illegible]	8.93	9.74	9.97	9.60	8.96	8.65	11.16	11.03	10.52	10.22
Ethylene/Ethane	1.52	1.74	1.71	1.64	1.46	1.41	2.54	2.54	2.53	2.54
CO2/CO	7.51	7.66	8.46	8.60	7.85	7.32	12.32	11.04	8.17	6.84

Table B12. **Comparison of Methane Coupling Results for Undoped and Alkali-Doped $K_2La_2Ti_3O_{10}$**

CATALYST:	**$K_2La_2Ti_3O_{10}$****	**$Na_2CO_3/La_2Ti_3O_{10}$**	**$K_2CO_3/K_2La_2Ti_3O_{10}$**	**$Li_2CO_3/K_2La_2Ti_3O_{10}$**
Weight (g):	4.01	4	4.03	4.04
$CH_4/O_2/N_2$:	2.0/1/3.8	2.0/1/3.8	2.0/1/3.8	2.0/1/3.8
Pressure (psig):	7	5	5	5
Temperature (°C)	800	801	801	801
Flow (cc/min)	200	200	200	200
GHSV (h 1)	3000	2857	3158	3288
CH_4 Conv., %	38.3	25.00	33.88	24.88
O_2 Conv., %	93.3	68.79	94.49	65.69
C Balance, %	100.9	101.57	100.63	101.77
C_2 Selectivity, %	40.7	39.15	39.17	38.45
C_3 Selectivity, %	1.8	1.78	1.55	2.42
C_2 Yield, %	15.8	9.94	13.36	9.74
Ethylene/Ethane	1.8	1.21	1.87	1.74
CO_2/CO	6.7	25.92	23.38	7.66

**: Results obtained previously (Third Quarterly Report).

Table B13. Methane Coupling Activity of K2CO3

CATALYST: K2CO3 **NOTEBOOK:** 6-KDC-X-88

Weight (g): 4.012 **Volume (cc):** 5

CH4/O2/N2: 2.02/1/3.84 **Pressure (psig):** 5

Temperature (°C)	805	805	805	805	805
Flow (cc/min)	50	50	50	50	50
GHSV (h-1)	600	600	600	600	600
Time (h)	1	3	11	19	29
CH4 Conv., %	28.91	28.12	23.04	21.64	20.26
O2 Conv., %	85.08	80.55	65.17	58.81	54.68
C Balance, %	103.34	101.57	101.82	101.12	101.15
C2 Selectivity, %	31.44	31.36	31.61	31.47	30.83
C3 Selectivity, %	3.44	1.82	2.03	1.98	1.99
C2 Yield, %	9.39	8.96	7.42	6.89	6.32
Ethylene/Ethane	2.56	2.46	2.35	2.17	2.09
CO2/CO	3.50	3.32	2.82	2.49	2.26

Table B14. Methane Coupling Activity of TiO2

CATALYST: TiO2 **NOTEBOOK:** 7-KDC-X-90

Weight (g): 4.017 **Volume (cc):** 3.2

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

Temperature (°C)	803	803	803	803	803
Flow (cc/min)	50	50	50	50	50
GHSV (h-1)	938	938	938	938	938
Time (h)	1	3	13	19	27
CH4 Conv., %	26.16	25.85	26.20	26.94	27.10
O2 Conv., %	94.63	94.66	94.63	94.64	94.63
C Balance, %	100.91	101.47	101.45	100.99	101.71
C2 Selectivity, %	7.42	9.35	12.60	14.27	16.08
C3 Selectivity, %	0.10	0.12	0.22	0.36	0.53
C2 Yield, %	1.96	2.45	3.35	3.88	4.43
Ethylene/Ethane	2.26	2.06	2.07	2.33	2.60
CO2/CO	5.75	6.41	7.29	7.23	6.68

Table B15. Methane Coupling Activity of La_2O_3

CATALYST: La_2O_3 **NOTEBOOK:** 7-KDC-X-113

Weight (g): 4.014 **Volume (cc):** 2.7

$CH_4/O_2/N_2$: 2.02/1/3.81 **Pressure (psig):** 5

Temperature (°C)	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200
GHSV (h^{-1})	4444	4444	4444	4444	4444	4444
Time (h)	1	3	9	17	25	31
CH_4 Conv., %	35.82	35.32	35.87	35.72	35.51	35.58
O_2 Conv., %	94.63	94.65	94.65	94.65	94.65	94.65
C Balance, %	101.62	102.53	101.44	101.54	101.68	101.66
C2 Selectivity, %	39.14	39.30	39.04	38.85	38.83	38.70
C3 Selectivity, %	2.32	2.39	2.43	2.43	2.44	2.44
C2 Yield, %	14.25	14.23	14.21	14.09	14.02	14.00
Ethylene/Ethane	1.55	1.49	1.49	1.50	1.50	1.50
CO_2/CO	5.12	5.40	5.47	5.47	5.45	5.44

Table B16. Methane Coupling Activity of Mixture of K_2CO_3 - La_2CO_3*

CATALYST: Mixture of K_2CO_3 - La_2CO_3 **NOTEBOOK:** 6-KDC-X-113

Weight (g): 2.64 **Volume (cc):** 3.3

$CH_4/O_2/N_2$: 2.18/1/3.79 **Pressure (psig):** 5

Temperature (°C)	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200
GHSV (h^{-1})	3636	3636	3636	3636	3636	3636	3636
Time (h)	1	3	9	13	17	23	49
CH_4 Conv., %	33.68	34.02	33.72	34.51	33.99	33.93	34.16
O_2 Conv., %	94.57	94.58	94.52	94.55	94.55	94.57	94.54
C Balance, %	100.77	101.16	102.37	100.51	101.63	101.59	101.54
C2 Selectivity, %	42.53	40.91	41.33	40.73	40.47	40.22	40.50
C3 Selectivity, %	2.38	2.34	2.35	1.75	2.35	2.34	2.39
C2 Yield, %	14.44	14.08	14.26	14.13	13.98	13.87	14.05
Ethylene/Ethane	1.51	1.54	1.53	1.57	1.56	1.57	1.57
CO_2/CO	20.27	17.90	15.51	15.52	14.75	14.00	13.00

*: K/La ratio is 1/1.

Table B17. **Methane Coupling Activity of Mixture of K2CO3 - La2O3 - TiO2***

CATALYST: Mixture of K2CO3 - La2O3 - TiO2 **NOTEBOOK:** 7-KDC-X-123

Weight (g): 4.022 **Volume (cc):** 3.6

CH4/O2/N2: 2.18/1/3.79 **Pressure (psig):** 5

Temperature (°C)	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200
GHSV (h-1)	3333	3333	3333	3333	3333	3333
Time (h)	1	3	9	13	17	23
CH4 Conv., %	34.54	34.16	34.43	34.80	34.26	34.28
O2 Conv., %	94.57	94.69	94.69	94.70	94.69	94.68
C Balance, %	100.25	101.46	101.27	101.12	101.70	101.56
C2 Selectivity, %	43.13	42.30	41.88	40.72	40.66	40.39
C3 Selectivity, %	0.67	1.79	1.78	1.84	1.88	1.86
C2 Yield, %	14.94	14.66	14.60	14.33	14.17	14.06
Ethylene/Ethane	1.19	1.22	1.24	1.31	1.33	1.35
CO2/CO	29.06	20.84	18.92	15.18	13.68	13.12

*: K/La/Ti ratio is 2/2/3.

Table B18. **Comparison of Methane Coupling Results for Layered Perovskite Components**

CATALYST:	**K2CO3**	**La2O3**	**TiO2**	**K2La2Ti3O10****	**K2CO3-La2O3**	**K2CO3-La2O3-TiO2**
Weight (g):	4.01	4.01	4.02	4.01	2.64	4.02
CH4/O2/N2:	2.0/1/3.8	2.0/1/3.8	2.1/1/3.8	2.0/1/3.8	2.2/1/3.8	2.2/1/3.8
Pressure (psig):	5	5	5	7	5	5
Temperature (°C)	805	800	803	800	800	800
Flow (cc/min)	50	200	50	200	200	200
GHSV (h 1)	600	4440	940	3000	3636	3333
CH4 Conv., %	28.1	35.3	27.1	38.3	34.02	34.16
O2 Conv., %	*80.5*	*94.6*	*94.6*	*93.3*	*94.58*	*94.69*
C Balance, %	101.6	102.5	101.7	100.9	101.16	101.46
C2 Selectivity, %	31.4	39.3	16.1	40.7	40.91	42.30
C3 Selectivity, %	1.8	2.4	0.5	1.8	2.34	1.79
C2 Yield, %	9	14.2	4.4	15.8	14.08	14.66
Ethylene/Ethane	2.5	1.5	2.6	1.8	1.54	1.22
CO2/CO	3.3	5.4	6.7	6.7	17.90	20.84

**: Results obtained previously (Third Quarterly Report).

Table B19. Methane Coupling Activity of K2La2Ti3O10

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 8-KDC-X-15

Weight (g): 2.01 **Volume (cc):** 1.7

CH4/O2/N2: 2.22/1/3.74 **Pressure (psig):** 5

Temperature (°C)	800	800	800	800	800	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200	200	200	200	200	200
GHSV (h-1)	7059	7059	7059	7059	7059	7059	7059	7059	7059	7059	7059	7059
Time (h)	1	4	6	10	14	18	22	26	30	34	38	42
CH4 Conv., %	31.12	30.28	29.92	29.41	28.58	28.30	28.10	27.74	27.19	26.80	26.06	25.91
O2 Conv., %	90.85	89.02	87.31	85.60	84.75	83.69	83.13	81.95	80.87	79.81	79.06	78.42
C Balance, %	99.73	100.56	99.85	99.60	100.08	99.90	100.07	99.72	99.86	99.74	100.52	100.32
C2 Selectivity, %	40.58	41.45	40.23	39.21	38.54	38.14	38.17	37.25	36.68	36.22	35.60	35.25
C3 Selectivity, %	1.58	1.51	1.45	1.39	1.36	1.34	1.45	1.30	1.27	1.26	1.21	1.19
C2 Yield, %	12.59	12.62	12.02	11.48	11.03	10.78	10.73	10.30	9.96	9.68	9.32	9.16
Ethylene/Ethane	1.22	1.23	1.25	1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.21	1.22
CO2/CO	36.11	27.89	22.75	22.05	19.45	19.25	18.14	17.34	16.56	15.95	15.06	15.38

Table B19. Methane Coupling Activity of K2La2Ti3O10 (Continued)

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 8-KDC-X-15

Weight (g): 2.01 **Volume (cc):** 1.7

CH4/O2/N2: 2.22/1/3.74 **Pressure (psig):** 5

	***							***				
Temperature (°C)	800	800	800	800	800	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200	200	200	200	200	200
GHSV (h-1)	7059	7059	7059	7059	7059	7059	7059	7059	7059	7059	7059	7059
Time (h)	46	50	54	58	62	66	70	74	78	82	86	90
CH4 Conv., %	26.65	26.06	26.00	25.51	25.17	25.32	25.35	27.16	27.07	26.80	26.56	26.60
O2 Conv., %	80.16	78.60	78.55	77.75	77.23	76.90	77.02	82.00	81.30	80.14	79.45	79.13
C Balance, %	99.63	99.86	99.72	100.11	100.02	99.69	99.78	100.38	99.87	100.18	100.19	99.80
C2 Selectivity, %	35.27	34.93	34.50	34.05	33.67	33.34	33.29	36.62	36.42	36.41	36.36	36.07
C3 Selectivity, %	1.21	1.20	1.18	1.16	1.14	1.12	1.13	1.25	1.29	1.24	1.23	1.26
C2 Yield, %	9.36	9.09	8.94	8.70	8.47	8.41	8.42	9.98	9.84	9.78	9.68	9.58
Ethylene/Ethane	1.26	1.24	1.25	1.24	1.24	1.24	1.24	1.35	1.36	1.33	1.33	1.34
CO2/CO	14.42	14.58	13.60	14.16	13.13	12.96	13.55	13.32	12.62	12.51	12.05	12.18

***: Temperature had drifted down. Temperature adjusted such that the highest observed temperature in the catalyst bed was 800 °C.

Table B19. Methane Coupling Activity of K2La2Ti3O10 (Continued)

CATALYST: K2La2Ti3O10 **NOTEBOOK:** 8-KDC-X-15

Weight (g): 2.01 **Volume (cc):** 1.7

CH4/O2/N2: 2.22/1/3.74 **Pressure (psig):** 5

	***								***	
Temperature (°C)	800	800	800	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200	200	200	200
GHSV (h-1)	7059	7059	7059	7059	7059	7059	7059	7059	7059	7059
Time (h)	94	98	106	110	114	118	122	126	130	134
CH4 Conv., %	28.09	28.22	28.04	27.96	27.44	27.14	26.25	25.59	26.68	26.45
O2 Conv., %	83.26	82.63	82.80	82.47	81.43	80.36	77.68	75.64	78.19	77.67
C Balance, %	100.03	99.57	100.09	99.96	100.04	100.15	99.99	99.95	99.89	99.82
C2 Selectivity, %	37.77	37.61	38.10	38.23	37.67	37.56	36.92	36.34	37.51	37.45
C3 Selectivity, %	1.32	1.36	1.35	1.55	1.39	1.38	1.38	1.41	1.52	1.54
C2 Yield, %	10.61	10.57	10.69	10.68	10.34	10.21	9.69	9.29	10.00	9.89
Ethylene/Ethane	1.46	1.47	1.47	1.48	1.48	1.48	1.46	1.44	1.56	1.56
CO2/CO	11.69	11.67	11.09	10.63	10.48	10.55	9.52	9.23	9.31	8.76

***: Temperature had drifted down. Temperature adjusted such that the highest observed temperature in the catalyst bed was 800 °C.

Table B20. Methane Coupling Activity of Mixture of K2CO3 - La2O3*

CATALYST: Mixture of K2CO3 - La2O3 **NOTEBOOK:** 9-KDC-X-19

Weight (g): 1.406 **Volume (cc):** 1.4

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

Temperature (°C)	800	800	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200	200	200
GHSV (h-1)	8571	8571	8571	8571	8571	8571	8571	8571	8571
Time (h)	1	3	9	15	21	27	33	39	45
CH4 Conv., %	32.52	31.74	32.11	32.52	32.54	33.10	32.77	33.23	32.73
O2 Conv., %	94.64	94.46	94.48	94.53	94.56	94.51	94.57	94.57	94.56
C Balance, %	98.70	99.24	99.44	99.29	99.19	98.32	98.73	98.28	99.07
C2 Selectivity, %	41.48	39.02	39.23	39.04	38.74	38.43	38.44	38.22	38.41
C3 Selectivity, %	2.30	1.91	1.96	1.97	1.97	1.97	1.97	1.97	2.00
C2 Yield, %	13.32	12.29	12.53	12.61	12.51	12.51	12.44	12.48	12.46
Ethylene/Ethane	1.80	1.51	1.55	1.58	1.60	1.61	1.63	1.64	1.64
CO2/CO	17.37	9.97	8.35	7.67	6.98	6.67	6.41	6.42	6.28

*: Molar ratio K/La equals 1/1.

Table B20. Methane Coupling Activity of Mixture of K2CO3 - La2O3* (Continued)

CATALYST: Mixture of K2CO3 - La2O3 **NOTEBOOK:** 9-KDC-X-19

Weight (g): 1.406 **Volume (cc):** 1.4

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

			***					
Temperature (°C)	800	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200	200
GHSV (h-1)	8571	8571	8571	8571	8571	8571	8571	8571
Time (h)	51	63	69	75	81	87	89	91
CH4 Conv., %	32.25	32.24	32.66	33.10	33.09	33.03	33.05	33.23
O2 Conv., %	94.57	94.63	94.55	93.65	93.57	93.52	93.51	93.52
C Balance, %	99.47	99.39	99.45	99.37	99.45	99.39	99.32	99.28
C2 Selectivity, %	37.94	37.82	39.01	41.17	41.09	41.09	41.15	41.16
C3 Selectivity, %	2.08	2.15	1.98	2.30	2.30	2.32	2.32	2.32
C2 Yield, %	12.17	12.12	12.67	13.54	13.52	13.49	13.51	13.58
Ethylene/Ethane	1.71	1.75	1.59	1.43	1.43	1.44	1.44	1.44
CO2/CO	6.19	6.23	5.98	6.56	6.48	6.35	6.27	6.40

*: Molar ratio K/La equals 1/1.
***: Temperature had drifted down. Temperature adjusted such that the highest observed temperature in the catalyst bed was 800 °C.

Table B21. Methane Coupling Activity of K2Pr2Ti3O10

CATALYST: K2Pr2Ti3O10 **NOTEBOOK:** 6-KDC-X-83

Weight (g): 4.882 **Volume (cc):** 3.9

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

Temperature (°C)	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	100
GHSV (h-1)	3077	3077	3077	3077	3077	3077	1538
Time (h)	1	3	7	11	15	17	19
CH4 Conv., %	30.61	26.94	23.88	22.19	19.96	18.46	23.88
O2 Conv., %	87.79	78.98	71.12	64.34	58.07	55.73	81.71
C Balance, %	103.20	102.35	102.36	101.32	101.55	102.31	105.33
C2 Selectivity, %	33.85	33.57	31.42	29.61	28.14	28.00	30.40
C3 Selectivity, %	1.33	1.05	1.03	0.88	0.72	0.72	1.16
C2 Yield, %	10.69	9.26	7.68	6.66	5.70	5.29	7.64
Ethylene/Ethane	1.51	1.39	1.31	1.22	1.16	1.13	1.64
CO2/CO	31.11	18.41	12.22	9.30	7.25	6.51	9.76

Table B21. Methane Coupling Activity of K2Pr2Ti3O10 (Continued)

CATALYST: K2Pr2Ti3O10 **NOTEBOOK:** 6-KDC-X-83

Weight (g): 4.882 **Volume (cc):** 3.9

Pressure (psig): 5

CH4/O2/N2: 2.04/1/3.81			**CH4/O2/N2:** 2.12/1/17.8			
Temperature (°C)	800	800	800	800	800	800
Flow (cc/min)	100	100	100	100	100	100
GHSV (h-1)	1538	1538	1538	1538	1538	1538
Time (h)	21	23	25	27	33	41
CH4 Conv., %	24.90	23.68	22.03	21.97	21.95	20.92
O2 Conv., %	78.38	75.53	61.51	60.01	56.93	54.04
C Balance, %	103.13	103.56	99.98	100.20	98.79	98.89
C2 Selectivity, %	29.46	28.90	36.60	37.13	37.27	37.65
C3 Selectivity, %	1.06	1.02	0.73	0.74	0.81	1.14
C2 Yield, %	7.56	7.09	8.06	8.17	8.08	7.79
Ethylene/Ethane	1.62	1.57	1.14	1.16	1.13	1.10
CO2/CO	8.59	7.58	8.82	8.85	7.48	6.17

Table B22. Methane Coupling Activity of K2Ce2Ti3O10

CATALYST: K2Ce2Ti3O10 5-KDC-X-27 **NOTEBOOK:** 7-KDC-X-83

Weight (g): 4.222 **Volume (cc):** 4.2

Pressure (psig): 5

CH4/O2/N2: 2.11/1/3.81							**CH4/O2/N2:** 2.12/1/17.8			
Temperature (°C)	800	800	800	800	800	800	800	800	800	800
Flow (cc/min)	50	50	50	40	40	40	40	40	40	40
GHSV (h-1)	714	714	714	571	571	571	571	571	571	571
Time (h)	1	11	15	17	19	21	23	25	31	37
CH4 Conv., %	28.96	26.87	26.54	28.31	28.67	28.91	27.42	27.60	27.28	27.28
O2 Conv., %	76.38	74.66	74.65	90.23	90.04	90.33	71.86	72.35	71.92	71.43
C Balance, %	103.25	101.64	101.90	104.12	103.73	103.62	100.07	99.72	99.54	99.38
C2 Selectivity, %	36.06	33.46	33.02	33.07	33.10	33.01	40.81	40.63	40.79	40.61
C3 Selectivity, %	2.01	1.87	1.81	2.05	2.04	2.04	1.44	1.59	1.44	1.55
C2 Yield, %	10.78	9.14	8.93	9.75	9.84	9.89	11.20	11.18	11.08	11.01
Ethylene/Ethane	1.75	1.85	1.81	1.97	1.99	2.01	1.43	1.45	1.42	1.42
CO2/CO	12.12	6.97	6.83	14.64	13.29	13.14	9.14	8.96	8.51	8.28

Table B23. Methane Coupling Activity of K2CO3-Tb4O7-TiO2

CATALYST: K2Tb2Ti3O10 **NOTEBOOK:** 6-KDC-X-119

Weight (g): 4.001 **Volume (cc):** 2.9

CH4/O2/N2: 2.15/1/3.77 **Pressure (psig):** 5

Temperature (°C)	808	808	808	808	808	808	751	751	751	705	705	705
Flow (cc/min)	200	200	200	200	200	200	200	200	200	100	100	100
GHSV (h-1)	4138	4138	4138	4138	4138	4138	4138	4138	4138	2069	2069	2069
Time (h)	1	4	16	28	44	58	62	66	70	72	76	82
CH4 Conv., %	34.70	34.84	34.38	34.31	34.41	33.77	25.65	24.12	24.00	21.57	21.68	21.70
O2 Conv., %	94.43	94.74	94.75	94.73	94.74	94.74	84.27	83.11	82.91	85.42	85.48	85.48
C Balance, %	100.13	102.10	101.74	102.14	101.50	102.75	101.06	102.29	102.39	101.86	101.90	101.43
C2 Selectivity, %	45.81	45.98	45.24	45.05	44.55	44.17	28.61	28.01	27.81	14.40	14.41	14.57
C3 Selectivity, %	1.06	1.10	1.15	1.30	1.19	1.40	1.00	0.97	0.95	0.39	0.39	0.39
C2 Yield, %	15.92	16.35	15.82	15.79	15.56	15.33	7.42	6.91	6.84	3.16	3.18	3.21
Ethylene/Ethane	1.23	1.49	1.50	1.50	1.51	1.53	0.76	0.74	0.74	0.47	0.48	0.48
CO2/CO	23.48	18.47	17.85	18.71	18.45	17.79	56.50	50.94	55.10	59.74	63.83	54.32

Table B24. Methane Coupling Activity of K2CO3-Lu2O3-TiO2

CATALYST: K2Lu2Ti3O10 **NOTEBOOK:** 8-KDC-X-1

Weight (g): 4.039 **Volume (cc):** 3.9

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

Temperature (°C)	800	800	800	800	800	800	800	800	750	750	750	750
Flow (cc/min)	200	200	200	200	200	300	300	300	250	250	250	250
GHSV (h-1)	3077	3077	3077	3077	3077	4615	4615	4615	3846	3846	3846	3846
Time (h)	1	3	7	11	15	17	19	21	23	25	31	39
CH4 Conv., %	30.50	30.48	30.41	30.13	30.61	29.25	28.39	28.58	16.53	16.32	16.04	16.50
O2 Conv., %	94.71	94.58	94.50	94.45	94.46	84.15	82.72	82.10	54.96	54.59	54.01	54.07
C Balance, %	101.28	100.78	100.65	101.38	100.32	100.63	101.03	100.86	100.88	100.85	101.00	100.62
C2 Selectivity, %	36.63	36.14	35.56	35.82	35.67	39.35	38.72	38.79	22.32	22.13	21.81	21.73
C3 Selectivity, %	1.77	0.82	1.60	1.73	1.60	1.66	1.64	1.77	0.61	0.60	0.58	0.57
C2 Yield, %	11.32	11.10	10.88	10.94	10.95	11.58	11.10	11.18	3.72	3.64	3.53	3.61
Ethylene/Ethane	1.50	1.54	1.57	1.56	1.58	1.41	1.40	1.38	1.00	1.00	0.99	1.00
CO2/CO	22.58	21.01	19.53	19.64	19.18	10.45	9.73	9.60	8.10	8.03	7.94	7.89

Table B25. Methane Coupling Activity of K2CO3-Er2O3-TiO2

CATALYST: K2Er2Ti3O10 NOTEBOOK: 8-KDC-X-21

Weight (g): 4.006 Volume (cc): 2.7

CH4/O2/N2: 2.20/1/3.70 Pressure (psig): 5

Temperature (°C)	800	800	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200	200	200
GHSV (h-1)	4444	4444	4444	4444	4444	4444	4444	4444	4444
Time (h)	1	3	15	21	27	33	39	45	51
CH4 Conv., %	32.31	31.40	32.10	31.87	31.60	31.54	31.43	32.33	32.29
O2 Conv., %	94.73	94.73	94.72	94.73	94.72	94.74	94.73	94.74	94.73
C Balance, %	100.54	101.37	101.42	101.15	101.13	101.07	101.10	101.48	101.46
C2 Selectivity, %	42.45	40.78	41.84	40.21	39.77	39.42	39.39	41.83	41.70
C3 Selectivity, %	1.14	1.06	1.01	0.98	0.98	0.98	0.98	1.03	1.04
C2 Yield, %	13.79	12.98	13.63	12.96	12.71	12.57	12.52	13.73	13.66
Ethylene/Ethane	1.31	1.26	1.43	1.37	1.35	1.33	1.37	1.51	1.50
CO2/CO	22.73	22.64	15.24	15.18	15.04	15.77	14.80	13.47	13.81

Table B25 . Methane Coupling Activity of K2CO3-Er2O3-TiO2 (Continued)

CATALYST: K2Er2Ti3O10 **NOTEBOOK:** 8-KDC-X-21

Weight (g): 4.006 **Volume (cc):** 2.7

CH4/O2/N2: 2.20/1/3.70 **Pressure (psig):** 5

Temperature (°C)	800	800	800	800	800	800	800	800	800
Flow (cc/min)	200	200	200	200	200	200	200	200	200
GHSV (h-1)	4444	4444	4444	4444	4444	4444	4444	4444	4444
Time (h)	57	63	69	75	81	87	93	99	105
CH4 Conv., %	32.12	32.29	32.08	32.10	31.99	32.06	31.84	31.41	31.64
O2 Conv., %	94.71	94.71	94.70	94.70	94.70	94.73	94.69	94.73	94.69
C Balance, %	101.37	101.33	101.50	101.30	101.43	101.53	101.61	101.91	101.55
C2 Selectivity, %	41.54	41.51	41.54	41.38	41.30	41.39	40.95	40.87	40.83
C3 Selectivity, %	1.04	1.05	1.06	1.06	1.07	1.07	1.11	1.12	1.10
C2 Yield, %	13.53	13.58	13.53	13.46	13.40	13.47	13.25	13.08	13.12
Ethylene/Ethane	1.50	1.52	1.52	1.53	1.53	1.54	1.61	1.61	1.61
CO2/CO	13.14	13.60	12.94	12.85	12.79	12.89	12.72	13.23	13.32

Table B26. Comparison of Methane Coupling Results for Layered Perovskites

CATALYST:	K2La2Ti3O10	K2Nd2Ti3O10	K2Sm2Ti3O10	K2Dy2Ti3O10	K2Gd2Ti3O10	Rb2La2Ti3O10	Na2La2Ti3O10
Weight (g):	4.01	1.01	1.03	4.01	4.03	4.01	0.93
CH4/O2/N2:	2.0/1/3.8	2.0/1/3.8	2.1/1/3.8	2.0/1/3.7	2.0/1/3.7	2.0/1/3.7	2.0/1/3.8
Pressure (psig):	7	5	5	5	5	5	5
Temperature (°C)	800	800	801	800	800	807	800
Flow (cc/min)	200	50	50	200	150	150	100
GHSV (h 1)	3000	3750	5000	3430	1765	4500	4610
CH4 Conv., %	38.3	25.5	25.3	25.1	28.8	21.0	35.1
O2 Conv., %	93.3	77.6	70.3	78.5	91.3	51.5	93.4
C Balance, %	100.9	101.9	99.9	101.2	101.7	100.5	100.5
C2 Selectivity, %	40.7	24.2	23	15.3	19.6	31.0	27.8
C3 Selectivity, %	1.8	1.5	1.7	0.2	0.5	1.6	1.4
C2 Yield, %	15.8	6.3	5.3	3.9	5.7	6.6	9.8
Ethylene/Ethane	1.8	2.3	3.1	0.9	1	1.3	2.3
CO2/CO	6.7	2.8	2.3	6.6	15.5	2.8	3.8

Table B26. **Comparison of Methane Coupling Results for Layered Perovskites (Continued)**

CATALYST:	**K2CO3-La2O3-MnO2**	**K2CO3-Tb4O7-TiO2**	**K2CO3-Er2O3-TiO2**	**K2CO3-Lu2O3-TiO2**	**K2Pr2Ti3O10**	**K2Ce2Ti3O10**
Weight (g):	1.00	4.00	4.01	4.04	4.00	4.22
CH4/O2/N2:	2.1/1/3.8	2.2/1/3.8	2.2/1/3.7	2.0/1/3.8	2.1/1/3.8	2.1/1/3.8
Pressure (psig):	5	5	5	5	6.5	5
Temperature (°C)	798	808	800	800	800	800
Flow (cc/min)	50	200	200	300	200	50
GHSV (h 1)	3000	4140	4440	4620	3430	714
CH4 Conv., %	30.8	34.8	32.1	29.3	33.5	26.9
O2 Conv., %	94.5	94.7	94.7	84.2	87.4	74.7
C Balance, %	101.0	102.1	101.4	100.6	98.5	101.6
C2 Selectivity, %	27.2	46.0	41.8	39.4	40.0	33.5
C3 Selectivity, %	1.5	1.1	1.0	1.7	1.7	1.9
C2 Yield, %	8.5	16.4	13.6	11.6	13.2	9.1
Ethylene/Ethane	1.5	1.5	1.4	1.4	1.6	1.9
CO2/CO	25.1	18.5	15.2	10.5	19.4	7.0

Table B27. Methane Coupling Activity of Li2SiO3

CATALYST: Li2SiO3
Weight (g): 4.012
CH4/O2/N2: 2.07/1/3.79

NOTEBOOK: 6-KDC-X-100
Volume (cc): 3.5
Pressure (psig): 4.5

Temperature (°C)	699	699	699	699	699	750	750	750	750	802	802	802
Flow (cc/min)	100	100	100	100	100	100	100	100	100	100	100	100
GHSV (h-1)	1714	1714	1714	1714	1714	1667	1667	1667	1667	1667	1667	1667
Time (h)	1	3	6	14	18	22	26	30	38	42	46	50
CH4 Conv., %	9.65	8.29	7.57	6.78	6.71	13.72	13.38	12.37	12.33	27.21	26.24	26.00
O2 Conv., %	28.66	23.18	21.18	17.95	17.25	34.56	33.17	32.46	31.22	63.20	60.69	59.89
C Balance, %	100.11	100.00	100.42	100.65	100.53	100.97	100.75	101.62	101.19	100.62	100.91	101.03
C2 Selectivity, %	10.85	11.82	12.49	12.38	12.81	29.50	30.29	30.68	31.16	37.88	38.08	38.00
C3 Selectivity, %	0.08	0.08	0.08	0.08	0.08	0.85	0.85	0.87	0.88	2.31	2.26	2.32
C2 Yield, %	1.05	0.98	0.95	0.85	0.86	4.09	4.08	3.86	3.89	10.37	10.08	9.98
Ethylene/Ethane	0.36	0.34	0.34	0.32	0.35	0.79	0.78	0.76	0.76	2.45	2.44	2.44
CO2/CO	1.89	1.57	1.46	1.40	1.43	1.51	1.52	1.50	1.49	1.31	1.21	1.15

Table B28. Methane Coupling Activity of Li4SiO4

CATALYST: Li4SiO4 **NOTEBOOK:** 7-KDC-X-98

Weight (g): 4.012 **Volume (cc):** 3.5

CH4/O2/N2: 2.07/1/3.79 **Pressure (psig):** 4.5

Temperature (°C)	705	705	705	705	705	752	752	752	752	752
Flow (cc/min)	100	100	100	100	100	100	100	100	100	100
GHSV (h-1)	1714	1714	1714	1714	1714	1714	1714	1714	1714	1714
Time (h)	1	5	9	13	17	21	25	29	33	37
CH4 Conv., %	14.33	11.11	9.46	9.15	9.76	21.30	20.71	20.07	18.80	18.90
O2 Conv., %	25.78	18.88	16.83	16.28	16.02	43.74	42.54	40.95	39.02	38.08
C Balance, %	99.93	100.70	101.86	101.75	100.63	101.45	101.13	100.91	101.42	100.73
C2 Selectivity, %	55.08	55.01	55.22	55.23	54.47	51.81	50.57	50.34	50.05	50.06
C3 Selectivity, %	2.26	2.22	2.19	2.13	2.07	3.35	3.27	3.20	3.12	3.11
C2 Yield, %	7.89	6.16	5.32	5.14	5.35	11.20	10.59	10.19	9.54	9.53
Ethylene/Ethane	0.78	0.73	0.70	0.69	0.68	1.45	1.50	1.50	1.49	1.49
CO2/CO	4.41	3.45	3.39	3.18	2.88	3.41	3.06	2.87	2.68	2.57

Table B28. Methane Coupling Activity of Li4SiO4 (Continued)

CATALYST: Li4SiO4 **NOTEBOOK:** 7-KDC-X-98

Weight (g): 4.012 **Volume (cc):** 3.5

CH4/O2/N2: 2.07/1/3.79 **Pressure (psig):** 4.5

Temperature (°C)	752	752	804	804	804	804	804	700	700
Flow (cc/min)	100	100	100	100	100	100	100	100	100
GHSV (h-1)	1714	1714	1714	1714	1714	1714	1714	1714	1714
Time (h)	41	49	37	41	45	49	53	57	53
CH4 Conv., %	18.29	19.51	29.48	27.11	24.98	21.18	23.69	3.58	4.88
O2 Conv., %	37.21	41.13	69.49	63.36	56.69	59.46	53.24	7.01	7.51
C Balance, %	100.97	100.91	101.16	101.15	100.85	105.57	100.50	100.08	98.84
C2 Selectivity, %	49.74	48.01	39.55	38.71	38.51	37.94	38.73	12.76	12.43
C3 Selectivity, %	3.03	2.98	2.48	2.43	2.36	2.22	2.32	0.00	0.45
C2 Yield, %	9.19	9.45	11.79	10.62	9.70	8.48	9.22	0.46	0.60
Ethylene/Ethane	1.48	1.67	3.04	2.84	2.59	2.45	2.41	0.26	0.26
CO2/CO	2.40	2.18	1.96	1.63	1.32	1.11	1.13	0.79	0.77

Table B29. Methane Coupling Activity of Li4SiO4

CATALYST: Li4SiO4 **NOTEBOOK:** 7-KDC-X-102

Weight (g): 5.063 **Volume (cc):** 4.5

CH4/O2/N2: 2.07/1/3.79 **Pressure (psig):** 4.5

Temperature (°C)	705	705	705	705	705	705	705	705	705	705	705
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	667	667	667	667	667	667	667	667	667	667	667
Time (h)	1	3	5	7	11	13	17	21	25	29	33
CH4 Conv., %	17.77	16.86	15.78	15.12	14.66	14.16	13.46	12.65	12.06	11.63	11.69
O2 Conv., %	43.20	44.93	42.90	41.56	39.35	37.70	36.36	35.51	34.33	33.42	32.99
C Balance, %	104.94	105.58	105.88	106.21	105.38	105.40	105.21	105.50	105.78	105.86	105.36
C2 Selectivity, %	51.88	50.36	50.97	50.79	50.44	50.27	50.02	49.69	49.53	49.43	49.07
C3 Selectivity, %	2.88	3.15	2.96	2.90	2.78	2.73	2.64	2.57	2.50	2.45	2.41
C2 Yield, %	9.67	8.96	8.52	8.16	7.79	7.50	7.08	6.63	6.32	6.09	6.04
Ethylene/Ethane	1.15	1.21	1.18	1.15	1.11	1.08	1.05	1.02	1.01	0.99	0.98
CO2/CO	5.88	5.23	4.88	4.68	4.25	4.08	3.81	3.65	3.50	3.40	3.31

Table B29. Methane Coupling Activity of Li4SiO4 (Continued)

CATALYST: Li4SiO4 **NOTEBOOK:** 7-KDC-X-102

Weight (g): 5.063 **Volume (cc):** 4.5

CH4/O2/N2: 9.19/1/3.84** **Pressure (psig):** 4.5

Temperature (°C)	705	705	705	705	705	705	705	705	705	705	705
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	667	667	667	667	667	667	667	667	667	667	667
Time (h)	35	37	41	45	49	53	55	59	63	67	69
CH4 Conv., %	9.10	7.48	7.54	7.41	7.16	7.20	7.30	6.93	6.72	6.87	6.91
O2 Conv., %	52.96	51.94	51.78	51.53	50.65	50.22	49.90	49.34	49.13	48.83	48.52
C Balance, %	99.16	100.98	100.72	100.73	100.95	100.79	100.66	100.97	101.22	100.93	100.84
C2 Selectivity, %	67.77	68.08	68.01	67.76	67.79	67.66	67.81	67.57	67.47	67.35	67.32
C3 Selectivity, %	4.30	4.23	4.10	4.15	4.10	4.05	4.04	3.96	3.96	3.93	3.91
C2 Yield, %	6.12	5.14	5.17	5.06	4.90	4.91	4.98	4.73	4.59	4.67	4.69
Ethylene/Ethane	0.70	0.70	0.70	0.70	0.70	0.69	0.69	0.68	0.68	0.68	0.67
CO2/CO	3.41	3.32	3.32	3.28	3.22	3.18	3.28	3.11	3.06	3.03	3.03

****: Feed gas composition changed.**

Table B30. Methane Coupling Activity of MgO

CATALYST: MgO NOTEBOOK: 9-KDC-X-13

Weight (g): 4.001 Volume (cc): 4

CH4/O2/N2: 2.04/1/3.81 Pressure (psig): 7.5

Temperature (°C)	700	700	700	700	750	750	750	750
Flow (cc/min)	100	100	100	100	100	100	100	100
GHSV (h-1)	1500	1500	1500	1500	3000	3000	3000	3000
Time (h)	1	3	7	9	17	19	21	23
CH4 Conv., %	3.53	2.61	3.49	2.79	9.02	9.70	9.87	10.24
O2 Conv., %	6.24	6.01	5.59	6.97	22.33	23.46	24.22	24.65
C Balance, %	99.40	100.33	99.30	99.99	100.31	100.41	100.36	100.20
C2 Selectivity, %	16.25	17.96	19.20	20.17	29.89	29.98	31.14	31.23
C3 Selectivity, %	0.12	0.13	0.15	0.24	1.21	3.39	1.36	1.40
C2 Yield, %	0.57	0.47	0.67	0.56	2.71	2.92	3.08	3.21
Ethylene/Ethane	0.32	0.32	0.31	0.31	1.10	1.17	1.20	1.22
CO2/CO	0.45	0.41	0.38	0.36	0.28	0.26	0.25	0.25

Table B30. Methane Coupling Activity of MgO (Continued)

CATALYST: MgO **NOTEBOOK:** 9-KDC-X-13

Weight (g): 4.001 **Volume (cc):** 4

CH4/O2/N2: 2.04/1/3.81 **Pressure (psig):** 7.5

Temperature (°C)	800	800	800	800	800	850	850	850	850	850
Flow (cc/min)	100	100	100	150	150	150	150	150	150	150
GHSV (h-1)	3000	3000	3000	3750	3750	3750	3750	3750	3750	3750
Time (h)	25	29	31	33	35	37	39	43	47	51
CH4 Conv., %	30.03	31.43	31.71	30.89	31.23	35.43	35.83	36.82	36.60	37.46
O2 Conv., %	82.49	86.39	87.14	83.12	83.62	94.65	94.75	94.77	94.78	94.76
C Balance, %	100.54	100.54	100.76	100.37	100.11	99.28	99.24	98.60	99.23	98.42
C2 Selectivity, %	21.55	20.49	20.42	21.69	21.51	15.94	15.06	14.03	13.99	13.99
C3 Selectivity, %	1.23	1.12	1.09	1.18	1.16	0.74	0.76	0.68	0.68	0.84
C2 Yield, %	6.51	6.48	6.52	6.73	6.72	5.61	5.35	5.09	5.08	5.16
Ethylene/Ethane	4.17	4.64	4.73	4.22	4.28	8.63	9.71	11.57	11.81	11.13
CO2/CO	0.27	0.27	0.27	0.26	0.27	0.27	0.25	0.24	0.24	0.23

Table B31. Methane Coupling Activity of 0.65 wt% Ba(NO3)2/ MgO

CATALYST: 0.65 wt% Ba(NO3)2/ MgO   **NOTEBOOK:** 9-KDC-X-4

Weight (g): 4.006   **Volume (cc):** 3.9

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

Temperature (°C)	600	600	600	600	650	650	650	650	700	700	700	700
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	50	50
GHSV (h-1)	769	769	769	769	769	769	769	769	769	769	769	769
Time (h)	1	3	7	11	15	17	21	25	27	29	31	35
CH4 Conv., %	**	**	**	**	4.68	4.49	4.74	4.55	11.71	11.63	11.52	11.85
O2 Conv., %	4.42	3.59	3.37	3.63	16.63	16.72	16.33	16.18	40.42	39.77	38.81	39.94
C Balance, %	100.59	100.27	99.79	100.33	100.27	100.46	100.13	100.27	100.57	100.61	96.79	100.95
C2 Selectivity, %	**	**	**	**	2.13	2.19	2.31	2.39	6.80	7.09	7.34	9.24
C3 Selectivity, %	**	**	**	**	0.00	0.00	0.00	0.00	0.09	0.10	0.00	0.14
C2 Yield, %	**	**	**	**	0.10	0.10	0.11	0.11	0.80	0.83	0.82	1.11
Ethylene/Ethane	**	**	**	**	0.18	0.18	0.18	0.18	0.71	0.73	0.81	0.83
CO2/CO	**	**	**	**	3.02	2.91	3.02	3.00	2.11	2.03	2.01	1.91

**: Conversion too low for meaningful results.

Table B31. Methane Coupling Activity of 0.65 wt% Ba(NO3)2/ MgO (Continued)

CATALYST: 0.65 wt% Ba(NO3)2/ MgO NOTEBOOK: 9-KDC-X-4

Weight (g): 4.006 Volume (cc): 3.9

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

Temperature (°C)	750	750	750	750	800	800	800	800	800	800	850	850
Flow (cc/min)	50	50	50	50	50	50	50	100	100	100	100	100
GHSV (h-1)	769	769	769	769	769	769	769	1538	1538	1538	1538	1538
Time (h)	37	39	43	47	49	51	59	61	63	67	69	71
CH4 Conv., %	22.74	22.76	22.84	22.71	29.50	29.51	29.10	22.97	22.06	21.66	31.16	30.76
O2 Conv., %	73.40	72.99	72.14	71.74	91.72	91.47	91.23	61.14	62.19	61.93	90.67	90.51
C Balance, %	100.90	100.48	100.49	100.60	99.96	99.99	100.43	100.01	101.50	101.79	101.40	101.73
C2 Selectivity, %	18.48	17.92	18.60	18.70	25.13	25.27	24.65	25.83	26.14	26.04	28.44	28.43
C3 Selectivity, %	0.73	0.79	0.75	0.75	1.50	1.51	1.52	1.14	1.16	1.15	1.65	1.66
C2 Yield, %	4.24	4.10	4.27	4.27	7.41	7.46	7.20	5.93	5.85	5.74	8.99	8.90
Ethylene/Ethane	1.94	2.03	1.99	1.99	3.15	3.13	3.26	2.12	2.16	2.15	3.96	3.99
CO2/CO	1.96	1.87	1.79	1.73	1.97	1.90	1.72	1.13	1.13	1.11	1.23	1.21

Table B32. Methane Coupling Activity of Ba(2+)/ MgO : ion-exchange

CATALYST: Ba(2+)/ MgO : ion-exchange   **NOTEBOOK:** 9-KDC-X-9

Weight (g): 4.009   **Volume (cc):** 4.3

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

Temperature (°C)	700	700	700	700	750	750	750	750
Flow (cc/min)	50	50	50	50	50	50	50	50
GHSV (h-1)	698	698	698	698	698	698	698	698
Time (h)	1	3	9	11	13	15	19	25
CH4 Conv., %	1.88	1.74	1.61	1.64	6.01	6.47	6.37	6.63
O2 Conv., %	7.16	6.93	6.49	6.90	22.44	23.53	23.59	23.63
C Balance, %	100.82	100.90	101.00	101.00	101.14	101.05	101.18	100.99
C2 Selectivity, %	6.23	6.28	6.58	6.19	13.44	15.09	15.21	15.20
C3 Selectivity, %	0.00	0.00	0.00	0.00	0.08	0.13	0.13	1.15
C2 Yield, %	0.12	0.11	0.11	0.10	0.82	0.99	0.98	1.02
Ethylene/Ethane	0.19	0.15	0.15	0.14	0.41	0.44	0.44	0.45
CO2/CO	2.33	2.22	2.13	1.94	2.90	2.90	2.90	2.88

Table B32. Methane Coupling Activity of Ba(2+)/ MgO : ion-exchange (Continued)

CATALYST: Ba(2+)/ MgO : ion-exchange **NOTEBOOK:** 9-KDC-X-9

Weight (g): 4.009 **Volume (cc):** 4.3

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

Temperature (°C)	800	800	800	800	800	850	850	850	850
Flow (cc/min)	50	50	50	100	100	100	100	100	100
GHSV (h-1)	698	698	698	1395	1395	1395	1395	1395	1395
Time (h)	29	31	33	43	45	47	49	53	57
CH4 Conv., %	16.75	16.38	16.96	14.11	13.45	27.57	27.44	28.00	28.27
O2 Conv., %	56.06	55.18	56.12	46.16	45.75	79.07	78.10	78.15	78.72
C Balance, %	101.74	101.80	101.21	101.11	101.94	101.64	101.37	101.28	101.25
C2 Selectivity, %	27.68	27.44	27.28	25.96	26.42	27.37	27.14	27.03	26.49
C3 Selectivity, %	0.88	0.87	0.89	0.74	0.74	1.67	1.69	1.62	1.55
C2 Yield, %	4.72	4.58	4.68	3.70	3.62	7.67	7.55	7.67	7.58
Ethylene/Ethane	1.02	1.02	1.05	0.96	0.97	3.14	3.40	3.41	3.52
CO2/CO	3.31	3.34	3.38	3.20	3.22	0.59	0.56	0.54	0.53

Table B33. Methane Coupling Activity of 0.53 wt% Sr(NO3)2/ MgO

CATALYST: 0.53 wt% Sr(NO3)2/ MgO **NOTEBOOK:** 8-KDC-X-4

Weight (g): 4.002 **Volume (cc):** 3.5

CH4/O2/N2: 2.21/1/3.74 **Pressure (psig):** 5

Temperature (°C)	700	700	700	750	750	750	800	800	800	800	850	850
Flow (cc/min)	50	50	50	50	50	50	50	50	50	50	100	100
GHSV (h-1)	857	857	857	857	857	857	857	857	857	857	1714	1714
Time (h)	1	3	13	17	19	21	23	25	31	35	39	41
CH4 Conv., %	10.09	10.31	9.99	18.16	18.04	17.72	26.79	27.60	26.86	26.47	30.96	31.89
O2 Conv., %	37.00	38.51	38.26	57.95	56.86	55.77	82.05	83.26	80.75	79.07	94.30	94.36
C Balance, %	98.90	98.91	98.98	99.05	99.04	99.02	98.93	98.89	98.96	98.91	97.79	96.49
C2 Selectivity, %	6.75	7.19	7.61	17.26	17.27	17.17	26.03	26.20	25.42	25.03	24.07	23.38
C3 Selectivity, %	0.04	0.05	0.05	0.56	0.57	0.57	1.42	1.45	1.41	1.39	1.84	1.63
C2 Yield, %	0.67	0.73	0.75	3.10	3.08	3.01	6.90	7.15	6.76	6.55	7.29	7.19
Ethylene/Ethane	0.47	0.49	0.48	1.18	1.20	1.20	2.35	2.54	2.63	2.72	4.40	4.47
CO2/CO	2.04	2.43	3.28	1.28	1.24	1.19	1.48	1.41	1.20	1.09	1.30	1.24

Table B34. Methane Coupling Activity of Sr(2+)/ MgO : ion-exchange

CATALYST: Sr(2+)/ MgO : ion-exchange **NOTEBOOK:** 9-KDC-X-16

Weight (g): 4.009 **Volume (cc):** 3.6

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

Temperature (°C)	700	700	700	750	750	750	800	800	800	800	800	800
Flow (cc/min)	50	50	50	50	50	50	50	50	100	100	100	100
GHSV (h-1)	833	833	833	833	833	833	833	833	1667	1667	1667	1667
Time (h)	1	3	9	13	15	19	31	23	25	27	29	35
CH4 Conv., %	6.28	6.00	7.25	24.13	25.90	26.37	32.26	34.27	31.79	31.71	32.21	32.54
O2 Conv., %	18.37	18.70	20.83	64.99	70.46	72.38	91.79	94.61	84.96	85.31	85.70	86.34
C Balance, %	98.00	98.69	98.15	98.31	98.34	98.84	98.96	98.62	98.74	99.09	98.70	98.71
C2 Selectivity, %	24.48	27.08	28.77	26.15	25.15	24.87	19.45	17.03	22.64	22.52	22.34	22.06
C3 Selectivity, %	0.39	0.53	0.70	1.52	1.45	1.42	0.94	0.73	1.14	1.11	1.10	1.06
C2 Yield, %	1.51	1.60	2.05	6.20	6.41	6.48	6.21	5.76	7.11	7.08	7.10	7.09
Ethylene/Ethane	0.61	0.69	0.78	2.94	3.22	3.35	5.16	6.91	4.63	4.73	4.75	4.86
CO2/CO	0.89	0.90	0.96	0.41	0.40	0.38	0.44	0.44	0.30	0.30	0.30	0.30

Table B35. **Methane Coupling Activity of 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO**

CATALYST: 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO **NOTEBOOK:** 7-KDC-X-108

Weight (g): 4.014 **Volume (cc):** 9.8

CH4/O2/N2: 2.02/1/3.78 **Pressure (psig):** 4.5

Temperature (°C)	800	800	800	800	800	800	851	851	851	851	851	851
Flow (cc/min)	100	100	100	100	100	100	250	250	250	250	250	250
GHSV (h-1)	612	612	612	612	612	612	1530	1530	1530	1530	1530	1530
Time (h)	1	2	4	8	12	16	18	20	24	28	30	32
CH4 Conv., %	33.70	33.95	34.23	34.62	34.80	34.73	36.62	36.98	37.08	35.97	37.03	36.90
O2 Conv., %	94.66	94.66	94.67	94.66	94.66	94.55	94.62	94.64	94.64	94.64	94.64	94.64
C Balance, %	100.61	100.62	100.78	100.62	100.67	101.15	100.94	100.48	100.43	101.65	100.57	100.70
C2 Selectivity, %	34.83	35.24	35.29	35.25	35.14	34.98	37.91	37.74	37.50	37.42	37.26	37.15
C3 Selectivity, %	3.17	3.09	3.18	3.20	3.19	3.26	3.43	3.38	3.37	3.35	3.36	3.35
C2 Yield, %	11.81	12.04	12.18	12.28	12.31	12.29	14.01	14.03	13.97	13.68	13.88	13.80
Ethylene/Ethane	3.28	3.32	3.37	3.54	3.64	3.78	3.55	3.63	3.72	3.75	3.77	3.80
CO2/CO	2.30	2.09	1.83	1.55	1.38	1.27	0.91	0.86	0.81	0.78	0.77	0.76

Table B36. **Methane Coupling Activity of 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO [Sequential Mode]**

CATALYST: 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO **NOTEBOOK:** 6-KDC-X-106

Weight (g): 10.009 **Volume (cc):** 22.3

CH4/O2/N2: Pure CH4 **Pressure (psig):** 0

Temperature (°C)	800	800	800	800	850	850	850
Flow (cc/min)	50	50	150	150	50	50	50
GHSV (h-1)	135	135	404	404	135	135	135
Collection Interval (min)	0 - 2	2 - 5	0 - 2	2 - 5	0 - 2	2 - 5	5 - 10
CH4 Conv., %	49.71	22.26	41.76	5.29	55.36	8.56	2.61
C2 Selectivity, %	28.22	42.49	31.89	77.82	25.21	46.44	64.21
C3 Selectivity, %	2.34	4.45	2.86	4.75	1.80	6.97	18.76
C2 Yield, %	14.03	9.46	13.32	4.11	13.96	3.98	1.67
Ethylene/Ethane	4.80	3.53	4.41	1.53	5.53	3.60	2.35
CO2/CO	4.25	5.32	4.46	2.59	2.76	3.92	0.85

Table B36. Methane Coupling Activity of 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO (Continued)
[Sequential Mode]

CATALYST: 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO **NOTEBOOK:** 6-KDC-X-106

Weight (g): 10.009 **Volume (cc):** 22.3

CH4/O2/N2: Pure CH4 **Pressure (psig):** 0

Temperature (°C)	850	850	850	825	825	825	825	825	825
Flow (cc/min)	150	150	150	50	50	50	150	150	150
GHSV (h-1)	404	404	404	135	135	135	404	404	404
Collection Interval (min)	*0 - 2*	*2 - 5*	*5 - 10*	*0 - 2*	*2 - 5*	*5 - 10*	*0 - 2*	*2 - 5*	*5 - 10*
CH4 Conv., %	26.50	5.48	1.93	44.63	7.27	1.70	21.20	8.85	4.10
C2 Selectivity, %	44.73	69.53	77.21	27.83	57.71	75.44	57.58	72.42	77.88
C3 Selectivity, %	4.47	8.24	10.78	2.46	8.93	9.01	5.70	6.50	8.01
C2 Yield, %	11.85	3.81	1.49	12.42	4.19	1.28	12.21	6.41	3.19
Ethylene/Ethane	3.88	2.26	1.10	4.85	3.18	1.71	3.35	2.23	1.39
CO2/CO	3.17	2.35	2.04	5.45	4.21	0.93	2.89	3.20	2.05

Table B36. **Methane Coupling Activity of 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO (Continued)**
[Sequential Mode}

CATALYST: 34.5 wt% Mn(OAc)2/ 2.7 wt% Na4P2O7/ silica - ARCO **NOTEBOOK:** 6-KDC-X-106

Weight (g): 10.009 **Volume (cc):** 22.3

CH4/O2/N2: Pure CH4 **Pressure (psig):** 0

Temperature (°C)	350	850	850	825	825	825	850	850
Flow (cc/min)	150	150	150	50	50	50	150	150
GHSV (h-1)	404	404	404	135	135	135	404	404
Collection Interval (min)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	0 - 2	2 to 5
CH4 Conv., %	20.76	7.27	1.65	36.83	5.94	2.70	29.93	5.94
C2 Selectivity, %	49.73	57.71	84.29	24.49	59.22	68.54	44.78	69.71
C3 Selectivity, %	0.54	8.93	5.84	2.37	8.40	9.85	3.23	8.89
C2 Yield, %	10.32	4.19	1.39	9.02	3.52	1.85	13.40	4.14
Ethylene/Ethane	3.89	3.18	1.16	4.71	3.63	2.99	4.34	2.44
CO2/CO	3.24	4.21	0.83	6.13	2.79	0.95	3.49	2.43

Table B37. Methane Coupling Activity of 20 wt% Na2CO3/ LaCaMnCoO6

CATALYST: 20 wt% Na2CO3/ LaCaMnCoO6 **NOTEBOOK:** 7-KDC-X-125

Weight (g): 4.002 **Volume (cc):** 4.9

CH4/O2/N2: 2.18/1/3.79 **Pressure (psig):** 8.0 - 12.0

Temperature (°C)	800	800	800	800	800	800	800
Flow (cc/min)	300	300	300	300	300	300	300
GHSV (h-1)	3673	3673	3673	3673	3673	3673	3673
Time (h)	1	3	6	24	30	48	66
CH4 Conv., %	32.44	32.35	32.46	30.11	28.90	28.45	28.72
O2 Conv., %	94.69	94.65	94.69	94.70	94.66	94.66	94.66
C Balance, %	100.52	100.50	100.96	101.04	102.13	97.42	97.10
C2 Selectivity, %	37.49	38.60	38.55	34.69	34.57	37.81	38.61
C3 Selectivity, %	2.17	2.33	2.35	1.73	1.68	1.87	1.93
C2 Yield, %	12.22	12.55	12.63	10.55	10.20	10.48	10.77
Ethylene/Ethane	1.76	1.85	1.92	1.43	1.42	1.36	1.38
CO2/CO	32.69	32.99	34.58	42.72	53.97	41.31	40.26

Table B38. Methane Coupling Activity of 20 wt% Na2CO3/ LaCaMnCoO6
[Sequential Mode]

CATALYST: 20 wt% Na2CO3/ LaCaMnCoO6 **NOTEBOOK:** 6-KDC-X-116

Weight (g): 10.011 **Volume (cc):** 17.2

CH4/O2/N2: Pure CH4 **Pressure (psig):** 0

Temperature (°C)	800	800	800	800	800	850	850	850	850	850
Flow (cc/min)	50	50	50	150	150	50	50	50	150	150
GHSV (h-1)	174	174	174	523	523	174	174	174	523	523
Collection Interval (min)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5
CH4 Conv., %	10.63	7.61	6.92	7.30	5.43	10.04	6.06	4.23	11.28	9.98
C2 Selectivity, %	88.57	85.47	78.39	90.59	85.32	80.27	60.87	24.99	77.21	65.24
C3 Selectivity, %	2.83	3.19	3.82	2.19	0.00	4.17	2.96	0.95	3.86	5.54
C2 Yield, %	9.42	6.50	5.43	6.62	4.64	8.06	3.69	1.06	8.71	6.51
Ethylene/Ethane	1.65	1.63	1.68	1.07	0.97	1.76	1.24	0.65	2.30	2.46
CO2/CO	**	**	46.52	13.59	19.07	20.45	21.70	5.59	68.09	30.26

**: CO too low for meaningful results.

Table B38. Methane Coupling Activity of 20 wt% Na2CO3/ LaCaMnCoO6 (Continued)
[Sequential Mode]

CATALYST: 20 wt% Na2CO3/ LaCaMnCoO6 **NOTEBOOK:** 6-KDC-X-116

Weight (g): 10.011 **Volume (cc):** 17.2

CH4/O2/N2: Pure CH4 **Pressure (psig):** 0

Temperature (°C)	825	825	825	825	825	800	800	800	800	800
Flow (cc/min)	50	50	50	150	150	150	150	150	50	50
GHSV (h-1)	174	174	174	523	523	523	523	523	174	174
Collection Interval (min)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5
CH4 Conv., %	12.18	11.47	10.84	9.69	8.24	9.04	8.04	5.22	10.61	9.35
C2 Selectivity, %	75.69	66.08	55.14	85.39	74.73	86.05	80.62	75.18	84.24	81.58
C3 Selectivity, %	3.86	4.68	4.41	3.21	3.19	2.42	2.61	2.17	2.72	0.00
C2 Yield, %	9.22	7.58	5.98	8.27	6.16	7.78	6.48	3.93	8.94	7.63
Ethylene/Ethane	2.40	2.49	2.35	1.47	1.30	1.30	1.18	0.90	1.92	2.08
CO2/CO	124.55	42.61	42.17	25.89	37.40	29.06	39.23	19.69	**	46.98

**: CO too low for meaningful results.

Table B39. **Methane Coupling Activity of 20 wt% Na2CO3/ LaCaMnCoO6 - Run 2**
[Sequential Mode]

CATALYST: 20 wt% Na2CO3/ LaCaMnCoO6   **NOTEBOOK:** 6-KDC-X-97

Weight (g): 3.015   **Volume (cc):** 3.8

CH4/O2/N2: Pure CH4   **Pressure (psig):** 0

Temperature (°C)	797	848	795	795	797	848	848	848	848	848	900
Flow (cc/min)	150	150	150	150	75	75	75	150	150	150	150
GHSV (h-1)	2368	2368	2368	2368	1184	1184	1184	2368	2368	2368	2368
Collection interval (min)	0 - 3	0 - 3	0 - 3	0 - 3	0 - 3	0 - 3	3 - 5	0 - 3	0 - 3	0 - 5	0 - 3
CH4 Conv., %	6.20	4.47	2.13	2.29	2.32	3.28	2.06	2.43	2.40	2.21	5.51
C2 Selectivity, %	91.05	86.29	94.51	94.93	95.18	88.59	90.47	91.33	89.92	93.02	85.70
C3 Selectivity, %	1.05	1.33	1.13	1.10	1.10	3.19	1.80	1.52	1.50	1.47	3.81
C2 Yield, %	5.65	3.86	2.01	2.17	2.21	2.91	1.87	2.22	2.16	2.06	4.72
Ethylene/Ethane	0.50	0.56	0.32	0.33	0.42	0.69	0.54	0.51	0.48	0.48	0.98
CO2/CO	43.59	10.73	4.65	4.41	**	**	8.07	7.65	7.90	7.73	11.91

**: CO too low for meaningful results.

Table B40. Methane Coupling Activity of 36 wt% K_2CO_3/ $LaCaMnCoO_6$
[Sequential Mode]

CATALYST: 36 wt% K_2CO_3/ $LaCaMnCoO_6$ **NOTEBOOK:** 6-KDC-X-129

Weight (g): 10.004 **Volume (** 13.5

$CH_4/O_2/N_2$: Pure CH_4 **Pressure (psig):** 0

Temperature (°C)	800	800	800	800	800	850	850	850	850	850	850
Flow (cc/min)	50	50	50	150	150	50	50	50	150	150	150
GHSV (h-1)	222	222	222	667	667	222	222	222	667	667	667
Collection Interval (min)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10
CH_4 Conv., %	6.81	5.38	3.82	4.70	3.24	5.94	4.36	2.39	7.26	3.89	18.01*
C2 Selectivity, %	75.48	68.43	45.18	83.17	54.07	66.33	62.73	31.78	76.94	43.18	1.29
C3 Selectivity, %	0.40	1.03	1.06	0.83	1.02	0.57	1.07	0.67	1.06	1.69	0.25
C2 Yield, %	5.14	3.68	1.73	3.91	1.75	3.94	2.73	0.76	5.58	1.68	0.23
Ethylene/Ethane	0.61	1.02	0.89	0.77	0.63	0.72	0.91	0.97	0.96	0.75	0.78
CO_2/CO	**	17.87	17.21	10.26	16.12	**	16.89	5.43	18.27	9.21	0.28

*: Detectable amounts of hydrogen present in the 5 to 10 minute sample
**: CO too low for meaningful results.

Table B40. Methane Coupling Activity of 36 wt% K2CO3/ LaCaMnCoO6 (Continued) [Sequential Mode]

CATALYST: 36 wt% K2CO3/ LaCaMnCoO6 **NOTEBOOK:** 6-KDC-X-129

Weight (g): 10.004 **Volume (** 13.5

CH4/O2/N2: Pure CH4 **Pressure (psig):** 0

Temperature (°C)	850	850	850	825	825	825	825	825	825
Flow (cc/min)	150	150	150	50	50	50	150	150	150
GHSV (h-1)	667	667	667	222	222	222	667	667	667
Collection Interval (min)	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10	0 - 2	2 - 5	5 - 10
CH4 Conv., %	7.60	3.59	10.95*	5.23	3.89	3.40	9.39	5.96	3.47
C2 Selectivity, %	79.48	42.31	0.37	83.54	83.43	68.38	79.64	57.79	24.16
C3 Selectivity, %	1.10	0.58	0.00	0.57	1.18	1.89	1.19	1.04	0.24
C2 Yield, %	6.04	1.52	0.04	4.37	3.25	2.32	7.48	3.45	0.84
Ethylene/Ethane	1.00	0.75	0.76	0.90	0.97	0.85	1.26	0.89	0.48
CO2/CO	6.84	9.04	0.06	**	**	11.41	23.10	28.35	19.25

*: Detectable amounts of hydrogen present in the 5 to 10 minute sample
**: CO too low for meaningful results.

Table B41. Methane Coupling Activity of 80 mole% Pr - 20 mole% Ce Oxide

CATALYST: 80 mole% Pr - 20 mole% Ce Oxide **NOTEBOOK:** 8-KDC-X-11

Weight (g): 4.007 **Volume (cc):** 9

CH4/O2/N2: 2.22/1/3.74 **Pressure (psig):** 5

Temperature (°C)	600	600	600	652	652	652	702	702	702	752	752	752
Flow (cc/min)	150	150	150	200	200	200	200	200	200	200	200	200
GHSV (h-1)	1000	1000	1000	1333	1333	1333	1333	1333	1333	1333	1333	1333
Time (h)	3	11	17	19	21	25	27	33	39	41	43	45
CH4 Conv., %	22.79	22.79	22.64	23.22	23.11	22.98	23.35	23.77	23.48	23.96	25.35	25.30
O2 Conv., %	94.71	94.71	94.72	94.71	94.71	94.71	94.71	94.73	94.73	94.72	94.73	94.73
C Balance, %	100.37	100.36	100.16	100.33	100.31	100.40	101.53	99.97	100.30	100.61	99.00	98.94
C2 Selectivity, %	10.89	10.71	9.58	12.81	12.56	12.45	13.47	14.14	14.32	15.58	15.64	15.52
C3 Selectivity, %	0.41	0.41	0.33	0.37	0.35	0.35	0.34	0.35	0.36	0.33	0.32	0.45
C2 Yield, %	2.49	2.45	2.17	2.98	2.91	2.87	3.19	3.36	3.37	3.76	3.92	3.89
Ethylene/Ethane	0.34	0.34	0.31	0.41	0.41	0.41	0.51	0.52	0.52	0.77	0.78	0.76
CO2/CO	67.73	79.76	81.36	60.92	61.55	61.97	44.27	54.94	54.68	28.31	28.93	29.46

Table B42. **Methane Coupling Activity of 20 wt% Na2CO3/ 80 mole% Pr - 20 mole% Ce Oxide**

CATALYST: 20 wt% Na2CO3/ 80 mole% Pr - 20 mole% Ce Oxide **NOTEBOOK:** 9-KDC-X-38

Weight (g): 4.034 **Volume (cc):** 4.6

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

Temperature (°C)	500	500	500	550	550	550	600	600	600
Flow (cc/min)	100	100	100	100	100	100	100	100	100
GHSV (h-1)	1304	1304	1304	1304	1304	1304	1304	1304	1304
Time (h)	1	3	5	7	9	13	15	17	21
CH4 Conv., %	**	**	**	4.47	4.89	4.92	21.50	21.41	20.71
O2 Conv., %	5.76	5.81	5.52	23.01	24.26	23.89	90.70	90.79	89.62
C Balance, %	100.83	100.55	100.74	101.53	101.49	101.10	101.38	101.53	101.43
C2 Selectivity, %	**	**	**	0.33	1.63	0.32	14.01	13.53	11.75
C3 Selectivity, %	**	**	**	0.00	0.00	0.00	0.58	0.56	0.44
C2 Yield, %	**	**	**	0.01	0.08	0.02	3.05	2.94	2.47
Ethylene/Ethane	**	**	**	2.82	1.37	3.08	0.59	0.58	0.53
CO2/CO	**	**	**	36.12	38.33	44.55	102.31	107.20	108.84

**: Conversion too low for meaningful results.

Table B42. **Methane Coupling Activity of 20 wt% Na_2CO_3/ 80 mole% Pr - 20 mole% Ce Oxide (Continued)**

CATALYST: 20 wt% Na_2CO_3/ 80 mole% Pr - 20 mole% Ce Oxide **NOTEBOOK:** 9-KDC-X-38

Weight (g): 4.034 **Volume (cc):** 4.6

$CH_4/O_2/N_2$: 2.04/1/3.81 **Pressure (psig):** 5

Temperature (°C)	650	650	650	700	700	700	750	750	750
Flow (cc/min)	100	100	100	100	100	100	100	100	100
GHSV (h-1)	1304	1304	1304	1304	1304	1304	1304	1304	1304
Time (h)	23	25	29	31	33	37	39	41	45
CH_4 Conv., %	31.24	30.67	30.53	32.22	32.49	32.05	31.84	31.38	30.67
O_2 Conv., %	94.69	94.72	94.70	94.72	94.71	94.73	94.71	94.69	94.72
C Balance, %	101.27	101.31	101.38	101.34	101.04	101.22	101.17	101.13	101.47
C2 Selectivity, %	41.38	40.24	39.81	44.02	44.11	43.81	42.64	41.85	40.85
C3 Selectivity, %	2.74	2.64	2.59	2.67	2.63	2.57	2.56	2.48	2.32
C2 Yield, %	13.09	12.51	12.32	14.37	14.48	14.21	13.74	13.28	12.71
Ethylene/Ethane	1.06	0.98	0.95	1.25	1.26	1.23	1.72	1.70	1.61
CO_2/CO	108.71	99.93	127.99	75.32	88.57	74.23	48.89	44.55	49.25

Table B43. **Methane Coupling Activity of 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce Oxide**

CATALYST: 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce Oxide **NOTEBOOK:** 9-KDC-X-24

Weight (g): 4.012 **Volume (cc):** 9.4

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

Temperature (°C)	500	500	**	550	550	**	600	600
Flow (cc/min)	100	100	100	100	100	200	200	200
GHSV (h-1)	638	638	638	638	638	1277	1277	1277
Time (h)	3	7	9	11	15	17	19	25
CH4 Conv., %	22.68	22.51	22.80	23.16	23.16	23.05	24.64	24.57
O2 Conv., %	94.73	94.74	94.73	94.73	94.73	94.74	94.72	94.74
C Balance, %	100.03	100.33	100.19	100.27	100.27	100.44	100.29	100.54
C2 Selectivity, %	10.18	10.25	11.02	12.69	12.83	13.18	18.67	19.19
C3 Selectivity, %	0.37	0.39	0.39	0.46	0.47	0.48	0.49	0.52
C2 Yield, %	2.31	2.32	2.52	2.95	2.98	3.05	4.61	4.74
Ethylene/Ethane	0.27	0.28	0.32	0.36	0.37	0.37	0.57	0.57
CO2/CO	***	125.22	511.65	326.74	219.68	80.85	43.11	42.75

**: Temperature changing.
***: CO too low for meaningful results.

Table B43. **Methane Coupling Activity of 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce Oxide (Continued)**

CATALYST: 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce Oxide **NOTEBOOK:** 9-KDC-X-24

Weight (g): 4.012 **Volume (cc):** 9.4

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

Temperature (°C)	650	650	650	650	700	700	750	750	750
Flow (cc/min)	200	200	200	200	200	200	200	200	200
GHSV (h-1)	1277	1277	1277	1277	1277	1277	1277	1277	1277
Time (h)	27	29	33	35	37	39	41	43	45
CH4 Conv., %	24.97	24.86	25.06	25.04	25.35	25.46	25.53	25.57	25.93
O2 Conv., %	94.72	94.73	94.74	94.73	94.73	94.72	94.72	94.72	94.73
C Balance, %	100.52	100.59	100.27	100.39	100.20	100.10	100.08	100.11	99.87
C2 Selectivity, %	19.68	19.25	19.07	19.16	18.16	17.42	17.54	17.62	17.48
C3 Selectivity, %	0.48	0.44	0.43	0.42	0.37	0.35	0.35	0.35	0.33
C2 Yield, %	4.94	4.81	4.79	4.82	4.61	4.44	4.48	4.51	4.53
Ethylene/Ethane	0.71	0.74	0.77	0.79	1.01	1.14	1.18	1.20	1.19
CO2/CO	32.24	29.21	25.68	25.72	16.62	12.79	11.94	11.67	11.76

Table B44. **Methane Coupling Activity of 20 wt% Na_2CO_3/ 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide**

CATALYST: 20 wt% Na_2CO_3/ 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide **NOTEBOOK:** 9-KDC-X-34

Weight (g): 4.005 **Volume (cc):** 4.8

$CH_4/O_2/N_2$: 2.04/1/3.81 **Pressure (psig):** 5

Temperature (°C)	500	500	500	550	550	600	600	600
Flow (cc/min)	100	100	100	100	100	100	100	100
GHSV (h-1)	1250	1250	1250	1250	1250	1250	1250	1250
Time (h)	1	3	5	7	9	13	15	19
CH_4 Conv., %	**	**	**	2.40	2.38	27.69	26.83	26.93
O_2 Conv., %	3.51	3.01	2.92	13.30	13.75	94.74	94.72	94.74
C Balance, %	100.93	100.70	100.68	100.87	100.95	100.79	101.22	101.16
C2 Selectivity, %	**	**	**	0.61	0.59	30.65	29.64	29.01
C3 Selectivity, %	**	**	**	0.00	0.00	1.97	1.88	1.78
C2 Yield, %	**	**	**	0.01	0.01	8.56	8.05	7.90
Ethylene/Ethane	**	**	**	2.81	2.88	0.84	0.81	0.78
CO_2/CO	**	**	**	21.54	22.16	155.35	119.56	624.81

**: Conversion too low for meaningful results.

Table B44. **Methane Coupling Activity of 20 wt% Na2CO3/ 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide (Continued)**

CATALYST: 20 wt% Na2CO3/ 2.9 mole% Ag - 77.7 mole% Pr - 19.4 mole% Ce oxide **NOTEBOOK:** 9-KDC-X-34

Weight (g): 4.005 **Volume (cc):** 4.8

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

Temperature (°C)	650	650	650	700	700	700	750	750
Flow (cc/min)	100	100	100	100	100	100	100	100
GHSV (h-1)	1250	1250	1250	1250	1250	1250	1250	1250
Time (h)	21	23	27	29	31	35	37	39
CH4 Conv., %	33.25	33.24	32.83	34.00	33.96	33.99	32.99	32.70
O2 Conv., %	94.73	94.72	94.73	94.71	94.75	94.71	94.73	94.74
C Balance, %	100.87	100.80	100.91	100.67	100.77	100.70	100.86	100.94
C2 Selectivity, %	44.78	44.56	44.03	46.41	46.52	46.38	44.19	43.84
C3 Selectivity, %	3.02	2.97	2.90	3.16	3.14	3.08	2.90	2.84
C2 Yield, %	15.02	14.93	14.58	15.89	15.92	15.87	14.70	14.47
Ethylene/Ethane	1.13	1.12	1.07	1.35	1.36	1.34	1.69	1.68
CO2/CO	113.13	115.06	115.53	64.75	64.16	65.00	44.92	44.80

Table B45. Methane Coupling Process Material Balance

Mlb/hr for a process producing 1,000MMppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10
H2										
N2	2.3	1887.9	3569.7	3569.7		3569.7		3569.7	1890.6	1679.0
O2		573.5	573.5							
CO			44.9	94.5		94.5		94.5	49.6	45.0
CO2	1.0		1.0	232.4	0.1	232.3	232.3			
CH4	328.5		575.2	299.3		299.3		299.3	10.5	246.9
C2H4			0.1	116.7		116.7		116.7	0.2	0.2
C2H6	3.4		4.2	23.5		23.5		23.5	0.8	0.9
C3H6			0.3	7.0		7.0		7.0	0.3	0.3
C3H8				1.4		1.4		1.4	0.0	0.0
C4s +			53.9	53.9		53.9		53.9	51.3	53.9
H2O				424.3	394.4	29.9	29.9			
Total	**335.2**	**2461.4**	**4822.8**	**4822.7**	**394.5**	**4428.2**	**262.2**	**4166.0**	**2003.3**	**2026.2**

Component	11	12	13	14	15
H2					
N2					
O2					
CO					
CO2					
CH4	41.9	41.9			
C2H4	117.1	116.3	0.8		0.8
C2H6	36.5	21.8	14.7		14.7
C3H6	31.5	6.4	25.1		25.1
C3H8	7.0	1.4	5.6		5.6
C4s +	29943.9	1.7	29942.2	53.0	29995.2
H2O					
Total	**30177.9**	**189.5**	**29988.4**	**54483.7**	**30041.4**

Table B46. Methane Coupling Process Material Balance

Mlb/hr for a process producing 1,000MMppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10
H2										
N2	1.7	4.6	63.7	63.7		63.7		63.7	6.3	57.4
O2		201.1	201.1							
CO			0.6	0.6		0.6		0.6		0.6
CO2	0.7		0.7	31.2		31.2	31.2			
CH4	245.1		907.9	731.1		731.1		731.1	68.2	662.9
C2H4			15.1	136.1		136.1		136.1	0.2	15.1
C2H6	2.5		2.8	15.8		15.8		15.8		0.4
C3H6				7.1		7.1		7.1		
C3H8				4.5		4.5		4.5		
C4s +				0.3		0.3		0.3		
H2O				201.4	190.4	11.0	11.0			
Total	**250.0**	**205.7**	**1191.9**	**1191.8**	**190.4**	**1001.4**	**42.2**	**959.2**	**74.7**	**736.4**

Component	11	12	13	14	15
H2					
N2					
O2					
CO					
CO2					
CH4					
C2H4	120.8	120.6	0.2	0.2	
C2H6	15.4	0.1	15.3	15.2	0.1
C3H6	7.1		7.1	0.1	7.0
C3H8	4.5		4.5		4.5
C4s +	0.3		0.3		0.3
H2O					
Total	**148.1**	**120.7**	**27.4**	**15.5**	**11.9**

Table B47. Methane Coupling Economics

	Price	Case 1 Ethylene/Ethane = 1		Ethylene/Ethane = 10	
	$/Unit	Volume Units/Yr	Value $MM/Yr	Volume Units/Yr	Value $MM/Yr
Investment					
ISBL		1000	311	1000	241
Oxygen Plant		3508	64	2451	42
OSBL			78		60
Total Fixed Investment			**453**		**343**
Working Capital			15		13
Total Utilized Investment			**468**		**357**
Ethylene Sales	**$0.320**	**1000**	**320**	**1000**	**320**
Variable Cost					
Methane, Lb	$0.043	3161	136	2071	101
Ethane, Lb	$0.055				
By-Product Credit					
Fuel Gas, MMBTU	$1.800	15	-26	13	-28
Hydrogen, Lb	$0.180				
Ethane, Lb	$0.055	920	-51	129	-8
Propylene, Lb	$0.205	87	-18	58	-14
Propane, Lb	$0.066	61	-4	38	-3
Crude C4s +, Lb	$0.120	4	-1	3	0
Total By-Product Sales			-99		-53
Utilities, MMBTU	$1.800	12	22	9	18
Catalyst & Chemicals			1		1
Total Variable Cost			**59**		**67**
Fixed Cost			**40**		**31**
Total Cash Cost			98		98
Operating Income			**222**		**222**
Depreciation (10%)			45		34
NIAT (37% Tax Rate)			**111**		**118**
ROIAT			**24%**		**33%**

Table B48. Methane Coupling Economics

		Case A1.2a		Case A1.2b	
	Price $/Unit	Volume Units/Yr	Value $MM/Yr	Volume Units/Yr	Value $MM/Yr
Investment					
ISBL		1000	330	1000	439
Oxygen Plant		3297	62	2280	50
OSBL			83		110
Total Fixed Investment			**475**		**599**
Working Capital			16		19
Total Utilized Investment			**491**		**618**
Ethylene Sales	**$0.320**	**1000**	**320**	**1000**	**320**
Variable Cost					
Methane, Lb	$0.049	2185	107	1941	95
Ethane, Lb	$0.064				
By-Product Credit					
Fuel Gas, MMBTU	$2.050	14	-28	12	-25
Propylene, Lb	$0.205	62	-13	62	-13
Propane, Lb	$0.077	20	-2	20	-2
Crude C4s +, Lb	$0.139	15	-2	15	-2
Total By-Product Sales			-44		-41
Utilities, MMBTU	$2.050	13	27	26	54
Catalyst & Chemicals			1		1
Total Variable Cost			**90**		**108**
Fixed Cost			**37**		**45**
Total Cash Cost			127		154
Operating Income			**193**		**166**
Depreciation (10%)			47		60
NIAT (37% Tax Rate)			**92**		**67**
ROIAT			**19%**		**11%**

Table B49. Case A1.2a Methane Coupling Process Material Balance

Mlb/hr for a process producing 1,000MMppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10
H2			3.5	1.8		1.8		3.9		3.9
N2	1.8	6.2	76.5	76.5		76.5		76.5		76.5
O2		271.3	271.3			0.0				
CO			15.8	17.5		17.5		17.6		17.6
CO2	0.8		0.8	84.7		84.7		84.7	84.7	
CH4	257.1		999.2	811.5		811.5		813.3		813.3
C2H4			2.5	94.4		94.4		124.1		124.1
C2H6	2.6		2.7	35.6		35.6		64.5		64.5
C3H6				6.9		6.9		9.7		9.7
C3H8				2.8		2.8		2.9		2.9
C4s +						0.0		1.8		1.8
H2O				235.6	206.0	29.6	27.3	4.0	4.0	
Total	**262.3**	**277.5**	**1372.3**	**1367.3**	**206.0**	**1161.3**	**27.3**	**1203.0**	**88.7**	**1114.3**

Component	11	12	13	14	15	16	17	18	19	20	21
H2	3.5	0.4							2.2		2.2
N2	68.5	7.6									
O2											
CO	15.8	1.7							0.1		0.1
CO2											
CH4	737.2	76.3							1.9		1.9
C2H4	2.5		121.5		121.5	120.9	0.6		29.6		29.6
C2H6	0.2		64.4	0.1	64.3	0.1	64.2		29.0		29.0
C3H6			9.7	7.5	2.2		2.2		2.8		2.8
C3H8			2.9	2.4	0.5		0.5		0.1		0.1
C4s +			1.8	1.8					1.8		1.8
H2O								11.9	11.9	8.9	3.0
Total	**827.7**	**86.0**	**200.3**	**11.8**	**188.5**	**121.0**	**67.5**	**11.9**	**79.4**	**8.9**	**70.5**

Table B50. Case A1.2b Methane Coupling Process Material Balance

Mlb/hr for a process producing 1,000MMppy of Ethylene

Component	1	2	3	4	5	6	7	8	9	10
H_2			3.9	1.9		1.9		4.1		4.1
N_2	1.6	4.3	117.0	117.0		117.0		117.0		117.0
O_2		187.6	187.6			0.0				
CO			5.6	5.9		5.9		5.9		5.9
CO_2	0.7		0.7	27.8		27.8		27.8	27.8	
CH_4	228.1		1626.2	1464.8		1464.8		1466.6		1466.6
C_2H_4			2.8	94.9		94.9		124.3		124.3
C_2H_6	2.3		2.5	35.4		35.4		64.2		64.2
C_3H_6				6.9		6.9		9.7		9.7
C_3H_8				2.8		2.8		2.9		2.9
C_4s +								1.8		1.8
H_2O				189.0	139.8	49.2	44.3	6.4	6.4	
Total	**232.7**	**191.9**	**1946.3**	**1946.4**	**139.8**	**1806.6**	**44.3**	**1830.7**	**34.2**	**1796.5**

Component	11	12	13	14	15	16	17	18	19	20	21
H_2	3.9	0.2							2.1		2.1
N_2	111.1	5.8									
O_2											
CO	5.6	0.3							0.1		0.1
CO_2											
CH_4	1398.1	68.4							1.9		1.9
C_2H_4	2.8		121.5		121.5	121.0	0.5		29.5		29.5
C_2H_6	0.2		64.0	0.1	63.9	0.1	63.8		28.8		28.8
C_3H_6			9.7	7.5	2.2		2.2		2.8		2.8
C_3H_8			2.9	2.4	0.5		0.5		0.1		0.1
C_4s +			1.8	1.8					1.8		1.8
H_2O								11.8	11.8	8.9	2.9
Total	**1521.7**	**74.7**	**199.9**	**11.8**	**188.1**	**121.1**	**67.0**	**11.8**	**78.9**	**8.9**	**70.0**

Appendix C. FIGURES

Figure C1. BaCO3/Al2O3, 33-BKW-1

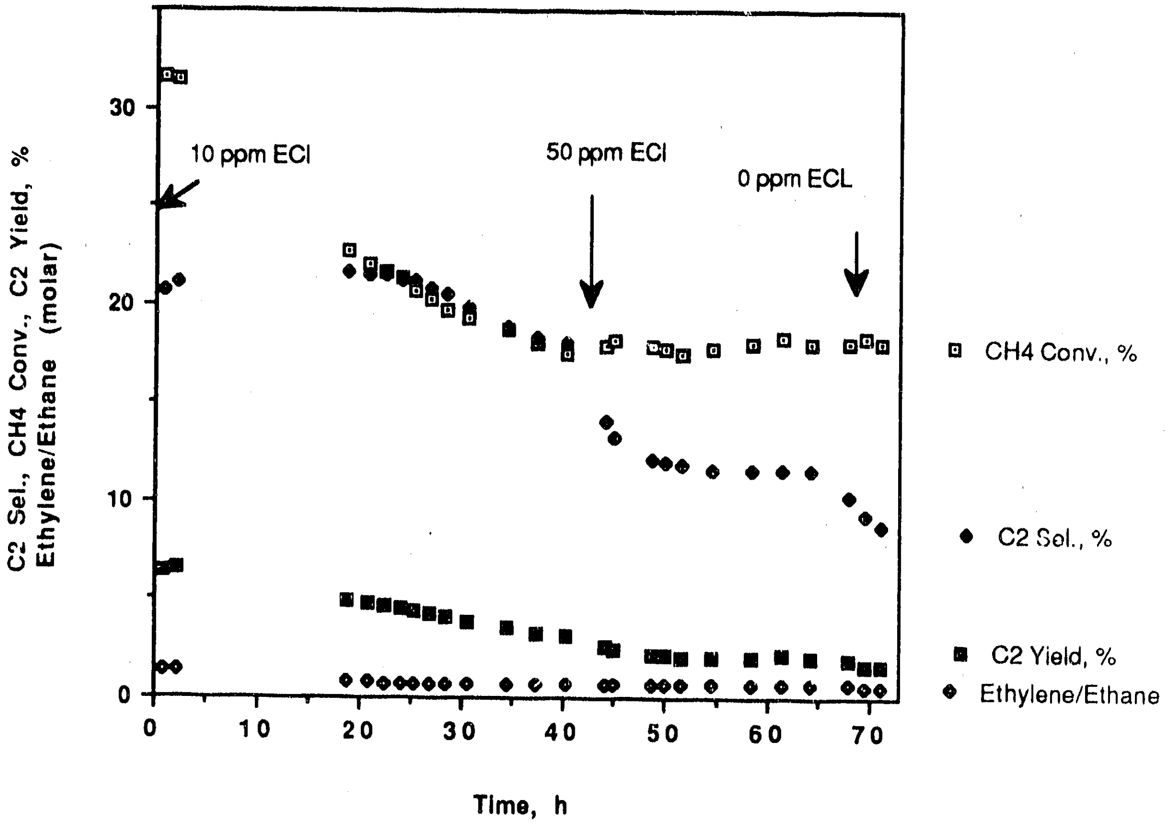

Figure C2. 33-BKW-2

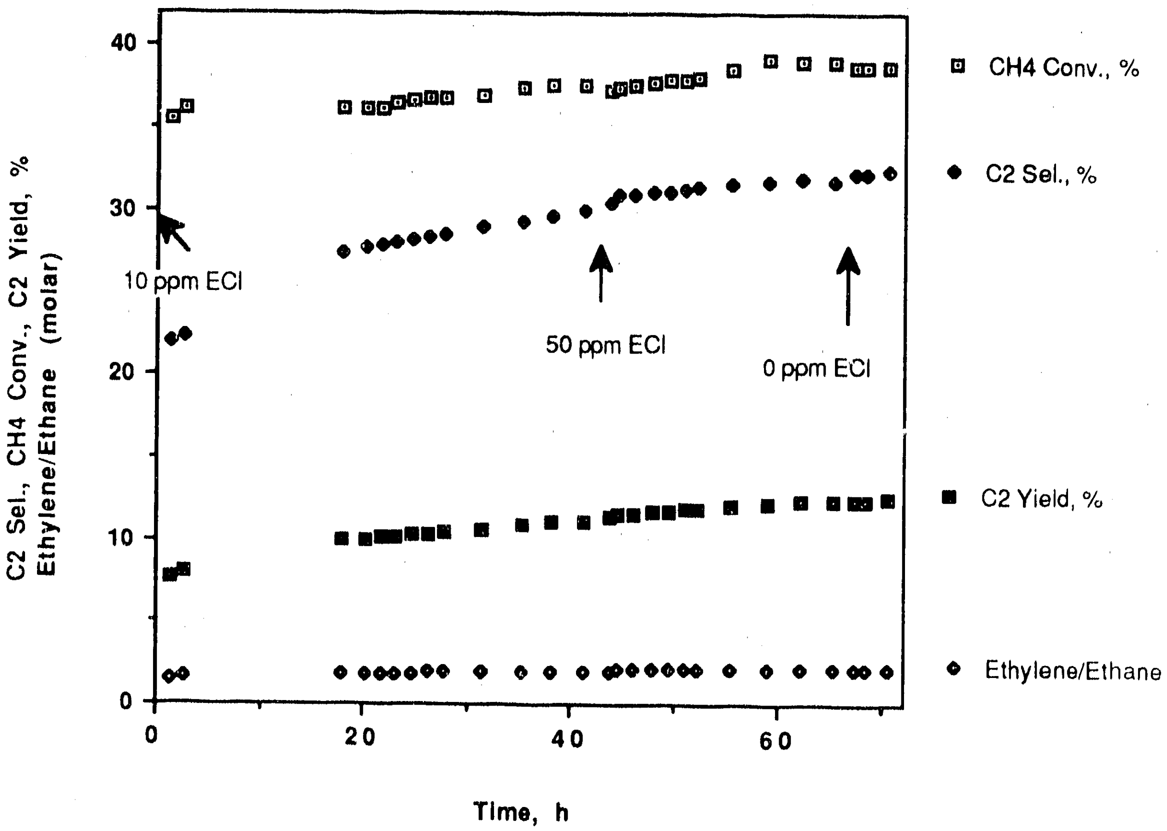

Figure C3. BaCO3/Al2O3, 33-BKW-7

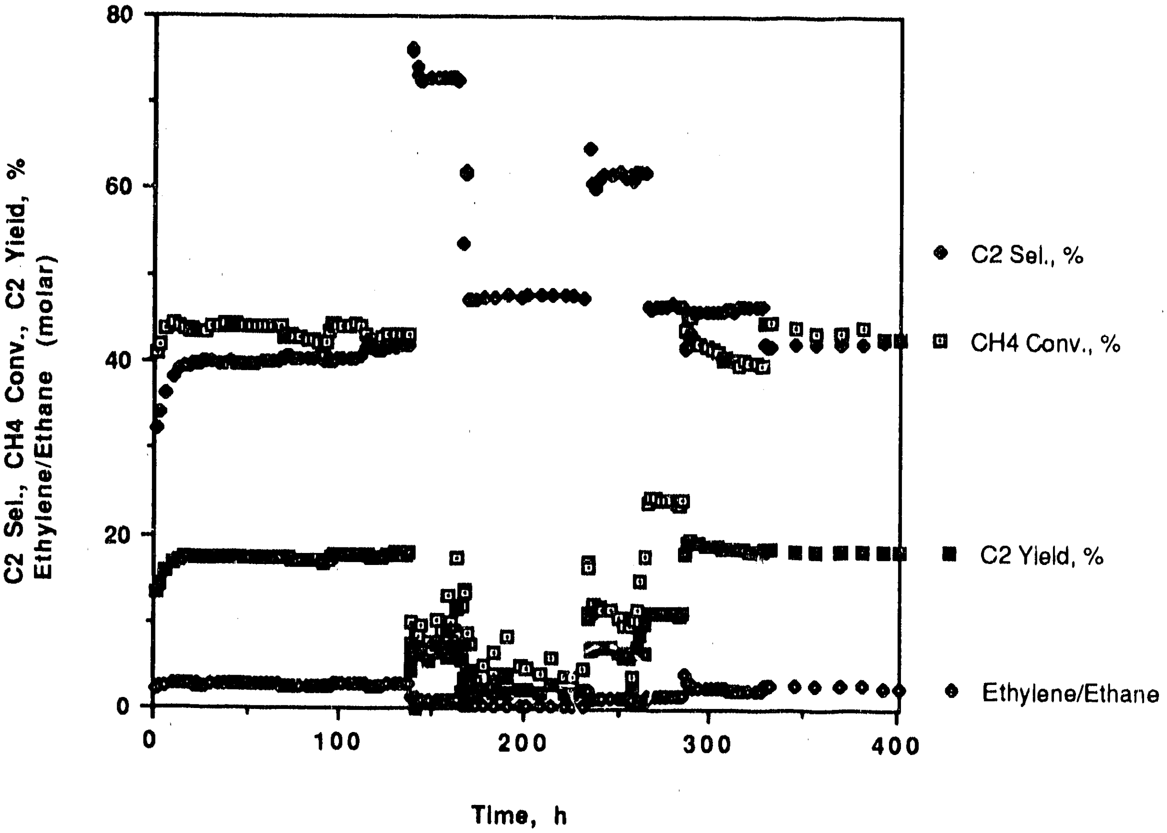

Figure C4

Methane Coupling Process Simplified Block Diagram

Absorber / Stripper Case

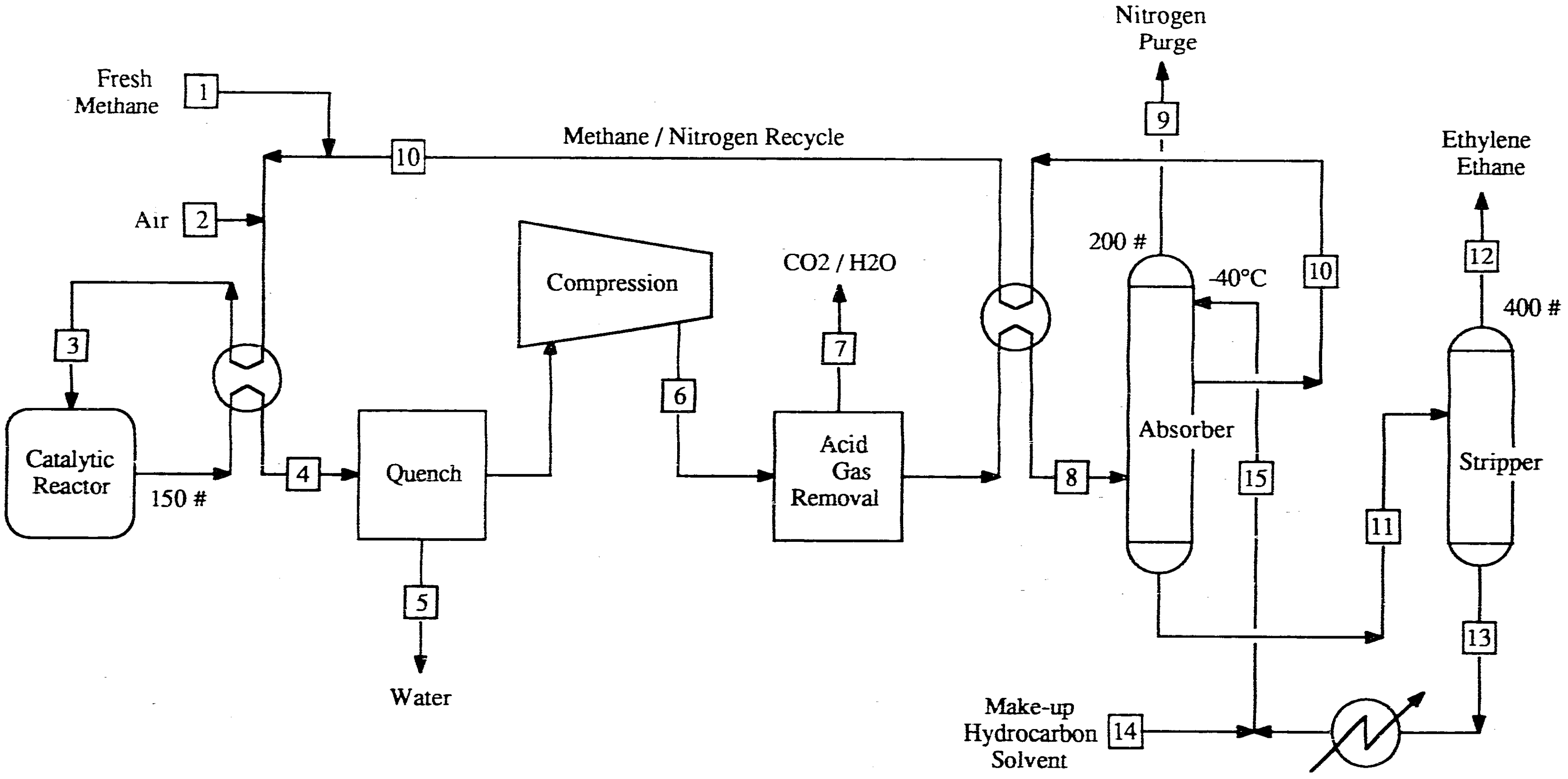

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Figure C5

Methane Coupling Process Simplified Block Diagram

High Ethylene / Ethane Production Ratio

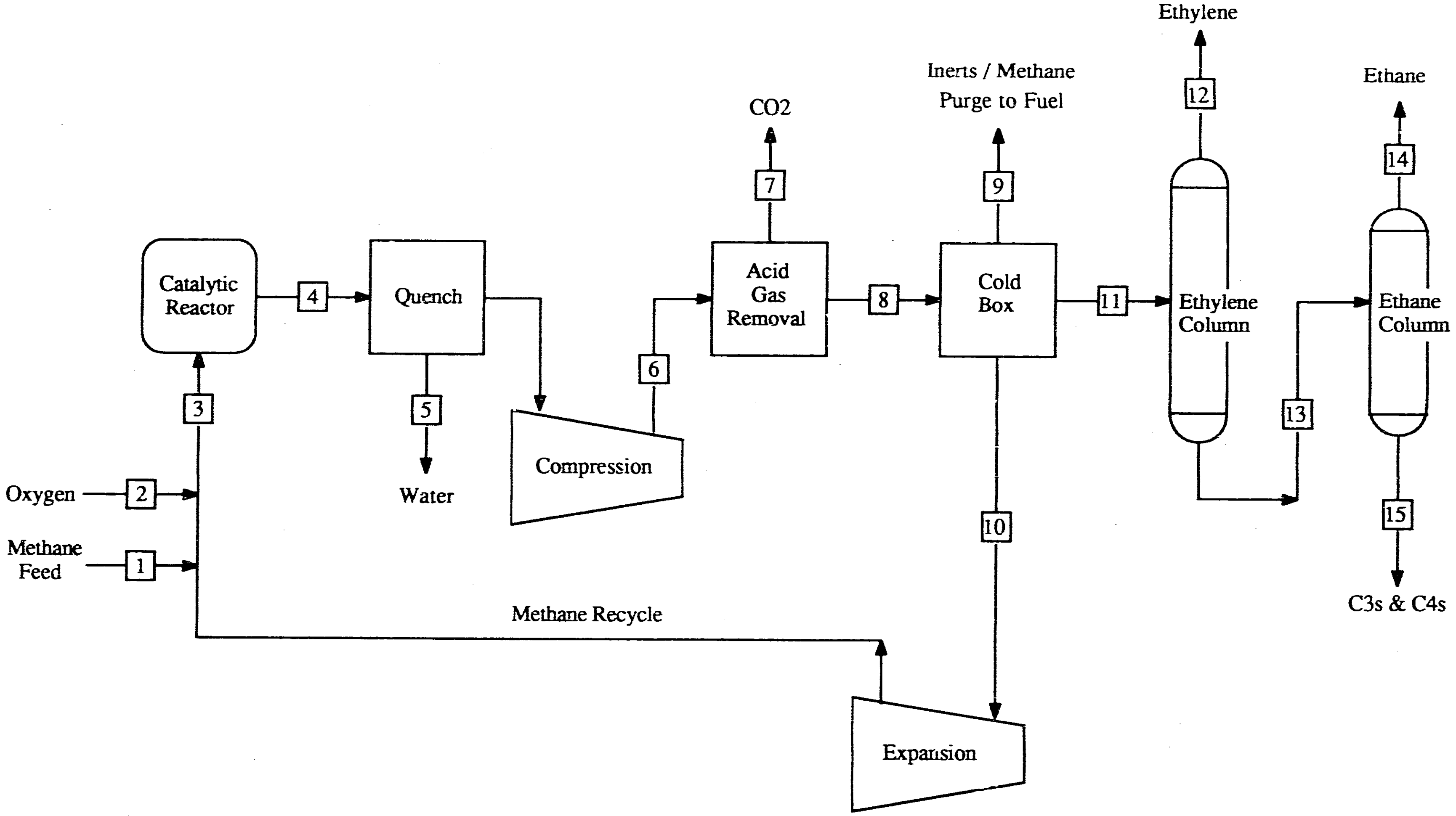

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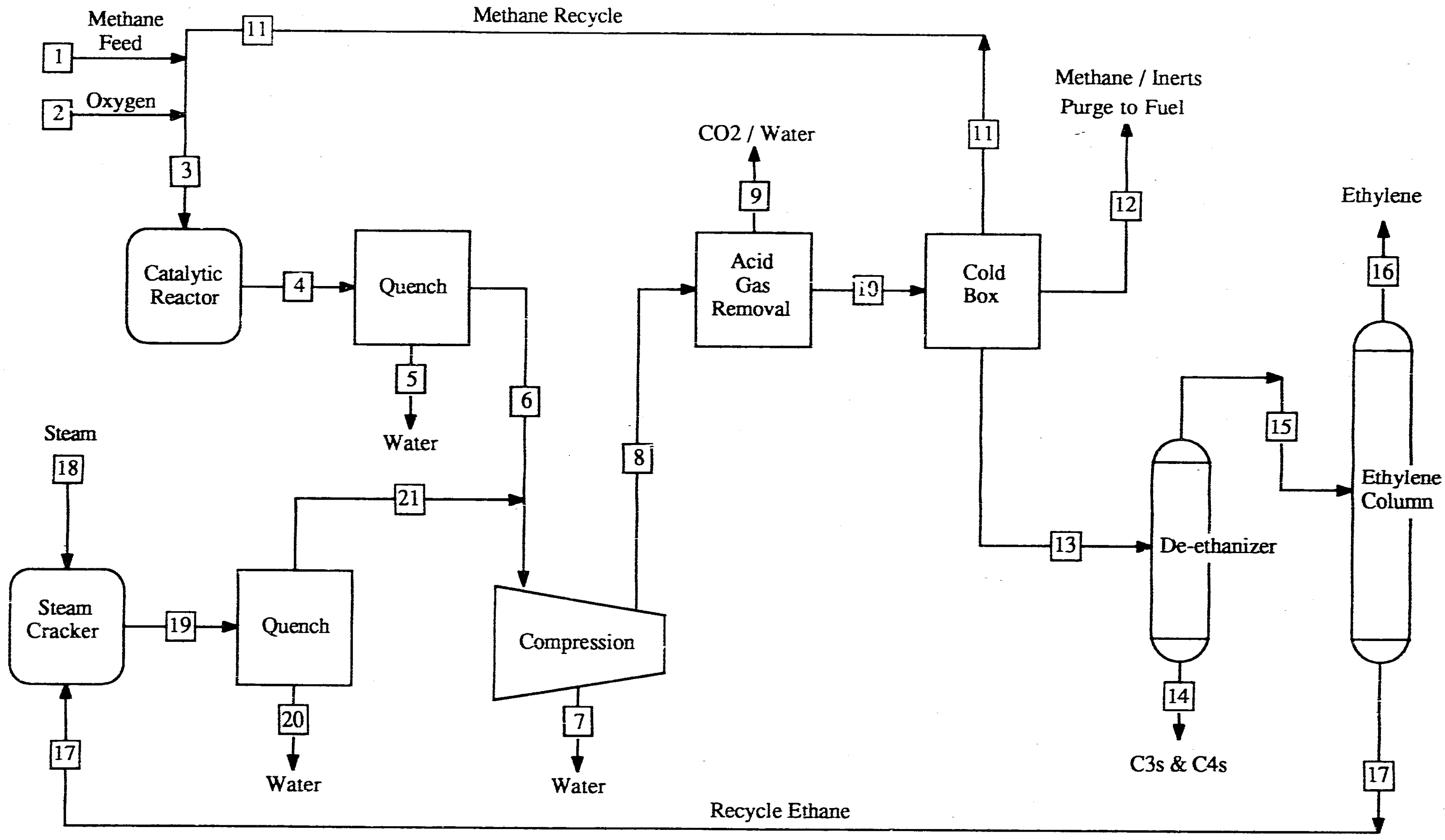
Figure C6

Case A1.2 Methane Coupling Process

Simplified Block Diagram



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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	Preparation Procedure	g Support or * g Cat.
32-BKW-120(R#4)	32-BKW-110(R#3) -- used catalyst						12/30/88			
32-BKW-122(R#3)	BaBr2.2H2O / Al2O3,Norton SA5451 (850 °C, 2hrs)	7.933	0.000254	1.09	60/100	32-BKW-118A	1/3/89	3.49	A	6
32-BKW-123(R#4)	gamma Al2O3, Norton SA6573	99.99		0.56	60/100		1/3/89			
32-BKW-128(R#3)	BaCO3 / ZrO2 (850 °C, 2hrs)	4.77	0.000254	2.63	60/100	32-BKW-118B	1/6/89	3.49	B	6
32-BKW-129(R#4)	BaCO3/gamma Al2O3,Norton SA6573 (850 °C, 2hrs	4.77	0.000254	0.63	60/100	32-BKW-118C	1/6/89	3.49	B	6
32-BKW-134(R#3)	Li2CO3 / MgO (600 °C, 12 hrs)	11.47	0.00175	0.5	30/60	32-BKW-132B	1/16/89	2.44	B#2(*)	(* 2.25 g of 32-BKW-132A)
32-BKW-135(R#4)	Li2CO3 / MgO (850 °C, 2 hrs)	11.47	0.00175	1	30/60	32-BKW-132C	1/16/89	2.44	B#2(*)	(* 2.25 g of 32-BKW-132A)
33-BKW-1(R#3)	BaCO3 / Al2O3, Norton SA5402 (600 °C, 16 hrs)	4.76	0.000254	1.14	60/100	32-BKW-132F(#1)	1/24/89	3.49	B#2(*)	(* 10 g of 32-BKW-132D)
33-BKW-2(R#4)	BaCO3 / Al2O3, Norton SA5402 (600 °C, 16 hrs)	29.87	0.00216	1.19	60/100	32-BKW-132G(#2)	1/24/89	29.65	B#2(*)	(* 10 g of 32-BKW-132E)
33-BKW-6(R#3)	BaCO3/Al2O3, SA5451 (600°C,14; 850°C,4)	4.76	0.000254	1.14	60/100	33-BKW-3A	1/27/89	3.49	B#2	6
33-BKW-7(R#4)	BaCO3/Al2O3, SA5451 (600°C,14; 850°C,4)	29.87	0.00216	1.11	60/100	33-BKW-3B	1/27/89	29.65	B#2	6
33-BKW-33(R#3)	MgAlOH hydrotalcite, 16341-93B-WTR (850 °C, 4)	100		0.366	60/100	33-BKW-15C	2/20/89		R	
33-BKW-34(R#4)	MgAlOH hydrotalcite, 16341-95B-WTR (850 °C, 4)	100		0.366	60/100	33-BKW-15D	2/20/89		R	
33-BKW-38(R#3)	BaF2 / Al2O3, Norton SA5451 (850 °C, 2 hrs)	4.26	0.000254	1.11	60/100	33-BKW-37A	2/23/89	3.49	A	6
33-BKW-39(R#4)	MgAlOH hydrotalcite, 16341-94B-WTR (850 °C, 4)	100		0.366	60/100	33-BKW-15E	2/23/89		R	
33-BKW-42(R#3)	BaCO3 / MgAlOH hydrotalcite, 93B (850 °C, 4 hrs)	4.76	0.000254	0.375	60/100	33-BKW-37B	2/28/89	3.49	R, B	3
33-BKW-43(R#4)	BaCO3 / MgAlOH hydrotalcite, 94B (850 °C, 4 hrs)	4.76	0.000254	0.375	60/100	33-BKW-37C	2/28/89	3.49	R, B	3
33-BKW-48(R#3)	BaCO3 / MgAlOH hydrotalcite, 95B (850 °C, 4 hrs)	4.76	0.000254	0.375	60/100	33-BKW-47A	3/3/89	3.49	R, B	3
33-BKW-49(R#4)	Ba(NO3)2 / Al2O3, Norton SA5451 (850 °C, 4 hrs)	6.22	0.000254	1.11	60/100	33-BKW-47B	3/3/89	3.49	B	6
33-BKW-54(R#3)	BaCl2 / Al2O3, SN:8855001 (850 °C, 2 hrs)	5.02	0.000254	1.22	18/60	33-BKW-51A	3/9/89	3.49	A	6
33-BKW-55(R#4)	BaCl2 / Al2O3, SN:8855011 (850 °C, 2 hrs)	5.02	0.000254	1.02	14/70	33-BKW-51D	3/9/89	3.49	A	6
33-BKW-62(R#3)	BaCl2 / Al2O3, SN:8855002 (850 °C, 2 hrs)	5.02	0.000254	0.98	18/60	33-BKW-51B	3/14/89	3.49	A	6
33-BKW-63(R#4)	BaCl2 / Al2O3, SN:8855003 (850 °C, 2 hrs)	5.02	0.000254	1.11	14/50	33-BKW-51C	3/14/89	3.49	A	6
33-BKW-66(R#3)	32-BKW-122(R#3) -- Used catalyst						3/17/89			
33-BKW-67(R#4)	BaCO3 / Al2O3, Norton SA5451 (850 °C, 4 hrs)	4.77	0.000254	1.16	60/100	33-BKW-64A(#1)	3/17/89	3.49	B(*)	(* 6 g of 33-BKW-64A)
33-BKW-74(R#3)	BaCO3 / Al2O3, Norton SA5451 (850 °C, 4 hrs)	4.77	0.000254	1.16	60/100	33-BKW-64A(#2)	3/22/89	3.49	B(*)	(* 6 g of 33-BKW-64A)
33-BKW-75(R#4)	BaCO3 (850 °C, 2 hrs)	99.997		1.16	40/100	33-BKW-15B	3/22/89		P	

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.

F.) Listed below are catalyst preparations referred to in the last column.

	Li2CO3 / MgO (B. Bartley, 3/16 pellets)	11.47	0.00175		30/60	32-BKW-132A		2.44	B#2	5
	BaCO3 / Al2O3, Norton SA5402	4.76	0.000254		30/100	32-BKW-132D		3.49	B#2	12
	BaCO3 / Al2O3, Norton SA5402	29.87	0.00216		30/100	32-BKW-132E		29.65	B#2	12
	BaCO3 / Al2O3, Norton SA5451	4.77	0.000254		60/100	33-BKW-64A		3.49	B	15

Appendix E. Catalyst Preparation Procedures

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). Most dried catalysts are tested without further treatment. Several were first calcined in air . In most cases, these are marked in Appendix D as procedure A(*). These were prepared in 15 gram batches prior to calcining, and 5.3 to 6 grams of material was calcined, as indicated in Appendix D. Metal or inorganic compound loadings are expressed as weight percent based on 100 weight percent of the support.

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#2 is the same as Procedure B except 100 mL of deionized, distilled water were used.

Procedure P

Compound was stirred as a slurry and heated in water. The paste was dried in a vacuum oven at 130 °C under a vacuum of 16-84 kPa. The solid was then heated at 850 °C for 2 hours, prior to being chopped and sieved to 40/100 mesh.

Procedure R

Hydrotalcites ($Mg_6Al_2(OH)_{16}(CO_3^{=})$•~$4H_2O$) were prepared by W. T. Reichle of the Specialty Chemicals Division of Union Carbide, at the Bound Brook, New Jersey Laboratory. The Mg/Al ratio of the bulk compounds is approximately 3. The surface composition of the hydrotalcites by ESCA for samples 16341-93A, 16341-94A, and 16341-95A by atomic percent are shown.

Sample	C	O	Mg	Al	Cl	Si	Na	Mg/Al
16341-93A	15	51	27	4.8	0.4	0.3	0.3	6.4
16341-94A	21	50	24	4.4	0.2	0.5	0.1	6.2
16341-95A	15.6	51.4	27.2	5.4	0.1	0.1	0.2	5.7

These samples were heated at 450 °C for 18 hours in air, then either heated at 850 °C for 4 hours in air (33-BKW-33, 34, and 39), or loped with barium carbonate using procedure B, then heated at 850 °C for 4 hours in air (33-BKW-42, 43, and 48).

Sources of Materials

Alpha-alumina supports were obtained from Norton, unless otherwise specified. Sample numbers are shown in tables, designating the type of alpha-alumina support. Alkaline earth salts and others salts, unless specified, were obtained from Johnson Matthey or AESAR, and are greater than 99.99% pure, unless specified. Metal oxides, unless specified, are also obtained from Johnson Matthey or AESAR, and are greater than 99.99% pure.

See Appendix E of the Fourth[20] and Fifth[4] Quarterly Reports for sources of most materials. Zirconium oxide, ZrO2, was obtained from Johnson Matthey, and was 99.9975% pure. MgO used in 32-BKW-134 and 135 was 3/16" pellets from Davison Chemicals.

Gamma-alumina used in 32-BKW-123 and 129 was SA6573, from Norton Co. The α-alumina samples used in 33-BKW-55 (SN:8855001), 33-BKW-55 (SN:8855011), 33-BKW-62 (SN:8855002), and 33-BKW-63 (SN:8855003) were obtained from Norton Co.

END

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