DIRECT CONVERSION OF METHANE TO C_2 's AND LIQUID FUELS

Chemistry

DOE Contract No. DE-AC22-87PC79817

September 17, 1987 - December 31, 1989

by

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Presented at the U. S. D. O. E.'s
Indirect Liquefaction Contractors' Review Meeting
November 15, 1989
by B. K. Warren

Date: November 20, 1989

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Contract Number: DE-AC22-87PC79817

Period of Performance: September 17, 1987 to December 31, 1989

Objective: The objective of this program is to discover and evaluate novel catalytic systems for the conversion of methane or byproduct light hydrocarbon gases through intermediate light gases rich in C_2's to liquid hydrocarbon fuels.

Technical Approach: Conversion of methane to ethylene in an efficient economical process would represent important technology for the future. Ethylene could be oligomerized to liquid hydrocarbon fuels, or converted to commodity and specialty chemicals. The approach for the chemistry part of this program has been to test several specific classes of potential catalysts for the conversion of methane selectively to C_2 products rich in ethylene. The conversion of C_2's to fuels was to be evaluated with a hypothetical stream from a methane to ethylene process, and by coupling the methane to ethylene reaction with the oligomerization step, using little or no separations.

Significant Accomplishments: Union Carbide is interested in developing novel, competitive technology for the conversion of methane to C_2's rich in ethylene. Three unique catalyst systems have been provided which appear to operate by the heterogeneous/homogeneous mechanism, where product distributions are largely dictated by the gas phase chemistry and process conditions. One type of catalyst gives very high ethylene to ethane ratios, and one catalyst appears to be significantly more stable than reported literature catalysts. The third catalyst type, a layered perovskite, exhibits a unique structure and shows performance competitive with literature catalysts. Process studies on the high ethylene to ethane catalysts have included pressure studies and the study of the effect of steam as diluent. Three other catalyst systems were designed in an attempt to change the heterogeneous/homogeneous methane coupling mechanism which is predicted to have a yield barrier. Metals known to activate methane unselectively (i.e., burn methane) at low temperatures were added to good methane coupling catalysts and provide catalysts which exhibit enhanced surface reactions and give yields of 20% to C_2's at lower temperatures. Catalysts which altered the gas phase chemistry were found to result in increased selectivities to C_2's by reduction of the formation of carbon oxides. The results of experiments integrating methane coupling and olefin oligomerization reactions to produce liquid hydrocarbons will be reviewed.

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OBJECTIVE:

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.

Technology exists for converting methane to liquid fuels,

$$CH_4 \longrightarrow CO/H_2 \longrightarrow CH_3OH \longrightarrow C_2H_4 \longrightarrow \text{GASOLINE / DISTILLATES},$$

where C_2H_4 indicates light hydrocarbon gases rich in ethylene. Union Carbide economic studies indicate that 75% of the cost of conversion of methane to fuels via commercial technology is in the conversion of methane through synthesis gas to methanol. The conversion of methanol to light olefins and the oligomerization of these olefins to liquid fuels with Mobil's Olefins to Gasoline and Distillate (MOGD) process[3] are a small portion of the investment and operating costs for this technology. Economic studies also indicate that a process to convert methane to fuels by direct oxidation of methane to light hydrocarbon gases rich in ethylene could be economically superior to the synthesis gas route in the near future (5-10 years). The economics of the conversion of methane to ethylene and/or liquid hydrocarbon fuels become more attractive for commercialization as the difference in costs of methane and higher hydrocarbons, currently used to produce ethylene or liquid fuels, becomes greater. This project proposes to invent the technology necessary to avoid the reforming step which is required in existing technology to convert methane to liquid fuels because it is capital intensive.

The objective of this program is to prepare and evaluate novel catalyst systems to convert methane to a mixture of hydrocarbons rich in ethylene. This step is the technological hurdle in a two-step process to convert methane or natural gas to liquid hydrocarbon fuels, including gasoline and distillates. Union Carbide predicts that in the future, this process will be more practical and economical than a single step process or other alternatives. The chemistry portion of this work is presented here, and the process economics are provided in a separate presentation.

TECHNICAL APPROACH:

Union Carbide's approach to accomplish the objectives of Task 1, the discovery of catalytic systems for converting methane to liquid fuels, has been to test several specific classes of potential catalysts for the conversion of methane selectively to C_2 products rich in ethylene. This approach concentrates on the technological hurdle in the conversion of methane to liquid fuels, the conversion of methane to light hydrocarbon gases, primarily ethane and ethylene. The integration of the conversion of methane to C_2's with the conversion of C_2's to fuels, with little or no separation between steps, was briefly explored.

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. Reported catalyst systems were predominantly variations on Li/MgO, the Mn-based ARCO catalyst, or lanthanide oxide systems. Catalysts which might provide high ethylene to ethane ratios were of particular interest. Studies began with exploration of a very simple NaCl on α-alumina catalyst discovered, but not reported, by Union Carbide's G. E. Keller and M. M. Bhasin in the late 1960's. They explored this catalyst only in a pulsed, rather than a continuous mode. Specific ideas were to be explored by the examination of several types of catalyst systems. Plans were then to design catalyst systems to alter the currently accepted heterogeneous/homogeneous mechanism for methane oxidation through several specific approaches. The cooxidation mode was preferred for all studies, although both cooxidation and sequential modes were explored.

Methane can be converted to C_2's by a two-step process in which methane is reacted with a metal oxide to produce C_2's, then the reduced metal oxide is reoxidized[4-6] with air. Methane can also be converted to C_2's in a cofeed mode, where methane and oxygen, with or without a diluent, are fed simultaneously[7,8] to a reactor containing catalyst. Active sites on the catalyst are continuously regenerated by the oxygen present in this mode. In both cases, the major inefficiencies are the formation of CO and CO_2. Smaller amounts of C_3's, C_4's, and higher hydrocarbons are formed, and in some cases traces of acetylene and hydrogen are observed. In the cofeed mode, hydrocarbons higher than C_4 are rare. Reactions are usually conducted at temperatures in the 700-950 °C range and operated at low pressures (5-50 psig), in fixed bed or fluidized bed reactors. Quartz and alumina[9-11] materials have been used for reactors. Stainless steel and alonized stainless steel[12] are suitable at lower pressures and temperatures. Oxygen concentration is limited to about 10 mole percent in any stream to avoid operation within the explosive limits.

Direct conversion of methane to C_2's is an increasingly active area of research internationally[13], industrially[14], academically[15], and in government laboratories[16]. Although several different mechanisms have been proposed for the catalytic oxidative coupling of methane, Lunsford and coworkers[17-20] have elegantly and convincingly demonstrated, and others[21-25] have agreed that the mechanism for conversion of methane to ethane and ethylene over the metal oxides studied (and probably over other selective methane coupling catalysts) 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. Ethane is then converted to ethylene through known gas phase free radical chemistry. This is shown in Figure 1.

Figure 1. Methane to Ethylene Current Technology

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

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

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

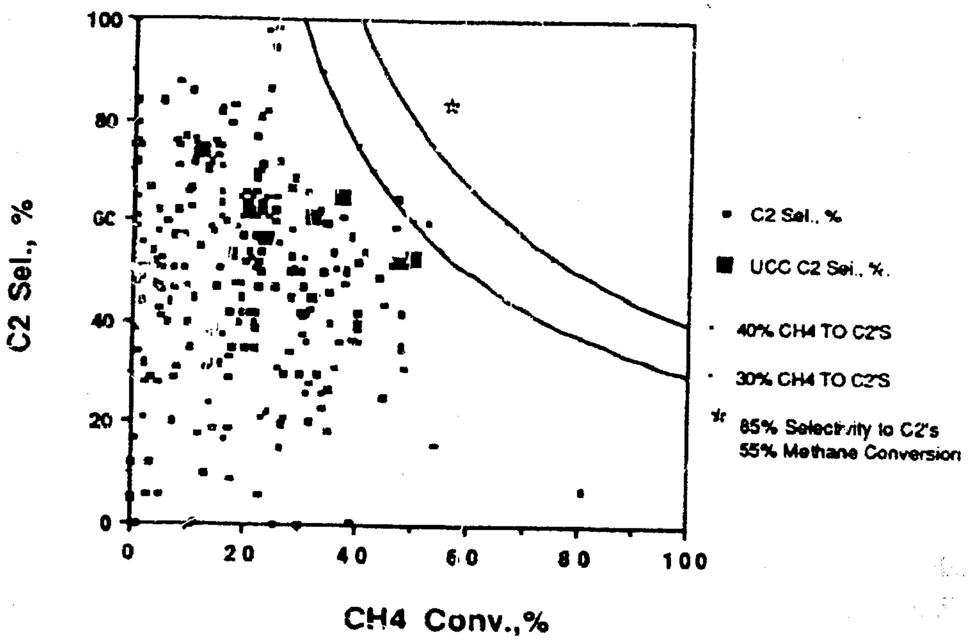
$$C_2H_6 \longrightarrow C_2H_4$$

This mechanism shows that much of the product distribution is dictated by gas phase chemistry, largely independent of catalyst, but dependent on the temperature and operating conditions. With this mechanism, one might at best approach C_2 yields above 50% if one reported model (J. Kimble and J. Kolts) of the mechanism are correct. Others (J. Labinger and J. McCarty) have proposed a yield barrier closer to 30%. Practically, literature results above a 30% yield to C_2's are very rare.

SIGNIFICANT ACCOMPLISHMENTS.

During the past two years, UCC has developed continuous, unattended operation capabilities and now has seven reactors operable and engaged in the study of methane coupling[26,27]. One of these reactors is capable of operating in the pulsed, sequential reaction mode. Union Carbide researchers have evaluated many classes of methane oxidation catalysts. Selectivity/conversion combinations per pass over several different types of catalysts, operated in both the cooxidation and sequential modes, provide results which are comparable to better literature results[28-32]. C_2 yields of 20-26% have been demonstrated. Figure 2 shows literature and Union Carbide results for methane coupling. The two lines are 30% and 40% yields to C_2's. The star represents 85% selectivity and 55% methane conversion, which might currently be economically competitive with existing technology for ethane/propane cracking in Texas.

Figure 2. Literature and Union Carbide Results for Methane Coupling



Almost all of the reported literature catalysts rapidly deactivate. A few metal oxide catalysts which are less volatile (e.g., Sm_2O_3) undergo phase changes resulting in deactivation. Most frequently, catalysts lose critical components due to volatilization at the high temperatures used for methane oxidation. Catalysts containing alkali metals lose the metal salts, e.g., the lithium is lost from the Li/MgO catalyst. As an example, a Li/MgO catalyst which contained less than 3% Li, and which had been roasted at >800 °C for 4 hours prior to exposure to methane and oxygen, exhibited a 12% loss in the rate to C_2's over 50 hours, presumably due to loss of Li. Often, initial results from literature catalysts indicate transient high selectivities to and/or yields of C_2's.

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[33], but this yield is considered low, since there are many literature yields in the 18% yield range. Union Carbide studied the causes for catalyst deactivation with several catalysts and designed new catalyst systems which did not deactivate for as long as 400 hours of operation (until tests were discontinued). C_2 yields of 18-20% could be obtained for the duration of the long catalyst tests, with product distributions containing ethylene to ethane ratios of 2.5-10.

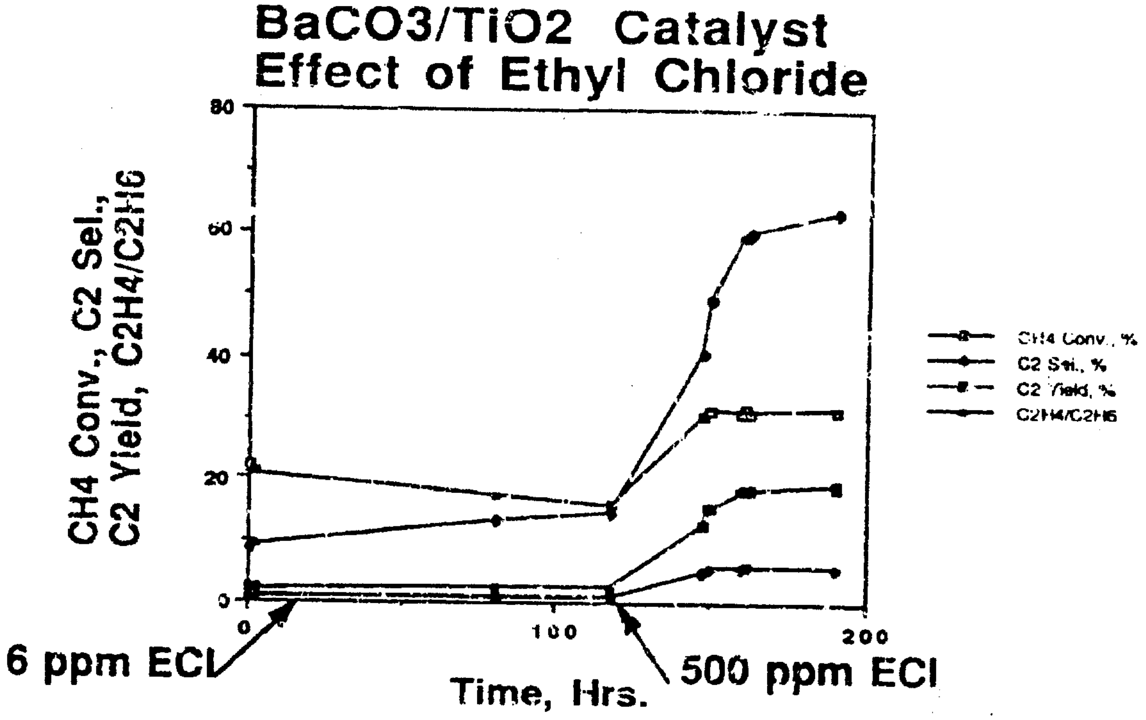
The sodium chloride/α-alumina catalysts discovered by Keller and Bhasin were run in the cooxidation mode, rather than a pulsed mode. They were competitive with literature catalysts in methane conversion and C_2 selectivity, but showed product distributions containing ethylene to ethane ratios of over 2.5, rather than the ethylene to ethane ratios of about 1 which were typical for literature catalysts. These catalysts were observed to deactivate rapidly under cooxidation conditions. It was first thought that this might be due to the loss of chloride, so a volatile chloride, ethyl chloride (ECl) was fed to partially deactivated catalysts, and selectivity and activity to C_2 products from the oxidation of methane rose, as did the ethylene to ethane ratio, although neither rose to initial levels. Even with ethyl chloride in the feed gas, catalyst deactivation occurs, and analysis of new and used catalysts reveals loss of most of the sodium. Methane coupling over sodium chloride based catalysts indicates that redox metals are not needed for this reaction, and it reasonable to assume that an oxide of sodium may abstract hydrogen from methane in the rate determining step of this reaction[34].

Other catalysts with alkali chlorides on alumina were also found to deactivate due to loss of alkali. Alkaline earth salts are less volatile, and oxides derived from alkaline earth compounds were considered good candidates for methane coupling catalysts. Catalysts with alkaline earth chlorides on alumina were tested and found to retain the alkaline earth metals, but the ethylene to ethane ratios, which were initially very high, dropped, and catalysts deactivated without the addition of volatile chloride. With added chloride, selectivity and activity could be retained with alkaline earth chlorides, and although the ethylene to ethane ratio initially dropped, it could be maintained at levels above 2.

The best catalysts for high ethylene to ethane ratios, which exhibit C_2 selectivities and C_2 yields competitive with literature catalysts, were found to be catalysts which contain Ba or Sr, with chloride on the catalyst and/or in the feed gas, and a non-basic metal oxide combustion promoter. Combustion promoters are metal oxides which alone, with methane and oxygen under reaction conditions, burn methane, for example, oxides of Ti, Zr, Ga, or Al. Examples of these catalysts are $BaCl_2/TiO_2$/ethyl chloride and $BaCO_3$/α-alumina/ethyl chloride. The best supports are acidic. Without added chloride, these catalysts deactivate rapidly. More acidic supports require more chloride. Some basic supports result in combustion without added promoters. Even when these basic supports are promoted with Ba or Sr, the ratios of ethylene to ethane produced are not high

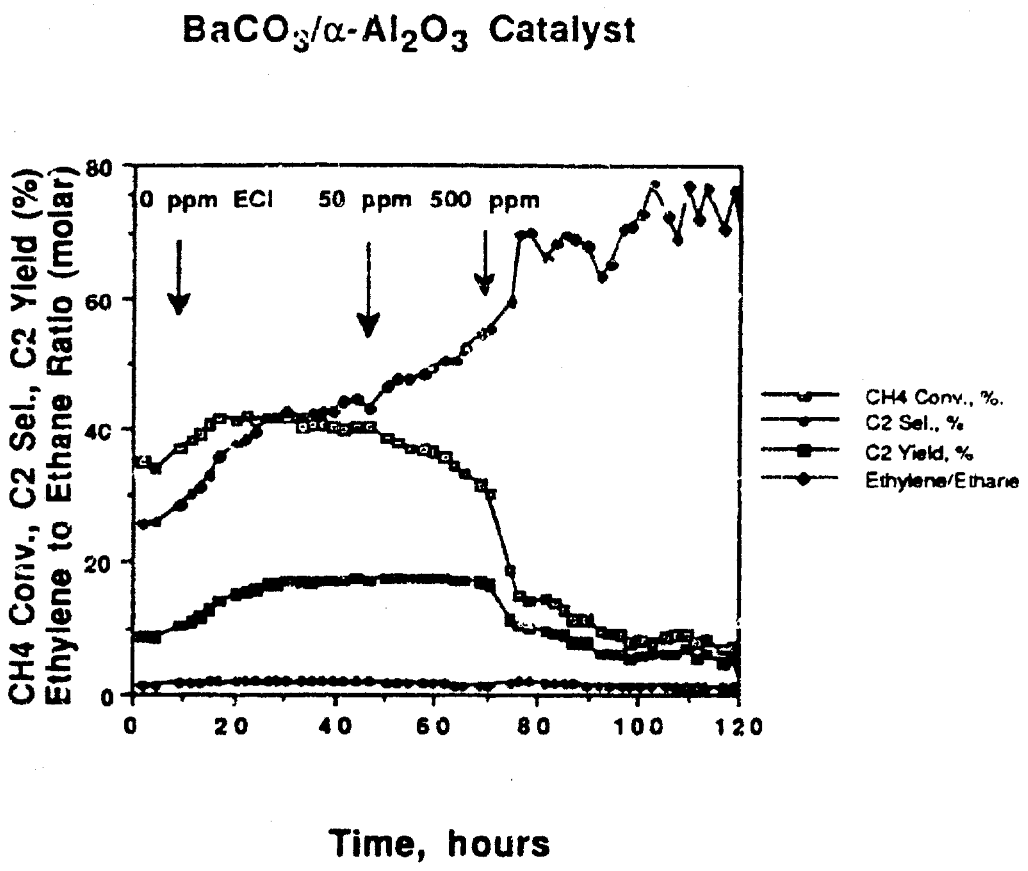
Ba or Sr catalysts with titanium dioxide combustion promoters require higher levels of ethyl chloride for high methane conversions and C_2 selectivities. This is illustrated in Figure 3, where a C_2 selectivity of 63%, methane conversion of 31%, and a C_2 yield of 19% are obtained with 500 ppm ethyl chloride in the gas feed using 5 g of a $BaCO_3/TiO_2$ catalyst at 750 °C, 11 psig, and a space velocity of 2743 hr^{-1}. With 6 ppm ethyl chloride, C_2 selectivities and yields are very low.

Figure 3. Metal Oxide Combustion Promoters



In contrast to this example, Figure 4 shows that after an initial catalyst activation period, the catalyst exhibits a C_2 yield of 17%, a C_2 selectivity of 44%, and a methane conversion of 40%, with 10 ppm of ethyl chloride initially in the gas feed, using 5 g of a $BaCO_3/\alpha\text{-}Al_2O_3$ catalyst, at 750 °C, 11 psig, and a space velocity of 2233 hr^{-1}. This catalyst requires lower levels of ethyl chloride. The higher level of ethyl chloride, which promotes higher selectivities and activities for the catalyst containing titanium oxide, causes catalyst deactivation with this catalyst.

Figure 4. Optimum Chloride Levels Depend on the Catalyst



Starting with the carbonate catalyst, which initially contains no chloride, Figure 4 shows lower selectivity to C_2's, lower methane conversion, and lower C_2 yields initially. The 10 ppm ECl fed from the beginning of the reaction increases the rate of methane activation and conversion to C_2 products. The chloride therefore appears to affect the catalyst. These data are consistent with chloride catalyzing the conversion of inactive catalyst sites to active sites. For instance, chloride can react with stable barium or strontium salts to produce less stable intermediates, which can then be converted to active sites for hydrogen abstraction by reaction with oxygen. In this same figure, the selectivity rises slowly over a period of time while the rate to C_2's remains constant. During this time, the rate to CO_2 is continuing to drop. This observation can be explained by chloride blocking CO_2 formation on the surface of the catalyst. The reduction of the rate to CO_2 occurs over a long period of time, indicating a slow catalyst change.

The type of support appears to be important to the initial and the final ethylene to ethane ratios. High ethylene to ethane ratios were not obtained with basic supports such as MgO or CaO under any conditions, as shown in Table 1. Addition of ethyl chloride to catalysts prepared using these basic supports does not appear to increase catalyst performance, rather performance drops in some cases with addition of volatile chloride. Activity, selectivity, and stability of catalysts on supports which are not significantly basic, e.g., Norton 5451 α-alumina, are higher in the presence of the right amount of added chloride than without added chloride after the catalyst has run for a period of time. Catalysts on more acidic supports, such as TiO_2 require higher levels of volatile chloride for stable performance and have higher ethylene to ethane ratios. Chloride catalysts on the acidic supports provide higher initial ethylene to ethane ratios, but deactivate more rapidly when less than optimum amounts of volatile chloride are added in the feed gas.

Table 1. High Ethylene to Ethane Catalysts

Support	Acidity µm/g	Acidity µm/m^2	ECl ppm	GHSV hr^{-1}	C_2H_4/C_2H_6
MgO	0.15	0.004	1-500	9796	1.6
Norton 5451 α-Alumina	0.31	1.03	200	2087	2.2
TiO_2	1.08	1.31	500	2743	10.2

Catalysts prepared using more acidic supports result in higher ethylene to ethane ratios. Chlorine radicals in the gas phase are responsible for higher ethylene to ethane ratios[35]. In control runs, addition of ethyl chloride to an uncatalyzed (homogeneous) reaction of methane and oxygen results in only a slight increase in methane conversion or shift in product distribution. This result indicates that chlorine radicals are produced on the acidic catalyst surface and released into the gas phase.

In summary:

- Higher ethylene to ethane ratios result from chlorine radicals in the gas phase.
- Higher activities (compared with no chloride) are consistent with the conversion by chloride of stable salts of Ba or Sr to active oxygen species.
- Higher selectivities can be explained by chloride blocking CO_2 formation on the surface of the catalyst.

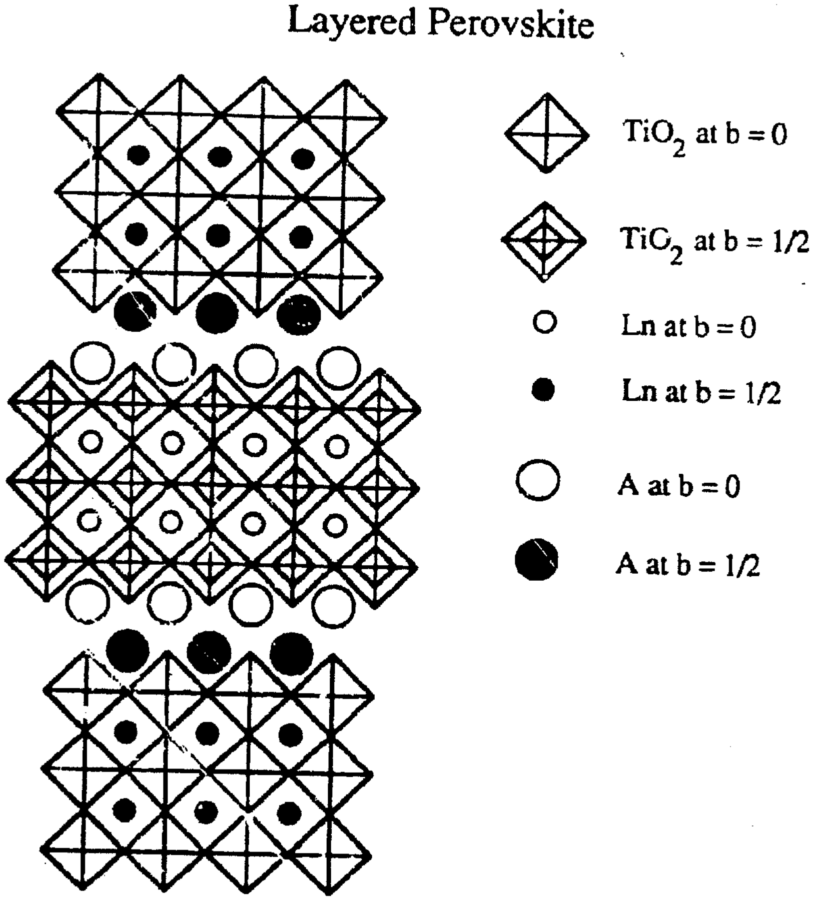
C_2 selectivity and methane conversion can be maintained for long periods of time over Ba and Sr catalysts. High selectivities and methane conversions have been demonstrated for over 400 hours. The optimum amount of a volatile chloride promoter must be used to obtain a stable rate to C_2's. This amount depends on the process conditions and the particular catalyst used. As described above, the amount depends on the type of metal oxide combustion promoter used. Catalyst stability is better, and higher C_2 selectivities and C_2 yields are obtained over long periods when catalysts are made with barium and strontium carbonates rather than the chlorides.

Process studies have been done to explore non-nitrogen diluents, and to study the effects of higher pressures on the reaction. The methane coupling reaction proceeds well with helium or argon as diluent. When running a methane oxidation over a barium catalyst with up to 15% steam substituted for either methane or inert gas diluent, little effect on catalyst activity or selectivity is observed. At steam levels greater than 25% of the feed gas, decreases in methane conversion and selectivity to C_2's are observed. At higher steam levels, initial increases in the ethylene to ethane ratio and activity are followed by catalyst deactivation. An increase in the pressure of the reaction from 11 to 16 psig results in a 4% increase in methane conversion and a 4% decrease in C_2 selectivity, with no change in C_2 yield using a barium catalyst under one set of reaction conditions. A C_2 yield of 21% with a C_2 selectivity of 57% was obtained at a pressures of about 20 psig. The increase in pressure has other effects. The rate of homogeneous reaction is increased and the catalytic and/or quenching effects of the reactor wall are more pronounced at otherwise constant conditions. Therefore, the high rate of the homogeneous reaction and the increased importance of wall effects under higher pressures using the cooxidation mode make it unlikely that studies of the catalyzed methane coupling reaction will provide meaningful results without significant engineering, reactor design, and materials science contributions.

Alkali doped lanthanide oxides have been reported to be very active catalysts for the oxidative coupling of methane. These materials are operated at high temperatures (usually 800 °C) and prepared using slurry or incipient wetness techniques. The high temperatures cause the loss of alkali components during reaction while the preparation methods result in catalysts in which the dispersion and location of the alkali components are not readily controlled. In order to alleviate some of these problems, layered perovskites containing layers of alkali ions dispersed and sandwiched between lanthanide perovskite layers were tested as methane coupling catalysts.

Layered perovskites of the form $A_2Ln_2Ti_3O_{10}$ (A=K,Rb; Ln=La,Nd,Sm,Gd,Dy) were first synthesized by J. Gopalakrishnan and V. Bhat[36]. These materials were prepared with the objective of forming Ruddlesden-Popper type layered oxides (with the 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. These materials are composed of three octahedra-thick perovskite slabs $[Ln_2Ti_3O_{10}]$ separated by alkali metal ions (shown below).

Figure 5. Structure of $A_2Ln_2Ti_3O_{10}$



In this structure the alkali and lanthanide species are in close contact with the lanthanide species in a perovskite environment. Potassium ions of $K_2Ln_2Ti_3O_{10}$ are easily exchanged with Na^+ or Li^+ by treating with molten alkali-metal nitrates.

Layered perovskites are prepared by grinding together appropriate mixtures (correct molar ratios of metals) of alkali carbonate, lanthanide oxide, and titanium dioxide and heating in air at 1000 °C for 8-12 hours. Mixtures are then reground and heated in air at 1000 °C for another 8-12 hours. Excess alkali carbonate (~20 mol%) is initially added to compensate for loss due to volatilization. More alkali is added after the first heating.

The layered perovskite $Na_2La_2Ti_3O_{10}$ is prepared by ion exchange of $K_2La_2Ti_3O_{10}$ in molten $NaNO_3$. Other layered perovskites prepared, including $K_2La_2Ti_3O_{10}$, $K_2Nd_2Ti_3O_{10}$, $K_2Sm_2Ti_3O_{10}$, $K_2Dy_2Ti_3O_{10}$, $K_2Gd_2Ti_3O_{10}$, $Rb_2La_2Ti_3O_{10}$, and $K_2Ce_2Ti_3O_{10}$, have powder x-ray diffraction patterns consistent with the structure of $K_2La_2Ti_3O_{10}$. Diffraction patterns were not obtained for $Na_2La_2Ti_3O_{10}$ or $K_2Pr_2Ti_3O_{10}$, which were also prepared.

These catalysts (1.0-4.0 g) were tested with flow rate of 50-200 ccm, a reactor pressure of 5 psig, and a $CH_4/O_2/N_2$ ratio of 2/1/3.8. The highest C_2 yield and selectivity to C_2's were obtained for $K_2La_2Ti_3O_2$, with a 39% methane conversion, a 42% selectivity to C_2's and a 16.4% C_2 yield, at 800 °C.

Layered perovskites of the form $A_2Ln_2Ti_3O_{10}$ represent a new type of methane coupling catalyst in which the alkali dopant is part of the crystal structure of the material. They give results comparable to many of the reported literature methane coupling catalysts.

The barium and strontium catalyst systems described above, as well as the layered perovskites, are thought to operate by the heterogeneous/homogeneous mechanism with creation of methyl radicals on the catalyst surface by hydrogen abstraction from methane, followed by release into the gas phase of the methyl radical, then coupling of two methyl radicals to form ethane. Since the product distribution for this mechanism is largely dictated by the gas phase chemistry, some models predict maximum yields of about 50% (Phillips presentation at the Los Angeles ACS meeting, 1988), and many predict yield barriers closer to 30% (Labinger and McCarty). In fact, although yields of up to 30% (transients) have been reported, yields of over 22% have not been reported under practical conditions.

Two approaches are suggested to avoid the heterogeneous/homogeneous mechanism in order to achieve higher C_2 selectivity/methane conversion combinations. One is to get away from the gas phase chemistry and make more of the reaction occur on the surface of the catalyst, at lower temperatures. The other is to change the gas phase chemistry to depart from the typical combustion reaction network.

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

In the Contractor's Review last year, results were described for a low temperature catalyst containing silver, barium chloride, and α-alumina (catalyst compositions were then coded). C_2 yields as high as 10% were obtained at 650 °C. Without the barium chloride, complete oxygen conversion occurs at temperatures of 300-500 °C, with methane converted only to carbon oxides. The exploration of other catalysts with metals which activate methane at low temperatures has continued with the Group VIII metals, using Sr. Results are shown in Table 2.

Table 2. Low Temperature Catalysts

Catalyst*	CH_4 Conv. %	C_2 Sel. %	C_2 Yield %
Ag/ $BaCl_2$/ α-alumina (1/0.32/21)	32	32	10
$SrCl_2$/ α-alumina (1/50)	7.5	61	4.6
Pd/ $SrCl_2$/ α-alumina (1/25/300)	18	30	5.4
Co/ $SrCl_2$/ α-alumina (1/9/204)	24	66	16
Ni/ $SrCl_2$/ α-alumina (1/9/200)	19	70	13
Fe/ $SrCl_2$/ α-alumina (1/9/206)	5.1	5.3	0.3
Cu/ $SrCl_2$/ α-alumina (1/14/323)	3.7	0.2	0
Rh/ $SrCl_2$/ α-alumina (1/17/198)	36	51	18
Co/ α-alumina (1/225)	19	0.4	0.1

Reaction conditions: $CH_4/O_2/N_2$ = 2.0-2.2/1/18-20; GHSV = 600-1700 hr^{-1}; 650 °C.

* Molar ratio of metals given in parentheses.

Unusually high C_3 selectivities are obtained with Pt/$SrCl_2$/α-alumina, Ag/$BaCl_2$/α-alumina, and Pd/$SrCl_2$/α-alumina catalysts under certain conditions (C_2/C_3 ratios are normally around 15-20). Also, the C_3 products in these cases were all propane instead of propylene, which is usually observed for oxidative methane coupling catalysts. The propylene has been proposed to result from methyl radical reaction with ethylene in the gas phase for typical methane coupling catalysts. These results demonstrate the principle of enhanced surface reaction during methane coupling.

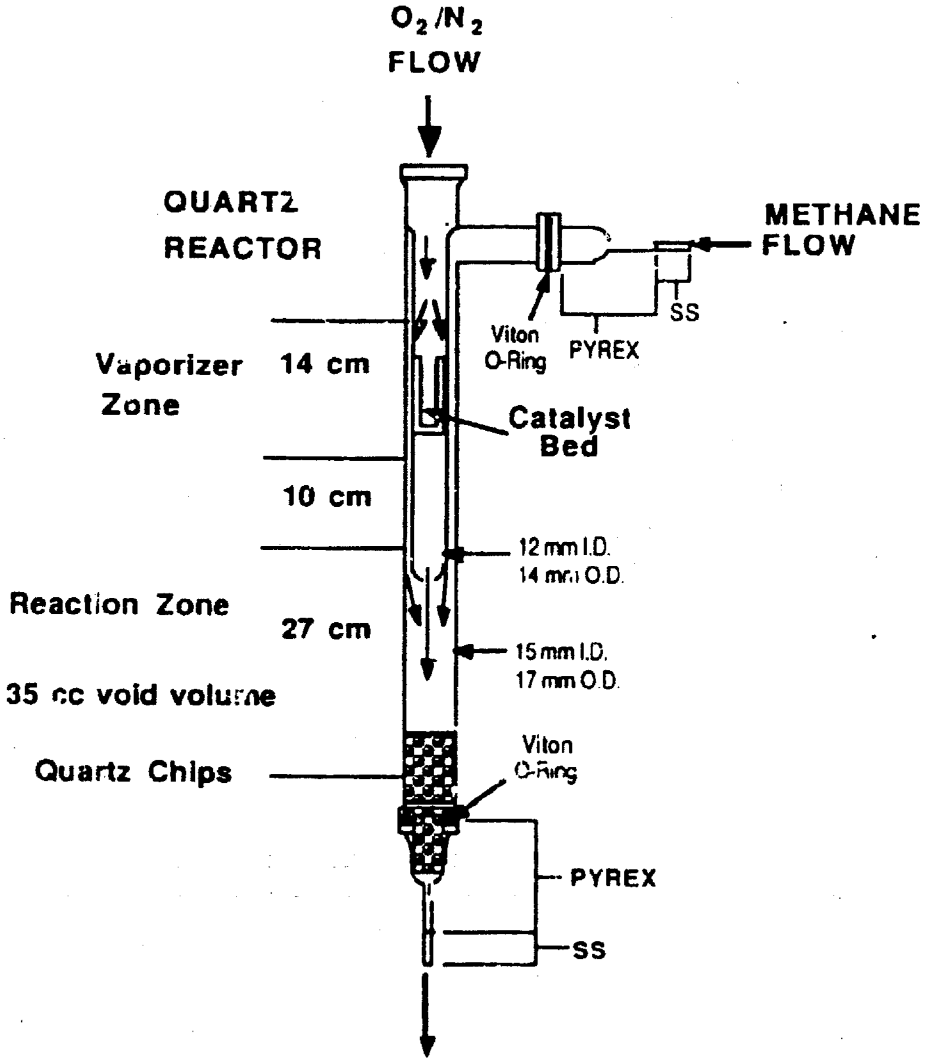
Since these results were obtained, Matsuhashi *et al.*[37] reported that a Na/ZrO_2 catalyst gives C_3 hydrocarbons as the main products during the oxidative coupling of methane. Their catalyst produced more C_3 than C_2 products with the C_3 hydrocarbons being 77% propane and 23% propylene.

The second approach suggested to avoid the heterogeneous/homogeneous mechanism is to change the gas phase chemistry to depart from the typical combustion reaction network. As an example, a volatile metal complex is oxidized to some state, for instance a superoxide, which abstracts a hydrogen from methane. The complex does not have as large a reservoir of oxygen to further oxidize the new methyl radical, as an oxidized surface would. Methyl radicals couple in the gas phase rather than be further oxidized.

Alternately, volatile complexes could be used to quench the hydroperoxides which convert methane coupling intermediates and products to carbon oxides. Volatile catalysts could also be used to increase the rate of hydrogen abstraction and shift the gas phase reaction away from the typical heterogeneous/homogeneous product distribution, as halogen radicals were shown to do in producing higher ethylene to ethane ratios

The reactor used for vapor phase catalyst studies is shown in Figure 6. Oxygen and nitrogen are introduced into the top of the reactor which is heated in the vaporizer zone by one oven. The catalyst or additive to be volatilized is in a quartz cup within the vaporizer zone. Methane is added so that it mixes with the oxygen/nitrogen/vapor phase catalyst mixture in a reactor heated by a second oven. In this way, reactions may be conducted with or without volatile catalysts present, since the vaporizer zone oven can be turned on or off as desired. When operating with vapor phase catalysts, the volatile catalyst components are trapped in the cool quartz chips located in the bottom of the reactor.

Figure 6. Vapor Phase Catalytic Reactor



Results are shown in Table 3. Methane conversion is decreased significantly by addition of volatile CsCl to a methane oxidation reaction in an empty, heated reactor space. Since the methane is essentially all converted to carbon oxides under these conditions, the volatile catalyst reduces the rate of homogeneous methane conversion to carbon oxides. This is shown for temperatures of 650 and 750 °C. The effect can be shown by either adding the vapor phase catalyst, which results in a drop in methane conversion, or by ceasing volatile catalyst addition, which is also shown in Table 3. Results for LiCl were similar to those of CsCl.

Table 3. Vapor Phase CsCl Catalyst

Vaporizer Zone T, °C	Reaction Zone T, °C	% CH4 Conv.
196	650	5.34
600	650	0.77
650	750	4.06
226	750	15.4

The discovery of the effect of volatile catalysts on homogeneous CH_4 conversion was studied in the presence of a catalyst. Catalyst conditions and volatile chloride levels were not optimized, but results in Table 4 show an increase in selectivity to C_2's and a decrease in CO_2 formation upon addition of volatile catalyst to a methane coupling reaction over a used $BaCO_3/Cl/\alpha\text{-}Al_2O_3$ catalyst. This is interpreted as a reduction in the gas phase conversion of methane to carbon oxides, allowing the methane which would have reacted in the gas phase to react on the catalyst surface to produce C_2's. These results demonstrate the concept of changing the gas phase chemistry during methane oxidation with volatile catalysts or promoters.

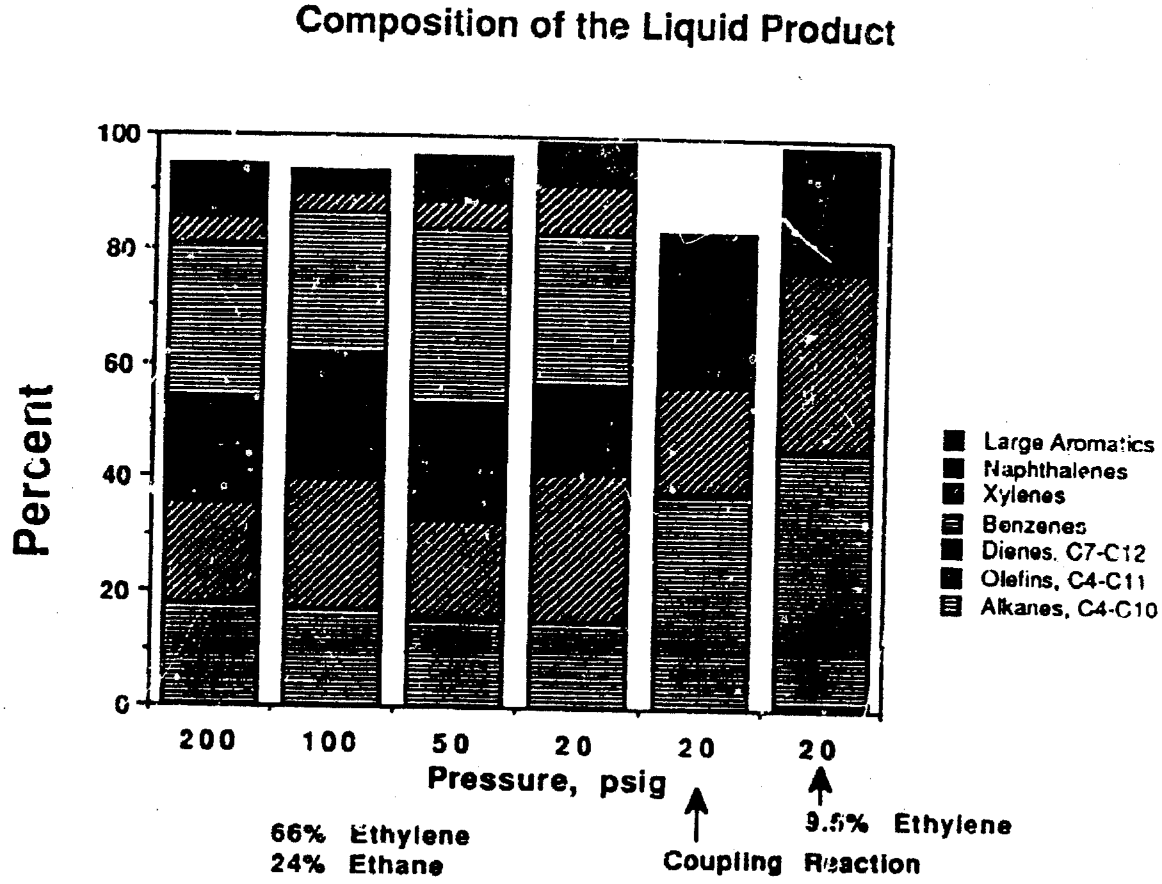
Table 4. Vapor Phase CsCl Over BaCO3/Cl/α-Al2O3 Catalyst

Vaporizer T, °C	Reaction T, °C	CH_4 Conv. %	C_2 Sel. %	CO_x Sel. %
185	750	21.08	46.49	51.10
750	750	21.32	53.06	43.57
40 ppm ethyl chloride:				
188	750	39.31	27.68	70.44
750	750	36.04	37.60	60.02

The ability to integrate a methane oxidative coupling reaction directly to an olefin oligomerization reaction would result in a process for the conversion of methane to liquid hydrocarbon products without any intermediate steps, such as separations or compression. This ability would also improve the economic viability of a methane to liquid hydrocarbons process since the separations part of the system could be simplified. Studies were performed to explore the oligomerization of methane coupling products (ethylene) to liquid hydrocarbons and determine the feasibility of integrating the methane coupling reaction directly to an oligomerization reaction.

Experiments were carried out using a reactant stream composed of 66% ethylene, 24% ethane, and 10% nitrogen at 350 °C. This is a hypothetical stream from a methane coupling reactor after separations. The oligomerization catalyst used was 5 grams of LZ-105-6/alumina, a ZSM-5 type material. This material was chosen due to its availability and the numerous reports in the literature on the use of ZSM-5 as an oligomerization catalyst. Gaseous reactants and products were analyzed using an online GC, and the liquid products were collected in a cooled trap for GC/MS analyses. The 350 °C temperature was chosen to ensure high ethylene conversion when the oligomerization and methane coupling reactions were integrated (very low ethylene pressure). At this temperature, the formation of aromatics as well as aliphatic hydrocarbons is expected[38]. A conventional continuous flow, high pressure stainless steel reactor was used for these experiments, at pressures of 200, 100, 50, and 20 psig. Since the flow rate was held constant, the contact time changed in these experiments. Surprisingly, the composition of the liquid does not vary greatly as the pressure is lowered from 200 to 20 psig. Results are shown in Figure 6.

Figure 6. Oligomerization Results



Experiments at 20 psig were run in which the effluent from a methane coupling reactor was passed directly into an oligomerization reactor containing 5 g of the LZ-105-6/alumina catalyst at 350 °C, using a single straight tube, quartz reactor, passing through two furnaces (reactant feed of $CH_4/O_2/N_2 = 8.2/1/0.6$, catalyst of 4.77 wt % $BaCO_3/\alpha$-alumina, ECl = 20 ppm, 750 °C, GHSV = 606 hr^{-1}, pressure = 20 psig). The figure above also shows the composition of the liquid products obtained from this coupling reaction experiment.

The product mix is entirely different from that of the ethylene-ethane-nitrogen (2.7/1/0.4) reaction at 20 psig. None of the aliphatic C_4 C_{12} products are observed. The main products are substituted benzenes, substituted naphthalenes, and xylenes. To determine if the low partial pressure of ethylene present in the methane coupling effluent was responsible for the shift in product distribution, an oligomerization run was performed using a reactant stream comprising 9.5% ethylene, 5.2% ethane, and 85.3% nitrogen. The product mixture from this run, also shown in Figure 6, is similar to that from the coupling run, indicating the possibility that the shift to aromatics is due to the low ethylene partial pressure produced in the coupling reaction.

Methane coupling products from low pressure reactions can be oligomerized to liquid hydrocarbons without separation and/or compression of the product stream. However, the formation of particular hydrocarbon fractions may require higher ethylene pressure in the oligomerization and/or separation of some components from the product stream.

SUMMARY:

In summary, Union Carbide has developed relatively long-lived novel catalysts for methane coupling which give performance which is competitive with that reported in the literature. High ethylene to ethane ratios (2.5-10) can be obtained. Enhanced surface reaction and altered vapor phase reaction concepts have been demonstrated. Oligomerization of hypothetical product streams and actual reaction mixtures has been demonstrated. Commercialization of direct methane coupling is considered to be 10-15 years away.

REFERENCES:

1. C. A. Jones, J. J. Leonard, and J. A. Sofranko, *Energy and Fuels*, **1**, 12 (1987).

2. F. M. Dautzenberg, R. L. Garten, and G. Klingman, "Fuels from Remote Natural Gas: Defining the Research and Development Challenge," paper presented at ACS 21st Symposium, Mares Island, Florida (1986).

3. S. A. Tabak "Production of Synthetic Diesel Fuel From Light Olefins," 1984 AIChE National Meeting, Philadelphia, 1984.

4. G. E. Keller and M. M. Bhasin, *J. Catal.*, 73, 9 (1982).

5. J. A. Sofranko, J. J. Leonard, and C. A. Jones, *J. Catal.*, **103**, 302 (1987).

6. C. A. Jones, J. J. Leonard, and J. A. Sofranko, *J. Catal.*, **103**, 311 (1987).

7. W. Hinsen and M. Baerns, *Chemiker Zeitung*, **107**, 223 (1983).

8. W. Hinsen, W. Bytyn, and M. Baerns, *Proc. 8th Int. Congr. Catal.*, 3, 81 (1984).

9. J. A. Sofranko, C. A. Jones, J. J. Leonard, A. M. Gaffney, and H. P. Withers, *Petr. Div. Preprints* **32**, 763 (1987).

10. G. S. Lane and E. E. Wolf, *J. Catal.* **113**, 144 (1988).

11. F. P. Larkin and M. R. Nordin, "Studies in Surface Science and Catalysis: Methane Conversion" Vol. **36**, 409, 1987.

12. B. K. Warren and K. D. Campbell, "Direct Conversion of Methane to C_2's and Liquid Fuels," Second Quarterly Progress Report, Contract DE-AC22-87PC79817, April 4, 1989.

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

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

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

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

17. D. J. Driscoll, W. Martin, J.-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.*, **107**, 58 (1985).

18. K. D. Campbell, E. Morales, and J. H. Lunsford, *J. Am Chem. Soc.*, **109**, 7900 (1987).

19. K. D. Campbell, H. Zhang, and J. H. Lunsford, *J. Phys. Chem.*, **92**, 750 (1988).

20. K. D. Campbell and J. H. Lunsford, *J. Phys. Chem.*, **92**, 5792 (1988).

21. J. A. Sofranko, J. J. Leonard, and C. A. Jones, *J. Catal.*, **103**, 302 (1987).

22. J. B. Kimble and J. H. Kolts, *Energy Progress*, **6**, 226 (1986).

23. K. Otsuka, K. Jinno, and A. Morikawa, *J. Catal.*, **100**, 353 (1986).

24. N. W. Cant, C. A. Lukey, P. F. Nelson, and R. J. Tyler, *J. Chem. Soc., Chem. Commun.*, 766 (1988).

25. A. Ekstrom and J. A. Lapszewicz, *J. Chem. Soc., Chem. Commun.*, 797 (1988).

26. B. K. Warren, "Direct Conversion of Methane to C_2's and Liquid Fuels," Light Hydrocarbon Gas Conversion/Bioconversion of Synthesis Gas/Slurry Bubble Columns Proceeding, Volume II, Indirect Liquefaction Contractors' Review Meeting, December 8-9, 1987, U.S. Department of Energy, Pittsburgh Energy Technology Center (National Information Service U. S. Dept. of Commerce, Springfield, VA 22161).

27. B. K. Warren, K. D. Campbell, J. L. Matherne, and G. L. Culp, "Direct Conversion of Methane to C_2's and Liquid Fuels," Indirect Liquefaction Contractors' Review Meeting Proceedings, November 15-17, 1988, pp 117-204, U. S. Department of Energy, Pittsburgh Energy Technology Center (National Information Service U. S. Dept. of Commerce, Springfield, VA 22161).

28. K. Otsuka and T. Komatsu, *J. Chem. Soc., Chem. Commun.*, 388 (1987).

29. K. Otsuka, M. Hatano, and T. Komatsu, *Studies in Surface Science and Catalysis: Vol. 36-Methane Conversion Symp.*, 383 (1987).

30. T. Ito, J.-X.. Wang, C.-H. Lin, and J. H. Lunsford, *J. Am. Chem. Soc.*, **107**, 5062 (1985).

31. I. Matsuura, Y. Utsumi, M. Nakai, and T. Doi, *Chem. Letts.*, 1981 (1986).

32. K. Otsuka, Q. Liu, and A. Morikawa, *J. Chem. Soc., Chem. Commun.*, 586 (1986).

33. V. R. Choudhary, S. T. Chaudhari, A. M. Rajput, and V. H. Rane, *J. Chem. Soc. Chem. Comm.*, 555 (1989).

34. N. W. Cant, C. A. Lukey, P. F. Nelson, and R. J. Tyler, *J. Chem. Soc., Chem. Commun.*, 776 (1988).

35. S. Ahmed and J. B. Moffat, *Applied Cat.*, in press (1989).

36. J. Gopalakrishnan and V. Bhat, *Inorg. Chem.*, **26**, 4301 (1987).

37. H. Matsuhashi, K. Sakurai, and K. Arata, *Chem. Lett.*, 585 (1989).

38. US Patent 3,775,501 to Mobil (1973).

Direct Conversion of Methane to C_2's and Liquid Fuels

Chemistry

DE-AC22-87PC79817

UNION CARBIDE
CHEMICALS AND PLASTICS COMPANY INC.
South Charleston, WV 25303

B. K. Warren
K. D. Campbell
N. E. Kinkade

11/15/89 BKW-1

Direct Conversion of Methane to C_2's and Liquid Fuels

Contract Objectives

Explore novel catalytic systems to convert methane through C2's to liquid hydrocarbon fuels.

Evaluate different conceptualized process flow schemes.

11/15/89 BKW-2

Methane to Ethylene Current Technology

The methane to ethylene reaction is a heterogeneous - homogeneous reaction.

Catalyst-O* + CH4 ⟶ CH3 • + Catalyst-OH

CH3 • (adsorbed) ⟶ CH3 • (gas phase)

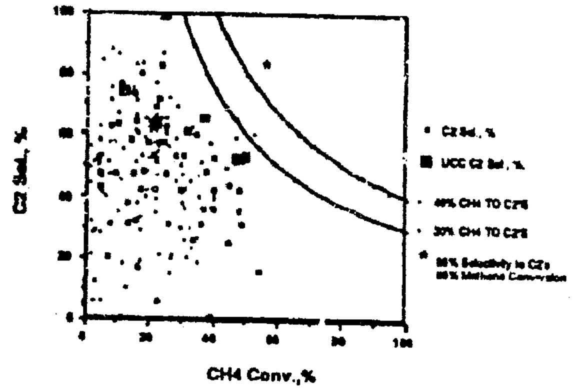
2 CH3 • ⟶ C2H6

C2H6 ⟶ C2H4

The product distribution is largely dictated by the gas phase chemistry and process conditions

BKW-3

Literature and Union Carbide Results for Methane Coupling



T = 700-950 °C p = 5-20 psig

11/15/88 BKW-4

High Ethylene to Ethane Catalyst Systems

Ba, Sr Compound

Chloride on Catalyst or in Vapor Phase
(ethyl chloride)

Metal Oxide Combustion Promoter -
e.g., Ti, Zr, Ga, Al oxides

BaCl2/TiO2	BaCO3/α-Al2O3

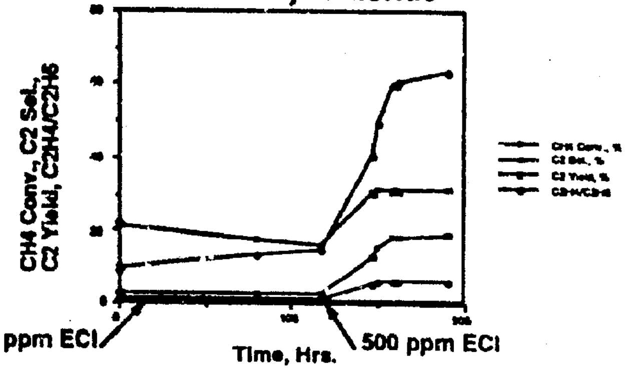
Best supports are acidic. Without added chloride, these deactivate rapidly. More acidic supports require more chloride.

Basic supports promote combustion, but do not result in higher ethylene to ethane ratios.

UNION CARBIDE 11/15/89 BKW-5

Metal Oxide Combustion Promoters

BaCO3/TiO2 Catalyst
Effect of Ethyl Chloride



6 ppm ECl

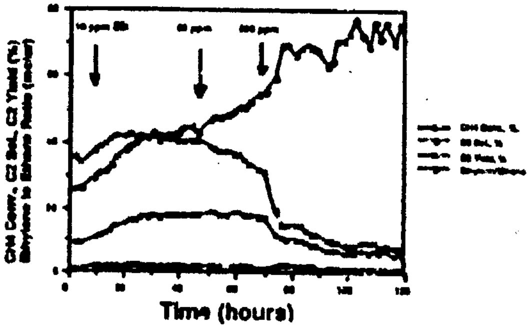
500 ppm ECl

TiO2 requires higher levels of ECl.

UNION CARBIDE 11/15/89 BKW-6

Optimum Chloride Levels Depend on Catalyst

BaCO3/α-Al2O3/Ethyl Chloride



This catalyst on α-Al2O3 required lower levels of ECl.

11/15/90 BKW-7

High Ethylene to Ethane Catalysts

Support	Acidity um/g	Acidity um/m2	ECl	GHSV	=/-
MgO	0.15	0.004	1-500	9796	1.6
Norton 5451 α-Alumina	0.31	1.03	200	2087	2.2
TiO2	1.08	1.31	500	2743	10.2

750 °C except for MgO: 700 °C

Catalysts with more acidic supports result in higher ethylene to ethane ratios.

11/18/90 BKW-8

Role of Chloride

Higher ethylene to ethane ratios from Cl radicals in the gas phase

Higher activities (vs. no Cl) from conversion of stable salts of Ba or Sr to active oxygen species

Higher selectivities from blocking of CO2 sites (slow change)

Selectivity and methane conversion can be maintained for over 400 hours

---

Process Studies

Steam Diluent

Little effect of replacing up to 15% of methane or inert diluent with steam.

>25% steam results in decreased activity and decreased selectivity to C2 hydrocarbons.

Pressure

Increasing pressure from 11 to 16 psig

- 4% increase in CH4 conversion
- 4% decrease in C2 selectivity
- (No change in yield)

Layered Perovskite

A2 Ln2 Ti3 O10 A = alkali; Ln = lanthanide

Composition

Contains alkali and lanthanide species in close contact
Lanthanide species present in perovskite environment

Unique Structure

Three octahedra-thick perovskite slabs [Ln2 Ti3 O10]
Alkali metal ions occupying interlayer positions

Advantages

Location and dispersion of alkali ions are known
Loss of alkali should be limited

Example

Catalyst	% CH4 Conv.	% C2 Sel.	% C2 Yield	T, °C
K2 La2 Ti3 O10	39	42	16.4	800

11/15/89 BKW-11

Technology Dilemma

AT BEST, some models predict yields of 59% at selectivities approaching 80%.

IN FACT, although yields up to 30% (transients) have been reported, yields of over 22% have not been reported under practical conditions.

Approaches

Get away from the gas phase chemistry.
Make more reaction occur on the surface of the catalyst, at lower temperature.

Change the gas phase chemistry.

11/15/89 BKW-12

Surface Reaction

Increase the reaction rate

Barium peroxide converts methane to C2's at 400 °C.

Certain metals activate hydrocarbons unselectively at low temperatures.

Highly activated metal sites exist in rigid frameworks, e.g., metal molecular sieves.

Results at 650 °C

Catalyst	% CH4 Conv.	% C2 Sel.	% C2 Yield
Ag/ BaCl2/ α-alumina	32	32*	10
SrCl2/ α-alumina	7.5	61	4.6
Pd/ SrCl2/ α-alumina	18	30*	5.4
Co/ SrCl2/ α-alumina	24	66	16
Ni/ SrCl2/ α-alumina	19	70	13
Fe/ SrCl2/ α-alumina	5.1	5.3	0.3
Cu/ SrCl2/ α-alumina	3.7	0.2	0
Rh/ SrCl2/ α-alumina	36	51	18
Co/ α-alumina	19	0.4	0.1

* : High C3 selectivity noted. (All propane)

Vapor Phase Chemistry

Catalyze with vapor phase catalysts

Change the mechanism of oxidation with volatile complexes which can not overoxidize, e.g., Li, Cs, Ru

Quench hydroperoxides

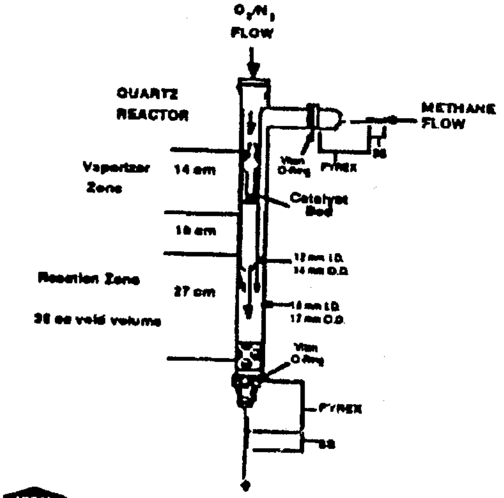
Metal complexes, water, quartz, other

Increase rate of hydrogen abstraction

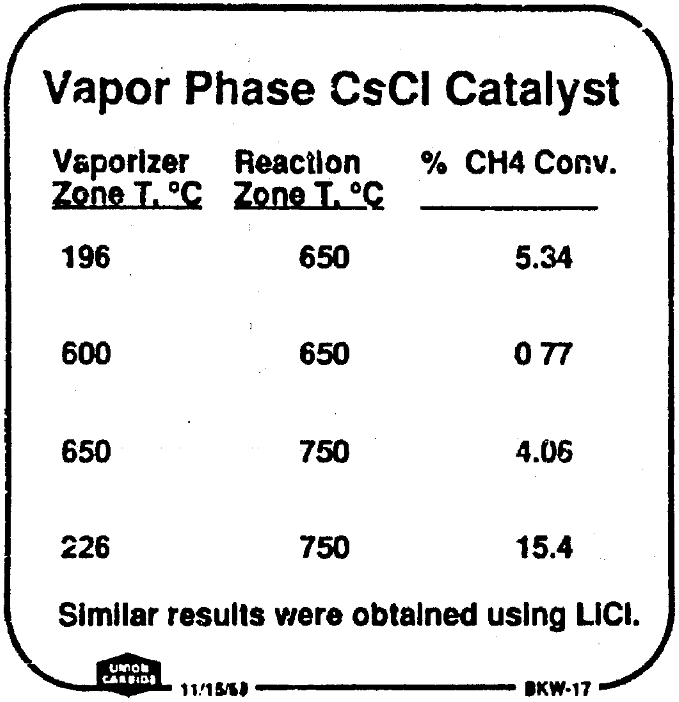
Halogens, hydrogen abstracting compounds

UNION CARBIDE 11/15/89 BKW-15

Vapor Phase Catalyst Reactor



UNION CARBIDE 11/15/89 BKW-16

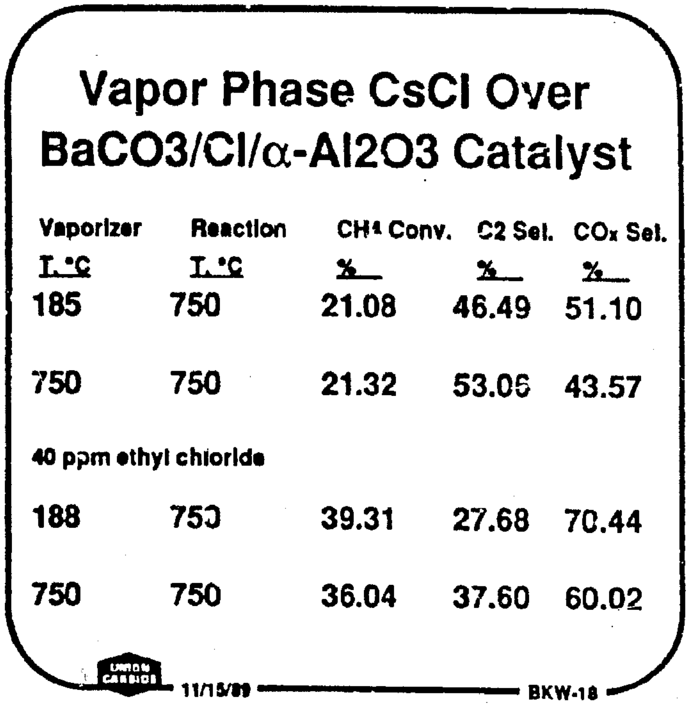


Vapor Phase CsCl Catalyst

Vaporizer Zone T. °C	Reaction Zone T. °C	% CH4 Conv.
196	650	5.34
600	650	0 77
650	750	4.06
226	750	15.4

Similar results were obtained using LiCl.

11/15/89 BKW-17



Vapor Phase CsCl Over BaCO3/Cl/α-Al2O3 Catalyst

Vaporizer T. °C	Reaction T. °C	CH4 Conv. %	C2 Sel. %	COx Sel. %
185	750	21.08	46.49	51.10
750	750	21.32	53.06	43.57
40 ppm ethyl chloride				
188	750	39.31	27.68	70.44
750	750	36.04	37.60	60.02

11/15/89 BKW-18

Oligomerization of Methane Coupling Products

Purpose

Explore the oligomerization of methane coupling products (ethylene) to liquid products

Determine feasibility of integrating methane coupling and oligomerization steps without (or with minimal) separations

Experimental

Oligomerization: ZSM-5 type catalyst, 350 °C

Methane Coupling: $BaCO_3/\alpha\text{-}Al_2O_3$ /ECI catalyst, 750 °C

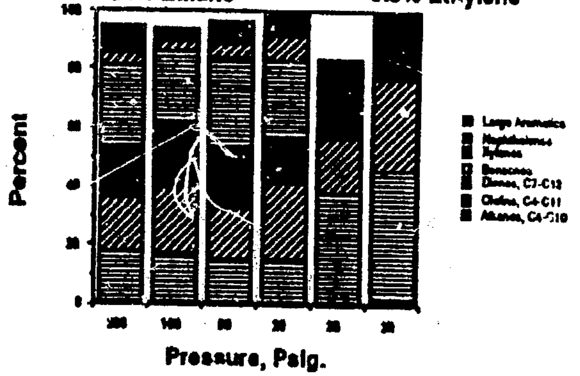
11/15/89 BKW-19

Composition of Liquid Products

Coupling Product (3% Ethylene)

66% Ethylene ~24% Ethane

9.5% Ethylene



11/16/89 BKW-20

Oligomerization Summary

Oligomerization of methane coupling products can be accomplished without separation and / or compression of the product stream

Formation of particular hydrocarbon fractions requires

    higher ethylene pressure in the oligomerization, and/or

    separation of some components from the product stream

UNION CARBIDE 11/15/89 BKW-21

Methane to Ethylene Current Status

Union Carbide has novel technology which is competitive with that reported in the literature, but with better catalyst lifetimes.

High ethylene to ethane ratios (2.5-20) can be obtained.

Enhanced surface reaction and altered vapor phase reaction concepts have been demonstrated.

Oligomerization of hypothetical product streams and actual reaction mixtures has been demonstrated.

Commercialization of direct methane coupling is 10-15 years away

UNION CARBIDE 11/15/89 BKW-22