SESSION 2B

NATURAL GAS TO LIQUIDS RESEARCH

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NATURAL GAS TO LIQUIDS RESEARCH

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ABSTRACT

The United States (U.S.) has substantial uncommitted reserves of natural gas and large quantities of undiscovered conventional resources. A large part of the uncommitted gas is on Alaska's North Slope. There are also large "unconventional" resources in tight sands, coalbed methane, and Devonian shales, some of which are not accessible by available pipelines. Conversion of gas to liquid fuels could unlock this resource, reduce the need for imported fuels, and provide a secure supply of liquid fuels in geographically distributed areas. Such chemical conversion technology could also be used to produce cheaper chemical feedstocks for industry.

In 1984, the U.S. Department of Energy (DOE) assumed the responsibility for expanding the knowledge base and for developing concepts, methods, and processes to convert natural gas to liquid fuels. The initial research activities focused on the development of a comprehensive understanding of the fundamental mechanisms and kinetics of the partial oxidation of methane directly to methanol for use as the basis for the design of a process. The goal is to achieve a sufficiently high yield that an operable and economically viable process can be applied to conversion of remote natural gas to liquids for transportation to markets in the United States. This effort is still ongoing; however, the research effort has progressed to include research in catalytic, non-catalytic, and biological conversion processes.

In conversion of gas to liquids, the promising prospect is a simple one- or two-step process carried out under mild temperature and pressure conditions which yields high conversions and selectivity of the gasoline and/or distillate fuels. Both catalytic and non-catalytic methods should be explored along with other unique methods, such as biological methods. Some high potential catalytic methods are in the conceptual stage and need further exploration.

Non-catalytic methods are being explored as potential means to initiate desired reactions. Biological methods are in their infancy but could develop into a promising approach, while possibly shedding light on catalytic improvements. In all processes, yield and selectivity tradeoffs must be considered.

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There is the need for new and improved separation techniques to remove desired products from unconverted feed and undesirable products. Techniques such as membrane, liquid membrane, or improved fractionation and absorption techniques should be studied to reduce costs. Recycling of unconverted feedstock and undesired product is also costly. Methods to reduce these costs need to be investigated.

HYDROCARBON CHEMICALS FROM NATURAL GAS

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ABSTRACT

The projects which are, or will be funded or cofunded by the Chemical Process Research Department of the Gas Research Institute in the Hydrocarbon Chemicals From Natural Gas area are:

"Experimental Demonstration of Methane Chlorination Reaction for Natural Gas Conversion", at Kinetics Technology International Corporation(KTI). The objectives are to validate ethylene yield as predicted by the KTI model, and to determine the ethylene to acetylene ratio in the yield.

"Conversion of Methane Into Ethylene and Acetylene Via Chlorine Catalyzed Oxidative Pyrolysis Process", at the Illinois Institute of Technology. The objetives are to determine the catalysis of hydrocarbon pyrolysis by chlorine, the suppression of carbon formation by oxygen, and the suppression of flame formation by chlorine.

and "Liquid Hydrocarbons and Chemicals From Pipeline Gas", at the Institute of Gas Technology(IGT). The objectives are to develop basic oxide catalysts for methane coupling and akyl aromatics coupling, and oxysulfide/sulfide catalysts for using natural gas as one of the feed stocks.

IGT's approach to oxidative coupling are:

to develop catalysts which promote high ehtylene and ethane selectivity, and high ethylene/ethane ratio in the yield.

to develop catalysts which promote the yield of high-value chemicals.

to determine the effect of sulfur compounds on the life and activity of these catalysts.

and to use pipeline gas as one of the feed stocks.

IGT found that the higher the base strength of the catalyst, the higher the ethylene/ethane yield and the lower the carbon oxides yield. To achieve the high base strength, IGT modified the alkaline earth based catalyst by doping it with ions of oxidation state one greater than the alkaline earth(US Patent 4,826,796). Results of oxidative coupling from literature and those from IGT are summarized in Figure 1 which was presented by SRI International originally. The target area represents a 40% yield of ethylene/ethane and is considered to be economical.To date, none of these findings is successful enough to be commercialized.

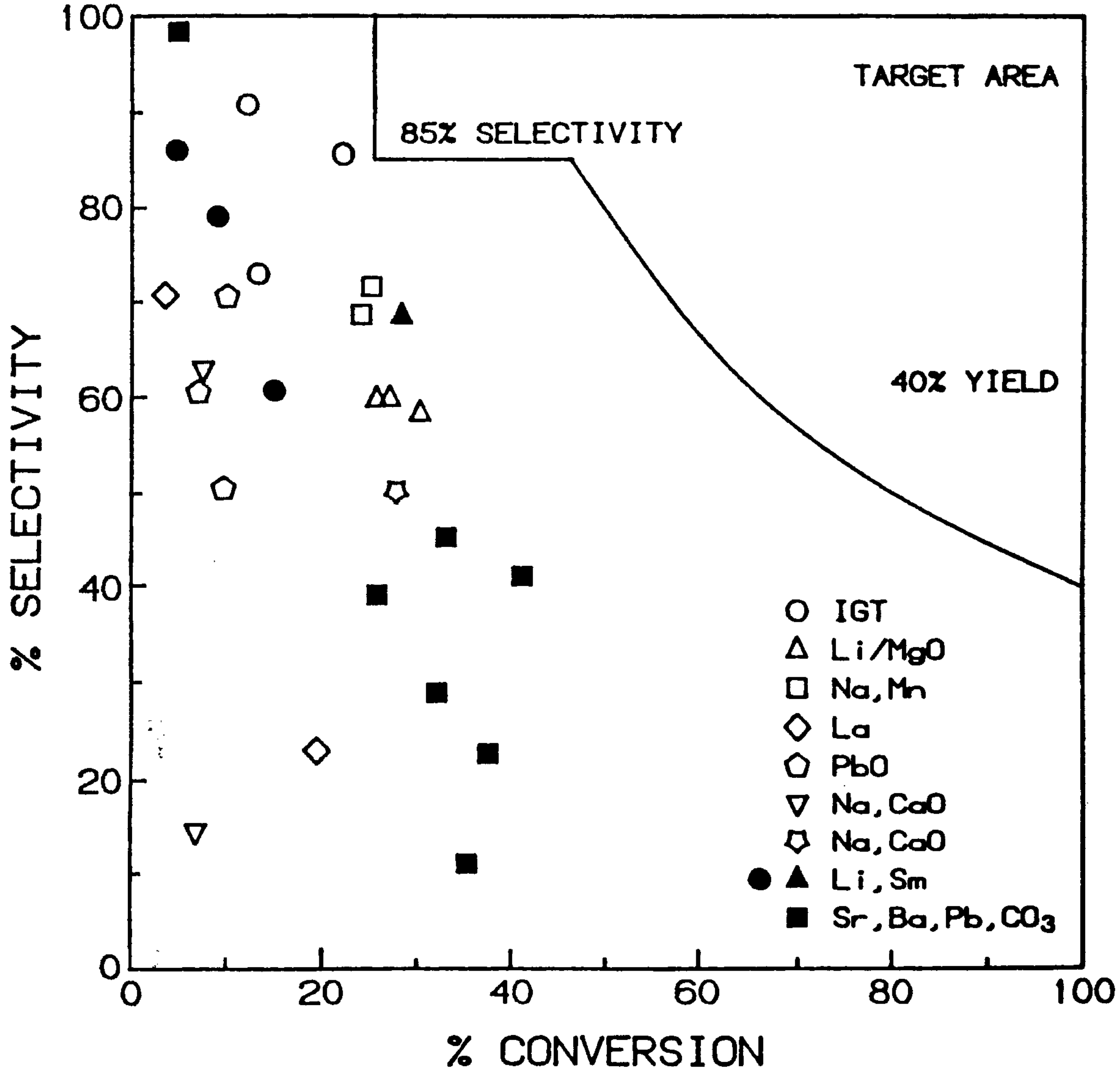

Figure 1. Ethylene/Ethane Yield

CONVERSION OF METHANE TO LIQUID HYDROCARBONS

1. CONTRACT NUMBER:	FEW-6030
CONTRACTOR:	Lawrence Livermore National Laboratory Livermore, CA 94550
PROGRAM MANAGER (CONTRACTOR):	Michael W. Droege, L-325 (415) 422-0155/FTS 532-0155
PRINCIPAL INVESTIGATORS:	M.W. Droege, L.M. Hair
METC PROJECT MANAGER:	Rodney D. Malone
PERIOD OF PERFORMANCE:	FY 1989

2. SCHEDULE/MILESTONES:

Milestones for FY89 were to complete a study of niobium and lanthanum catalyst systems (synthesis, characterization, and reactions) for methane oxidation and perform numerical chemical kinetic modeling of the gas-phase reactions of methane with oxygen and possible effects on catalyst reactions.

3. OBJECTIVE:

The effective utilization of "remote" natural gas requires research aimed at developing catalyzed reactions using oxygen that lead to partial oxidation or oxidative coupling of methane. Our efforts have been focused on the synthesis, characterization, and reactions of new catalysts that perform these oxidative processes with methane. Successful materials will serve as the basis for new processes that directly convert methane to liquid hydrocarbons.

4. BACKGROUND:

The future for methane conversion and natural gas processing depends on the development of catalyzed routes that directly convert methane to liquid hydrocarbons. The thermodynamically allowed, general reaction that transforms methane (CH_4) to higher hydrocarbons, summarized below,

$$nCH_4 + (y/2)O_2 \text{ -------->} C_nH_{4n-2y} + yH_2O$$

is an oxidative process that requires the use of a catalyst to facilitate the reaction. Non-catalyzed, simple thermal reactions of methane and oxygen require very high operating temperatures (700-800 °C) and, as a result, the desired product yield of hydrocarbons is unacceptably low, in large part due to the uncontrolled over-oxidation of methane to carbon monoxide (CO) and carbon dioxide (CO_2). The key to upgrading methane to liquid fuels is the controlled catalytic activation of the C–H bond preventing over-oxidation.

5. PROJECT DESCRIPTION:

The major emphasis of this project is the development of new catalyst materials which facilitate reactions that convert methane to liquid fuels. Reactions of interest include partial oxidation (forming methanol and formaldehyde) or oxidative coupling (forming ethane and ethylene) of methane using oxygen. Our efforts have focused both on describing the gas phase reactions of methane and oxygen that lead to methane oxidation and on development of new catalysts that select and accelerate the partial oxidation or coupling reactions. In order to better understand and describe the contribution of background reactions during catalyzed reactions, we have employed a chemical kinetic model (HCT: Hydrodynamics, Chemical kinetics, and Transport) that was developed at this Laboratory to describe such homogeneous gas phase reactions. In addition, we have focused on the synthesis and reactions of new catalyst materials that would serve as the basis for methane conversion processes. The catalysts typically consist of an inorganic oxide matrix such as SiO_2 in which early transition metal and lanthanide ions are incorporated into the oxide coordination environment of the matrix. Characterization studies including elemental analysis, surface area, and structural investigations by EXAFS (Extended X-ray Absorption Fine Structure) have been used to elucidate both the bulk properties of the catalysts as well as to determine details of the metal ion coordination environment. Reactor studies testing the foregoing catalysts for methane partial oxidation reactions are in progress and the results will be correlated with both the characterization data and with chemical kinetic modelling of the thermal reactions of methane and oxygen.

6. RESULTS/ACCOMPLISHMENTS:

During the study of some of the new catalysts, we observed, for even chemically quite distinct materials, similar reactivity patterns. An examination of the literature[1] shows that despite the wide range of catalyst materials that have been studied under an equally wide variety of experimental conditions, a common reactivity pattern emerges. This pattern, characterized by the inverse relationship between methane conversion and product selectivity, has been observed for both partial oxidation and oxidative coupling reactions.[1b] In considering the typical experimental conditions used for such catalyst studies, it is clear that significant potential exists for the appearance of non-catalyzed, thermally activated gas-phase reactions of methane and oxygen. These reactions can occur in the absence of catalysts and under the appropriate experimental conditions can be quite important. Experimentally, we have observed significant conversion of methane (30%) to light hydrocarbons and CO_x with appreciable selectivity (25%) to C_2^+ components due solely to gas-phase reactions. In recognition of these thermal reactions, more experimental consideration is being given to describing the thermally induced, homogeneous gas phase ("background") reactions of methane and oxygen occurring during catalysis studies.[2,3]

In order to better quantify the contribution of these background reactions and to determine whether gas-phase related reactions may in part be responsible for the common reactivity observed during catalyzed reactions, we have employed a chemical kinetic model (HCT) developed at this Laboratory to describe the overall homogeneous gas phase reaction of methane and oxygen. We have experimentally verified the model, applied to the case of methane oxidative coupling, in a series of tests comparing the effects of various experimental parameters such as temperature, residence time, feed gas composition.

As an example of the application of this model to describing catalyst systems, we have synthesized new catalysts containing niobium and lanthanum. Preliminary characterization of these catalysts as well as their catalytic effect have been studied. The observed catalytic reaction can be described in terms of the computational model.

EXPERIMENTAL

Reactor Experiments: The reactor itself was a 0.8 cm (ID) x 66.5 cm fused silica tube. It was centered in an electrically heated Lindberg furnace. The furnace ramp programs and set points were controlled by a programmable Micristar controller. The actual temperature was determined using a K-type wire thermocouple inserted either into the center of the reactor (the thermocouple was shielded in a quartz sleeve) or against the outer wall of the reactor. The measured temperature in the center of the reactor was found to be 5 to 12 °C hotter than that observed at the outer wall during reaction studies in the temperature region from 700 to 800 °C. Since temperature distribution was a concern in comparing our experimental data with model calculations (primarily in the determination of meaningful residence times), the exact temperature distribution was used in some of the model calculations as a check.

Methane containing 5% argon (Matheson, 99.9%) and oxygen (Amerigas, 99.9%) were the feed gases. Variable gas compositions and flow rates were obtained using mass flow controllers (Brooks 5850E). The presence of the argon tracer gas was used as a check on carbon balance. Product gases exiting the reactor were maintained at a temperature of 100-120 °C in heated lines to prevent condensation. Products were detected using a Questor quadrapole mass spectrometer and HP 5896 gas chromatograph. The mass spectroscopic determinations used the matrix method to determine volume percent products in the gas stream. The gas chromatographic determination used the sequence-reversal method employing 60/80 Chromosorb 102 (6' x 1/8") and 60/80 5A molecular sieve (3' x 1/8") columns.

Typical reactor parameters studied here were methane-to-oxygen ratios varying from 3:1 to 5:1, flow rates of 50 to 500 cc/min, temperatures ranging from 700 to 820 °C, with all reactions performed at atmospheric pressure. A standard experiment consisted of establishing a flow of mixed methane and oxygen at room temperature followed by ramping the reactor up to the desired operating temperature and allowing the temperature to stabilize. The reaction was allowed to continue at temperature until a steady-state reaction was established (0.25-1.0 hr depending on flow rate) before data was collected. Catalyst studies were performed using the reactor system already described. Catalysts were prepared by crushing the monolithic material (see next section) and sieving to 30 mesh. The sieved material was then loaded into the reactor and positioned and supported in the reactor hot zone using a plug of quartz wool. The catalyst was pretreated by ramping (15 °C/min) under a flow of oxygen to

500 °C and holding at that temperature for 30 min. This procedure removes surface water and alkoxide ligands. Reactor parameters used for the study were methane-to-oxygen ratio of 3:1, flow rate of 50 cc/min, temperature of 800 °C, and catalyst sample weight of 0.2-0.4 g, with all reactions performed at atmospheric pressure. The catalyst reactor experiments were performed using the procedure described above for the empty reactor.

Preparation of Catalyst Materials: A silica pre-gel is formed by the sub-stoichiometric hydrolysis of a silicon alkoxide as follows: A solution of 22.5 g (1.25 moles) of distilled water and 0.25 g concentrated sulfuric acid is slowly added to a solution of 200g of silicon tetratethoxide (TEOS; 0.96 moles) in 200 g of ethanol. The resulting clear solution is brought to reflux under a nitrogen atmosphere. After refluxing for two hrs, the resulting ethanol solvent (~400 mL) is removed by distillation under nitrogen. After cooling under nitrogen, the thick oil that remains is anaerobically transferred to a glove box and maintained under a dry, oxygen free atmosphere. A typical procedure for catalyst synthesis follows: La-Nb-Si Gel. A solution of niobium and lanthanum alkoxide and the silicon pre-gel in ethanol was prepared by dissolving 0.1 g lanthanum isopropoxide, 0.1 g niobium ethoxide, and 1.4 g of silicon pre-gel in 2.8 g of anhydrous, oxygen free ethanol (prepared by distillation from magnesium ethoxide under nitrogen) at room temperature in an dry, inert atmosphere glove box. This clear solution was sealed with a septum and removed from the glove box. A stock solution containing 2.5 g distilled water and 2.6 g of 48-50% tetrafluoroboric acid (in water) was prepared. Using a syringe, 0.5 g of the stock solution was added dropwise to the metal-silica-ethanol solution. The resulting clear solution was transferred to a plastic container, sealed with plastic wrap, and allowed to gel at room temperature (gel time = minutes to hours depending on formulation). After gelation, the metal-silica gel was aged at 50 °C for 16 hrs. The aged gel was dried using a critical point drying apparatus (Polaron) with liquid carbon dioxide. A colorless, transparent to translucent monolithic cylinder of metal-silica aerogel was obtained.

Elemental compositions were determined by ICP-AES and surface areas were evaluated by BET measurements. Catalyst surface areas ranged from 700-800 m^2/g.

Description of Chemical Kinetic Model: The chemical kinetic model used in the present study is the HCT (Hydrodynamics, Chemical kinetics, and Transport) model.[4] This model solves the coupled equations of conservation of mass, momentum, and energy, and determines each chemical species concentration in finite difference form. For this study, the reactor is assumed to be essentially a plug flow system where spatial variations in velocity, temperature, and species concentrations in the radial direction and diffusion of energy and species in the axial direction are assumed to be negligible. As a result, spatial changes in species concentration and temperature can be replaced by time variations. Thus only the energy equation and the species conservation equations must be solved. Surface reactions at the reactor wall were not considered. In the numerical model, coupling between the different chemical species takes place through the chemical kinetic terms, and these terms are introduced into the model through a detailed chemical reaction mechanism.[5]

The plug flow model is an approximation of the experimental reactor and assumes a radially-uniform velocity and temperature profile. In the actual reactor under isothermal conditions, the flow will attain a fully developed (parabolic) velocity and temperature profile after a short entry length of about 1 mm, since the Reynolds number (based on the inner diameter of the reactor) is about 3. The plug flow approximation was invoked since it results in considerable simplification of the numerical model.

The chemical reaction mechanism used here has developed from a number of studies of methane and natural gas combustion.[6-8] This mechanism has been extensively validated in a series of studies where numerical results were compared to experimental results from static reactors, stirred reactors, shock tubes, flames, and flow reactors.[9-16] The reaction mechanism does not consider carbon containing species C_3 or greater.

RESULTS AND DISCUSSION

1. Description of Overall Observed Reaction. The reaction between methane and oxygen occurring in the temperature range of 700-825 °C was studied in the quartz reactor. The major products of the reaction are CO, CO_2, C_2H_6, and C_2H_4 as determined by both gas chromatography and mass spectroscopy analysis and account for at least 98% of converted methane. Trace amounts of methanol, formaldehyde, and C_3^+ products are also observed. Under steady-state conditions, the products CO_2 and CO account for 75% of the observed products. Equilibrium or steady-state conditions are observed for residence times of about 5 sec and greater. Table 1 gives typical conversions and selectivities for this reaction at 800 °C and 10 sec residence times. These general observations agree well with the results of similar experiments recently reported by Lane and Wolf.[2]

2. Effect of Residence Time. Figure 1 compares model calculations and experimental results for methane

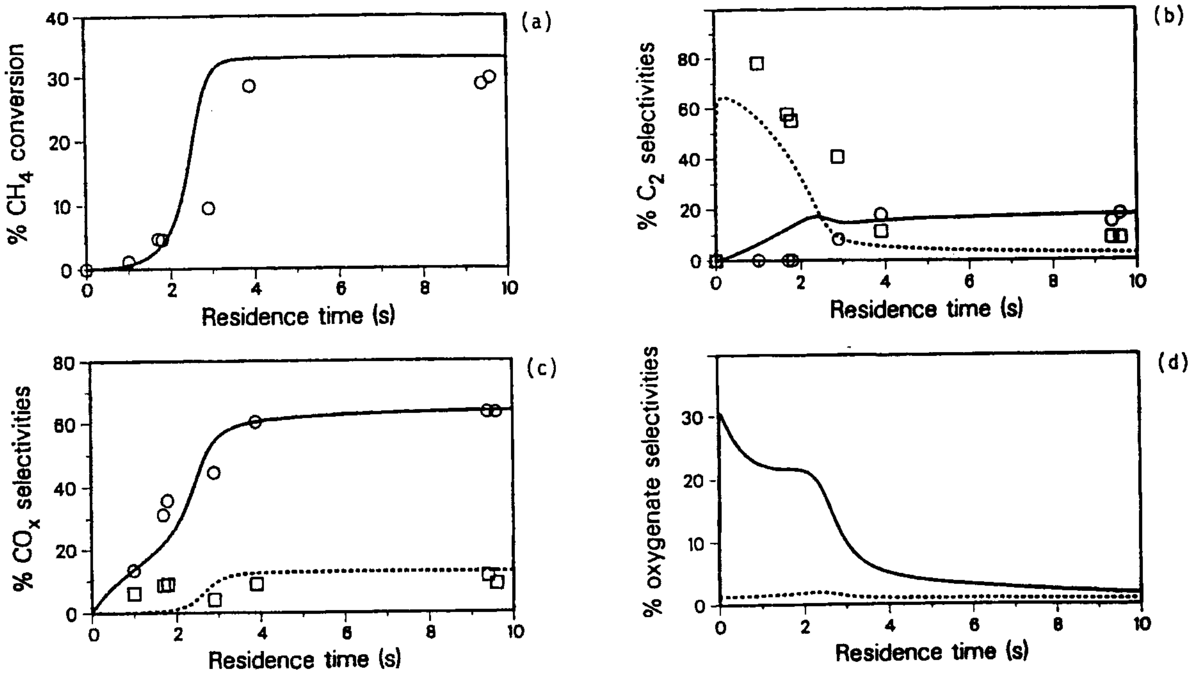

Fig. 1—Comparative plots of model calculations and experimental results for methane conversion and product selectivities at various residence times (800 °C, 3:1 methane-to-oxygen ratio). (a) Methane conversion predicted by model calculations (solid line) and experimentally determined methane conversion (open circles). (b) Ethane (broken line) and ethylene (solid line) selectivity predicted by model calculations. Experimentally measured selectivity for ethane (open squares) and ethylene (open circles). (c) Carbon monoxide (solid line) and carbon dioxide (broken line) selectivity predicted by model calculations. Experimentally determined selectivity for carbon monoxide (open circles) and carbon dioxide (open squares). (d) Formaldehyde (solid line) and methanol (broken line) predicted by model calculations.

conversion and product selectivities at various residence times. The overall picture is essentially one of the time evolution of the oxidation reaction of methane under these conditions. It is observed that residence times of about 4 sec and longer result in a steady-state reaction. At steady state, methane conversion and product selectivities are similar to those given in Table 1. Below about 1 sec residence time, essentially no methane is being converted. Under conditions for low methane conversion (~1%), coupling and partial oxidation products (C_2's, CH_2O) are the major products while over-oxidation products (CO, CO_2) are minor. In particular, predicted ethane and formaldehyde selectivities are as high as 65% and 30%, respectively, but drop off rapidly as methane conversion increases. As this occurs, the over-oxidation products become dominant, with CO being the major product, at the expense of the coupling and partial oxidation products. This inverse relationship between methane conversion and product selectivity is a common experimental observation for the partial oxidation or oxidative coupling of methane in catalyzed systems.[1b] Oxidative coupling products, ethane and ethylene, respond inversely to each other with ethane being the favored product at shorter residence times and declining in selectivity with respect to ethylene at longer residence times. It has been observed elsewhere[1j-k,2,17] that ethylene production occurs at the expense of ethane formation.

The model calculations do an excellent job of predicting both the trend and the numerical values of the experimental data. It should be noted that although the model predicts predicts 30% selectivity to formaldehyde at short residence times dropping to about 3% at steady-state, experimentally, formaldehyde is detected in only trace amounts (<1%) at steady-state. No attempt has yet been made to detect formaldehyde at shorter residence times.

3. Effect of Temperature. Figure 2a shows a plot of methane conversion as a function of residence time for three temperatures (700 °C, 750 °C, 800 °C) at a 3:1 methane-to-oxygen ratio as generated by model calculations. The effect of temperature on product selectivities is shown in Figures 2b-2d. The effect of temperature is simply to slow down (lower temperatures) or speed up the oxidation reaction of methane and does not significantly affect either intermediate or final (steady-state) conversion values. To test this prediction experimentally, separate oxidation reactions at the three temperatures were performed. These results are shown in Figures 3a-3c as a

Table 1. Typical Conversions and Selectivities for Methane-Oxygen Reaction at 800 °C, 3:1 Methane-to-Oxygen Ratio, and 55 cc/min Flow Rate.

Product	Selectivities[a] (%)
CO	63.2
CO_2	8.8
C_2H_6	8.4
C_2H_4	17.9

CH_4 Conversion[b] (%) = 29.7

C_2 Yield[c] (%) = 8.3

[a] Selectivities (%) = [(moles C in product)/(total moles C in all products)] x 100

[b] Conversion (%) = [total moles C in all products/(total moles C in products + moles C in unreacted methane)] x 100

[c] Yield (%) = Fractional Conversion x %Selectivity

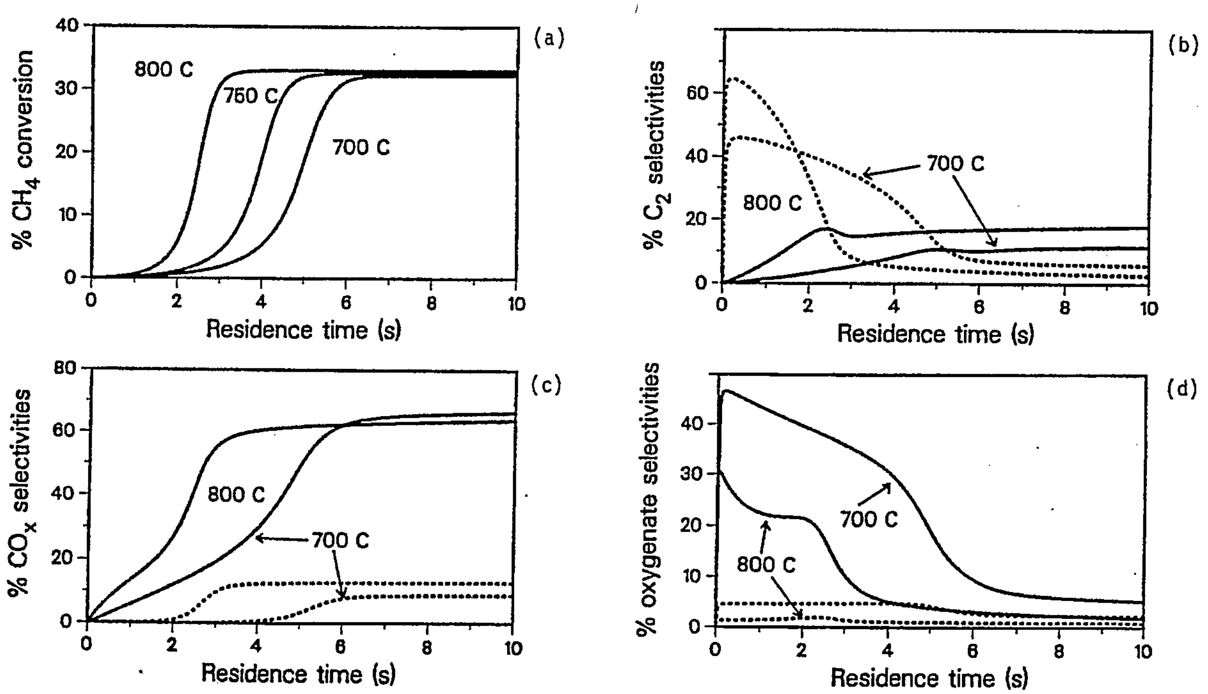

Fig. 2—Plots of methane conversion and product selectivities as a function of residence time for three temperatures (700 °C, 750 °C, 800 °C) generated by model calculations at a 3:1 methane-to-oxygen ratio. (a) Predicted methane conversion (solid line). (b) Predicted selectivities for ethane (broken line) and ethylene (solid line). (c) Predicted selectivities for carbon monoxide (solid line) and carbon dioxide (broken line). (d) Predicted selectivities for formaldehyde (solid line) and methanol (broken line).

function of inverse flow rate. This was done in preference to residence time because the exact reaction volume is difficult to determine. The trends are similar for product formation with temperature only slowing down or speeding up the approach to steady-state values. The experimental steady-state distributions (at long residence times) are essentially the same as those shown in Figure 1. Temperatures higher than about 900 °C serve only to facilitate destructive secondary reactions such as hydrocarbon pyrolysis.

4. Effect of Methane-to-Oxygen Ratio. Figure 4 compares model calculations and experimental results for methane conversion and product selectivities at methane-to-oxygen ratios of 5:1 at 800 °C (a plot of the 3:1 ratio

is shown in Figure 1). The effect of increasing the methane concentration relative to oxygen in the feed gas results in two general trends observed and predicted. The first is to lengthen the time required for the reaction to reach steady-state. This is similar to that observed for the effect of temperature. The second trend, which is more important, is to lower the overall conversion of methane during reaction. The steady state value of methane conversion is reduced from 30% (33% calculated) at methane-to-oxygen ratio of 3:1 to 18% (22% calculated) at 5:1. The relative product distributions for the 5:1 case are nearly the same as is observed in the 3:1 case. The only difference with the 5:1 case is that selectivity to over-oxidation products is slightly lower while selectivity to coupling products is slightly higher than is observed for the 3:1 case. This is a direct consequence of the lower conversion achieved at steady-state in the 5:1 case. The 3:1 case would exhibit product selectivities similar to the 5:1 if it were operated at ~20% conversion. The fit of the model to the experimental data at intermediate residence times is not as good as the 3:1 case. We attribute that to the difficulty in determining precise residence times.

5. Description of Reaction Pathways Derived from Chemical Kinetic Mechanism. The general features of the mechanism can be summarized quite easily. Initiation is assumed to occur primarily by H atom abstraction from methane by oxygen (Eq 1) due

$$CH_4 + O_2 = CH_3 + HO_2 \text{......................(1)}$$

to the high concentrations of O_2 present in the initial reactants. However, the rate of initiation reactions appear to have little influence on the computed results. After an initial radical pool is established, methane is consumed mainly by H atom abstraction, with OH and H being the most important radical species (Eq 2-6). These

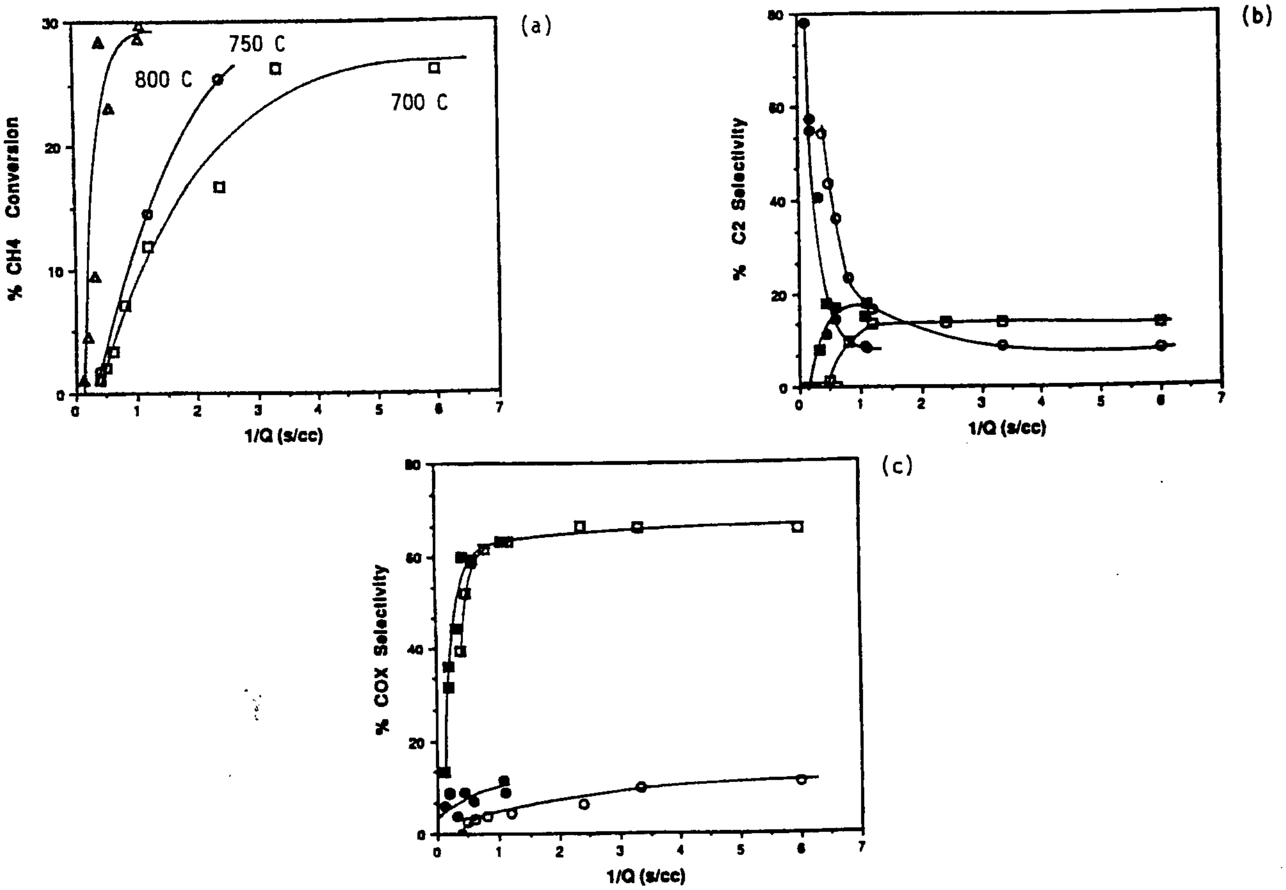

Fig. 3—Plots of experimentally measured methane conversion and product selectivities as a function of inverse flow rate for three temperatures (700 °C, 750 °C, 800 °C) at a 3:1 methane-to-oxygen ratio. (a) Measured methane conversion at 800 °C (open triangles), 750 °C (open circles), and 700 °C (open squares). (b) Measured ethane selectivity at 800 °C (closed circles) and 700 °C (open circles). Measured ethylene selectivity at 800 °C (closed squares) and 700 °C (open squares). (c) Measured carbon dioxide selectivity at 800 °C (closed squares) and 700 °C (open squares). Measured carbon monoxide selectivity at 800 °C (closed circles) and 700 °C (open circles).

reactions are important for significant methane conversion. The key to understanding thermally-activated methane oxidation is determining the fate of the methyl radicals

$$CH_4 + OH = CH_3 + H_2O \ldots\ldots (2)$$
$$CH_4 + H = CH_3 + H_2 \ldots\ldots (3)$$
$$CH_4 + HO_2 = CH_3 + H_2O_2 \ldots\ldots (4)$$
$$CH_4 + O = CH_3 + OH \ldots\ldots (5)$$
$$CH_4 + CH_3O = CH_3 + CH_3OH \ldots\ldots (6)$$

that are produced by consumption of methane. Unlike larger alkyl radicals,[16] methyl radicals react through only two major paths. The first of these involves direct oxidation of methyl radicals forming methoxy radicals (Eq 7) followed by decomposition of the methoxy radicals to formaldehyde (Eq 8). This reaction is the major source of H atoms

$$CH_3 + HO_2 = CH_3O + OH \ldots\ldots (7)$$
$$CH_3O + M = CH_2O + H + M \ldots\ldots (8)$$

under the present conditions. When formaldehyde (or methoxy radical) is produced, subsequent reactions rapidly yield formyl radicals (HCO), which then produce CO through reaction with O_2 (the primary pathway) or third bodies (Eq 9-10).

$$HCO + O_2 = CO + HO_2 \ldots\ldots (9)$$
$$HCO + M = CO + H + M \ldots\ldots (10)$$

At low conversion, high dilution, or lower temperature, these subsequent reactions (Eq 9-10) are minimized and greater selectivity to formaldehyde is expected (see Figure 2).

Carbon monoxide leads to CO_2 through reaction with HO_2 and OH radicals (Eq 11-12).

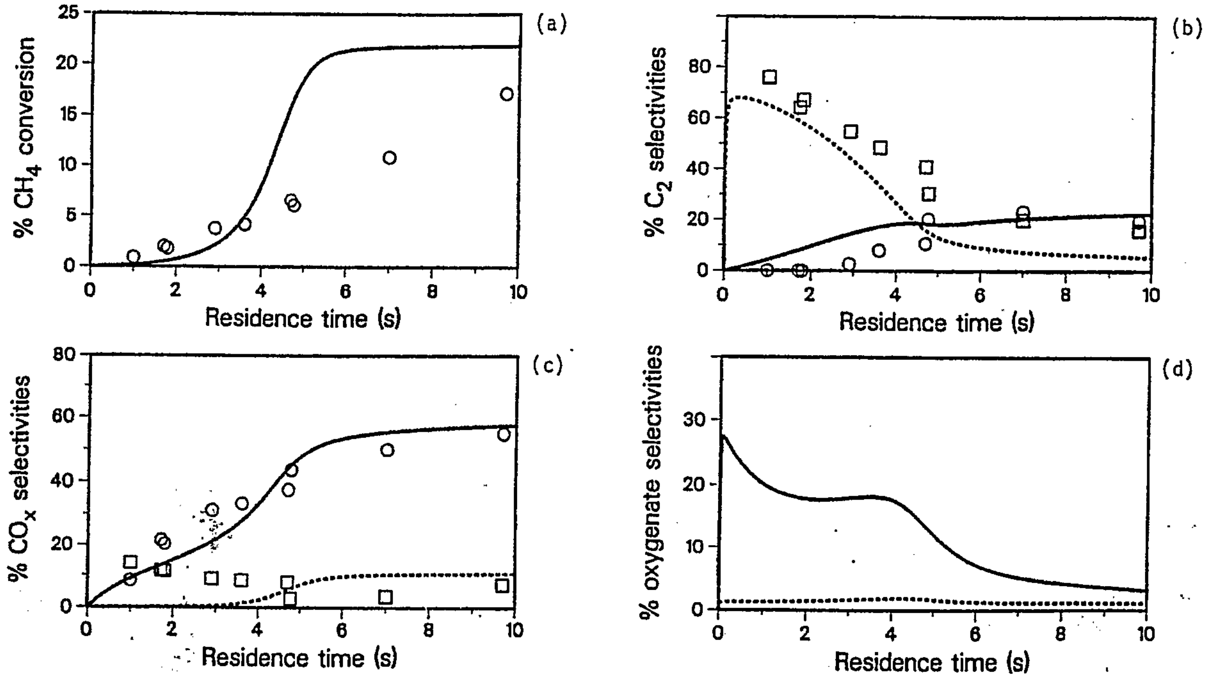

Fig. 4—Comparative plots of model calculations and experimental results for methane conversion and product selectivities as a function of residence times at a methane-to-oxygen ratio of 5:1 (800 °C). (a) Methane conversion predicted by model calculations (solid line) and experimentally determined methane conversion (open circles). (b) Ethane (broken line) and ethylene (solid line) selectivity predicted by model calculations. Experimentally measured selectivity for ethane (open squares) and ethylene (open circles). (c) Carbon monoxide (solid line) and carbon dioxide (broken line) selectivity predicted by model calculations. Experimentally determined selectivity for carbon monoxide (open circles) and carbon dioxide (open squares). (d) Formaldehyde (solid line) and methanol (broken line) predicted by model calculations.

$$\mathrm{CO} + \mathrm{HO_2} = \mathrm{CO_2} + \mathrm{OH} \ldots\ldots\ldots\ldots (11)$$
$$\mathrm{CO} + \mathrm{OH} = \mathrm{CO_2} + \mathrm{H} \ldots\ldots\ldots\ldots (12)$$

The second major reaction path for methyl radicals is the direct recombination to produce ethane (Eq 13) one of the major intermediate products. It is also chain termination since it results in the net consumption of two radicals. Thus increasing

$$\mathrm{CH_3} + \mathrm{CH_3}\ (+M) = \mathrm{C_2H_6}\ (+M) \ldots\ldots\ldots (13)$$

the rate of Eq 13 results both in the increased production of ethane and a decreased oxidation rate of methane (conversion).

The ethane produced by this reaction is then consumed by radical attack (Eq 14-16). The ethyl radicals which result are then consumed by thermal decomposition

$$\mathrm{C_2H_6} + \mathrm{CH_3} = \mathrm{C_2H_5} + \mathrm{CH_4} \ldots\ldots\ldots (14)$$
$$\mathrm{C_2H_6} + \mathrm{OH} = \mathrm{C_2H_5} + \mathrm{H_2O} \ldots\ldots\ldots (15)$$
$$\mathrm{C_2H_6} + \mathrm{H} = \mathrm{C_2H_5} + \mathrm{H_2} \ldots\ldots\ldots (16)$$

and by reaction with molecular oxygen resulting in the formation of ethylene (Eq 17-18).

$$\mathrm{C_2H_5} + \mathrm{O_2} = \mathrm{C_2H_4} + \mathrm{HO_2} \ldots\ldots\ldots (17)$$
$$\mathrm{C_2H_5}\ (+M) = \mathrm{C_2H_4} + \mathrm{H}\ (+M) \ldots\ldots\ldots (18)$$

The oxygenated product CH_3OH results primarily from reactions involving the methoxy radical (Eq 19-20).

$$\mathrm{CH_4} + \mathrm{CH_3O} = \mathrm{CH_3} + \mathrm{CH_3OH} \ldots\ldots\ldots (19)$$
$$\mathrm{CH_2O} + \mathrm{CH_3O} = \mathrm{HCO} + \mathrm{CH_3OH} \ldots\ldots\ldots (20)$$

As the concentration of stable intermediate species increases, methyl radicals are also consumed by reaction with these intermediates (Eq 21-23). These reactions

$$\mathrm{H_2} + \mathrm{CH_3} = \mathrm{H} + \mathrm{CH_4} \ldots\ldots\ldots (21)$$
$$\mathrm{CH_2O} + \mathrm{CH_3} = \mathrm{HCO} + \mathrm{CH_4} \ldots\ldots\ldots (22)$$
$$\mathrm{C_2H_6} + \mathrm{CH_3} = \mathrm{C_2H_5} + \mathrm{CH_4} \ldots\ldots\ldots (23)$$

convert the methyl radicals back to methane. These reactions become important late in the reaction.

6. Catalyst Reactions. Figure 5 shows the results of reactor screening experiments for mixed Nb-La-SiO_2 catalysts. Three mixed metal materials were prepared containing 4.33 wt% Nb and 1.25 wt% La, 2.43 wt% Nb and 3.74 wt% La. and 1.3 wt% Nb and 6.62 wt% La, respectively. These three materials have been compared to similar metal loading levels for pure Nb and La silica catalysts of 5.7% and 8.6% respectively. The all niobium material exhibits the tendency for deep oxidation and low C_2 selectivity. The addition of La to the mixed-metal catalyst causes an immediate increase in both methane conversion (~25%) and C_2 selectivity (~30%). Only the 61% La- 39% Nb case departs dramatically from these observations. In that case, a significant drop-off in methane conversion to about 13% along with an increase to 41% C_2 selectivity is observed. The origin of this

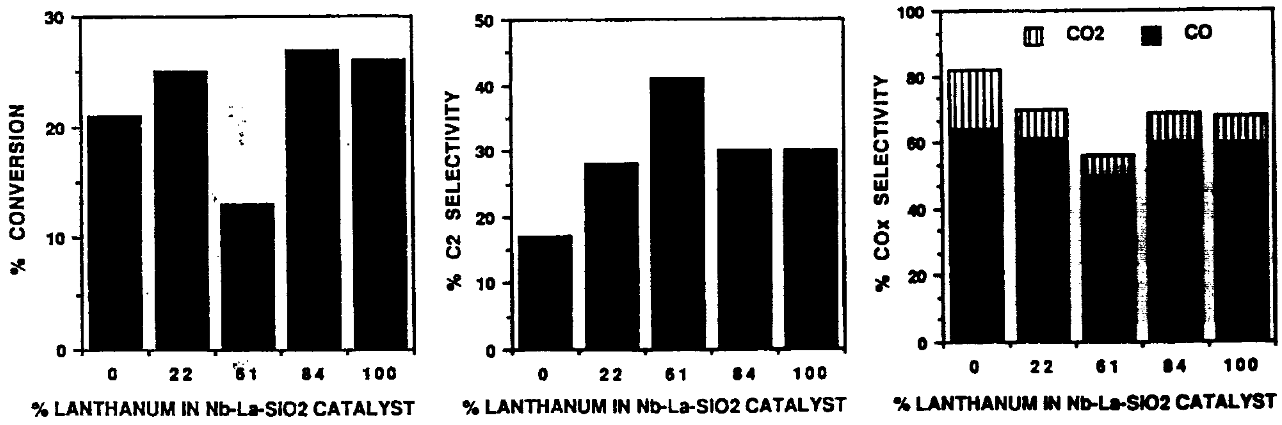

Fig. 5—Comparison plots of methane conversion and product selectivity (C_2 and CO_x) as a function of wt% La in the synthetic mixed niobium-lanthanum-silica based catalysts.

effect is unclear, but since this behavior is observed only for a particular catalyst composition, the possibility of a cooperative interaction between the two metal ions might be suggested. More or less lanthanum (than in the 61% La-39% Nb case) in the mixed-metal catalyst shows results similar to the pure lanthanum-silica catalysts described above. However, it should be noted that this new behavior can also be described using the model. A methane conversion of 13% is predicted to result in C_2 product selectivity of ~40%. This is what is observed experimentally for the mixed 61% La-39% Nb material.

CONCLUSIONS

Summary of Experimental and Modelling Efforts. The following conclusions are supported by the experimental and model results:

- Overall, the model predicts very well the trends and steady state results observed in the experimental parameter studies.
- Thermal reactions alone account for significant methane conversion (30% under the experimental conditions) and lead to an inverse relationship between conversion and C_2 selectivity.
- Reactor operating parameters affect conversion and product distribution:
  - -Reduced temperature increases reaction time to steady state with little effect on final conversion and product distribution.
  - -Increased residence increases methane conversion while decreasing C_2 selectivity.
  - -Increased methane proportion in the feed gas lengthens reaction time to steady state and decreases conversion.

Implications for Catalysis. Since most catalyst systems described for methane conversion reactions are operated under conditions where thermally-induced radical reactions potentially exist, it is very likely that these materials may be interacting with established radical pools and that aspects of the catalyst reaction chemistry can be described within the framework of these gas-phase reactions. The generally observed reaction trend for catalysts, characterized by the inverse relationship between methane conversion and product selectivity, is an important feature of the thermally-activated, gas-phase oxidation of methane with oxygen. The reaction mechanism indicates that methyl radical coupling is the major route for C_2 production. These methyl radicals are produced during propagation steps that consume methane. As coupling increases, the general radical pool is diminished and, as a result, propagation slows and less methane is consumed (converted). A catalyst that facilitates methyl radical coupling from an established radical pool would be inherently limited in methane conversion. On the other hand, oxygen and oxygen centered radicals are primarily responsible for the over-oxidation reaction to CO and CO_2. However, since these radicals are also important in propagation, catalysts that either terminate these radicals or facilitate partial oxidation reactions (forming CH_2O, CH_3OH) would also diminish the general radical pool and face a methane conversion barrier. It is likely that the new catalysts described here operate in this manner. The way to overcome this limit in conversion, is to provide an additional agent that produces methyl radicals and feeds the propagation steps. It is possible that the alkali metal promoted catalysts that exhibit the best C_2 product yields act in this manner. It has been shown that these catalysts tend to deactivate with time due to the loss of volatile metal oxides. The description of catalyzed systems that at low methane conversions result in appreciable selectivities to either ethane or formaldehyde (depending on temperature), even for systems that are not traditionally considered catalysts such as silica and silicon glasses,[3,18] can be described in a straightforward manner within the framework of the model used in this work.

In general, it appears that catalysts that interact with a gas-phase radical pool face inherent barriers in desirable product yields and will probably not be viable process catalysts. It is possible that catalysts that show a dramatic departure from the trends predicted by the gas-phase reactions may lead to useful process materials.

7. FUTURE WORK:

Future work includes continued catalyst synthesis and reactor screening experiments emphasizing new catalysts containing Y, V, and W. In addition, studies are in progress to extend the chemical kinetic modeling to include the interaction between catalyst surfaces and gas-phase methane reactions and the potential impact of this interaction on product distributions and yields.

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METHANE TO METHANOL CONVERSION

1. CONTRACT NUMBER: FEW A180

CONTRACTOR: Los Alamos National Laboratory
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CONTRACT PERIOD OF PERFORMANCE: May 1, 1984 through
September 30, 1989

2. SCHEDULE/MILESTONES:

Work on this project during FY85-88 involved mechanism development and modeling coupled with fundamental kinetics measurements and bench-scale reactor experiments. These efforts resulted in a detailed elementary reaction mechanism for the partial oxidation of methane with oxygen which has been partially validated for low pressure simulations. Experiments in a bench-scale static reactor have successfully demonstrated that methane can be converted into methanol with a selectivity >70% in a single pass although at low (<3%) methane conversion. During FY88, simulations performed with the computer kinetic model predicted methane conversions >25% while maintaining a selectivity for methanol >50%. Experimental validation of the code simulation is the objective of current research efforts. The focus of the project during FY89 is to complete the testing of a bench-scale prototype of a pulsed flow reactor. Experiments will be performed during FY89 and FY90 in the prototype to provide guidance for the design during FY90 of an advanced, supersonic, pulsed-flow reactor which will operate with a stoichiometric CH_4/O_2 mix within explosive limits. Various options for increasing the conversion efficiency will be explored concurrently during FY90.

3. OBJECTIVES:

The objective of this research effort is to understand the fundamental chemistry necessary to develop a process to effect the partial oxidation of methane to methanol using air or oxygen. The goal is to develop an economically viable process to convert natural gas or methane from coal gasification products to a liquid fuel that is readily transported.

4. BACKGROUND STATEMENT:

The purpose of this project is to develop a novel process by which natural gas or methane from coal gasification products can be converted to a transportable liquid fuel. It is proposed that methanol can be produced by the direct, partial oxidation of methane utilizing air or oxygen. It is anticipated that, compared to present technologies, the new process might offer significant economic advantages with respect to capital investment and methane feedstock purity requirements.

Methanol is presently manufactured by the catalytic reaction of synthesis gas (carbon monoxide and hydrogen) made by steam reforming of natural gas or heavier hydrocarbon fractions; several different, but related, processes exist (Danner 1970). Such two-step transformations require moderately high operating temperatures and pressures, reasonably pure feedstock, and are energy intensive. The present research effort attempts to avoid these requirements.

In the present research, the direct partial oxidation of methane to methanol utilizing air or oxygen is being studied. Methanol meets the requirements of improved transportability, can be utilized directly as a fuel, or can be transformed into long chain hydrocarbons via processes such as the Mobil MTG process. The overall transformation can be represented by reaction (1):

$$CH_4 + 1/2\ O_2 \rightarrow CH_3OH. \tag{1}$$

The essence of the project is to control the partial oxidation to produce useful yields of methanol. It is crucial that complete oxidation to the thermodynamically stable products, carbon dioxide and water, be avoided. Methanol has been obtained as a major product in the partial oxidation of methane at high pressure and temperatures (Gesser 1985; Luckett 1976; Newitt 1934; Newitt 1932; Mantashyan 1981). The further oxidation products CH_2O, CO, and CO_2 accounted for the remainder of the methane consumed.

5. PROJECT DESCRIPTION:

Our research approach is to achieve an economically attractive yield of methanol by developing and employing techniques to control the methane partial oxidation process. The application of control must arise from an understanding of the complex chemistry involved. It is based on exact control of the reaction kinetics of the direct oxidation of methane with termination of the reaction prior to reaching thermodynamic equilibrium to provide a high yield of methanol in a single step. The approach involves a homogeneous, gas-phase partial oxidation; it is non-catalytic. One focus of the project is a computer kinetic model describing all of the important free radical reactions. This model has no free parameters or fitting factors, only the rate constants for each of the individual reactions. The kinetic model has been improved and validated by extensive experimental efforts and is now used to guide the laboratory work.

An early approach which was investigated to control the partial oxidation process involved unconventional initiation of the chain reaction by laser irradiation or a plasma source. Subsequent work demonstrated that more effective control could be effected by conducting the process at high temperatures and unconventionally terminating the reaction by rapid expansion through a supersonic nozzle.

6. RESULTS/ACCOMPLISHMENTS:

During the course of the research effort, we have employed an integrated, multidisciplinary approach using state-of-the-art theoretical and experimental tools including computer kinetic modeling, fundamental kinetics measurements, theoretical rate constant calculations, bench-scale reactor experiments, and systems analysis. We have made significant advances in understanding the detailed chemistry of the reactive intermediates and of the possible reaction pathways under various conditions and have been able to specify the reaction parameters necessary to obtain high yields of methanol.

Major accomplishments to date include the following:

- Demonstrated scientific proof-of-principle by achieving 70% selectivity for methanol formation for 99:1 $CH_4:O_2$ mixtures.
- Developed a comprehensive kinetic working model with predictive capabilities and identified key reactions and reaction intermediates.
- Measured removal rate constants for methoxy radical interacting with O_2, CH_4, and a variety of unreactive gases over a wide temperature range.

- Developed a general procedure based on RRKM theory for calculation of rate constants of unimolecular reactions at high temperatures and pressures.

- Benchmarked the computer kinetic model against real experiments in a microprocessor controlled bench-scale static reactor.

- Predicted experimental conditions for high methane conversion (>25%) and high methanol selectivity (>50%) for single-pass conditions.

- Designed a high-temperature, high-pressure prototype of a pulsed-flow reactor based on results of hydrodynamic calculations.

- Fabricated, assembled, and began testing the bench-scale prototype reactor.

- Initiated discussions of collaboration and technology transfer with several U.S. industries.

A key accomplishment in the project has been the identification of experimental parameters to achieve high methane conversion while maintaining a high methanol selectivity. An extensive series of simulations was carried out for process conditions of 60 atmospheres with 25% initial oxygen, both at fixed (isothermal) temperatures and at various initial (adiabatic) temperatures. Some of the results are shown in Figure 1. Also shown in Figure 1 are 8, 10, and 12% yield contours; we consider a single pass yield of 8-9% to be a minimum acceptable for an industrial process. The 1000K isothermal simulation is very encouraging with a peak yield of 14.1% achieved at 29.9% methane conversion with a methanol selectivity of 47.3%. At slightly lower methane conversion (25%), the methanol selectivity is 51.6% for a predicted yield of 12.9%. Numerous other simulations were performed to determine the sensitivity of the overall yield to variations in pressure, temperature, methane/oxygen ratios, isothermal versus adiobatic conditions, added nitrogen, and seeding with a source of methyl free radicals.

Although the projected methanol conversion/selectivity per pass depicted in Figure 1 is most encouraging, it will be difficult to achieve an essentially isothermal reaction of a flammable methane/oxygen mixture at 1000K with rapid quenching prior to complete oxidation. It is possible that an adaptation of supersonic nozzle flow and expansion might provide the necessary technology. However, the funding available for the project would not allow the design and construction of such a supersonic reactor. Instead, it was

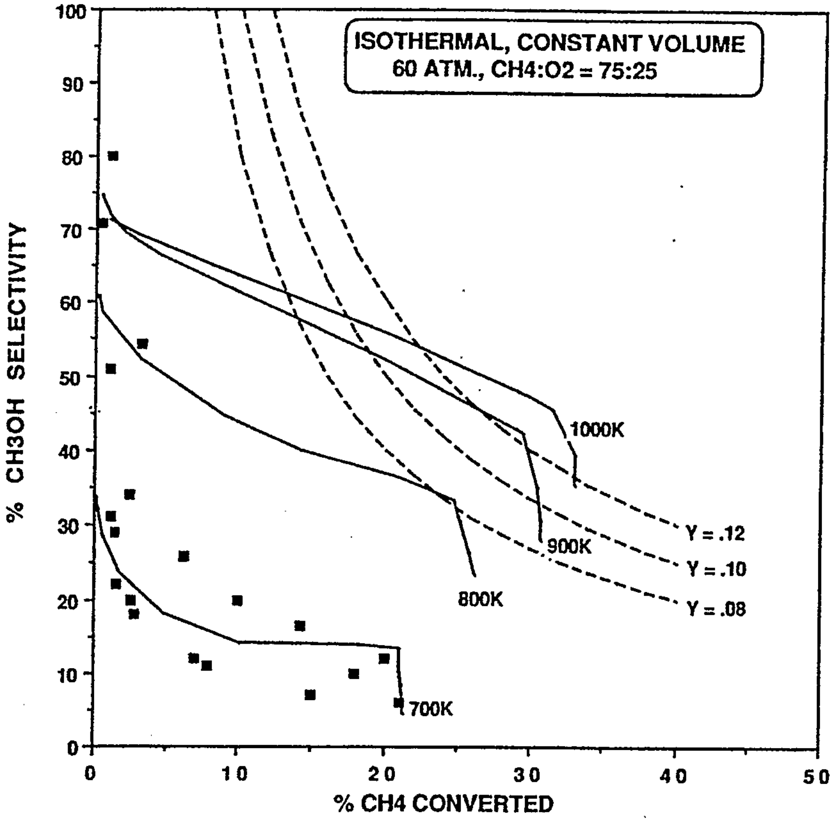

Figure 1. Kinetic model simulation of percent methanol selectivity versus percent methanol conversion at 1000K, 800K, and 700K for CH_4/O_2 = 75/25 at 60 atmospheres. The blackened squares are assorted literature data.

deemed desirable to demonstrate the validity of the model predictions at some yield value sufficiently removed from all previously reported efforts to engender interest from potential sponsors. For that purpose we envisioned a turbulent fast-flow reactor with free-jet expansion quenching at the end. Because the flow tube would not be isothermal, we wanted to achieve the highest yield possible prior to combustion. This required an allowance for a temperature rise of several hundred degrees before the expansion quenching. An adiabatic simulation with an initial temperature of 850K predicted that a yield of 8.3% with a 14.3% methane conversion and a methanol selectivity of 58% can be achieved when the temperature has risen to 1266K. Quenching must then be achieved on a millisecond time scale to prevent combustion.

Based on the results of the kinetic modeling described above and additional hydrodynamic model calculations, the design, construction, and assembly of a turbulent, pulsed-flow, bench-scale reactor was completed during FY88 and FY89. A schematic of the reactor design is shown in Figure 2. In this design, a 1-2 second duration pulse of high-pressure methane flows through a high-temperature reactor tube. During this transient methane flow, a pulse of oxygen is injected from a center-positioned coaxial tube. The partial oxidation chemistry that produces methanol occurs during residence in the tube and is subsequently quenched as the reaction mixture is expanded through the supersonic nozzle into a low-pressure "dump" tank. The reacted gases in the dump tank are analyzed using mass spectrometric and gas chromatographic techniques.

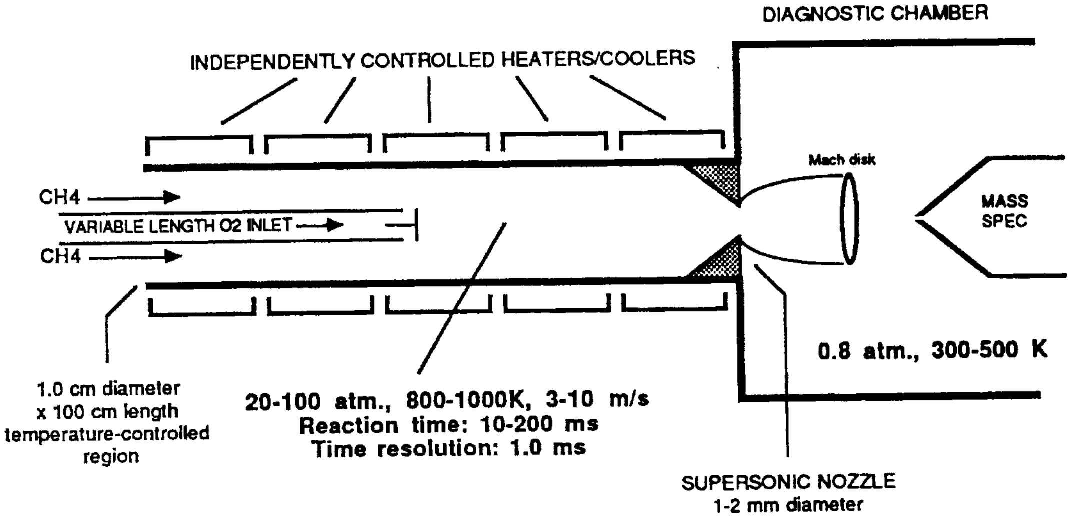

Figure 2. Schematic of reaction tube of pulsed, high-pressure flow reactor.

The methane and oxygen are introduced from separate preheated ballast tanks with solenoid-operated valves. The anticipated process conditions for this reactor are in the range 20-100 atmospheres and 800-1000K. The residence time of the reacting gases at process conditions in the tube is approximately 10-200 ms. The sizes of ballast tanks, tubing, valves, the supersonic nozzle orifice, etc., depend upon the parameters of pressure, temperature, pulse length, and throughput, and are based on a set of computer-generated relationships for the operating parameters and conditions of the reactor. Transient temperatures and pressures throughout the reactor tube are measured with fast-response thermocouples and pressure transducers. The timed operations of the valves and data logging of pressures and temperatures is computer-controlled using LabVIEW (National Instruments, Inc.) software on a Macintosh II personal computer equipped with a multi-channel 12-bit analog-to-digital converter. This computer is also used for data reduction, analysis, and display.

Preliminary experiments have begun to test and refine the system operation and to assess the heat transfer rates between the gas flow and the reactor tube wall. The results of these measurements will be compared to predicted transfer rates and will be used to determine the final configuration of the apparatus. For safety reasons, these preliminary experiments employ nitrogen, rather than methane and oxygen.

7. FUTURE WORK:

During FY89, emphasis will be focused on completing the fabrication, assembly, and testing of the bench-scale prototype of a pulsed-flow reactor. Experiments will be performed during FY89 and FY90 in the prototype to provide guidance for the design during FY90 of an advanced, supersonic, pulsed-flow reactor which will operate with a stoichiometric methane/oxygen mix within explosive limits. Concurrently during FY90, various options for increasing the conversion efficiency will be explored. These include, but are not limited to, (a) seeding the reaction with independently-generated free radicals, (b) using zeolite catalysts to convert the partial oxidation product mix to higher hydrocarbons, and (c) utilizing multistaging techniques. The advanced, supersonic reactor will be fabricated, assembled, and tested during FY90 and FY91 and methanol synthesis studies will be initiated in late FY91.

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OXIDATIVE COUPLING RESEARCH FOR THE CONVERSION OF NATURAL GAS TO LIQUID FUELS

1. CONTRACT NUMBER: 896/AB0520

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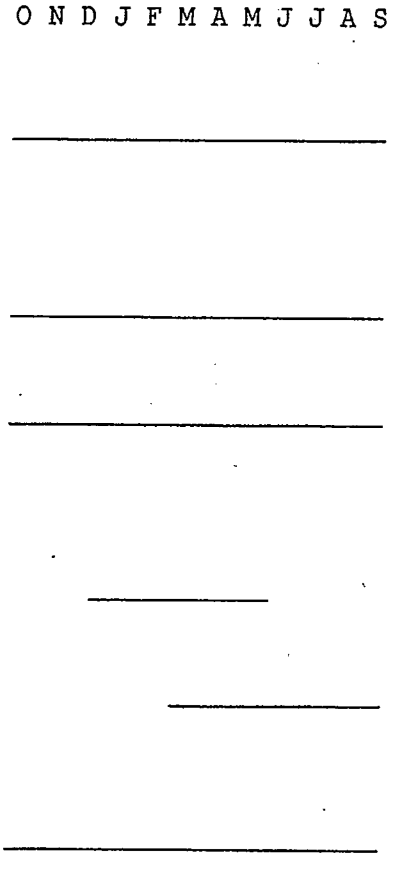
METC PROJECT MANAGER: Rodney D. Malone

CONTRACT PERIOD OF PERFORMANCE: October 1, 1988 through September 30, 1989

2. SCHEDULE/MILESTONES:

FY 89 Program Schedule



Catalyst Development/Testing:

a. Catalyst Preparation/Testing and Characterization

Reaction Mechanism/Pathways:

a. Surface (XPS) and Temperature-Programmed Studies

b. Surface Studies, Using Fourier Transform Infrared (FTIR)

Novel Concepts Evaluation:

a. Evaluation/Testing of Ceramic Membrane Reactor (CMR)

b. Barrier Catalyst Synthesis/Evaluation

Computer Modeling:

a. Synthesis/Evaluation of Numerical Integration/Implication

3. OBJECTIVES:

The overall objective of this project is to develop a process with a minimum level of complexity and acceptable rates of conversion and selectivity for the conversion of natural gas to liquid fuels. The specific objectives are (1) to prepare, test, and characterize new methane conversion catalysts; (2) to investigate the reaction kinetics in an effort to elucidate the overall mechanism; (3) to explore and develop novel concepts for the conversion of natural gas; and (4) to develop a model which is capable of predicting the optimum experimental conditions for maximum C_2+ (olefins) yield.

4. BACKGROUND:

Methane is the principal component of natural gas which is found in porous reservoirs generally associated with crude oil. Some of these abundant reserves of natural gas exist in locations too remote from market areas to be recovered on a commercial basis by present methods. A promising new methane conversion technology uses catalytic oxidative coupling as the first step in the process (Ekstrom and Lapszewicz 1988; Labinger and Ott 1987; Zang, et al. 1988). The oxidative coupling step converts natural gas to olefins which are subsequently converted to higher hydrocarbons (Jezl, et al. 1988). A key to developing this technology is optimization of the oxidative-coupling step, primarily via the use of novel catalytic materials. We have shown that by proper cation substitution in perovskite-type oxides, superior catalysts for the oxidative coupling of methane to higher hydrocarbons can be obtained (France, et al. 1988). Recent studies showed that gas-phase reactions, especially at higher pressures, play a significant role in the partial oxidation of methane (Yates and Zlotin 1988; Lane and Wolf 1988; Asami, et al. 1987). Furthermore, there appears to be a discrepancy between the results obtained by Ito, et al. (1985) and the results obtained by Yates and Zlotin (1988) for empty reactors. Therefore, in order to gain further insight into this catalytic and noncatalytic system, the oxidative coupling of methane was investigated under a wide variety of reaction conditions, both in the presence and absence of the perovskite-type oxide $La_{0.9}Na_{0.1}MnO_3$.

One of the most important factors which govern the catalytic oxidation process is the metal-oxygen bond strength (Kung 1986). For metal oxide catalysts, usually three different types of oxygen may be detected, namely, lattice oxygen, adsorbed oxygen, and absorbed oxygen (Seiyame, et al. 1985). These activated oxygen species have widely different properties in catalytic oxidation and can affect the activity of a particular catalyst. In the case of metal oxide catalysts, reactivity of these oxygen species depends largely upon the kind of component metal cation present. Therefore, a knowledge of the oxygen-sorptive properties of any metal oxide is essential for the understanding of a catalytic oxidation process.

Temperature-programmed desorption (TPD) is one of the techniques that can be used to obtain useful information on the existence of oxygen species in discrete states and/or over a broad distribution of energies (Seiyame, et al. 1985; Iwamoto, et al. 1978; Falconer and Schwartz 1983). Such information when combined with the results of catalytic reaction studies, carried out under identical conditions, can provide an insight into the catalytic oxidative conversion of methane to hydrocarbons. In this paper, we report the oxygen-sorptive properties of perovskite-type catalysts in relation to their catalytic activity and selectivity.

EXPERIMENTAL

The details of preparing the perovskite-type oxide, $La_{0.9}Na_{0.1}MnO_3$, have been reported elsewhere (France, et al. 1988). A laboratory-scale reactor system was used to evaluate the catalysts. A 0.235 m long downflow alumina reactor tube (9.53 mm o.d., 6.35 mm i.d., estimated heated volume 2.0 cm^3) with a quartz thermowell was used as a fixed-bed reactor with 0.5 g of catalyst (-28/+48 mesh) held in place by quartz wool. Electronic mass flow controllers were used to feed methane (99.99 percent), oxygen (99.8 percent), and helium (99.999 percent). The reactor was electrically heated to reaction temperatures under a flow of helium. All transfer lines and valves were 316 stainless steel and held at 423 K. Product analyses were performed by on-line gas chromatography (GC) and mass spectrometry (MS). The products were sampled but not analyzed until performance stabilized and this never exceeded 30 minutes. Samples were analyzed for carbon monoxide, methane, ethane, ethylene, propylene, propane, hydrogen, carbon oxides, formaldehyde, and water. A thermal conductivity detector was used with a 1 m x 3.2 mm o.d. stainless steel molecular sieve 5A column and a 3.7 m x 3.2 mm o.d. stainless steel Porapak Q (80/100 mesh) column at isothermal oven temperatures of 373 and 393 K, respectively. Results are reported on a carbon-mol percent basis (Table 1).

Temperature-programmed studies were performed by passing oxygen (99.8 percent) over the catalyst and raising the temperature from room temperature to 1,093 K with a heating rate of 0.08 K/sec and cooling the catalyst to room temperature under oxygen atmosphere. Any excess oxygen not consumed by the catalyst was then flushed out by using high purity He (99.999 percent). Oxygen desorption was performed by raising the temperature linearly (heating rate = .1 K/sec) with time and using high purity He (30 cm^3/min) as carrier gas. Products were analyzed by on-line gas chromatography (GC) and mass spectrometry (MS). The TPD chromatogram were obtained from the analysis of total ion chromatogram for m/e = 32 and it was plotted versus temperature. For the blank

Table 1. Comparison of Activity and Selectivity of Oxidative Coupling of Methane in the Presence and Absence of Catalyst at 1118 K, Alumina Reactor, $CH_4/He/O_2$ = 20/20/10 cm^3/min NPT Flow Rate.

	Conversion (mol %)		Selectivity (carbon-mol %)			
Catalyst/ Conditions	Methane	Oxygen	C_2H_4	C_2H_6	CO_2	CO
Empty, Contact Time 2.4 Seconds, 1 atm	29.9	62.9	19.0	5.7	8.8	66.5
Empty, Contact Time < 1 Second, 1 atm	1.0	0.5	34.8	51.5	1.2	12.5
Empty, Contact Time < 1 Second, 3.6 atm	18.5	37.7	21.8	12.4	8.9	56.9
$La_{0.9}Na_{0.1}MnO_3$, 0.5 g, Contact Time 0.4 Second, 1 atm	19.8	44.5	30.0	17.4	41.5	11.1
$La_{0.9}Na_{0.1}MnO_3$, 0.5 g, Contact Time 2.4 Seconds, 1 atm	37.2	85.1	36.6	13.7	43.2	6.5

experiment, where no catalyst was present in the reactor, no appreciable traces of oxygen were detected.

5. RESULTS:

CATALYST EVALUATION

The oxidative coupling of methane co-fed with oxygen was studied in an empty alumina reactor with and without dead volume (Table 1). The results showed that extensive conversion of methane and oxygen occurred in the empty reactor, especially at higher pressures and contact times. The heated volume of the reactor was estimated to be 2.0 cm^3 with a contact time of 2.4 seconds at maximum dead volume. However, as the contact time was reduced (< 1 second), by minimizing the dead volume in the reactor, the contribution from the gas-phase reaction was significantly reduced. Since we were not able to measure the exact volume of the reactor with the minimized dead volume, the contact time is reported as "< 1 second."

Pressure also appears to be an important factor affecting conversion and selectivity both in the gas phase and on the surface of the catalyst. For example, at 1.0 atm pressure and 1013 K (not shown in Table 1), about 1.5 percent of the methane and about 1.7 percent of the oxygen were converted to products (9 percent C_2H_4, 38 percent C_2H_6, 3 percent CO_2, and 49 percent CO) in the empty reactor (contact time = 2.4 seconds and $CH_4:O_2 = 2:1$). When the pressure was raised to 3.6 atm, the methane and oxygen conversions increased to 35.7 and 96.8 percent, respectively. The product distribution in this case was 11.2 percent C_2H_4, 4.6 percent C_2H_6, 15.8 percent CO_2, and 68.4 percent CO.

The effects of temperature and pressure on conversion and selectivity to C_2+ hydrocarbons, over a $La_{0.9}Na_{0.1}MnO_3$ catalyst, are shown in Figure 1.

At 3.6 atm pressure and temperatures below 1053 K, higher methane and oxygen conversions and higher selectivity to C_2+ hydrocarbons were observed compared to those at 1 atm. However, as the temperature increased the C_2+ selectivity at low pressure (1 atm) increased to a maximum value, while at the higher pressure the C_2+ selectivity slightly decreased. Furthermore, a higher molar ratio of $C_2H_4:C_2H_6$ was observed at higher pressure. In the presence of the catalyst, the major portion of the carbon oxides was carbon dioxide, indicating that the catalyst played a significant role in the reaction sequences and altered the product distribution.

The dependence of conversion and selectivity on the methane-to-oxygen ratio over $La_{0.9}Na_{0.1}MnO_3$ was also studied. Lower conversion of methane and higher selectivity to C_2+ hydrocarbons were obtained when the methane-to-oxygen ratio was raised to 5:1. This result indicates that methane and higher hydrocarbon products, at higher oxygen partial pressures and in the presence of the catalyst, were increasingly converted to carbon oxides (CO in the absence and CO_2 in the presence of catalysts).

Catalysts promoted with sodium pyrophosphate such as $Na_4P_2O_7/CaO$ and $Na_4P_2O_7/Gd_2O_3$ were also studied. These catalysts were also found to be active, selective, and stable for oxidative coupling of methane. The C_2 yields for these catalysts at 1101 K and $CH_4:O_2$ ratio = 2 ranged from 17 to 19 percent. Surface analysis indicated that phosphorous stabilizes the sodium on the surface and enhances the longevity of these catalysts without being consumed during the reaction (see posters for details).

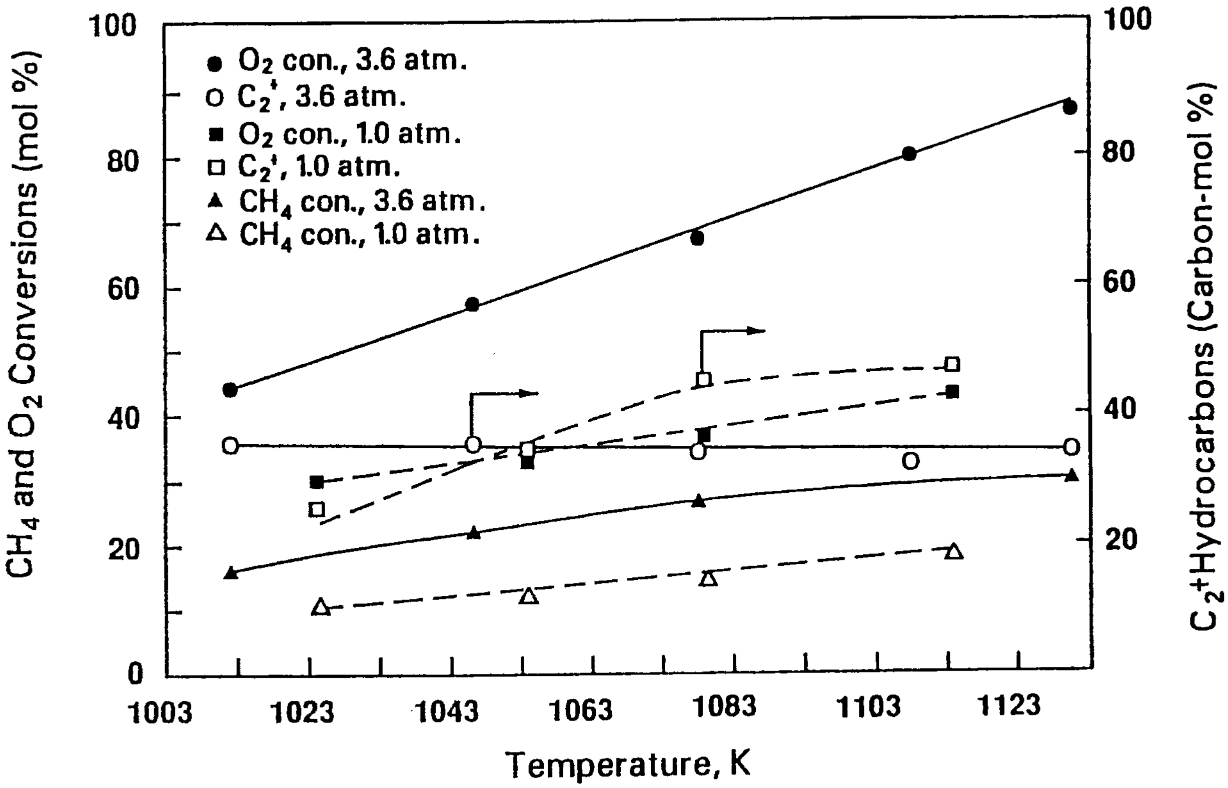


Figure 1. Dependence of Conversion and Selectivity on Temperature and Pressure Over $La_{0.9}Na_{0.1}MnO_3$: $CH_4/He/O_2$ = 20/20/10 cm^3/min NTP Flow Rates; Contact Time = 0.4 Second; 0.50 g Catalyst.

TEMPERATURE-PROGRAMMED DESORPTION

Temperature-programmed desorption studies on a series of perovskite-type catalysts with general formula $A_{1-x}B_xMnO_3$ (where A is Gd, Sm, La, or Ho, B is either Na or K and x = 0 or 0.1) were carried out and the temperature at which maximum oxygen desorbed (T_{max}) was correlated with the C_2 selectivity. The TPD chromatograms for oxygen desorption are shown in Figure 2 as plots of mass spectrometer signal (desorption rate) for oxygen (m/e = 32) versus temperature. All chromatograms are characterized by the appearance of two types of oxygen. The first type, (α)

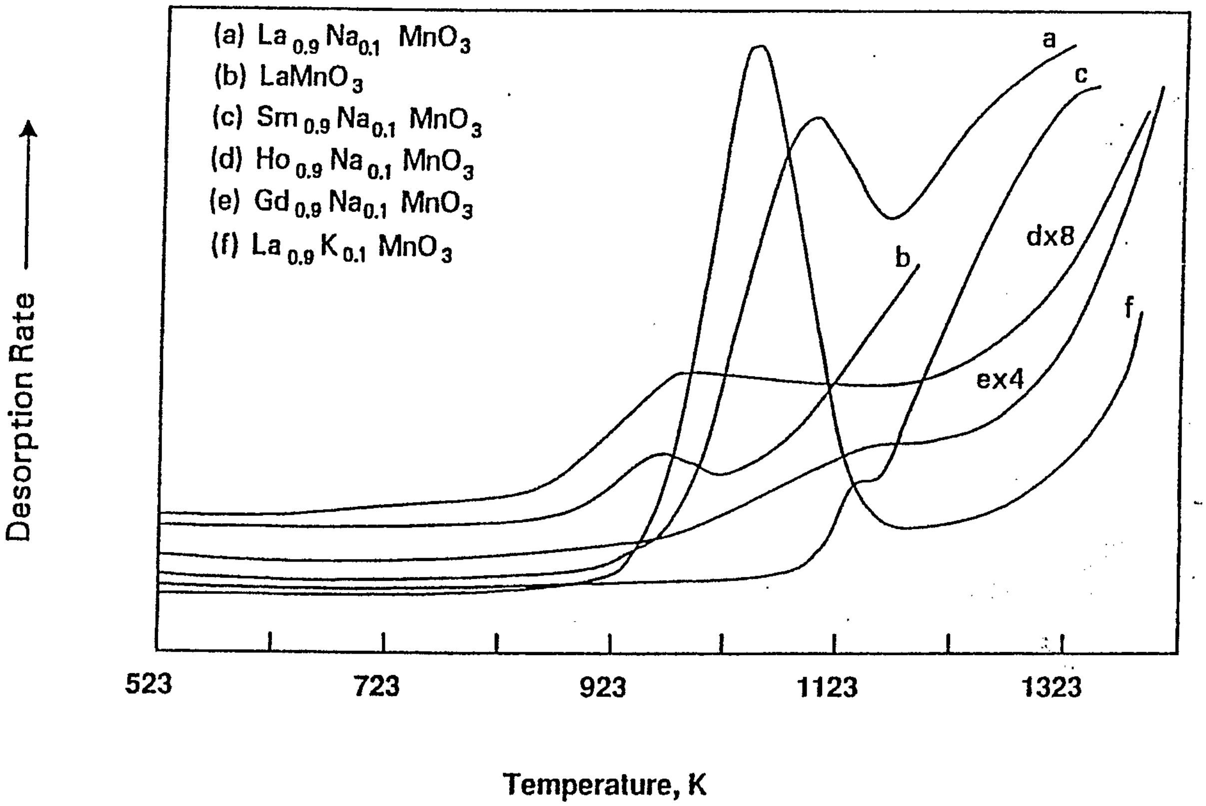


Figure 2. Temperature-Programmed Desorption of Oxygen (m/e = 32) from Perovskite-Type Catalysts; Heating Rate = 1 K/sec, He Flow Rate = 0.5 cm^3/sec, 0.25 g Catalyst.

oxygen, desorbs over a wide range of temperatures (900-1200 K), whereas the second type, (ß) oxygen, starts appearing after 1023 K. The values for T_{max}, corresponding to the maxima for (α) oxygen desorption, are plotted in Figure 3 along with the C_2 selectivities obtained in the earlier studies (France, et al. 1988[a] and [b]). T_{max} ranges from 1133 K for $Gd_{0.9}Na_{0.1}MnO_3$ to 968 K for $LaMnO_3$ and is sensitive to the presence of alkali metal ion B as well as to substitution at site A.

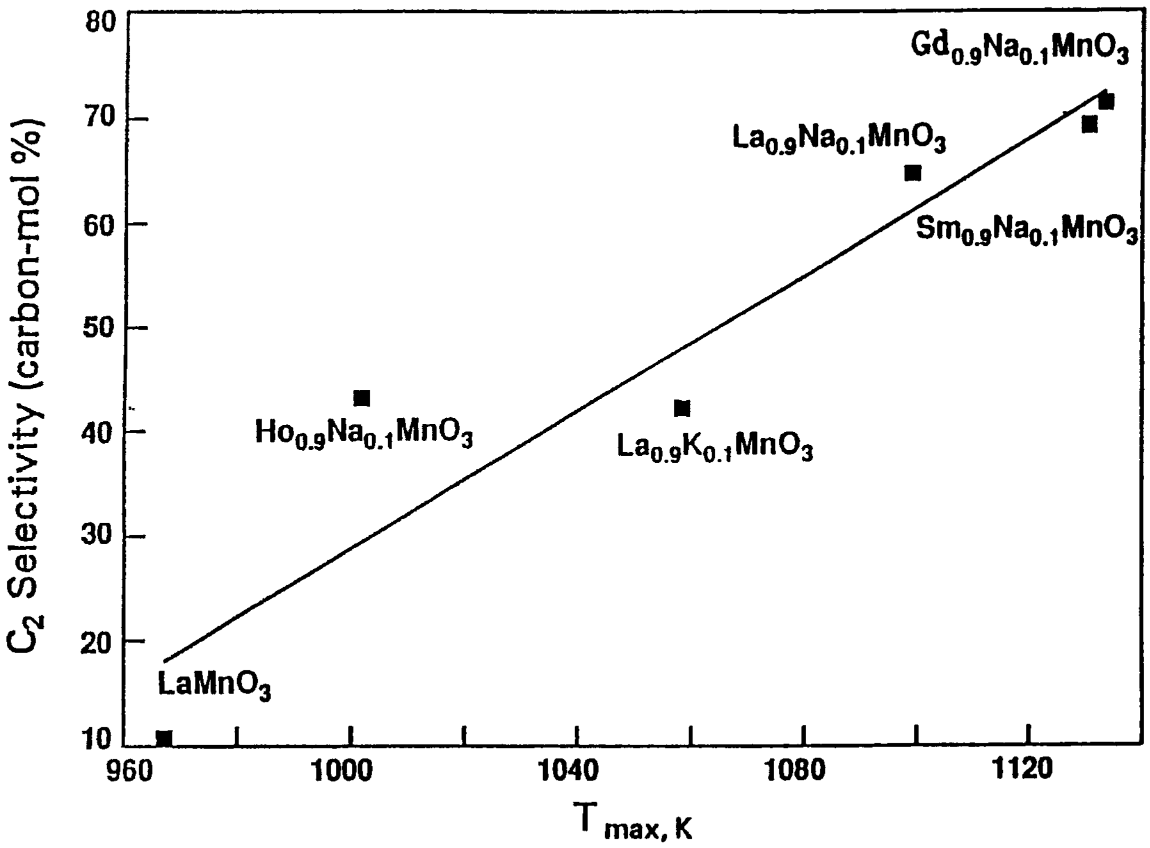


Figure 3. Correlation of C_2 Selectivity With the Temperature at Which Maximum O_2 Desorbed (T_{max}) from Perovskite-Type Catalysts; 0.25 g Catalyst Tested at 1093 K, CH_4/O_2 Ratio = 5.

The results presented in Figure 3 show that T_{max} for (α) oxygen desorption correlates very well with the C_2 selectivity. The catalyst with (α) oxygen desorbing at the highest temperature (1138 K) showed the highest selectivity for C_2 products whereas $LaMnO_3$ which desorbs oxygen at the lowest temperature (968 K) is the least selective for the conversion of methane to C_2 products. It is interesting to note that optimum conditions (higher C_2 selectivity) for conversion of methane over $La_{0.9}Na_{0.1}MnO_3$ catalyst correspond to the temperature (1093 K) which matches very nicely with the T_{max} for that catalyst. For the perovskite-type catalysts examined, it has been speculated earlier that the oxygen binding energy decreases in this order $(La,Na)MnO_3$ > $(La,K)MnO_3$ > $(La,[])MnO_3$ (Voorhoeve, et al. 1975). Present TPD studies provide an experimental basis for that trend in oxygen binding energies for these compounds and also similar information on other catalysts. For example, when comparing $LaMnO_3$ with $La_{0.9}K_{0.1}MnO_3$ and $La_{0.9}Na_{0.1}MnO_3$, it becomes apparent that it is the nature of metal-oxygen bond that controls the catalytic activity of oxide catalysts. Therefore, we suggest that in catalytic oxidation of methane to higher hydrocarbons, the most important factor may very well be the binding energy of oxygen to a surface site of the catalyst. This observation also agrees well with the earlier claim that some of the common selective oxidation catalysts (e.g., V_2O_3, MoO_3, and Bi_2MoO_6) did not contain weakly adsorbed oxygen (Iwamoto, et al. 1978).

CERAMIC MEMBRANE REACTOR STUDIES

A ceramic membrane reactor (CMR) has been constructed to evaluate new concepts which are based on solid oxide membranes that conduct only oxygen ions. This new technology may improve the selectivity and possibly minimize the separation/recycle requirements in the process. The membrane is made of zirconia stabilized with 8 mol percent yttria andthe catalyst can be embedded in a nonactive metal or affixed directly to the disk to serve as both a catalyst and electrode to enhance the methane conversion and selectivity to higher hydrocarbons.

MODELING

A phenomenological model program was conducted in parallel with the METC experimental program for the oxidative coupling of methane. The purpose of the modeling was two-fold: (1) to elucidate possible mechanistic aspects of the oxidative coupling reaction on metal-oxide surfaces, and (2) to guide experimental results by predicting the probable outcome of experimentation under as yet untried conditions. The model was fitted to actual data under various conditions of temperature and methane/oxygen ratios. The success of the model is exemplified by the excellent prediction of a nonmonotonic yield curve given only two end-point data sets as initial conditions. The optimum conditions for the modeled catalyst were determined as a function of temperature and methane/oxygen ratio (see posters for details).

6. SUMMARY AND CONCLUSIONS:

It has been shown that by proper cation substitution in perovskite-type oxides and by supporting sodium pyrophosphate on metal oxides ($Na_4P_2O_7$/Gd_2O_3 and $Na_4P_2O_7$/CaO) superior catalysts for the oxidative coupling of methane to higher hydrocarbons can be obtained. The results show that surface reactions are important in oxidizing the intermediates $CH_3\cdot$, C_2H_6, and CO to carbon dioxide.

It was found that contact time, temperature, methane-to-oxygen ratio, and pressure were the major factors affecting the conversion and selectivity in the presence and absence of the catalyst. Furthermore, the high activity observed by Yates and Zlotin (1988) for the empty reactor could be a result of the higher contact time and possible back pressure (caused by the capillary tube) when compared with the results reported by Ito, et al. (1985). The activation of methane occurred both in the gas phase and on the surface of the catalyst. In the gas phase, methane was possibly activated by diatomic oxygen. The oxidation of methane in the gas phase by diatomic oxygen has been discussed in other reports (Bone 1932; Walker 1975). The results also indicated that simultaneous operation at high pressure and temperature is a major problem, and, at these conditions, a significant amount of higher hydrocarbons are being converted to carbon oxides. Therefore, finding a catalyst that operates at lower temperature is more desirable.

The types of oxygen species on the surfaces of the catalyst responsible for activation of methane are not well defined. However, the activation of methane by surface oxygen species has been proposed by several researchers. Liu, et al. (1984) have shown O^- ions; Driscoll, et al. (1985) have proposed $[Li^+O^-]$ centers; and Otsuka and Jinno (1986) have proposed adsorbed diatomic oxygen, as being responsible for the activation of methane.

From the TPD studies, we can conclude that for the perovskite-type catalysts examined, a strong binding of oxygen to the surface site is essential to selectively produce C_2 hydrocarbons from methane as opposed to complete oxidation leading to undesirable carbon oxides. Present results suggest a possibility that TPD technique can be utilized to find more effective catalysts by selecting a proper combination of A and B site substitution in perovskite-type catalysts.

A phenomenological model, consistent with experimental results, was developed. The combined result, produced from minimal initial experimental data, was able to correctly predict the optimum conditions for maximum C_2 yield for the selected catalyst.

7. ACCOMPLISHMENTS:

- A series of perovskite-type catalysts and sodium pyrophosphate supported on metal oxides (e.g., CaO, Gd_2O_3) have been prepared/characterized and tested for their catalytic activity and selectivity.

- A ceramic membrane reactor (CMR) for evaluating new concepts has been constructed.

- A paper titled "Oxidative Coupling Research for the Conversion of Natural Gas to Liquid Fuels" was presented by A. Shamsi at the AIChE 1988 Spring National Meeting in New Orleans, Louisiana, March 6-10, 1988.

- A paper titled "Oxidative Coupling Research for the Conversion of Natural Gas to Liquid Fuels" has been published in Energy Progress, Vol. 8, No. 4, 185 (1988).

- A communication paper titled "Oxidative Coupling of Methane Over Perovskite-Type Oxides" by J. E. France, A. Shamsi, and M. Q. Ahsan has been published in Energy & Fuels, Vol. 2, No. 2, 235 (1988).

- A model which can predict the optimum experimental conditions for a maximum C_2 selectivity has been developed.

8. FUTURE WORK:

- Continue working on catalyst preparation, characterization (using XPS, AES, and FTIR), and testing.

- Study reaction mechanism to understand the chemistry of oxidative coupling reactions.

- Explore new concepts which may lead us to a new technology.

- Improve the existing model to include both gas-phase and surface reactions.

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ECONOMICS OF NATURAL GAS CONVERSION TO GASOLINE

1. CONTRACT TITLE: Natural Gas to Liquids Economics and Systems Analysis

CONTRACT NUMBER: PTPA 9-896

CONTRACTOR: Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507-0880
(304) 291-4546

PRINCIPAL INVESTIGATOR: Hsue-peng Loh

CO-INVESTIGATORS: Louis H. Berkshire
J. Christopher Ludlow

METC PROJECT MANAGER: Rodney D. Malone

3. OBJECTIVE:

The objective of the project is to perform an economic study of a plant converting natural gas to gasoline based on oxidative coupling chemistry and a fixed-bed reactor system. The result will also be presented with economics based on other process configurations.

4. BACKGROUND STATEMENT:

Utilization of natural gas has been discussed by Dautzenberg (1986) and Green (1988), and natural gas can be converted to a variety of products chemically, biochemically, thermally, or electrochemically. By far the most active recent research effort has been in the area of chemical conversion, particularly in processes using heterogeneous catalysis. The target products for these research efforts are gasoline and methanol because they are easy to handle and transport. Among chemical conversion pathways the process based on oxidative coupling chemistry is one of the most energy efficient. In the oxidative coupling reaction, oxygen reacts with methane to form ethylene, higher olefins, and higher paraffins. The most important products are ethylene and higher olefins because they are the precursors to motor fuels.

The oxygen required for this reaction can be supplied from two possible sources: the oxygen atom from the crystal lattice of the catalytic metal oxide or the oxygen molecule from oxygen gas or air fed along with the methane. The REDOX mode of operation occurs when the catalyst is reduced by giving up part of the oxygen that makes up a portion of its crystal lattice. The catalyst is later oxidized to the oxygen-rich state in a separate step by contacting the catalyst with air or pure oxygen. On the other hand, the reaction is in the COFEED mode if the oxygen is continuously supplied to the reactor as a gas with methane. The catalyst used in the COFEED mode is typically the same as the one used in the REDOX mode.

Loh conducted an economic study in 1987 for a natural gas-to-gasoline plant based on the REDOX oxidative coupling scheme. For that study, which was sited on the North Slope of Alaska, a series of fluidized-bed reactors were used. The study concluded that the selling price for the gasoline produced is currently uncompetitive with petroleum-derived fuel.

This paper discusses the economics and the technological aspects of a process based on the COFEED mode of operation using a fixed-bed reactor system. Again, siting is on the North Slope of Alaska. Results from this study are also compared with those based on other process configurations.

5. PROJECT DESCRIPTION:

Process Description of Fixed-Bed System -- COFEED Mode

The process studied is based on a fixed-bed reactor system and is shown in Figure 1. Oxygen from an air separation plant is catalytically reacted with natural gas at 1,500°F in a methane conversion reactor to form olefins and higher paraffins as well as three by-products: water, carbon dioxide, and carbon monoxide. Effluent gas is cooled in a waste heat boiler which generates high-pressure steam. The gas then enters a quench column which quenches it and removes by-product water. The by-product carbon dioxide is removed, and the remaining gas goes through an absorber-stripper system which removes unreacted oxygen and carbon monoxide from the gasoline precursors. These precursors are then fed into an ethylene conversion reactor which uses Mobil olefin to gasoline and distillates (MOGD) technology, a pilot plant-proven process, to form gasoline components. After the gasoline components are condensed as a liquid product, they are stabilized. The plant can produce various product slates between 10 percent gasoline/90 percent diesel fuel and 90 percent gasoline/10 percent diesel fuel.

The gasoline plant under study produces 50,000 barrels per day of gasoline and diesel fuel from natural gas (97 percent methane). The waste heat boiler generates part of the electricity required for the plant. The balance of the required electricity is generated on site by a natural gas-fired power plant. Total natural gas consumed (as raw material and fuel) is 480 million standard cubic feet per day (MMscf/d).

The catalyst used is a mixed oxide of lanthanum and manganese doped with sodium. The methane conversion is assumed to be 20 percent with

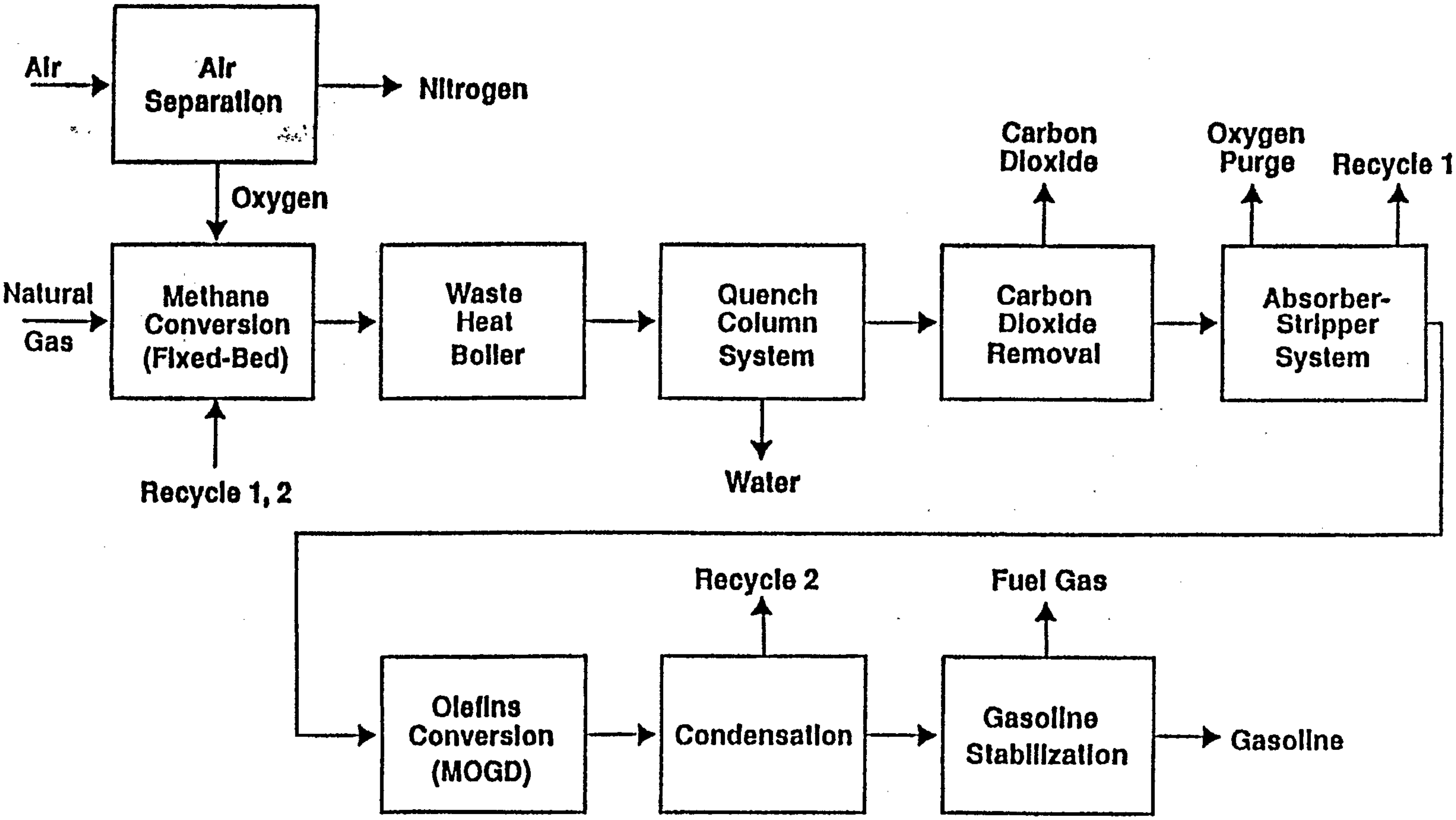

Figure 1. Natural Gas to Gasoline
(Based on Fixed-Bed Oxidative Coupling)

63 percent C_2 selectivity. These values are based on experimental results obtained by the Morgantown Energy Technology Center (METC) (France).

Comparison With Fluid-Bed System -- REDOX Mode

A study conducted previously at METC (Loh 1987) was based on the REDOX mode of operation with a fluidized-bed reactor system. Three major concerns surfaced as a result of this study. The first was the potential for catalyst attrition within the fluidized beds. The second was the possibility of short catalyst life. The third was the increased capital cost required by the fluidized-bed system. It was concern and uncertainty centering on these three questions that prompted the current study. The major features of COFEED-based and REDOX-based processes are listed in Table 1.

Table 1. Comparison of COFEED Mode and REDOX Mode

	COFEED Mode	REDOX Mode
Reactor System for Oxidative Coupling	Fixed Bed	Fluidized Bed
Capital Cost	Possibly Lower	High
Catalyst Attrition	Not Expected	Severe
Catalyst Life	Much Longer	Very Short
Catalyst Regeneration	Off-Line Operation	On-Line Operation
Source of Oxygen	Gas	Catalytic Metal Oxide
Air Separation Unit	Required	Not Required

6. RESULTS/ACCOMPLISHMENTS:

Product Quality

The anticipated gasoline produced via the COFEED oxidative coupling process is nearly identical to the high-octane unleaded gasoline currently available on the market and performs identically to petroleum-based gasoline. The distillate products (jet and diesel fuels) should have better burning quality and lower pour points than petroleum-based fuels. The low sulfur and aromatic content of the distillate make it a premium blending stock for jet fuel. The gasoline quality is shown in Table 2.

Capital Cost

The capital cost for the plant was estimated for both items of equipment and package units. For the sections of the process responsible for methane conversion, product gas quenching, ethylene conversion, gasoline

Table 2. Gasoline Product Quality

Research Octane	92	
Motor Octane	79	
Specific Gravity	.78	
Sulfur, Weight %	.002	
Bromine Number	4	
Pour Point	- 65°F	
Cumulative Distillation	20%	390°F
	50%	457°F
	90%	648°F

condensation, and gasoline stabilization, an equipment list was prepared. For these lists, each piece of equipment was individually sized and costed. For other sections such as the air separation plant, waste heat boiler, carbon dioxide removal, hydrocarbon absorber system, and electric power plant, capital cost was determined as a function of section capacity without detailed equipment specifications.

The capital cost was developed for a standard U.S. Gulf Coast location first, and a location factor of 1.9 was then used to determine the North Slope, Alaska, cost. The breakdown of the total installed cost is shown in Table 3.

Manufacturing Cost

Natural gas at the North Slope is primarily an associated gas that is produced along with crude oil. Since the state law prohibits the flaring of this gas into the atmosphere, the gas has in the past been compressed and reinjected into the oil reservoir for additional oil recovery. As the oil production at the North Slope peaks in 1989, the return on the gas compression cost in terms of additional crude oil revenue is expected to decline. Eventually, the produced natural gas will become a liability rather than a credit. With this liability in mind, a cost of $0.00 (zero) has been assigned to the natural gas feedstock. Other assumptions for determination of the manufacturing costs are listed in Table 4.

The calculated manufacturing costs are shown in Table 5. The capital recovery charge of $510 million includes return on equity, depreciation, and Federal income tax and amounts to 69 percent of the total manufacturing cost of $727 million. The high cost of the capital is not uncommon for a large-scale synfuel plant. The required selling price based on the financial assumptions listed in Table 4 is $44/bbl, free on board (F.O.B.), at the entrance to the Alaskan pipeline. The gasoline will be blended with crude oil at the pipeline entrance, pumped to the pipeline

Table 3. Capital Cost Estimation
(1988 Dollars)

Equipment/Section	Installed Cost ($ Million)	
Methane Conversion	91	
Quench Column	29	
Carbon Dioxide Removal	15	
Absorber-Stripper	40	
Olefins Conversion	53	
Gasoline Stabilization	5	
Air Separation Plant	124	
Waste Heat Boiler	45	
Power Plant	84	
Off-Site	250	
Total Installed Cost (TIC)	737	
Catalyst	14	
Contingency (15% of TIC)	111	
Working Capital (7% of TIC)	52	
Total Capital Requirement	914	(U.S. Gulf Coast)
Location Factor	x 1.9	
North Slope Cost	1,737	

Table 4. Financial Assumptions

Natural Gas Price	0 $/MMBtu
Equity	100%
Return on Equity	20%
Federal Income Tax	38%
Tax Credit	0%
Inflation	0%
Rate of Return	20%
Plant Life	20 Years
On-Stream Factor	330 Days/Year

Table 5. Annual Manufacturing Cost
(1988 Dollars)

	$ Million/Year
Natural Gas ($0.00/1,000 scf)	0
Raw Water	10
Annual Catalyst	14
Labor: Operating	24
Overheads	37
Maintenance	80
Local Tax and Insurance	52
Total Operating Cost	217
Capital Recovery (29.4% Capital Cost)	510
Total Required Selling Price	727

Service Factor: 330 Days/Year
Capacity: 50,000 bbl/d
Shipping/Processing: $20/Barrel

Gasoline Unit Price = $727,000,000 ÷ 330 ÷ 50,000
= $44/Barrel (F.O.B. North Slope)
= $64/Barrel (U.S. Gulf Coast)

terminal, barged to the U.S. Gulf Coast, and separated from the crude oil at a Gulf Coast location. The combined charge for shipping and processing is estimated to be $20/bbl. The required gasoline selling price at the Gulf Coast is $64/bbl. The $20/bbl charge is an estimate made three years ago based on then current market condition. It is believed that the charge could be significantly lower today.

Comparison of Capital and Manufacturing Costs

Results from the current study have been presented along side results obtained from the study by Loh in 1987 using REDOX oxidative coupling technology and more "conventional" steam reforming technology. This presentation is shown in Figure 2. Scheme A represents the current study, Scheme B is the REDOX oxidative coupling study conducted in 1987, and Scheme C is a commercially proven process. The differences between Scheme A and Scheme B were compared in Table 1. In Scheme C, natural gas is steam reformed, hydrogen shifted, synthesized to methanol by the low-temperature Imperial Chemical Industries (ICI) process, and finally converted to gasoline by the methanol-to-gasoline (MTG) process. Based on these three process schemes, three sets of economics have been generated. They are shown in Table 6.

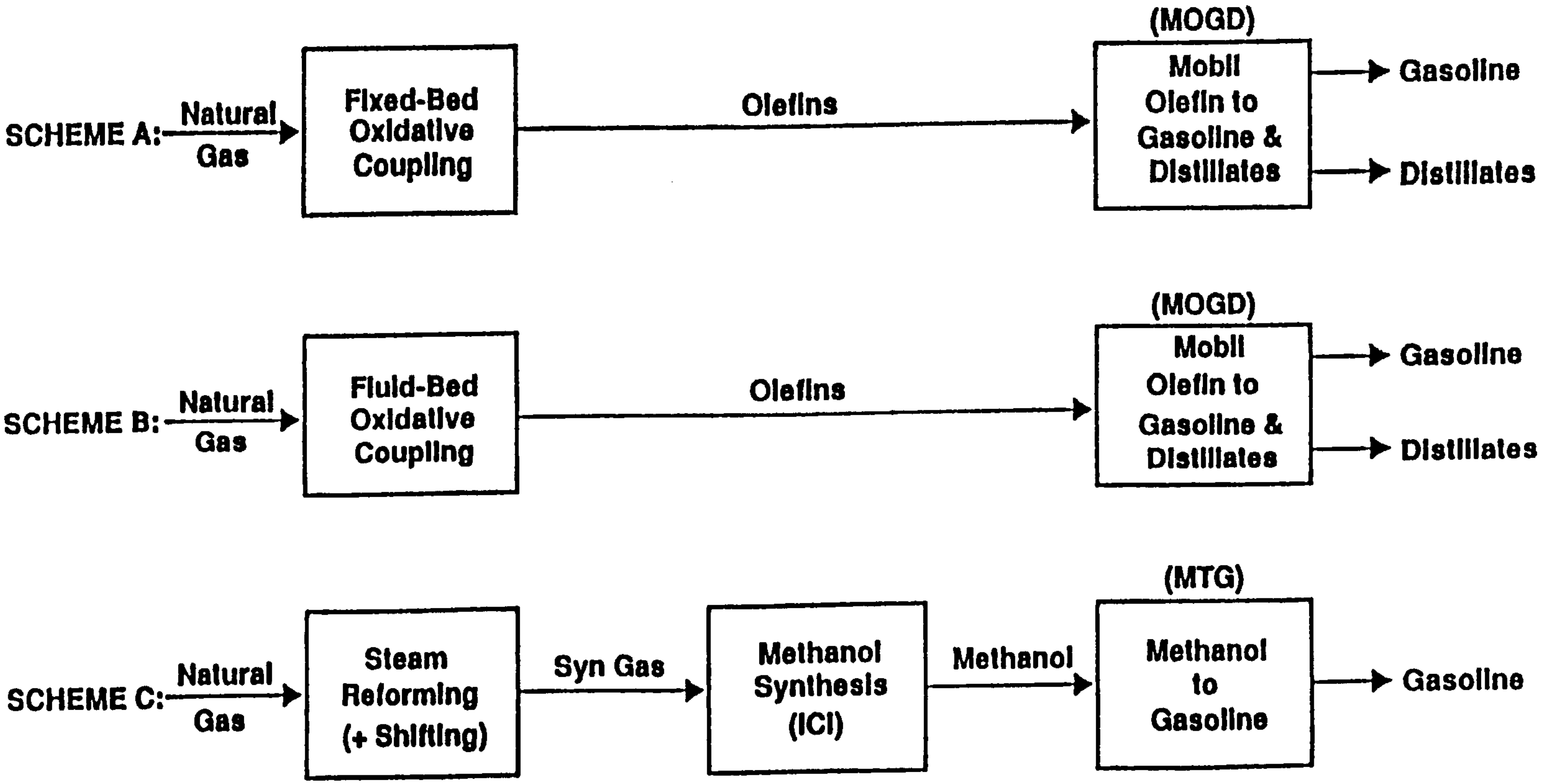

Figure 2. Natural Gas to Gasoline Process Options

Table 6. Results of Cost Estimation

Case	1	2	3
Process Scheme (See Figure 2)	A	B	C
Methane Conversion	Oxidative Coupling Fixed Bed	Oxidative Coupling Fluidized Bed	Steam Reforming
Plant Location	Alaska	Alaska	Gulf Coast
Capacity (bbl/d Gasoline)	50,000	50,000	10,700
Natural Gas Price ($/Million Btu)	0.0	0.0	1.65
Capital Cost ($ Million)	1,735	1,900	504
Capital Cost Per Unit Rate ($ Million/1,000 bbl/d)	35	38	47
Rate of Return (%)	20	20	10
Gasoline Price ($/bbl, Gulf Coast)	64	70	72

It is important to note that while an attempt has been made to present these systems on an equal basis, in some cases this has been impossible because the assumptions made are different. Therefore, extreme caution is needed in using the data in Table 6 for rigorous case-to-case comparisons. However, the cost data can be used to assess the state of oxidative coupling technology in general.

Both Case 1 (the current study) and Case 2 (Loh 1987) use oxidative coupling with a plant capacity of 50,000 barrels per day (bbl/d) of gasoline located on the North Slope of Alaska, and both have assumed zero cost for natural gas feed. Case 3 (Warren 1988) is based on commercially proven steam reforming technology and uses a natural gas cost of $1.65/MMscf/d.

The capital cost of Case 1 ($1,737 million) is lower than that of Case 2 ($1,900 million). The manufacturing cost for Case 1 is $64 per barrel of gasoline; the cost for Case 2 is $70. The manufacturing cost in both cases includes the production cost at the North Slope, the shipping cost to the U.S. Gulf Coast, and the processing cost at a Gulf Coast refinery.

Case 3 is a steam reforming system with $504 million capital cost and $72 per barrel gasoline price.

Discussion and Conclusion

The capital costs per production rates for the three cases are $35, $38, and $47 million per Mbb/d, respectively. The lower capital cost for Case 1 compared to Case 2 is attributed to the lower cost of the fixed-bed system and is expected. Note that the steam reforming-based (Case 3) cost is significantly higher than the cost for Cases 1 and 2.

The selling prices for the three cases are $64, $70, and $72 per bbl/d of gasoline, respectively. For Cases 1 and 2, the price includes shipping and processing. A reduction of $14/bbl selling price can be realized for Cases 1 and 2 if the rate of return is changed from 20 percent (as assumed in Table 6) to 10 percent. In other words, for the same 10 percent rate of return, the selling price will be $50, $56, and $70 per barrel for Cases 1, 2, and 3, respectively. Refiners have been selling gasoline at $25 to $30/bbl since 1986, though it approached $50/bbl in the early 1980's. The current selling price is $29/bbl. Based on these current and historical facts, it appears that gasoline production based on oxidative coupling technology will not be competitive until oil prices rise to levels higher than ever experienced to date. This suggests that a critical improvement is needed for oxidative coupling technology to become an economically viable alternative.

7. FUTURE WORK:

Future work will include identification of promising alternative reaction pathways and assessment of technical and economical feasibility of emerging technologies for conversion of natural gas to liquids.

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CATALYTIC CONVERSION OF LIGHT ALKANES

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Applied Research and Development Department
P.O. Box 1135
Marcus Hook, PA 19061

AUTHORS: James E.Lyons
Paul E. Ellis, Jr.
Vincent A. Durante

PRESENTER: James E. Lyons

2. SCHEDULE/MILESTONES:

This paper presents aspects of research on light alkane oxidation as a means of converting natural gas to liquid fuels which was carried out at Sun Company during the past three years.

3. OBJECTIVE:

The objective of the research to be presented in this paper is to develop new, efficient catalysts for the selective transformation of light alkanes to alcohols for use as fuels, fuel precursors and chemical products. As petroleum reserves dwindle, all hydrocarbon raw materials which could be converted to usable liquid fuels become more dear. Often the search for oil yields extensive gas reservoirs. The small aliphatic hydrocarbons present in natural gas are among the most refractory of organic substrates, yet among the most abundant and inexpensive. These substrates are also being generated in increasing amounts in refineries due to greater operating severity needed to process heavier crudes. There exist few processes for the efficient upgrading of these hydrocarbons to valuable products and no DIRECT one-step catalytic functionalization of these substrates to produce chemical or fuel products. Such a one-step route to fuels or chemicals would represent superior useful technology for the utilization of natural gas and similar refinery-derived light hydrocarbons streams.

4. BACKGROUND STATEMENT:

We have uncovered a new catalytic approach to the direct production of alcohols from light hydrocarbons which will impact this problem significantly. In this paper we discuss the nature of some new catalytic materials and the mechanism of their action specifically as it applies to the oxidation of isobutane and propane. Our approach grew out of the recognition that high oxidation state metal oxo complexes will react with alkanes to give alcohols under mild conditions. Iron oxo intermediates are, no doubt, involved in the enzymatic hydroxylation of C-H bonds in vivo (Cytochrome P-450). To date, no one has been able to synthesize these Fe=O species under mild conditions using ONLY molecular oxygen as the oxidant. Even nature requires the stoichiometric consumption of a co-reductant which donates the electrons and protons needed for closing the catalytic oxidation cycle. This stoichiometric requirement imposes severe and usually prohibitive constraints on commercial applications of such a catalytic process.

Conversion of methane to methanol, ethane to ethanol, propane to either acetone or isopropyl alcohol, butane to either sec-butyl alcohol or methyl ethyl ketone, and isobutane to tert-butyl alcohol have all been achieved in our laboratories. No expensive co-reductants are needed. This work represents the first selective liquid phase catalytic air oxidation of C_1-C_3 aliphatic hydrocarbons under mild conditions. Our catalysts have also been placed on suitable support materials or used directly as solid catalysts for vapor phase oxidation of methane to methanol, and natural gas to a methanol-rich oxidate.

5. PROJECT DESCRIPTION:

In order for commercially useful processes to be developed, increases in catalyst life, reaction rate and selectivity are required. An experimental program geared to the further improvement of these novel and potentially useful catalysts is underway. Using concepts generated during the initial research stage and described herein, together with advanced techniques of catalyst synthesis, we will prepare and test novel catalytic materials which are electronically tuned to provide superior results in the direct reaction of light alkanes to alcohols including the conversion of natural gas to a methanol-rich liquid oxidate. This program of work will involve nearly 100 man-months of chemist, engineer and technician manpower for a duration of 33 months.

6. RESULTS AND ACCOMPLISHMENTS:

ISOBUTANE OXIDATIONS

Azide Promoted Catalysts

It is believed that monooxygenase enzymes such as cytochrome P-450 catalyze the conversion of alkanes to alcohols through metal oxo intermediates (1). The high oxidation state metal oxo intermediates that are generated in the biological systems require stoichiometric consumption of two electrons and two protons, eq. 1. Most biomimetic analogs require oxygen atom transfer reagents such as iodosylbenzene (2,3), peroxides (4,5), hypohalites (6), or others (7-9) to generate the active metal oxo. The catalytic hydroxylation of alkanes using oxygen as the source of O-atoms has been accomplished with added co-reductants such as Pt/H_2 (10) or ascorbic acid (11). Recent work (12) has shown that a low oxidation state porphyrinatoruthenium complex can form metal oxo by direct reaction with molecular oxygen. This complex catalyzes the epoxidation of cyclooctene using O_2 and no added co-reductant (13).

$$\mathrm{Fe(II)} + O_2 + 2H^+ + 2e^- \longrightarrow \text{"Fe=O"} + H_2O \qquad (1)$$

We report results that demonstrate for the first time that that the first row azido(tetraphenylporphyrinato)metal(III) complexes: $M(TPP)N_3$ (M = Cr, Mn, Fe) are active catalysts for the selective formation of *tert*-butyl alcohol from isobutane and molecular oxygen at low temperature, Eq. 2, Table 1. These catalysts efficiently hydroxylate the alkane without the addition of stoichiometric co-reductants. In contrast to the catalytic activity of the first row metal azides, the chloro- or acetato(tetraphenylporphyrinato)-metal(III) complexes (metal = Cr, Mn, Fe) were found to be ineffective as catalysts for the low temperature oxidation of isobutane.

$$(CH_3)_3CH + {}^1/_2\, O_2 \xrightarrow{M(TPP)N_3} (CH_3)_3COH \qquad (2)$$

The azido(tetraphenylporphyrinato)metal(III) complexes (M = Cr, Mn, Fe) are more active than typical radical initiators or cobalt salts and have activity which is quite comparable to the highly active alkylperoxo[*bis*(pyridylimino)isoindolinato]cobalt(II) complexes (14,15), Table 2, which have been investigated recently. We have also found that azido[*bis*(pyridylimino)isoindolinato]-cobalt(II), $Co(BPI)N_3$, is of comparable activity to the alkylperoxo complex, $Co(BPI)OOBu^t$, but far more active than the acetate, Co(BPI)OAc. ($Co(BPI)N_3$ is prepared by reacting Co(BPI)OAc (17) with sodium azide in methanol. IR(KBr) shows the N-N stretch of the azide ligand at 2030 cm^{-1}).

In contrast to the first row azido(tetraphenylporphyrinato)-metal(III) complexes, the corresponding nitrides are not active under mild conditions, Table 1. In fact, it is possible to observe the transformation of the tetraphenylporphyrinatoiron-(III)azide, $Fe(TPP)N_3$, into the corresponding μ- nitride, $[Fe(TPP)]_2N$, in benzene using FTIR spectroscopy (17). The azide N-N stretch at 2050 cm^{-1} disappears and new bands at 920 and 870 cm^{-1} attributable to the μ-nitrido species appear. This may be a catalyst deactivation process. Whereas the μ-oxo diiron species, $[Fe(TPP)]_2O$, was active for autoxidation of allylic and benzylic C-H bonds, (18), it is not active for hydroxylation of isobutane at low temperatures. Thus, it would appear that any catalyst which is converted to this species loses activity for alkane hydroxylation.

Another deactivation process involves the oxidative decomposition of the porphyrin ring structure which can be followed by electronic absorption spectroscopy.

Table 1. Oxidation of Isobutane Catalyzed by Metalloporphyrin Complexes[a]

Catalyst	mmoles Catalyst	Catalyst Turnovers[b]	Selectivity To *tert*-Butyl Alcohol,%
Fe(TPP)Cl	0.025	0	-
Mn(TPP)OAc	0.050	0	-
Cr(TPP)Cl	0.025	0	-
$Fe(TPP)N_3$	0.013	130	93
$Mn(TPP)N_3$	0.013	180	88
$Cr(TPP)N_3$	0.025	280	89
$[Fe(TPP)]_2N$	0.013	0	-
Mn(TPP)N	0.025	0	-
Cr(TPP)N	0.013	0	-

[a] Isobutane, 6-7 g., was added to a solution of the catalyst in 25 ml benzene. The solution was stirred under 100 psig of O_2 at 80°C for 6 hrs. (O_2 added as used).

[b] Moles oxygen consumed/mole catalyst used.

7. CATALYSTS WITH FLUORINATED LIGANDS:

We have discovered that huge increases in catalytic activity for the reaction of isobutane with molecular oxygen to give *tert*-butyl alcohol, Eq. 1, are observed when the *meso*-phenyl groups in the porphyrin ligand are replaced by pentafluorophenyl substituents (19).

Oxidations of isobutane catalyzed by *tetrakis*(pentafluorophenyl)-porphyrinatometal(III) complexes, M(III)(TFPP)X (20), are summarized in Table 3. Increases in activity of more than an order of magnitude over the analogous tetraphenylporphyrinato complexes,

Table 2. Oxidation of Isobutane Catalyzed by Cobalt Complexes[a]

Complex	mmoles Catalyst	Catalyst Turnovers	Selectivity To *tert*-Butyl Alcohol,%
None	0	0	-
AIBN	1.00	5	78
	0.10	17	70
$Co(acac)_2$	0.100	52	89
$Co(acac)_3$	0.100	15	88
Co(BPI)(OAc)	0.025	24	88
$Co(BPI)N_3$	0.025	200	87
$Co(BPI)(O_2Bu^t)$	0.025	260	89

[a] Isobutane, 6-7 g., was added to a solution of the catalyst in 25 ml benzene. The solution was stirred under 100 psig of O_2 at 80°C for 6 hrs. (O_2 added as used).

M(TPP)X, are observed for the iron(III)TFPP chloride, azide and μ-oxide. On the other hand, both the μ-nitrido TPP and TFPP iron complexes are completely inactive for low temperature isobutane oxidation as are the corresponding manganese and chromium acetates and chlorides. It seems that in the case of manganese and chromium complexes, axial activation with azide is required for high activity even in the fluorinated systems. Fluorination of the *meso*-phenyl groups enhances the catalytic activity of the manganese and chromium azides, Table 3, but not as much as that of the iron azide.

Since $Fe(TFPP)N_3$ was such an active catalyst for the direct hydroxylation of an alkane with molecular oxygen, its activity was examined over a range of temperatures, Table 4. Room temperature hydroxylation of isobutane to *tert*-butyl alcohol could be achieved with a very high selectivity (94-95%). The iron catalyst retained good life and still had considerable activity after 24 hours at room temperature, Table 4.

Just as was found in the case of $Fe(TPP)N_3$ (21), the fluorinated complex, $Fe(TFPP)N_3$, could be converted to the μ-nitride, $[Fe(TFPP)]_2N$, by warming in benzene. This suggests a possible deactivation pathway. It is of particular interest that although the diiron TPP μ-oxo complex is not active, the fluorinated complex, $[Fe(TFPP)]_2O$, has high catalytic activity. No doubt, this point has significant mechanism implications and may be related to

Table 3. Oxidation of Isobutane Catalyzed by Metalloporphyrin Complexes[a]

COMPLEX	MMOLES COMPLEX	CATALYST TURNOVERS[b]	SELECTIVITY TO tert-BUTYL ALCOHOL[c],%
Fe(TPP)Cl	0.025	0	-
Fe(TFPP)Cl	0.016	2040	90
Mn(TPP)OAc	0.050	0	-
Mn(TFPP)OAc	0.016	0	-
Cr(TPP)Cl	0.025	0	-
Cr(TFPP)Cl	0.016	0	-
Fe(TPP)N_3	0.013	130	93
Fe(TFPP)N_3	0.016	2060	89
Mn(TPP)N_3	0.013	180	88
Mn(TFPP)N_3	0.016	750	87
Cr(TPP)N_3	0.025	280	89
Cr(TFPP)N_3	0.016	450	97
[Fe(TPP)]$_2$N	0.013	0	-
[Fe(TFPP)]$_2$N	0.013	0	-
[Fe(TPP)]$_2$O	0.013	0	-
[Fe(TFPP)]$_2$O	0.007	1730	92

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[a] Isobutane, 6-7 g., was added to a solution of the catalyst in 25 ml benzene. The solution was stirred under 100 psig of O_2 at 80°C for 6 hrs. (O_2 added as used).

[b] Moles oxygen consumed/mole catalyst used.

[c] (Moles *tert*-butyl alcohol produced/total moles liquid product) x 100. The only products detected were *tert*-butyl alcohol, acetone and CO_2.

Table 4. Isobutane Oxidations Catalyzed by $Fe(TFPP)N_3$[a]

REACTION TIME, HRS.	REACTION TEMPERATURE, °C	CATALYST TURNOVERS
6	80	2060
6	60	1050
6	40	470
6	27	54
24	27	440

[a] Isobutane, 6-7 g., was added to a solution of the catalyst, 0.016 mmole, in 25 ml benzene. The solution was stirred under 100 psig of O_2 at the designated temperature (O_2 added as consumed).

the high catalytic activity of the TFPP complexes. The hydroxo complex, Fe(TFPP)(OH), is also catalytically active producing over 1700 moles of tert-butyl alcohol per mole of complex used over a six hour period. Although somewhat more stable than the tetraphenylporphyrinato complexes, the tetrakis(pentafluorophenyl)-porphyrinato species are still too fragile for prolonged alkane oxidation at elevated temperatures.

PROPANE OXIDATIONS

We have shown that When the meso-phenyl substituents bear five fluorines, as in azidotetrakis(pentafluorophenyl)porphyrinatometal(III), $M(TFPP)N_3$, catalytic activity can be increased by more than an order of magnitude. Because of the unusually high activity of these complexes we were encouraged to attempt the catalytic oxidation of a more difficult secondary C-H bond. The substrate which we chose to study was propane. Propane is an interesting substrate not only because of the difficulty of C-H bond cleavage, but also because of the possibility of further oxidation of the alcohol, Eq. 3, produced. The ability to form either acetone or isopropyl alcohol allows us to examine another aspect of reaction selectivity not provided by hydroxylation of isobutane.

In this paper we report that: a) the tetrakis(pentafluorophenyl)-porphyrinatometal(III) complexes: Fe(TFPP)N_3, Fe(TFPP)Cl, and $[Fe(TFPP)]_2O$, are active catalysts for the selective conversion of propane to a mixture of isopropyl alcohol and acetone at temperatures as low as 100°C; b) the tetraphenylporphyrinato complexes, Fe(TPP)N_3, Fe(TPP)Cl, and $[Fe(TPP)]_2O$, on the other hand, are inactive below 125°C; and c) in contrast to their ability to catalyze isobutane hydroxylation, the analogous manganese and chromium complexes - M(TFPP)X and M(TPP)X (M = Mn, Cr; X = N_3,Cl) have little or no activity for propane oxidation below 150°C.

$$CH_3CH_2CH_3 + O_2 \xrightarrow{Fe(TFPP)X} CH_3CH(OH)CH_3 + CH_3C(O)CH_3 \qquad (3)$$

Table 5 shows the pronounced effect of the porphyrin ligand on the activity of iron(III)-catalyzed oxidation of propane in benzene at 125°C. The high activity of iron TFPP complexes for air oxidation is reminiscent of that observed for alkane oxidations using iodosylbenzene as the oxidant in which iron oxo species were implicated (19). It is of interest that the diiron μ-oxo complex, $[Fe(TFPP)]_2O$, has activity comparable to the chloride and the azide. It is likely that the μ-oxo species is a reactive intermediate in all cases and work continues in an attempt to demonstrate this unambiguously. Table 6 demonstrates that Fe(TFPP)N_3 has considerable activity even at 100°C, and appears to be more active in acetonitrile than in benzene. The activity of Fe(TFPP)N_3, though initially very high, diminishes with time. At 150°C the catalyst is nearly inactive after three hours whereas at 125°C there is still considerable activity after three hours. The loss of activity and the considerable bleaching of the catalyst after long times, especially at higher temperatures indicates that the fluorinated ligand, though far more oxidation resistant than TPP, is still subject to significant oxidative degradation and demetallation.

Table 5. Propane Oxidations Catalyzed by Iron(III) Porphyrin Complexes[a]

IRON(III) COMPLEX	CATALYST TURNOVERS	ISOPROPYL ALCOHOL/ ACETONE
$Fe(TPP)Cl$	0	-
$Fe(TPP)N_3$	2	na
$[Fe(TPP)]_2O$	0	-
$Fe(TFPP)Cl$	230	0.8
$Fe(TFPP)N_3$	330	0.8
$[Fe(TFPP)]_2O$	440	0.8

[a] Propane, 1.36 moles was added to benzene, 42.2 grams, containing the catalyst, 0.023 mmoles. The solution was stirred for 3 hours at 125°C under 1000 psig of air in a glass-lined autoclave. Liquids and gases were analyzed by gc. Production of carbon oxides never exceeded 5% of total products. Isopropyl alcohol and acetone exceeded 90% of reaction products in all cases.

Table 6. Propane Oxidations Catalyzed by $Fe(TFPP)N_3$[a]

REACTION TEMP.,°C	REACTION TIME, HRS.	CATALYST TURNOVERS	ISOPROPYL ALCOHOL/ ACETONE
150	1	490	1.1
100	3	30	0.6
125	3	330	0.8
125	3	250	0.9
150	3	620	1.0
150	3	870[b]	0.5
100	6	190	0.7
125	6	410[b]	0.7
125	7.5	430	0.8
150	7.5	640	0.8

[a] See Ref. [a], Table 5 [b] Reactions run in acetonitrile

THE ROLE OF THE FLUORINATED MACROCYCLE:

The fluorinated porphyrinic macrocycle may play several important roles in generating more stable and more oxidation active metal catalysts. These roles center about the strong electron-withdrawing character of the fluorinated ligands. The first effect may be to attract an electron and to stimulate the ejection of an X• radical to produce a reduced iron (II) species which can interact with molecular oxygen. More importantly, however, the fluorinated ligand will destablilize a diiron μ-oxo intermediate relative to its disproportionation to give a high-oxidation state Fe=0 complex. Fluorination of C-H bonds in the macrocycle will stablilize this very active Fe=0 species toward destructive oxidative degradation and allow it to survive to hydroxylate the alkane. Figure 1 presents a proposal of a possible reaction mechanism for the Fe(TFPP)X-catalyzed oxidation of an alkane to an alcohol.

We have generated <u>in situ</u> UV/VIS evidence that Fe(TFPP)X (X= N_3 or Cl) first forms the iron (II) species shown in Figure 1 which gradually is converted to the μ-oxo iron (III) form as reaction proceeds. Evidence from both crystal structure determination and from electrochemical experiments shows that the μ-oxo dimer should be far more prone to disproportionation to the active Fe=0 intermediate than is the un-fluorinated analog.

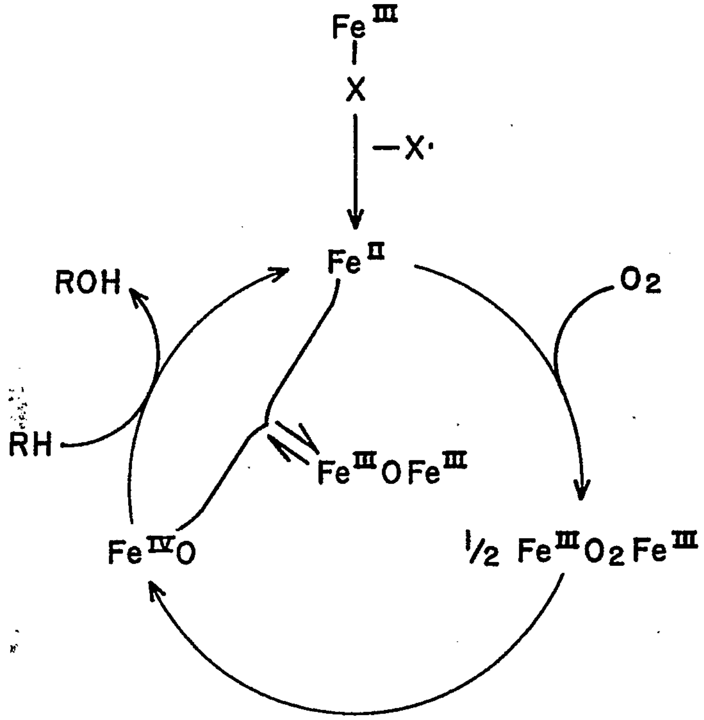

Figure 1. Proposed Mechanism for Suprabiotic Alkane Hydroxylation

POLYOXOANIONS AND HETEROPOLY ACIDS:

Having formulated the postulate that a stable electron-withdrawing macrocyclic ligand environment for oxidation-active first row transition metals could produce a catalyst active enough to hydroxylate a light alkane using only molecular oxygen and no co-reductant, we proceeded to make a large number of compounds having this characteristic. One such family of compounds is the framework-substituted polyoxoanions or heteropoly acids. Table 7 shows that using a silicotungstate ligand system for first row transition metal centers results in active isobutane oxidation catalysts. Table 8 demonstrates the enormously beneficial effect of azide ion on catalytic properties. The Keggin structure, Figure 2, is particularly suited for metal incorporation and gives an all-inorganic analog to the porphyrin systems. It also encouraged us to incorporate first row transition metals into solid inorganic structures and investigate alkane oxidation in the gas phase. We can now catalytically oxidize even methane in good (70%) selectivity to methanol using catalytic systems of this type.

8. FUTURE WORK

Future work is concerned with refining our understanding of the mechanism of these unique catalyst systems and in creating more active and more robust catalysts which can achieve commercially acceptable rates, yields and product selectivities.

Table 7. Isobutane Oxidations Catalyzed by First Row Transition Metal Centers in Polyoxoanions Having the Keggin Structure[a]

Complex	mmoles Catalyst	Catalyst Turnovers	Selectivity to *tert*-ButylAlcohol, %
$K_4SiMo_{12}O_{40}$	0.025	0	-
$K_6SiMo_{11}FeO_{39}$	0.025	70	86
$K_5SiMo_{11}CrO_{39}$	0.025	140	84
$K_6SiMo_{11}MnO_{39}$	0.025	0	-

[a] See Ref. [a], Table 1

Table 8. Effect of Azide on Propane Oxidation Activity of First Row Transition Metal Centers in Polyoxoanions Having the Keggin Structure[a]

Complex	mmoles Catalyst	Catalyst Turnovers	Isopropyl Alcohol/ Acetone
$K_3PW_{12}O_{40}$	0.025	> 20	na
$K_4PW_{11}CrO_{39}$	0.010	40	na
$K_5PW_{11}CrO_{39}N_3$	0.010	2290	1.0
$K_5PW_{11}VO_{40}$	0.010	60	na
$K_5PW_{11}VO_{40}N_3$	0.010	2090	0.8

[a] Propane, 1.36 moles, was added to a solution of the catalyst in a solution of aqueous acetic acid and o-dichlorobenzene (48 ml) which was stirred 3 hours at 150°C under 100 psig of air. Liquids and gases were analyzed by gc.

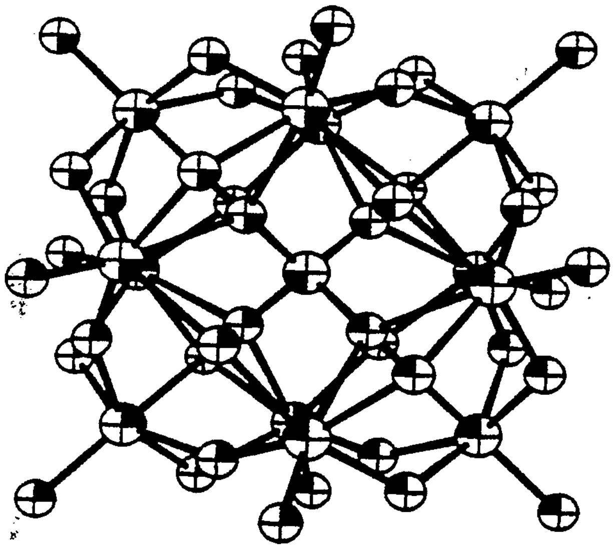

Figure 2. Polyoxoanion, $[PM_{12}O_{40}]^{-3}$, of the Keggin Structure

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DIRECT CONVERSION OF LIGHT HYDROCARBON GASES TO LIQUID FUELS

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Introduction

Significant amounts of methane and other light hydrocarbon gases (C_1-C_4) are produced in the indirect liquefaction of coal. Both gasification and Fischer-Tropsch (FT) synthesis give rise to C_1-C_4 byproducts. Current technology involves reforming these hydrocarbon gases to synthesis gas which is then recycled to the FT reactor for conversion to liquids. Reforming is an expensive process step. Higher thermal efficiency and reduced capital cost will be achieved if these by-product, light hydrocarbon gases can be directly converted to liquids. A brief summary of the objectives and accomplishments of the projects funded by the Department of Energy in the Indirect Liquefaction Program administered by the Pittsburgh Energy Technology Center will be provided in this report.

The conversion routes being investigated include the following:

1. Oxyhydrochlorination [1].
2. Oxidative Coupling [2].
3. Partial Oxidation [3].

In addition, a techno-economic assessment of the above routes has been performed. Exploratory studies on novel catalysts that can mimic enzymatic conversion of methane are being conducted.

Description of Projects

1. Project Title: Direct Conversion of Methane to Liquid Hydrocarbons through Chlorocarbon Intermediates

Organization: Pittsburgh Energy Technology Center

Investigators: C. E. Taylor and R. P. Noceti

Technical Approach: A novel combination of two existing process concepts has been examined and appears capable of producing higher hydrocarbons from methane with high yield and selectivity. Methane, oxygen and hydrogen chloride are reacted over an oxyhydrochlorination catalyst in the first stage to produce methyl chloride and water. In the second stage, the methyl chloride is converted to higher hydrocarbons, namely paraffins, olefins, aromatics, and cycloparaffins, over a zeolite such as ZSM-5. The final hydrocarbon mixture is largely in the gasoline (C_4-C_{10}) boiling range [1].

Accomplishments: The conversion of methane to chloromethane has been observed at 300-350°C, 0.1 MPa, and GHSV of 47-156. The reaction rate exhibited a marked temperature dependence, with a maximum at 345°C. This temperature is slightly below the eutectic melting point of the supported catalyst which consisted of 41.7% CuCl, 37.5% SiO_2, 11.5% KCl, and 9.4% $LaCl_3$. At temperatures above 350°C, a decrease of conversion was observed, probably owing to loss of active surface area. Methane conversion and polychlorination both decrease with space velocity. The conversion of chloromethane over ZSM-5 to gasoline-range hydrocarbons occurred under conditions comparable to those for the conversion of methanol (350°C, 1 atm). The ZSM-5 catalyst was stable under extended exposures to chloromethanes.

Investigations in progress seek to identify optimum operating conditions for both reactor stages. This information will be used for the design of a continuous, integrated, bench-scale system.

2. Project Title : Direct Conversion of Methane to C_2's and Liquid Fuels.

Organization : Union Carbide Corporation

Investigators : B. K. Warren, K. D. Campbell, J. L. Matherne, and G. L. Culp

Technical Approach: The strategy is 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 will be evaluated briefly during the contract. In addition, the development and economic evaluation of conceptual processes for converting methane to C_2's and C_2's to liquid fuels will be conducted.

Accomplishments: Several classes of catalysts have been evaluated [4] for the oxidative conversion of methane to C_2's. These include catalysts with metals in unusual oxidation or coordination states. C_2 selectivities as high as 74%, C_2 yields as high as 26%, and ethylene to ethane ratios of 5 to 20 have been obtained with one class of promoted metal oxide catalysts. UCC-A catalysts have long lifetimes (~ 300 h) if operated under the proper process conditions. Two mechanisms of catalyst deactivation were defined, and it was possible to design catalysts to avoid the first type of deactivation. A way to retard and/or reverse the second type of deactivation was discovered.

A first pass economic analysis (Case 1 study) of a process for oxidatively coupling methane to form heavier hydrocarbons, predominantly ethylene and ethane, has been completed based on selectivities in a

Phillips patent example [5]. The results of the initial analysis indicate that a commercial scale Methane Coupling Unit could produce ethylene at a variable cost of $0.0588 per pound, with a return on investment of 24% (after tax). Case 2 study will involve the conversion of methane to liquid fuels through intermediate light gases rich in C_2's (Case 1 integrated with MOGD).

3. Project Title : Direct Catalytic Conversion of Methane and Light Hydrocarbon Gases

Organization : SRI International

Investigators : R. B. Wilson Jr., Y. W. Chan, and B. Posin

Technical Approach : The goal is to convert methane and light hydrocarbon gases to intermediates such as olefins and alcohols that can be used in a subsequent conversion to give either motor fuels or petrochemical products as economics dictate. Two technical directions, both involving the development of supported organometallic catalysts, are being pursued. The first is to dehydrocouple the hydrocarbons to yield olefins, without coke formation. The second direction is to develop selective oxidation catalysts for the oxidation of the hydrocarbons to the corresponding alcohol. The catalysts are based on heterogenizing homogeneous catalysts that have been developed as models for oxygenase enzymes similar to those active in methanogenic bacteria. The catalysts are heterogenized by synthesizing the complexes within the pores of zeolites.

Accomplishments:

Novel supported organometallic Ru catalysts, on a variety of supports (alumina, 5A molecular sieves, Na-Y-Zeolite, or magnesia), were synthesized and tested for methane dehydrogenation. Three different sizes of ruthenium clusters: monomer(Ru), tetramer(Ru_4), and hexamer(Ru_6) were examined. Selectivities to hydrocarbons of upto 60% were observed with conversions of methane in the range 1 to 20% in the temperature range 600 to 750°C. The amount of coke retained on the catalyst varied with the support and the nature of the catalyst precursor.

Catalytic oxidation of methane with molecular oxygen was investigated in a fixed bed flow reactor with various anchored metal pthalocyanine (PC) and porphyrins as the catalysts. These supported organometallic species were stable at temperatures as high as 400°C. Methanol was formed from zeolite encased RuPC, CoTPP, and MnTPP at 375°C. In contrast, a PdPC complex attached to magnesia produced ethane rather than methanol. The other surface-supported catalysts gave carbon dioxide and water as the sole observable products (by GC).

4. Project Title : Direct Synthesis of Alcohol Fuels over Molybdenum-Based Catalysts

Organization : Lehigh University

Investigators : K. Klier and R. G. Herman

Technical Approach : To explore and develop novel multi-component catalysts for the conversion of light hydrocarbons to liquid hydrocarbon fuels. To examine the influence of additives to the feed such as chlorinated hydrocarbons on the product selectivity.

Accomplishments :

It was found that Pd/SiO_2 catalyzed the oxidation of methane under mild reaction conditions (375°C and 250 kPa). Reactions that were observed included the oxidation of methane to formaldehyde and the oxidation to synthesis gas. Methanol production was not observed over the present catalysts under the reaction conditions employed. For the oxidation of methane, the surface of the palladium catalysts exists in a partial oxidation state with an optimum amount of oxygen coverage. The selectivity to partial oxidation products is enhanced by the addition of a small amount of dichloromethane to the feed. The enhanced selectivity may be an ensemble-control effect caused by the partial coverage of the surface by chlorine. Addition of water to the reactants caused a similar behavior to be observed. However, passing too much dichloromethane or water over the catalyst results in greatly suppressing the overall catalytic activity. Higher temperatures would then be needed to observe appreciable methane conversion,but will result in a decrease of the selectivity to partial oxidation products.

The decomposition of methanol, a possible transient product of the methane oxidation reaction, was studied over Pd/SiO_2 in the temperature range of 150-375°C at 0.1 MPa and at 5.0 MPa. It was found that elevated pressure and gas flows decreased the rate of methanol decomposition. Thus, reaction engineering of the oxidation of methane over palladium-based catalysts should be carried out such that the yields of selective oxidation products can be enhanced by balancing the reaction temperature with surface reactant and promoter concentrations, reactor pressure, and reactant gas flow.

5. Project Title : Computer-Aided Molecular Design of Methane-Activation Catalysts

Organization : Sandia National Laboratories

Investigator : J. A. Shelnutt

Technical Approach : The objective is to develop a methodology for computer-aided molecular design of catalysts. Emphasis is on the design of biomimetic catalysts for alkane activation, with emphasis on methane-to-methanol conversion. The design activities are guided by structural and chemical information about naturally occurring biological catalysts such as cytochrome P450, methyl reductase, methyl transferase, and methyl monooxygenase. Specifically, cytochrome P450 carries out the hydroxylation of many hydrocarbons. The active site of P450 contains an iron porphyrin.Since the reaction occurs at ambient temperature and pressure, two one-electron reductions are required to activate O_2 resulting in the reactive intermediate, an oxo-iron(IV) porphyrin radical cation. (In high temperature direct conversion, a reductant is not required to activate O_2.) This intermediate then reacts with the bound alkane inserting the Fe bound oxygen atom in the alkane C-H bond, and regenerating the starting Fe(III)-porphyrin catalyst. The active Fe center in cytochrome P450 is embedded deep within the protein matrix. The active site also has, adjacent to the Fe porphyrin, a pocket of a size and shape suited for binding the substrate molecule. Having the active site buried deep in the protein provides selective access of the substrate molecule to the catalytic center, thereby preventing the oxidation of other system components, including P450 itself. This insures the stability of the catalytic system as a whole.

Accomplishments:

It has been demonstrated that an iron porphyrin will catalyze the hydroxylation of methane and ethane. In batch reactions, it was confirmed that methane, ethane and hexane are converted to the corresponding alcohols. The batch reactions were run under ambient conditions except that the gaseous hydrocarbons were run at elevated pressures to increase solubility. For simplicity in interpretation, the catalyst used in this work is not one of the designed catalysts, but a sterically unhindered one (Fe tetra(pentafluorophenyl) porphyrin). Iodosylbenzene was used as the oxidant. Hexane is hydroxylated at moderate rates (~9 catalyst turnovers/min for hexanols) to give mainly 2-, and 3-hexanol and some 1-hexanol and hexanones. Ethane is converted catalytically (~3 catalyst turnovers), but much less efficiently.

The product yields are much less than could be expected if a stable oxidant system could be found. The oxidant inactivation problem should be amenable to catalyst design efforts, since it is possible that a protected cavity can be devised which allows oxygen transfer from iodosylbenzene to the Fe, but which does not allow the active Fe-porphyrin intermediate to attack iodosylbenzene via the destructive pathway. Several designed porphyrins have been synthesized and are being tested for alkane activation activity.

6. Project Title : Direct Methane Conversion Process Evaluations

Organization : Bechtel National Inc.

Investigators : J. M. Fox, T. P. Cheng, and B. D. Degen

Technical Approach : The objective of this study is to compare direct methane conversion technologies using the same rigorous methods employed for the assessment of conventional technology. Three of the most promising new developments, selected in a screening study, have been subjected to evaluation. These are: (i) Oxyhydrochlorination [1], (ii) Partial Oxidation [6], and (iii) Oxidative Coupling [7]. Since the key issue is how these new technologies compare with conventional technology, costs of syngas based processes [8] have been adjusted to the same basis to provide this comparison.

Accomplishments :

The primary conclusion from this study is that direct methane conversion technology has the potential for a significant economic breakthrough provided improvements in selectivity and conversion are achieved. The direct conversion technologies considered in this study have yet to achieve this potential. The best of the three (oxyhydrochlorination) is competitive with synthesis gas based processing only when no differential contingency allowance is made.

Potential improvements in each of the cases have been identified and the ultimate potential of direct conversion technology has been examined by looking at a process with ideal selectivity and improved conversion. It is shown that breakthrougn economics (i.e. competitive with gasoline from $20/barrel crude oil) can be achieved if good selectivity can be achieved in a relatively uncomplicated process environment.

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