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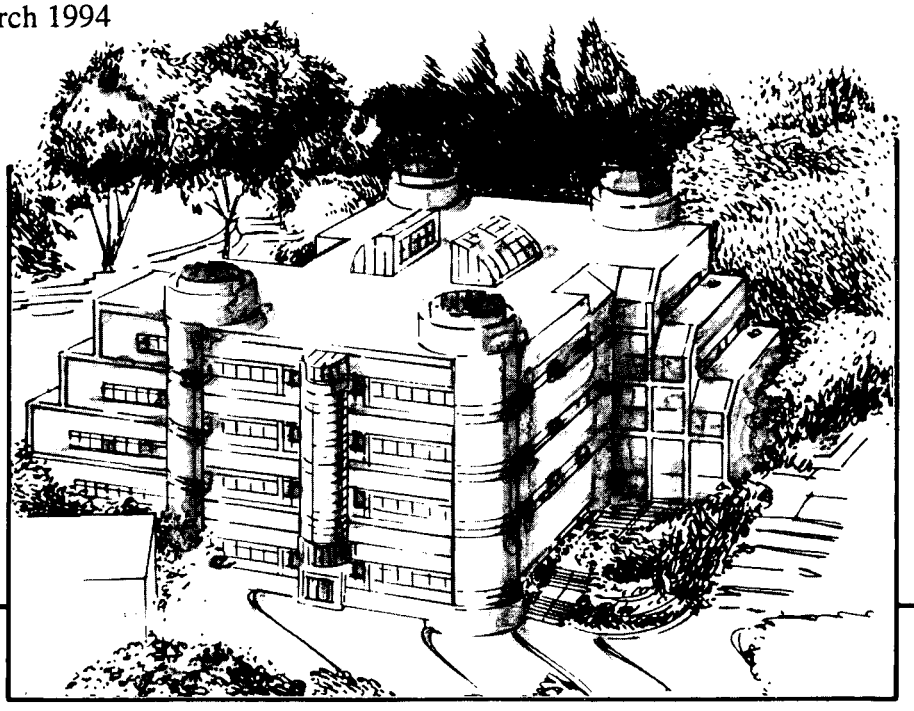
Fundamental Studies of the Mechanism of Catalytic Reactions with Catalysts Effective in the Gasification of Carbon Solids and the Oxidative Coupling of Methane

Quarterly Report

January 1–March 31, 1994

E. Iglesia, H. Heinemann, and D.L. Perry

March 1994



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QUARTERLY REPORT

January 1, 1994 to March 31, 1994

FUNDAMENTAL STUDIES OF THE MECHANISM OF CATALYTIC REACTIONS WITH CATALYSTS EFFECTIVE IN THE GASIFICATION OF CARBON SOLIDS AND THE OXIDATIVE COUPLING OF METHANE

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This work was supported by the Assistant Secretary for Fossil Energy, Office of Technical Coordination, U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Morgantown Energy Technology Center, Morgantown, West Virginia 26505.

TABLE OF CONTENTS

I. Task Description for FY1994

II. Introduction

III. Highlights

a) Catalytic Steam Gasification of Coals and Cokes

b) Oxidative Coupling of Methane

c) Synthesis and Characterization of Catalysts

IV. Progress of Studies

a) Catalytic Steam Gasification of Coals and Cokes

b) Oxidative Coupling of Methane

c) Synthesis and Characterization of Catalysts

ATTACHMENT: Slides: Keynote Address on "Reaction-Transport Models and the Design of Catalysts and Reactors for the Oxidative Coupling of Methane" by Iglesia and Reyes

I. Task Description for FY 1994

Task 1 - *Catalytic Steam Gasification of Coals and Cokes*: Work on the catalytic steam gasification of coals, chars, and petroleum coke will be phased out in 1994. Experimental work will be limited to a better understanding of the reaction of carbonaceous materials with steam in the presence of alkali introduced with the steam. A final report will be written, which will cover more than six years of research results.

Task 2 - *Oxidative Methane Coupling:* The CRADA between LBL and Orion ACT resulted in appreciable work and significant progress during FY1993. The positive effect of steam was recently shown to be a general phenomenon that applied not only to Ca-Ni-K oxides but also to several other widely studied oxidative coupling catalysts. Additional increases in ethylene and ethane yields will be pursued through the use of membrane and cyclic reactors. A membrane reactor has been constructed and proton-transfer membranes will be synthesized and tested in the oxidative coupling reactions. A unit is being redesigned to permit the testing of catalytic materials under cyclic condition, in which methane is sequentially decomposed and the reaction products scavenged by O_2, H_2, and hydrocarbons. Detailed fundamental models of chemical reactions and of reactor hydrodynamics in cyclic and membrane reactors will be developed and used in the design of concept demonstration tests.

Task 3 - *Synthesis and Characterization of Catalysts*: Detailed spectrographic and wet chemical analyses of fresh and spent catalysts have shown significant differences, which have permitted conclusions as to the sources of deactivation; this work will continue in FY 1994. In addition, pulsed laser deposition techniques have shown the ability to form stoichiometric mixed metals oxides; this technique will be exploited in the synthesis of catalytic materials and thin film membranes.

II. Introduction

Catalytic gasification work was completed during the second quarter of FY1994 with the completion of written reports describing research performed during the last several years. A graduate student has been trained in the operation of the membrane reactors and has begun experimental and theoretical work during the second quarter of

FY1994. Task 2 has operated without a post-doctoral fellow during the quarter while we await the arrival of Dr. S. Sundararajan, a recent graduate of Professor A. Datye's group at the University of New Mexico and an expert in the synthesis of thin metal oxide films for membrane and catalytic applications. The cyclic experimental unit has been plagued with analytical difficulties but preliminary results were obtained in the last two weeks.

III. Highlights

A keynote lecture was presented at the Symposium on Methane Conversion during the 204th Meeting of the American Chemical Society in San Diego, California on March 13, 1994. The subject was the design of reaction-separation schemes for the selective conversion of methane-oxygen mixtures to ethane and ethylene. A copy of the slides used is included as an Attachment to this Quarterly Report.

a) Catalytic Steam Gasification of Coals and Cokes

A final report has been written and forwarded under separate cover to Mr. Rodney Malone, Project Manager, Morgantown Energy Technology Center. This requested final report completes our activities in coal gasification for FY1994 due to the termination of financial support mentioned in the previous quarterly report..

b) Oxidative Methane Coupling

- High temperature densification under applied pressure in high-temperature dies has proven effective in the sintering of disks of stoichiometric metal oxide powders into pre-forms. These pre-forms have been successfully sliced into membranes of 0.5-1 mm thickness; they maintained the perovskite structure required for fast proton transport during the densification process. We have synthesized five different compositions of these proton-conducting mixed metal oxides with high bulk densities (83-94% of theoretical solid density values). Initial testing suggests that these membranes are free of percolation paths that would cause unwanted mixing of the methane and oxygen reactants present at each side of the disk in our membrane reactor.

- Initial experiments using a supported Ni catalyst for the cyclic partial oxidation of methane have demonstrated the experimental capabilities of the recently redesigned unit to characterize the metal surface area and to measure the ability of Ni to decompose methane at about 500°C to form surface CH_x species and to remove such carbon species with oxygen to form CO and CO_2. The objective of this work is to carry out the partial oxidation of methane to CO and hydrogen at temperature significantly lower than those used in non-catalytic thermal partial oxidation processes.

- Theoretical models of chemical reactions and of reactor-separator hydrodynamics have been developed and used to predict the benefits of reaction-separation schemes in increasing the yield of ethane and ethylene in oxidative coupling reactions. These models are also essential in guiding the experimental tests of these concepts in our laboratory reactors. Our research was recognized by the Keynote Address at the *Symposium on Methane Conversion* held during the *204th Meeting of American Chemical Society*.

- The correspondence between cyclic reactor operation and membrane reactors in separating hydrocarbons from oxygen temporally and spatially, respectively, has been demonstrated theoretically by an analysis of the reaction-transport equations describing both operating protocols. This treatment demonstrates the relationship between cycle frequency in transient reactors and membrane thickness in membrane configurations using similar materials.

c) Synthesis and Characterization of Catalysts.

- The initial studies of the morphology of calcium-nickel-potassium oxide films have been completed

- Research has begun on the use of the x-ray fluorescence microprobe at the Advanced Light Source at the Lawrence Berkeley Laboratory to study the homogeneity of these calcium-nickel-potassium samples.

-A journal paper describing the magnetochemical data for calcium-nickel-potassium oxide powdered catalysts is being prepared.

IV. Progress of Studies

a) Catalytic Steam Gasification of Coals, Chars, and Cokes.

The final report on this task has been completed and issued. No further work is planned in this area because of termination of financial support.

b) Oxidative Coupling of Methane

Mr. Richard W. Borry, a graduate student from the Chemical Engineering Department at the University of California at Berkeley, joined the group in January, 1994. A post-doctoral fellow will join this project at the end of April 1994.

Membrane Reactors

We have prepared five different membrane disks with x-ray diffraction patterns corresponding to stoichiometric compositions: $CaZr_{0.9}Y_{0.1}O_{2.95}$, $SrZr_{0.9}Y_{0.1}O_{2.95}$, $BaZr_{0.9}Y_{0.1}O_{2.95}$, $SrCe_{0.9}Y_{0.1}O_{2.95}$, and $BaCe_{0.9}Y_{0.1}O_{2.95}$. Membrane disks of 0.5-1 mm thickness are being tested in a single-pass flow reactor at 500-700°C using methane on one side of the membrane and a dilute oxygen stream in the opposite side. The combination of stoichiometric powder synthesis with high-temperature pressing of the samples into disks has overcome previous technical hurdles in the synthesis of defect-free membranes. This technique leads to disks with 83-95% of the theoretical bulk density for the corresponding composition. These high densities suggest that we have prepared for the first time sintered disks without significant residual voids, which would lead to gas percolation through the resulting diffusion channels and to loss of membrane selectivity for exclusive proton transport.

The ceramic membrane disks have proven susceptible to cracking during high-temperature catalytic reactions. These high temperature are required because proton conduction through these relatively thick membrane disks is slow at lower temperatures. We have taken two approaches at overcoming these hurdles. One is the use of slip casting

or laser ablation film deposition in order to decrease the thickness of defect-free membrane films. The other is to use recirculating gradientless membrane reactors instead of single-pass reactors in order to be able to obtain measurable methane conversion at lower proton fluxes available at lower temperature, where cracking of the membrane disks is less likely to occur. The latter approach allows demonstration of the concept using existing reactor capabilities and available membrane disks at lower temperatures; this approach is proceeding concurrently with the development of the new synthetic techniques.

Cyclic Methane Conversion Reactors

We are also studying an alternate method for preventing the full oxidation of methane during partial oxidation and oxidative coupling reactions of methane-oxygen mixtures. In cyclic membrane reactors, contact between methane and oxygen reactants is prevented by a temporal separation between methane and oxygen pulses, instead of the spatial separation achieved with membrane reactors.

Modifications of existing equipment to allow cyclic operations and in-situ catalyst characterization of the number of exposed metal atoms and of hydrocarbon and hydrogen species at the surface were completed after significant difficulties in the refurbishing of existing analytical equipment. This time-consuming effort was carried almost exclusively by project personnel in order to minimize external costs, but at a significant loss of research time for the personnel involved. It appears that these difficulties are now behind us. Initial results with supported Ni catalysts have proven their ability to decompose methane at around 500°C and the significant reactivity of the resulting hydrocarbon fragments in oxygen at 100-300°C. We are presently synthesizing and characterizing other supported metal catalysts and attempting to characterize the nature and reactivity of carbonaceous and hydrogen species on the surface of Ni catalysts.

Theoretical Descriptions of Reaction-Separation Schemes

Oxidative coupling reactions occur by complex reaction networks involving both gas phase and surface-catalyzed reactions. The design and testing of reaction-separation concepts to avoid deleterious full oxidation of reactive C_2 products to CO_x requires the development of detailed models. These models must combine credible simulations of these complex kinetics and also their equally complex interplay with the hydrodynamics of plug-

flow, backmixed, and recycle or membrane reactor. We have developed such models in order to predict the expected benefits of such reaction-separation schemes and in order to guide our laboratory experiments using membrane and cyclic reactors.

The details of the model structure, the simulation results, and the predicted benefits are described in the Attachment. Both hydrogen transport membranes and recycle reactors with separation of C_2 products from the recycled stream (Figures 1 and 2) achieve yields above 50%, in contrast with the best reported yields of about 20-25% at uneconomical conditions in cofeed tubular reactors. The simulations show that C_2 separation from the recycle stream increases C_2 yields by preventing secondary reactions that decrease the high initial selectivity to C_2 in oxidative coupling (Figure 2). This effect increases as we increase the recycle ratio in these reactors.

Interstage removal of C_2 products can be achieved using existing technology for low-temperature (cryogenic) separations or more desirably by the use of emerging technologies for chemical complexing, selective C_2 membranes, or absorption/chromatographic ethylene and ethane separation processes. Separation or protection of reactive C_2 products could also be achieved by the conversion of these C_2 products to less reactive or more condensable products using catalytic reactions that occur near oxidative coupling temperatures and which can convert C_2 to aromatic molecules. We are continuing to exploit this model to examine other novel schemes for increased yields as a useful complement to our experimental efforts in catalyst design and testing for membrane and cyclic reactors.

The detailed results of this research have been described in a manuscript that is in final review before submission to *Chemical Engineering Science*.

Time-Space Relationships in Cyclic and Membrane Reactors

We have developed rigorous descriptions of transient (cyclic) and membrane reactors in order to explore the relative advantages and disadvantages of their respective operation. We are presently examining the relationship between the time required to achieve a certain throughput in both types of reactors. This time requirements will ultimately determine the reactor and separation requirements in any commercial applications of the two approaches that we have proposed for selective synthesis of ethane and ethylene using oxidative coupling reactions. Our initial results demonstrate that there is clear mathematical and

physical correspondence between the spatial separation achieved in membrane reactors and the temporal separation achieved in cyclic reactors containing the same catalyst and diffuser as in the membrane reactors.

These results are being prepared for publication in *Industrial and Engineering Chemistry or Chemical Engineering Communications.*

c) Synthesis and Characterization of Catalysts

Initial studies have begun concerning the use of x-ray fluorescence probe approaches to look at the chemical composition, homogeneity, and spatial resolution of the elements in the calcium-nickel-potassium oxide film systems. This experimental system is capable of detecting elements at femtogram concentration levels in a solid matrix, while yielding micron-level resolution of the spatial distribution within the sample. Chemical defects and surface-bulk heterogeneity can be easily studied using this approach, with the investigator being able to observe these phenomena at concentrations lower than by any other available techniques.

In the case of a calcium-nickel matrix into which potassium is doped at a low concentration level, both calcium and nickel are observed to exist in equilibrium with one another in the surface plane but with various islands being present. Within these islands, both elements are shown to be in variable concentration with respect to the surface and with respect to other islands. This is presumably due to clustering effects of the elements during the condensation of the elements from the laser ablation plume that is generated in the process of forming the film. Alternately, the islands of segregation may also be due to point defects in the substrate onto which the filmed is formed.

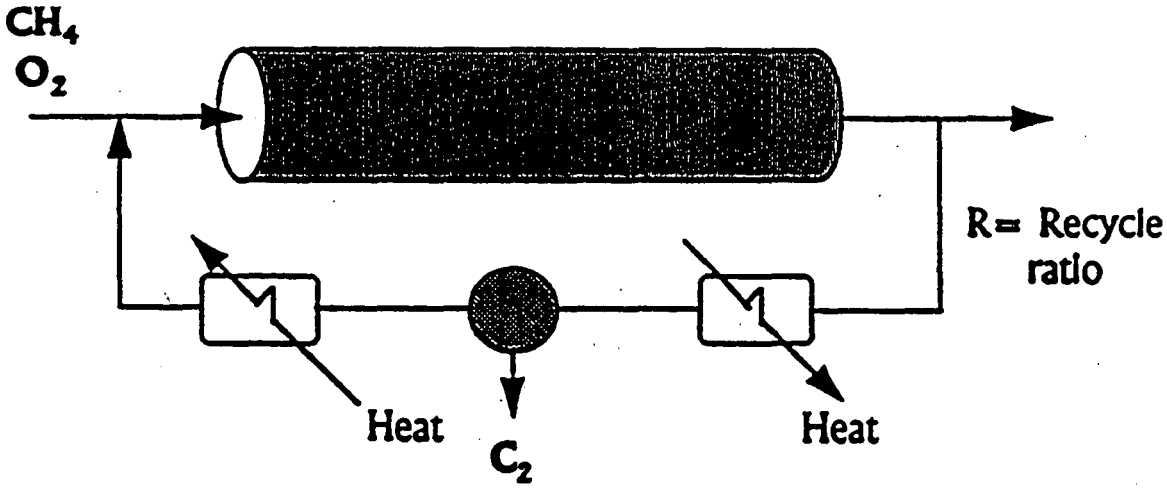


Figure 1. Schematic Diagram of a Recycle Reactor with Ethylene/Ethane Separation

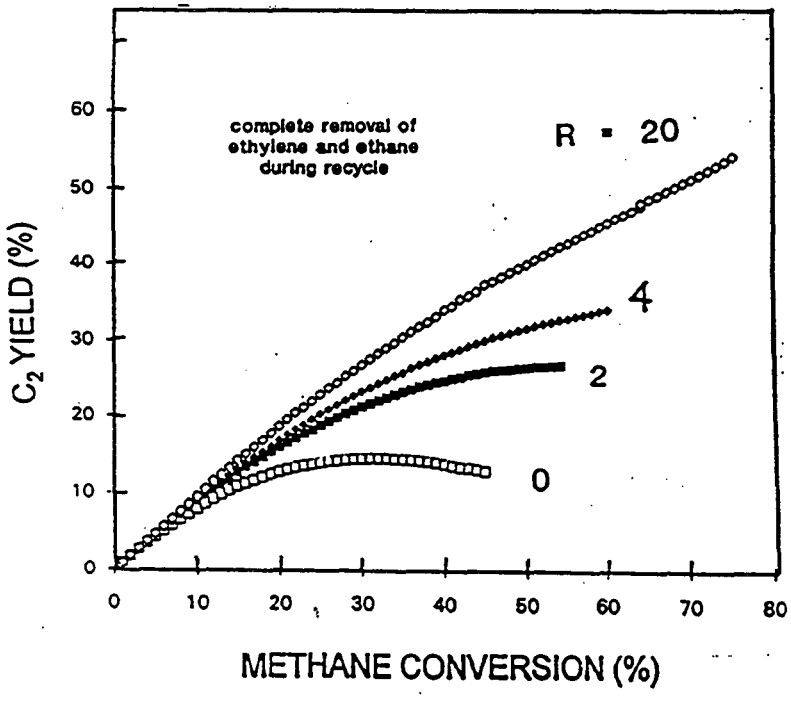


Figure 2. Effect of Recycle Ratio on C_2 Yields Attainable in Oxidative Coupling of Methane [Simulation results at 1073 K, 1 bar, and CH_4/O_2= 2.0]

ATTACHMENT

SLIDES PRESENTED AS THE KEYNOTE LECTURE

AT THE SYMPOSIUM ON METHANE CONVERSION HELD DURING THE

204th MEETING OF THE AMERICAN CHEMICAL SOCIETY

SAN DIEGO, CALIFORNIA

MARCH 13, 1994

TITLE

"Reaction-Transport Models and the Design of Catalysts and Reactors for the Oxidation and Coupling of Methane"

by

Enrique Iglesia and Sebastian C. Reyes

REACTION-TRANSPORT MODELS AND THE DESIGN OF CATALYSTS AND REACTORS FOR THE OXIDATIVE COUPLING OF METHANE

Enrique Iglesia

Department of Chemical Engineering
University of California at Berkeley

Sebastian C. Reyes

Corporate Research Laboratories
Exxon Research and Engineering Co.

Keynote Address: Symposium on Methane Activation
207th Meeting of the American Chemical Society
San Diego, California
13 March 1994

OXIDATIVE COUPLING OF METHANE TO ETHANE/ETHYLENE

$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]\,[O_2]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$

- Homogeneous kinetic network and reactors
- Homogeneous-Heterogeneous kinetics and reactors

- Staged injection of oxygen reactant along tubular reactors
- Membrane wall reactors for oxygen injection or hydrogen removal
- Intrapellet oxygen sieving by pore diffusion restrictions

- Interstage removal of ethylene/ethane along tubular reactors
- Recycle and backmixed reactors with reactive or adsorptive C_2 separation

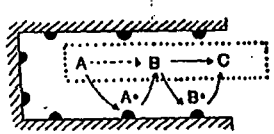
OXIDATIVE METHANE COUPLING..A BIMODAL HOMOGENEOUS-HETEROGENEOUS REACTION WITHIN POROUS SOLIDS

$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]\,[O_2]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$

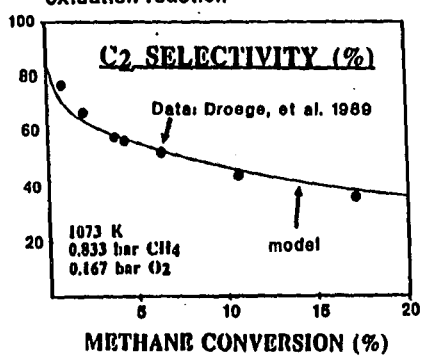
Increase rate of methyl radical generation

Inhibit secondary oxidation reaction

HOMOGENEOUS REACTION NETWORK

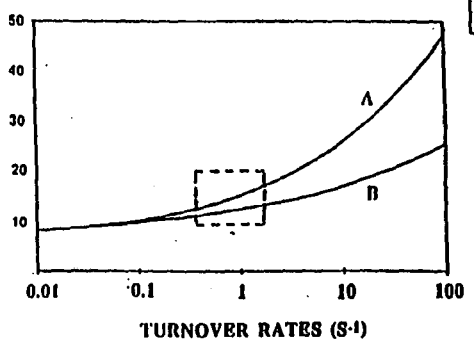


- 29 reactive species
- 145 reversible free-radical reactions with unadjusted literature rate constants



CATALYTIC SITES..... yield improvements require high site activity and selectivity

MAXIMUM C_2 YIELDS (%)



$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]\,[O_2]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$

A: sites activate only methane

$k_{C_2H_6}/k_{CH_4} = 0$

B: sites activate methane and

$k_{C_2H_6}/k_{CH_4} = 4$

- yields limited by homogeneous oxidation of reactive C_2 products ..... inhibited by lower O_2 concentrations

[1073 K, 1 bar, $CH_4/O_2 = 2.0$]

OXIDATIVE COUPLING OF METHANE TO ETHANE/ETHYLENE

$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]\,[O_2]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$

- Homogeneous kinetic network and reactors
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- Staged injection of oxygen reactant along tubular reactors
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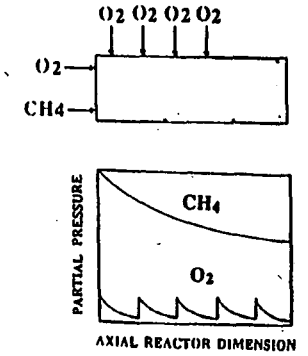
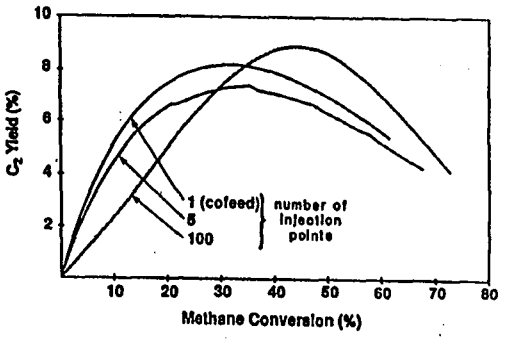
- Interstage removal of ethylene/ethane along tubular reactors
- Recycle and backmixed reactors with reactive or adsorptive C_2 separation

STAGED OXYGEN INJECTION -- HOMOGENEOUS REACTORS

- control oxygen concentration while supplying stoichiometric oxygen requirement

$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]\,[O_2]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$



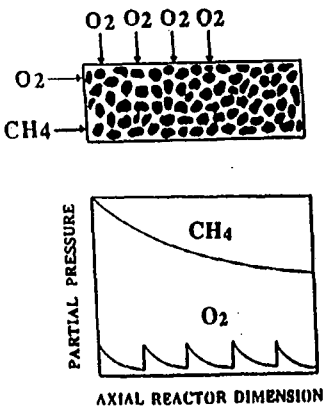


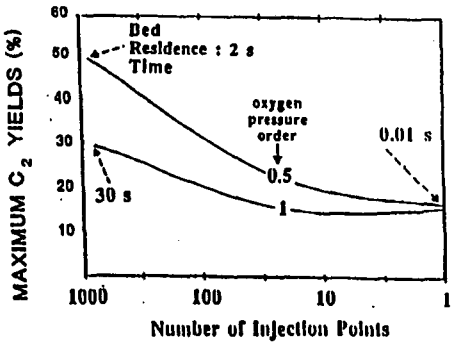
[1073 K, 0.5 bar CH_4, total reactant supply (CH_4/O_2)=1.0]

- but requires larger reactor volumes and low O_2 kinetic order for heterogeneous methyl radical generation step

STAGED INTRODUCTION OF STOICHIOMETRIC OXYGEN REACTANT INCREASES C_2 YIELDS .....

$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$





decreasing oxygen concentration

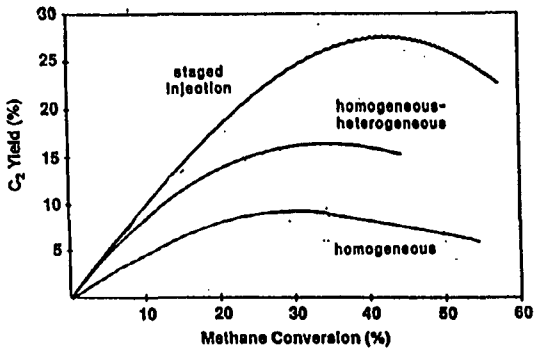
YIELD LIMITATIONS IN OXIDATIVE COUPLING OF METHANE

$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]\,[\ddot{O}_2]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$

Increase rate of methyl radical generation

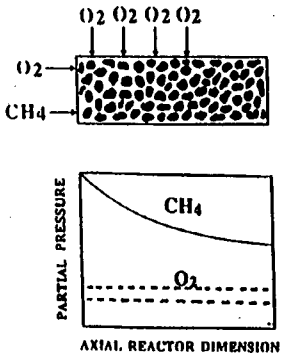
Inhibit secondary oxidation reaction

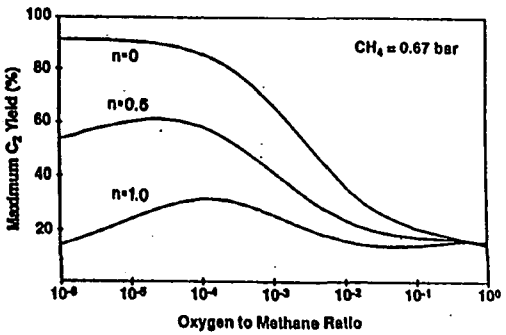
- catalytic methyl radical generation
- staged oxygen injection and membrane reactors
- intrapellet oxygen sieving



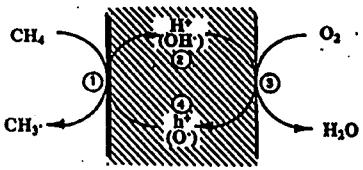
MEMBRANE REACTORS .....require very active sites and low heterogeneous kinetic order in oxygen

$$CH_4 \xrightarrow[{[\bullet]\,[\Delta]}]{[CH_3]\,[\ddot{O}_2]} C_2 \xrightarrow[{[\bullet]\,[\Delta]}]{[O_2]} CO_x$$





CATALYTIC MEMBRANE REACTORS USING PROTON CONDUCTORS



REACTION/TRANSPORT PATHWAYS

1. H Abstraction from CH_4 by Surface O^-.
   - $CH_4 + O^- \longrightarrow CH_3^{\cdot} + OH^-$
2. Proton (H^+/OH^-) Transport Across Membrane.
   - Flux = $-D_{H^+}(\Delta[H^+]/\Delta x)$
3. O^- Regeneration by O_2.
   - $2\,OH^- + 1/2\,O_2 \longrightarrow 2\,O^- + H_2O$
4. Hole (h^+/O^-) Transport Across Membrane.
   - Flux = $-D_{h^+}(\Delta[h^+]/\Delta x)$

MEMBRANE MATERIALS

- known materials with high proton mobility and low oxygen ion conductivity at 600-700 C

$SrM_{0.9}Yb_{0.1}O_{2.95}$

M = Ce, Zr

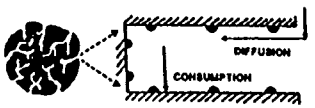
[Iwahara, et al. Solid State Ionics 18/19 (1986) 1003]

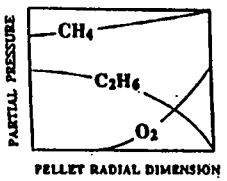
with H. Heinemann, R.W. Borry, and D.M. Ginter

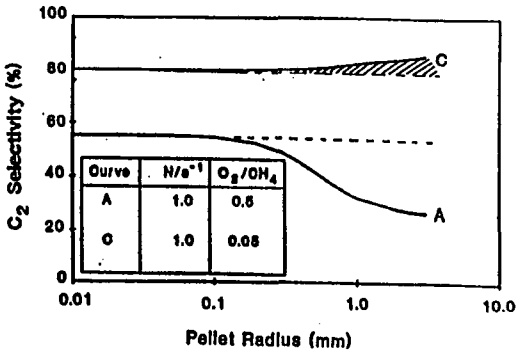
C_2 REMOVAL LIMITS POTENTIAL BENEFITS OF INTRAPELLET OXYGEN SIEVING

- staged injection reactors required to avoid deleterious effects of severe transport restrictions

DIFFUSION-LIMITED PELLETS







Curve	N/s^{-1}	O_2/CH_4
A	1.0	0.5
C	1.0	0.05

[1073 K, 1 bar, CH_4/O_2 = 2.0]

OXIDATIVE COUPLING OF METHANE TO ETHANE/ETHYLENE

$$CH_4 \xrightarrow[{[*]\,[\Delta]}]{[CH_3]\,[O_2]} C_2 \xrightarrow[{[*]\,[\Delta]}]{[O_2]} CO_x$$

- Homogeneous kinetic network and reactors
- Homogeneous-Heterogeneous kinetics and reactors

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- Interstage removal of ethylene/ethane along tubular reactors
- Recycle and backmixed reactors with reactive or adsorptive C_2 separation

SIMULATION CONDITIONS

REACTOR: total CH_4/O_2 ratio = 2.0

1 bar total pressure

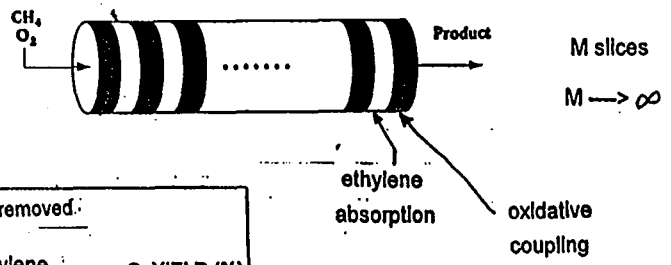
1073 K

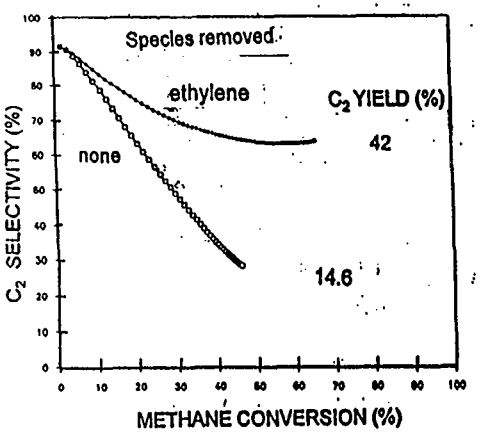
CATALYST: Turnover Rate = 1 s^{-1}

k_{C2H6}/k_{CH4} = 0.4

n = 0.5 (kinetic oxygen order for heterogeneous radical generation step)

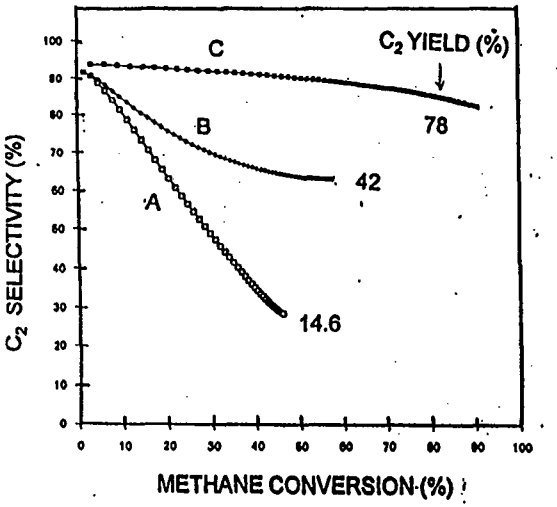
REACTOR-SEPARATION SCHEMES: INSTANTANEOUS ETHYLENE REMOVAL WITHIN TUBULAR REACTOR





1073 K 0.67 bar methane 0.33 bar oxygen

INSTANTANEOUS SEPARATION OF ETHANE AND ETHYLENE ALONG A TUBULAR REACTOR



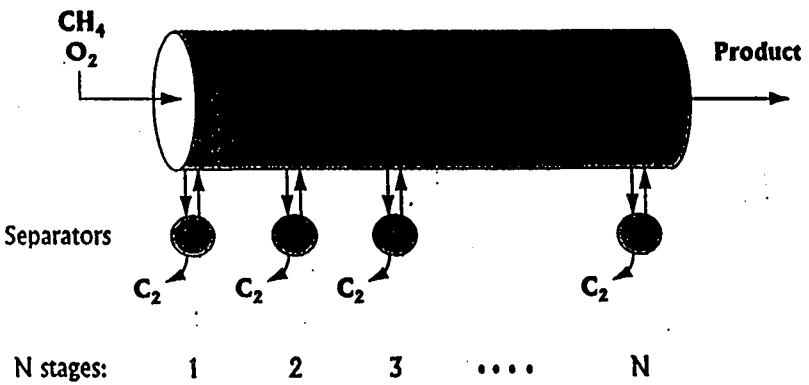
- additional yield improvement when ethane is also removed

Species removed

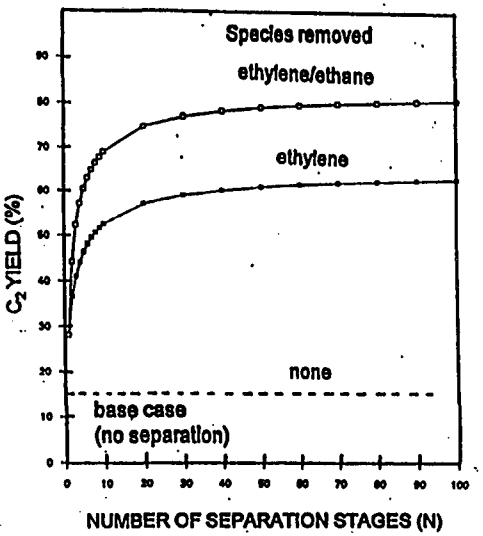
A: none
B: ethylene
C: ethylene/ethane
N= number of separation stages

[1073 K, total CH_4/O_2 = 2, 1 bar total pressure]

C_2 REMOVAL IN N-STAGES ALONG A TUBULAR REACTOR

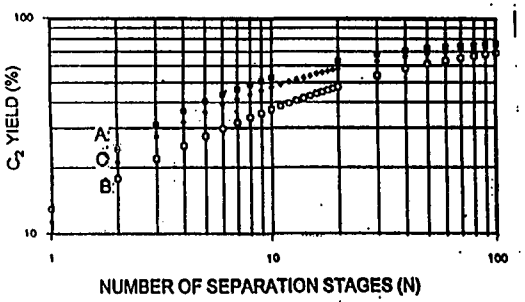


EFFECT OF REMOVAL FREQUENCY AND EFFICIENCY
Ethylene vs. Ethylene/Ethane Removal



[1073 K, total CH_4/O_2 = 2, 1 bar total pressure]

STAGED ETHYLENE/ETHANE REMOVAL IN TUBULAR REACTORS

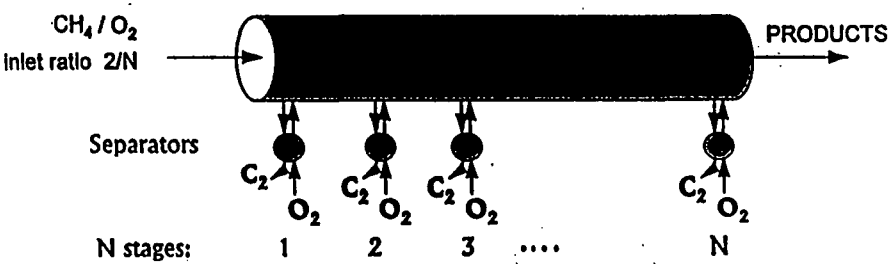


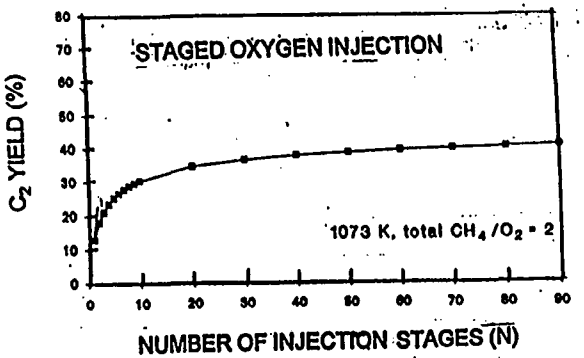
	surface (k_{C2H6}/k_{CH4})	β C_2 removal efficiency
A	0	1.0
B	0	0.5
C	4.0	1.0

$$N^* = N \times \beta / k_{C2H6}$$

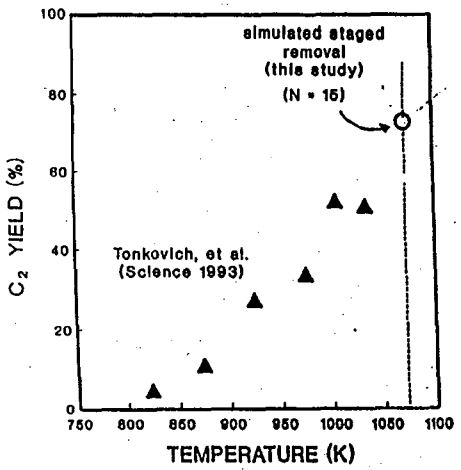
[1073 K, total CH_4/O_2 = 2, 1 bar total pressure]

EFFECT OF OXYGEN INJECTION AND C2 REMOVAL FREQUENCY
STAGED INTRODUCTION OF OXYGEN ALONG A TUBULAR REACTOR

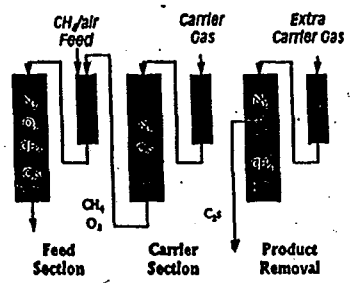




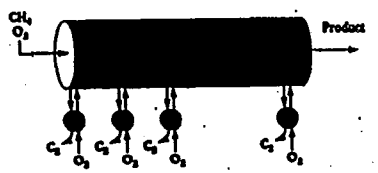
COUNTERCURRENT "MOVING BED ABSORBER" vs. TUBULAR REACTOR WITH STAGED SEPARATORS



"MOVING BED ABSORPTION"

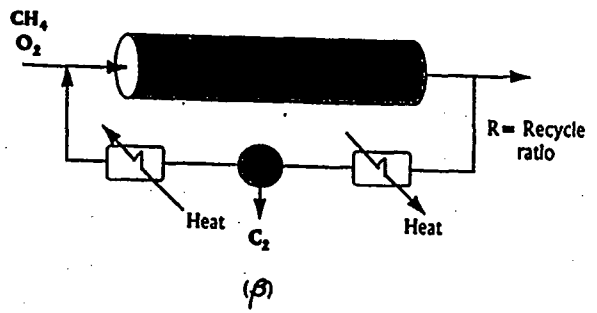


STAGED REMOVAL IN TUBULAR REACTOR



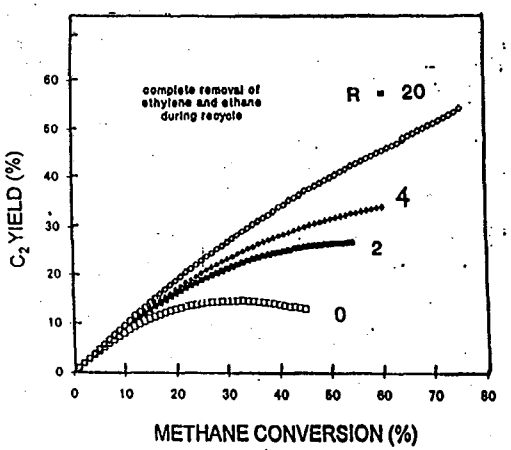
RECYCLE REACTORS WITH ETHYLENE/ETHANE REMOVAL

- ethylene and ethane removed from recycle stream
- inhibits full combustion of C_2 products .... but dilutes inlet feed with partially converted stream



removal efficiency

YIELDS INCREASE WITH INCREASING RECYCLE RATIO



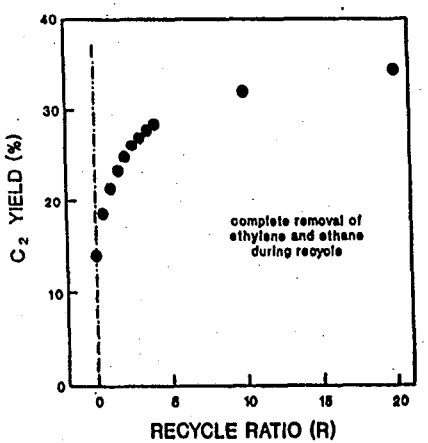
- initial selectivity preserved at higher conversions
- O_2/CH_4 consumption ratio decreases as R increases

1073 K, INLET CH_4/O_2 = 2.0

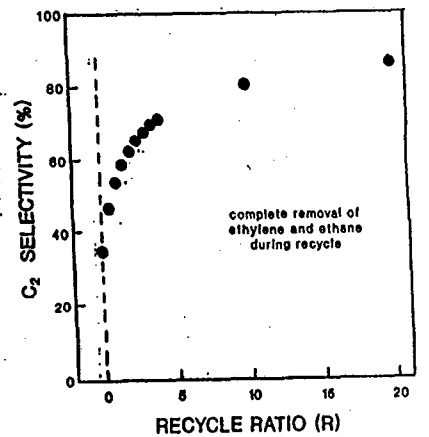
RECYCLE REACTORS WITH C_2 REMOVAL .....C_2 yield and selectivity increase with recycle ratio

at 40% methane conversion level

C_2 YIELD



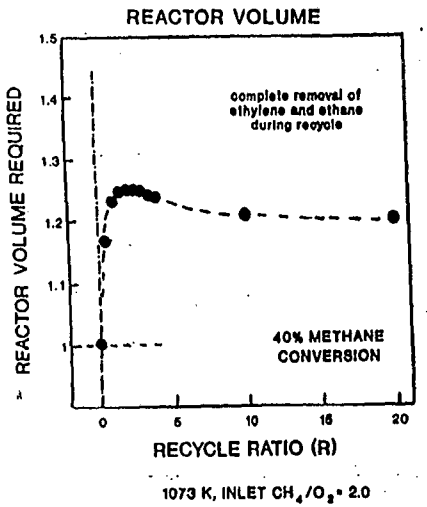
C_2 SELECTIVITY



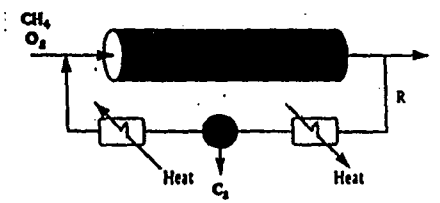
1073 K, INLET CH_4/O_2 = 2.0

DILUTION OF FEED WITH RECYCLE STREAM DECREASES REACTOR PRODUCTIVITY ONLY SLIGHTLY

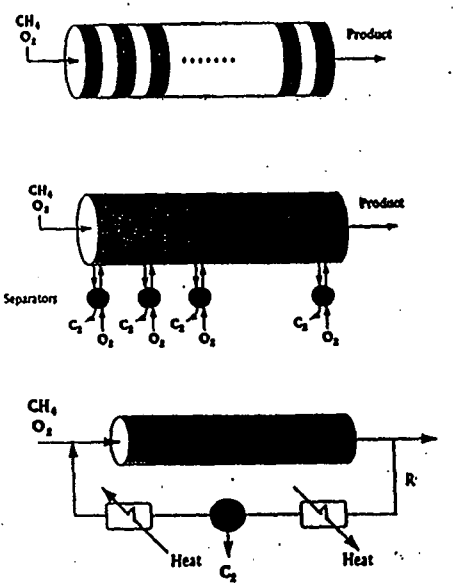
- cooling/heating of recycle stream to carry out separation requires efficient heat integration



RECYCLE REACTOR WITH SEPARATION



REACTION-SEPARATION SCHEMES



C_2 REMOVAL OPTIONS

- cryogenic separation
- adsorption/stripping
- chemical complexing
- C_2 conversion to (easier to separate) products
  - oligomerization
  - cyclodimerization (CYCLAR)
  - aromatics alkylation (EBZ)
  - carbonylation, hydration, ...

CATALYST/REACTOR DESIGN OPTIONS

- high density of (selective) methyl radical generation sites
- (very) distributed oxygen injection in tubular reactors
- hydrogen (and oxygen) transport membrane reactors
- interstage ethylene and ethane removal
- recycle reactors with separators/reactors in recycle streams
- high oxygen conversion backmixed reactors

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