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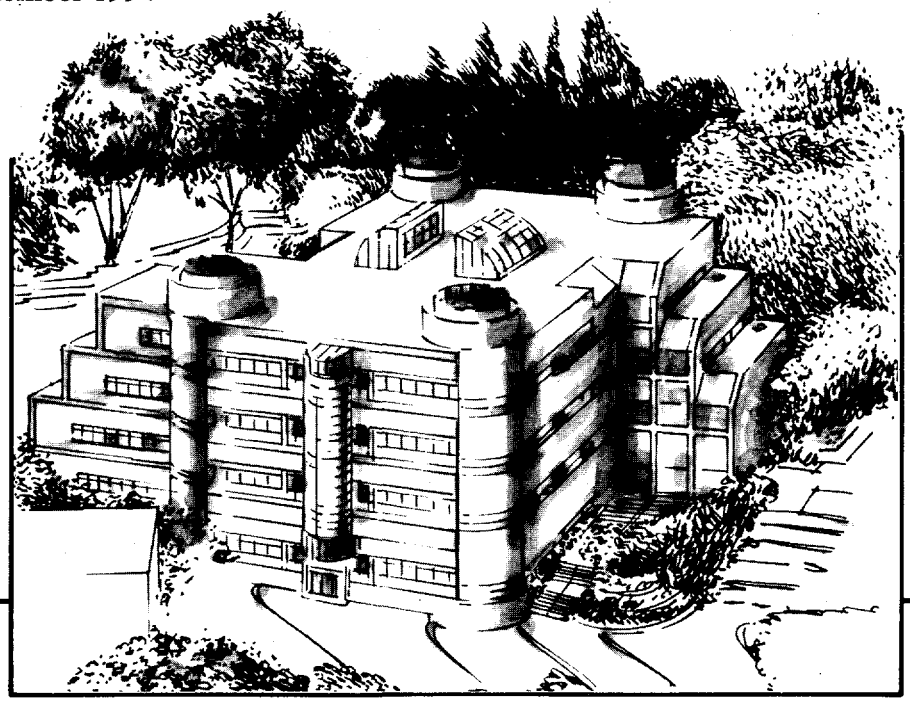
Fundamental Studies of the Mechanism of Catalytic Reactions with Catalysts Effective in the Gasification of Carbon Solids and the Oxidative Coupling of Methane

Quarterly Report

July 1–September 30, 1994

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

September 1994



Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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QUARTERLY REPORT

July 1, 1994 to September 30, 1994

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

Principal Investigators: Enrique Iglesia
Dale L. Perry
Heinz Heinemann

Center for Advanced Materials
Materials Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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a) Catalytic Steam Gasification of Coals and Cokes

b) Oxidative Coupling of Methane

c) Synthesis and Characterization of Catalysts

ATTACHMENTS: Slides: Presentation by Richard W. Borry at California Catalysis Society Meeting, June 1994 and by E. Iglesia at Catalytica, Inc., July 1994.

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 has been completed and no other work is planned in the general area of Catalytic gasification of Coals and Chars. A graduate student (Richard W. Borry) is assigned full-time to the project. A post-doctoral fellow (Dr. Srinivasan Sundararajan) joined the project during the third quarter of FY94 and is

assigned to the project part-time. Both group members are assigned to the operation of the membrane and cyclic reactors; in addition Mr. Borry has carried out a novel treatment of the theoretical relationships between the two types of reactors, which has proven critical in guiding our research towards the synthesis of thinner membrane materials and the design of faster hydrogen-conducting materials. Budgetary constraints have slowed down the re-design and start-up of the cyclic reactor unit (CRU) by requiring that group personnel repair electronic components in the mass spectrometer and gas chromatography system. Both are now operational and have been used in initial experiments in both cyclic and membrane reactors.

III. Highlights

Our experimental and theoretical studies of the selective activation of methane were described in recent presentations by R.W. Borry and E. Iglesia at the Spring 1994 Meeting of the California Catalysis Society and at an invited seminar at Catalytica, Inc.. Copies of these presentations are included as attachments to this Quarterly Report. E. Iglesia has been invited to present one of the plenary lectures at the 1995 International Natural Gas Conversion Symposium in Johannesburg, Republic of South Africa.

In the synthesis and characterization area, a manuscript describing the magnetochemical aspects of the calcium-nickel-potassium oxide powdered catalysts has been accepted for publication in the Journal of Materials Research. An abstract describing details of x-ray fluorescence data has been accepted for presentation at the Fall Meeting of the Materials Research Society.

a) Catalytic Steam Gasification of Coals and Cokes

A final report was written and forwarded to Mr. Rodney Malone, Project Manager, Morgantown Energy Technology Center during 2Q'1994. This requested final report completed our activities in coal gasification for FY1994. No further studies are planned.

b) Oxidative Methane Coupling

-Our cyclic-membrane model, which compares the predicted performance of membrane and cyclic processes, has been enhanced to incorporate the different

geometries of the two systems (slab in membrane, spherical in particles used in cyclic packed bed reactors). The results describe more rigorously the relative hydrogen transport and methane conversion rates in the membrane and cyclic configurations.

- The membrane reactor has been tested in both continuous flow and recirculating modes. The first experiment to measure the steady-state and equilibrium conditions in the reactor with a pure methane feed has been completed at 750°C using both an empty reactor and a membrane with both sides exposed to pure methane reactants. These data are currently being analyzed while we perform the remaining control experiments.

- We have carried out a thorough review of the scientific and patent literature in membrane and thin film fabrication in order to provide alternate routes for the synthesis of inorganic metal oxide films with perovskite structure. Controlled precipitation and hydrolysis methods combined with spin coating will be experimentally examined for their ability to form thin and hole-free films of these hydrogen transport materials.

- Extensive repairs of analytical instruments and of vacuum systems were carried out in the Cyclic Reactor Unit (CRU). Experiments with a low surface area perovskite solid suggest that all analytical and vacuum problems have been resolved.

- The research group met to discuss the program plan for FY95; as a result of this meeting we have assembled a research agenda document that is being drafted for internal distribution.

c) Synthesis and Characterization of Catalysts

- Synthetic approaches for the targets and membrane films fabricated using pulsed laser deposition have been further studied, including considerations of pore sizes in the materials used as support substrates for the membrane films.

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

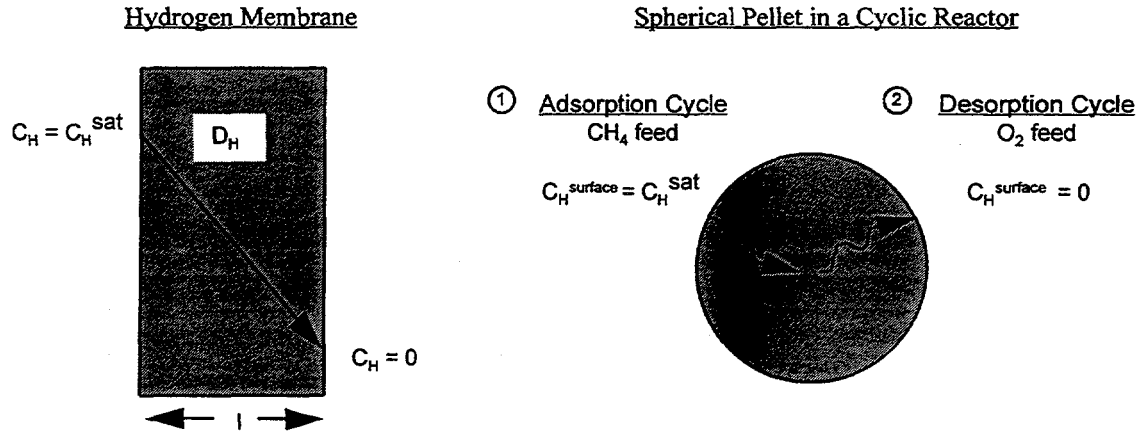
IV. Progress of Studies

b) Oxidative Coupling of Methane

Time-Space Relationships in Cyclic and Membrane Reactors

In the last quarter we described a rigorous mathematical comparison of the maximum hydrogen throughput available in the transient (cyclic) and membrane reactors. This model assumed an infinite slab geometry for both reactors. In reality, a membrane reactor would likely consist of thin cylindrical tubes, which indeed resemble an "infinite" slab; a cyclic reactor, however, consists of packed particles, which are better described by spherical geometry. The model has been modified to reflect this fact. Figure 1 shows a schematic diagram of these two situations.

Figure 1: Reactor Models



The new model assumes very fast surface reaction rates and non-porous particles or membranes. In this case, the overall rate of reaction equals the rate of hydrogen transport through the membrane (or between cycles in the cyclic reactor). Since the dominating cost of any such processes is likely to be the amount of hydrogen conducting/storage material used, the fluxes were normalized by the volume of the solid material used in each case. Detailed simulations using this model show a direct mathematical relationship for the maximum possible rate of hydrogen transport using the two types of reactors.

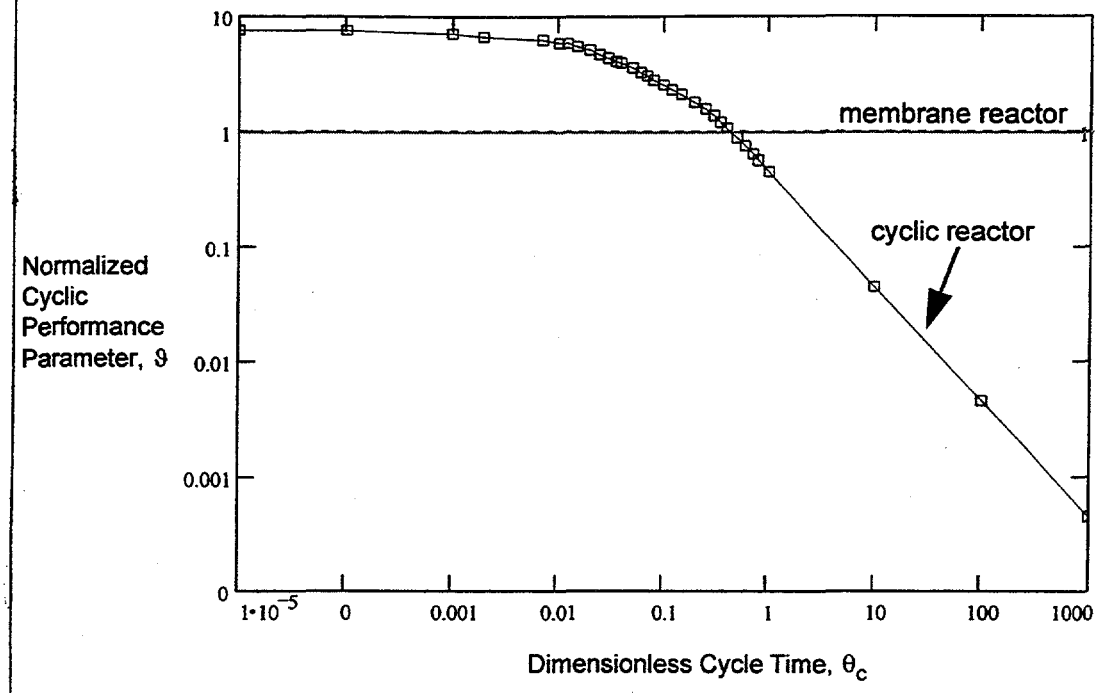
The graph shown in Figure 2 shows ϑ as a function of θ_c. ϑ is a complex, dimensionless function that describes the rate of hydrogen transfer from the methane cycle to the oxygen one in the cyclic reactor. As an example of the use of these simulation results, we estimate the relative performance of $SrCe_{0.9}Y_{0.1}O_{2.95}$ one of the perovskite materials presently under study.

For $SrCe_{0.9}Y_{0.1}O_{2.95}$, the approximate parameters are a cycle half-length (t_c) of 5 seconds (typical of cyclic and pressure swing processes), a diffusion coefficient (D_H) of 10^{-6}-cm^2/s at 900°C, and a particle radius (r_p) of 1 μm. The calculated dimensionless cycle time is then 500. From Figure 2, the value of ϑ for this dimensionless time is then about 9×10^{-4}, at 900°C.

For a minimum membrane thickness (ℓ) of 0.5 mm, the length ratio ($(\ell/r_p)^2$) is 2.5×10^5. Therefore the ratio of the flux (per volume) of the two systems is 225. This indicates that for this specific example, the cyclic system can achieve a much higher hydrogen throughput than a membrane of 0.5 mm thickness. In other words, the thickness of a $SrCe_{0.9}Y_{0.1}O_{2.95}$ membrane must be about 50 μm in order for the membrane reactor to outperform an ideal cyclic reactor using 1 micron spherical particles as the hydrogen transport material.

The results shown in Figure 2 indicates two parameters are important to compare the performance of these two reactors. The first is the dimensionless half-cycle time (θ_c) in the cyclic reactor. The second number (η) is the ratio of the two characteristic lengths, i.e. the membrane thickness and the particle radius. This accounts for the larger surface area to volume ratio in the cyclic system.

Figure 2: Cyclic to Membrane Hydrogen Flux Ratio versus Material Properties.



D_H	= Diffusion coefficient of hydrogen in conducting / storage material	(mol/m^2 s)
t_c	= Half length of one full feed cycle in cyclic operation	(s)
r_p	= Radius of particles used in cyclic operation	(m)
ℓ	= Thickness of membrane in membrane operation	(m)

$\theta_C = (D_H t_c / r_p^2)$ = Dimensionless cycle time
$\vartheta = f(\theta_C)$ = Dimensionless rate of hydrogen transport between feed cycles
$\eta = (\ell / r_p)$ = Ratio of characteristic lengths of each system
$F = \eta^2 N(\theta_C)$ = Ratio of flux per volume (cyclic reactor) / flux per volume (membrane reactor)

Procedure for using model simulation results

For a given cyclic system, calculate the dimensionless cycle time, θ_C. From the graph, find the normalized performance parameter, ϑ. Then calculate F to get the ratio of the flux per volume of the cyclic system to that of the membrane system. If this ratio is greater than one, then the cyclic system will perform better than a membrane system, for equal amounts of this particular material.

Figure 2 shows that hydrogen-conducting materials with high diffusivities favor a membrane configuration. A higher diffusion coefficient moves the dimensionless cycle time to the right, towards better membrane performance (ϑ<1). Also, the benefit of

reducing the cycle time in a cyclic reactor has several limitations. The first is that the performance curve levels sharply at low values of θ_c, corresponding to short cycles; thus additional improvements in performance cannot be achieved by further decreases in cycle time. The second is that shorter and more frequent cycles will introduce unavoidable mixing between the two feed cycles, containing methane and oxygen, respectively, and could result in loss of C_2+ selectivity.

Membrane Reactor Equilibrium Experiments

Catalytic evaluation studies are being conducted following delays associated with the imperfect sealing of membranes in this reactor and with the move of the reactor unit from Building 66 in the Lawrence Berkeley Laboratory to Hildebrand Hall in the Berkeley Campus. This move was required in order to provide for a hood exhaust environment in which to carry out studies with oxygen-methane mixtures. As part of this move, the reactor has been re-designed to incorporate a recirculating reactor module in order to extend the range of experimental conditions that can be achieved experimentally in our study of membrane reactors.

The membrane reactor now contains both continuous flow and recirculating reactor modules. The recirculating mode is required in order to increase the residence time over our very small surface area (16 mm disks) membranes. A feed mixture of 50% CH_4 in argon is being used in all experiments. This reactant mixture allows the use of the argon component as an internal standard for the gas chromatography (GC) measurements and thus ensures rigorous and accurate mass balances during the course of experiments. The gas chromatograph was re-calibrated to use this new method for the measurement of concentrations in reactor streams.

The purpose of the membrane reactor is to improve (beyond equilibrium) the conversion of methane to ethane, ethylene, and higher hydrocarbons. Therefore, a controlled experiment is needed to establish the baseline conversion from which we will measure improvement. The first series of experiments has examined the steady-state (continuous flow mode) and thermodynamic equilibrium (recirculating mode) performance of the reactor with a pure methane feed at 750°C. This has recently been completed and will also be examined at 850°C and 950°C. The results of these experiments are being analyzed in order to provide direction for the remaining control experiments.

Synthesis and Characterization of Thin Membranes

We have recently carried out a thorough review of the literature describing the fabrication of ceramic materials in thin film configurations in order to meet the requirements for thinner hydrogen transport membranes suggested by the model simulations described above. We have chosen to pursue several techniques concurrently in order to maximize the chances of success. Our objective is to fabricate perovskite films of stoichiometric compositions and 50 micron thickness.

One of the techniques is vapor deposition of perovskite on a porous alumina substrate using a technique called laser ablation. This work is being carried out in Dr. Dale Perry's laboratory and it is described in the Synthesis and Characterization of Materials section of this report.

The other techniques involve the synthesis of high surface area perovskite solids by controlled precipitation or hydrolysis methods and the spin coating of these materials in a slurry or gel mixture onto porous substrates, where they will be sintered in controlled humidity conditions in order to ensure uniform coverage of the pore structure within the underlying support. These methods have been widely used for the preparation of uniform ceramic materials and thin films of low porosity, although 50 micron films remain at the edge of what can be presently achieved reproducibly by using these techniques. Our plan is to spin a porous alumina disc or cylinder in a solution of perovskite precursors. Upon the controlled addition of water, hydrolysis reactions lead to the formation of sol-gel precursors that will be deposited by spin coating to form uniform, hole-free structures sustained structurally on top of the porous substrate support.

Methane Activation Studies in Cyclic Reactors

This part of the project was plagued by vacuum and mass spectrometer problems caused by the age of the equipment and by restricted budgets, which have prevented access to manufacturer's expertise in repairing this equipment. As of mid-September, this cyclic reactor appears to be fully operational. It was tested using a sample of $SrCe_{0.9}Y_{0.1}O_{2.95}$ with low surface area. All system components were operational but

reaction rates were very low because of the low surface area of this sample. A more detailed description of the experimental difficulties and the repair strategy is included as an attachment at the end of this report.

We are presently testing two additional samples: a high surface area version of $SrCe_{0.9}Y_{0.1}O_{2.95}$ prepared by co-precipitation techniques and a supported Pd sample. The latter is being tested because of its known properties to absorb and transport hydrogen at fairly low temperatures, characteristics that make Pd an attractive alternate composition for hydrogen transport membranes in methane activation studies.

c) Synthesis and Characterization of Catalysts

Studies of Strontium-Zirconium-Yttrium Oxide Films and Membranes

Initial membranes of Sr-Zr-Y oxide have been fabricated using pulsed laser deposition techniques and Y-stabilized zirconia as the substrate. The target composition for these studies was $SrZr_{0.9}Y_{0.1}O$. X-Ray diffraction lines attributable to the target composition phase were identified based on previous data from our laboratory. Other target/membrane compositions that have been fabricated include: Ce-Sr-Y oxide systems with stoichiometries similar to those of the Sr-Zr-Y system presently being studied as a fast proton conductor. These stoichiometries will be further studies as ablated films. Variations in porosity involving the substrate onto which the film is ablated are also being studied.

X-Ray Fluorescence Microprobe Studies on Ca-Ni-K Films

Continued studies of calcium-nickel-potassium films using the x-ray fluorescence microprobe approach have been conducted at the Advanced Light Source synchrotron facility at the Lawrence Berkeley Laboratory. Emphasis has been placed on studying the degree of heterogeneity with respect to the calcium, nickel, and potassium in the film matrices. The films have been fabricated in a wide range of stoichiometries in order to show that the films (coatings) can be experimentally ordered with respect to different, desired compositions. Studies of these films have also been made using x-ray diffraction to document the various phases that have been made, including new ones that have been heretofore unreported. Energy dispersive x-ray spectroscopy has been used to obtain

stoichiometries. A manuscript describing the x-ray synchrotron results will be prepared for submission to a journal.

ATTACHMENT

Description of Experimental Difficulties and Solutions in Cyclic Methane Activation Reactor

The mass spectrometer had a faulty ionizer with problems arising due to internal shorts and several missing pieces of ceramic insulation. The spectrometer electronics did not allow communication with external data collection ports. These problems have been corrected during this quarter. The mass-spectrometer was operated using a peak programmable selector in order to allow data collection and analysis. This instrument lacked an operating manual and a trial and error approach was required to make it functional because even the manufacturer had no available information on the operation of this obsolete instrument. After this obstacle was overcome, we implemented computer software to allow a personal computer to display data in 'real time' as the experiment is performed and to record it in a manner that standard spreadsheet software can accept. Also, we have interfaced the temperature output from the thermocouple so that the reactor temperature can be precisely and automatically recorded by the computer.

Major problems were also encountered with the diffusion-pumped vacuum system. This vacuum system was plagued by gas bursts at irregular intervals, which made data collection irreproducible. Removal of leaks, both on the ultra-high vacuum side as well as the foreline side of the diffusion pump did not correct these problems. This problem was later found to be caused by carbon scaling on the internal walls of the diffusion pump, which were then cleaned with a mild abrasive and this problem disappeared. Other problems in the automatic fill apparatus for liquid nitrogen were fixed as well. In order to introduced samples of the reactor streams into the mass analyzer, we designed and fabricated with existing parts a leak-in mechanism in which most of stream is vented while a reproducible fraction of it makes it to the mass-spectrometer.

ATTACHMENT

SLIDES AND ABSTRACT PRESENTED AT

1. 1994 MEETING OF THE CALIFORNIA CATALYSIS SOCIETY, BERKELEY, CA

2. CATALYTICA INC., MOUNTAIN VIEW, CA

DESIGN OF REACTION-SEPARATION SCHEMES FOR THE OXIDATIVE COUPLING OF METHANE

Enrique Iglesia
Richard W. Borry
Department of Chemical Engineering
University of California at Berkeley

Sebastian C. Reyes
Corporate Research Laboratories
Exxon Research and Engineering Co.

Catalytic dehydrodimerization of methane to form ethane and ethylene is described using detailed reaction-transport models that include surface and gas phase kinetic models and convective and diffusive transport within catalytic pellets and membranes. Simulations using these models suggest that distributed injection of the stoichiometric oxygen reactant and ethylene/ethane removal along tubular reactors increase C_2 yields by inhibiting undesirable secondary homogeneous oxidation pathways.

Yield improvements using staged oxygen injection require catalysts with high density of sites on which radical generation rates depend weakly on oxygen concentration. Interstage removal of ethylene and ethane require recycle tubular reactors or multistage separators; these reaction-separation schemes benefit from removal processes that operate with high separation efficiency near oxidative coupling temperatures. C_2 yields well above 50% are predicted using interstage or recycle stream separators. Similar yield improvements can be achieved using proton transport membranes and backmixed high conversion reactors.

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 model
- Homogeneous - heterogeneous kinetics in catalytic reactors
- Staged Oxygen injection
- Reactor - separation schemes:

Separate Products

Interstage removal of C_2 products

Recycle reactor with C_2 removal

Separate Reactants

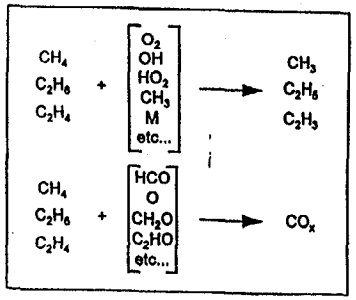
Hydrogen transport membrane

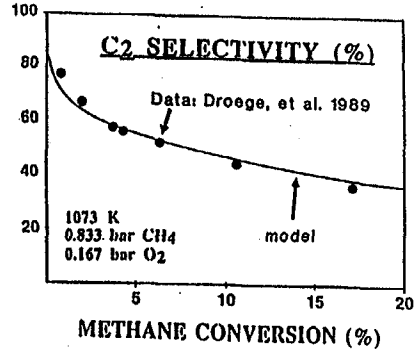
Cyclic methane decomposition and hydrogen scavenging

Homogeneous Reaction Model

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

Reaction Network





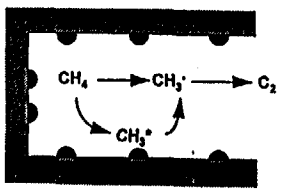
- 29 reactive species
- 145 reversible free-radical reactions with unadjusted literature rate constants

Reyes, Iglesia, and Kelkar, Chem. Eng. Sci. 48 (1993) 2643.

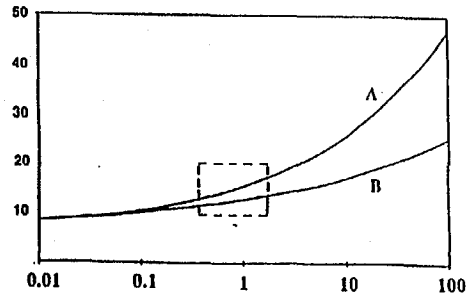
Heterogeneous Reaction Model

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

Oxidative Methane Coupling- a bimodal reaction within porous solids



Maximum C_2 Yields (%)



A: sites activate only methane

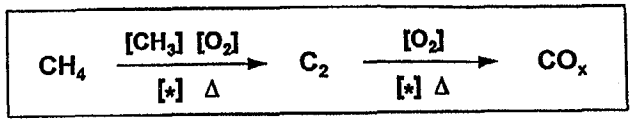
$k_{C_2H_6} / k_{CH_4} = 0$

B: sites activate methane and C_2 products

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

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

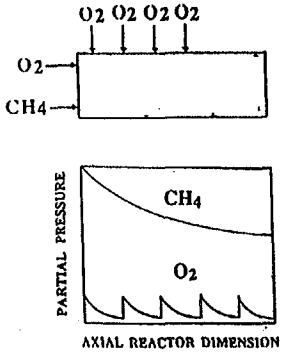
Yield Limitations in Oxidative Coupling of Methane



Increase rate of methyl radical generation

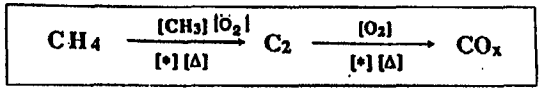
Inhibit secondary oxidation reaction

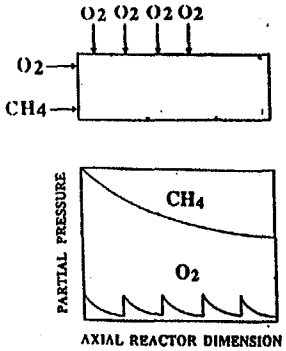
Prevent contact between C_2 product and O_2

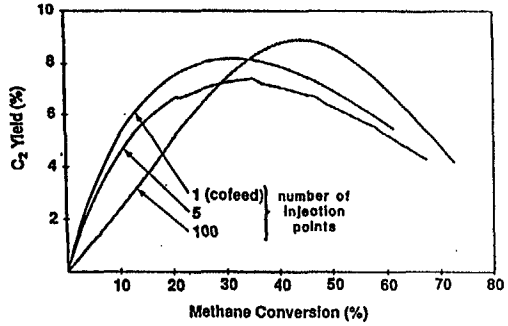


STAGED OXYGEN INJECTION -- HOMOGENEOUS REACTORS

- control oxygen concentration while supplying stoichiometric oxygen requirement



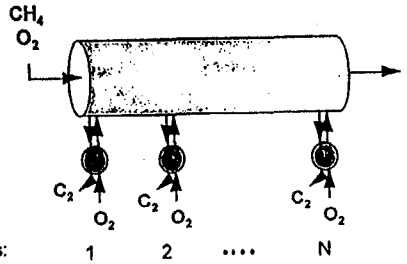




[1073 K, 0.5 bar CH_4, total reactant supply (CH_4 /O_2)=1.0]

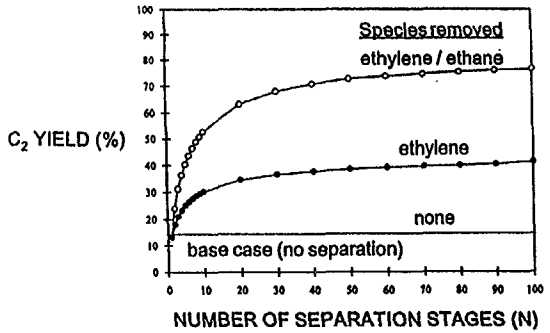
Staged C_2 Separation

- Removes C_2 product before the oxidation reaction can occur



C_2 Separators:

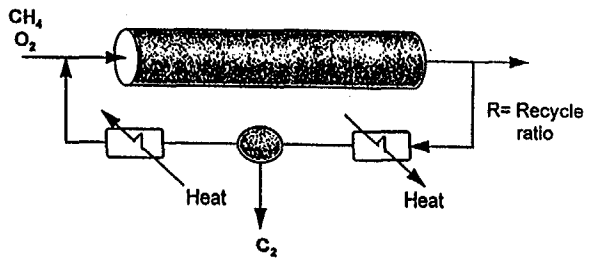
Number of stages: 1 2 .... N



[1073 K, total CH4 / O2 = 2, 1 bar total pressure]

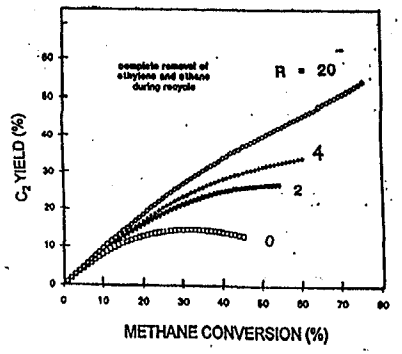
Recycle Reactor with Ethylene/Ethane Removal

- Ethylene and Ethane are removed from recycle stream
- Inhibits full combustion of C_2 products.. but dilutes inlet feed with partially converted stream

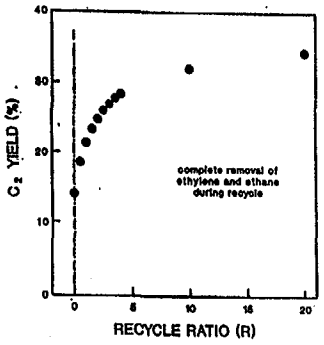


Recycle Reactor Performance

Yields Increase with Recycle Ratio



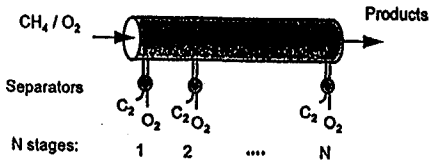
C_2 Yield at 40% CH_4 Conversion



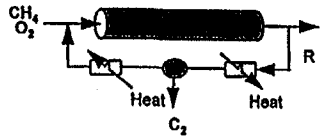
[1073 K, Inlet $CH_4/O_2 = 2.0$]
Complete removal of ethylene and ethane during recycle

Product Separation Schemes for Methane Oxidative Coupling

Staged C_2 Separation



Recycle with C_2 Removal



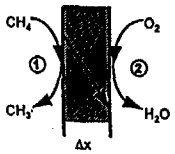
How to Separate C_2 Product?

- cryogenic separation
- adsorption/stripping
- ethylene removal through a microporous membrane
- conversion to separable products

Oxidative Coupling of Methane to Ethane/Ethylene

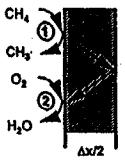
Separate Reactants:

Hydrogen Membrane



vs.

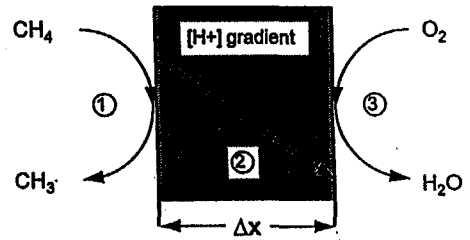
Hydrogen Cycles



Prevent oxidation reaction without stopping thermodynamic driving force

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

Catalytic Membrane Reactor Using Hydrogen Conductors



Reaction / Transport Model

1) H abstraction from CH_4 at surface

2) Proton transport across membrane

$$J_{membrane} = -(Area) \cdot D_{H+} \frac{\Delta[H+]}{\Delta x}$$

3) H removal by O_2

Membrane Materials

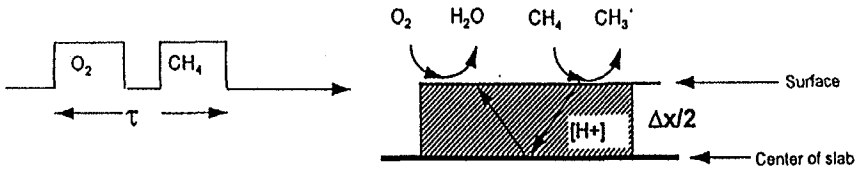
- high proton mobility and low oxygen ion conductivity at 500 - 700 °C
- $SrM_{0.9}Yb_{0.1}O_{2.95}$ M = Ce, Zr

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

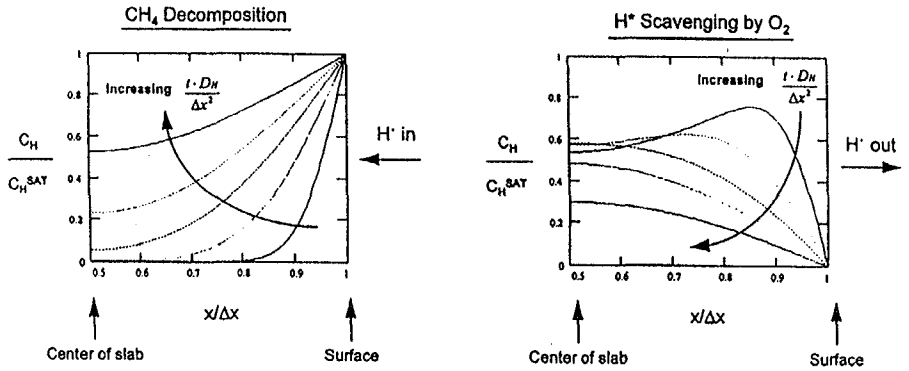
- Pd

(with H. Heinemann)

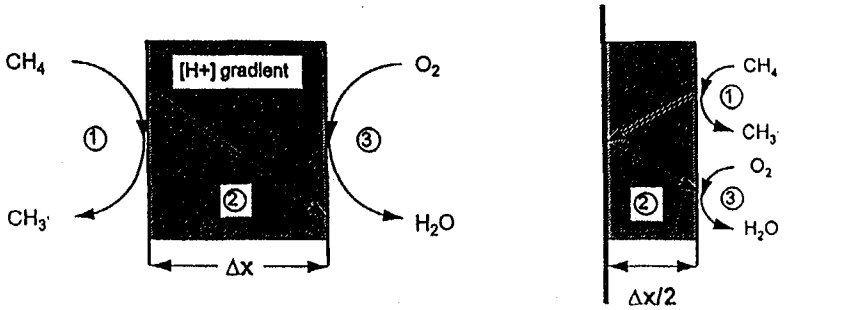
Cyclic Feed Reactor



- Separation of Reactants in Time
- Assume fast surface kinetics



Membrane vs. Cyclic Feed Reactor

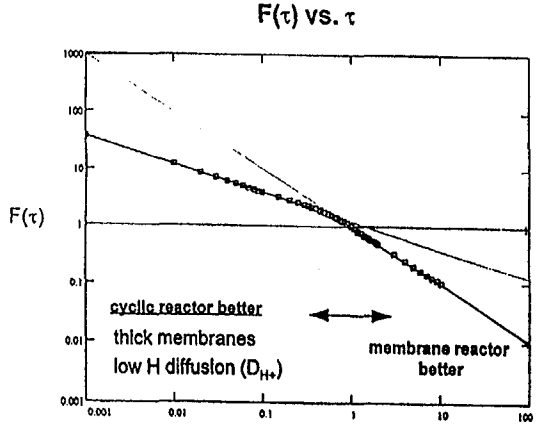


- Separate hydrocarbons from O_2 in space
- Separate hydrocarbons from O_2 in time

$$J_{membrane} = -(Area)\cdot D_{H+}\frac{\Delta[H+]}{\Delta x}$$

$$\frac{J_{cyclic}}{J_{membrane}} = F(\tau)$$

Cyclic Reactor: Dimensionless flux vs. dimensionless cycle time



$$F(\tau) = \frac{J_{cyclic}}{J_{membrane}}$$

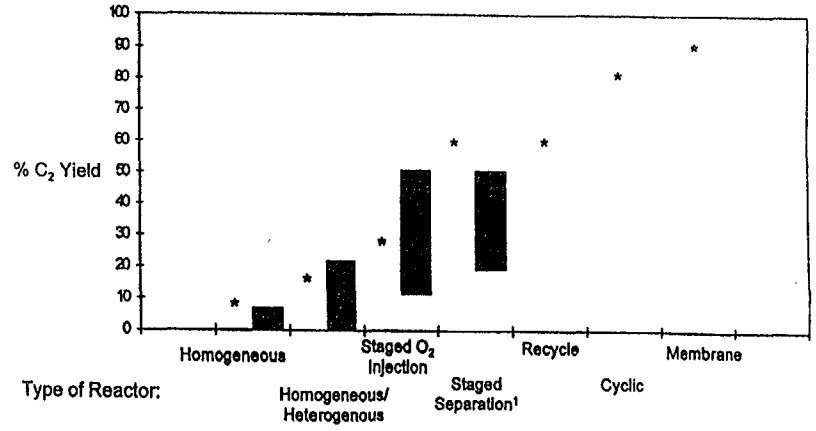
$$\tau = \frac{t\cdot D_H}{\Delta x^2}$$

(Dimensionless cycle time)

Thin membrane must be:

- non-porous
- mechanically strong
- catalytically active

Summary: Progression of Methane Oxidative Coupling



(1) Tonkovich, et al., 1993

Acknowledgements

D. G. Barton, J. A. Biscardi, D. Petrakis, S. Sundararajan

- Division of Fossil Energy (Department of Energy)