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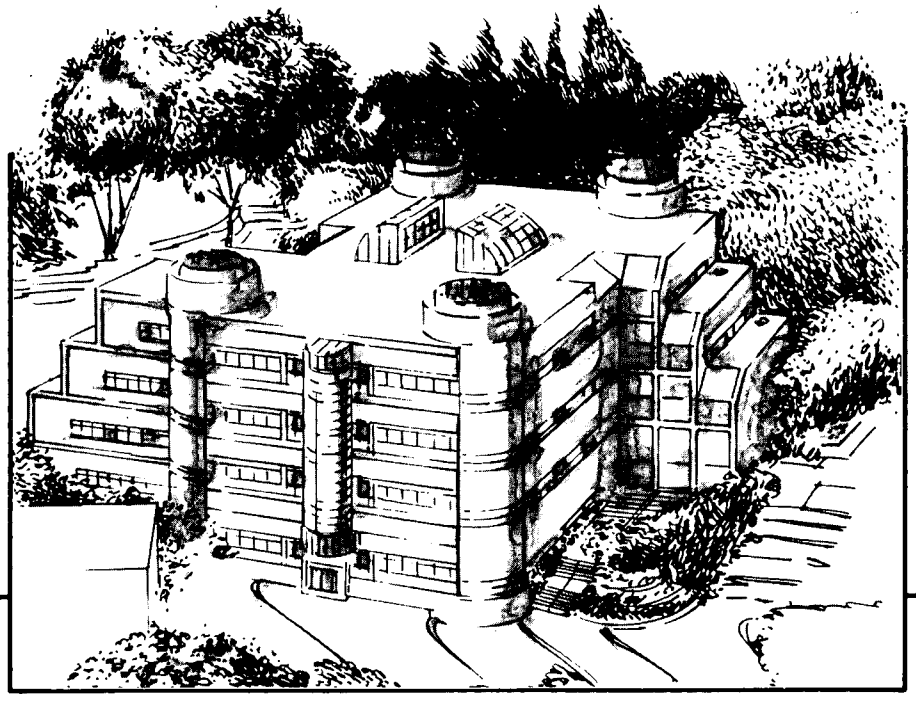
Fundamental Studies of the Mechanism of Catalytic Reactions with Catalysts Effective in the Gasification of Carbon Solids and the Oxidative Coupling of Methane

Quarterly Report

October 1–December 31, 1993

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

December 1993



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QUARTERLY REPORT

October 1, 1993 to December 31, 1993

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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ATTACHMENT: Manuscript: "Steady-State and Transient Catalytic Oxidation and Coupling of Methane", by Heinemann, Iglesia, and Perry

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 has 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 selectivity 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.

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 impeded during the first quarter of 1994 by the temporary cancellation of funding for this part of the project; funding was not reinstated until November. In addition, a change in post-doctoral fellows, the addition of a graduate student, and the redesign of both membrane and cyclic methane conversion units slowed to some extent the experimental output in the methane oxidation project.

III. Highlights

A paper was presented at the Fuels Technology Contractors Meeting summarizing the accomplishments of this project during FY 1993. A copy of the manuscript submitted for the Proceedings of this meeting is included as an Attachment to this Quarterly Report.

a) Catalytic Steam Gasification of Coals and Cokes

- A series of catalysts has been tested in the gasification of chars prepared in the presence of small amounts of alkali

- Some ternary catalyst oxides give better gasification rates than the previously used binary Ca-K oxide catalysts. The best catalysts are K-Ca-Co and K-Ca-Fe_3 oxides.

b) Oxidative Methane Coupling

- Five different compositions of proton-conducting mixed metal oxides have been prepared in the form of dense disks using high temperature densification under applied pressure; the synthesis procedures developed lead to stoichiometric compositions, densities within 94% of theoretical values, and crack-free disk configurations.

- An experimental unit has been redesigned to permit cyclic operation of oxidative coupling catalysts. The new design will also permit in-situ characterization of catalytic materials using site titration techniques to identify the nature and density of active sites and the composition and reactivity of surface fragments formed during methane decomposition cycles.

- Two journal papers describing the characterization of oxygen reactivity and the effect of steam in Li/MgO and Ca-Ni-K Oxides appeared in the Journal of Catalysis

c) Synthesis and Characterization of Catalysts.

- Thin films of calcium-nickel-potassium oxides have been made using laser ablation/deposition from variable composition targets.

- These films have been characterized using a variety of techniques including x-ray diffraction, x-ray photoelectron, and Fourier transform infrared and Raman spectroscopy.

- Initial work has begun on the selection of components to be used in the laser ablation synthesis of strontium-yttrium-zirconium and calcium-yttrium-zirconium films for use as catalytic membranes.

- A journal paper describing the initial thin film work on calcium-nickel oxides appeared in the Journal of Materials Research

IV. Progress of Studies

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

It has been reported in previous quarterly reports that charring coals or coking petroleum resids in the presence of small amounts of alkali results in chars or cokes that are easier to gasify than those prepared in the absence of alkali. It has also been shown that the rate of gasifying chars prepared with alkali is further enhanced by impregnating the char with binary catalysts, such as Ca-K oxides.

Recently, we have extended this study to ternary catalyst oxides, e.g., mixtures of K-Ca-Mo oxide or K-Ca-W oxide. Table 1 presents early results. In the "Catalysts" column of this table, the designation NaOH refers to charring with the indicated amount of alkali prior to gasification with the indicated catalyst.

It is apparent from the data in Table 1 that the combination of alkali charring and catalytic gasification gives the best results. Further, some ternary catalyst oxides, but not

all, perform better than binary oxides. The best catalysts were K-Ca-Co oxide and K-Ca-Fe_3 oxide.

b) Oxidative Coupling of Methane

The post-doctoral fellow involved in this program has left for an academic position at the University of Missouri. We have identified a new candidate for the post-doctoral position and we expect that he will arrive by the end of the next reporting period.

Membrane Reactors

Five different materials were prepared in powder form ($CaZr_{0.9}Y_{0.1}O_{2.95}$, $SrZr_{0.9}Y_{0.1}O_{2.95}$, $BaZr_{0.9}Y_{0.1}O_{2.95}$, $SrCe_{0.9}Y_{0.1}O_{2.95}$, and $BaCe_{0.9}Y_{0.1}O_{2.95}$). All of these mixed metal oxides showed x-ray diffraction patterns corresponding to the stoichiometric perovskite structures. The Zr-containing samples are prepared by a simple calcination of the individual metal oxides and alkaline earth carbonates at 1100 °C. We have found that at this temperature, the alkali earth carbonates decompose and react with the remaining oxides to form perovskite mixed-oxide structures. In contrast, the Ce-containing powders require calcination at significantly higher temperatures (up to 1400 °C) to decompose the carbonates. Technical hurdles in the reproducible formation of proton-conducting oxides in powder form have been overcome and we can now reproducibly prepare a wide range of compositions using available equipment.

The yttrium-doped zirconate powders were successfully fabricated into dense membrane disks by sintering preformed disks in a die press at high temperatures. The synthesis procedure involves the grinding of the above oxide compositions into a fine powder, the pressing of the fine powders at room temperature under isostatic pressure into a cylindrical pre-form, the sintering of these cylinders at 1600 °C overnight without applied pressure, and finally the in-situ sintering in a graphite die under isoostatic pressure at 1650-1700 °C. This final step was critical in obtaining cylinders with 90-94% of the theoretical oxide density, compared with much lower densities obtained by sintering without applied pressure (73-83%). These results are summarized in Table 2. These high densities suggest that we have prepared for the first time sintered disks without significant residual voids, which would provide deleterious gas phase diffusion

channels in our attempt to use the materials a solid-state proton conductors in membrane configurations.

Cylinders of doped zirconate compositions were sliced into 0.5 mm thick membrane disks, which appeared to be free of cracks when analyzed by optical microscopy. These materials will be tested in our membrane reactor during the next report period.

Y-doped calcium zirconates decomposed during calcination in air. Thus, we were unable to sinter these materials into cylindrical pre-forms with high density without significant decomposition. This suggests that the use of these materials as proton-conducting membranes will require that we replace the Y dopant with a smaller cation, such as In, in order to improve the stability of these samples against decomposition to the separate constituting oxides. The Ce-based materials could not be sintered at high temperature under isostatic pressure because they reacted with the graphite dies. However, doped cerate membranes appear to sinter at lower temperatures than zirconates of similar compositions and could be formed by sintering under pressure at lower temperatures (1400-1500 ^{o}C), where solid state reactions with graphite can be minimized.

A previously obtained crack-free $SrCe_{0.9}Y_{0.1}O_{2.95}$ sample, prepared during last quarter, led to cracking of the quartz reactor during thermal expansion of the cerate at oxidative coupling temperatures. We have re-designed the membrane reactor and replaced quartz with alumina in order to minimize thermal expansion differences between the membrane disks and the reactor. We are presently attempting to seal the disks against the new reactor materials.

In parallel, we are studying the alternate use of supported membrane films instead of sintered disks in order to increase the proton flux across these proton conducting membranes. Laser ablation techniques described below provide a promising route to these materials.

Cyclic Methane Conversion Reactors

We are also studying an alternate method for preventing the full oxidation of methane during oxidative coupling. 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.

Our proposed schemes for sequential decomposition of methane and scavenging of the surface fragments are shown in Figure 1. In all cases, deleterious full combustion of methane to carbon dioxide is prevented by a temporal separation between methane and oxygen.

We have modified existing equipment to permit cyclic reactor operation as well as the in-situ characterization of the site density and of the composition of the fragments formed during decomposition of pure methane streams on supported metal catalysts. Initial experiments using supported Ni catalysts show the integrity and capability of the unit. We are presently synthesizing and characterizing other supported metal catalysts and interfacing the cyclic reactor with a refurbished mass spectrometer in order to allow direct on-line sampling of transient changes in reactant and product process streams.

Experimental testing of the proposed cyclic schemes will begin as soon as we interface the required analytical equipment.

c) Synthesis and Characterization of Catalysts

The work involving the synthesis and characterization of calcium-nickel-potassium oxide films continued, with the emphasis being placed on learning the different stoichiometric possibilities for the different elements. These films have been initially fabricated on a MgO surface, and they have been made using a wide range of compositions of potassium, including up to a 40% load. This high load was used in order to be sure that there was no upper maximum limiting level of this component in any films of interest. Conversely, films with small amounts of the potassium in the matrix are also possible to synthesize.

The x-ray diffraction studies show variations in the phases in the films as a function of the elemental composition. In some of the films, one can detect NiCaO solid solution phases, while for other compositions, the generated films are amorphous. Also, the compositions of the targets used in the laser ablation process tend to have a marked effect on the composition of the films that are formed. X-ray photoelectron spectroscopy shows the oxygen 1s core photoelectron line to vary as a function of the composition of the films. Initial data have also been obtained on the films using Fourier transform infrared and Raman spectroscopy.

Table 1. Selectivities of Catalysts in the Steam Gasification of Illinois #6 Char (640 °C)

Catalysts	Selectivity CO %	Selectivity Methane %	Selectivity CO_2 %	Cumulative* Cov. %
NaOH-free	39.4	6.0	54.6	3.12
NaOH (0.2%)	36.2	6.8	57.0	7.65
K-Ca/NaOH (0.2%)	12.7	3.3	86.0	19.20
K-Ca-Ni/ NaOH (0%)	22.2	2.6	75.3	8.56
K-Ca-Ni/ NaOH (0.2%)	23.3	3.1	73.6	21.50
K-Ca-Co/ NaOH (0.2%)	16.1	1.9	82.0	27.30
K-Ca-Mo/ NaOH (0.2%)	22.3	2.8	74.9	16.01
K-Ca-W/ NaOH (0.2%)	23.3	4.4	72.3	14.50
K-Ca-V/ NaOH (0.2%)	28.2	3.4	68.4	12.10
K-Ca-Fe^{+2}/ NaOH (0.2%)	19.4	1.9	78.7	17.20
K-Ca-Fe^{+3}/ NaOH (0.2%)	16.0	2.0	82.1	21.35

*Cumulative conversion of carbon after 300 minutes.

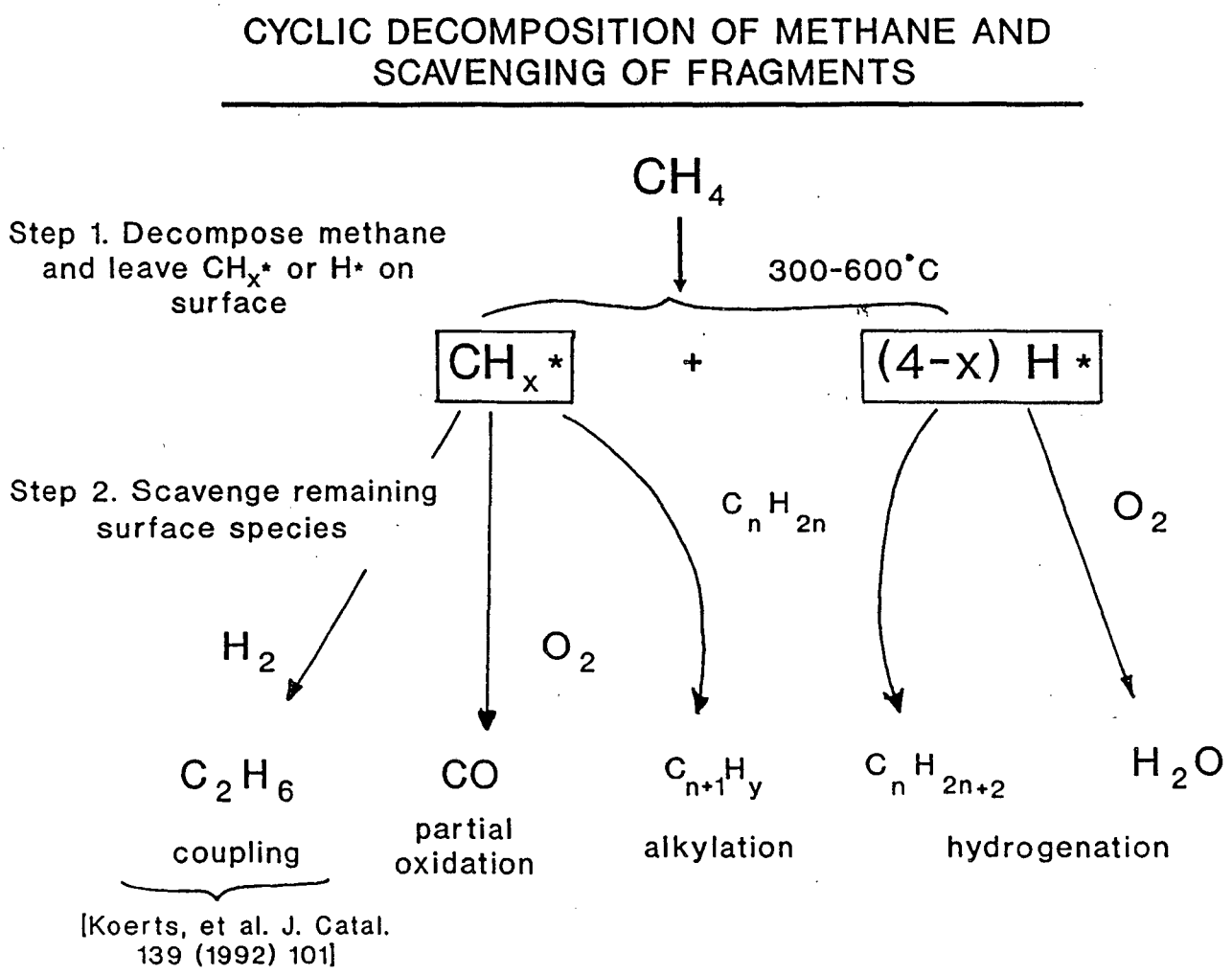
Table 2. Density of Sintered Cylinders of Doped Zirconates

Composition	Theoretical Density (g/cc)	Density (% of theoretical) Sintered [1] (g/cc)	Sintered [2]
$CaZr_{0.9}Y_{0.1}O_{2.95}$	4.78	3.49 (73%)	4.31 (90%)
$SrZr_{0.9}Y_{0.1}O_{2.95}$	5.45	4.52 (83%)	5.10 (94%)
$BaZr_{0.9}Y_{0.1}O_{2.95}$	6.25	--------	5.69 (90%)

1. sintered at 1600 C overnight without applied pressure

2. sintered at 1650-1700 C overnight in graphite die under isostatic pressure

Figure 1. Proposed Schemes for the Decomposition of Methane on Solids and the Scavenging of Surface Fragments by Reactive Gas Phase Species.



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MORGANTOWN ENERGY TECHNOLOGY CENTER MORGANTOWN, WEST VIRGINIA

TITLE

"Steady-State and Transient Catalytic Oxidation and Coupling of Methane"

by

Heinz Heinemann, Enrique Iglesia, and Dale Perry

Steady-State and Transient Catalytic Oxidation and Coupling of Methane

CONTRACT INFORMATION

Contract Number	DE-AC03-76SF00098
Contractor	Lawrence Berkeley Laboratory One Cyclotron Road Berkeley, CA 94720
Contractor Project Manager	Dr. Heinz Heinemann
Principal Investigators	Dr. Heinz Heinemann Professor Enrique Iglesia Dr. Dale L. Perry
METC Project Manager	Mr. Rodney D. Malone
Period of Performance	August 1, 1992 to September 30, 1993

Schedule and Milestones

Four papers have been published on the mechanisms and site requirements for the oxidative coupling of methane to ethane and ethylene [1-3] and on the synthesis of thin catalytic films [12] during fiscal 1993. These publications also describe a unique inhibiting effect of water on the rate of undesired full oxidation pathways during oxidative coupling. Five quarterly reports have been written and submitted during the covered period [4]. These findings and recently reported models of surface and gas phase reactions of methane [5,6] suggest the use of membrane reactors and of cyclic methane decomposition schemes in order to avoid deleterious full oxidation reactions and to increase C_2 yields above 25%. In fiscal 1994, we will proceed with the testing of proton-conducting membranes that we have recently fabricated. We will also continue our emerging effort in cyclic decomposition of methane and scavenging of fragments on supported metal catalysts.

OBJECTIVES

This project addresses the conversion of methane and other components in natural gas using catalytic materials in packed-bed and membrane reactors. Our strategy is to identify catalytic sites responsible for selective methyl radical generation, in order to prevent direct oxidation of methane to CO_2, and to separate reactive products (ethane and ethylene) from O_2 using membrane or cyclic reactors, in order to prevent their sequential oxidation to CO_2. A CRADA between LBL, Orion ACT, and DOE went into effect on January 1, 1992 and covers most of the work reported here.

BACKGROUND INFORMATION

Oxidative coupling of methane is widely known to produce ethane and ethylene as

primary products and CO and CO_2 in both primary direct oxidation of methane and secondary combustion of C_2 products; these reactions combine methyl radical generation on oxide surfaces with coupling and oxidation of hydrocarbon free radicals in the gas phase. Full oxidation reactions also occur on surfaces during desired radical generation steps and lead to high yields of undesired CO_2.

We have previously reported that the oxidative coupling of methane to higher hydrocarbons occurs at temperatures below 600°C on Ca-Ni-K oxides. We have shown previously that water enhances the C_2 selectivity on Ca-Ni-K by inhibiting the oxidation of methane and of C_2 products to CO and CO_2. We propose that its role is to decrease the concentration of sites capable of multiple exchange between gas phase and lattice oxygen and extend these findings to Li/MgO catalysts. These sites, where oxygen availability appears to be high, appear to be responsible for deleterious total oxidation pathways on these materials.

RESULTS

Effects of Added Water on the Oxidative Coupling of Methane on Li/MgO.

Li/MgO materials have been widely studied for the oxidative coupling of methane at relatively high temperatures [7], where secondary gas phase reactions of desired C_2 products decrease their yields. Lower temperatures do not appear to increase C_2 yields because direct catalytic oxidation of methane becomes competitive with the formation of methyl radicals.

We have studied the reactions of CH_4/O_2 mixtures at low temperatures (550-650°C) on Li/MgO in the presence and absence of added water. The presence of water is essential for the formation of C_2 products at these low reaction temperatures. Water inhibits oxidative reactions of methane that lead to the formation of CO and CO_2 products. For example, the hydrocarbon selectivity increases from 5 to 30 % when water is added to the CH_4/O_2 reactants at 600°C (Table 1). The selectivity increases even though the water also increases the level of methane conversion and thus the likelihood of secondary oxidation of primary C_2 products. The rate of the reaction also increases slightly, causing the CH_4 conversion to increase from 14 to 18% when water is added to the reactant mixture (Table 1). These effects occur without any direct involvement of water in steam reforming reactions, which would have led to higher selectivities to CO and CO_2 products. The presence of water allows the use of these metal oxide catalysts in low-temperature schemes for the oxidative coupling of methane.

The effect of water becomes weaker at higher reaction temperatures (Table 1), where oxidative coupling selectivity appears to be higher because of a smaller contribution of surface-catalyzed full oxidation of the methane reactant. This is consistent with our proposal, suggested by the findings reported below, which show that water inhibits surface-catalyzed oxidation steps by modifying the density and nature of oxygen species on metal oxide surfaces.

X-Ray photoelectron studies of selective and unselective preparations of Li/MgO and MgO preparations showed that high surface densities of oxygen species having a XPS binding energy of 534.1 eV. These oxygen surface species differ markedly in their binding energy from lattice oxygen (BE=532.4 eV) and appear to be responsible for oxygen activation

Table 1. Effect of Steam on Reactions of Methane with Oxygen on Li/MgO Catalysts

Temperature (°C)	Steam	Conversion (%) CH_4	Selectivity (%)		
			CO_x[b]	Hydrocarbons	$C_2^=/C_2^\circ$
550	Yes	6	85 (0)	15	<0.2
600	Yes	18	70 (0)	30	0.6
600	No	14	95 (2)	5	0.3
650	Yes	19	77 (3)	23	0.8
650	No	16	81 (2)	19	0.2

[a] Methane, 1.5 $cm^3 \cdot min^{-1}$; O_2, 0.5 $cm^3 \cdot min^{-1}$; H_2O, 3.3 $cm^3 \cdot min^{-1}$.
[b] Amount of carbon monoxide in brackets; CO_x selectivity is the sum of CO and CO_2 in gas phase and CO_2 on catalyst due to the formation of carbonate.

and for the formation of methyl radicals on MgO surfaces.

Active Surface Sites for Oxidative Coupling on Ca-Ni-K Oxides and Li/MgO

These effects of added water on Li/MgO catalysts resemble those we previously reported on Ca-Ni-K oxide catalysts [1], which also convert methane to CO_x and C_2 species at temperatures around 600°C. This resemblance led us to study both types of materials using temperature-programmed isotopic exchange (TPIE) and temperature-programmed desorption (TPD) of water and CO_2 on these materials [3].

TPIE studies were carried out by exchanging ^{16}O-containing metal oxide catalysts with $H_2{}^{18}O$ at 680°C until no further exchange was noted. These isotopically labeled solids were then exposed to unlabeled $^{16}O_2$ at room temperature and the temperature was increased linearly to 750°C at 10°C/min. The kinetics of exchange between surface and lattice oxygen and gas phase O_2 were measured by monitoring the concentrations of $^{18}O^{16}O$ (single exchange) and $^{18}O_2$ (multiple exchange) in the gas phase [3].

TPIE profiles for single exchange ($^{18}O^{16}O$) and double exchange ($^{18}O_2$) oxygens are shown in Figure 1 for Li/MgO and in Figure 2 for Ca-Ni-K. The appearance of these exchange products did not result from oxygen desorption from the labeled oxide precursors, as shown by the absence of gas phase oxygen species during heating of these samples in an inert He stream. On Li/MgO, two types of kinetically-distinct surface oxygen species give rise to single exchange and result in noticeable desorption maxima at 550 and 660°C

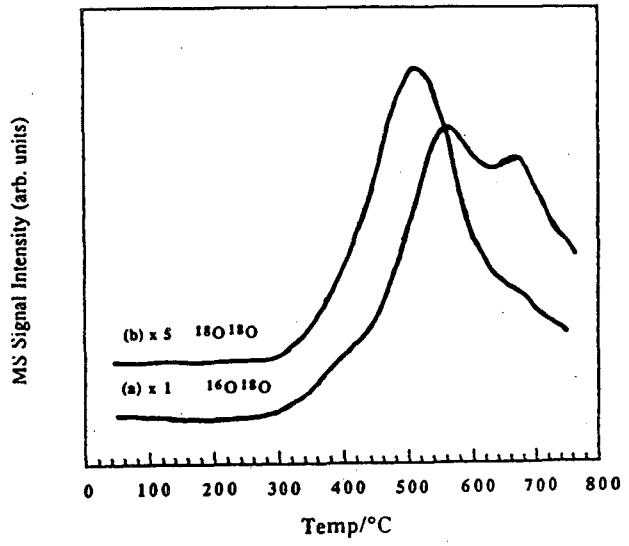

Figure 1 TPIE of ^{18}O in Li/MgO with gas phase $^{16}O_2$. (a) single exchange; (b) multiple exchange.

(Figure 1). Multiple exchange TPIE profiles show only a single maximum at about 500°C. About 20% of the available oxygen species are capable of multiple exchange reactions. Significant exchange between gas phase oxygen and Li/MgO occurs only above 400°C, a temperature range also required for detectable amounts of methane oxidation and oxidative coupling products.

Multiple exchange occurs on Li/MgO during a single surface sojourn and not by sequential single exchange processes. In fact, the multiple exchange process appears to occur at even lower temperatures than single exchange. This single-step multiple exchange process occurs on active sites with kinetic access to more than one oxygen atom, such as peroxide sites present on metal oxide surfaces. McCarty [9] has recently suggested the involvement of both superoxide (O_2^-) and peroxide (O_2^{-2}) anions in reactions of methane on metal oxides. Oxygen reactivity and availability appear to be greater in peroxide species, suggesting the involvement of these sites in multiple exchange pathways and in deeper oxidation reactions of methane.

Single and multiple exchange sites are also present on Ca-Ni-K oxides catalysts, but their relative abundance is more difficult to detect because sequential single exchange steps also lead to $^{18}O_2$ products on these catalysts. Also, the TPIE profiles depend on the method of catalyst synthesis. At least three types of sites catalyze single exchange reactions on Ca-Ni-K oxides (Figure 2), with TPIE maxima at 430, 580, and >750°C. Multiple exchange TPIE products also reveal three kinetically distinct processes with maxima at 450, 520, and >720°C. After sequential single step processes are taken into account, we find that about 7% of the available exchange sites promote single-sojourn multiple exchange reactions.

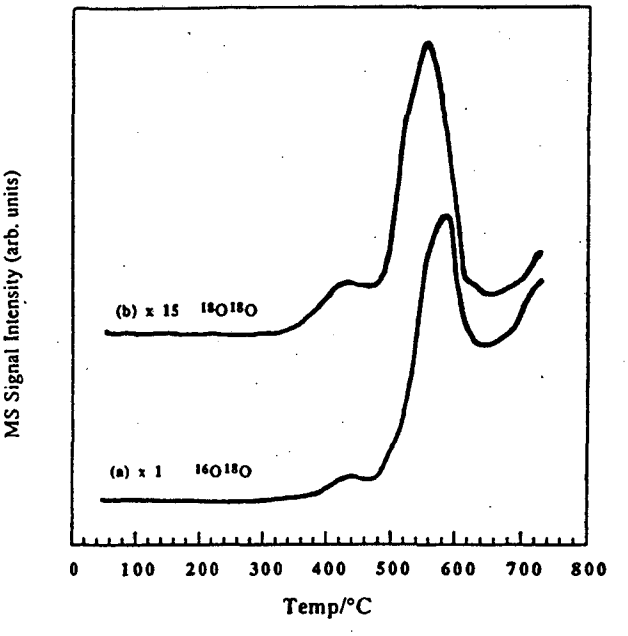

Figure 2. TPIE of ^{18}O in Ca-Ni-K oxides with gas phase $^{16}O_2$. (a) single exchange; (b) multiple exchange.

The presence of water appears to inhibit the extent of multiple exchange occurring on Li/MgO and Ca-Ni-K oxide catalysts. It also inhibits full oxidation reactions during the oxidative coupling of methane at low temperatures. We suggest that water can catalyze the decomposition of peroxide anions (O_2^{-2}) by stabilizing surface OH^- surface species that act as intermediates in the formation of highly mobile charge carriers such as O^-, which are likely to lead to both single exchange and single H-abstraction from CH_4 molecules. At higher temperatures, peroxide decomposition can apparently occur without the assistance of adsorbed water species, and the effect of water on oxidative coupling selectivity is much less marked than at lower temperatures.

Characterization of Ca-Ni-K Oxide Powders

These studies have been complemented with detailed surface characterization of CaNiK

materials, specifically the surface density and location of K, and its essential role in the oxidative coupling reaction. X-Ray Photoelectron Spectroscopy (XPS) studies show that K species segregate to the surface of Ca-Ni oxides in oxidative environments at usual oxidative coupling reaction temperatures. The required K promotion of oxidative coupling reactions on Ca-Ni oxides requires segregation of K to their surface and their strong interaction with the underlying oxide in order to prevent alkali loss during pretreatment and catalytic reactions. Magnetochemical characterization techniques have also been used to determine the structure and oxidation state of Ni cations within the oxide lattice in Ca-Ni-K catalysts

Reaction-Transport Models of Oxidative Coupling and Predicted Benefits of Membrane Reactors.

Computer simulations using recently reported detailed reaction-transport models of oxidative coupling reactions [5,6] confirm previous suggestions that selective methyl radical generation sites are necessary but not sufficient to achieve high C_2 yields. Increasing turnover rates or site densities increase C_2 yields by increasing gas-phase methyl radical concentrations and the probability of bimolecular coupling reactions. Such sites, however, also activate ethane and ethylene to C_2 radicals that undergo facile oxidation in homogeneous gas-phase reactions. Thus, C_2 yields above about 25% in conventional reactors require not only sites that form methyl radicals from methane without total oxidation pathways but also sites that can activate methane without catalyzing similar C-H abstraction steps in ethane and ethylene molecules. This type of selectivity is unlikely to occur because of the structural and chemical similarities between methane and ethane.

Homogeneous C_2 oxidation reactions can be inhibited by lowering oxygen concentrations, but this approach also limits the availability of the required stoichiometric oxygen reactant and the driving force for the catalytic generation of methyl radicals. The required stoichiometry can be maintained by introducing oxygen continuously as it is consumed along the reactor, while maintaining a low and constant oxygen concentration in the reactor gas phase. This approach depends on the availability of surface sites that activate methane to methyl radicals with low kinetic dependence on oxygen concentration, so that homogeneous oxidation pathways can be selectively inhibited compared with methyl radical generation steps as we decrease the oxygen concentration.

Figure 3 illustrates the improved C_2 yields predicted as oxygen transport membranes lower local oxygen concentrations near catalytic sites and in the contacting gas phase. C_2 yield improvements become significant only when the oxygen kinetic dependence for the catalytic methyl radical generation step becomes less than one. Then, gas phase oxidation reactions are influenced more strongly by lower oxygen concentrations than the desired surface-catalyzed methyl radical generation steps.

Hydrogen Transport Membranes for the Oxidative Coupling of Methane

An alternate approach that totally excludes contact between the hydrocarbon and oxygen components of the stoichiometric reaction mixture is the use of hydrogen transport membranes. Metal oxides with high protonic and electronic conductivity are especially appealing because they avoid the extensive fouling inherent in the use of metal membranes (e.g., Pd). One side of the membrane would catalyze hydrogen abstraction

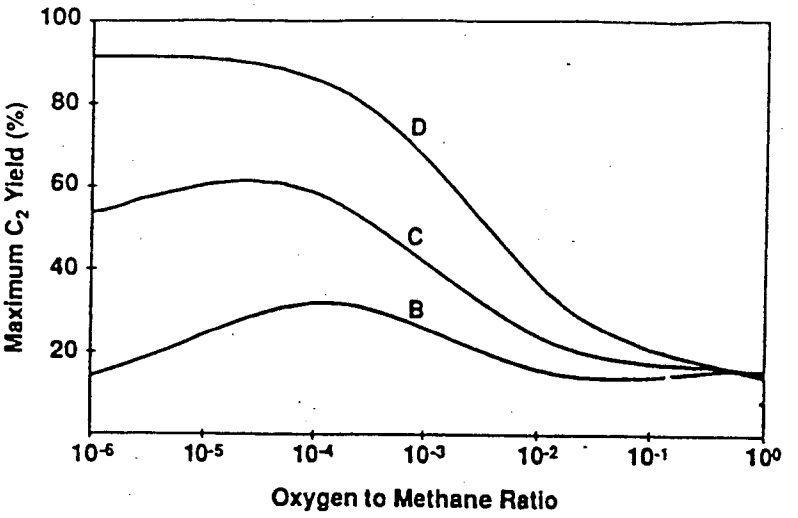

Figure 3. Simulated effect of oxygen concentration on C_2 yields in tubular membrane reactors at 800°C and 67 kPa CH_4 [membrane catalyzes formation of methyl but not ethyl radicals; kinetic order in oxygen for methyl radical generation (n); Curve B (n=1); C (n=0.5); D (n=0)]

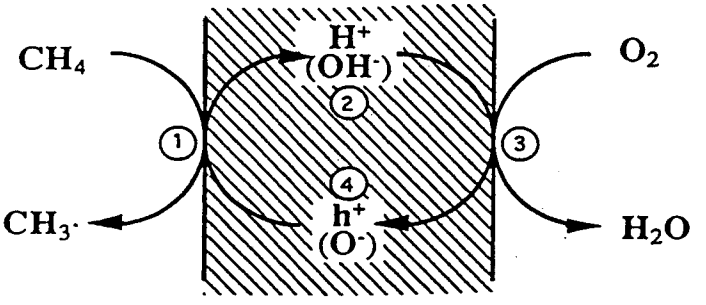

Figure 4. Catalytic Membrane Reactors Using Proton Conductors

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 = $-D_{h+}(\Delta[h^+]/\Delta x)$

Figure 5. Reaction Pathways Involved in Non-Electrochemical Activation of Methane in Proton-Conducting Membrane Reactors

steps and the formation of methyl radicals and hydrogen atoms from methane. Hydrogen atoms would move across the membrane under a concentration gradient imposed by the CH_4 activation step and react with O_2 or other hydrogen acceptor species on the opposite side of the membrane (Figures 4 and 5).

Recent reports suggest that these reactor configurations allow the selective conversion of methane to C_2 hydrocarbons but conversions were limited by the slow transport of protons and holes across relatively thick membranes [10]. Our objective is to demonstrate the feasibility of this approach, to develop techniques for the synthesis of thinner disks and films (<0.5 mm), required for faster proton transport, and to combine these membranes with catalyst films in order to optimize the catalytic chemistry at each side of the proton conducting membrane.

We have recently prepared $SrM_{0.9}Y_{0.1}O_{2.95}$ (M=Ce, Zr) perovskites in the form of thin disks (1 mm) suitable for use in a membrane reactor that we have recently designed and constructed in our laboratory. These materials allow the selective transfer of the abstracted H-atoms from one side, where the CH_4 activation occurs, to the opposite side, where they are oxidized to provide the thermodynamic driving force for the overall conversion reaction, without allowing direct contact between hydrocarbons and O_2.

Initial membrane fabrication procedures involved spin coating alcohol solutions of mixed metal alkoxides onto porous alumina disks. These synthesis procedures failed to produce membranes of uniform thickness. Dried and calcined forms of these membranes showed extensive defects and porosity within the metal oxide film even after densification; these supported membranes were also difficult to seal against the reactor.

Synthesis procedures were developed in order to produce thicker unsupported metal oxide disks. These membranes were prepared by calcining mixtures of $SrCO_3$, ZrO_2 , and Y_2O_3 at 1000°C in order to form mixed oxides with X-ray diffraction lines and compositions corresponding to $SrZr_{0.9}Y_{0.1}O_{2.95}$ in perovskite structures. The resulting powder was then pressed into a disk and sintered by heating in air first to 1300°C in order to make a disk preform and then to 1600°C overnight in order to densify the materials and eliminate internal porosity and bypass channels. The density of the resulting material was 85% of the theoretical solid density, with the top and bottom of the disk much closer to this theoretical density

A thin sample of this disk was obtained by cutting a 1 mm slice off the end of this disk and mounting it within the reactor using a zirconia-based ceramic paste. The membrane developed a small (2 x 0.1 mm) crack during reaction, allowing some intermixing of the two reactants streams during testing. Additional slices of the same disk are being prepared for testing. In addition, we have found that preforms where Zr has been replaced with Ce ($SrCe_{0.9}Y_{0.1}O_{2.95}$) sinter to disks with 90% of the theoretical density at lower densification temperatures (1500°C). These lower temperatures may ultimately allow the use of graphite as a membrane barrier in order to block remaining channels across the membranes. Both Zr and Ce forms of these perovskites materials are being prepared for measurements of oxidative coupling catalytic activity and proton conductivity.

Membrane and Catalytic Films of Metal Oxides.

We are also studying alternate methods for the fabrication of coherent thin films in order to decrease the ultimate thickness of the membrane materials well below the 1 mm thickness presently attainable. These methods can also be used to deposit thin films of catalytic materials on the surface of metal oxides and thus remove the need for catalyzing the methane activation reaction and the hydrogen oxidation reactions on the actual metal oxide used as the membrane material.

Specifically, we have demonstrated the formation of $Ca_{(1-x)}Ni_xO$ solid solution films using pulsed laser deposition from sintered targets of NiO and CaO. This technique involves the vaporization of a target by a pulsed laser beam, the formation of plasma plume, and the deposition of the plume materials on a heated substrate. The resulting films were approximately 150 nm thick and showed X-ray diffraction patterns corresponding to crystalline bulk materials with sodium chloride structures. This technique allows the formation of coherent films of varying stoichiometries and thickness, which cannot be formed directly by thermal treatment of NiO and CaO powder precursors.

This techniques was also used successfully to prepare Ca-Ni-K oxide films with K contents spanning the entire range of catalytically relevant compositions. The pulsed laser deposition prevents the extensive loss of volatile K species that occurs during conventional thermal synthesis of these materials at high temperatures.

These synthesis techniques are quite general and can be applied to the synthesis of most metal oxide materials. In particular, we will attempt to extend this pulse laser deposition techniques to the synthesis of proton-conducting oxides in thin film configurations and of catalytic films of optimum composition for the non-oxidative generation of methyl radical on one side of the membrane and for the oxidation of hydrogen using O_2 on the opposite side. Additional control of film density, adhesion to substrate, and oxide orientation may be obtained using ion-assisted pulsed laser deposition, a technique under active research in our laboratory.

Cyclic Decomposition of Methane and Scavenging of Hydrogen or Hydrocarbon Fragments

The separation between the CH_4 and O_2 stoichiometric reactants can occur spatially, as it does in our proposed catalytic membrane configuration, or temporally, as in recently reported cyclic schemes for the sequential decomposition of methane to surface carbides on metals surface followed by hydrogenation of these species to C_2 hydrocarbons using gas phase H_2 [11]. In these schemes, the coupling is thermodynamically driven by changes in temperature between the two cycles, rather than by providing an oxidative pathway for the removal of the hydrogen reaction products.

We have recently started an experimental program to examine the feasibility of alternate cyclic schemes for methane conversion on supported metal catalysts. Three specific approaches differing significantly from those described in reference [11] are being examined:

1. Decomposition of methane to CH_x surface species and oxidative removal using O_2 to form H_2 and CO mixtures with high selectivity.

2. Decomposition of methane on metal surfaces to form CH_x species and scavenging of such

species by alkylation of hydrocarbons such as ethylene, ethyne, or benzene.

3. Decomposition of CH_4 on metals, sub-oxides, or alloys that form stable interstitial hydride compounds (e.g., Zr_2Fe, Pd, Ga, La and W oxides, ...) and scavenging of the interstitial hydrogen in a subsequent cycles by transfer to hydrogen acceptor species.

FUTURE WORK

1. Develop thin film deposition techniques and other fabrication techniques for membranes with higher proton fluxes.

2. Determine catalytic and proton conduction properties of $SrM_{0.9}Y_{0.1}O_{2.95}$ (M=Ce, Zr) perovskites

3. Develop rigorous reaction-transport models of methane activation under non-oxidative (pyrolysis) conditions

4. Explore potential of proposed approaches for cyclic methane decomposition followed by scavenging of the CH_x or H reaction products.

5. Exploit magnetochemical techniques for the characterization of the structure and oxidation state of transition metal cations within catalytic oxide films.

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