DOE/MC/00098-95/C0463

Conf-950494--21

Steady-State and Transient Catalytic Oxidation and Coupling Methane

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Contract Number:

DE-AC03-76SF00098

Conference Title:

Natural Gas RD&D Contractor's Review Meeting

Conference Location:

Baton Rouge, Louisiana

Conference Dates:

April 4 - 6, 1995

Conference Sponsor:

Co-Hosted by Department of Energy (DOE)
Morgantown Energy Technology Center
Morgantown, West Virginia
and
Southern University and
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Steady-State and Transient Catalytic Oxidation and Coupling of Methane

CONTRACT INFORMATION

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Period of Performance	January 1, 1994 to January 31, 1995

Schedule and Milestones

Two papers have been published on calcium-nickel-potassium oxide catalytic thin films.[1,2] Three presentations,[3-5] including a keynote lecture at the 204th ACS meeting, were given in 1994 describing reaction-separation schemes using oxidative coupling of methane, and two more are scheduled for 1995.[6,7] Four quarterly reports have been written and submitted during this time.[8] These findings have led us to develop membrane and cyclic feed reactor designs for methane coupling. We have completed initial membrane trials using two methods of metal oxide film preparation, pulsed laser deposition and co-precipitation. In 1995, we will prepare non-porous membrane films using these techniques and test them in a membrane reactor.

OBJECTIVES

This project addresses the conversion of methane from natural gas into ethane, ethylene and higher hydrocarbons. Our research explores the mechanistic and practical implications of carrying out the methane oxidative coupling reaction in reactor designs other than conventional packed-beds with co-fed reactants. These alternate reactor designs are needed to prevent the full oxidation of methane, which limits C_{2+} yields in methane oxidative coupling reactions.

BACKGROUND INFORMATION

Oxidative coupling of methane (OCM) leads to ethane and ethylene as primary products and CO and CO_2 by primary direct oxidation of methane and by secondary combustion of C_2 products. The oxidative coupling reaction combines methyl radical generation on various oxide surfaces with coupling and oxidation of alkyl radicals in the gas phase.

Maximum C_{2+} yields of about 25% have been achieved using single-pass catalytic reactors with mixed methane and O_2 feeds. Higher C_{2+} yields will require catalytic solids that activate methane but not ethane or ethylene, the existence of which appears improbable at this time.

PROJECT DESCRIPTION

The research strategy focuses on preventing contact between the O_2 reactant required for favorable overall thermodynamics and the C_{2+} products of methane coupling. The behavior of various reactor designs are simulated using detailed kinetic-transport models. These simulations have suggested that the best way to prevent high CO_2 yields is to separate the oxygen and hydrocarbon streams altogether. As a result, the project has focused on the experimental demonstration of proton transport membrane reactors for the selective conversion of methane into higher hydrocarbons.

RESULTS

Reaction-Transport Models of Oxidative Coupling

Kinetic-transport models of the oxidative coupling reactions have been used to predict the C_{2+} yields in various reactor configurations. These models combine a detailed gas phase kinetic network and surface reactions with rigorous descriptions of the convective and diffusive transport processes within catalytic reactors.[9,10] We have previously reported simulation results from staged oxygen injection and oxygen-transport membrane reactors.[9,10] More recently, we have used these models to simulate the behavior of two additional reactor designs:

1) tubular flow reactor with interstage separation of ethane and/or ethylene
2) recycle reactor with ethane and ethylene removal from the recycle stream

Figure 1 shows a tubular reactor with C_2 separators along its length. As the reaction proceeds, the gas stream is periodically diverted from the reactor into a separator with 100% C_2 removal efficiency. The function of this separator is to remove the C_2 products before they undergo complete oxidation, and to add a small amount of oxygen in order to satisfy the OCM reaction stoichiometry while maintaining low O_2 concentration.

Realistically, such a separator would require cooling (and subsequent re-heating) of the gas stream from reactor temperatures of 800°C to below 100°C, the lowest operating temperature of current C_2 adsorbents. These repeated heating/cooling cycles severely reduce the second-law efficiency of this process.

Figure 2 shows the predicted C_2 yield for ethylene or ethane/ethylene separation. As the number of separators

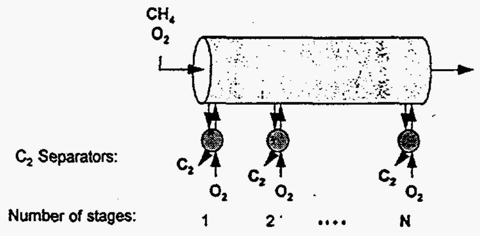

Figure 1. Staged C_2 Separation

increases, the overall reactor performance (and complexity) also increases. Fortunately, a small number of separators (<10) gives a significant improvement in C_2 yield. The maximum C_2 yield ($N = \infty$) is about 90%, corresponding to the selectivity of the surface methane oxidation reaction.

[800°C, $CH_4/O_2 = 2$, 1 bar total pressure]

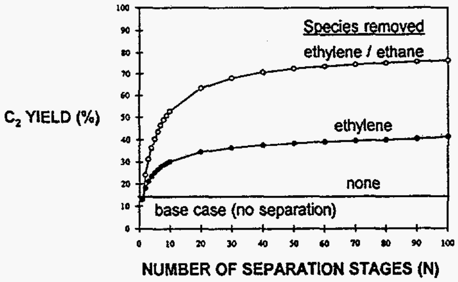

Figure 2. C_2 Yield Improves with an Increasing Number of Separators

This reactor is very similar to the simulated counter-current chromatographic moving-bed reactor reported by Tonkovich, et al.[11] Using an unpromoted Sm_2O_3 catalyst, and periodically removing both the ethane and ethylene product, they report a maximum C_2 yield of about 50% at a reactor temperature of 750°C. For large N, this value is between that predicted in figure 2 for ethane/ethylene removal and ethylene removal only. As noted by the authors,[11] this reactor could be optimized to achieve a C_2 yield closer to the 75% maximum predicted by our model for a large number of separators.

A more conventional reactor-separator design is the recycle reactor with C_2 removal from the recycle stream, as shown in figure 3. The recycle reactor operates on the same principle as the staged separation design: removal of the C_2 product before it can be completely oxidized. Figure 4 shows the simulated effect of increasing the recycle ratio on the overall C_2 yield, assuming the complete removal of both ethane and ethylene from the recycle loop. For a large recycle ratio (R=20), the C_2 yield is predicted to approach 60% at a methane conversion of 80%.

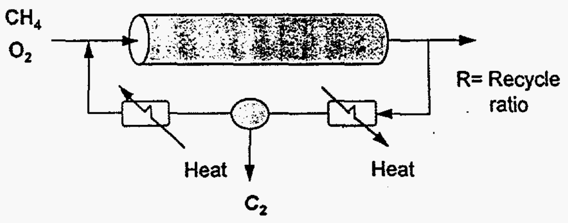

Figure 3. Recycle Reactor with C_2 Separation from Recycle Stream

Experimental results using a recycle reactor have been reported recently by Vayenas and coworkers.[12] Their reactor had a per-pass methane conversion of less than 3%. However, at steady-state, they report a maximum C_2 yield of 49%, at a CH_4 conversion of 65%. Furthermore, in batch operation ($R = \infty$), the reactor achieved a C_2 yield of 88%, the highest value reported to date for the oxidative coupling reaction. As

[800°C, $CH_4/O_2 = 2$, 1 bar total pressure]

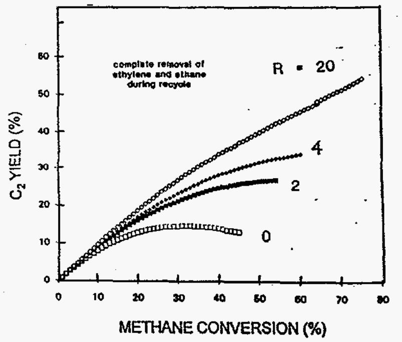

Figure 4. Predicted C_2 Yield in a Recycle Reactor with Increasing Recycle Ratio

noted by the authors[12] and demonstrated by our model, the dramatic C_2 yields attained were due to the separation of ethylene prior to oxidation, rather than any special aspect of the reactor design or the electrochemical catalyst employed.

A significant problem with these two reactor schemes is the availability of efficient C_1/C_2 separators. The low-temperature processes currently used to separate the light gases in an OCM product stream require efficient heat integration and cause large entropy losses (i.e., reduced second-law efficiency). Also, the dilution effect of a recycle stream leads to large reactors and high capital costs. Therefore, we are pursuing reaction-separation schemes that place less emphasis on the methane-C_2 gas separation process.

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. Figure 5 shows the membrane reactor concept. One side of the membrane must activate the C-H bond in methane to generate methyl radicals and surface hydrogen. The hydrogen moves through the membrane under a concentration gradient developed by the removal of hydrogen from the opposite side by O_2 from air. The overall reaction is that of the OCM reaction, which is thermodynamically favorable and does not require an externally applied voltage.

The key to this reactor is the nature of the membrane and of the catalytic surface. Metal oxides with high protonic and electronic conductivity are appealing beacause they avoid the extensive fouling inherent in the use of metal membranes (e.g. Pd alloys). These properties have been demonstrated in perovskites of composition $SrB_{1-x}B'_xO_{3-0.5x}$ (B=Ce, Zr; B'=Yb, Y; x=0.01-0.1).[13,14] In these materials, the B'^{3+} cation substitutes into the lattice position of the B^{4+} cation, creating lattice oxygen vacancies by charge compensation. Uchida et al, have shown that in the presence of oxygen these vacancies form electron holes (lattice O^- species), which can abstract hydrogen from gas phase molecules.[15] Within the oxide, the abstracted hydrogen forms a proton, which behaves as a point-charge interstitial species that can migrate among lattice oxygen ions.[16] At temperatures between 500 to 1000°C, these perovskites have a hydrogen diffusion coefficient of about 10^{-6} cm^2/sec, and practically no oxygen conductivity.[16]

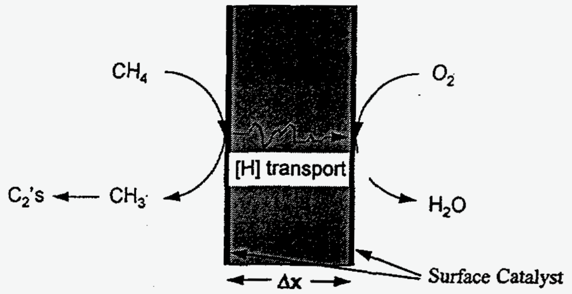

Figure 5. Methane Coupling in a Hydrogen Transport Membrane Reactor

The methane coupling reaction has been conducted using a $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ membrane in an electrochemical cell.[17] Although this configuration did enhance the conversion of methane to C_2 hydrocarbons, the rates were low due to slow transport of protons through the thick membrane and extensive coking on the metal electrodes at the high reaction temperature (900°C). Our goal is to demonstrate the feasibility of this approach, emphasizing thinner membrane films (<0.5 mm), more active and selective surface catalysts, and much lower reaction temperatures (<700°C).

Membrane and Catalytic Thin Films of Metal Oxides

We are currently studying three methods of preparing ceramic thin films:

1) Pressed discs (~0.5 mm thick)
2) Pulsed laser deposition of a 1 μm film on a ceramic substrate,
3) Spin- or dip-coating of films (<0.1 mm) using dispersed precursors.

A general problem with preparing mixed metal oxides is the creation of a homogeneous mixture of the metal cations. The traditional method is to mix the (solid) metal salt precursors and sinter at high temperature to induce diffusion and formation of the desired phase in the solid state. We have prepared discs of various perovskite phases by grinding and calcining at 1000°C mixtures of the oxide precursors. This powder was then pressed to 30,000 psi and sintered at 1300°C in air, followed by another cold press and sintering at 1600°C overnight. These discs achieved 85-90% of the theoretical density. When we repeated the method, replacing the second cold press step with a hot press, we were able to achieve up to 95% theoretical density for some samples. These results are summarized in table 1.

We have attempted to test these membranes inside an alumina membrane reactor. Samples with less than 90% theoretical density proved to be permeable to methane. With the other samples, we have experienced cracking of the membranes and the zirconia cement used to attach the samples as the temperature is raised above 200°C. An alumina cement has been recently selected, to more closely match the thermal expansion of the reactor and perovskite discs.

Table 1. Per Cent of Theoretical Density of Perovskite Membrane Samples

Cold Press (30,000 psi, 25°C)	
$BaZr_{0.9}Y_{0.1}O_{2.95}$	85.3%
$CaZr_{0.9}Y_{0.1}O_{2.95}$	90.1
Hot Press (8,000 psi, 1600°C)	
$SrZr_{0.9}Y_{0.1}O_{2.95}$	93.8%
$SrCe_{0.9}Y_{0.1}O_{2.95}$	93.2
$BaCe_{0.9}Y_{0.1}O_{2.95}$	93.2

Using this technique, the minimum thickness for dense, unsupported ceramic membranes is about 0.5 mm.[17] Since a reduction in the membrane thickness will give a proportional increase in proton conductivity, we have begun to explore two alternate methods for the synthesis of thin films.

Pulsed-Laser Deposition of Thin Films

We have previously reported the preparation of $Ca_{1-x}Ni_xO$ catalytic thin films using pulsed laser deposition (PLD).[18] This technique involves the vaporization of a target by a high-energy pulsed laser beam, the formation of a plasma plume, and the deposition of the plume on a heated substrate. Recently, we have used an eximer laser with nanosecond pulses of 3-5 J/cm^2 energy density to deposit $SrZr_{0.9}Y_{0.1}O_{3-\delta}$ films of approximately 0.2 to 0.5 μm thickness on a porous Al_2O_3 substrate. (Coors Ceramics Company, average pore diameter <0.5 μm)

The resulting film was studied in a scanning electron microscope with energy dispersive spectroscopy (EDS) to examine the film composition and integrity. Figure 6 shows the EDS results. After film deposition, the peaks due to impurities in the Al_2O_3 substrate have disappeared, being covered by peaks corresponding to $SrZr_{0.9}Y_{0.1}O_{3-\delta}$, in the same ratio as the target composition.

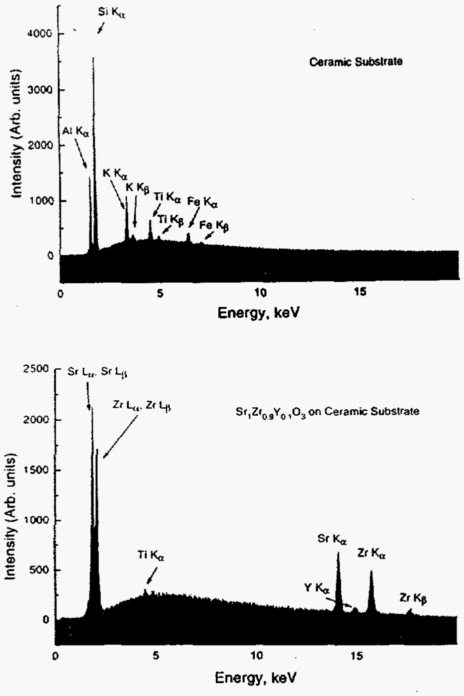

Figure 6. EDS Patterns of $SrZr_{0.9}Y_{0.1}O_{3-\delta}$ Film and Al_2O_3 Substrate

X-ray diffraction patterns of the substrate were taken before and after film deposition. Figure 7 shows the XRD pattern due to the film and substrate compared to the pattern of the substrate alone. The three strongest lines of $SrZrO_3$ at d = 2.91, 2.06, and 1.68 are the only peaks appearing after the film deposition, indicating the formation of a phase-pure film of $SrZrO_3$ in the distorted perovskite structure. As expected, the Y^{3+} cations have been substituted for Zr^{4+} cations with little alteration of the original lattice structure.

We are currently testing the film porosity in an alumina reactor at temperatures from 25 to 800°C. The earliest samples proved to be porous, allowing >14% gas flow (compared to the substrate alone) through the membrane. We have prepared samples with thicker films (~1 μm) in order to obtain a non-porous film for hydrogen transport and OCM studies.

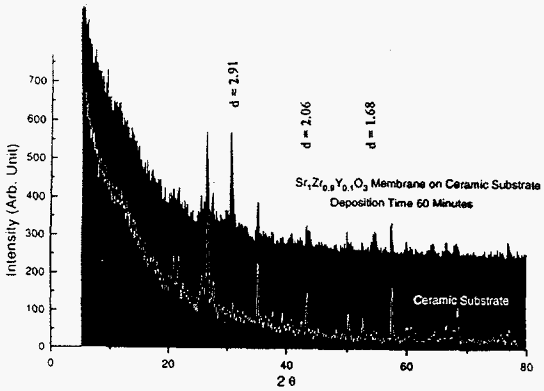

Figure 7. XRD Patterns of $SrZr_{0.9}Y_{0.1}O_{3-\delta}$ Film and Al_2O_3 Substrate

In pulsed-laser deposition, the target material and the substrate must fit inside an UHV chamber, which limits the utility of the method to small-scale applications. However, for experimental studies it provides a method to test the limit of improving the membrane concept via a reduction in the film thickness.

Preparation of Mixed Metal Oxide Precursors Via Co-Precipitation

The solid state reaction synthesis route for the Sr-Ce(Zr)-Yb(Y)-O perovskites requires reaction temperatures in excess of 1450 °C for 24 hours.[13] In order to form a dense perovskite phase at lower temperatures, we are exploring methods that allow the formation of high-surface area precursors with intimate contact among the desired metal cations.

Recently, high-temperature superconductors with the perovskite structure have been prepared using precursors formed via co-precipitation.[19,20] This involves dissolving the appropriate metal salts in an acidic mixture, which is rapidly added to a basic solution to induce precipitation of the metals as hydroxides or carbonates. After thermal treatment, this method gives dense, homogenous sinters with the perovskite phase only. These sinters can then be sliced into thin discs or used as targets for pulsed laser deposition on a ceramic substrate. Alternately, the precursor can be dissolved and coated on a ceramic substrate prior to thermal treatment. Repeated coatings yield homogeneous thin films.[19]

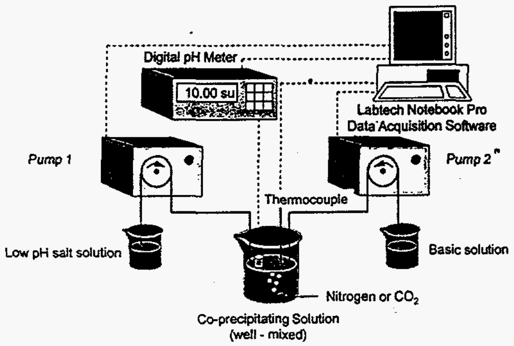

Figure 8. Constant pH Co-Precipitation

We have constructed a computer-controlled constant pH co-precipitation unit to prepare these precursors in a controlled and reproducible manner. The unit is shown in figure 8. In order to maintain stoichiometry and minimize waste, the precipitation is conducted at the pH value corresponding to the minimum solubility of the cations in solution. From potentiometric titration and solubility data for the cations Ce^{3+}, Yb^{3+}, and Y^{3+}, a pH of 9 was determined to be high enough to precipitate the metal hydroxides. This allows use of ammonium hydroxide as the base, which is readily removed upon heating. As expected from similar data for Ba^{2+}, $Sr(OH)_2$ is soluble at all values of pH. However, Sr^{2+} will precipitate as a carbonate over a wide range of pH. The addition of an excess amount of ammonium bicarbonate to the precipitating solution allows for the recovery of Sr^{2+} along with the other cations.

We have prepared several samples of mixed metal salts of stoichiometry $SrCe_{0.95}Yb_{0.05}$ at pH = 9. We are currently testing the effects of various heat treatments upon forming dense discs for eventual testing in the membrane reactor. We anticipate this method will allow the use of lower sintering temperatures in forming the perovskite phase.

FUTURE WORK

1. Test proton transport membranes prepared using pulsed-laser deposition and co-precipitation techniques.

2. Develop thin film deposition techniques and other fabrication methods for ceramic membranes.

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

4. Screen potential surface catalysts for medium temperature, pyrolytic methane activation.

ACKNOWLEDGMENTS

The authors wish to acknowledge Sebastian C. Reyes of Exxon Research and Engineering (Annandale, NJ) for work on the OCM model, and Richard W. Borry III of the University of California at Berkeley

for work on the hydrogen transport membrane experiments.

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