The influence of carbon dioxide on the catalytic oxidative coupling of methane over A-La2O3 and II-La2O2CO3

Richard Paul Taylor
Iowa State University

Follow this and additional works at: http://lib.dr.iastate.edu/rtd

Part of the Chemical Engineering Commons

Recommended Citation
http://lib.dr.iastate.edu/rtd/10390

This Dissertation is brought to you for free and open access by Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600
The influence of carbon dioxide on the catalytic oxidative coupling of methane over A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$

Taylor, Richard Paul, Ph.D.

Iowa State University, 1992
The influence of carbon dioxide on the catalytic oxidative coupling of methane over A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$

by

Richard Paul Taylor

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Approved:
Signature was redacted for privacy.

In Charge of Major Work
Signature was redacted for privacy.

For the Major Department
Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa
1992
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ............................................................................................................................. vi

GENERAL INTRODUCTION ...................................................................................................................... 1
   Explanation of Dissertation Format ........................................................................................................ 1
   Introduction ........................................................................................................................................ 1

Literature Review .................................................................................................................................... 4
   Homogeneous versus Heterogeneous Reactions .................................................................................... 5
   Methane Activation via Hydrogen Abstraction ...................................................................................... 6
   The Active Site for Methane Activation .................................................................................................. 8
   Ethane Production via Coupling of Methyl Radicals .......................................................................... 10
   Ethene Production via Ethane Dehydrogenation ............................................................................... 11
   Reactive Intermediates .......................................................................................................................... 12
   Routes for the Production of Carbon oxides ......................................................................................... 12
   Previous Work Conducted in our Laboratory ....................................................................................... 13

Research Objectives ............................................................................................................................... 16

PAPER I. THE INFLUENCE OF CO-FED CO\textsubscript{2} ON THE OXIDATIVE COUPLING OF METHANE OVER A-La\textsubscript{2}O\textsubscript{3} AND II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}

ABSTRACT .................................................................................................................................................. 21

1. INTRODUCTION ..................................................................................................................................... 22

2. EXPERIMENTAL PROCEDURE ............................................................................................................. 26
   2.1 Catalyst Characterization ............................................................................................................... 26
      2.1.1 Fourier Transform Infrared Spectroscopy .............................................................................. 26
      2.1.2 Laser Raman Spectroscopy .................................................................................................... 27
   2.2 Catalyst Preparation ....................................................................................................................... 27
      2.2.1 Preparation of A-La\textsubscript{2}O\textsubscript{3} ...................................................................................... 28
      2.2.2 Preparation of II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} ........................................................................... 29
   2.3 Catalytic Performance Evaluation .................................................................................................. 29

3. EXPERIMENTAL RESULTS .................................................................................................................. 34
   3.1 Co-feeding CO\textsubscript{2} over A-La\textsubscript{2}O\textsubscript{3} ............................................................................... 34
      3.1.1 Influence on Feed Conversions .............................................................................................. 34
      3.1.2 Influence on C\textsubscript{2} Selectivities ..................................................................................... 34
      3.1.3 Influence on CO\textsubscript{2} Selectivities ................................................................................... 37
   3.2 Co-feeding CO\textsubscript{2} over II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} ........................................................................ 37
      3.2.1 Influence on Feed Conversions .............................................................................................. 37
3.2.2 Influence on C₂ Selectivities ................................................. 40
3.2.3 Influence on CO₂ Selectivities ............................................... 40
3.3 Post-reaction Catalyst Characterization ...................................... 43

4. DISCUSSION OF RESULTS .................................................................. 44

5. CONCLUSIONS ..................................................................................... 47

ACKNOWLEDGEMENTS ........................................................................... 48

REFERENCES .......................................................................................... 49

PAPER II. THE AFFINITY OF A-La₂O₃ AND II-La₂O₂CO₃ FOR CO₂ AT TYPICAL OCM REACTION TEMPERATURES

ABSTRACT .................................................................................................. 51

1. INTRODUCTION .................................................................................... 52
  1.1 Uptake of CO₂ on A-La₂O₃ and II-La₂O₂CO₃ ........................................ 53

2. EXPERIMENTAL PROCEDURE ............................................................ 56
  2.1 Catalyst Characterization ................................................................. 56
    2.1.1 Fourier Transform Infrared Spectroscopy ................................... 56
    2.1.2 Laser Raman Spectroscopy ....................................................... 57
  2.2 Catalyst Preparation ......................................................................... 57
    2.1.1 Preparation of A-La₂O₃ ............................................................ 58
    2.1.2 Preparation of II-La₂O₂CO₃ ..................................................... 59
  2.3 Thermal Decomposition Studies ...................................................... 59
  2.4 CO₂ Pulsing Studies ......................................................................... 63

3. EXPERIMENTAL RESULTS ................................................................. 65
  3.1 Thermal Decomposition of A-La₂O₃ and II-La₂O₂CO₃ ....................... 65
  3.2 CO₂ Uptake by A-La₂O₃ and II-La₂O₂CO₃ at Elevated Temperatures .... 68
  3.3 CO₂ Uptake by A-La₂O₃ and II-La₂O₂CO₃ during Thermal Decomposition ... 72

4. DISCUSSION OF RESULTS ................................................................. 75
  4.1 Thermal Decomposition of II-La₂O₂CO₃ ........................................... 75
  4.2 The Structure of A-La₂O₃ and II-La₂O₂CO₃ ...................................... 77
    4.2.1 A-La₂O₃ .................................................................. 77
    4.2.2 II-La₂O₂CO₃ ................................................................. 79

5. CONCLUSIONS ..................................................................................... 85
ACKNOWLEDGEMENTS ......................................................................................................................... 86
REFERENCES .................................................................................................................................................. 87

PAPER III. THE FATE OF THE C AND O ATOMS OF THERMALLY EVOLVED CO₂ DURING THE OXIDATIVE COUPLING OF METHANE OVER II-La₂O₂CO₃

ABSTRACT .................................................................................................................................................. 90

1. INTRODUCTION ........................................................................................................................................ 92

2. EXPERIMENTAL PROCEDURE .................................................................................................................. 95
  2.1 Catalyst Characterization ....................................................................................................................... 95
    2.1.1 Fourier Transform Infrared Spectroscopy ....................................................................................... 95
    2.1.2 Laser Raman Spectroscopy ............................................................................................................ 96
  2.2 Catalyst Preparation ................................................................................................................................ 96
    2.2.1 Preparation of A-La₂O₃ and A-La₁⁸O₁ ............................................................................................ 97
    2.2.2 Preparation of II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ .................................................. 98
  2.3 Reactor Studies ....................................................................................................................................... 99
    2.3.1 Thermal Decomposition of II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ............................ 105
    2.3.2 Pulse Studies over II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ............................... 106

3. EXPERIMENTAL RESULTS ....................................................................................................................... 108
  3.1 Preparation of ¹⁸O- and ¹³C-Labeled and Unlabeled Catalysts .............................................................. 108
    3.1.1 Preparation of A-La₂O₃ and A-La₁⁸O₁ ........................................................................................... 108
    3.1.2 Preparation of II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ................................................ 111
  3.2 Thermal Decomposition of II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ............................ 116
  3.3 Pulsing He/CH₄/O₂ over II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ................................. 119
    3.3.1 Isotopic Composition of CO₂ in the Reactor Exit Stream ......................................................... 119
    3.3.2 Isotopic Composition of CO in the Reactor Exit Stream ............................................................ 126
    3.3.3 Isotopic Composition of O₂ in the Reactor Exit Stream ............................................................. 129
    3.3.4 Isotopic Composition of C₂H₆ in the Reactor Exit Stream ......................................................... 129
    3.3.5 Isotopic Composition of C₂H₆ in the Reactor Exit Stream ......................................................... 134
  3.4 Pulsing He/O₂ over II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ................................................ 134
  3.5 Pulsing He/CH₄ over II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ........................................... 136
  3.6 Post-reaction Catalyst Characterization ............................................................................................... 140

4. DISCUSSION OF RESULTS ..................................................................................................................... 141
  4.1 Preparation of ¹⁸O- and ¹³C-Labeled and Unlabeled Catalysts ........................................................ 141
  4.2 Thermal Decomposition of II-La₂O₂CO₃, II-La₁⁸O₂CO₃, and II-La₂O₂¹³CO₃ ........... 141
4.3 Pulse Studies ........................................................................................................ 142

5. CONCLUSIONS ...................................................................................................... 145

ACKNOWLEDGEMENTS ............................................................................................. 148

REFERENCES ............................................................................................................. 149

GENERAL SUMMARY .................................................................................................. 150

ADDITIONAL REFERENCES ....................................................................................... 155
ACKNOWLEDGEMENTS

I have many people to thank for their support and encouragement in completing this project. First of all, I would like to acknowledge the advice and guidance of my major professor, Dr. Glenn L. Schrader. Secondly, I owe a great deal to the people of the Ames and Iowa State University communities who helped me learn so much during my time here. These include my colleagues in the Schrader research group, the secretarial and custodial staff in the Department of Chemical Engineering, the personnel of the Ames Laboratory who greatly facilitated my experimental work, and all my friends and acquaintances in Ames. You all contributed to the enormous personal growth I have experienced in the last five years.

Finally, I wish to express my appreciation, love, and respect for my partner, Jeanne Massey. Her companionship, support, encouragement, tolerance, and unconditional love lightened the load more than she will ever know. I look forward to our future life together.
GENERAL INTRODUCTION

Explanation of Dissertation Format

This dissertation consists of three distinct papers, each written in a form suitable for publication in a technical journal. A general introduction precedes the three papers in order to inform the reader of both the background and industrial relevance of the work. References cited in the general introduction are given at the end of the dissertation along with a summary of the overall findings of the work.

The research presented in each paper represents original work conducted in both the Ames Laboratory and the Department of Chemical Engineering at Iowa State University by the author.

Introduction

In 1982, it was reported that a large number of reducible metal oxides were catalytically active for the conversion of methane to C2 hydrocarbons (ethane, C2H6, and ethene, C2H4) [1]. Since the presence of gas phase oxygen was found to be required for methane activation to occur¹, the process became known as the oxidative coupling of methane (OCM).

It was well known at the time of this study that C2 hydrocarbons could be used as a feedstock for the production of synthetic crude oil. Thus, the OCM process directly linked

¹ In this original study, oxygen and methane were fed in a cyclic mode; co-feeding became the accepted mode in later studies.
the production of synthetic crude to the utilization of natural gas (of which approximately 90 mol. % is methane). The industrial significance of this initial study was immediately recognized and resulted in a strong commitment being made to the field of OCM by researchers around the world.

The OCM process is of particular interest currently because of the problems associated with a continued dependence on natural crude as the primary source of automotive fuel and industrial plastics:

(i) Global crude reserves are finite and existing fields are being depleted faster than new fields are being discovered.

(ii) The quality of crude reserves is decreasing. Most often, this translates into crudes with higher sulfur contents. If not completely removed, sulfur results not only in the poisoning of catalysts used in downstream processing but also in the presence of sulfur dioxide (the main precursor to acid rain) appearing in exhaust streams. With society’s ever increasing sensitivity towards environmental pollution and the subsequent strict legislation regarding industrial emissions, the continued use of such crudes will require large capital investments to be made in air pollution abatement technology.

(iii) Increasingly, crude oil reserves (at least those the exploitation of which is economically viable) lie in politically unstable areas of the (typically third) world. In order to ensure continued unrestricted access to and control of these reserves, it is likely that the crude-importing (primarily first world) countries will increasingly resort to military force. This has already been demonstrated by the U. S.-led action against Iraq during the Gulf War of 1991.
One way to decrease U. S. dependence on foreign crude is to exploit the abundant reserves of domestic natural gas. There are, however, two problems with this approach:

(i) Most natural gas reserves are located in remote regions, e. g. in the Gulf of Mexico, off the Pacific coast, and beneath the North Slope of Alaska. The logistics and expense of transporting a gaseous resource (or the expense of pressurizing the gas for its transportation as a liquid) over large distances and difficult terrain to a processing plant is often prohibitive. One solution is to locate near to the gas reserves, a process which converts the gas to a higher value, more easily transportable (i.e., liquid phase) product.

(ii) Conventional processes for utilizing natural gas have severe drawbacks which make them less than ideal for such large scale implementation. One route is to convert natural gas to syngas via steam reforming. Syngas can then be converted to methanol or to synthetic crude, the latter via Fischer-Tropsch chemistry. However, steam reforming is both capital- and energy-intensive and the Fischer-Tropsch process produces a blend of synthetic crude biased towards lighter hydrocarbons (and therefore, with a lower octane rating). A second route for the utilization of natural gas is to convert the feedstock to methanol directly. This has the advantage over steam reforming of being more energy efficient (on the molecular level, fewer bonds are being broken and made in this process). The intermediate methanol can then be used as a gasoline additive or it can be further converted to synthetic gasoline via Mobil’s MTG (Methanol-to-Gasoline) process.

The attraction of the OCM process, especially relative to the natural gas-MTG route, is really twofold:

2 "Synthesis gas", a 3-to-1 (by volume) mixture of H₂ and CO.
(i) The intermediate \( \text{C}_2 \) hydrocarbons may be used as feedstocks in the production of polyethylene and other polymers, thereby serving to decouple the plastics industry from the oil industry.

(ii) The coupling process is conceptually extremely simple; on the molecular level, a \( \text{CH}_3-\text{H} \) bond is broken on two methane molecules and the resulting methyl radicals couple to yield ethane, which may then dehydrogenate to ethene. Predictably perhaps, the large number of studies undertaken since 1982 have revealed the actual process to be more complex, as the literature review in the next section demonstrates.

**Literature Review**

Most early studies of the OCM process investigated the relative performance of several types of catalyst systems [2-8]. The results, however, are difficult to compare due to the wide variety of operating conditions used. Several process parameters appear to strongly influence catalytic performance, regardless of the particular catalyst system under investigation. Among these are reaction temperature, the ratio of methane to oxygen in the feed stream, the specific oxidant employed (e.g., \( \text{O}_2 \), air, or \( \text{N}_2\text{O} \)), the space velocity, and the partial pressures of the reactive feed components.

Catalysts studied to date include oxides of the first transition metal series [9], group IIA alkaline earth metals [10-13], most of the elements of groups IIIB, IVB, and VB [11, 14-15], and several of the rare earth elements [2-3, 16-18]. Other catalyst systems have been developed using *promoters* (most commonly alkali metal salts) [11, 19-25], different high surface area *supports* [26-27], and *mixtures* of several basic oxides [12, 28-30]. The goal in
all of these studies has been to develop catalyst systems capable of promoting methane
coupling (preferably with high selectivity to the more valuable ethene) while minimizing its
deeper oxidation to carbon oxides.

Several excellent reviews of work performed in the OCM field have been published in
recent years [31-36].

It appears likely that the fundamental steps of the OCM process are similar regardless
of the particular oxide system being used. The first step involves the heterogeneous
abstraction of an hydrogen atom from methane. This is followed by the coupling of the
resulting methyl radicals to give ethane. Ethane can then dehydrogenate in the gas phase
yielding ethene. The nature of the steps giving rise to carbon oxides (i.e., both CO and CO₂)
is less well understood.

**Homogeneous versus Heterogeneous Reactions**

Much of the early debate in the OCM field centered on whether the process depended
on the presence of a catalyst or whether homogeneous³ gas phase reactions alone could
account for the observed conversion of methane to C₂ hydrocarbons.

Several studies have reported negligible conversion of methane under typical reaction
conditions in a blank reactor (i.e., either an empty reactor or, more commonly, one filled
with either quartz wool or quartz chips) [5, 37-38]. Many others, however, either have not
tested for the blank reactor case or have not reported their findings.

³ i.e., reactions not initiated by a catalyst.
The dispute over the degree to which homogeneous reactions affect OCM has been especially vociferous in the case of Li/MgO catalysts [39-46]. However, it now seems to be accepted that such reactions become important when the reaction temperature exceeds 650 °C, the dilution ratio, $P^*$ \(^4\), exceeds 0.4, the residence times of the reaction gases exceed 6 seconds [41, 46], and the reaction pressure exceeds 3 atmospheres [42]. Under such conditions, methane conversions as high as 32% are observed, with selectivities to $C_2$ products as high as 29%.

These results clearly indicate that, under certain operating conditions, homogeneous reactions can be just as important as heterogeneous reactions in converting methane to $C_2$ hydrocarbons. The remainder of this work concerns itself with OCM under reaction conditions at which homogeneous reactions are negligible.

**Methane Activation via Hydrogen Abstraction**

It is widely accepted that methane is activated during OCM by cleavage of its first C-H bond (bond strength 435 kJ/mol) [6, 47]. Whether the resulting methyl radicals, $CH_3•$, couple to form ethane on the catalyst surface [1] or in the gas phase [39, 48] seems to have been decided in favor of the latter due to the detection of methyl radicals in the gas phase. Such species have been detected during OCM over MgO, CaO, and rare earth oxide (REO) catalysts using matrix isolation electron spin resonance (MIESR) [6, 47] and over MnO$_x$/SiO$_2$ using a Paneth lead mirror technique [29]. This evidence suggests that methane activation proceeds via the abstraction of a single hydrogen atom. Other researchers,

---

\(^4\) i.e., the ratio of the sum of methane and oxygen partial pressures to the total pressure.
however, have proposed that a second hydrogen atom can be abstracted, yielding a methylene radical, CH₂• [49]. It was also suggested that the methylene radical played a role in activating methane as follows:

\[ \text{CH}_2\cdot + \text{CH}_4 \rightarrow 2\text{CH}_3\cdot \] (1)

If this were true, one would expect a combined CH₄/CD₄ + O₂ feed (where D refers to deuterium) to yield the isotopically labeled products CH₂CD₄ and CH₄CD₂. However, such an experiment over a Li/MgO catalyst [50] resulted in ethanes of the form CH₃CD₃, CH₃CH₃, and CD₃CD₃ being produced with virtually no other isotopic combinations being detected. Thus, methylene radicals are unlikely to be involved in OCM.

Among the REO catalysts, it was shown that selectivity towards coupling products was strongly related to the catalyst’s ability to generate (as opposed to consume) methyl radicals [51]. Thus, the most effective REOs for the OCM reaction (La₂O₃, Sm₂O₃, and Nd₂O₃) were found to be excellent methyl radical generators whereas poor OCM catalysts (CeO₂, Pr₆O₁₁, and Tb₂O₃) were found to be good methyl radical scavengers. It would appear from these results that the REO’s effectiveness as an OCM catalyst is related to its crystallographic structure and/or the oxidation state of the rare earth element; Ce, Pr, and Tb are unique among the rare earths for their ability to form stable oxides with oxidation states higher than the Ln(III+) of the sesquioxide (Ln₂O₃).

The facility for generating methyl radicals is common to other (non-REO) catalysts effective for OCM, for example Li/MgO and Na/CaO [51]. In the case of Na/CaO, it was established that varying the loading of the promoter from 0 to 43% resulted in a strong
correlation between the rate of methyl radical formation and the yield of coupling products. A maximum in both was found at a Na loading of around 20 wt.\%.

It has also been established \([52-53]\) via CH\(_4\) and CD\(_4\) isotopic studies that the abstraction of an hydrogen atom from methane is the rate limiting step in OCM over Li/MgO. This can be concluded since the expected kinetic isotope effect of 1.5 was observed between a CH\(_4\) + O\(_2\) feed and a CD\(_4\) + O\(_2\) feed over this catalyst at 750°C.

The Active Site for Methane Activation

As discussed above, it is clear that the activation of methane proceeds via the abstraction of an hydrogen atom. Exactly how this process takes place is much less certain. Many studies indicate that an oxygen species is responsible for methane activation. Indeed, it has been reported that methane cannot couple to C\(_2\)S without the presence of molecular oxygen \([54-56]\) although results presented in this work dispute this.

Among the oxygen species considered as potential candidates for methane activation, the O\(^-\) species has been proposed to form through the combination of gas phase oxygen with anion vacancies, V\(_{\text{surface}}\), on the catalyst surface \([57-58]\):

\[
O_2(g) \leftrightarrow O_2(\text{surface}) \tag{2}
\]

\[
O_2(\text{surface}) + 2 V_{\text{surface}} \leftrightarrow 2 O^- \tag{3}
\]

Besides being suggested as the species responsible for methane activation \([59]\), O\(^-\) is also proposed to undergo exchange with lattice oxygen \([57]\):

\[
^{18}O^- + ^{16}O_{\text{lattice}} \leftrightarrow ^{18}O^- + ^{16}O_{\text{lattice}} \tag{4}
\]
Evidence for this process comes from isotopic exchange studies between $^{18}\text{O}_2(g)$ and the lattice oxygens in Sm$_2$O$_3$ [60-61], La$_2$O$_3$ [62], and 1% Sr/La$_2$O$_3$ [56], with $^{18}\text{O}_2$ undergoing reactions (2) and (3) prior to (4).

Other oxygen species considered include the superoxide, O$_2^-$, the peroxide, O$_2^{2-}$, and the lattice oxide, O$^2$. One study over Sm$_2$O$_3$ investigated the kinetics of the OCM process and proposed a reaction scheme which involved initiation by a diatomic oxygen species [63]. Because it is the only paramagnetic diatomic oxygen species, electron paramagnetic resonance (EPR) spectroscopy has been successfully applied to the study of the superoxide ion [64-65]. Exposure of A-La$_2$O$_3$ to a flow of oxygen at room temperature was shown to result in the formation of O$_2^-$ on the catalyst surface. At a temperature of 650 °C, 85% of the O$_2^-$ species formed on the surface while the remainder was shown to incorporate between the (LaO)$_2^{2+}$ layers of the catalyst [65]. However, the same species could not be detected after OCM on the same catalyst for two reasons: (i) O$_2^-$ is known to be thermally unstable at the low oxygen partial pressures existing over a working catalyst and (ii) O$_2^-$ cannot be detected in the presence of oxycarbonates formed during the OCM reaction [65]. This result is consistent with another study which determined that O$_2^-$ species contained in peroxide catalysts are ineffective for methane activation [66].

This leaves the peroxide ion, O$_2^{2-}$, as the only viable diatomic oxygen species for the activation of methane. Although no direct proof has been presented for its existence, it has been proposed to exist in equilibrium with suboxide ions, O' [67] and superoxide ions [65] as follows;

\[ 2\text{O}^- \leftrightarrow \text{O}_2^{2-} \]
\[ O_2 + O_2^{2-} \rightleftharpoons 2O_2^- \]  \hspace{1cm} (6)

where \( O^- \) is formed [67] through an equilibrium between carbonate, superoxide and peroxycarbonate species;

\[ CO_3^{2-} + O_2^- \rightleftharpoons CO_4^{2-} + O^- \]  \hspace{1cm} (7)

Finally, it has been suggested that the main difference between the oxygen species responsible for methane activation over REO catalysts and alkali/alkaline earth oxide catalysts is that, in the former, it is an adsorbed oxygen species and, in the latter, part of the lattice [54]. For example, over Li/MgO, the activation was proposed to occur at \([\text{Li}^-\text{O}^-] \) centers since a strong correlation was found between the amount of methyl radicals produced and the number of \([\text{Li}^-\text{O}^-] \) sites as the lithium content of the catalyst was varied [48].

Formation of these active sites was suggested to occur by the combination of a lattice oxide species with a vacant oxygen hole, \{\}, in the presence of lithium ions and gas phase oxygen.

\[ 2\text{Li}^-\text{O}^{2-} + \{\} + \frac{1}{2}O_2 \rightleftharpoons 2[\text{Li}^+\text{O}^-] + O_2^2^- \]  \hspace{1cm} (8)

\[ [\text{Li}^+\text{O}^-] + \text{CH}_4 \rightarrow \text{Li}'\text{OH}^- + \text{CH}_3\cdot \]  \hspace{1cm} (9)

Methane activation produces lithium hydroxide which is proposed to regenerate the \([\text{Li}^-\text{O}^-] \) centers [39].

**Ethane Production via Coupling of Methyl Radicals**

The main evidence for the direct coupling of methyl radicals in the formation of ethane lies in the \( \text{CH}_4/\text{CD}_4 + O_2 \) experiments referred to above [50] which used mass spectrometry and Fourier transform infrared spectroscopy to detect isotopically labeled products. Clearly,
the fact that ethanes composed of only CH₃ and/or CD₃ groups were detected implies that these groups are the basic building blocks for product ethane [50, 53].

**Ethene Production via Ethane Dehydrogenation**

The same study which detected ethanes of the form CH₃CD₃, CH₃CH₃, and CD₃CD₃ [50] also detected ethenes limited to CH₂CD₂, CH₂CH₂, and CD₂CD₂. This would seem to imply that ethene is not derived directly from methane but from the sequential dehydrogenation of ethane.

Other evidence comes from a study of the relationship between product selectivities and the reaction contact time [68]. It was found that when the product selectivities were extrapolated back to zero contact time (and, therefore, zero methane conversion), ethane, CO₂, and CO gave non-zero intercepts - unlike ethene and the C₃ products. This suggests that ethane, CO, and CO₂ are primary products of OCM and that they result from parallel routes whereas ethene and C₃ hydrocarbons probably result from secondary reactions of ethane, most likely occurring in the gas phase.

Another study compared the OCM process with the oxidative dehydrogenation of ethane over several REO catalysts [69]. It was discovered that the latter proceeded four times as fast as the OCM process and was less catalyst dependent, possibly confirming that the ethene product in OCM results from the homogeneous dehydrogenation of ethane. Finally, ethane fed over a LiCl/Sm₂O₃ catalyst under typical OCM reaction conditions was found to produce ethene in addition to carbon oxides [54].
Reactive Intermediates

Under reaction conditions different from those of OCM, oxygenated products such as formaldehyde and methanol can be formed from \( \text{CH}_4 + \text{O}_2 \) feeds [9]. For example, lower reaction temperatures (350-500°C) encourage the formation of formaldehyde [9, 70], and high reaction pressures (50-150 atm) favor methanol [71]. These processes are believed to involve intermediate methoxy, \( \text{CH}_3\dot{O} \), or methoxide, \( \text{CH}_3\text{O}^- \), adsorbed species [72]. At even lower temperatures (200 °C or lower), methane undergoes rapid oxidation to a number of oxygenated products, including formaldehyde, methanol and formic acid [73]. In these reactions, the peroxy, \( \text{HO}_2\dot{\bullet} \), and methylperoxy, \( \text{CH}_3\text{O}_2\dot{\bullet} \), radicals play important roles as reactive intermediates.

At the higher temperatures and \( \text{CH}_4\)-to-\( \text{O}_2 \) ratios involved in the OCM process, however, it is believed that the role played by these radicals is negligible relative to that played by methyl radicals [39, 54, 74]. This would seem to be confirmed by the fact that the OCM process yields no oxygenated hydrocarbon products.

Routes for the Production of Carbon oxides

As stated above, it appears that one route to carbon oxides is the primary heterogeneous reaction of methane [75-76]. Another route involves the combustion of product \( \text{C}_2\)s [54, 77-78]. The former is more prevalent at reaction temperatures below 700 °C, the latter above 740 °C (at which temperatures it may account for between 30 and 80 % of the carbon oxides produced [77]).

In the case of both methane oxidative coupling and ethane oxidative dehydrogenation over REO catalysts, a correlation was found between the CO-to-CO\(_2\) product ratio and the
catalyst's oxidizing power [69]. The CO-to-CO\textsubscript{2} ratio maximized at a value of around 0.4 for La\textsubscript{2}O\textsubscript{3} and Sm\textsubscript{2}O\textsubscript{3} (good OCM catalysts but weak oxidizers) at temperatures between 500 and 625 °C. In contrast, CeO\textsubscript{2} and Pr\textsubscript{6}O\textsubscript{11} (poorer OCM catalysts but strong oxidizers) yielded very little CO relative to CO\textsubscript{2} in either reaction and over the entire temperature range of interest (450-750 °C).

Another study based on experiments using CH\textsubscript{4} + O\textsubscript{2}, C\textsubscript{2}H\textsubscript{4} + O\textsubscript{2}, C\textsubscript{2}H\textsubscript{6} + O\textsubscript{2} feeds over La\textsubscript{2}O\textsubscript{3} and a blank reactor at 800 °C, reported that carbon oxides could be formed via both homogeneous and heterogeneous reactions [79].

**Previous Work Conducted in our Laboratory**

Lanthanum sesquioxide, La\textsubscript{2}O\textsubscript{3}, was identified in several of the earliest catalyst screening studies to be both active and selective towards coupling products in the OCM process [2-3, 5, 8] and work in our laboratory has focused on catalysts based on this material [37, 80].

In addition to their ability to catalyze OCM, it is known that REOs (and particularly La\textsubscript{2}O\textsubscript{3}) are highly sensitive to hydration and carbonation in the presence of atmospheric H\textsubscript{2}O and CO\textsubscript{2} [81-84]. In the case of La\textsubscript{2}O\textsubscript{3}, stabilization in air is achieved within 24 hours at room temperature and results in conversion to a partially carbonated hydroxide, with carbonation restricted to the formation of hydroxycarbonates in the outer layers.

Despite the presence of H\textsubscript{2}O in the gas phase above a working OCM catalyst (as a product of complete combustion), it is unlikely that any hydrated phase could exist at typical OCM reaction temperatures due to their thermal instability. In contrast, since CO\textsubscript{2} is also
present in the reacting atmosphere and since the oxycarbonate phase is known to be thermally stable to around 850 °C in a CO₂ environment [80], it appears likely that the oxycarbonate could exist on a working "lanthanum oxide" catalyst.

Since the precise conditions of catalyst preparation, interim storage, and pretreatment prior to their use as OCM catalysts was not always reported in previous studies [2-4, 85-86], it is possible that the differences in catalytic performance in these studies could be partially accounted for by the presence of contaminating phases. Thus, several pure lanthanum-based compounds were prepared in our laboratory and their catalytic performance evaluated. The phases prepared were A-La₂O₃, La(OH)₃, II-La₂O₂CO₃, and La₂(CO₃)₃. Characterization was performed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and laser Raman spectroscopy (LRS) both before and after reaction at several temperatures. Catalytic performance was quantified by gas chromatography (GC).

As shown in Figure 1, the C₂ product yield was quite different for each starting catalyst. Of most significance is the fact that the pure A-La₂O₃ starting catalyst (which had previously been considered the active phase in lanthanum oxide catalysts) gave the lowest C₂ yields at all reaction temperatures. Calculating the ratio of C₂ yield for the most effective starting catalyst (II-La₂O₂CO₃, 10.3 % at 800 °C) with that of A-La₂O₃ (4.7 % at 800 °C) results in a value of 2.19. The corresponding ratio for the yield of the most desirable product, C₂H₄, is 3.87. Thus, by using pure II-La₂O₂CO₃ as the starting material for OCM, it is possible to improve the yield of C₂H₄ by almost 400 %, a phenomenal difference.
Figure 1: \(C_2\) yield versus reaction temperature for OCM over various starting catalysts [80]
Post-reaction characterizations for all four catalysts are presented in Table 1. Relating these compositions to the catalytic performance suggested a strong correlation between the presence of oxycarbonate and the ability to selectively promote the coupling of methane.

Other points to note from this study are that (i) no hydrated phases existed on any catalysts after reaction at temperatures of 600 °C or higher and (ii) all four starting catalysts exhibited different catalytic performance at a reaction temperature of 850 °C despite the fact that characterization showed that all four materials had fully converted to A-La\textsubscript{2}O\textsubscript{3} after reaction at this temperature.

**Research Objectives**

On the basis of the results of earlier studies in our laboratory [37, 80], it is clear that the presence of carbonate (and particularly oxycarbonate) in "lanthanum oxide" catalysts greatly enhances catalytic performance. The primary objective of this work is to investigate the nature of this phenomenon by considering the role played by CO\textsubscript{2} in the OCM process over lanthanum-based catalysts.

Since characterization of A-La\textsubscript{2}O\textsubscript{3}, La(OH)\textsubscript{3}, II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}, and La\textsubscript{2}(CO\textsubscript{3})\textsubscript{3} starting catalysts after reaction at temperatures in excess of 600 °C revealed the presence of just A-La\textsubscript{2}O\textsubscript{3} and II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} phases [80], the current work deals exclusively with these two materials as starting catalysts. These materials are also of particular interest because they displayed the poorest (A-La\textsubscript{2}O\textsubscript{3}) and the best (II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}) catalytic performance of the four materials studied earlier and because they may be prepared from each other via the loss and gain, respectively, of CO\textsubscript{2}. 
Table 1: Catalyst compositions after reaction at various temperatures [80]

<table>
<thead>
<tr>
<th>Starting Catalyst</th>
<th>200°C</th>
<th>400°C</th>
<th>600°C</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>800°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-La$_2$O$_3$</td>
<td>A-La$_2$O$_3$</td>
<td>A-La$_2$O$_3$</td>
<td>A-La$_2$O$_3$</td>
<td></td>
<td></td>
<td>A-La$_2$O$_3$</td>
<td>A-La$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>La(OH)$_3$ (CO$_2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-La$_2$O$_2$CO$_3$</td>
<td></td>
<td></td>
<td>II-La$_2$O$_2$CO$_3$</td>
<td>II-La$_2$O$_2$CO$_3$</td>
<td>II-La$_2$O$_2$CO$_3$</td>
<td>A-La$_2$O$_3$ (II-La$_2$O$_2$CO$_3$)</td>
<td>A-La$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>La$_2$(CO$_3$)$_3$</td>
<td>La$_2$(CO$_3$)$_3$</td>
<td>La$_2$(CO$_3$)$_3$ (II-La$_2$O$_2$CO$_3$)</td>
<td></td>
<td></td>
<td>A-La$_2$O$_3$ (II-La$_2$O$_2$CO$_3$) (CO$_2$)</td>
<td>A-La$_2$O$_3$ (II-La$_2$O$_2$CO$_3$) (CO$_2$)</td>
<td>A-La$_2$O$_3$ (II-La$_2$O$_2$CO$_3$)</td>
<td>A-La$_2$O$_3$</td>
</tr>
</tbody>
</table>
Assuming pure starting catalysts, there are three potential sources of CO$_2$ which may influence the working catalyst:

- Co-fed CO$_2$,
- CO$_2$ resulting from the deep oxidation of feed methane and coupling products, ethane and ethene, and
- CO$_2$ evolving from II-La$_2$O$_2$CO$_3$ during its thermal decomposition at typical OCM reaction temperatures.

The first paper investigates the influence of co-fed CO$_2$ on the catalytic performance of A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ starting catalysts. This study was based on the premise that, by co-feeding CO$_2$ over a working "lanthanum oxide" catalyst, the equilibrium of the reaction:

$$\text{A-La}_2\text{O}_3 + \text{CO}_2 \rightleftharpoons \text{II-La}_2\text{O}_2\text{CO}_3$$  \hspace{1cm} (10)

could be forced to the right and that stabilization of the II-La$_2$O$_2$CO$_3$ phase could enhance the catalytic performance.

The second paper determines the affinity for gas phase CO$_2$ exhibited by both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ at typical reaction temperatures. It also investigates the nature of the thermal decomposition of II-La$_2$O$_2$CO$_3$ to A-La$_2$O$_3$ (i.e. the reverse of reaction 10 above) which occurs during the standard pretreatment procedure prior to catalytic testing of II-La$_2$O$_2$CO$_3$. The objectives of this study are (i) to examine the possibility of (oxy)carbonate phases forming on A-La$_2$O$_3$ when exposed to gas phase CO$_2$ at typical reaction temperatures and (ii) to determine the thermal stability of any carbonated phases so formed.
The third paper uses gas chromatography in series with mass spectrometry (GC/MS) and isotopically-labeled catalysts to determine the fate of the C and O atoms incorporated into $\text{II-La}_2\text{O}_2\text{CO}_3$ (during its preparation from $\text{A-La}_2\text{O}_3$) during OCM. Of particular interest, is whether or not these atoms are to be found in the reaction products (and, if so, in which products) and whether they are able to exchange with the C and O atoms in the feed components.

With these three approaches it is expected that a deeper understanding will be gained of how CO$_2$ interacts with these two materials and the role(s) played by its C and O atoms in the OCM process.
PAPER I.

THE INFLUENCE OF CO-FED CO₂ ON THE OXIDATIVE COUPLING
OF METHANE OVER A-La₂O₃ AND II-La₂O₂CO₃
ABSTRACT

It is known from X-ray photoelectron and Fourier transform infrared spectroscopic studies that trace amounts of an oxycarbonate phase form on a working A-La$_2$O$_3$ catalyst during the oxidative coupling of methane (OCM). It is also known that a pure II-La$_2$O$_3$CO$_3$ starting material gives ethene yields up to 400% larger than a pure A-La$_2$O$_3$ starting material operating under the same conditions. Since A-La$_2$O$_3$ readily converts to II-La$_2$O$_3$CO$_3$ in a CO$_2$ environment between 415 and 815 °C, the influence of co-fed CO$_2$ on the catalytic performance of A-La$_2$O$_3$ is of obvious interest.

This work investigated the influence of various quantities of co-fed CO$_2$ on the catalytic performance of both A-La$_2$O$_3$ and II-La$_2$O$_3$CO$_3$ starting materials. It was determined that, under the conditions employed in this study, co-fed CO$_2$ is detrimental to the objective of maximizing the yield of ethene since it depresses both methane conversion and ethene selectivity over both catalysts.

It was concluded that co-fed CO$_2$ plays at least two roles in OCM over A-La$_2$O$_3$; that of a catalyst modifier (decreasing the catalyst's ability to activate methane) and that of a gas phase modifier (inhibiting the oxidative dehydrogenation of ethane to ethene by interfering with the homogeneous reaction pathway). It seems likely that the best catalytic performance of such catalysts depends on the presence of both A-La$_2$O$_3$ and II-La$_2$O$_3$CO$_3$ phases.
1. INTRODUCTION

Few studies to date have considered the influence of co-fed CO₂ on the OCM process and it is difficult to compare the results of those that have because of the wide variety of catalyst systems and operating conditions employed. For example, CO₂ can be co-fed in at least three different ways: as the diluent in a CH₄ + O₂ feed [1], as the sole oxidant in a CH₄ feed [2], or as a second oxidant in a CH₄ + O₂ + Inert feed [3-6].

Using CO₂ as a second oxidant, a He + CH₄ + O₂ + CO₂ feed (in the molar ratios 400:100:100:1) over Sm₂O₃, 20 mol. % BaO-MgO [5], and 15 mol. % PbO-MgO [4] catalysts gave C₂ yields between two and four times higher than a He + CH₄ + O₂ feed (in the molar ratios 400:100:100) over the same catalysts. However, this desirable outcome was accompanied by even larger undesirable increases in the amount of CO produced. To explain the simultaneous increases in C₂ and CO products, it was proposed that gas phase CO₂ converts to CO by losing an oxygen atom to the catalyst surface:

\[ \text{CO}_2 \rightarrow \text{CO} + \text{O} \_\text{(a)} \] (2.1)

This oxygen species then activates methane according to the following scheme:

\[
\begin{align*}
2 \text{CH}_3 + \text{O} \_\text{(a)} & \rightarrow \text{CH}_3 \bullet + (\text{OH}) \_\text{(a)} \\
2 \text{CH}_3 \bullet & \rightarrow \text{C}_2\text{H}_6 \\
2 (\text{OH}) \_\text{(a)} & \rightarrow \text{H}_2\text{O} + \text{O} \_\text{(a)}
\end{align*}
\] (2.2)

Promoting the Sm₂O₃ catalyst with 20 wt. % Li₂O [4], increased the C₂ yield (by a factor of 3.85 compared with unpromoted Sm₂O₃) for the feed without CO₂. On co-feeding CO₂, the C₂ yield was reduced to one fifth of this value and catalyst deactivation was
observed after three hours on stream. No explanation was offered for this behavior although it is likely that CO₂ altered the lithium-related active sites by forming a less active carbonate phase.

Addition of lithium (this time in the form of Li₂CO₃) is also known to promote the performance of MgO catalysts for OCM although the resulting mixed phase catalyst deactivates over a period of 15 hours [3]. Since deactivation was characterized by a loss of activity but no loss in selectivity, it was concluded that the number but not the nature of the active sites had changed during reaction. Post-reaction characterization revealed that the lithium and carbonate contents had fallen from 3.1 to 0.1 wt.% and from 8.24 to 0.1 wt.%, respectively. Dosing the deactivated catalyst with CO₂ was found to restore catalytic performance, but subsequent deactivation occurred much more rapidly thereafter. When CO₂ was co-fed over a fresh Li₂CO₃/MgO catalyst in the feed ratio N₂:CH₄:O₂:CO₂ of 4:10:1:1, the catalytic activity fell to about half of its previous value, the C₂ selectivity remained approximately the same, but no deactivation occurred.

From the studies described above, it is evident that co-fed CO₂;

(i) increases the yields of both C₂S and CO over Sm₂O₃, 20 mol. % BaO-MgO, and 15 mol. % PbO-MgO catalysts,

(ii) decreases the C₂ yield over Li₂O-promoted Sm₂O₃ and causes rapid deactivation, and

(iii) decreases the C₂ yield over Li₂CO₃-promoted MgO but stabilizes it against deactivation.
Clearly, the role played by co-fed CO\textsubscript{2} depends strongly on the catalyst system being used. It would be most unwise, therefore, to extend the knowledge gained in the above studies to the co-feeding of CO\textsubscript{2} over A-La\textsubscript{2}O\textsubscript{3} and II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}.

Co-fed CO\textsubscript{2} has also been studied for its influence on the exchange reactions of methane and oxygen with OCM catalysts. Over La\textsubscript{2}O\textsubscript{3}, co-feeding CO\textsubscript{2} was found to destroy the active sites for the equilibration reaction between CH\textsubscript{4} and CD\textsubscript{4} (i.e., the sites responsible for methane activation) at 700-800 °C [7]. Since the addition of lithium to the catalyst produces the same effect, it was concluded that the active sites for methane exchange are the basic sites of the oxide surface. These sites were reported to be poisoned by the formation of Li\textsubscript{2}CO\textsubscript{3} in the latter case and by neutralization in the former case.

Another study reported that, during OCM\textsuperscript{1} over an \textsuperscript{18}O-doped 1 % Sr/La\textsubscript{2}O\textsubscript{3} catalyst, the rate of oxygen exchange between the catalyst and gas phase oxygen decreased relative to that occurring with just oxygen in the feed [8]. Since co-feeding CO\textsubscript{2} with O\textsubscript{2} led to the same result, it was concluded that the species responsible for the decreased oxygen exchange was CO\textsubscript{2}. It was proposed that a surface carbonate formed in the presence of CO\textsubscript{2} and that it was this phase which decreased the number of sites suitable for the exchange reaction. Similar results were reported over Li/MgO [9]; co-fed CO\textsubscript{2} in this case was proposed to form a Li\textsubscript{2}CO\textsubscript{3} layer on the catalyst surface which discouraged oxygen exchange between the catalyst and gas phase oxygen.

\textsuperscript{1} i.e., with both oxygen and methane in the feed.
Clearly, there is little information in the existing literature regarding the influence of co-fed CO$_2$ on OCM over A-La$_2$O$_3$ and II-La$_2$O$_3$CO$_3$. This paper attempts to address the issue by investigating its impact on feed conversions and product selectivities at various reaction temperatures and feed compositions.
2. EXPERIMENTAL PROCEDURE

2.1 Catalyst Characterization

From earlier work involving several characterization techniques [10], it was determined that Fourier transform infrared spectroscopy (FTIR) and laser Raman spectroscopy (LRS) could identify the bulk composition of the lanthanum compounds of interest in this work.

2.1.1 Fourier Transform Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Instruments 60SX spectrometer equipped with a water-cooled globar source and a mercury-cadmium-telluride (MCT) detector. Samples were prepared in the form of pressed wafers thin enough to permit the transmittance of at least 25 % of the intensity of the incident infrared beam. Each wafer was prepared from approximately 0.15 g of a mixture composed of 1-2 wt. % of sample in potassium bromide, KBr (Fisher, IR grade). This mixture was ground in an agate mortar and pestle for two and a half minutes. It was then pressed between the faces of a hardened stainless steel die under a load of 9 tons (20000 lb) on a Model C-12 press (Fred S. Carver, Inc.). The resulting wafer was 20.6 mm in diameter and approximately 0.03 mm thick at the center. All spectra involved the accumulation of 512 scans at either 1 or 5 wavenumber (WN) resolution and were ratioed to that of a 100 % KBr wafer collected under the same conditions.
2.1.2 Laser Raman Spectroscopy

Laser Raman spectra were obtained using a Spex Triplmate triple monochromator spectrometer. The primary excitation source was the 514.5 nm line of a Spectra-Physics argon ion laser, Model 164, operating at powers ranging from 20 to 200 mW at the source. The resolution of the resulting spectra was 5 WN. The spectrometer was calibrated over the range 80 to 850 WN using a powder sample of MoO₃. Catalyst samples were prepared by sealing approximately 0.01 g in a 0.8 mm inside diameter (i. d.), 90 mm long quartz capillary tube. Spectra were obtained in a single scan with the scan time dependent upon the intensity of the Raman scattering.

2.2 Catalyst Preparation

A-La₂O₃ and II-La₂O₂CO₃ catalysts were prepared according to techniques developed in earlier work [10]. Both used La₂O₃ (Aldrich Chemical Company, 99.99 %) as the starting material. Since La₂O₃ is known to be sensitive to atmospheric hydration and carbonation, it had been stored in an argon-filled dry box since its initial purchase. However, although characterization by LRS indicated the sole presence of A-La₂O₃ (bands at 107, 194, and 410 WN), characterization by FTIR revealed bands at 3610 and 642 WN corresponding to the presence of some La(OH)₃ in the Aldrich material.

A heat treatment was therefore performed in order to regenerate a bulk supply of pure A-La₂O₃. This was done by placing approximately 5 g of La₂O₃ (from the dry box) in a quartz boat inside a quartz tube in a tube furnace (Lindberg, Model 54232, with Lindberg Console, Model 59544, and Eurotherm Controller, Model 211). An inert gas, in this case
oxygen-free nitrogen (Matheson, <5 ppm O₂), was passed through the tube at a flow rate of 100 standard cubic centimeters per minute (sccm). The sample was heated to 900 °C at 10 °C/min and maintained at 900 °C for 12 hours. The furnace was then switched off and allowed to cool over a period of several hours to room temperature. A-La₂O₃ was removed from the quartz boat and samples were taken for analysis by FTIR and LRS. The remainder was placed in a vial under a helium atmosphere and stored in a dessicator.

### 2.2.1 Preparation of A-La₂O₃

Although A-La₂O₃ prepared in the tube furnace was pure (as indicated by FTIR and LRS characterizations), it was found that a small but finite degree of contamination occurred in the time it took to load the sample in the reactor. It was therefore necessary to regenerate pure A-La₂O₃ in situ for subsequent catalytic performance testing. This was done by loading 0.050 g of A-La₂O₃ (prepared in the tube furnace) on top of a small plug of quartz wool in the quartz reactor (described in the next subsection). The sample was then heated to 900 °C at 10 °C/min in a 100 sccm flow of helium (Matheson, Zero grade). During the heating process, the reactor effluent was fed directly to the Porapak Q column of the gas chromatograph (Varian, Model 3600) in order to observe eluting species. Since each batch of catalyst was prepared in situ and in an amount required for subsequent testing, characterization of each starting catalyst could not be performed. However, the FTIR and LRS spectra of a representative sample of A-La₂O₃ prepared by the above technique matched those of the pure A-La₂O₃ sample prepared in the tube furnace.
2.2.2 Preparation of II-La$_2$O$_2$CO$_3$

Since A-La$_2$O$_3$ served as the starting material for the preparation of II-La$_2$O$_2$CO$_3$, the latter was also prepared in situ. In this case, 0.044 g of A-La$_2$O$_3$ (prepared in the tube furnace) was loaded in the reactor and heated to 900 °C at 10°C/min in a 100 sccm flow of helium (Matheson, Zero grade). This served to regenerate pure A-La$_2$O$_3$. After cooling to room temperature, the helium carrier gas was changed to a 30 sccm flow of CO$_2$ and the sample was heated to 650 °C at 5 °C/min, from 650 to 700 °C at 2 °C/min, and maintained at 700 °C for 30 minutes. Given the initial starting mass of 0.044 g of A-La$_2$O$_3$, the stoichiometry of the reaction at completion yielded 0.050 g of II-La$_2$O$_2$CO$_3$. As for A-La$_2$O$_3$, II-La$_2$O$_2$CO$_3$ was prepared batchwise in situ in an amount required for subsequent testing; therefore characterization of each starting catalyst could not be performed. However, characterization by FTIR and LRS of a representative sample prepared using this technique gave spectra indicating the sole presence of II-La$_2$O$_2$CO$_3$.

2.3 Catalytic Performance Evaluation

Reactor studies were undertaken using the system shown schematically in Figure 1. The reacting feed stream had a total flow of 100 sccm, of which the component flows were as follows: methane (Matheson, 99.99 %), 18 sccm; oxygen (Air Products, 99.6 %), 2 sccm; carbon dioxide (Air Products, 99.7 %), 0, 2, 4, or 6 sccm; and helium (Air Products, 99.997 %), balance. Amounts of CO$_2$ to be co-fed were chosen with two requirement in mind. First, the smallest amount should be several times greater than the amount of CO$_2$ produced during the OCM process. The latter depends on the reaction temperature and the catalyst being used.
Figure 1: Schematic of OCM gas feed/reactor/analytical system
but typically ranges from zero to approximately 0.6 sccm (for OCM over II-La$_2$O$_2$CO$_3$ at 800 °C). Second, the amounts were selected to be comparable with the amount of oxygen in the feed (2 sccm). The gas feed system for each gas stream included a molecular sieve/Drierite™ water trap, an Alltech Oxytrap™ (not on the oxygen stream), and a Tylan mass flow controller (Model FC-260 or FC-280). Valco 10- and 4-port sampling valves allowed the reactants to be fed either in continuous or pulse flow modes although only the former was used in this study.

The catalyst bed was supported on a plug of quartz wool in a quartz reactor, shown schematically in Figure 2. The reactor was made by fusing a 195 mm long, 6 mm outside diameter (o. d.), 1 mm i. d. quartz capillary to a 200 mm long, 8 mm o. d., 6 mm i. d. quartz tube. Use of the narrow bore tube significantly reduced gas-phase reactions that can occur downstream of the catalyst bed. An 18"-long, 0.02" o. d., K-type thermocouple with a 0.02" i. d. quartz sheath was forced through a high temperature septum at the reactor inlet; the tip was positioned at the center of the catalyst bed. The reactor was positioned vertically along the furnace axis. Temperatures above and below the catalyst bed were measured at 750 °C and found to vary by no more than 2 °C at distances of 1" above or below the bed. All transfer lines downstream of the reactor were maintained at 150 °C to prevent condensation of products.

Product analysis was accomplished by gas chromatography (GC) using a Varian 3600 gas chromatograph equipped with a thermal conductivity detector (TCD) and temperature ramping. Two chromatographic columns (Alltech Associates, Inc.) were used; a 7' long, $\frac{1}{8}$" o. d., 80/100 mesh Porapak Q column separated H$_2$, O$_2$/CO, CH$_4$, CO$_2$, C$_2$H$_4$, C$_2$H$_6$, and C$_3$H$_8$.
Figure 2: Schematic of OCM reactor
components and a 6' long, \( \frac{\sqrt{2}}{8} \) o. d., 60/80 mesh molecular sieve 5A column separated O\(_2\), CO, and CH\(_4\) components.

The reactor was loaded with A-La\(_2\)O\(_3\) (0.050 g for in situ preparation of A-La\(_2\)O\(_3\) and 0.044 g for in situ preparation of II-La\(_2\)O\(_2\)CO\(_3\)) and the catalyst prepared as described above. The reactant stream was started and the catalyst bed was heated from room temperature to 700 °C at 10 °C/min. The temperature was then raised in 50 °C increments to 850 °C at a heating rate of 10 °C/min. At each temperature, 2 hours were allowed for catalyst stabilization before 25 µL samples were taken for analysis by GC. The same procedure was repeated for each feed stream (i.e., with varying amounts of co-fed CO\(_2\)) and each catalyst.

Feed conversions for reactants methane and oxygen were calculated as the ratio of the number of moles reacted to the number of moles in the feed. Selectivities to carbon-containing compounds were calculated on a per-carbon-atom basis as the ratio of the number of moles of carbon in the product\(^2\) to the number of moles of carbon in all products. Product yields were calculated by multiplying the methane conversion by the product selectivity and therefore corresponded to the number of moles of product per mole of methane fed.

After reaction at 850 °C, the catalyst was removed from the reactor and samples were taken for immediate analysis by FTIR and LRS.

\(^2\) Less the number of moles of carbon in co-fed carbon dioxide in the case of carbon dioxide selectivities.
3. EXPERIMENTAL RESULTS

3.1 Co-feeding CO\textsubscript{2} over A-La\textsubscript{2}O\textsubscript{3}

3.1.1 Influence on Feed Conversions

As shown in Figure 3, the reaction temperature greatly influenced methane and oxygen feed conversions regardless of whether or not CO\textsubscript{2} was co-fed. The addition of 2 mol. %\textsuperscript{3} of CO\textsubscript{2} to the reactant stream, however, depressed both methane and oxygen conversions, the effect being more significant at lower reaction temperatures. There was an approximately 35 % reduction in both conversions at 700 °C compared to a 15 % reduction at 800 °C. Increasing the amount of co-fed CO\textsubscript{2} to 4 or 6 mol. % did not further influence the feed conversions significantly.

3.1.2 Influence on C\textsubscript{3} Selectivities

Co-fed CO\textsubscript{2} decreased the combined selectivity to C\textsubscript{2} hydrocarbons at all reaction temperatures. Perhaps of more significance is that the C\textsubscript{2}H\textsubscript{4}-to-C\textsubscript{2}H\textsubscript{6} ratio in the reaction products (Figure 4) was lowered significantly by co-feeding just 2 mol. % CO\textsubscript{2}. At 700 °C, co-feeding CO\textsubscript{2} resulted in no ethene being produced; at higher reaction temperatures, the decrease in the C\textsubscript{2}H\textsubscript{4}-to-C\textsubscript{2}H\textsubscript{6} ratio ranged from 23 to 29 %. Co-feeding increasing amounts of CO\textsubscript{2} did not further influence the C\textsubscript{2}H\textsubscript{4}-to-C\textsubscript{2}H\textsubscript{6} ratio to any great extent.

\textsuperscript{3} i.e., 2 sccm CO\textsubscript{2} in a total feed flow of 100 sccm. In all cases the flow rates of CH\textsubscript{4} and O\textsubscript{2} in the feed stream were maintained at 18 and 2 sccm, respectively.
Figure 3: Influence of co-fed CO$_2$ on feed conversions over A-La$_2$O$_3$ at various reaction temperatures:

(---) oxygen conversion; (---) methane conversion; ■ 700°C; ● 750°C; ▲ 800°C
Figure 4: Influence of co-fed CO$_2$ on the C$_2$H$_4$-to-C$_2$H$_6$ selectivity ratio over A-La$_2$O$_3$ at various reaction temperatures; ■ 700°C; ● 750°C; ▲ 800°C
3.1.3 Influence on CO$_2$ Selectivities

Adding 2 mol. % CO$_2$ to the feed stream resulted in a significant decrease in the ratio of CO$_2$-to-CO products, as shown in Figure 5. As the amount of co-fed CO$_2$ was increased, however, the trend reversed and more CO$_2$ was produced at the expense of CO. The same trend was observed for all three reaction temperatures (700, 750, and 800 °C), but the increase in the CO$_2$-to-CO ratio at 750 °C was not as pronounced as for those at lower and higher reaction temperatures.

3.2 Co-feeding CO$_2$ over II-La$_2$O$_2$CO$_3$

3.2.1 Influence on Feed Conversions

As shown in Figure 6, the influence of co-fed CO$_2$ on feed conversions over II-La$_2$O$_2$CO$_3$ differed significantly to that over A-La$_2$O$_3$. With 2 mol. % CO$_2$ in the feed stream, both methane and oxygen conversions at lower reaction temperatures (700 and 750 °C) were drastically reduced. In fact, at 700 °C, methane activation was completely suppressed. Increasing the amount of co-fed CO$_2$ at these temperatures did not greatly affect conversions further. At a reaction temperature of 800 °C, both methane and oxygen conversions were reduced by around 18 % on adding 2 mol. % CO$_2$ to the feed. Doubling the amount of CO$_2$ caused a further 8 % decrease and tripling it to 6 sccm resulted in a significant 34 % further decrease$^4$. At a reaction temperature of 850 °C, co-feeding CO$_2$ had no effect on feed conversions; the methane conversion remained constant at approximately

$^4$ All percentages expressed relative to the feed conversions over the catalysts with no co-fed CO$_2$. 
Figure 5: Influence of co-fed CO₂ on the CO₂-to-CO selectivity ratio over A-La₂O₃ at various reaction temperatures;

- ■ 700°C
- ● 750°C
- ▲ 800°C
Figure 6: Influence of co-fed CO₂ on feed conversions over H₂-La₂O₃CO₃ at various reaction temperatures:

(____) oxygen conversion; (____) methane conversion;  ■ 700°C;  ● 750°C;  ▲ 800°C;  • 850°C
17%. It should be noted, however, that oxygen was fully consumed at this temperature, and therefore, the reaction conditions differed significantly from the runs at lower temperatures where oxygen was non-limiting.

3.2.2 Influence on C₂ Selectivities

Co-feeding CO₂ at reaction temperatures of 800 or 850 °C did not significantly affect the combined selectivity to coupling products, it remaining fairly constant at between 68 and 74%. At lower reaction temperatures, however, a strong effect was observed. At 700°C, only trace amounts of ethane and no ethene were detected regardless of the quantity of CO₂ co-fed. At 750 °C, co-feeding CO₂ in increasing amounts decreased the selectivity to C₂s. Considering the C₂H₄-to-C₂H₆ ratio in the product stream (Figure 7), it was seen that adding 2 mol. % CO₂ to the feed depressed the production of ethene relative to ethane at all reaction temperatures. The ratio was not greatly affected by increasing the amount of co-fed CO₂.

3.2.3 Influence on CO₂ Selectivities

The relationship between the amount of co-fed CO₂ and the CO₂-to-CO ratio in the product stream is difficult to interpret (Figure 8). Adding 2 mol. % of CO₂ to the feed reduced the ratio at all reaction temperatures investigated. Further increases in the amount of co-fed CO₂ had little impact at 850 °C. At lower temperatures, however, a doubling of co-fed CO₂ to 4 mol. % resulted in a large increase in the amount of CO₂ detected in the product stream relative to CO. Increasing the CO₂ feed component further to 6 mol. % returned the CO₂-to-CO ratio to lower values.
Figure 7: Influence of co-fed CO$_2$ on the C$_2$H$_4$-to-C$_2$H$_6$ selectivity ratio over II-La$_2$O$_3$CO$_3$ at various reaction temperatures; ▲ 700°C; ● 750°C; ▲ 800°C; • 850°C
Figure 8: Influence of co-fed CO\textsubscript{2} on the CO\textsubscript{2}-to-CO selectivity ratio over Il-La\textsubscript{2}O\textsubscript{3}CO\textsubscript{3} at various reaction temperatures;  
- 700°C; • 750°C; ▲ 800°C; ● 850°C
Due to the uncertainties in how much CO\textsubscript{2} is taken up by the catalyst under these reaction conditions\textsuperscript{5}, the quantity of product CO\textsubscript{2} calculated in these experiments is subject to a large error. This will lead to a large margin of error in the calculated CO\textsubscript{2}-to-CO ratios, especially at those temperatures at which CO\textsubscript{2} uptake is strongest.

3.3 Post-reaction Catalyst Characterization

Characterization by FTIR and LRS revealed that all catalysts consisted purely of A-La\textsubscript{2}O\textsubscript{3} after reaction at 850 °C regardless of the reactant feed composition.

\textsuperscript{5} Results reported in Paper II of this dissertation reveals that II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} is much more susceptible than A-La\textsubscript{2}O\textsubscript{3} to CO\textsubscript{2} uptake at these temperatures, especially at 700 and 750 °C.
4. DISCUSSION OF RESULTS

The results presented above reveal a complex relationship between the amount of co-fed CO$_2$, the reaction temperature, and the catalytic performance of A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ under typical OCM reaction conditions.

In summary, several trends are apparent:

(i) As the reaction temperature is increased from 700 °C to 800 °C over both catalysts, increases are observed in methane and oxygen conversions, the C$_2$H$_4$-to-C$_2$H$_6$ selectivity ratio, and the CO$_2$-to-CO selectivity ratio. Higher temperatures therefore correspond to more complete oxidation, reinforcing the suggestion that C$_2$H$_4$ is produced as a secondary oxidation product of C$_2$H$_6$ [11-12].

(ii) Co-feeding CO$_2$ at the flow rates examined in these experiments is detrimental to the desired objective of maximizing the yield of C$_2$H$_4$ since doing so typically lowers both the conversion of methane and depresses the selectivity towards C$_2$H$_4$ over both starting materials.

Returning to the theory that initiated this study, namely, that co-feeding CO$_2$ over a working "lanthanum oxide" catalyst would stabilize the presence of the II-La$_2$O$_2$CO$_3$ phase and therefore lead to improved catalytic performance, several comments can be made. Firstly, at a reaction temperature of 700 °C (at which the II-La$_2$O$_2$CO$_3$ phase is known to be thermally stable in a CO$_2$ environment and at which the co-feeding of CO$_2$ over A-La$_2$O$_3$ is expected to encourage its formation), we see no improvement in the performance of the
A-La₂O₃ starting catalyst. On the contrary, co-feeding 2 mol. % CO₂ reduces methane and oxygen feed conversions, reduces the selectivity to coupling products, and precludes the production of ethene. This suggests that co-fed CO₂ plays at least two roles over A-La₂O₃; that of a catalyst modifier (leading to deactivation of the catalyst with respect to methane activation) and that of a gas phase modifier (negating the homogeneous mechanism by which product ethane dehydrogenates to ethene). Since characterization of the catalyst was not performed after reaction at this temperature, it is unknown whether (and to what extent) II-La₂O₃CO₃ was formed on the catalyst. We can only speculate therefore that co-fed CO₂ resulted in the formation of II-La₂O₃CO₃ at 700 °C and that this phase alone is a poor catalyst for methane activation.

That this may be so could be implied from the corresponding experiments over the pure II-La₂O₃CO₃ starting material in which co-feeding CO₂ at 700 and 750 °C resulted in dramatic reductions in both methane and oxygen conversions. It is known that the thermal decomposition of II-La₂O₃CO₃ begins at approximately 570 °C in a flowing helium environment [Paper II] and at 815 °C in a pure flowing CO₂ environment [10]. It is also known that a II-La₂O₃CO₃ starting catalyst is composed of primarily II-La₂O₃CO₃ with a minor A-La₂O₃ component after reaction at 700 °C and of primarily A-La₂O₃ with a minor II-La₂O₃CO₃ component after reaction at 750 °C in a reacting OCM environment (i.e. a He + CH₄ + O₂ feed) [10]. Thus, it is expected that by co-feeding an amount of CO₂ several times greater than that produced during OCM, the composition of the catalyst in this study at a reaction temperature of 700 °C (and possibly also at 750 °C) is pure II-La₂O₃CO₃. That this
catalyst was extremely inactive towards OCM at these temperatures may confirm the
unsuitability of the pure II-La$_2$O$_2$CO$_3$ compound for OCM.
5. CONCLUSIONS

Co-feeding CO$_2$ over A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ starting catalysts, under the conditions employed in this study, is detrimental to the objective of maximizing the yield of ethene since it depresses both methane conversion and ethene selectivity over both catalysts. Degradation in the catalytic performance is especially severe under reaction conditions at which pure II-La$_2$O$_2$CO$_3$ is believed to be stable. It seems likely, therefore, that the best catalytic performance depends on the presence of both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ phases.

Furthermore, co-fed CO$_2$ appears to play at least two distinct roles in the OCM process over A-La$_2$O$_3$; that of a catalyst modifier (decreasing the catalyst's ability to activate methane) and that of a gas phase modifier (inhibiting the oxidative dehydrogenation of ethane to ethene by interfering with the homogeneous reaction pathway).
ACKNOWLEDGEMENTS

This work was performed at Ames Laboratory under contract number W-7405-eng-82 with the U. S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1615 to this thesis.
REFERENCES


10 Taylor, R. P. M. S. Thesis (1989) Iowa State University


PAPER II.

THE AFFINITY OF A-La₂O₃ AND II-La₂O₂CO₃ FOR GAS-PHASE CO₂

AT TYPICAL OCM REACTION TEMPERATURES.
ABSTRACT

It has been shown that the presence of both II-La$_2$O$_2$CO$_3$ and A-La$_2$O$_3$ is beneficial for maximizing the yield of ethene during the oxidative coupling of methane (OCM) over lanthanum oxide-based catalysts. For example, a pure II-La$_2$O$_2$CO$_3$ starting material (which partially decomposes to A-La$_2$O$_3$ under OCM conditions) is known to give ethene yields up to 400 % larger than pure A-La$_2$O$_3$. However, pure II-La$_2$O$_2$CO$_3$ (stabilized by the addition of gas phase CO$_2$ to the reactant feed) is a much poorer OCM catalyst.

This work investigated the potential for oxycarbonate formation on both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ starting catalysts at typical OCM reaction temperatures by considering the uptake of gas phase CO$_2$ by both materials. The results revealed that CO$_2$ uptake between 700 and 800 °C is not restricted to the surface and probably proceeds by the incorporation of CO$_2$ between the (LaO)$_2$ layers present in both materials. II-La$_2$O$_2$CO$_3$ takes up significantly more CO$_2$ than A-La$_2$O$_3$, probably because of its more open structure along the c axis of the unit cell (i.e., perpendicular to the (LaO)$_2$ planes).

The fact that the A-La$_2$O$_3$ phase resulting from the thermal decomposition of II-La$_2$O$_2$CO$_3$ is a much more active and selective OCM catalyst than a pure A-La$_2$O$_3$ starting material is attributed to its higher basicity resulting from the trace presence of carbonate groups.
1. INTRODUCTION

Previous work conducted in this laboratory tested the catalytic performance of several pure hydrated and carbonated lanthanum compounds for the oxidative coupling of methane (OCM) [1] and found that a pure II-La$_{2}$O$_{3}$CO$_{3}$ starting material gave an ethene yield almost 400% higher than a pure A-La$_{2}$O$_{3}$ starting material. Multi-technique post-reaction characterization revealed that the II-La$_{2}$O$_{3}$CO$_{3}$ starting material had partially decomposed to A-La$_{2}$O$_{3}$ but that the A-La$_{2}$O$_{3}$ starting material had remained pure. It was concluded that the presence of the oxycarbonate phase was highly beneficial for the selectivity to ethene over a working "lanthanum oxide" catalyst.

More recent work co-fed CO$_{2}$ over both A-La$_{2}$O$_{3}$ and II-La$_{2}$O$_{3}$CO$_{3}$ starting materials in an attempt to encourage oxycarbonate formation on the former and to discourage decomposition of the latter during OCM. The catalytic performance of each catalyst was determined as the amount of co-fed CO$_{2}$ was varied [Paper I]. The results revealed that co-feeding CO$_{2}$ over A-La$_{2}$O$_{3}$ and II-La$_{2}$O$_{3}$CO$_{3}$ depressed the conversion of methane and the selectivity to ethene over both catalysts. Degradation in the catalytic performance was found to be especially severe under reaction conditions at which pure II-La$_{2}$O$_{3}$CO$_{3}$ was believed to

---

1 It should be noted, however, that the characterization techniques used were not surface sensitive. Other researchers have observed the presence of an oxycarbonate phase on the surface of a La$_{2}$O$_{3}$ catalyst after OCM at 700 °C using X-ray photoelectron spectroscopy (XPS) [2] and in situ FTIR spectroscopy [3].
exist. It was concluded that optimal catalytic performance depended on the presence of both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ phases.

It is the purpose of this study to investigate the potential for partial oxycarbonate formation on both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ at typical OCM reaction temperatures by considering the uptake of small amounts of gas phase CO$_2$ by both materials. In contrast to our earlier work [Paper I], the goal here is not to use excess quantities of gas phase CO$_2$ to influence the equilibrium between bulk phase A-La$_2$O$_3$ and bulk phase II-La$_2$O$_2$CO$_3$, but rather to use sub-monolayer quantities to probe the incomplete conversion of A-La$_2$O$_3$ to II-La$_2$O$_2$CO$_3$.

1.1 Uptake of CO$_2$ on A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$

Since many of the most selective OCM catalysts are basic materials, several studies have considered the adsorption and temperature programmed desorption (TPD) of CO$_2$ as a way to quantify surface basicity [4-5]. The basicity of an oxide material is related to the difference in the size of the partial charge on the lattice oxygen relative to that on the cation (i.e., the difference in electronegativity between the oxygen anion and the cation). Ionic solids, such as A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ have highly electropositive cations which result in high partial charges on the lattice oxygens and hence, high basicity [6].

Unfortunately, the use of CO$_2$ as a probe molecule for determining surface basicity is of little value for A-La$_2$O$_3$ because of the formation of carbonated phases upon exposure of this material to CO$_2$. Even so, one recent study used CO$_2$ adsorption / TPD to determine the basicity / base strength distribution of several REOs by the stepwise thermal desorption
(STD) of CO₂ chemisorbed at 50 °C [4]. It was reported that CO₂ desorbed steadily from
A-La₂O₃ between 50 and 900 °C with approximately 40% of the chemisorbed CO₂ desorbing
between 500 and 700 °C and a further 22% desorbing between 700 and 900 °C. Because
A-La₂O₃ chemisorbed more CO₂ at 50 °C and desorbed CO₂ at higher temperatures than the
other REOs, it was concluded to be the most basic of the REOs tested and to possess the
strongest basic sites. However, no characterization was performed in this study and no
consideration was given to the formation or decomposition of carbonated phases. From the
STD data and our previous work which confirmed the susceptibility of A-La₂O₃ to
carbonation, it is likely that part of the CO₂ chemisorbed at 50 °C produced an oxycarbonate
phase as the temperature was increased to around 500 °C and that decomposition of this
phase occurred as the temperature was raised further.

One early study used in situ infrared spectroscopy to investigate the interaction between
A-La₂O₃ and 50 Torr of CO₂ at 25 °C [7]. It was revealed that such exposure to gas phase
CO₂ resulted in the formation of a unidentate carbonate species with a surface coverage of
7-8 CO₂ molecules / 100 Å² (approximately 1 CO₂ molecules / surface O³⁻ ion). Upon
evacuation at 275 °C, the unidentate carbonate partially desorbed as CO₂ but also rearranged
to give a bidentate carbonate species. Surface coverage at this temperature was reported to
be 1-2 CO₂ molecules / 100 Å². By 300 °C, the unidentate species had fully decomposed and,
by 350 °C, so had the bidentate species. No oxycarbonate formation was reported on this
material although similar experiments on La(OH)₃ reported the formation of La₂O₂CO₃ at
150-200 °C which was thermally stable to 700 °C.
No investigation of the interaction between CO₂ and II-La₂O₃CO₃ has been published to date. Clearly then, the current state of knowledge on the influence of gas phase CO₂ on lanthanum oxide-based OCM catalysts is inadequate. The objectives of this work have been to address these shortcomings by employing several different approaches.

Firstly, in order to determine the stability of A-La₂O₃ and II-La₂O₃CO₃ phases at elevated temperatures, thermal decompositions to 900 °C in a flowing helium environment were conducted. Secondly, the susceptibility for uptake of CO₂ by both materials was investigated by pulsing small quantities of CO₂ over both materials once stabilization had been attained at typical OCM reaction temperatures. Finally, in order to determine if the non-equilibrium state (i.e., during which both oxycarbonate and sesquioxide phases are present as II-La₂O₃CO₃ decomposes to A-La₂O₃) is particularly susceptible to CO₂ uptake, small quantities of CO₂ were pulsed while the temperature of a II-La₂O₃CO₃ starting material was ramped from 550 to 750 °C.
2. EXPERIMENTAL PROCEDURE

2.1 Catalyst Characterization

From earlier work involving several characterization techniques [8], it was determined that Fourier transform infrared spectroscopy (FTIR) and laser Raman spectroscopy (LRS) could identify the bulk composition of the lanthanum compounds of interest in this work.

2.1.1 Fourier Transform Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Instruments 60SX spectrometer equipped with a water-cooled globar source and a mercury-cadmium-telluride (MCT) detector. Samples were prepared in the form of pressed wafers thin enough to permit the transmittance of at least 25 % of the intensity of the incident infrared beam. Each wafer was prepared from approximately 0.15 g of a mixture composed of 1-2 wt. % of sample in potassium bromide, KBr (Fisher, IR grade). This mixture was ground in an agate mortar and pestle for two and a half minutes. It was then pressed between the faces of a hardened stainless steel die under a load of 9 tons (20000 lb) on a Model C-12 press (Fred S. Carver, Inc.). The resulting wafer was 20.6 mm in diameter and approximately 0.03 mm thick at the center. All spectra involved the accumulation of 512 scans at either 1 or 5 wavenumber (WN) resolution and were ratioed to that of a 100 % KBr wafer collected under the same conditions.
2.1.2 Laser Raman Spectroscopy

Laser Raman spectra were obtained using a Spex Triplemate triple monochromator spectrometer. The primary excitation source was the 514.5 nm line of a Spectra-Physics argon ion laser, Model 164, operating at powers ranging from 20 to 200 mW at the source. The resolution of the resulting spectra was 5 WN. The spectrometer was calibrated over the range 80 to 850 WN using a powder sample of MoO$_3$. Catalyst samples were prepared by sealing approximately 0.01 g in a 0.8 mm inside diameter (i. d.), 90 mm long quartz capillary tube. Spectra were obtained in a single scan with the scan time dependent upon the intensity of the Raman scattering.

2.2 Catalyst Preparation

A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ catalysts were prepared according to techniques developed in earlier work [8]. Both used La$_2$O$_3$ (Aldrich Chemical Company, 99.99 %) as the starting material. Since La$_2$O$_3$ is known to be sensitive to atmospheric hydration and carbonation, it had been stored in an argon-filled dry box since its initial purchase. However, although characterization by LRS indicated the sole presence of A-La$_2$O$_3$ (bands at 107, 194, and 410 WN), characterization by FTIR revealed bands at 3610 and 642 WN corresponding to the presence of some La(OH)$_3$ in the Aldrich material.

A heat treatment was performed in order to regenerate a bulk supply of pure A-La$_2$O$_3$. This was done by placing approximately 5 g of La$_2$O$_3$ (from the dry box) in a quartz boat inside a quartz tube in a tube furnace (Lindberg, Model 54232, with Lindberg Console, Model 59544, and Eurotherm Controller, Model 211). An inert gas, in this case oxygen-free
nitrogen (Matheson, <5 ppm O₂), was passed through the tube at a flow rate of 100 standard cubic centimeters per minute (scm). The sample was heated to 900 °C at 10 °C/min and maintained at 900 °C for 12 hours. The furnace was then switched off and allowed to cool over a period of several hours to room temperature. A-La₂O₃ was removed from the quartz boat and samples were taken for analysis by FTIR and LRS. The remainder was placed in a vial under a helium atmosphere and stored in a dessicator.

2.2.1 Preparation of A-La₂O₃

Although A-La₂O₃ prepared in the tube furnace was pure (as indicated by FTIR and LRS characterizations), it was found that a small but finite degree of contamination occurred in the time it took to load the sample in the reactor. It was therefore necessary to regenerate pure A-La₂O₃ in situ for subsequent catalytic performance testing. This was done by loading 0.050 g of A-La₂O₃ (prepared in the tube furnace) on top of a small plug of quartz wool in the quartz reactor (described in the next subsection). The sample was then heated to 900 °C at 10 °C/min in a 100 sccm flow of helium (Matheson, Zero grade). During the heating process, the reactor effluent was fed directly to the Porapak Q column of the gas chromatograph (Varian, Model 3600) in order to observe eluting species. Since each batch of catalyst was prepared in situ and in an amount required for subsequent testing, characterization of each starting catalyst could not be performed. However, the FTIR and LRS spectra of a representative sample of A-La₂O₃ prepared by the above technique reproduced those of the pure A-La₂O₃ sample prepared in the tube furnace.
2.2.2 Preparation of \( \text{II-La}_2\text{O}_2\text{CO}_3 \)

Since \( \text{A-La}_2\text{O}_3 \) served as the starting material for the preparation of \( \text{II-La}_2\text{O}_2\text{CO}_3 \), the latter was also prepared in situ. In this case, 0.044 g of \( \text{A-La}_2\text{O}_3 \) (prepared in the tube furnace) was loaded in the reactor and heated to 900 °C at 10 °C/min in a 100 sccm flow of helium (Matheson, Zero grade). This served to regenerate pure \( \text{A-La}_2\text{O}_3 \). After cooling to room temperature, the helium carrier gas was changed to a 30 sccm flow of \( \text{CO}_2 \) and the sample was heated to 650 °C at 5 °C/min, from 650 to 700 °C at 2 °C/min, and maintained at 700 °C for 30 minutes. Given the initial starting mass of 0.044 g of \( \text{A-La}_2\text{O}_3 \), the stoichiometry of the reaction at completion yielded 0.050 g of \( \text{II-La}_2\text{O}_2\text{CO}_3 \). As for \( \text{A-La}_2\text{O}_3 \), \( \text{II-La}_2\text{O}_2\text{CO}_3 \) was prepared batchwise in situ in an amount required for subsequent testing, therefore characterization of each starting catalyst could not be performed. However, characterization by FTIR and LRS of a representative sample prepared using this technique gave spectra indicating the sole presence of \( \text{II-La}_2\text{O}_2\text{CO}_3 \).

2.3 Thermal Decomposition Studies

These studies were undertaken using the system shown schematically in Figure 1. A molecular sieve / Drierite™ water trap and an Alltech Oxytrap™ removed contaminating water and oxygen from the helium (Matheson, Zero grade) carrier stream. The helium flow rate was regulated to 100 sccm by a Tylan mass flow controller (Model FC-260). Valco 10- and 4-port sampling valves were set such that the helium was fed to the reactor in the continuous (as opposed to pulse) flow mode.
Figure 1: Schematic of OCM gas feed/reactor/analytical system
The catalyst bed was supported on a plug of quartz wool in a quartz reactor, shown schematically in Figure 2. The reactor was made by fusing a 195 mm long, 6 mm outside diameter (o. d.), 1 mm i. d. quartz capillary to a 200 mm long, 8 mm o. d., 6 mm i. d. quartz tube. Use of the narrow bore tube significantly reduced gas-phase reactions that can occur downstream of the catalyst bed. An 18"-long, 0.02" o. d., K-type thermocouple with a 0.02" i. d. quartz sheath was forced through a high temperature septum at the reactor inlet; the tip was positioned at the center of the catalyst bed. The reactor was positioned vertically along the furnace axis. Temperatures above and below the catalyst bed were measured at 750 °C and found to vary by no more than 2 °C at distances of 1" above or below the bed. All transfer lines downstream of the reactor were maintained at 150 °C.

Effluent gas analysis was accomplished by gas chromatography (GC) using a Varian 3600 gas chromatograph equipped with a thermal conductivity detector (TCD) and a 7 ft long, 0.02" o. d., 80/100 mesh Porapak Q (Alltech Associates, Inc.) chromatographic column. The TCD signal was fed to an analog-to-digital convertor (ADC) board installed in an Apex 386/25 personal computer. The signal was recorded and processed using Varian's GC Star software package.

The reactor was loaded with A-La$_2$O$_3$ (0.050 g for in situ preparation of A-La$_2$O$_3$ and 0.044 g for in situ preparation of II-La$_2$O$_2$CO$_3$) and the catalyst prepared as described above. With the helium carrier flowing, the catalyst bed was heated from room temperature to 900 °C at 10 °C/min and the effluent stream was fed directly into the GC column. This allowed any evolved species to be collectively detected by the TCD (i.e., no separation of evolved components was effected). The procedure was repeated for both A-La$_2$O$_3$ and
Figure 2: Schematic of OCM Reactor
II-La₂O₂CO₃ prepared in situ. Finally, the thermal decomposition of II-La₂O₂CO₃ was repeated twice more but, in these runs, the final temperatures were limited to 700 and 750 °C, respectively. These final temperatures were maintained for as long as was necessary for complete decomposition to occur.

2.4 CO₂ Pulsing Studies

These studies used the same experimental setup as the thermal decomposition studies described above with the exception that the feed streams were fed in the pulse mode. The amount of CO₂ in each pulse was set to approximately 10 % of a monolayer. Assuming one monolayer corresponds to 8 CO₂ molecules /nm² [7], a BET surface area of 1 m² / g for each catalyst [1], and a 50 µL pulsing loop in the Valco 10-port valve, the feed flow rates were set as follows; helium carrier (MFC 1), 100 sccm; helium make-up (MFC 2), 96.75 sccm; CO₂ (MFC 6), 3.25 sccm; helium purge (MFC 3), 100 sccm.

The pulsing experiments were conducted over A-La₂O₃, II-La₂O₂CO₃ (both freshly prepared in situ), and a blank reactor (i.e., empty except for a plug of quartz wool) at temperatures of 700, 750, 800, and 850 °C using pulses of CO₂ and N₂ (both 3.25 % in helium). Each experiment started by heating the reactor to 700 °C at 10 °C/min in a 100 sccm flow of helium. After allowing 2 hours for stabilization, a series of 20 pulses was fed at 3 minute intervals. The temperature was then raised in 50 °C increments (10 °C/min) to 850 °C with the same procedure being followed at each temperature. The CO₂ not taken up by the catalyst was detected downstream of the reactor as a peak on the TCD chromatogram. The
peak area was integrated and ratioed to that of a feed pulse. Using this value, the percentage of a monolayer of CO$_2$ taken up by the catalyst was calculated.

In a separate set of experiments, CO$_2$ adsorption on A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ was investigated while the catalysts were heated between 550 and 750 °C. In these runs, the catalysts were first ramped from room temperature to 550 °C at 10 °C/min in flowing He (100 sccm). Pulses of CO$_2$ (3.25 % in He) were then fed to the catalyst bed at 3 minute intervals while heating continued to 750 °C at 2 °C/min. The final temperature was maintained until no further change in CO$_2$ uptake were observed.

In all experiments, the switching of the Valco 10-port (pulsing) valve was controlled by the GC via a pre-written program and an electric actuator attached to the valve.
3. EXPERIMENTAL RESULTS

3.1 Thermal Decomposition of A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$

As shown in Figure 3, A-La$_2$O$_3$ (freshly prepared in situ) was thermally stable when heated from room temperature to 900 °C at 10 °C/min in a 100 sccm flow of helium. This confirms the purity of the sample since any contamination via hydration and/or carbonation would be detected through the evolution of H$_2$O and/or CO$_2$. In fact, such evolutions were observed in the thermal decomposition of the contaminated La$_2$O$_3$ supplied by Aldrich (also shown for comparison in Figure 3). Major evolutions from this material occur at 320, 440, and 610 °C.

The oscillations in both thermal decomposition curves at temperatures below 250 °C resulted from the large heating mass of the reactor furnace causing nonlinearities in the heating profile (plotted in Figure 3). These nonlinearities produced variations in the flow rate of the helium carrier gas through the sample side of the TCD and hence the observed oscillations.

Subjecting II-La$_2$O$_2$CO$_3$ to the same heating profile revealed a two-stage evolution of CO$_2$ (with peaks centered at 685 and 840 °C$^2$) as the oxycarbonate phase decomposed to the sesquioxide (Figure 4). Decomposition in a flowing CO$_2$ environment, however, is known to proceed via a single evolution of CO$_2$ centered at 870 °C (as indicated by thermogravimetric

---

$^2$ It should be noted that when a slower heating rate was used (2 °C/min) these same maxima were observed at 625 and 775 °C, respectively.
Figure 3: Thermal decomposition of Al$_2$O$_3$ to 900°C.
Figure 4: Thermal decomposition of H₂, H₂O, CO, to 900°C.
analysis reported in earlier work [8]). Decomposition in a flowing CO₂ environment is expected to occur at a higher temperature than that in a flowing He environment because of the influence of CO₂ on shifting the equilibrium shown below to the right:

\[ \text{A-La}_2\text{O}_3 + \text{CO}_2 \rightleftharpoons \text{II-La}_2\text{O}_2\text{CO}_3 \]  

(4.1)

When II-La₂O₂CO₃ was heated at 10 °C/min to 700 °C and 750 °C in a flowing helium environment, it took 5 hours and 1.7 hours, respectively, at the upper temperatures for complete decomposition to occur.

3.2 CO₂ Uptake by A-La₂O₃ and II-La₂O₂CO₃ at Elevated Temperatures

Feeding a series of twenty pulses, each containing 10% of one monolayer of CO₂, over A-La₂O₃, II-La₂O₂CO₃, and a blank reactor at elevated temperatures gave no variation in the amount of CO₂ adsorbed with the pulse number. Therefore, the average amount of CO₂ taken up per pulse was calculated and plotted against temperature for each run, as shown in Figure 5.

For the blank reactor run, the results indicated that the quartz wool plug and the reactor itself displayed no affinity for CO₂, regardless of reactor temperature.

For runs with a loaded reactor, the extent of CO₂ uptake at elevated temperatures was very different for each catalyst. Over A-La₂O₃, there was a small, and decreasing, uptake of CO₂ as the temperature increased from 700 to 800 °C. At 850 °C, no uptake of CO₂ was observed. Over II-La₂O₂CO₃, the amount of CO₂ taken up at the lower temperatures was significantly higher. For example, that taken up at 700 °C corresponded to almost half of the CO₂ fed in each pulse, or approximately 4.4% of one monolayer per pulse. This is
Carbon dioxide Adsorbed per Pulse (% of one monolayer)

Figure 5: CO₂ adsorption on A-La₂O₃, ( ), II-La₂O₃, CO₂, ( ), and a blank reactor (○) at elevated temperatures.
particularly interesting since we know from the thermal decomposition experiments described above that II-La$_2$O$_2$CO$_3$ begins to thermally decompose to A-La$_2$O$_3$ at 570 °C and continues to evolve CO$_2$ up to 870 °C (when heated at 10 °C/min). Thus, CO$_2$ was being simultaneously taken up and evolved by the material. As for A-La$_2$O$_3$, no uptake of CO$_2$ was observed on II-La$_2$O$_2$CO$_3$ after 2 hours at 850 °C.

Uptake of CO$_2$ by II-La$_2$O$_2$CO$_3$ was accompanied by a broadening of the CO$_2$ peaks in the TCD chromatogram, as evidenced by the full width at half maximum (FWHM) values plotted in Figure 6. This wider distribution of retention times while CO$_2$ is being taken up by the catalyst implies that some of the CO$_2$ molecules are in some way held up before passing out of the catalyst bed to the GC detector, perhaps by some kind of temporary (i.e., not permanently binding) interaction(s) with the catalyst. In support of this observation, a significant delay has been observed between the $^{13}$CH$_4$ and $^{13}$CO$_2$ MS traces when a He/$^{13}$CH$_4$/O$_2$ feed was switched to a He/CH$_4$/O$_2$ feed over La$_2$O$_3$ at 750 °C [9]. The delay was attributed to the readsorption and redesorption of CO$_2$ along the catalyst bed.

An alternative explanation for the peak broadening is that the CO$_2$ molecules follow highly tortuous paths as they pass through (the necessarily highly porous) catalyst bed. This is an unlikely explanation in the case of II-La$_2$O$_2$CO$_3$, however, because of its apparent low porosity (it has a BET surface area of just 1.1 m$^2$/g). Furthermore, one would expect to see peak broadening even when no uptake of CO$_2$ occurred (i.e. at 850 °C). Clearly, because the FWHM value for II-La$_2$O$_2$CO$_3$ at 850 °C approached that for A-La$_2$O$_3$ and the blank reactor, the porosity explanation cannot hold. However, to investigate further, the experiments were
Figure 6: Peak full widths at half maximum for CO\textsubscript{2} ( ), N\textsubscript{2} ( ) adsorption on A-La\textsubscript{2}O\textsubscript{3} (■), II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} ( ), and a blank reactor (○) at elevated temperatures.
repeated using pulses of nonadsorbing \( N_2 \) (3.25 % in He). As shown in Figure 6, the FWHM values for \( N_2 \) over \( \text{II-La}_2\text{O}_2\text{CO}_3 \) were similar to those over \( \text{A-La}_2\text{O}_3 \) and the blank reactor at 700 to 850 °C (the latter two overlap at all temperatures). This confirmed that peak broadening for \( \text{CO}_2 \) adsorption over \( \text{II-La}_2\text{O}_2\text{CO}_3 \) was caused by specific (but unknown) interactions between \( \text{CO}_2 \) molecules and the catalyst.

Of further interest is the fact that the \( \text{CO}_2 \) peak broadening over \( \text{II-La}_2\text{O}_2\text{CO}_3 \) was 17 % higher at 750 than at 700 °C, despite the fact that \( \text{CO}_2 \) uptake was 34 % lower.

### 3.3 \( \text{CO}_2 \) Uptake by \( \text{A-La}_2\text{O}_3 \) and \( \text{II-La}_2\text{O}_2\text{CO}_3 \) during Thermal Decomposition

Analysis of the reactor effluent by GC while heating \( \text{A-La}_2\text{O}_3 \) and \( \text{II-La}_2\text{O}_2\text{CO}_3 \) at 10 °C/min from room temperature to 550 °C in flowing helium gave no indication of any evolved species, confirming the results of subsection 4.1 above. Further heating from 550 to 750 °C with simultaneous pulsing of \( \text{CO}_2 \) at 3 minute intervals gave very different results for each catalyst.

Over \( \text{A-La}_2\text{O}_3 \), there was a small and decreasing uptake of \( \text{CO}_2 \) (corresponding to less than 1 % of a monolayer per pulse) between 550 and 730°C (Figure 7). Over \( \text{II-La}_2\text{O}_2\text{CO}_3 \), two regions of strong \( \text{CO}_2 \) uptake were observed (Figure 8). The first occurred between 620 and 650 °C, the second between 670 and 750 °C. After one and a half hours at 750 °C, \( \text{CO}_2 \) uptake attained a fairly steady value of approximately 1.5 % of one monolayer per pulse.
Figure 7: CO$_2$ adsorption on A$_2$La$_4$O$_9$ during heating from 550 to 750°C.

Carbon dioxide Adsorbed per Pulse (% of one monolayer)

Temperature (deg. C)
Figure 8. CO₂ adsorption on 11-La₂O₃·CO₃O₄ during heating from 550 to 750°C.
4. DISCUSSION OF RESULTS

4.1 Thermal Decomposition of II-La$_2$O$_2$CO$_3$

As described in earlier work [8], A-La$_2$O$_3$ is easily converted to II-La$_2$O$_2$CO$_3$ via a heat treatment in a CO$_2$ environment. Observation of the process by thermogravimetric analysis (TGA) revealed that, at a heating rate of 5 °C/min in a 60 sccm flow of CO$_2$, the phase transformation begins at 415 °C and is complete by 600 °C. The II-La$_2$O$_2$CO$_3$ so formed decomposes between 815 °C and 950 °C to give A-La$_2$O$_3$. This decomposition temperature is much higher than can be expected in an inert environment due to the influence of gas phase CO$_2$ on the equilibrium between A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$;

$$\text{A-La}_2\text{O}_3 + \text{CO}_2 \leftrightarrow \text{II-La}_2\text{O}_2\text{CO}_3 \quad (5.1)$$

Other studies have reported the II-La$_2$O$_2$CO$_3$ to A-La$_2$O$_3$ decomposition temperature as 590-760 °C in vacuum ($10^{-5}$ mmHg) [10], 700 °C in air [11], 790-870 °C in 15 mmHg of water vapor [10], and 915 °C [12], 950-970 °C [10, 13], and 960 °C [14-15] in CO$_2$. However, parameters such as heating rate, sample preparation method [16-17], carbon content, and particle size, all influence the decomposition temperature greatly [12].

The results of this work reveal the thermal decomposition of II-La$_2$O$_2$CO$_3$ in a flowing helium environment to be a two-step process. However, no intermediate has ever been reported for this decomposition and it is unlikely that a stable intermediate exists since this transformation is well known as the last step in the thermal decomposition of hydrated lanthanum carbonate [11];
La₂(CO₃)₃.8H₂O → La₂(CO₃)₃ → La₂O₂CO₃ → La₂O₃

A possible explanation for the two-step decomposition process observed in this work is that, during the decomposition, the oxycarbonate lattice undergoes an internal restructuring which produces two, differently bonded forms of CO₂. The first, more weakly bound form accounts for approximately 5 % of the total CO₂ evolved³ and is liberated from the lattice between 570 and 700 °C. The second form constitutes the remainder and evolves between 700 and 870 °C.

Since these evolution temperatures are so high, it is unlikely that even the more weakly bound form corresponds to a surface adsorbed CO₂ species. Both are more likely to result from the decomposition of the (CO₃)²⁻ anions between the planes of (LaO)²⁺ cations in the oxycarbonate lattice (see below). The difference in their thermal stabilities may be accounted for by their different orientations within the crystal lattice.

The thermal decomposition of II-La₂O₂CO₃ to 750 °C revealed that decomposition to A-La₂O₃ was complete after 1.7 hours at the upper temperature. Thus, the II-La₂O₂CO₃ starting catalyst used in our earlier work [1] must have been essentially pure A-La₂O₃ prior to its catalytic evaluation at this temperature since a 2 hour stabilization period was allowed. That this catalyst and the pure A-La₂O₃ starting catalyst gave very different catalytic performance seems to indicate that the thermal decomposition of II-La₂O₂CO₃ results in a form of A-La₂O₃ particularly suited for the activation of methane. It is possible that the A-La₂O₃ so formed retains trace amounts of carbonate groups, possesses particular structural

³ Based on an integration of the areas under each peak in the thermal decomposition curve shown in Figure 4.
defects and/or retains a more open crystallographic structure than the A-La$_2$O$_3$ starting material.

In order to discuss the results further it is useful to review the literature regarding the crystallographic structures of both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$.

4.2 The Structure of A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$

4.2.1 A-La$_2$O$_3$

Although dioxides (LnO$_2$), suboxides (LnO), and nonstoichiometric mixed oxides are known for other members of the lanthanide series, the sesquioxide (Ln$_2$O$_3$) is the only stable form of lanthanum oxide [18]. Its stability is explained in part by the empty 4f subshell in the La$^{3+}$ cation. Lanthanum is also unique among the rare earth sesquioxides in that it exists only in the hexagonal form, A-La$_2$O$_3$, at normal temperatures [19]. At temperatures approaching its melting point of 2300 °C, however, two other phases are formed [20]. The hexagonal H-form appears at around 2050 °C and the (probably cubic) X-form appears at 2100 °C.

The atomic structure of A-La$_2$O$_3$ has proven fairly difficult to determine [18]. One early study [21] reported a layered structure composed of an hexagonal P lattice with space group $P 3m1$ ($D_3^{3h}$). Each cation was surrounded by seven anions, four of which were closer than the other three. This structure stood for thirty seven years before being rejected in favor of a micro-twinning modification [22] with the space group $P 6_3/mmm$ ($D_{6h}^4$). A more recent study [23] suggested a structure formed by layers of two-dimensionally packed (OLa$_4$) tetrahedra separated by layers of oxygen (see Figure 9). The tetrahedra are joined to one
Figure 9: The atomic arrangement in A-La$_2$O$_3$ another along their edges, forming the complex "lanthanyl" cation, (LnO)$_2^{2+}$. Although the La-O bonds within the (LaO)$_2^{2+}$ layers are mainly covalent, the ionic nature of the material prevails in the La-O bonds between the layers. A view in the plane of the lanthanyl layers reveals the hexagonal close-packed arrangement of the lanthanum atoms (Figure 10). The oxygen atoms in the oxide layers occupy positions above the centers of these hexagons, as shown in Figure 10 (dotted circles).

Lattice parameters, $a$ and $c$, for the hexagonal unit cell at room temperature have been assigned values of 3.9373 Å and 6.1299 Å, respectively [24]. On heating, the lattice
undergoes thermal expansion with expansion being greater along the \( c \) axis (i.e., in the direction perpendicular to the ion planes) than along the \( a \) axis [25].

4.2.2 II-La\(_2\)O\(_2\)CO\(_3\)

Lanthanum oxycarbonate exists in three polymorphic forms; type I (tetragonal), type Ia (a monoclinic distortion of type I), and type II (hexagonal) [12]. All three forms are
layer-type structures based on the complex lanthanyl cation, \((\text{LaO})_2^{2+}\). Type I has the square \((\text{LaO})_2^{2+}\) layers found in \(\text{LaOCl}\); type II has the hexagonal \((\text{LaO})_2^{2+}\) layers found in \(\text{A-La}_2\text{O}_3\) (and described above).

In the type II form, the planar \(\text{CO}_3^{2-}\) groups exist in only one orientation, in contrast to the I and Ia forms in which there are two and three possible orientations, respectively. Figure 11 shows all three possible orientations superimposed on the hexagonal closed-packed arrangement of the lanthanum atoms in the \((\text{LaO})_2^{2+}\) layers. The second orientation is the one believed to exist in \(\text{II-La}_2\text{O}_2\text{CO}_3\).

Linear thermal expansion coefficients for the I and II forms of the oxycarbonate have been reported for temperatures up to 800 °C [12] and compared with those for \(\text{A-La}_2\text{O}_3\) [25]. The coefficients along the \(a\) and \(c\) axes for \(\text{II-La}_2\text{O}_2\text{CO}_3\) are approximately 127 % and 40 % of those for \(\text{A-La}_2\text{O}_3\) in the same directions. The large difference in the coefficient along the \(c\) axis is to be expected since the bonding between the \((\text{LaO})_2^{2+}\) layers and \(\text{CO}_3^{2-}\) in \(\text{II-La}_2\text{O}_2\text{CO}_3\) and that between the \((\text{LaO})_2^{2+}\) layers and \(\text{O}^{2-}\) in \(\text{A-La}_2\text{O}_3\) differs mainly in the \(c\) direction. Absolute values for the lattice parameters have not been reported for the II form but correspond to 4.16 Å and 14.05 Å for the \(a\) and \(c\) directions, respectively, in \(\text{I-La}_2\text{O}_2\text{CO}_3\) [12].

It is likely that it is the layered nature of both \(\text{A-La}_2\text{O}_3\) and \(\text{II-La}_2\text{O}_2\text{CO}_3\) which facilitates (through the insertion of \(\text{O}_2\), \(\text{H}_2\text{O}\), and \(\text{CO}_2\) between the layers) the high oxygen exchange rates and susceptibility to hydration and carbonation observed on these materials.

The results of the \(\text{CO}_2\) pulsing experiments reveal several interesting points:
Since the amount of CO₂ taken up from each pulse remained constant over a series of pulses (irrespective of temperature or whether the catalyst was II-La₂O₂CO₃ or A-La₂O₃), it is likely that each catalyst is able to take up multi-monolayer quantities, implying a process not restricted to surface adsorption. This is to be expected since the uptake of CO₂ is likely to proceed via its incorporation between the (LaO)²⁺ layers present in both materials rather than (or in addition to) via a surface adsorption mechanism.

II-La₂O₂CO₃ clearly takes up more CO₂ than A-La₂O₃ at all temperatures below 850 °C. This is also in accordance with expectations since crystallographic studies...
discussed above indicate that the cell length along the c axis (i.e., perpendicular to the 
(LaO)$_2^{2+}$ planes) for II-La$_2$O$_2$CO$_3$ is more than twice that for A-La$_2$O$_3$ making CO$_2$
insertion between layers that much easier. Although the linear thermal expansion
coefficient for A-La$_2$O$_3$ in the c direction is larger than that for II-La$_2$O$_2$CO$_3$ at these
temperatures, the absolute spacing between layers is much smaller.

- No uptake of CO$_2$ is observed at 850 °C on either catalyst. As noted in the thermal
decomposition studies, at this temperature the II-La$_2$O$_2$CO$_3$ phase is unstable in a
helium environment. Thus, its crystal structure collapses to that of A-La$_2$O$_3$ and the
insertion of CO$_2$ into the O$_{2-}$ layers (between (LaO)$_2^{2+}$ layers of A-La$_2$O$_3$) becomes
thermodynamically unfavorable.

- The observation that the FWHM values for CO$_2$ pulses over II-La$_2$O$_2$CO$_3$ increases
between 700 and 750 °C while the amount of CO$_2$ taken up simultaneously decreases
seems to indicate that the ability of CO$_2$ to permanently incorporate into the catalyst
lattice decreases with increasing temperature. At 700 °C, approximately 44 % of the
CO$_2$ in each pulse is taken up by the catalyst; at 750 °C, just 30 % is taken up but the
broader GC peaks indicate more nonbinding interactions between CO$_2$ and
II-La$_2$O$_2$CO$_3$ at this temperature.

- The experiments pulsing CO$_2$ during the thermal decomposition of II-La$_2$O$_2$CO$_3$ are
more difficult to interpret. It appears that the temperatures at which CO$_2$ is most
readily taken up correspond to those at which CO$_2$ is being most rapidly evolved from
a decomposing II-La$_2$O$_2$CO$_3$ sample. There is therefore likely to be a significant degree of exchange occurring between co-fed CO$_2$ and CO$_2$ evolving from the oxycarbonate lattice as II-La$_2$O$_2$CO$_3$ decomposes to A-La$_2$O$_3$.

As reported in earlier work [1], the A-La$_2$O$_3$ material resulting from the thermal decomposition of II-La$_2$O$_2$CO$_3$ is a much more active and selective OCM catalyst than a pure A-La$_2$O$_3$ starting material. There are several possible explanations which could account for this enhancement in catalytic performance. First, since the decomposition process involves the simultaneous collapse of the oxycarbonate crystal structure$^4$ and evolution of CO$_2$ from the carbonate layers, it is conceivable that significant structural defects appear in the resulting sesquioxide. These defects may provide specific active sites on the catalyst, accounting for the observed increases in the selectivities to coupling products.

A second explanation relates catalytic performance to the basicity of the oxygen atoms in the (LaO)$_2^{2+}$ layers. As described in the introduction, the basicity of an oxide is related to the difference in the size of the partial charge on the lattice oxygen relative to that on the lanthanum cation. In the sesquioxide, the oxygen atoms located in the oxide layer compete with the oxygen atoms in the neighboring (LaO)$_2^{2+}$ layers for the negative charge attracted from the lanthanum cations. This competition lowers the charge difference between the oxygen and lanthanum atoms in the (LaO)$_2^{2+}$ layers and hence the basicity. Since the electronegativity of the carbonate groups in II-La$_2$O$_2$CO$_3$ is lower than that of the oxide atoms in A-La$_2$O$_3$, the basicity of the former is higher. It is proposed that the A-La$_2$O$_3$ phase

$^4$ With significant contraction in the c direction as the (LaO)$_2^{2+}$ layers pack closer together.
atoms in A-La₃O₇, the basicity of the former is higher. It is proposed that the A-La₂O₃ phase resulting from the thermal decomposition of II-La₂O₂CO₃ displays better catalytic performance than a pure A-La₂O₃ starting material due to the trace presence of carbonate groups which serve to increase the material's basicity.

It would follow from this theory that a pure II-La₂O₂CO₃ phase would display even better catalytic performance. However, it should be remembered that at typical OCM reaction temperatures, II-La₂O₂CO₃ is thermally unstable. Attempting to stabilize this phase by co-feeding CO₂, as demonstrated in Paper I, results in severe degradation in catalytic performance. This degradation is assumed to result from gas phase CO₂ both interfering with the homogeneous mechanism by which product ethane dehydrogenates to ethene and disrupting the charge separation between the oxygen and lanthanum atoms in the (LaO)₂⁺ layers, thereby reducing the catalyst's basicity.
5. CONCLUSIONS

The thermal decomposition of II-La$_2$O$_2$CO$_3$ proceeds via a two-step process and probably involves some kind of internal restructuring at temperatures exceeding 550 °C which results in two distinct evolutions of CO$_2$.

The uptake of CO$_2$ by A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ at temperatures in the range 700 to 800 °C is not restricted to the surface and most probably proceeds by the incorporation of CO$_2$ between the (LaO)$_{2+}$ layers present in both materials.

II-La$_2$O$_2$CO$_3$ is capable of taking up significantly more CO$_2$ than A-La$_2$O$_3$ at typical reaction temperatures, probably because of its more open structure along the c axis of the unit cell (i.e., perpendicular to the (LaO)$_{2+}$ planes). As the temperature is increased from 700 to 750 °C, co-fed CO$_2$ is less likely to incorporate permanently into the crystal structure but undergoes numerous nonbinding interactions. Also, as II-La$_2$O$_2$CO$_3$ thermally decomposes to A-La$_3$O$_3$, it exhibits a higher susceptibility to CO$_2$ uptake than pure A-La$_2$O$_3$.

The fact that the A-La$_2$O$_3$ phase resulting from the thermal decomposition of II-La$_2$O$_2$CO$_3$ is a much more active and selective OCM catalyst than a pure A-La$_2$O$_3$ starting material is attributed to its higher basicity resulting from the trace presence of carbonate groups. These carbonates lessen the charge sharing between the oxygen atoms in the (LaO)$_{2+}$ layers and the oxygen atoms in the oxide layers, thereby increasing the relative charge difference between the oxygen and lanthanum atoms in the (LaO)$_{2+}$ layers and hence the material's basicity.
ACKNOWLEDGEMENTS

This work was performed at Ames Laboratory under contract number W-7405-eng-82 with the U. S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1615 to this thesis.
REFERENCES


17 Stecura, S. U. S. Bureau of Mines Report 6616 (1964) 1-44

18 Lejus, A. M.; Collongues, R. Topics in Mat. Sci. 4 (1980) 9, 481-577

19 Warshaw, I.; Roy, R. J. Phys. Chem. (1961) 65, 2048-2051


21 Pauling, L. Z. Krist. (1929) 69, 415-421


23 Caro, P. E. J. Less Common Metals (1968) 16, 367-

24 Swanson; Fuyat NBS. Circ. (1954) 3, 33-34

PAPER III.

THE FATE OF THE C AND O ATOMS OF THERMALLY EVOLVED CO₂ DURING THE OXIDATIVE COUPLING OF METHANE OVER II-La₂O₂CO₃
ABSTRACT

Previous work conducted in this laboratory concluded that the presence of both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ phases was necessary for high yields of coupling products in the oxidative coupling of methane (OCM) over a "lanthanum oxide" catalyst. This work studied the influence of the oxycarbonate phase during OCM by investigating the roles of the C and O atoms located in the (CO$_3$)$^{2-}$ groups of II-La$_2$O$_2$CO$_3$. Preparing II-La$_2^{18}$O$_2$CO$_3$ and II-La$_2^{13}$O$_2$CO$_3$ from A-La$_2$O$_3$ and C$^{18}$O$_2$ and $^{13}$CO$_2$, respectively, enabled the isotopically labeled C and O atoms to be followed by mass spectrometry (MS).

Carbon dioxide used in preparing oxycarbonate from sesquioxide was found to insert directly into the oxide layers which exist in A-La$_2$O$_3$. II-La$_2^{18}$O$_2$CO$_3$ consists, therefore, of alternating layers of (C$^{18}$O$_2$O)$^{2-}$ anions and (LaO)$_2^{2+}$ cations.

During the thermal decomposition of II-La$_2^{18}$O$_2$CO$_3$ to 750 °C in flowing helium, it was determined that carbon dioxide evolves only from the (CO$_3$)$^{2-}$ layers of the oxycarbonate and that all C-O bonds within the carbonate groups are equivalent.

During OCM, the C atoms in the catalyst are the carbon source of 46 % of the CO$_2$ produced. The remaining 54 % results from the deep oxidation of feed CH$_4$ and/or coupling products. No C atoms originating in the catalyst appear in either of the hydrocarbon products. Thus, C$_2$H$_6$ and C$_2$H$_4$ are produced from feed CH$_4$ alone.

The O atoms present in the (CO$_3$)$^{2-}$ layers of the catalyst also appear in products CO$_2$ and CO during OCM. It was calculated that $^{18}$O accounts for 48.5 % of all oxygen detected...
in carbon dioxide produced over II-La$_2^{18}$O$_2$CO$_3$. The same O atoms are also observed to exchange with O$_2$ in the feed. After a He/O$_2$ pulse was fed over II-La$_2^{18}$O$_2$CO$_3$, it was calculated that $^{18}$O accounts for 48.5% of all post-reactor gas phase oxygen.

Since the ratios of single-, double-, and non- $^{18}$O-substituted CO$_2$ (from a He/CH$_4$/O$_2$ feed) and O$_2$ (from a He/O$_2$ feed) were the same, carbon dioxide was determined to be produced on the catalyst rather than in the gas phase. The ratios suggest that the O and $^{18}$O available for substitution are equally plentiful. Since, the amount of O$_2$ in the feed stream is small relative to that in the catalysts (the ratio is approximately 1:700), it follows that the O and $^{18}$O available in the catalyst for substitution are equally plentiful.

Finally, oxygen present in the catalyst was found to be capable of activating methane. The amounts of coupling products detected following a He/CH$_4$ pulse were equivalent to approximately 2% of those observed following a He/CH$_4$/O$_2$ feed pulse.
1. INTRODUCTION

Previous work conducted in this laboratory tested the catalytic performance of several pure hydrated and carbonated lanthanum compounds for the oxidative coupling of methane (OCM) [1] and determined that the presence of an oxycarbonate phase significantly improved the selectivity to ethene over a working "lanthanum oxide" catalyst.

Other work [Paper I] co-fed CO₂ over both A-La₂O₃ and II-La₂O₂CO₃ starting materials in an attempt to encourage oxycarbonate formation on the former and to discourage its decomposition on the latter during OCM. The results indicated that co-feeding CO₂ depressed the catalytic performance of both starting materials. Degradation in the catalytic performance was found to be especially severe under reaction conditions at which pure II-La₂O₂CO₃ was believed to exist. It was concluded that optimal catalytic performance depended on the presence of both A-La₂O₃ and II-La₂O₂CO₃ phases. Furthermore, it was concluded that gas phase CO₂ acted (i) as a catalyst modifier by decreasing the catalyst's ability to activate methane and (ii) as a homogeneous reaction (gas phase) modifier by inhibiting the oxidative dehydrogenation of ethane to ethene.

A more recent study conducted in our laboratory [Paper II] probed further the role of CO₂ as a catalyst modifier by investigating the affinity for gas phase CO₂ of both II-La₂O₂CO₃ and A-La₂O₃ at typical OCM reaction temperatures. The study revealed that CO₂ uptake by both materials at temperatures between 700 and 800 °C was not restricted to the surface and probably proceeded by the incorporation of CO₂ between the (LaO)₂⁺ layers.
present in both materials. Secondly, II-La$_2$O$_5$CO$_3$ was found to take up significantly more
CO$_2$ than A-La$_2$O$_3$ at these temperatures, probably because of its more open structure along
the e axis of the unit cell (i.e. perpendicular to the (LaO)$_2$$^{2+}$ planes). Finally, as II-La$_2$O$_5$CO$_3$
thermally decomposed to A-La$_2$O$_3$ between 550 and 750 °C, it displayed a higher
susceptibility to CO$_2$ uptake than pure A-La$_2$O$_3$, subjected to the same heating profile.

It was proposed that the superior catalytic performance of the A-La$_2$O$_3$ material
resulting from the thermal decomposition of II-La$_2$O$_5$CO$_3$ relative to a pure A-La$_2$O$_3$ starting
material was due to the higher basicity of the former caused by the trace presence of
carbonate groups.

Our previous work, therefore, has revealed the importance of a partial presence of the
oxycarbonate phase for improving the catalytic performance of "lanthanum oxide" catalysts
relative to pure A-La$_2$O$_3$ and II-La$_2$O$_5$CO$_3$ materials. As discussed previously [Paper II],
both A-La$_2$O$_3$ and II-La$_2$O$_5$CO$_3$ contain layers of (LaO)$_2$$^{2+}$ cations. The two materials differ
from one another by the groups occupying the space between these layers. The sesquioxide
has layers of O$^{2-}$ anions between the (LaO)$_2$$^{2+}$ layers whereas the oxycarbonate has layers of
(CO$_3$)$_2$$^{2-}$ anions. The intent of this work is to investigate the role played by the oxycarbonate
phase under OCM conditions, by following the fate of the C and O atoms incorporated into
the (CO$_3$)$_2$$^{2-}$ groups during the preparation of II-La$_2$O$_5$CO$_3$ from A-La$_2$O$_3$. Isotopic labeling of
these C and O atoms enables such tracking to be done.

Although several studies have employed isotopic labeling techniques to investigate
different aspects of the OCM process over La$_2$O$_3$ materials [2-4], none have studied the
formation of an oxycarbonate phase on the working catalyst\textsuperscript{1}.

\textsuperscript{1} Despite the fact that its importance in enhancing the catalytic performance of $\text{La}_2\text{O}_3$ has been recognized [2-3, 5-6].
2. EXPERIMENTAL PROCEDURE

2.1 Catalyst Characterization

From earlier work involving several characterization techniques [7], it was determined that Fourier transform infrared spectroscopy (FTIR) and laser Raman spectroscopy (LRS) could identify the bulk composition of the lanthanum compounds of interest in this work.

2.1.1 Fourier Transform Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Instruments 60SX spectrometer equipped with a water-cooled globar source and a mercury-cadmium-telluride (MCT) detector.

Samples were prepared in the form of pressed wafers thin enough to permit the transmittance of at least 25 % of the intensity of the incident infrared beam. Each wafer was prepared from approximately 0.15 g of a mixture composed of 1-2 wt. % of sample in potassium bromide, KBr (Fisher, IR grade). This mixture was ground in an agate mortar and pestle for two and a half minutes. It was then pressed between the faces of a hardened stainless steel die under a load of 9 tons (20000 lb) on a Model C-12 press (Fred S. Carver, Inc.). The resulting wafer was 20.6 mm in diameter and approximately 0.03 mm thick at the center. All spectra involved the accumulation of 512 scans at 1 wavenumber (WN) resolution and were ratioed to that of a 100 % KBr wafer collected under the same conditions.
2.1.2 Laser Raman Spectroscopy

Laser Raman spectra were obtained using a Spex Triplamate triple monochromator spectrometer. The primary excitation source was the 514.5 nm line of a Spectra-Physics argon ion laser, Model 164, operating at powers ranging from 20 to 200 mW at the source. The resolution of the resulting spectra was 5 WN. The spectrometer was calibrated over the range 80 to 850 WN using a powder sample of MoO₃. Catalyst samples were prepared by sealing approximately 0.01 g in a 0.8 mm inside diameter (i. d.), 90 mm long quartz capillary tube. Spectra were obtained in a single scan with the scan time dependent upon the intensity of the Raman scattering.

2.2 Catalyst Preparation

A-La₂O₃ and II-La₂O₂CO₃ catalysts were prepared according to techniques developed in earlier work [1]. Both used La₂O₃ (Aldrich Chemical Company, 99.99%) as the starting material. Since La₂O₃ is known to be sensitive to atmospheric hydration and carbonation, it had been stored in an argon-filled dry box since its initial purchase. However, although characterization by LRS indicated the sole presence of A-La₂O₃ (bands at 107, 194, and 410 WN), characterization by FTIR revealed bands at 3610 and 642 WN corresponding to the presence of some La(OH)₃ in the Aldrich material.

A heat treatment was performed in order to regenerate a bulk supply of pure A-La₂O₃. This was done by placing approximately 5 g of La₂O₃ (from the dry box) in a quartz boat inside a quartz tube in a tube furnace (Lindberg, Model 54232, with Lindberg Console, Model 59544, and Eurotherm Controller, Model 211). An inert gas, in this case oxygen-free
nitrogen (Matheson, <5 ppm O₂), was passed through the tube at a flow rate of 100 standard cubic centimeters per minute (sccm). The sample was heated to 900 °C at 10 °C/min and maintained at 900 °C for 12 hours. The furnace was then switched off and allowed to cool over a period of several hours to room temperature. A-La₂O₃ was removed from the quartz boat and samples were taken for analysis by FTIR and LRS. The remainder was placed in a vial under a helium atmosphere and stored in a dessicator.

2.2.1 Preparation of A-La₂O₃ and A-La₂¹⁸O₃

Although A-La₂O₃ prepared in the tube furnace was pure (as indicated by FTIR and LRS characterizations), it was found that a small but finite degree of contamination occurred in the time it took to load the sample in the reactor. It was therefore necessary to regenerate pure A-La₂O₃ in situ for subsequent use. This was done by loading 0.050 g of A-La₂O₃ (prepared in the tube furnace) on top of a small plug of quartz wool in the quartz reactor (described in the next subsection). With both reactor inlet and outlet valves (valves V₁ and V₂, respectively) fully open, the sample was then heated to 900 °C at 10 °C/min in a 100 sccm flow of helium (Matheson, Zero grade). During the heating process, the reactor effluent was fed directly to the Porapak Q column of the gas chromatograph (Varian, Model 3600) in order to observe eluting species. Since the catalyst was prepared in situ in an amount required for subsequent testing, characterization of each batch of starting catalyst could not be performed. However, the FTIR and LRS spectra of a representative sample of A-La₂O₃ prepared by the above technique reproduced those of the pure A-La₂O₃ sample prepared in the tube furnace.
A-La$_2^{18}$O$_3$ was prepared using a syringe-injection technique. After pure A-La$_2$O$_3$ had been regenerated in situ and the reactor had cooled to room temperature, a septum was placed on the downstream side of V$_o$ and the reactor was sealed by closing V$_i$. The helium carrier gas line at the inlet to V$_i$ was exchanged for a vacuum line connected to a roughing pump (Sargent-Welch, Model 1004). After the line had been evacuated to a base pressure of approximately $10^{-4}$ Torr, V$_i$ was opened slowly and the reactor was evacuated for 30 minutes. V$_i$ was then closed and 12 cm$^3$ of $^{18}$O$_2$ (MSD Isotopes, 99.8 atom % $^{18}$O) was injected through the septum on V$_o$ into the reactor. V$_o$ was then closed and the $^{18}$O$_2$ was allowed to exchange with the catalyst while the reactor was heated to 900 °C at 10 °C/min. Characterization of the resulting labeled material was performed by FTIR and LRS.

2.2.2 Preparation of II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$

Since A-La$_2$O$_3$ served as the starting material for the preparation of II-La$_2$O$_2$CO$_3$, the latter was also prepared in situ. In this case, 0.044 g of A-La$_2$O$_3$ (prepared in the tube furnace) was loaded in the reactor and heated to 900 °C at 10 °C/min in a 100 scm flow of helium (Matheson, Zero grade). This served to regenerate pure A-La$_2$O$_3$.

All three oxycarbonate materials (i.e., $^{18}$O-, $^{13}$C-, and un-labeled) were prepared using the same technique as that developed for the preparation of A-La$_2^{18}$O$_3$. However, in these runs, 12 cm$^3$ injections of C$^{18}$O$_2$ (MSD Isotopes, 97 atom % $^{18}$O), $^{13}$CO$_2$ (MSD Isotopes, 99.2 atom % $^{13}$C), and CO$_2$ (Air Products, 99.7 %), respectively, were used and the heating profile ramped the reactor from room temperature to 650 °C at 5 °C/min, from 650 to 700 °C at 2 °C/min, and maintained it at 700 °C for 30 minutes.
Given the initial starting mass of 0.044 g of A-La$_2$O$_3$, the stoichiometry of the reaction at completion yielded 0.050 g of (labeled or unlabeled) II-La$_2$O$_2$CO$_3$. As for A-La$_2$O$_3$, the oxycarbonate materials were prepared batchwise in situ in an amount required for subsequent testing. Therefore, characterization of each starting catalyst could not be performed. However, characterization by FTIR and LRS of a representative sample prepared using this technique gave spectra indicating the sole presence of (labeled or unlabeled) II-La$_2$O$_2$CO$_3$.

2.3 Reactor Studies

Reactor studies were undertaken using the system shown schematically in Figure 1. The gas feed system consisted of methane (Matheson, 99.99%), oxygen (Air Products, 99.6%), carbon dioxide (Air Products, 99.7%), and helium (Air Products, 99.997%) gas streams. Each gas line included a molecular sieve/Drierite$^\text{TM}$ water trap, an Alltech Oxytrap$^\text{TM}$ (not on the oxygen line), and a Tylan mass flow controller (Model FC-260 or FC-280). Valco 10- and 4-port sampling valves allowed the reactants to be fed either in continuous or pulse flow modes. In continuous mode, a stream containing one, two or all three reactants could be fed continuously to the catalyst bed in a flow of carrier helium. In pulse mode, known volumes of the same stream could be pulsed into a pure helium stream fed continuously over the catalyst bed. It was also possible to pulse a methane and/or helium mixture and an oxygen and/or carbon dioxide and/or helium mixture alternately into the pure helium stream. The catalyst bed was supported on a plug of quartz wool in a quartz reactor, shown schematically in Figure 2. The reactor was made by fusing a 200 mm long, 8 mm outside diameter (o. d.), 6 mm i. d. quartz tube to a 195 mm long, 6 mm o. d., 1 mm i. d. quartz capillary.
Use of the narrow bore capillary significantly reduced gas-phase reactions that can occur downstream of the catalyst bed. The reactor was positioned vertically along the furnace axis. In earlier work [1], the temperature of the catalyst bed had been measured by an 18" long, 0.02" o. d., K-type thermocouple placed inside the reactor. However, in this work, the incorporation of valves $V_i$ and $V_o$ precluded this arrangement. Thus, the tip of the same thermocouple was positioned against the outside wall of the reactor next to the
Figure 2: Schematic of OCM Reactor
catalyst bed. Temperatures above and below the catalyst bed were measured at 750 °C and found to vary by no more than 2 °C at distances of 1" above or below the catalyst bed.

Product analysis was accomplished by gas chromatography (GC) in series with mass spectrometry (MS) as shown schematically in Figure 3. The Varian 3600 gas chromatograph was equipped with a thermal conductivity detector (TCD), a 7' long, $\frac{1}{8}$" o. d., 80/100 mesh Porapak Q column which separated H$_2$, O$_2$/CO, CH$_4$, CO$_2$, C$_2$H$_4$, C$_2$H$_6$, and C$_3$H$_8$ components, and a 6' long, $\frac{1}{8}$" o. d., 60/80 mesh molecular sieve 5A column which separated O$_2$, CO, and CH$_4$ components. Due to the extremely high pressure drop over the GC's Porapak Q and molecular sieve 5A columns in series, it was impossible to feed the reactor effluent directly through both columns without the pressure in the reactor approaching 80 psig. Consequently, component separation was performed on the Porapak Q column alone.

The TCD signal was fed to an analog-to-digital convertor (ADC) board installed in an Apex 386/25 personal computer. The signal was recorded and processed using Varian's GC Star software package.

After passing through the TCD, the product stream (now separated into the above components) was passed through a leak valve which directed approximately 6 % by volume of the product stream to the Atmospheric Pressure Sampling Module (APSM, supplied by UTI Instruments, Inc.). Most of the product stream flowing through the first of two orifices in the APSM was pumped to vent. The remainder passed through the second orifice and into the mass spectrometer chamber. The net effect of the APSM was to reduce the sampling pressure of the product stream from atmospheric to ultra high vacuum (UHV) without
Figure 3: Schematic of OCM Analytical System
component discrimination. A satisfactory mass spectrometer signal-to-noise (S/N) ratio was obtained by using a chamber pressure of $5.0 \times 10^7$ Torr and a pulse loop size of 250 µL.

The quadropole mass spectrometer (UTI 100C) was interfaced (UTI Spectralink) to a personal computer (Hewlet Packard Vectra ES/12) and controlled via a commercial software package (UTI Spectrasoft). The software enabled the fast tracking of up to twelve mass-to-charge (m/e) ratios as a function of time. In this work, m/e values of 16, 28, 29, 30, 31, 32, 34, 36, 44, 45, 46, and 48 were followed. Each m/e was monitored in turn for a period of 100 ms. A single cycle through all twelve m/e values took approximately 2 s.

The m/e values to be monitored were selected based on the known MS cracking patterns of the species eluting from the GC. The intensities of the largest fractions for each component are presented in Table 1 (expressed as a percentage of the main fraction). Because of the degree of overlap in the respective cracking patterns (e.g., CO, C$_2$H$_4$, and C$_2$H$_6$ all have m/e = 28 as their main fraction), deconvoluting the resulting MS trace would be very difficult if all components entered the MS chamber at the same time. By feeding the reactor exit stream through the GC first, the components in the stream were separated on the GC column and each component (with the exception of O$_2$ and CO which could not be separated on the Porapak Q column) appeared sequentially in the MS traces. This greatly simplified the interpretation of results.

With the experimental conditions used in this study, O$_2$ and CO were detected in the MS chamber approximately 35 s after the pulse valve had been switched; CH$_4$ appeared after approximately 46 s; CO$_2$ after 70 s; C$_2$H$_4$ after 97 s; and C$_2$H$_6$ after 132 s. The separating of
Table 1: Cracking patterns of the components present during OCM

<table>
<thead>
<tr>
<th>Component</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>25</th>
<th>26</th>
<th>27</th>
<th>28</th>
<th>29</th>
<th>30</th>
<th>32</th>
<th>44</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.1</td>
<td>7.4</td>
<td>15</td>
<td>83</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>6.3</td>
<td></td>
<td>13</td>
<td></td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>C₂H₄</td>
<td></td>
<td>8.1</td>
<td></td>
<td>12</td>
<td>6.1</td>
<td>59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>C₂H₆</td>
<td></td>
<td></td>
<td>5.7</td>
<td>24</td>
<td>33</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21</td>
<td></td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>

components upstream of the MS typically enabled the main fraction (with its higher S/N ratio) to be used as the unique identifier for each component. Thus, m/e = 28 was used to monitor CO, 32 for O₂, 16 for CH₄, 44 for CO₂, and 28 for both C₂H₄ and C₂H₆.

The matter was complicated somewhat by the use of isotopically labeled species. Thus, $^{13}$CO, $^{13}$CO₂, $^{13}$CH₄, $^{13}$CCH₄, $^{13}$C₂H₄, $^{13}$C₂H₆, and $^{13}$C₂H₈ would be expected to give main fractions at m/e = 29, 45, 17, 29, 30, 29, and 30, respectively. Similarly, $^{18}$O₂, $^{18}$O₃, C$^{18}$O, C$^{18}$OO and C$^{18}$O₂ would give main fractions at m/e = 34, 36, 30, 46, and 48, respectively.

2.3.1 Thermal Decomposition of II-La₂O₂CO₃, II-La₂$^{18}$O₂CO₃, and II-La₂O₂$^{13}$CO₃

Each starting catalyst (II-La₂O₂CO₃, II-La₂$^{18}$O₂CO₃, and II-La₂O₂$^{13}$CO₃) was heated in a 100 sccm flow of helium (Air Products, 99.997%) from room temperature to 750 °C at a rate of 10 °C/min. The helium effluent was fed directly to the GC/MS system and the isotopically
labeled species evolved from the catalysts were identified. This experiment served to
determine whether the oxygen atoms in the carbon dioxide evolved from II-La$_2^{18}$O$_2$CO$_3$
during its thermal decomposition were the same as those incorporated into the material
during its preparation from A-La$_2$O$_3$ and C$^{18}$O$_2$ or whether exchange with other (unlabeled)
lattice oxygens took place.

2.3.2 Pulse Studies over II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$

After heating to 750 °C, the temperature of the reactor was held steady for at least two
hours to allow any thermal decomposition of the starting materials to reach completion. Then
a series of ten 250 μL He/CH/O$_2$ (80:18:2) pulses were fed to the catalysts and the products
detected by GC/MS as described above. The main objective of this experiment was to
determine if the carbon and/or oxygen atoms incorporated into the oxycarbonate during its
preparation from A-La$_2$O$_3$ and carbon dioxide appeared in any of the components in the
reactor exit stream. The m/e traces of particular interest here, therefore, would be 28, 29, and
30 corresponding to CO, $^{13}$CO, and $^{18}$O, respectively; 44, 45, 46, and 48 corresponding to
CO$_2$, $^{13}$CO$_2$, $^{18}$OO, and $^{18}$O$_2$, respectively; 28, 29, and 30 corresponding to C$_2$H$_4$, $^{13}$CCH$_4$,
and $^{13}$C$_2$H$_4$, respectively; and 30, 31, and 32$^2$ corresponding to C$_2$H$_6$, $^{13}$CCH$_6$, and $^{13}$C$_2$H$_6$,
respectively. It should be remembered that $^{13}$C- and $^{18}$O-substituted components (e.g.,
$^{13}$C$^{18}$O) are not possible with the experimental procedure being followed in this work.

$^2$ Note that, although the main fraction of C$_2$H$_6$ is at m/e = 28, detecting single- and
double-$^{13}$C substituted species at m/e = 29 and 30 would not be wise since, unlabeled C$_2$H$_6$
displays peaks with these m/e values.
To determine if oxygen in the feed stream was able to exchange with the oxygen atoms present in the oxycarbonate materials, a series of ten 250 µL He/O₂ (98:2) pulses were fed to each catalyst and the exit stream analyzed by GC/MS as above. The m/e traces of interest in this case are 32, 34, and 36 corresponding to O₂, ¹⁸OO, and ¹⁸O₂, respectively, which would be produced over II-La₂¹⁸O₂CO₃.

Finally, to test whether or not the catalysts are able to utilize their own oxygen content to activate methane, a series of ten 250 µL He/CH₄ (82:18) pulses were fed to each catalyst, the products again being analyzed by GC/MS. The m/e traces of interest here are 32, 34, and 36 corresponding to O₂, ¹⁸OO, and ¹⁸O₂, respectively; 28 and 30 corresponding to CO and C¹⁸O, respectively; and 44, 46, and 48 corresponding to CO₂, C¹⁸OO, and C¹⁸O₂, respectively which would be produced over II-La₂¹⁸O₂CO₃.

Since no trends in peak heights were observed with increasing pulse number in any of these experiments, the results presented in the following section present the MS signal intensity versus time traces of representative pulses for each component.

Finally, after the above experiments were performed on each catalyst, the sample was removed from the reactor and taken for immediate analysis by FTIR and LRS.
3. EXPERIMENTAL RESULTS

3.1 Preparation of $^{18}$O- and $^{13}$C-Labeled and Unlabeled Catalysts

With the exception of A-La$_2$O$_3$ (which was prepared in a flowing helium environment), all the materials studied in this work were prepared using the syringe-injection method described in the previous section. The FTIR and LRS spectra presented here are of representative samples prepared using these methods.

3.1.1 Preparation of A-La$_2$O$_3$ and A-La$_2^{18}$O$_3$

As shown in Figure 4, the FTIR spectrum of A-La$_2$O$_3$ shows no adsorption bands in the 400 to 4000 WN range consistent with that reported in earlier work [7]. The same holds true for A-La$_2^{18}$O$_3$. In contrast, the FTIR spectrum of the 99.99 % La$_2$O$_3$ material supplied by Aldrich (also presented in Figure 4) shows two bands, at 642 and 3610 WN, corresponding to the presence of La(OH)$_3$. Two weaker bands at 757 and 847 WN could not be identified although they had also been detected in our earlier work [7].

The LRS spectra of A-La$_2$O$_3$ and La$_2$O$_3$ (Aldrich) shown in Figure 5 both indicate the sole presence of A-La$_2$O$_3$ with its three characteristic bands at 107, 194, and 410 WN. In the case of A-La$_2^{18}$O$_3$, however, a large 15 WN downward shift is observed in the band at 410 WN.

It has been reported that the three oxygen atoms in the unit cell of the sesquioxide occupy two different oxygen sites, referred to as O(I) and O(II) [8]. The single oxygen atom
Figure 4: FTIR spectra of La$_2$O$_3$ (supplied by Aldrich), A-La$_2$O$_3$, and A-La$_2^{18}$O$_3$
Figure 5: LRS spectra of La$_2$O$_3$ (supplied by Aldrich), A-La$_2$O$_3$, and A-La$_2^{18}$O$_3$
in the O(I) site is octahedrally surrounded by six lanthanum atoms. The two oxygens occupying the O(II) site are surrounded by lanthanum atoms at the corners of a distorted tetrahedron. Only the vibrational modes of the O(II) site are Raman active and neither those of O(I) nor those of O(II) are ir-active [8]. Of the four vibrational modes of the O(II) site which are known to be Raman active, two are responsible for the 410 WN band. This band is associated with a stretching vibration of the La-O(II) bonds, while the 107 and 194 WN bands are both associated with bending modes of the same bonds [9]. The observed shift in the band at 410 WN in the LRS spectrum of A-La\textsuperscript{18}O\textsubscript{3} seems therefore to be related to a decrease in the frequency of the La-O(II) stretching vibration. This may be expected due to the increased mass of the \textsuperscript{18}O atom relative to the \textsuperscript{16}O atom. Thus, the evidence suggests that \textsuperscript{18}O occupies the O(II) site, but it is not possible to say if it also occupies the O(I) site.

3.1.2 Preparation of II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}, II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3}, and II-La\textsubscript{2}O\textsubscript{2}\textsuperscript{13}CO\textsubscript{3}

The FTIR spectra of II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}, II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3}, and II-La\textsubscript{2}O\textsubscript{2}\textsuperscript{13}CO\textsubscript{3} materials are shown in Figure 6. That of II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} fully agrees with the results of our previous work [7] and clearly exhibits the characteristic vibrational modes at 746, 856, 1087, 1464 and 1501 WN [10].

The FTIR spectrum of II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3} differs significantly from that of the unlabeled oxycarbonate as follows:

\[ \text{O(I) site corresponds to the oxygen atoms in the oxide layers; the O(II) site corresponds to the oxygen atoms in the (LaO)\textsuperscript{2+} layers of A-La\textsubscript{2}O\textsubscript{3}, as described in Paper II of this dissertation.} \]
Figure 6: FTIR spectra of II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$. 
• The major bands at 484, 856, 1464, and 1501 WN are shifted between 8 and 13 WN lower.

• The bands at 746 and 1087 WN degenerate into a series of four bands with a spacing of approximately 10 WN.

• Bands at 1751 and 1834 WN are replaced by two series of four bands with spacings of 32, 9, and 23 WN between the bands in each series.

Differences in the FTIR spectrum of II-La$_2$O$_2^{13}$CO$_3$ relative to the unlabeled oxycarbonate may be summarized as follows:

• Major bands at 856, 1464 and 1501 WN are shifted 27, 41 and 35 WN lower, respectively.

• The bands at 746 and 1087 WN undergo splitting to give less intense bands at 735 and 1067 WN.

• Bands at 1751 and 1834 WN are replaced by a series of eight bands with no discernible regularity in interband spacings.

Figure 7 shows the LRS spectra of the same three materials. That of II-La$_2$O$_2$CO$_3$ is in complete agreement with the results of our previous work [7] and shows characteristic bands at 86, 115, 129, 208, 260, 367, 398, and 748 WN. The 260, 367, and 398 WN bands in the LRS spectrum of II-La$_2^{18}$O$_2$CO$_3$ are shifted 9, 14, and 13 WN lower, respectively and the band at 748 WN degenerates into a series of four bands spaced approximately 10 WN apart.
Figure 7: LRS spectra of II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$
No significant shifts in band positions nor degeneracy are observed in the LRS spectrum of II-La$_2$O$_2^{13}$CO$_3$.

For the oxycarbonate, the assignment of each Raman and ir band to particular bonds in the crystal structure has not been previously reported. In fact, with the exception of our earlier work [7], no LRS spectrum of II-La$_2$O$_2$CO$_3$ has been published before. However, it is known that the very strong bands at 746, 856, 1087, 1464, and 1501 WN in the FTIR spectrum are all related to the carbonate groups positioned between the (LaO)$_2^{2+}$ layers [10]. Since these bands all correspond to various C-O vibrations, it is no surprise that all five are affected similarly in both the $^{18}$O- and $^{13}$C-labeled materials. For example, the bands at 856, 1464, and 1501 WN are shifted downwards in both II-La$_2^{18}$O$_2$CO$_3$ and II-La$_2$O$_2^{13}$CO$_3$. Those at 746 and 1087 WN degenerate to give a series of four lower intensity bands in II-La$_2^{18}$O$_2$CO$_3$, whereas the same two bands split in II-La$_2O_2^{13}$CO$_3$ to give a small shoulder band. Since the planar carbonate group is reported to exist in only one orientation in II-La$_2$O$_2$CO$_3$ [10], it is likely that all three C-O bonds in the carbonate group are equivalent.

It has not been reported which, if any, bands in the FTIR spectrum are associated with the La-O bonds of the (LaO)$_2^{2+}$ layers. Since the same layers are known to be present in A-La$_2$O$_3$, and since this material displays no bands in the 400 to 4000 WN range of its FTIR spectrum, it is likely that the La-O bonds in the (LaO)$_2^{2+}$ layers of II-La$_2$O$_2$CO$_3$ will also be ir-inactive.

As stated above, no previous work has assigned the Raman bands of II-La$_2$O$_2$CO$_3$ to particular bonds of the crystal lattice. In this work, no differences were observed between the
LRS spectra of II-La$_2$O$_2^{13}$CO$_3$ and II-La$_2$O$_2$CO$_3$. However, that of II-La$_2^{18}$O$_2$CO$_3$ indicated shifts in the bands at 260, 367, and 398 WN and degeneracy of the band at 748 WN. These bands may therefore correspond to La-O bonds rather than C-O bonds. No other information can be interpreted from this spectrum.

3.2 Thermal Decomposition of II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$

The GC chromatograms resulting when each starting material was heated from room temperature to $750^\circ$C at $10^\circ$C/min in flowing helium are presented in Figure 8. All three materials exhibit a two-step decomposition, the first step centered at approximately $670^\circ$C. All three starting materials ceased decomposing after less than two hours at the upper temperature.

When the reactor exit stream was analyzed by MS, it was seen that carbon dioxide was the only species evolved from each starting material. However, comparing the relative intensities of mass fractions of the carbon dioxide evolved from II-La$_2^{18}$O$_2$CO$_3$ (m/e = 44, 46, and 48) to those of C$^{18}$O$_2$ used in its preparation (Figure 9), we see that a significant degree of oxygen exchange had occurred in the bulk of the material under these conditions. This exchange resulted in the evolution of CO$_2$ and C$^{18}$OO, in addition to C$^{18}$O$_2$.

Deconvoluting the three forms of carbon dioxide revealed the ratios of CO$_2$, C$^{18}$OO, and C$^{18}$O$_2$ to be 13 : 41 : 46 and that $^{18}$O accounted for approximately 67% of the total oxygen content in the evolved CO$_2$. 
Figure 8: Thermal decompositions of II-La$_2$O$_2^{13}$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$ to 750°C
Figure 9: Relative intensities of m/e = 44, 46, and 48 in C^{18}O_{2} (97 atom %^{18}O_{2}) and C^{18}O_{2} evolved during the thermal decomposition of II-La_{2}^{18}O_{2}CO_{3} to 750°C
3.3 Pulsing He/CH₄/O₂ over II-La₂O₂CO₃, II-La₂¹⁸O₂CO₃, and II-La₂O₂¹³CO₃

As stated earlier, the Porapak Q column was able to separate O₂/CO, CH₄, CO₂, C₂H₆, and C₂H₄. Since O₂ was not separated from CO, it proved impossible to calculate oxygen conversions and product selectivities with this experimental setup. However, it was possible to calculate methane conversions and doing so revealed all three catalysts to give the same value of 16.8%. This compared well with the value of 17% calculated for II-La₂O₂CO₃ operating in the continuous mode [Paper I] at 850 °C.

Furthermore, the relative ratios of the GC area counts (with that of CO₂ = 1) for all the products detected on the Porapak Q column were calculated and compared with those calculated for II-La₂O₂CO₃ operating in the continuous mode at various reaction temperatures (Table 2). The results confirm that the catalysts operating in the pulse mode at 750 °C give similar performance to II-La₂O₂CO₃ operating in the continuous mode at 850 °C with the exception that less C₂H₆ is produced.

3.3.1 Isotopic Composition of CO₂ in the Reactor Exit Stream

As discussed in the experimental procedure section above, the m/e traces of particular interest in determining the isotopic composition of the carbon dioxide in the reactor effluent are 44, 45, 46, and 48 corresponding to CO₂, ¹³CO₂, C¹⁸O₂O, and C¹⁸O₂, respectively.

The m/e = 45 traces for each starting catalyst are presented in Figure 10. Since the cracking pattern of unlabeled CO₂ (Table 1) contains a minor fraction at this m/e value, a small peak is expected around an elapsed time of 70 s for all three starting catalysts.

---

¹ i.e., the time at which product CO₂ eluting from the GC is detected in the MS chamber.
Table 2: Relative amounts of products detected by GC for II-La$_2$O$_2$CO$_3$ operating in continuous mode and II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$ operating in pulse mode.

<table>
<thead>
<tr>
<th>Starting Catalyst</th>
<th>Reaction Temperature</th>
<th>O$_2$/CO</th>
<th>CH$_4$</th>
<th>CO$_2$</th>
<th>C$_2$H$_4$</th>
<th>C$_2$H$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous mode:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-La$_2$O$_2$CO$_3$</td>
<td>700 °C</td>
<td>5.8</td>
<td>65.4</td>
<td>1</td>
<td>0.6</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>750 °C</td>
<td>2.7</td>
<td>42.5</td>
<td>1</td>
<td>1.2</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>800 °C</td>
<td>1.3</td>
<td>31.6</td>
<td>1</td>
<td>1.5</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>850 °C</td>
<td>1</td>
<td>27.1</td>
<td>1</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Pulse Mode:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-La$_2$O$_2$CO$_3$</td>
<td>750 °C</td>
<td>0.7</td>
<td>30.8</td>
<td>1</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>II-La$_2^{18}$O$_2$CO$_3$</td>
<td>750 °C</td>
<td>0.7</td>
<td>29.5</td>
<td>1</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>II-La$_2$O$_2^{13}$CO$_3$</td>
<td>750 °C</td>
<td>0.6</td>
<td>28.3</td>
<td>1</td>
<td>0.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Figure 10: Selected peak monitoring (m/e = 45); He/CH₄/O₂ pulse over II-La₂O₂CO₃, II-La₂¹⁸O₂CO₃, and II-La₂O₂¹³CO₃, at 750°C
However, the trace for II-La\textsubscript{2}O\textsubscript{2}\textsuperscript{13}CO\textsubscript{3} showed a disproportionately large peak, indicating that its \textsuperscript{13}C atoms incorporated into product CO\textsubscript{2}. It should be noted here that the second "peak" appearing around 130 s is caused by a switch in the Amps decade on the MS as the signal intensity falls from the 10\textsuperscript{-10} Amp range to the more sensitive 10\textsuperscript{-11} Amp range.

Integrating the area under the carbon dioxide peaks in the m/e = 45 trace for II-La\textsubscript{2}O\textsubscript{2}\textsuperscript{13}CO\textsubscript{3} (using Jandel Scientific's PeakFit 3.0 software) and comparing it with the area under the corresponding m/e = 44 trace (corresponding to unlabeled CO\textsubscript{2}) revealed that approximately 46 % of the carbon dioxide detected was \textsuperscript{13}CO\textsubscript{2} and the remaining 54 % unlabeled CO\textsubscript{2} (i.e., resulting from the deep oxidation of co-fed methane).

Figure 11 shows the m/e = 48 traces for all three starting catalysts. The large peak in the trace for II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3} indicates that its \textsuperscript{18}O atoms incorporated into product carbon dioxide. Again, the switching of the Amps decade resulted in a small peak in the m/e = 48 trace for II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3}, in this case at an elapsed time of around 150 s. Similarly, the m/e = 46 traces shown in Figure 12 reveal the presence of C\textsuperscript{18}OO (i.e. with the exchange of just one \textsuperscript{18}O atom) over II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3}.

In Figure 13, the traces for m/e = 44, 46, and 48 are shown for II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} and II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3} in order to emphasize the different distributions of CO\textsubscript{2}, C\textsuperscript{18}OO, and C\textsuperscript{18}O\textsubscript{2} produced over each catalyst. Integrating the areas under each trace and deconvoluting, we find that carbon dioxide produced over II-La\textsubscript{2}\textsuperscript{18}O\textsubscript{2}CO\textsubscript{3} consists of CO\textsubscript{2}, C\textsuperscript{18}OO, and C\textsuperscript{18}O\textsubscript{2} in
Figure 11: Selected peak monitoring (m/e = 48); He/CH\textsubscript{4}/O\textsubscript{2} pulse over II-La\textsubscript{2}O\textsubscript{2}CO\textsubscript{3}, II-La\textsubscript{2}O\textsubscript{2}^{18}O\textsubscript{2}CO\textsubscript{3}, and II-La\textsubscript{2}O\textsubscript{2}^{13}CO\textsubscript{3}, at 750°C
Figure 12: Selected peak monitoring (m/e = 46); He/CH$_4$/O$_2$ pulse over II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$, at 750°C.
Figure 13: Selected peaks monitoring (m/e = 44, 46, and 48); He/CH₄/O₂ pulse over II-La₂O₂CO₃ and II-La₂¹⁸O₂CO₃ at 750°C
the ratios 29 : 45 : 26 and that $^{18}$O accounts for almost 50% of all oxygen detected in product carbon dioxide (Table 3).

### 3.3.2 Isotopic Composition of CO in the Reactor Exit Stream

The m/e values of interest in determining the isotopic composition of the carbon monoxide in the reactor effluent are 28, 29, and 30 corresponding to CO, $^{13}$CO, and $^{18}$O, respectively. Unfortunately, the areas under the m/e = 28 traces could not be integrated accurately due to experimental difficulties. It proved impossible, therefore, to calculate the relative amounts of CO, $^{13}$CO, and $^{18}$O produced over each catalyst.

However, the data could still be evaluated qualitatively by considering the m/e = 29 and 30 traces. As shown in Figure 14, the m/e = 29 trace for II-La$_2$O$_2$$^{13}$CO$_3$ reveals a disproportionately large peak corresponding to the presence of $^{13}$C in product CO. A second (broad) peak appears in the same trace at an elapsed time of around 65 s, probably corresponding to a minor fraction of $^{13}$C-labeled CO$_2$. It should also be noted from this figure that all three starting catalysts exhibit a large peak corresponding to the elution of C$_2$H$_6$ and a smaller peak corresponding to the elution of C$_2$H$_4$. This reinforces the benefit of employing the GC/MS technique since the use of MS alone would result in the overlap of all three peaks, precluding their deconvolution.

---

5 The background level (of approximately 8.8 x $10^{-9}$ Amps) was high relative to the CO peak maxima and occurred close to the upper range of the $10^{-9}$ Amp decade of the mass spectrometer. As a consequence, when the CO peak began to be detected by the mass spectrometer, the detector switched to the next highest decade. This caused a shift in the signal intensity which, because the quantity of CO was so small, masked the CO peak.
Table 3: Relative amounts of CO₂, C¹⁸O₂O, and C¹⁸O₂ produced by II-La₂O₂CO₃ and II-La₂¹⁸O₂CO₃ during a 250μL He/CH₄/O₂ (80:18:2) pulse at 750 °C.

<table>
<thead>
<tr>
<th>Starting Catalyst</th>
<th>m / e</th>
<th>Area {Amps.seconds}</th>
<th>Area {% of total}</th>
<th>^1₈O Content {% of total O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-La₂O₂CO₃</td>
<td>44</td>
<td>1.29 x 10⁻⁷</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sum:</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>II-La₂¹⁸O₂CO₃</td>
<td>44</td>
<td>3.31 x 10⁻⁸</td>
<td>27.6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>46</td>
<td>6.02 x 10⁻⁸</td>
<td>50.3</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>2.65 x 10⁻⁸</td>
<td>22.1</td>
<td>26.5</td>
</tr>
<tr>
<td>Sum:</td>
<td></td>
<td></td>
<td></td>
<td>48.9</td>
</tr>
</tbody>
</table>
Figure 14: Selected peak monitoring (m/e = 29); He/CH$_4$/O$_2$ pulse over II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$, at 750°C
The m/e = 30 traces, presented in Figure 15 show that $^{18}$O from II-La$_2^{18}$O$_2$CO$_3$ is also incorporated into product carbon monoxide. A second peak appears in the same trace at an elapsed time of approximately 65 s, corresponding to a minor fraction of $^{18}$O-labeled CO$_2$.

Again, major peaks are observed over all three starting materials corresponding to the elution of product C$_2$H$_6$.

3.3.3 Isotopic Composition of O$_2$ in the Reactor Exit Stream

The m/e values of interest in this case are 32, 34, and 36 corresponding to O$_2$, $^{18}$OO, and $^{18}$O$_2$, respectively. As shown in Figure 16, the m/e = 34 trace for the three starting materials indicated that the unconsumed portion of the oxygen feed contains oxygen originating from the catalyst. The apparently high noise level in these traces is due to the very low signal intensities (note the $10^{-11}$ Amps scale). Thus, it appears that the O$_2$ feed component undergoes exchange with the oxygen present in the catalyst. This is confirmed in the m/e = 36 traces presented in Figure 17 which shows an (extremely small) amount of $^{18}$O$_2$ in the unreacted oxygen. By integrating the areas under the m/e = 32, 34, and 36 traces for II-La$_2$O$_2$CO$_3$ and II-La$_2^{18}$O$_2$CO$_3$ and deconvoluting, we find that the unreacted oxygen consists of O$_2$, $^{18}$OO, and $^{18}$O$_2$ in the ratios 84 : 13 : 4 and, therefore, that $^{18}$O accounts for approximately 10 % of all unconsumed oxygen (Table 4).

3.3.4 Isotopic Composition of C$_2$H$_4$ in the Reactor Exit Stream

Of interest in this experiment are peaks detected in the traces with m/e = 28, 29, and 30 corresponding to C$_2$H$_4$, $^{13}$CH$_4$, and $^{13}$C$_2$H$_4$. If $^{13}$C originating in the catalyst incorporated into product ethene, a disproportionately large peak would be expected in the m/e = 29 and
Figure 15: Selected peak monitoring (m/e = 30); He/CH₄/O₂ pulse over II-La₂O₂CO₃, II-La₂¹⁸O₂CO₃, and II-La₂O₂¹³CO₃, at 750°C
Figure 16: Selected peak monitoring (m/e = 34); He/CH₄/O₂ pulse over II-La₂O₂CO₃, II-La₂¹⁸O₂CO₃, and II-La₂O₂¹³CO₃, at 750°C
Figure 17: Selected peak monitoring (m/e = 36); He/CH4/O pulse over II-La2O2CO3, II-La218O2CO3, and II-La2O213CO3, at 750°C
Table 4: Relative amounts of $O_2$, $^{18}O_O$, and $^{18}O_2$ detected over II-La$_2$O$_2$CO$_3$ and II-La$_2^{18}O_2$CO$_3$ during a 250μL He/CH$_4$/O$_2$ (80:18:2) pulse at 750°C.

<table>
<thead>
<tr>
<th>Starting Catalyst</th>
<th>m / e</th>
<th>Area [Amps.seconds]</th>
<th>Area [% of total]</th>
<th>$^{18}O$ Content [% of total O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-La$_2$O$_2$CO$_3$</td>
<td>32</td>
<td>$8.47 \times 10^{-9}$</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sum:</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>II-La$_2^{18}O_2$CO$_3$</td>
<td>32</td>
<td>$6.80 \times 10^{-9}$</td>
<td>83.6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>$1.04 \times 10^{-9}$</td>
<td>12.7</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>$3.00 \times 10^{-10}$</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Sum:</td>
<td></td>
<td></td>
<td></td>
<td>10.1</td>
</tr>
</tbody>
</table>
30 traces of $^{13}$CO$_3$ at an elapsed time of around 97 s. As shown in Figures 14 and 15, however, no such peaks were observed, implying the improbability of this proposal.

### 3.3.5 Isotopic Composition of C$_2$H$_6$ in the Reactor Exit Stream

Although the main fraction of the C$_2$H$_6$ cracking pattern is at m/e = 28 (Table 1), there is little value in looking for evidence of $^{13}$C incorporation by considering the m/e = 29 and 30 traces since even unlabeled C$_2$H$_6$ displays significant peaks with these m/e values. However, if such incorporation does occur, then a disproportionately large peak would be expected in the m/e = 31 trace of II-La$_2$O$_2^{13}$CO$_3$ at an elapsed time of around 132 s. These traces are presented in Figure 18 and indicate an equal (trace) presence of C$_2$H$_6$ for all three catalysts. It is therefore concluded that no C originating in the catalyst incorporates into product C$_2$H$_6$. This confirms the widely-held belief that C$_2$H$_6$ results from the direct coupling of two methyl radicals, each created by the single abstraction of a hydrogen atom from a methane molecule.

### 3.4 Pulsing He/O$_2$ over II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$

Analysis of the post-reactor effluent by GC revealed no species other than oxygen. It is therefore concluded that no long-term adsorption of CH$_4$ occurs on the working catalysts since this would be expected to result in the production of typical OCM products (C$_2$ hydrocarbons and carbon oxides). This conclusion has been independently reached in other studies which followed the CH$_4$ MS trace following a switch between labeled and unlabeled CH$_4$ in an OCM reactant feed stream doped with nonadsorbing Ar [3-4, 11]. The CH$_4$ trace in all cases showed no delay relative to that of Ar, indicating no adsorption on the catalyst.
Figure 18: Selected peak monitoring (m/e = 31); He/CH₄/O₂ pulse over II-La₂O₂CO₃, II-La₂¹⁸O₂CO₃, and II-La₂O₂¹³CO₃, at 750°C
Of more interest in this work, however, is the degree of oxygen exchange between feed
O₂ and oxygen in the catalysts observed by MS. Figure 19 shows the m/e = 32, 34, and 36
traces for II-La₂O₂CO₃ and II-La₂¹⁸O₂CO₃. The oxygen component of the effluent consisted
of O₂, ¹⁸O₂, and ¹⁸O₂ in the ratios 27 : 49 : 24. Therefore, ¹⁸O accounts for approximately
48 % of all post-reactor oxygen (Table 5). These values agree remarkably with those
calculated earlier for ¹⁸O incorporation into product carbon dioxide during a He/CH₄/O₂
pulse (presented in Table 3 above).

3.5 Pulsing He/CH₄ over II-La₂O₂CO₃, II-La₂¹⁸O₂CO₃, and II-La₂O₂¹³CO₃

Analysis by GC reveals trace amounts of O₂/CO, C₂H₄, and C₂H₆ (but no CO₂) when
pulses of He/CH₄ (82:18) are fed to each starting catalyst. Figure 20 shows an enlarged
chromatogram for a He/CH₄ pulse over II-La₂O₂CO₃. Although the quantities of the products
were too small to be detected by MS, integration of the areas under the GC peaks (using the
Varian GC Star software) gave an average of 80 area counts for the most abundant product,
C₂H₆. This corresponds to approximately 2 % of the amount of C₂H₆ generated by the
catalysts exposed to a He/CH₄/O₂ pulse. The amount of C₂H₄ produced was also found to
correspond to approximately 2 % of that resulting from a He/CH₄/O₂ pulse.

Since the single GC column used in these studies was incapable of separating O₂ and
CO₂, no conclusion can be drawn as to whether or not carbon monoxide is produced without
cold fed O₂. Certainly, no CO₂ is produced under these conditions.

Finally, although only ten pulses were fed to each catalyst, little deactivation of the
catalysts was observed.
Figure 19: Selected peaks monitoring (m/e = 32, 34, and 36); He/O₂ pulse over II-La₂O₂CO₃ and II-La₂¹⁸O₂CO₃ at 750°C
Table 5: Relative amounts of \( \text{O}_2 \), \( ^{18}\text{O}_2 \), and \( ^{16}\text{O}_2 \) detected over II-La\( _2\text{O}_2\text{CO}_3 \) and II-La\( _2^{18}\text{O}_2\text{CO}_3 \) during a 250\( \mu L \) He/O\( _2 \) (98:2) pulse at 750°C.

<table>
<thead>
<tr>
<th>Starting Catalyst</th>
<th>m / e</th>
<th>Area [Amps.seconds]</th>
<th>Area [% of total]</th>
<th>(^{18}\text{O} ) Content [% of total O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-La( _2\text{O}_2\text{CO}_3 )</td>
<td>32</td>
<td>3.95 x 10^{-7}</td>
<td>99.6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>1.57 x 10^{-9}</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Sum:</td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>II-La( _2^{18}\text{O}_2\text{CO}_3 )</td>
<td>32</td>
<td>1.14 x 10^{-7}</td>
<td>27.3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>2.05 x 10^{-7}</td>
<td>48.9</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>9.92 x 10^{-8}</td>
<td>23.7</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>Sum:</td>
<td></td>
<td>48.2</td>
<td></td>
</tr>
</tbody>
</table>
Figure 20: GC chromatogram resulting from a He/CH₄ pulse over 11-La₂O₃CO₃ at 750°C
3.6 Post-reaction Catalyst Characterization

All three post-reaction catalysts showed traces of II-\(\text{La}_2\text{O}_2\text{CO}_3\) in their FTIR spectra although the intensities of the bands are not large enough to reveal differences due to isotope content. The LRS spectra of II-\(\text{La}_2\text{O}_2\text{CO}_3\) and II--\(\text{La}_2\text{O}_2^{13}\text{CO}_3\) both indicate bands at 107, 194, and 410 WN corresponding to the presence of A-\(\text{La}_2\text{O}_3\). That of II--\(\text{La}_2^{18}\text{O}_2\text{CO}_3\) shows a downward shift in the 410 WN band to 399 WN indicating that the sesquioxide resulting from its partial decomposition still contains a significant \(^{18}\text{O}\) content.
4. DISCUSSION OF RESULTS

4.1 Preparation of $^{18}$O- and $^{13}$C-Labeled and Unlabeled Catalysts

$A$-$La_2^{18}$O$_3$, $II$-$La_2^{18}$O$_2$CO$_3$, and $II$-$La_2O_2^{13}$CO$_3$ prepared in this work showed significant differences in their FTIR and/or LRS spectra relative to those of the unlabeled materials. Clearly, the $^{13}$C atoms incorporated into $II$-$La_2O_2^{13}$CO$_3$ could occupy only one site. Assigning the $^{18}$O atoms taken up by $A$-$La_2^{18}$O$_3$ and $II$-$La_2^{18}$O$_2$CO$_3$ to any specific sites, however, proved to be difficult.

It appears that the oxygen atoms in $C^{18}$O$_2$ used to convert $A$-$La_2O_3$ to $II$-$La_2O_2^{18}$CO$_3$ occupy sites in the (CO$_3$)$^{2-}$ groups. For $A$-$La_2^{18}$O$_3$, it has been established that exchanged $^{18}$O occupies the $O$(II) site (i.e., in the (LaO)$_2^{2+}$ layers) but it is not known if these atoms also occupy the $O$(I) site.

4.2 Thermal Decomposition of $II$-$La_2O_2$CO$_3$, $II$-$La_2^{18}$O$_2$CO$_3$, and $II$-$La_2O_2^{13}$CO$_3$

That lanthanum oxycarbonate thermally decomposes in a two-step process has been observed in our recent work [Paper II]. Since both steps involve the evolution of CO$_2$, there must be at least two different types of carbonate bonding. Although it has been reported that the (CO$_3$)$^{2-}$ groups in $II$-$La_2O_2$CO$_3$ exist in only one orientation [10], it was proposed in our recent work that, during thermal decomposition, internal restructuring produced a second orientation, similar to that observed in $I$-$La_2O_2$CO$_3$ [10].
With regard to the isotopes detected in the carbon dioxide evolved from \( \text{II-La}_{2}^{18}\text{O}_{2}\text{CO}_{3} \), it is clear that unlabeled \( \text{CO}_2 \) and singly-substituted \( \text{C}^{18}\text{O} \) were evolved in addition to \( \text{C}^{18}\text{O}_2 \). Furthermore, it was calculated that \( ^{18}\text{O} \) accounted for 67% of the total oxygen content in the evolved \( \text{CO}_2 \). This is consistent with a mechanism in which (i) the \( \text{C}^{18}\text{O}_2 \) used to prepare the oxycarbonate from \( \text{A-La}_2\text{O}_3 \) inserted directly into the \( \text{O}^2^- \) layers to give layers of \( (\text{CO}^{18}\text{O})^2^- \) ions between the \( (\text{LaO})^2^+ \) layers of the oxycarbonate and (ii) the carbon dioxide evolved during thermal decomposition contained oxygen atoms coming only from the carbonate groups, and (iii) all three C-O bonds in these groups were equivalent. In such a scenario, one would expect the ratio of \( ^{18}\text{O} \) to O in the evolved carbon dioxide to be 2:1, in agreement with our observations.

### 4.3 Pulse Studies

The results of the pulse studies conducted in this work reveal that the C and O atoms of the \( \text{CO}_2 \) used to convert \( \text{A-La}_2\text{O}_3 \) to \( \text{II-La}_2\text{O}_2\text{CO}_3 \) appear in products \( \text{CO} \) and \( \text{CO}_2 \) when pulses of \( \text{He}/\text{CH}_4/\text{O}_2 \) (80:18:2) are fed to the oxycarbonate catalyst at 750 °C. The mechanism by which this happens, however, is not obvious.

Of the carbon appearing in product carbon dioxide, it was determined that around 54% came from deep oxidation of methane in the feed pulse and the other 46% came from oxidation of carbon present in the \( (\text{CO}_3)^2^- \) layers of the catalyst. Whether this same ratio applied to carbon appearing in product \( \text{CO} \) could not be determined due to experimental difficulties in integrating the area under the m/e = 28 trace.
Oxygen atoms may end up in the oxygenated products either (i) through exchange with O$_2$ in the feed pulse which then proceeds to react with CH$_4$ and C in the catalyst to give CO$_2$ and CO or (ii) through exchange with CO$_2$ and CO after they have been formed by O$_2$ in the feed pulse reacting with CH$_4$ and C in the catalyst. It is also conceivable that both of these mechanisms occur simultaneously. The proposition that O atoms in the catalyst exchange with O$_2$ in the feed pulse was confirmed by the runs feeding He/O$_2$ pulses to the catalysts.

Of further interest is the extent of single- and double-$^{18}$O substitution in product CO$_2$ (following a He/CH$_4$/O$_2$ pulse) and in gas phase O$_2$ (following a He/O$_2$ pulse). The results show that approximately 25% of the total amount of each species is double-$^{18}$O substituted (i.e., C$^{18}$O$_2$ or $^{18}$O$_2$), 50% is single-$^{18}$O substituted (i.e., C$^{18}$OO or $^{18}$OO), and the remaining 25% is unsubstituted. These distributions are what would be expected if the probability of incorporating $^{18}$O and unlabeled O were identical.

It should be recalled that the carbon dioxide evolved from II-La$_2^{18}$O$_2$CO$_3$ during its thermal decomposition contained two $^{18}$O atoms for every one O atom, reflecting the isotopic composition of the carbonate groups in the oxycarbonate. However, since the amount of $^{18}$O remaining after the catalyst has finished thermally decomposing is unknown, no argument can be made for relating the $^{18}$O : O ratio in the partially decomposed catalyst to that in product carbon dioxide (after a He/CH$_4$/O$_2$ pulse) and in gas phase oxygen (after a He/O$_2$ pulse). Interestingly, the same proportions of single- and double-$^{18}$O substituted carbon dioxide products were observed following an O$_2$ to $^{18}$O$_2$ switch made under OCM conditions.
over La$_2$O$_3$ [3]. It was concluded that product carbon dioxide formed on the catalyst surface from a pool of scrambled O and $^{18}$O atoms.

Finally, oxygen present in the catalyst was found to be capable of activating methane and producing coupled hydrocarbons when exposed to a He/CH$_4$ feed pulse. These findings contradict those of some other studies in which the presence of gas-phase O$_2$ was determined to be a requirement for methane activation over La$_2$O$_3$ and 1 % Sr/La$_2$O$_3$ [4], and for C$_2$ formation over several REOs (including La$_2$O$_3$) [12]. However, one study reported that the ratio of methyl radicals generated in the absence and presence, respectively, of gas phase O$_2$ was 0.04 for a La$_2$O$_3$ catalyst which had been pretreated in O$_2$ at 630 °C [13]. This level of activity is consistent with that observed in our experiments. Unfortunately, since the quantities of oxygenated products were too small to be detected by MS, it was impossible to determine whether the oxygen atoms involved were those in the carbonate groups (which would contain $^{18}$O atoms) or those in the (LaO)$_2$$^{2+}$ groups. Further work may resolve this question.
5. CONCLUSIONS

A-La$_2^{18}$O$_3$, II-La$_2$O$_2$CO$_3$, II-La$_2^{18}$O$_2$CO$_3$, and II-La$_2$O$_2^{13}$CO$_3$ can be prepared using a syringe-injection technique. Characterization of the sesquioxide by LRS revealed that $^{18}$O occupies the O(II) site. However, neither FTIR nor LRS are able to determine if $^{18}$O also occupies the O(I) site since the La-O(I) bonds are both ir- and Raman-inactive. FTIR characterization and information from the CO$_2$ evolved during thermal decomposition together indicate that the carbon dioxide used in preparing oxycarbonate from sesquioxide inserts directly into the oxide layers which exist between layers of (LaO)$_2^{2+}$ in A-La$_2$O$_3$. The oxycarbonate in the case of II-La$_2^{18}$O$_2$CO$_3$ consists, therefore, of layers of (C$^{18}$O$_2$O)$^{2-}$ anions between layers of (LaO)$_2^{2+}$ cations.

During the thermal decomposition of II-La$_2$O$_2$CO$_3$ to 750 °C at 10°C/min, two evolutions of CO$_2$ are observed. The first begins at around 570 °C and the second at around 650 °C. Evolution ceases within two hours at 750 °C. The carbon dioxide evolved from II-La$_2^{18}$O$_2$CO$_3$ consists of CO$_2$, C$^{18}$OO, and C$^{18}$O$_2$ in the ratios 13 : 41 : 46. Consequently, $^{18}$O accounts for approximately 67 % of the total oxygen content in the evolved carbon dioxide. This is consistent with the proposal that carbon dioxide evolves only from the (CO$_3$)$^{2-}$ layers of the oxycarbonate and that all C-O bonds within the carbonate groups are equivalent.

During OCM (which proceeds as a He/CH$_4$/O$_2$ pulse passes through the catalyst bed), the C atoms originating in the catalyst account for 46 % of the CO$_2$ produced. The remaining
54% of the CO₂ product results from the deep oxidation of CH₄ in the feed. The C atoms in the catalyst also appear in product CO but its proportion cannot be quantified with the experimental setup used in this study. None of the C atoms originating in the catalyst appear in either of the hydrocarbon products. Therefore, it is concluded that products C₂H₆ and C₂H₄ are produced only from the CH₄ in the feed pulse, probably via the abstraction of a single hydrogen atom from each CH₄ molecule and the coupling (and dehydrogenation) of the resulting methyl radicals.

The O atoms present in the (CO₂)²⁻ layers of the catalyst also appear in products CO₂ and CO. How much of the oxygen in product CO originates from the feed pulse and how much originates from the catalyst cannot be determined with the experimental setup used in this study. Carbon dioxide produced over a Ir-La₂¹⁸O₂CO₃ catalyst consists of CO₂, C¹⁸OO, and C¹⁸O₂ in the ratios 29 : 45 : 26. Consequently, ¹⁸O accounts for almost 50% of all oxygen detected in product carbon dioxide.

The O atoms present in the (CO₂)²⁻ layers of the catalyst are also observed to exchange with the O₂ feed. In a He/O₂ feed pulse, the ratios of O₂, ¹⁸O₂, and ¹⁸O appearing in the post-reactor oxygen are 27 : 49 : 24. Thus, ¹⁸O accounts for approximately 48% of all post-reactor gas phase oxygen.

That the ratios of single-, double-, and non-¹⁸O-substituted CO₂ (from a He/CH₄/O₂ feed) and O₂ (from a He/O₂ feed) are the same indicates that carbon dioxide is produced on the catalyst rather than in the gas phase. Obviously, these ratios suggest that the O and ¹⁸O available for substitution are equally plentiful. Since, the amounts of O₂ in the feed streams
are small relative to that in the catalysts (the ratio is approximately 1:700), it follows that the O and $^{18}$O available in the catalyst for substitution are equally plentiful.

Finally, trace amounts of $\text{O}_2$/CO, $\text{C}_2\text{H}_4$, and $\text{C}_2\text{H}_6$ (but no CO$_2$) are observed in the product stream when pulses of He/CH$_4$ (82:18) are fed over II-La$_2$O$_2$CO$_3$. Thus, oxygen present in the catalyst is capable of activating methane. The amounts of coupling products detected were equivalent to approximately 2 % of those observed following a He/CH$_4$/O$_2$ feed pulse.
ACKNOWLEDGEMENTS

This work was performed at Ames Laboratory under contract number W-7405-eng-82 with the U. S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1615 to this thesis.
REFERENCES

12 Choudhary, V. R.; Rane, V. H. *J. Catal.* (1992) 135, 310-316
GENERAL SUMMARY

As discussed in the general introduction, several catalyst screening studies revealed lanthanum oxide to be an effective catalyst for the oxidative coupling of methane. Few researchers, however, have acknowledged the influence of a co-existing oxycarbonate phase on its catalytic performance. Of these, surface spectroscopic techniques revealed simply that an oxycarbonate phase was formed on the surface of a lanthanum oxide catalyst under OCM conditions [76, 87]. Previous work conducted in our laboratory, however, suggested a strong correlation between the presence of II-La$_2$O$_2$CO$_3$ and the ability to selectively promote the coupling of methane [37]. This observation has been the focus of our current work.

In an attempt to encourage the presence of the II-La$_2$O$_2$CO$_3$ phase during OCM, CO$_2$ was co-fed in varying amounts over both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$ starting catalysts [Paper I]. The results indicated that co-feeding CO$_2$ depresses both methane conversion and $C_2$ selectivity. Furthermore, at 700 °C, co-feeding CO$_2$ over both catalysts totally suppresses $C_2H_4$ formation.

It was concluded that co-fed CO$_2$ plays at least two distinct roles in the OCM process over A-La$_2$O$_3$; that of a catalyst modifier (decreasing the catalyst's ability to activate methane) and that of a gas phase modifier (inhibiting the oxidative dehydrogenation of ethane to ethene by interfering with the homogeneous reaction pathway). Since catalytic performance was particularly poor under conditions at which it is believed that II-La$_2$O$_2$CO$_3$
was the only phase present, it was concluded that superior catalytic performance depends on
the presence of both A-$\text{La}_2\text{O}_3$ and II-$\text{La}_2\text{O}_2\text{CO}_3$ phases.

The second part of this work investigated the potential for oxycarbonate formation on
both A-$\text{La}_2\text{O}_3$ and II-$\text{La}_2\text{O}_2\text{CO}_3$ at typical OCM reaction temperatures by considering the
uptake of gas phase CO$_2$ by both materials [Paper II]. The results revealed that CO$_2$ uptake
between 700 and 800 °C is \textit{not} restricted to the surface and probably proceeds by the
incorporation of CO$_2$ between the (LaO)$_2^{2+}$ layers present in both materials. II-$\text{La}_2\text{O}_2\text{CO}_3$
takes up significantly more CO$_2$ than A-$\text{La}_2\text{O}_3$, probably because of its more open structure
along the \textit{c} axis of the unit cell (i.e., perpendicular to the (LaO)$_2^{2+}$ planes). The fact that the
A-$\text{La}_2\text{O}_3$ phase resulting from the thermal decomposition of II-$\text{La}_2\text{O}_2\text{CO}_3$ is a much more
active and selective OCM catalyst than a pure A-$\text{La}_2\text{O}_3$ starting material was attributed to its
higher basicity resulting from the trace presence of carbonate groups. These results reinforce
the conclusion of Paper I that good catalytic performance depends on the presence of both
A-$\text{La}_2\text{O}_3$ and II-$\text{La}_2\text{O}_2\text{CO}_3$ phases.

In the third part of this study, the influence of the oxycarbonate phase during OCM was
investigated by following the fate of the C and O atoms located in the (CO$_3$)$_2^{2-}$ groups of
II-$\text{La}_2\text{O}_2\text{CO}_3$ [Paper III]. Preparing II-$\text{La}_2^{18}\text{O}_2\text{CO}_3$ and II-$\text{La}_2\text{O}_2^{13}\text{CO}_3$ from A-$\text{La}_2\text{O}_3$ and
C$^{18}\text{O}_2$ and $^{13}\text{CO}_2$, respectively, enabled the isotopically labeled C and O atoms to be followed
by mass spectrometry (MS). It was found that the carbon dioxide used in preparing
II-$\text{La}_2\text{O}_2\text{CO}_3$ from A-$\text{La}_2\text{O}_3$ inserts directly into the oxide layers of the latter to give layers of
(CO$_3$)$_2^{2-}$ anions. The carbon dioxide evolved during the thermal decomposition of
II-La$_2$O$_2$CO$_3$ was determined to originate from the same (CO$_3$)$^{2-}$ layers of the oxycarbonate. However, since the carbon dioxide evolved was equally likely to contain oxygen atoms from the original oxide layer as those from the inserted CO$_2$ molecules, it was concluded that all C-O bonds within the carbonate groups are equivalent.

During OCM, C atoms originating in II-La$_2$O$_2$CO$_3$ were detected in products CO and CO$_2$ but not in either of the hydrocarbon products. It was concluded, therefore, that C$_2$H$_6$ and C$_2$H$_4$ are produced only via methane coupling. The O atoms originating in the (CO$_3$)$^{2-}$ layers of the catalyst were also detected in products CO and CO$_2$ during OCM. It was calculated that $^{18}$O accounts for 48.5 % of all oxygen detected in carbon dioxide produced over II-La$_2^{18}$O$_2$CO$_3$. The same O atoms are also observed to exchange with O$_2$ in the feed. After a He/O$_2$ pulse was fed over II-La$_2^{18}$O$_2$CO$_3$, it was calculated that $^{18}$O accounts for 48.5 % of all post-reactor gas phase oxygen.

Since the ratios of single-, double-, and non-$^{18}$O-substituted CO$_2$ (from a He/CH$_4$/O$_2$ feed) and O$_2$ (from a He/O$_2$ feed) were the same, carbon dioxide was concluded to be produced on the catalyst rather than in the gas phase. The ratios suggest that the O and $^{18}$O available for substitution are equally plentiful. Since, the amount of O$_2$ in the feed stream is small relative to that in the catalysts (the ratio is approximately 1 : 700), it follows that the O and $^{18}$O available in the catalyst for substitution are equally plentiful.

Finally, oxygen present in the catalyst was found to be capable of activating methane. The amounts of coupling products detected following a He/CH$_4$ pulse were equivalent to approximately 2 % of those observed following a He/CH$_4$/O$_2$ feed pulse.
In summary, the results of this work have shed new light on the importance of the oxycarbonate phase in enhancing the catalytic performance of lanthanum oxide-based materials for the oxidative coupling of methane.

In particular, it has been shown that pure II-La$_2$O$_2$CO$_3$ is a poor OCM catalyst and that good catalytic performance relies upon the presence of both A-La$_2$O$_3$ and II-La$_2$O$_2$CO$_3$. It is proposed that the effectiveness of A-La$_2$O$_3$ for OCM is due to the charge separation between the electronegative O atoms and the electropositive La atoms in the (LaO)$_2$$^{2+}$ layers resulting in high basicity. However, the basicity of A-La$_2$O$_3$ is reduced somewhat by the O$^{2-}$ anions in the oxide layers competing with the O atoms in the (LaO)$_2$$^{2+}$ layers for the negative charge. Since the (CO$_3$)$^{2-}$ groups of the oxycarbonate phase are less electronegative and are located at larger distances from the (LaO)$_2$$^{2+}$ layers than the oxide layers in pure A-La$_2$O$_3$, they compete less effectively for the negative charge. Thus, the presence of oxycarbonate results in higher basicity. From this reasoning, one would expect pure II-La$_2$O$_2$CO$_3$ to be a superior catalyst for OCM. That this is not the case is due to the fact that a relatively high partial pressure of gas phase CO$_2$ is required to stabilize II-La$_2$O$_2$CO$_3$ against thermal decomposition at typical OCM reaction temperatures. The excess CO$_2$ not only competes with the O atoms in the (LaO)$_2$$^{2+}$ layers for the negative charge (thereby reducing the basicity) but also inhibits the oxidative dehydrogenation of ethane to ethene by interfering with the homogeneous reaction pathway.

Further work is necessary to confirm the foregoing propositions. In situ, surface-specific spectroscopic techniques such as X-ray photoelectron spectroscopy may
offer the most promise for correlating the presence of trace amounts of the oxycarbonate phase on a working "lanthanum oxide" catalyst with catalytic performance.
ADDITIONAL REFERENCES


<table>
<thead>
<tr>
<th></th>
<th>Authors</th>
<th>Journal/Conference Title</th>
<th>Year</th>
<th>Volume</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>Choudhary, V. R.; Rane, V. H.</td>
<td>J. Catal.</td>
<td>1991</td>
<td>130</td>
<td>411-422</td>
</tr>
<tr>
<td>41</td>
<td>Lane, G. S.; Wolf, E. E.</td>
<td>J. Catal.</td>
<td>1988</td>
<td>113</td>
<td>144-163</td>
</tr>
</tbody>
</table>


80 Taylor, R. P. M. S. Thesis (1989) Iowa State University


<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Journal/Preprint Details</th>
</tr>
</thead>
</table>