Fueling the mission to Mars and Earth’s transition to renewable energy: Increasing catalyst performance for carbon dioxide methanation

Elspeth Petersen
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Fueling the mission to Mars and Earth’s transition to renewable energy: Increasing catalyst performance for carbon dioxide methanation

by

Elspeth Morgan Petersen

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Chemical Engineering

Program of Study Committee:
Jean-Philippe Tessonnier, Major Professor
Theodore J. Heindel
Luke T. Roling

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2019

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# TABLE OF CONTENTS

LIST OF FIGURES iv

LIST OF TABLES vi

ABSTRACT vii

CHAPTER 1. INTRODUCTION 1
   General Introduction and Motivation ................................................................. 1
   Preliminary Work at NASA .................................................................................. 3
   Thermodynamic, Kinetic, and Mechanistic Considerations .................................... 5
   Catalyst Activity on Silicon Carbide ...................................................................... 7
   Effects of Support Thermal Conductivity ............................................................ 11
   Silicon Carbide as Unique Platform ..................................................................... 13
   References ............................................................................................................ 14

CHAPTER 2. EXPERIMENTAL 20
   Catalyst Preparation ............................................................................................. 20
   Reactor Setup ........................................................................................................ 21
   Characterization ................................................................................................... 23
   Activity Calculations ............................................................................................ 24
      Carbon Dioxide Conversion ............................................................................. 24
      Methane Selectivity ......................................................................................... 24
   References ............................................................................................................ 25

CHAPTER 3. SILICON CARBIDE AS A UNIQUE PLATFORM FOR ISOLATING EFFECTS OF SUPPORT THERMAL CONDUCTIVITY ON CARBON DIOXIDE REDUCTION CATALYSTS 26
   Abstract ............................................................................................................... 26
   Introduction .......................................................................................................... 27
   Experimental ....................................................................................................... 33
      Catalyst Preparation ......................................................................................... 33
      Characterization .............................................................................................. 34
      Methanation Reaction ..................................................................................... 35
      Modelling Study .............................................................................................. 36
   Results and Discussion .......................................................................................... 37
      Preliminary Study ............................................................................................. 37
      Catalyst Characterization .............................................................................. 38
      Activity Tests .................................................................................................. 46
      Modelling Study .............................................................................................. 49
   Conclusions .......................................................................................................... 50
   Acknowledgements ............................................................................................... 51
   References ............................................................................................................ 51
CHAPTER 4. FUTURE WORK

Confirm Support Thermal Conductivity Trend .......................................................... 55
Improve Model Fidelity ................................................................................................. 56
Incorporate Metal Oxides to Enhance Silicon Carbide Activity .............................. 56
References ..................................................................................................................... 57
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>The 0.5%Ru/γ-alumina catalyst pellets used in the Mars atmosphere conversion</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Sabatier reactor at Kennedy Space Center. The unused catalyst (left) changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>in appearance drastically following deactivation in the reactor (right).</td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>Thermodynamic equilibrium for the Sabatier reaction based on temperature</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>assuming a stoichiometric feed of H₂ to CO₂ (4:1).</td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>Catalyst performance for 5%Ru on γ-alumina, silicon carbide and titania.</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Error bars represent variation among three repeated runs for each catalyst.</td>
<td></td>
</tr>
<tr>
<td>2-1</td>
<td>A close up image of the reactor bed showing the glass wool resting on the</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>dimples and supporting the catalyst and inert alumina mixture.</td>
<td></td>
</tr>
<tr>
<td>2-2</td>
<td>The down flow quartz reactor is fixed in stainless steel tubing with Cajon</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>fittings. A pressure gauge upstream ensures there is not pressure drop across</td>
<td></td>
</tr>
<tr>
<td></td>
<td>the reactor, and a condenser removes water from the stream prior to GC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>analysis.</td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>Bronkhorst flow controllers supply reactant gases, and an i-series Omega PID</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>controls bed temperature monitored by a thermometer placed on the outer wall</td>
<td></td>
</tr>
<tr>
<td></td>
<td>of the reactor and secured by an aluminum heat sink.</td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>The thermodynamic equilibrium composition of a Sabatier reaction at varying</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>temperatures given a stoichiometric feed of H₂ to CO₂ (4:1).</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>The 0.5%Ru/γ-alumina catalyst pellets used in the Mars atmosphere conversion</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Sabatier reactor at Kennedy Space Center. The unused catalyst (left) changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>in appearance drastically following deactivation in the reactor (right).</td>
<td></td>
</tr>
<tr>
<td>3-3</td>
<td>Performance of CO₂ methanation over 5%Ru supported catalysts. Error bars</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>represent variation among three repeated runs.</td>
<td></td>
</tr>
<tr>
<td>3-4</td>
<td>Thermal gravimetric analysis of silicon carbide undergoing calcination in air</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>over 48 hours. The silicon dioxide layer thickness and thermal conductivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>calculated from mass gain during calcination.</td>
<td></td>
</tr>
<tr>
<td>3-5</td>
<td>Surface morphology of 5%Ru/Calcined SiC supports. Upper level left to right:</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1h, 2h, 4h, and lower left to right 8h, 36h. Joel JSM-7500F Field Emission</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SEM WD 8mm, 15.0kV, 2700x.</td>
<td></td>
</tr>
<tr>
<td>3-6</td>
<td>Catalyst composition collected by Oxford AZtec X-MAXN EDS.</td>
<td>41</td>
</tr>
</tbody>
</table>
Figure 3-7 XRD spectra of 5%Ru catalyst supported on a) Calcined SiC 1h 1000C, b) Calcined SiC 2h 1000C c) Calcined SiC 4h 1000C, d) Calcined SiC 8h 1000C, e) Calcined SiC 36h 1000C. Peaks associated with SiC (★), Ru (●), SiO₂ (●●), and RuO₂ (●●●) are marked.......................................................... 41

Figure 3-8 Temperature programmed oxidation on the catalysts following ex-situ reduction (a) and supports without any pretreatment (b). Temperature programmed reduction carried out on catalysts following TPO (c) and supports without any pretreatment (d). ....................................................................................................... 43

Figure 3-9 TEM images of catalysts with inset of ruthenium particle size distribution taken from over 200 particles per catalyst. Top: L to R 5%Ru/Calcined SiC 1h 1000C, 5%Ru/Calcined SiC 2h 1000C 5%Ru/Calcined SiC 4h 1000C. Bottom: L to R 5%Ru/Calcined SiC 8h 1000C, 5%Ru/Calcined SiC 36h 1000C. ................ 44

Figure 3-10 Pore size distribution of a) 5%Ru/Calcined SiC 1h 1000C, b) 5%Ru/Calcined SiC 8h 1000C, and c) 5%Ru/Calcined SiC 36h 1000C determined by BJH desorption. ................................................................................................................ 45

Figure 3-11 (Left) Carbon dioxide turnover frequency and methane selectivity for the tested 5%Ru/Calcined SiC catalysts plotted based on calculated silicon dioxide layer thickness. Error bars represent variation from three repeated runs. (Right) The thermodynamic equilibrium carbon dioxide conversion and methane selectivity for a reactor fed a stoichiometric ratio of H₂ to CO₂ (4:1) with overlay of experimental selectivity of 5%Ru/Calcined SiC (1h to 36h left to right). ............... 47

Figure 3-12 Results from model of catalyst particle within reactor bed. Temperature gradient along radius from the center to the surface of a particle calculated for a bed temperature of (top) $T_\varnothing=325°C$ and (bottom) $T_\varnothing=350°C$. The largest gradient represents 5%Ru/Calcined SiC 36h 1000C and smallest is 5%Ru/Calcined SiC 1h 1000C for both bed temperature sets. ........................................ 50
LIST OF TABLES

Table 1-1 Physical properties and tabulated performance of the tested catalysts. Reduction temperatures were collected from TPR, and surface area was calculated from nitrogen physisorption using multi-point BET ................................. 9

Table 3-1 Catalyst characterization from preliminary study. .......................................................... 37

Table 3-2 Ruthenium particle size collected by hydrogen chemisorption and XRD (before and after 325°C reaction) and surface area found by nitrogen physisorption for all tested catalysts. ................................................................. 42

Table 3-3 Tabulated values for activation energy, carbon dioxide turnover frequency, and methane selectivity for the 5%Ru/Calcined SiC catalysts tested. ........................................ 48
Carbon dioxide methanation, also called the Sabatier reaction, has a wide range of applications. It can provide a means of carbon-neutral energy storage and transport by converting atmospheric or point-source carbon dioxide to methane using renewably generated hydrogen. This allows for energy transport and storage for intermittent renewable energy using the existing natural gas infrastructure. The Sabatier reaction will also play a large role in the human exploration of space. A reactor is currently under development by NASA to produce fuel on Mars for an ascent vehicle to return a crewed mission or planetary samples back to Earth. Synthesizing the fuel on-site eliminates the need to transport it from Earth, greatly decreasing the launch volume, weight, and cost requirements of the mission. The catalyst developed for this reactor can also be applied in crewed spacecraft to recycle oxygen from metabolic carbon dioxide and to produce fuel and water from trash.

However, issues related to catalyst deactivation currently limit the implementation of this technology. In order to ensure proper and long-term operation of a Sabatier reactor for such applications, catalyst durability and activity must be improved, and to do so, the effects of support properties, such as electronic interactions with the active phase, thermal conductivity, and behavior under typical reaction conditions must be understood. For this exothermic reaction, thermodynamics dictate that conversion and selectivity are favored at lower reactor temperatures, but supports with low thermal conductivity are not effective at transferring heat away from the active phase during the reaction. This buildup of heat results in localized elevated temperatures, higher than the overall bed temperature that detrimentally affect catalyst activity and longevity.

In order to increase catalyst longevity, beta silicon carbide, a material with exceptional heat conductivity and mechanical strength, has been chosen as a possible replacement for the
traditional, low-thermal conductivity, metal-oxide supports currently in use. To test the effects of support thermal conductivity in the absence of other interfering variables, the thermal conductivity of silicon carbide was tuned via controlled oxidation to silicon dioxide. By strategically controlling the calcination duration, supports with a range of silicon carbide to silicon dioxide ratios were produced. As silicon dioxide has a much lower thermal conductivity, the increased calcination time resulted in a lower support thermal conductivity. Composition supports consisting of silicon carbide with a natural silicon dioxide washcoat were impregnated with an active Sabatier catalyst, ruthenium, and tested for conversion rates and methane selectivity in a packed bed reactor. The study found a trend of decreasing selectivity with an increasing proportion of silicon oxide in the support and thus a decrease in thermal conductivity. The trends in selectivity and conversion are likely due to localized hot spots and match those predicted by thermodynamics at elevated reaction temperatures, where carbon dioxide conversion shifts to the production of carbon monoxide at the expense of methane. These findings are also supported by reaction modelling of a catalyst particle, which shows increasing surface temperature on the supports with reduced thermal conductivity. In addition to the negative impact the elevated surface temperatures have on selectivity due to thermodynamic constraints, it can also reduce catalyst longevity by means of active phase and support sintering, fouling via coke formation, and physical degradation.

The use of silicon carbide for the Sabatier reaction to improve support thermal conductivity shows great promise for improving catalyst activity and longevity, but further study is still required to build on these initial findings to further enhance catalyst stability and activity. Incorporating metal oxides into the silicon carbide matrix will likely address some of the drawbacks seen with the silicon carbide supports. Metal oxides, such as alumina and titania,
interact electronically with the active metal to increase catalyst dispersion, prevent sintering, and improve activity through participation in the reaction pathway. The knowledge gained in this and future studies will provide a more complete understanding of the deactivation pathways for Sabatier catalysts and enable the design of a new generation of robust, highly active catalysts. The development of a durable Sabatier reactor will enable the human exploration of Mars and the transition to renewable energy on Earth.
CHAPTER 1. INTRODUCTION

General Introduction and Motivation

Carbon dioxide levels in the atmosphere are reaching increasingly higher levels, recently reaching a record-breaking monthly average of 410ppm [1], causing numerous negative effects related to the rise of this greenhouse gas and global warming: sea level rise, changing weather patterns, ocean acidification, melting permafrost, and so on. Shifting the energy supply from fossil fuels to renewable energy sources will stem the flow of anthropogenic CO\(_2\) into the atmosphere; however, as we transition from petroleum-based to renewable energy, energy storage will be required to meet continuous power needs. By converting carbon dioxide (CO\(_2\)) into methane, the Sabatier reaction (Equation 1.1) provides a net carbon-neutral energy source

\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{\text{rxn}} = -165 \text{ kJ/mol}
\] (1.1)

that solves the problem of intermittent power availability. The proposed process, known as Power-to-Gas, produces methane by reacting hydrogen, produced from water electrolysis during peak energy availability, with CO\(_2\), which can be harvested from natural gas power plants or fermentation vats, such as those found at ethanol plants [2]. Methane is much easier to store than hydrogen and has a higher energy density. Also, by using methane as an energy storage and transport medium, Power-to-Gas can be implemented quickly due to the existing natural gas infrastructure including power plants and trans-country pipelines [3].

In addition to this terrestrial application, uses for the Sabatier reaction extend into outer space. This reaction has historically been used on the International Space Station to recycle oxygen from metabolic CO\(_2\), via water production, reducing the need to resupply breathable oxygen from earth in the form of water, thus avoiding the launch of up to 2000 lb/year and considerable cost savings for the program [4, 5]. Based on this legacy, NASA has recently
demonstrated interest in the Sabatier reaction to provide fuel for an ascent vehicle to return a
crewed or sample-return mission from Mars. The approaching Mars mission target date does not
allow for investigation of alternate methane production systems. A Mars Pathfinder will be sent
ahead of a crewed mission to convert carbon dioxide from the Martian atmosphere and water
from its regolith into methane (CH\textsubscript{4}) and oxygen for use as rocket propellant to launch spacecraft
from the surface of Mars on the return trip to Earth. The application of the Sabatier reaction for
in-situ fuel synthesis greatly decreases the volume, weight, and cost requirements of Mars
missions by eliminating the need to transport ascent vehicle fuel from Earth. The current analysis
requires the production of 7.0 metric tons of methane over a 480 day continuous operating period
for every ascent vehicle [6].

NASA also plans to use the Sabatier reaction for an application in conjunction with the
Orbital Syngas/Commodity Augmentation Reactor (OSCAR) project, converting the syngas
produced from gasifying trash into usable fuel aboard crewed spacecraft and extraterrestrial
human habitats. OSCAR has been designed to use high temperature plasma to gasify common
waste products from long-duration missions including the hygienic disposal of medical and
human waste. This will reduce odor and bulk and increase sanitation during crewed missions
while providing useful products including water and fuel [7].

Due to the importance of CO\textsubscript{2} conversion for both space and terrestrial applications, a
robust and active Sabatier catalyst must be designed. This new catalyst for the Sabatier reaction
will pave the way for crewed space exploration beyond lower Earth orbit and support the
transition to renewable energy on Earth.

The Sabatier reaction was discovered over a century ago [8] and has traditionally been
used in industry to remove trace amounts of carbon monoxide from hydrogen streams for use in
ammonia production and fuel cells [9, 10]. Because of its long heritage, many attempts have been made to understand and optimize the reaction and CO₂ conversion in general. These methods include electrochemistry, thermochemistry, biochemistry, and photocatalysis. Each method faces its own challenges and benefits. The two methods which have garnered the most attention recently are electrocatalytic and thermocatalytic carbon dioxide conversion.

Electrochemistry valorizes CO₂ into four main products using various catalysts. Copper catalysts produce mainly hydrocarbons; one study found 16 different C₁-C₃ products resulting from a single reactor [11]. Other target products include CO (using Au, Ag, and Zn), methanol, and formates (from In, Pb, Sn, and Cd catalysts) [12-14]. The electrochemical route faces challenges for CO₂ conversion including a low solubility of CO₂, low selectivity, and high overpotentials [11, 14]. Additionally, much of the recent work has focused on production of CO, methanol, C₂⁺ hydrocarbons and formate, not methane [15].

Because of the limitations faced by electrochemistry and the constraints set by NASA, this study will examine the thermochemical route to conversion. From the work that has been done on the Sabatier reaction, we know it provides a direct conversion to methane with high selectivity on a number of metal catalysts. However, further investigation is required to maximize conversion and selectivity for applications in a compact system and increase catalyst stability.

**Preliminary Work at NASA**

The catalyst (0.5wt% Ru/γ-Al₂O₃ 3.2mm pellets, Sigma-Aldrich) in the Mars atmosphere conversion Sabatier reactor being tested at NASA’s Kennedy Space Center deactivated after a timescale much shorter than required for the Mars mission. The Sabatier reactor operated for approximately 110 hours with a nominal inlet temperature of 400°C, a WHSV of
2800mL gcat$^{-1}$ h$^{-1}$ and a stoichiometric feed ratio of H$_2$ to CO$_2$ (4:1). The failure occurred following higher flow condition testing and resulted in an elevated catalyst bed temperature of 586°C, instability in the reactor temperature profile, and production of CO [16]. The catalyst underwent significant physical changes following deactivation including color change and pellet fragmentation (Figure 1-1). Characterization testing of spent pellets was inconclusive in determining the pathway(s) of deactivation, but pellet fracture and dusting strongly hint toward thermally induced deactivation. The reaction’s high exothermicity can generate hot spots at the surface of the ruthenium particles due to the support’s insufficient thermal conductivity, causing mechanical stress leading to cracking and fragmentation. The elevated surface temperatures can also cause sintering of the active phase and support [17, 18], coke formation through methane breakdown, and/or carbon monoxide production via methane steam reforming and the reverse water-gas shift. While the exact nature and cause of the failure is not yet known, catalyst stability is a major issue that plagues this NASA project and prevents implementation of commercial Power-to-Gas energy storage.

Figure 1-1 The 0.5%Ru/γ-alumina catalyst pellets used in the Mars atmosphere conversion Sabatier reactor at Kennedy Space Center. The unused catalyst (left) changes in appearance drastically following deactivation in the reactor (right).
Thermodynamic, Kinetic, and Mechanistic Considerations

This exothermic reaction is thermodynamically favored at lower temperatures, but the extreme stability of CO$_2$ requires higher temperatures and a catalyst to overcome the kinetic barrier for the reaction. As can be seen in Figure 1-2, showing the equilibrium concentration for the reaction at increasing temperatures, the methane selectivity is best at low temperatures with CO production occurring at higher temperatures where competing reactions dominate. The reverse water gas shift (RWGS) (Equation 1.2) and steam reforming (Equation 1.3) are the main side-reactions for the Sabatier system over heterogeneous catalysts [19].

\[
CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{rxn} \leftrightarrow 40.6 \frac{kJ}{mol} \tag{1.2}
\]

\[
CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_{rxn} \leftrightarrow 206 \frac{kJ}{mol} \tag{1.3}
\]

Figure 1-2 Thermodynamic equilibrium for the Sabatier reaction based on temperature assuming a stoichiometric feed of H$_2$ to CO$_2$ (4:1).
Previous studies have mostly focused on metal support interactions (MSI) on oxide supports to improve catalyst activity and durability. The active phase support can affect the reaction in many ways such as by providing a surface for CO\(_2\) adsorption, allowing hydrogen spillover, providing a heat sink to remove heat from the active metal, stabilizing metal to increase dispersion and avoid sintering, and affecting conversion rates and selectivity through electronic metal support interactions [20]. Much research has focused on testing supports in an empirical way. Reducible oxides and supports with oxygen vacancies, such as CeO\(_x\), can provide a large area for CO\(_2\) adsorption and may help transition CO\(_2\) into its intermediates by donating an electron pair [21-26]. Hydrogen spillover enhances catalyst activity for this reaction, potentially opening up alternate mechanisms for conversion or transition states on the support surface [27-30]. Metal loading, H\(_2\) pressure, catalyst metal species, dispersion, and support oxide [31] affect hydrogen spillover. Electronic metal support interactions from the support or dopants can affect the catalyst in many ways including anchoring the metal and stabilizing it to prevent sintering [32, 33], preventing coke formation and catalyst fouling [34], increasing selectivity, for example by affecting Ru-CO and C-O binding strength at the metal-oxide interface [35, 36], and detrimental effects such as strong metal support interactions, like those exhibited by Ru/TiO\(_2\) resulting in active metal encapsulation [37, 38].

The mechanism for the Sabatier reaction is still under debate, and the reaction pathway and intermediates seem to alter depending on the support and catalytic metal being used. Most researchers agree that hydrogen undergoes dissociative adsorption on the active metal, and CO\(_2\) adsorbs on the catalyst metal or on basic sites, hydroxyl groups, or oxygen vacancies on the support [25, 27, 39]. CO\(_2\) either directly dissociates to CO\(_{\text{ads}}\) at the support metal-interface or transitions through a formate to an adsorbed CO with help from hydrogen spillover on the
support. Ultimately, the CO\textsubscript{(ads)} is reduced to CH\textsubscript{x(ads)} with stepwise, facile addition of H\textsubscript{(ads)} until the product, CH\textsubscript{4}, is reached and desorbed [40-43].

The traditional oxide supports offer a number of key benefits as stated above, but beta silicon carbide (SiC), a relatively new support in catalysis, possesses characteristics that could prove beneficial to this reaction, especially to the space-related applications [44, 45]. Silicon carbide has a very high thermal conductivity, which has been shown to assist with temperature control for other exothermic reactions [46, 47]. Its exceptional mechanical strength will prevent physical catalyst degradation during the intense vibrations experienced during liftoff [48] and the landing impact on Mars. It possesses a surface area comparable to oxides and can be manufactured in many shapes including pellet, foam, and honeycomb to accommodate any reactor configuration and increase mixing within the reactor [49, 50]. Another beneficial property is a very low thermal expansion [50]. As seen in the KSC reactor, the Al\textsubscript{2}O\textsubscript{3} pellets fractured likely due to rapid temperature changes during reactor startup and shutdown. The Mars reactor will experience extremes in temperature between the Martian surface temperatures (-73°C to +20°C) and reactor operating temperatures (300°C +). A high thermal conductivity will disperse heat quickly to maintain reaction temperature control; however, should a temperature gradient exist, the low thermal expansion will prevent cracks and breaking. In order to take advantage of the positive physical characteristics, it must be determined if catalysts supported on SiC can perform as well as oxides for the Sabatier reaction with both high conversion and selectivity. Then tests for improvements in catalyst longevity can be carried out.

**Catalyst Activity on Silicon Carbide**

In order to compare support efficacy, one noble catalyst was selected for the study. Vannice [51] ranked several Sabatier catalysts by turnover frequency (TOF) and found that Ru had a turnover number over three times larger than the next most active catalyst. The metal
activity ranking determined in the study is as follows: Ru >> Fe > Ni > Co > Rh > Pd > Pt > Ir. Other studies have confirmed the premier activity of Ru [52-55]. A majority of recent studies have focused on nickel as the catalyst for commercial systems due to cost. Nickel is an effective catalyst; however, it generally requires much higher loading than Ru for reasonable conversion and is more prone to coking and sintering [56-58]. As ruthenium has been shown to provide high conversion, selectivity for methane, and longevity, it will be the catalyst of choice for our work.

Preliminary reaction activity tests were carried out on gamma alumina, rutile and anatase titania (TiO$_2$), and silicon carbide supports with five weight percent ruthenium as the active phase. Of the traditional supports, alumina and rutile-titania have been shown to be the most effective at enhancing catalyst performance [39, 59, 60]. Though the mechanisms by which they enhance performance are still not entirely understood, oxygen vacancies and basic sites on the supports appear to assist with CO$_2$ adsorption, a challenging step in the reaction mechanism [25, 39, 61]. For this preliminary study, gamma-alumina ($\gamma$-Al$_2$O$_3$) was chosen to provide a baseline to compare the activity, selectivity, and longevity of other supports with the catalyst support in NASA’s Sabatier reactor at Kennedy Space Center. Beta silicon carbide was selected for testing as a replacement for alumina due to its favorable thermal properties, which have proven beneficial in other reactions [47, 62]. The silicon carbide support either underwent no treatment (Non-calcined SiC) or was calcined in static air for 2 hours at 800°C or 8 hours at 1000°C (Calc SiC 2h800C and 8h1000C, respectively). The calcining step oxidized the surface layers of silicon carbide to silicon dioxide, providing anchoring sites for the ruthenium precursor to enhance dispersion. Titania (rutile and anatase) were selected, because they have shown interesting results in other CO and CO$_2$ methanation studies [35, 63, 64]. Anatase TiO$_2$ performs much less favorably than rutile possibly, because the rutile TiO$_2$ crystal structure is similar to that of
ruthenium, resulting in better dispersion during synthesis and anchoring during reaction [63, 65]. However, the complete reason for the superior performance of rutile TiO$_2$ compared to anatase remains unknown.

In the activity study, Al$_2$O$_3$ and TiO$_2$ catalysts generally behaved as expected based on previous work. Rutile TiO$_2$ exhibited very good activity, anatase performed poorly, and Al$_2$O$_3$ had excellent selectivity and good carbon dioxide conversion. The non-calc SiC shows promise with similar performance to the benchmark catalyst supports, Al$_2$O$_3$ and rutile TiO$_2$ (Table 1-1). Unlike alumina and titania, the silicon carbide/silicon dioxide supports are unlikely to participate in the reaction by adsorbing carbon dioxide, and, as a support, SiO$_2$ generally ranks near the bottom for studies testing MSI [39, 66]. The reason for its promising performance is not clear.

Table 1-1 Physical properties and tabulated performance of the tested catalysts. Reduction temperatures were collected from TPR, and surface area was calculated from nitrogen physisorption using multi-point BET.

<table>
<thead>
<tr>
<th>Ru Particle Size</th>
<th>H$_2$ Chemi (nm)</th>
<th>XRD (nm)</th>
<th>SA (m$^2$/g)</th>
<th>Thermal Conductivity (W/mK)</th>
<th>Initial Reduction Temperature (°C)</th>
<th>Peak Reduction Temperature (°C)</th>
<th>CO$_2$ Conversion (%)</th>
<th>CO$_2$ TOF (s$^{-1}$)</th>
<th>CH$_4$ Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Ru/γ-Al$_2$O$_3$</td>
<td>9.0</td>
<td>14.0</td>
<td>195</td>
<td>25</td>
<td>90.5</td>
<td>151.7</td>
<td>31.7</td>
<td>2.4</td>
<td>94.0</td>
</tr>
<tr>
<td>5%Ru/Non-Calc SiC</td>
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<td>13.6</td>
<td>35</td>
<td>100</td>
<td>55.0</td>
<td>84.1</td>
<td>26.9</td>
<td>3.5</td>
<td>92.8</td>
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<tr>
<td>5%Ru/Calc SiC 2h800C</td>
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<td>16.2</td>
<td>34</td>
<td>99.6</td>
<td>71.1</td>
<td>132.2</td>
<td>20.1</td>
<td>2.4</td>
<td>89.5</td>
</tr>
<tr>
<td>5%Ru/Calc SiC 8h1000C</td>
<td>10.4</td>
<td>16.9</td>
<td>18</td>
<td>93</td>
<td>90.9</td>
<td>119.9</td>
<td>14.1</td>
<td>1.9</td>
<td>84.4</td>
</tr>
<tr>
<td>5%Ru/TiO$_2$-Rutile</td>
<td>11.9</td>
<td>/</td>
<td>5</td>
<td>11</td>
<td>82.9</td>
<td>114.9</td>
<td>16.5</td>
<td>3.1</td>
<td>84.6</td>
</tr>
<tr>
<td>5%Ru/TiO$_2$-Anatase</td>
<td>13.8</td>
<td>13.4</td>
<td>15</td>
<td>11</td>
<td>90.5</td>
<td>121.6</td>
<td>10.3</td>
<td>2.2</td>
<td>75.3</td>
</tr>
</tbody>
</table>

As Table 1-1 shows, within each support species, there is a positive relationship between a lower initial reduction temperature determined by TPR and increased methane selectivity. However, when examining the complete data set, the behavior of the catalysts is perplexing. In the SiC group and TiO$_2$ catalysts, a lower initial reduction temperature is associated with a higher methane selectivity, but the trend does not continue across all the catalysts. The turnover
frequency, selectivity, initial and peak reduction temperatures vary, seemingly, randomly among the TiO$_2$, Al$_2$O$_3$, and SiC catalysts (Table 1-1).

From this study, it is difficult to draw conclusions about metal-support interactions on catalyst performance, because a few factors could be affecting activity other than the MSI. The drastically different surface areas may play a role in transport effects and could affect the degree of electronic metal support interactions [35, 67]. It may also be due to hot spot formation at the surface of the catalyst due to insufficient thermal conductivity of the supports resulting in different thermal environments for each catalyst.

The calcined SiC supported catalysts should behave comparably to each other considering they have the same surface material, surface area, and ruthenium particle size, but a trend exists with the selectivity decreasing with increasing oxidation treatment time. This trend could be the result of changes in support thermal conductivity, an important variable among the different SiC catalysts. The increased calcination time of the SiC increased the amount of SiO$_2$ in the support, thereby decreasing the thermal conductivity of each particle as silicon dioxide has a much lower thermal conductivity than SiC. This decrease in thermal conductivity in the calcined supports inhibits the effectiveness of the support at drawing heat away from the active metal. If the heat generated by the exothermic reaction is not diffused, the catalyst particles will experience an elevated temperature, or localized hot spots, resulting in decreases in performance (Figure 1-3). While additional experiments are needed, these early results suggest that insufficient thermal conductivity in catalyst supports may be responsible for the formation of detrimental hot spots during exothermic reactions.
Figure 1-3 Catalyst performance for 5%Ru on γ-alumina, silicon carbide and titania. Error bars represent variation among three repeated runs for each catalyst.

Effects of Support Thermal Conductivity

As mentioned earlier, conversion and selectivity are thermodynamically favored at lower temperatures (Figure 1-2). Temperature management has historically been addressed by drastically increasing H₂ concentration or recycling gas in the reactor feed to carry heat away, by fluidized bed reactors or by using multiple reactors with interstage cooling [19, 68]. These options result in higher operation costs and still allow for the possibility of a runaway reaction.

Existing literature does not provide supporting work for the trend seen among the SiC catalysts as it relates to thermal conductivity and reactor temperature control. Some studies have compared supports with high thermal conductivity, such as SiC and carbon felt, with traditional oxide supports. While the work provides interesting results, typically showing either higher activity or stability for the high thermal conductivity (TC) support, other variables that could affect the outcome were not always controlled, such as in the following studies:
• Nguyen et al. [69] compared cobalt on Al₂O₃ foam and SiC foam for the Fischer-Tropsch reaction. The difference in selectivity between the two catalysts were partially attributed to differences in pore size or surface chemistry. The more favorable selectivity exhibited by the SiC-supported catalyst could also be caused by enhanced reactor temperature control. The Al₂O₃ catalyst bed reached a higher temperature (10°C higher) during the reaction, and higher temperature hot spots could favor the secondary cracking reaction, which would also lower selectivity.

• Frey et al. [70] used SiC, Al₂O₃, and aluminum foams with a wash-coat of Ni/ceria-zirconia for CO₂ methanation. They noticed better heat distribution, CH₄ selectivity, and CO₂ conversion with the silicon carbide support. Unfortunately, they experienced problems with consistency in washcoat dispersion due to the very low surface areas of the foams, meaning the results for each catalyst are difficult to compare with each other, limiting the conclusions that can be drawn.

• Zhang et al. [71] performed syngas methanation using nickel supported on silicon carbide that had been calcined at 500˚C, 700˚C, and 900˚C for four hours prior to impregnation. The methane selectivity was comparable for all the catalysts, but the more calcined supports experienced a decrease in CO conversion over time. Variation in deactivation from sintering or carbon formation on the three supports could have been affected by differences in nickel particle sizes and support chemistry complicating possible conclusions about thermal conductivity.

• Zarubova [72] tested cobalt on the platelet and fishbone configurations of carbon nanofibers (CNFs) attached to carbon felt for the Fischer Tropsch reaction. The CNF supports provided similar chemical environments for the cobalt while allowing for
thermal conductivity manipulation. The fishbone CNF orientation provided a larger thermal conductivity throughout the bed and heat dissipation through the reactor wall. The catalyst with the fishbone configuration support showed better selectivity and a constant bed temperature along the length of the reactor. However, these results are complicated by the fact that the two supports caused drastically different flow regimes in the reactor, which could influence conversion and selectivity by altering heat transfer via convection and the residence time in the reactor.

- Zhang et al. [45] examined nickel on alumina and silicon carbide for carbon dioxide methanation. They found that conversion was comparable for both catalysts, but the selectivity dropped over time for the Al₂O₃ catalyst. The loss of selectivity over time for the alumina catalyst likely resulted from sintering and coke formation, both of which would be exacerbated by local hot spot formation due to the low thermal conductivity of the oxide support, but it was also reported that the alumina support had smaller nickel particle size, which could cause a similar effect.

**Silicon Carbide as Unique Platform**

This lack of clarity in the effect of support thermal conductivity on exothermic reaction activity lead us to design a study to isolate and examine the effects of support thermal conductivity without the interference of other variables. In order to do this, we will use SiC as a platform in an innovative way to test the effects of support thermal conductivity on exothermic reactions.

The results of this study will provide information needed to design a robust catalyst for the Sabatier reaction that can maintain tight reactor temperature control. This control is needed not only to prevent reactor run away and catalyst deactivation but also to promote catalyst activity and selectivity. Elevated reactor temperatures apply opposing forces on selectivity and
reactivity via kinetic and thermodynamic influences. An optimized temperature for this reaction must accommodate both for optimal reactor performance, and deviations caused by insufficient support thermal conductivity need to be eliminated.

References


41. Pan, Q., et al., Insight into the reaction route of CO\textsubscript{2} methanation: Promotion effect of medium basic sites. Catalysis Communications, 2014. 45: p. 74-78.


CHAPTER 2. EXPERIMENTAL

Catalyst Preparation

Gamma-Al₂O₃ (3.2mm pellets, Alfa Aesar, CAS: 1344-28-1), TiO₂ (pure Rutile phase (powder, Alfa Aesar, CAS: 1317-80-2) and pure Anatase phase (powder, Alfa Aesar, CAS: 1317-70-0)), and β-SiC (extruded pellet, SiCat) were impregnated with 5wt% Ru to perform characterization and reaction activity studies.

The β-SiC and γ-Al₂O₃ used in this work were purchased in the form of pellets (SBET=28 m² g⁻¹ and SBET=220 m² g⁻¹, respectively). Prior to impregnation, both support pellets were crushed and sieved to 45-65 mesh (212-425µm) to maintain a column to particle diameter ratio of approximately 10-20 to avoid channeling and pressure drop. Also before impregnation, the β-SiC support was divided into three synthesis method groups. All three treatments underwent a nitric acid wash to remove metallic impurities. The nitric acid wash alone treatment is referred to as non-calcined SiC. The other two treatment groups underwent calcination in static air at either 800°C for two hours or 1000°C for eight hours prior to impregnation (Calc SiC 2h800C and Calc SiC 8h1000C). The purpose of this calcination is to provide –OH anchoring sites for the ruthenium during synthesis [1, 2]. The non-calc SiC possesses a surface of disorganized SiCₓOᵧ species, and the calcined SiC have an increasing thickness of SiO₂, predicted to be approximately 20 and 60µm thick determined by mass gain during thermal gravimetric analysis calcining measurements. The pure phase rutile and anatase titania were purchased as a fine powders (SBET=13 m² g⁻¹ and SBET=5 m² g⁻¹, respectively). Due to the low surface area of the titania powders, they were synthesized using wetness impregnation by stirring the Ru precursor with the TiO₂ powder at 80°C for 2 hours, dried overnight, crushed and sieved to the same mesh size as the alumina and SiC catalysts. Following
ruthenium impregnation and drying, all catalysts were calcined at 300°C in static air to decompose the precursor.

**Reactor Setup**

The catalysts were tested in a down flow, quartz reactor at 325°C with a GHSV of 33000 h\(^{-1}\) and a stoichiometric ratio of H\(_2\) to CO\(_2\) (4:1). The catalyst underwent in-situ reduction for 30 minutes at 300°C prior to the reaction. To maintain constant bed height and shape, 35mg of each catalyst was mixed with 165mg inert alumina powder the same size as the catalyst. The inner diameter of the reactor was 0.37cm, and the bed height was 2.6cm. The bed was supported by a glass wool plug held by three dimples at the midpoint of the reactor (Figure 2-1).

![Figure 2-1](image)

*Figure 2-1 A close up image of the reactor bed showing the glass wool resting on the dimples and supporting the catalyst and inert alumina mixture.*

Reactant gases were fed to the reactor using Bronkhorst El-Flow mass flow controllers. The gas entered the bed at atmospheric pressure with no pressure drop (Figure 2-2). An Omega i-
Series PID maintained the bed temperature using heat tape and monitoring via a thermocouple placed on the outer wall at the center of the reactor bed and secured by an aluminum heat sink (Figure 2-3).

![Image](image_url)

Figure 2-2 *The down flow quartz reactor is fixed in stainless steel tubing with Cajon fittings. A pressure gauge upstream ensures there is not pressure drop across the reactor, and a condenser removes water from the stream prior to GC analysis.*

The reactor product stream was measured by a SRI gas chromatograph (GC) with molesieve 13X and silica gel packed columns in series to detect CH$_4$, N$_2$, CO$_2$, and CO. The only reaction byproduct detected by the GC was carbon monoxide.
Characterization

Characterization of the catalysts was carried out on the synthesized catalysts. X-ray Powder Diffraction (XRD) (PANalytical Cu anode, 40 mA, 45 kV) and hydrogen chemisorption (Micromeritics 2020C) were used to determine ruthenium particle size. The surface area was measured using nitrogen physisorption with multi-point BET analysis (Micromeritics 2020), and temperature programmed reduction (TPR) (20mg, Micromeritics 2920, 10°C min^{-1}) was used to determine trends in reduction temperature for the supported ruthenium particles.
Activity Calculations

The carbon dioxide turnover frequency (TOF) was calculated as the moles of reacted carbon dioxide per mole of ruthenium active sites per second. The ruthenium loading was normalized by the relative area under the TPR curve, and active site dispersion was calculated by hydrogen chemisorption.

Carbon Dioxide Conversion

Because the GC was not able to detect hydrogen, nitrogen was used as an internal standard as it does not interfere with the reaction or any of the GC peaks. A 5ml min$^{-1}$ stream of N$_2$ was fed into the reactor with the reactant gases for this purpose. For GC peak analysis, the total flow was calculated using the nitrogen peak (Equation 2.1), then conversion was calculated by comparing the carbon dioxide flow rate out of the reactor with that entering the reactor (Equation 2.2). Finally, the turnover frequency was calculated based on the number of moles of carbon dioxide converted per number of moles of ruthenium active sites (Equation 2.3).

\[
F_{tot,prod} (mL \cdot min^{-1}) = \frac{F_{N_2,in}}{\%N_2,prod} \tag{2.1}
\]

\[
CO_2 \ Conversion \ (%) = \left(1 - \frac{\%CO_2,prod \times F_{tot,prod}}{F_{CO_2,in}}\right) \times 100 \tag{2.2}
\]

\[
TOF_{CO_2} = \frac{n_{mol \ converted \ CO_2}}{n_{mol \ Ru \ exposed \cdot s}} \tag{2.3}
\]

Methane Selectivity

The methane selectivity was calculated by dividing the percent methane in the product stream by the total products (methane and carbon monoxide) as shown in Equation 2.4.

\[
Methane \ Selectivity \ (%) = \frac{\%CH_4,prod}{\%CH_4,prod + \%CO,prod} \times 100 \tag{2.4}
\]
References


CHAPTER 3. SILICON CARBIDE AS A UNIQUE PLATFORM FOR ISOLATING EFFECTS OF SUPPORT THERMAL CONDUCTIVITY ON CARBON DIOXIDE REDUCTION CATALYSTS

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Abstract

The conversion of carbon dioxide to methane can assist in the transition to renewable energy by serving as a carbon-neutral means of storing and transporting energy from wind and solar energy using the existing natural gas infrastructure. Applying the reaction to crewed space exploration allows for in-situ fuel production on Mars, oxygen recovery from metabolic carbon dioxide, and safe disposal of waste on long-duration missions. The high exothermicity and reactor temperatures required for this reaction have made catalyst stability an issue. This study explores the extent to which catalyst deactivation is exacerbated by the formation of local hot spots developed on the surface of the catalyst particles due to insufficient support thermal conductivity. Silicon carbide was used as a unique platform for this work; the support thermal conductivity was tuned prior to catalyst impregnation by oxidizing the outer layers to silicon dioxide. Increasing the silica content of the support decreases its thermal conductivity. The catalysts were characterized by XRD, SEM/EDS, nitrogen chemisorption, TEM, and hydrogen chemisorption to ensure activity results were not influenced by variables other than support thermal conductivity. Decreasing the thermal conductivity of the support greatly impacts the selectivity of the catalyst for this exothermic reaction, indicating an elevated surface temperature exists. A reduction in the support thermal conductivity by 20 W m\textsuperscript{-1} K\textsuperscript{-1} reduced methane selectivity by approximately 15\% for Ru/Calcined Silicon Carbide. The results are supported by a modeling study of the catalyst particle and a longevity test.
Introduction

The Earth has entered the Anthropocene era, a time period marked by rapid environmental changes caused by human activity [1, 2]. Global warming ranks as a chief concern as levels of greenhouse gases in the atmosphere continue to rise. Mitigating human-caused environmental impact necessitates a reduction of CO$_2$ production by using renewable, clean energy generation for electricity instead of fossil fuels. Currently, electricity production accounts for over 28% of the greenhouse gas emissions in the U.S. [3]. Fortunately, solar and wind energy generation is growing rapidly as the cost of renewable energy from these sources falls, but these energy sources experience intermittent availability and are frequently produced far from population centers. These challenges require the implementation of large-scale energy storage and transportation [4]. A process called power-to-gas provides a compelling solution that can be implemented in the near-term. This process splits water to produce hydrogen during peak energy production. The hydrogen then reduces carbon dioxide to methane, which can be transported, stored, and burned using the existing natural gas infrastructure to create carbon-neutral electricity on demand.

In addition to this terrestrial application, NASA is targeting CO$_2$ conversion to methane, the Sabatier reaction, for applications in space to enable human exploration of the solar system. One such application seeks to produce rocket fuel on the surface of Mars to return a crewed or sample-return mission from the planet. The reaction will produce methane from the carbon dioxide in the Martian atmosphere thereby reducing mission costs by eliminating the need to transport fuel for a return vehicle from Earth. Each mission will require the remote operation of a reactor for 16 months to produce 7 tons of methane [5].

The Sabatier reaction can also be applied to synthesize fuel from waste produced during long-duration, crewed missions using the Orbital Syngas/Commodity Augmentation Reactor
(OSCAR), an emerging technology being developed at Kennedy Space Center (KSC) [6]. In OSCAR, all the waste generated by the crew, such as food packaging, clothing, and washcloths, is processed through a high temperature plasma zone where the waste ionizes and forms syngas. This syngas is composed of hydrogen, carbon dioxide, carbon monoxide and methane. The CO and CO$_2$ in this output stream can be reduced to CH$_4$ via the Sabatier reaction to produce a valuable fuel from nuisance waste, while also decreasing waste volume and odor and increasing sanitation. The heat of the plasma arc allows for the safe disposal of biohazards including human waste and medical supplies. The micro-scale plasma arc gasifier is applicable to all long-duration human exploration systems, including the International Space Station and human habitation on the moon or Mars, eliminating solid waste pollution of other planets. These two NASA projects are based on the reaction’s legacy aboard the International Space Station, where it recycled oxygen from metabolic CO$_2$ collected from the crew cabin via water formation and electrolysis for seven years, though it regularly required crew time for repairs and was decommissioned in 2018 [7].

For terrestrial and space applications, the reliability of the Sabatier catalytic reactor is crucial. In order to design a catalyst for peak performance and longevity, the factors that affect catalyst performance must be fully understood. For the above applications, the Sabatier reaction converts carbon dioxide into methane and water in a highly exothermic reaction (Equation 1).

$$\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{\text{rxn}} = -165 \text{ kJ mol}^{-1}$$

(1)

The carbon dioxide molecule is incredibly stable, so the reaction typically requires high temperatures to overcome the kinetic barrier and reach reasonable reaction rates. However, conversion and selectivity are thermodynamically favored at lower temperatures as shown in
Figure 3-1. The main competing reactions, the reverse water gas shift and steam reforming [8], produce CO and decrease methane selectivity, especially at elevated temperatures.

![Figure 3-1](image)

Figure 3-1 *The thermodynamic equilibrium composition of a Sabatier reaction at varying temperatures given a stoichiometric feed of H$_2$ to CO$_2$ (4:1).*

A great deal of work has gone into studying CO$_2$ valorization with most recent attention focusing on electrochemical and thermochemical conversion. Electrochemical reactions offer milder conditions and an array of products including CO, methanol, formates, and C$_1$-C$_3$ hydrocarbons, but they typically suffer from low selectivity to methane, low CO$_2$ solubility, and high overpotentials [9-11]. Thermochemical conversion with heterogeneous catalysts have also been studied extensively on a wide range of catalysts and supports. In general, recent studies have reported high selectivity and conversion at a relatively narrow set of operating conditions, typically 250-450°C with stoichiometric or hydrogen-rich feed ratios using single and bimetallic...
catalysts consisting of Ni, Ru, Fe, Co, and Rh on oxide supports [12-16]. However, reactor temperature control and catalyst deactivation are major hurdles to the use of the thermal catalytic conversion of CO$_2$ for NASA applications and on an industrial scale. For example, at NASA’s Kennedy Space Center (KSC), a Mars atmosphere conversion reactor is currently undergoing testing. A packed bed reactor containing 0.5wt% Ru/γ-alumina catalyst underwent deactivation after approximately 110 hours on stream (figure 2 figure catalyst pictures from KSC). The

![Catalyst Images](image)

**Figure 3-2** The 0.5%Ru/γ-alumina catalyst pellets used in the Mars atmosphere conversion Sabatier reactor at Kennedy Space Center. The unused catalyst (left) changes in appearance drastically following deactivation in the reactor (right).

deactivation occurred after high flow testing during which the bed temperature reached nearly 600°C (an increase 200°C above the nominal reaction temperature) [17]. Despite this drawback, NASA has decided to pursue the thermochemical conversion route for a number of reasons. One is the legacy for the reaction aboard the ISS; the packed-bed reactor offers a straight-forward conversion process without moving parts that can potentially operate without user interaction in zero gravity. Another is that the approaching Mars mission dates do not allow for development of new processes. Also, the exothermicity of this reaction can be used to create an autothermal reactor, a trait especially useful for space applications where power availability is limited. Even with all that is known about the Sabatier reaction, a greater understanding of catalyst properties is required to ensure catalyst longevity for the timespans of the missions mentioned previously
while maintaining high conversion and selectivity to allow for a compact system with minimal product stream processing.

Like the reactor at KSC, much of the recent work on Sabatier catalysts has been done using oxide supports including alumina, zeolites, titanium oxide, silica, and cerium oxide [15, 18-24]. The catalyst support affects the reaction in many ways e.g. by providing a surface for CO$_2$ adsorption, allowing hydrogen spillover, stabilizing the active phase to increase dispersion and avoid sintering, and affecting conversion rates and selectivity through electronic metal support interactions. In general, alumina and titania have been found to be among the most effective supports for the reaction, which is attributed to metal support interactions (MSI) improving active phase dispersion and carbon dioxide adsorption on the support surface [21, 25, 26].

Much work on studying metal oxide supports is aimed at improving catalyst longevity by determining a catalyst systems capable of lowering the kinetic barrier in order to operate the reactor at lower temperatures. Regardless of the operating temperature, the exothermic Sabatier reaction will inevitably produce a great deal of heat at high conversion, so temperature control and heat removal must be considered. Silicon carbide has gained interest in recent years because of its excellent physical characteristics including high thermal conductivity (TC), and the development of a novel synthesis technique that allows for reliable production of the support with a surface area and surface morphology similar to typical oxide supports [27-29].

The use of silicon carbide can benefit a Sabatier reactor by using its exceptional thermal conductivity to pull heat from the catalyst metal particles during the reaction. It can provide physical strength to prevent physical degradation during taxing lift off and landing events. Also, its low thermal expansion will prove useful during the anticipated temperature changes the
Sabatier reactor will go through in space, on the Martian surface, and during reaction conditions [27]. However, first it must be determined if SiC can function as an appropriate catalyst support to carry out the reaction.

To this end, a preliminary study was carried out to determine SiC performance as a support compared to alumina and titania (Preliminary Study). Gamma alumina is the benchmark support as it is undergoing testing at KSC, and TiO$_2$ is a support widely recognized to improve Ru performance for the reaction [19, 30, 31]. The SiC supported catalyst performed as well as the traditional oxide supports with comparable conversion and selectivity. Exactly why the catalysts have similar performance is not entirely clear, because SiC lacks the beneficial metal support interactions exhibited by the oxide supports. However, it is likely related to the high thermal conductivity of silicon carbide drawing heat away from the ruthenium particles and avoiding hot spots to boost SiC performance compared with the low thermally conductive oxides. We hypothesize that support thermal conductivity plays a vital role in catalyst activity for exothermic reactions and that insufficient support thermal conductivity results in elevated catalyst surface temperatures greater than the overall bed temperature. To test this hypothesis, β-SiC was used in an innovative way as a platform to carry out a study on effects of support thermal conductivity. SiC has the unique feature of a tunable thermal conductivity, which can be adjusted by calcining the support in air at high temperatures. This treatment oxidizes the outer layers of the SiC to SiO$_2$ (a natural washcoat), and the thickness of the SiO$_2$ layer is related to the duration of the calcining treatment (Equation 2). SiO$_2$ has a much lower thermal conductivity than SiC, so the greater the fraction of SiO$_2$ in the support composition, the lower the thermal conductivity. This alteration of TC does not affect the morphology of the SiC,
meaning the surface area, chemical environment of the surface, and mass transport for the reaction are constant.

Several catalytic metals including nickel, iron, cobalt, rhodium, and ruthenium are active for this reaction [32-36]. A majority of recent studies examine Ni-based catalysts, because nickel is an active and selective catalyst with a much lower cost than precious metals, like ruthenium. The drawbacks are that nickel requires much higher loading and is more prone to sintering and coke formation [37-39]. The space Sabatier applications necessitate the most active and durable catalyst in order to design a compact, reliable reactor, and ruthenium is widely recognized as the most active catalyst for the reaction [16, 36, 40-42]. This work will study ruthenium as the catalyst and attempt to further improve its performance and more completely understand support effects for the Sabatier reaction, specifically to determine the effect of support thermal conductivity on catalyst performance for highly exothermic reactions. In order to isolate and study the effects of support thermal conductivity, this study will eliminate other variables that impact activity including variation in MSI, catalyst particle size, transport effects, and support surface area. We believe that increasing thermal conductivity of the support (even in a powder form) will reduce the formation of localized hotspots at the catalyst particle thereby increasing selectivity as predicted by thermodynamics.

**Experimental**

**Catalyst Preparation**

The β-SiC (SICAT extruded pellet) was ground with an agate mortar and pestle to 250-300μm (50-60 mesh). A tight sieve fraction was used to maintain constant support characteristics (i.e. weight percent SiO₂ after calcination) from one particle to the next. The SiC was then washed in nitric acid overnight and rinsed to a neutral pH with nanopure water to remove metallic contaminants.
Following the washing procedure, the SiC was dried at 110°C for 72 hours then calcined at 1000°C to oxidize the outer layer of SiC to SiO$_2$. The calcination took place in a Lindberg/Blue tube furnace for a specified amount of time, 1, 2, 4, 8, or 36 hours under 200 ml min$^{-1}$ synthetic air. The calcined SiC was loaded with five weight percent ruthenium over six serial incipient wetness impregnations using a ruthenium nitrosyl nitrate solution in pH 4 nitric acid water (Alfa Aesar crystalline ruthenium nitrosyl nitrate (Ru 31.3% min)). The samples were dried overnight at ambient conditions between impregnation rounds. Subsequent to the final impregnation, the 5%Ru/Calcined SiC catalysts were calcined at 250°C in 200 ml min$^{-1}$ synthetic air to decompose the precursor followed by ex-situ reduction for two hours at 400°C in 200 ml min$^{-1}$ hydrogen. The catalysts were cooled in nitrogen to ambient before exposure to air to limit bulk ruthenium oxidation.

**Characterization**

Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS) was carried out using both a Joel JSM-7500F Field Emission SEM and a Zeiss EVO 50 SEM with Oxford AZtec X-MAXN EDS. The composition of each catalyst was collected by averaging EDS scans taken from two high-point locations on five different particles for each catalyst. Before and after reaction, each catalyst was scanned by X-ray Powder Diffraction analysis (XRD: PANalytical – Empyrean, step size: 0.01°, counting time: 29s per step, anode material: Cu, generator settings: 40 mA, 45 kV). The resulting diffractograms were used to calculate Ru particle size using the Debye-Scherrer method at the following Ru (JCPDS 00-006-0663) 2θ angles, 44°(101), 58°(102), 68°(110), and 78°(102).

A Micromeritics 2020c was used to measure the hydrogen adsorption volume (assuming dissociative adsorption) to determine active phase dispersion [43]. Catalyst samples weighing
60-100mg were placed in a u-shaped quartz tube, degassed at 200°C under He, pre-reduced at 400°C for 30 min followed by 2 hours of evacuation. Isotherms were collected under H2 at 35°C.

For transmission electron microscope (TEM) preparation, samples were ground to a fine powder and sonicated in ethanol for 5 minutes. A 10μL drop of solution was dispersed on a 200 mesh carbon film with copper grid. Imaging took place in a 200kV JEOL 2100 Field Emission transmission electron microscope with a LaB₆ cold emitter. A minimum of 200 particles were measured for the particle size distribution.

The surface area was determined using a Micrometics ASAP 2020 using multiple point N₂ analysis at 77K with Brunauer–Emmett–Teller (BET) calculations in a relative pressure range of 0.065-0.2. The BJH Desorption dV/dlog(D) Pore Volume values were used for pore size distribution.

Temperature programmed oxidation (TPO) and temperature programmed reduction (TPR) took place in a Micromeritics 2920 using 20 mg of catalyst packed with glass wool in a u-shaped quartz tube. For both analyses, the sample was dried under helium at 120°C for 30 min followed by analysis. The outlet stream was measured by TCD during a 10°C min⁻¹ ramp to 850°C. For TPO, the analysis took place under 50 ml min⁻¹ 10%O₂/He. TPR was carried out on the same catalyst sample following TPO using 20 ml min⁻¹ 10%H₂/Ar during analysis.

**Methanation Reaction**

The reaction took place at atmospheric pressure with no pressure drop across the bed. The reactor bed consisted of a 15 cm long quartz tube with a 3.7 mm inner diameter with three dimples at the midpoint to support a plug of quartz wool on which rested the catalyst bed. The dimples were designed so as not to constrict air flow. Cajon fittings attached the reactor bed in a down flow reactor otherwise fitted with stainless steel tubing. A thermocouple was secured on the outer wall of the reactor at the catalyst bed center by an aluminum heat sink. Heat tape
controlled by an Omega i-series PID temperature controller surrounded the heat sink and maintained a constant bed temperature. A condenser located directly below the reactor and cooled by a 5°C chilled water loop removed water from the product stream prior to analysis.

The reactant gases consisted of 120 ml min\(^{-1}\) H\(_2\) and 30 ml min\(^{-1}\) CO\(_2\) with 5 ml min\(^{-1}\) N\(_2\) as an internal calibration for GC measurements. All gases were 99.999% purity and controlled by Bronkhorst El-Flow Select flow controllers calibrated with an Agilent ADM 1000 Universal Flowmeter. The reactor bed was made of 35mg catalyst (50-60 mesh) and 165mg inert γ-Al\(_2\)O\(_3\) (40-45 mesh) in a uniform mixture. The alumina was added to the catalyst in order to maintain bed height and shape among reactor beds. The product stream was measured using a GC SRI 8610 C Multi-gas #1 configuration with TCD detector, 10-port sampling valve and loop, and two packed columns in series containing molecular sieve 13X and silica gel, respectively, capable of detecting N\(_2\), CO, CH\(_4\), and CO\(_2\).

The catalysts were reduced in-situ at 300°C under 120 ml min\(^{-1}\) H\(_2\) and 5 ml min\(^{-1}\) N\(_2\) for 30 minutes prior to the reaction. The temperature was then changed to the desired set point and stabilized prior to introducing carbon dioxide. For the activity reaction runs, the temperature set point was 325°C. These reaction conditions were selected to maintain conversion below 30% to reduce transport effects. Arrhenius plots for each catalyst using the initial turnover frequency at four temperatures between 292-340°C for each catalyst were used to calculate the activation energies.

**Modelling Study**

An energy balance was carried out on a singular catalyst support and catalyst particle from within the bed to predict the temperature gradient from the center of the support to the surface where the ruthenium catalyst is located. The model assumed a spherical, radially symmetric catalyst particle with 1-D heat flow, and a uniform heat generation throughout the
particle based on TOF data and active ruthenium sites calculated from 5wt% ruthenium loading corrected by dispersion measurements. The boundary conditions were an adiabatic particle center with the temperature equal to that of the reactor bed and heat loss through convection to the gas flowing at an average velocity based on the reactor cross section. Heat transfer within the particle was calculated using a heat conductivity of 100 W m\(^{-1}\) K\(^{-1}\) for the silicon carbide core and 1.4 W m\(^{-1}\) K\(^{-1}\) for the SiO\(_2\) with the support composition (SiC:SiO\(_2\)) calculated from TGA measurements. Matlab was used to solve the energy balance and construct the temperature gradient graphs.

### Results and Discussion

#### Preliminary Study

Gamma alumina, phase pure rutile TiO\(_2\), and SiC were ground into powders and impregnated with 5wt% ruthenium using ruthenium nitrosyl nitrate as the precursor. The catalysts had comparable ruthenium particle sizes but varied in reduction temperature, surface area, and thermal conductivities (Table 3-1).

**Table 3-1 Catalyst characterization from preliminary study.**

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Ru Particle Size</th>
<th>SA (m(^2)/g)</th>
<th>Thermal Conductivity (W/mK)</th>
<th>Initial reduction temperature (°C)</th>
<th>Peak reduction temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Ru/Y-Al(_2)O(_3)</td>
<td>9.0</td>
<td>195</td>
<td>25</td>
<td>90.5</td>
<td>151.7</td>
</tr>
<tr>
<td>5%Ru/Non-Calc SiC</td>
<td>10.2</td>
<td>35</td>
<td>100</td>
<td>55.0</td>
<td>84.1</td>
</tr>
<tr>
<td>5%Ru/TiO(_2)-Rutile</td>
<td>11.9 /</td>
<td>5</td>
<td>11</td>
<td>82.9</td>
<td>114.9</td>
</tr>
</tbody>
</table>

Activity tests took place in a down flow, packed bed reactor with a stoichiometric flow of H\(_2\) to CO\(_2\), a GHSV of 33000h\(^{-1}\), and a reaction temperature of 325°C. The SiC supported catalyst performed as well as the traditional oxide supports with comparable conversion and selectivity (Figure 3-3). The exact reason for its commensurate performance is not entirely understood, but it can likely be attributed to its high thermal conductivity drawing heat away
from the ruthenium particles and avoiding detrimental hot spot formation on the particle surface. While the heat conduction from one powder particle to the next within the reactor is negligible [44, 45], the high thermal conductivity of each particle distributes heat from the active metal sites to the entire volume of the particle where convective heat exchange with the gas flow can take place over the total surface area of the support particle. Although the oxide supports assist in adsorbing CO$_2$ and through metal support interactions, their much lower thermal conductivity (TC) likely results in localized hot spots surrounding the ruthenium particles caused by the reaction heat production.

![Performance of CO$_2$ methanation over 5%Ru supported catalysts. Error bars represent variation among three repeated runs.](image)

**Catalyst Characterization**

The goal of this work was to isolate the effect of support thermal conductivity on catalyst activity for the exothermic Sabatier reaction. In order to do this, all variables that could affect activity other than support thermal conductivity must be constant among all the catalysts. The catalyst characterization shows that the average ruthenium particle size, the surface chemical
environment, the support pore size and surface area, and the ruthenium loading are constant among the synthesized catalysts.

To determine the amount of SiO\textsubscript{2} growth on the calcined silicon carbide supports, thermal gravimetric analysis (TGA) was used to measure the mass gain of the support during calcination in air at 1000°C for 48 hours (Figure 3-4). During the initial temperature ramp, the SiC lost mass. The mass spectrometer (MS) signal showed only carbon dioxide in the outlet during this time, and it is believed that some carbonaceous species remaining from the SiC synthesis process were burning off [46]. When the TGA reached the target temperature of 1000°C, the SiC support quickly increased in mass as the surface layers were oxidized to SiO\textsubscript{2}. Again, during this period, the only product measured by MS was carbon dioxide. After four hours of calcination, a passivation layer developed on the surface greatly decreasing the rate of oxidation. Support calcination times of 1h, 2h, 4h, 8h and 36h were selected to examine the effects of a range of oxide thicknesses on the reaction. The SiO\textsubscript{2} thicknesses and thermal conductivities were determined from the percent mass of SiO\textsubscript{2} for each support particle based on the mass gain measured by TGA (Figure 3-4).

![Figure 3-4](Figure_3-4.png)

**Figure 3-4** Thermal gravimetric analysis of silicon carbide undergoing calcination in air over 48 hours. The silicon dioxide layer thickness and thermal conductivity calculated from mass gain during calcination.

\[
\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2
\]

\[
\frac{M_{\text{SiC}}}{\text{mol}} = 40 \text{ g/mol}
\]

\[
\frac{M_{\text{SiO}_2}}{\text{mol}} = 60 \text{ g/mol}
\]
From low magnification SEM images, the general morphology of the catalyst surface is constant across all SiC catalysts (Figure 3-5). From the EDS scans, the average Ru loading is constant, whereas the carbon content decreases and oxygen content increases as the oxidation time of the SiC support increases demonstrating the surface conversion of SiC to SiO$_2$ (Figure 3-6). While inductively coupled plasma (ICP) analysis is possible with catalysts on SiC [47], we were unable to obtain reliable data due to the chemical inertness of SiC resulting in the inability to digest it for ICP sample preparation. Therefore, the loading was assumed to be uniform across all catalysts at 5wt% based on the EDS measurements.

Figure 3-5 Surface morphology of 5%Ru/Calcined SiC supports. Upper level left to right: 1h, 2h, 4h, and lower left to right 8h, 36h. Joel JSM-7500F Field Emission SEM WD 8mm, 15.0kV, 2700x.
Figure 3-6 Catalyst composition collected by Oxford AZtec X-MAXN EDS.

The XRD spectra for all the catalysts are very similar with the only exception being the 22° peak representing SiO₂, which increases in intensity with the increase in calcination time (figure 5 figure of XRD spectra), and there are no unexpected peaks. The Ru particle size

Figure 3-7 XRD spectra of 5%Ru catalyst supported on a) Calcined SiC 1h 1000C, b) Calcined SiC 2h 1000C c) Calcined SiC 4h 1000C, d) Calcined SiC 8h 1000C, e) Calcined SiC 36h 1000C. Peaks associated with SiC (★), Ru (○), SiO₂ (●), and RuO₂ (●) are marked.
calculated by the Debye-Sherrer equation using XRD data and from H₂ chemisorption show constant average Ru particle size of 20nm across all catalysts (Table 3-2). The particle size of the Ru is large (likely resulting from the serial impregnation synthesis) but consistent, which allows us to rule out particle size effects in the comparison of catalyst performance (Table 3-2). From the XRD data, the ruthenium particle size did not change following reaction at 325°C.

Table 3-2 Ruthenium particle size collected by hydrogen chemisorption and XRD (before and after 325°C reaction) and surface area found by nitrogen physisorption for all tested catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru particle size (nm)</th>
<th>BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂ Chemi</td>
<td>XRD Unused</td>
</tr>
<tr>
<td>5%Ru/CaSiC 1h1000C</td>
<td>19.9</td>
<td>23.4</td>
</tr>
<tr>
<td>5%Ru/CaSiC 2h1000C</td>
<td>23.3</td>
<td>20.9</td>
</tr>
<tr>
<td>5%Ru/CaSiC 4h1000C</td>
<td>21.3</td>
<td>21.9</td>
</tr>
<tr>
<td>5%Ru/CaSiC 8h1000C</td>
<td>23.3</td>
<td>22.2</td>
</tr>
<tr>
<td>5%Ru/CaSiC 36h1000C</td>
<td>21.2</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Considerable variation in Ru particle size is exhibited by the TEM images (Figure 3-9). Even with the vigorous grinding during TEM sample preparation, the particles exhibit multiple layers of SiC and ruthenium making it difficult to differentiate ruthenium particles. The size distribution was collected from the distinct
ruthenium particles and shows the particles are rather large, with nearly all of them existing at larger than 2nm in diameter. It is generally accepted that catalyst particles of greater than a few nanometers in diameter do not experience MSI on a scale that would affect activity, and prior work has shown that particle size effects are minimal for this reaction at temperatures greater than 200°C [48]. With such large average particle size and the fact that all the supports are coated in SiO₂, it is unlikely that MSI impacted the results; however, TPO and TPR were carried out on the catalyst to ensure that this was the case.
All catalysts show a similar oxidation pattern with the ruthenium reaching maximum oxidation at approximately 560°C (Figure 3-8). The extent of oxidation was not quantified, so it is unknown if the entirety of the large ruthenium particles were fully oxidized during this process. The support oxidizes slightly at approximately 650°C, the region marking the SiC to SiO$_2$ transformation seen in TGA. A single, narrow reduction peak located near 115°C for all catalysts indicates the chemical environment for the ruthenium was constant among the supports [49, 50], limiting the possibility of metal support interactions or Ru particle size distribution affecting activity results. Also, the in-situ reduction at 300°C for 30 min prior to the reaction is sufficient to fully reduce the catalysts based on these results. The bump at 435°C can be attributed to a slight reduction of the SiC/SiO$_2$ support as seen in Figure 3-8. These TPO and TPR results show a singular relationship between the support and catalyst.
The final variable that was controlled in this study was the surface area, which can influence activity via MSI [19] and by affecting mass and heat transport. Based on nitrogen physisorption and BET analysis, the catalysts exhibit a slight decrease in surface area as the calcination time of the SiC support increased (Table 3-2). The pores in the support are predominantly well above the micropore region as seen in the pore size distribution graph from the 5%Ru/1hSiC, 5%Ru/8hSiC, and 5%Ru/36hSiC (Figure 3-10). The pore size distribution remains constant for the catalysts until 36 hours of calcination. The loss of smaller pores could affect the transport properties of this reactor, although all the catalysts show a low surface area and large pore diameters, minimizing the variation among the catalysts and their effects on activity.

Figure 3-10 Pore size distribution of a) 5%Ru/Calcined SiC 1h 1000C, b) 5%Ru/Calcined SiC 8h 1000C, and c) 5%Ru/Calcined SiC 36h 1000C determined by BJH desorption.
Activity Tests

The activity tests show that selectivity decreases as the SiO$_2$ thickness increases as anticipated (Figure 3-11). The higher thermal conductivity of the support particles with lower SiO$_2$ content helps distribute heat produced at the ruthenium particle throughout the support allowing for a larger area of heat exchange via convection to the flowing gas, reducing surface temperature/localized hot spots. Lower temperatures are favored thermodynamically for the reaction as higher temperatures introduce side reactions that produce CO and decrease selectivity. The activity for the 5%Ru/Calc SiC 1h1000C and 5%Ru/Calc SiC 2h 1000C catalysts is nearly identical, as expected by the small difference in the SiO$_2$ layer thickness between the two treatments, while the decrease in selectivity becomes quite exaggerated as the calcination time and SiO$_2$ layer thickness increases to the 5%Ru/Calcined SiC 36h1000C catalyst.

The turnover frequency for the catalysts is relatively stable across the catalysts regardless of the SiO$_2$ thickness (Figure 3-11). This can be explained by the fact that this exothermic reaction is affected by temperature positively and negatively. Because of the stability of CO$_2$ molecules, the reaction is kinetically limited at low temperatures, but Le Chatelier's principle dictates that conversion decreases at high temperatures for exothermic reactions. The conversion is thus caught between two competing effects, remaining constant across the tested catalysts as the surface temperature varies.

Figure 3-11 also shows the thermodynamic equilibrium conversion and selectivity for this reaction in the range of 500-600°C found by minimizing Gibbs free energy. Over this temperature range, selectivity drops dramatically, and CO$_2$ conversion stays relatively constant as CO$_2$ conversion shifts to CO production. Overlaying the experimental results for selectivity shows a nearly identical pattern between the experimental results and thermodynamic equilibrium. This further supports that a decrease in support thermal conductivity increases
localized hot spots, and the resulting elevated surface temperatures detrimentally affect catalyst performance.

The apparent activation energies calculated for each catalyst fall in a range between 60 and 80 kJ mol$^{-1}$ (Table 3-3). Due to limitations regarding the GC, samples could be taken only every 20 minutes, so it was difficult to accurately capture the initial reaction rate, leading to some variation in the Arrhenius plot slopes that is unlikely reflective of actual differences. The activation energy calculations provide some evidence that the chemical environment for the Ru metal is constant among all the catalysts, and thus variation in MSI is not a contributing factor to the trend in selectivity seen during the activity testing. The apparent activation energies for Ru/Calc SiC in this study average to around 70 kJ mol$^{-1}$, which agrees well with the value calculated by Weatherbee and Bartholomew [35] who found an activation energy of 72 kJ mol$^{-1}$ for Ru/SiO$_2$. Apparent activation energies ranging from 60-100 kJ mol$^{-1}$ have been reported for supported Ru catalysts in the literature, which is a wide distribution but does agree well with our findings [24, 30, 34, 40, 51]. It is difficult to draw conclusions about reaction path based on the
apparent activation energies. Catalysts like Ru/Alumina and Ru/SiO$_2$ have been reported to have the same reaction pathway based on surface properties, specifically the absence of oxygen vacancies where CO$_2$ can be adsorbed and transformed to formate intermediates. The assumed rate limiting step of this pathway is the direct dissociation of CO$_2$(ads) to CO$_2$(ads) [18, 52].

From the XRD data showing no change in Ru particle size following reaction and the constant conversion displayed during reaction runs up to 15 hours long, it appears as though SiO$_2$ provides reasonable anchoring for the ruthenium particles to prevent sintering during reaction. Many researchers perform an oxidation treatment on the SiC prior to metal impregnation to provide hydroxyl group anchoring sites [53, 54]. While a higher thermal conductivity of the support appears to benefit the catalyst, caution must be taken to ensure the surface is still able to support the active metal. The calcination treatment of the SiC support must ensure both ample metal anchoring and high thermal conductivity.

Table 3-3 Tabulated values for activation energy, carbon dioxide turnover frequency, and methane selectivity for the 5%Ru/Calcined SiC catalysts tested.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>325°C TOF$_{CO_2}$ (s$^{-1}$)</th>
<th>325°C CH$_4$ Selectivity (%)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Ru/Calc SiC 1h1000C</td>
<td>2.7±0.03</td>
<td>85.8±0.37</td>
<td>79</td>
</tr>
<tr>
<td>5%Ru/Calc SiC 2h1000C</td>
<td>3.3±0.06</td>
<td>86.2±0.40</td>
<td>82</td>
</tr>
<tr>
<td>5%Ru/Calc SiC 4h1000C</td>
<td>2.7±0.04</td>
<td>84.4±0.72</td>
<td>74</td>
</tr>
<tr>
<td>5%Ru/Calc SiC 8h1000C</td>
<td>2.8±0.09</td>
<td>80.0±0.62</td>
<td>61</td>
</tr>
<tr>
<td>5%Ru/Calc SiC 36h1000C</td>
<td>2.3±0.06</td>
<td>70.7±0.67</td>
<td>72</td>
</tr>
</tbody>
</table>

Lastly, a longevity study was carried out on the 5%Ru/Calc SiC 1h and 5%Ru/Calc SiC 36h catalysts, during which the reactors were operated for 96 hours continuously using the same reaction conditions as previously described. The 5%Ru/Calc SiC 1h experienced a smaller decrease in selectivity over the longevity test than the 5%Ru/Calc SiC 36h catalyst. The 36h
catalyst showed a higher stability in the conversion over the same time span, which may have resulted from the overall conversion for the 36h catalyst being near the level of detection for the gas chromatograph. The 1h calcined catalyst exhibited an overall decrease in selectivity to methane of less than 2 percent, whereas the 36h catalyst experienced a greater loss during the 96 hour test.

**Modelling Study**

The conclusions drawn from this work are also supported by a modeling study that carried out an energy balance on an individual catalyst particle from within the reactor bed. The thermal conductivity of the SiC supports was calculated using the particle composition based on the weight percent of SiO$_2$ from TGA measurements. This model predicts a temperature gradient within each catalyst particle resulting in an elevated surface temperature. The gradient is larger with higher surface temperatures on the catalysts with longer SiC support calcination times (Figure 3-12). This corroborates our hypothesis that the thicker SiO$_2$ layer lowers the thermal conductivity of the support resulting in the formation of localized hotspots on the surface of the catalyst. The model also shows that the temperature gradient throughout the particle becomes much more intense as the bed temperature (and thus the assumed temperature at the center of the particle) increases. A bed temperature increase of only 25°C (from 325°C to 350°C) increases the temperature gradient seen in the 5%Ru/Calc SiC 36h1000C catalyst by over 40°C meaning that small changes in particle temperature resulting from variation in thermal conductivity can have compounding impacts on the surface temperature, the temperature experienced by the metal particles carrying out the reaction.
Figure 3-12 Results from model of catalyst particle within reactor bed. Temperature gradient along radius from the center to the surface of a particle calculated for a bed temperature of (top) $T_\infty=325°C$ and (bottom) $T_\infty=350°C$. The largest gradient represents 5%Ru/Calcined SiC 36h 1000C and smallest is 5%Ru/Calcined SiC 1h 1000C for both bed temperature sets.

In the model, the predicted surface temperatures are much lower than those predicted by plotting the selectivity using the thermodynamic equilibrium values. This likely results from the low fidelity of the model. Further work is required to develop a model that can predict catalyst performance based on the support thermal conductivity.

**Conclusions**

This study was able to eliminate interfering variables such as catalyst metal particle size, support chemistry, surface morphology, and mass transport in order to isolate and examine the effects of support thermal conductivity on an exothermic reaction. Silicon carbide was used as a distinct scaffold for the study due to its unique ability to alter its thermal conductivity by oxidation to SiO$_2$ without altering its surface morphology. Silicon carbide was calcined in air for varying periods of time to build up silicon dioxide surface layers of increasing thickness prior to catalyst metal impregnation. By increasing the silicon dioxide proportion of the support particle composition, the thermal conductivity of the support was decreased. Decreasing the thermal
conductivity of the support appears to reduce heat transfer from the active catalyst sites to the overall volume of the particle where the heat can be dissipated via convection to the gas flow. This resulted in the formation of localized hot spots at the metal active sites, thus lowering selectivity for this exothermic reaction as predicted by thermodynamics. The effect of particle surface hot spots must be taken into account when designing catalysts and predicting outcomes for exothermic reactions.

Acknowledgements

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CHAPTER 4. FUTURE WORK

Confirm Support Thermal Conductivity Trend

The trend in thermal conductivity will be confirmed using another highly exothermic reaction that is active for this catalyst. If an increase in support thermal conductivity is effective at dispersing heat from the surface and the ruthenium particle, a similar trend in performance should be seen in another exothermic reaction. Carbon monoxide oxidation is of interest for the purpose, because the reaction has three distinct, temperature-dependent phases. The first consists of low conversion during which the temperature is insufficient to overcome the kinetic barrier for \( \text{CO}_{\text{ads}} \) activation. As the temperature increases, different reaction pathways become available, and conversion quickly increases, partly due to surface temperature increases from heat produced by the reaction. Finally, the conversion stabilizes at higher reactor temperatures [1, 2].

The 5%Ru/Calcined SiC catalysts will be tested in the same flow reactor setup as the Sabatier reaction experiments. Testing will consist of introducing the reactant gases in the flow reactor while the temperature is systematically increased. The product stream will be analyzed by the GC to monitor reaction progress. As previously mentioned, the reactor will reach specific temperature where conversion rapidly increases, this is the reaction light-off. The light-off temperature will be determined during this phase and defined as the temperature at which 50% CO conversion occurs. During the temperature ramp, localized hot spots on the surface of the catalysts should result in light-off earlier for the low TC supports, giving more validation to the hypothesis that the surface thermal environment varies greatly for exothermic reactions over catalysts with a range of support thermal conductivities.
Improve Model Fidelity

A high-fidelity model is currently under development with the goal of using reaction kinetics and heat transfer to predict conversion and selectivity for a given set of reaction conditions [3-5]. The goal is to reach a point where support thermal conductivity can be used to predict catalyst behavior for exothermic reactions. This model can also be used to estimate ideal reactor conditions and predict behavior during off-nominal operation.

Incorporate Metal Oxides to Enhance Silicon Carbide Activity

Another goal for this work is to focus on increasing catalyst activity to enhance methane production and decrease launch mass. As anticipated from results of other studies on exothermic reactions, SiC performed well for this application, but it exhibited undesirable traits, including reduced Ru dispersion and lower methane selectivity. Oxide supports have been shown to interact with ruthenium favorably to promote CO$_2$ conversion and methane selectivity, increase dispersion, and reduce sintering. Ascertaining the metal support interaction effects between the various metal oxides and ruthenium will facilitate the design of a flight-ready catalyst.

Constraints imposed by transportation and operation in outer space will be taken into account including launch mass, mechanical durability to vibrations [6], reactor thermal control, and the ability to withstand an anticipated range of off-nominal flows and temperatures. We hypothesize a hybrid structure consisting of a SiC matrix intermixed with a small amount of metal-oxide impregnated with Ru will allow us to harness the beneficial characteristics of each support [7]. The SiC will provide elevated thermal conductivity and mechanical strength [8], while the metal-oxide will enhance the activity of Ru and catalyst dispersion through metal support interaction with Ru and potentially via an alternate reaction mechanisms that takes place at the metal-support interface [9]. By immobilizing a Ru/TiO$_2$ powder onto a three-dimensional SiC structure, Shima et al. [10] were able to eliminate the temperature differential along the length of the
reactor while achieving 93% CO\textsubscript{2} conversion at 260°C. This is in contrast to the temperature in the Sabatier reactor that was used on the International Space Station, which varied almost 450°C along the length of the reactor, generating thermal stress on catalyst at the inlet [11]. Vibration testing and reaction runs at a range of flows, feed ratios, and temperatures will indicate whether the catalyst will succeed in the flight-readiness review process for space applications.

References


