Compact and Lightweight Sabatier Reactor for Carbon Dioxide Reduction

Christian Junaedi[1], Kyle Hawley[2], Dennis Walsh[3] and Subir Roychoudhury[4]
Precision Combustion, Inc., North Haven, CT, 06473

Morgan B. Abney [5] and Jay L. Perry[6]
NASA George C. Marshall Space Flight Center, Huntsville, AL, 35812

The utilization of CO_2 to produce life support consumables, such as O_2 and H_2O, via the Sabatier reaction is an important aspect of NASA's cabin Atmosphere Revitalization System and In-Situ Resource Utilization architectures for both low-earth orbit and long-term manned space missions. In the current International Space Station (ISS) and other low orbit missions, metabolically-generated CO_2 is removed from the cabin air and vented into space, resulting in a net loss of O_2. This requires a continuous resupply of O_2 via water electrolysis, and thus highlights the need for large water storage capacity. For long-duration space missions, the amount of life support consumables is limited and resupply options are practically nonexistent, thus atmosphere resource management and recycle becomes crucial to significantly reduce necessary O_2 and H_2O storage. Additionally, the potential use of the Martian CO_2-rich atmosphere and Lunar regolith to generate life support consumables and propellant fuels is of interest to NASA. Precision Combustion, Inc. (PCI) has developed a compact, lightweight Microlith®-based Sabatier (CO_2 methanation) reactor which demonstrates the capability of achieving high CO_2 conversion and near 100% CH_4 selectivity at space velocities of 30,000-60,000 hr^{-1}. The combination of the Microlith® substrates and durable, novel catalyst coating permitted efficient Sabatier reactor operation that favors high reactant conversion, high selectivity, and long-term durability. This paper presents the reactor development and performance results at various operating conditions. Additionally, results from 100-hr durability tests and mechanical vibration tests are discussed.

Nomenclature

C	=	Celcius
d	=	diameter
GHSV	=	gas hourly space velocity
Gs	=	gravity (force)
GSA	=	geometric surface area
hr	=	hour
Hz	=	hertz
in	=	inch
kJ	=	kilojoules
L	=	length
m	=	meter
ml	=	milliliter

---

[1] Research Engineer, Microlith® Products, 410 Sackett Point Rd., North Haven, CT 06473.

[2] Development Engineer, Engineering Division, 410 Sackett Point Rd., North Haven, CT 06473.

[3] Catalyst System Engineer, Microlith® Products, 410 Sackett Point Rd., North Haven, CT 06473.

[4] Director, Microlith® Products, 410 Sackett Point Rd., North Haven, CT 06473.

[5] Aerospace Engineer, Environmental Control and Life Support Systems Development Branch, Bldg 4755 Room 403-7, NASA MSFC, Huntsville, AL 35812.
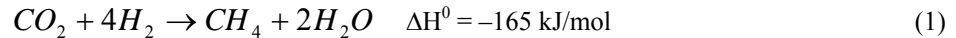
[6] Senior Engineer, Environmental Control Systems, Engineering Directorate, Space Systems Department, ECLS System Development Branch/ES62, NASA MSFC, Huntsville, AL 35812.

mol	=	mole
psia	=	pound per square inch absolute
slpm	=	standard liter per minute (21°C, 14.7 psia)
WHSV	=	weight hourly space velocity
wt %	=	percent by weight

I. Introduction

The closed-loop cabin Atmosphere Revitalization System (ARS), which includes the CO_2 Removal Assembly (CDRA), Oxygen Generator Assembly (OGA), and CO_2 Reduction Assembly (CRA), has become an integral part of NASA mission architectures for future long-duration human space exploration to the Moon and Mars.[1,2] In the current International Space Station (ISS) and other low orbit missions, the metabolically generated CO_2 is removed from the cabin air and vented into space, resulting in a net loss of O_2. This requires a continuous resupply of O_2 via water electrolysis, and thus highlights the need for large water storage.[3] For long-duration space missions, the amount of life support consumables (e.g., O_2 and H_2O) is limited and the resupply option is practically nonexistent, and thus atmosphere resource management and recycle become crucial. To achieve a complete closure of O_2 and H_2O, the CO_2 produced by metabolic processes is removed from the cabin air by CDRA and is then reacted with H_2 from OGA in a Sabatier CO_2 methanation reactor (i.e., part of CRA) to produce methane and water.[4,5] A highly efficient closed-loop ARS will result in a near complete closure of O_2, which would significantly reduce the required amount of water resupply, providing cost and logistics savings. Additionally, the use of the Sabatier process as part of the In-Situ Resource Utilization (ISRU) application for on-site production of life support consumables and propellants from Lunar and Martian regolith (i.e., CO_2 and CO from carbothermal reduction of regolith or from the Martian atmosphere) is of interest to NASA.[6-8]

In the Sabatier or CO_2 methanation process, CO_2 reacts with hydrogen in the presence of catalysts to produce methane and water, as shown in Eq. (1) below:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H^0 = -165 \text{ kJ/mol} \qquad (1)$$

Similarly, trace CO can also catalytically react with hydrogen to produce methane and water as shown in Eq. (2). Additionally, a competing reverse water gas shift (RWGS) reaction, Eq. (3), is typically present. Under certain operating conditions, CO_2 reduction via the Bosch reaction may also occur, where CO_2 reacts with hydrogen to form carbon and H_2O, as shown in Eq. (4). Both Eqs. (3) and (4) reduce the selectivity towards methane formation. Furthermore, the Bosch process is undesireable in this system since the resulting carbon can deposit on the catalyst surface, thus reducing the catalyst activity and performance as well as increasing the pressure drop.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (3)$$

$$CO_2 + 2H_2 \rightarrow C_{(s)} + 2H_2O \qquad (4)$$

The water produced by the Sabatier process can then be collected via centrifugation, condensation, or an adsorption method and used as is or it can be further electrolyzed using photovoltaic solar energy to form O_2 and H_2. Hydrogen can be recycled back to the Sabatier reactor for carrying out more CO_2 reduction. Methane can be vented overboard, stored and used as a rocket propellant or passed through a pyrolysis reactor to recover H_2 for recycle, depending on the applications. For safety reasons, the Sabatier reactor for space applications would be operated at slightly less than ambient pressure in order to prevent leakage of combustible gasses to the atmosphere surrounding the unit.

The Sabatier process is an exothermic reaction and is limited by the thermodynamic equilibrium. Lower operating temperatures, typically around 250-400°C, are desirable for higher CO_2 conversion and higher CH_4 selectivity. To date, extensive studies have been performed by others to evaluate and to compare the activity and selectivity of various catalysts, such as Ni, Ru, and Rh for the Sabatier reaction. Nickel is the traditional Sabatier catalyst that has been extensively investigated, while ruthenium was reported as the most active catalyst with the highest selectivity toward CH_4.[9,10] The Sabatier reaction tests performed in these studies, however, were carried out

in packed-bed reactors consisting of catalyst pellets. Recently, researchers at Pacific Northwest National Lab (PNNL) have designed and tested catalytic microchannel reactors for the Sabatier process, and have shown improved CO_2 conversion due to better heat and mass transfers compared to the traditional packed-bed reactors.[7,8] Despite the performance improvement demonstrated by the microchannel reactors, the highest obtainable CO_2 conversion was still relatively low at high throughputs (i.e., ≥30,000 hr^{-1}).[6,7] Additionally, the CO_2 conversion decreased from 70% to ~62% during 4 days of operation (i.e., ~100 hours) and further decreased to ~50% at the end of the 14-day testing period indicating significant catalyst deactivation.[6]

In this paper, we describe the development of a compact and lightweight Microlith-based Sabatier reactor prototype capable of achieving high CO_2 conversion and near complete CH_4 selectivity (i.e., ≥90% of the thermodynamic equilibrium values) at high space velocities. The reactor was operated at 30,000-60,000 hr^{-1} gas hourly space velocity (GHSV) and at average operating temperatures of ≤400ºC. Additionally, the versatility of the reactor was demonstrated by operating under H_2-rich (H_2/CO_2 ratio of >4), stoichiometric (ratio of 4), and CO_2-rich (ratio of <4) conditions. The ability to operate the Microlith-based reactor at high space velocities results in a compact and lightweight Sabatier reactor that will reduce size and launch costs. Based on the test results, an approximately 14 ml reactor (excluding the heat exchanger) is sufficient for a 4-crew unit. The current estimate of the required Microlith catalytic substrate is 3.1 grams per crew. These performance metrics would reduce the size and weight of the overall CRA unit to meet NASA's target values for specific mass and specific volume.[11] Finally, both performance durability for 100 hours and mechanical durability of the Microlith catalytic substrates are discussed. In general, the high surface area per volume of the catalytic Microlith substrates is expected to help with the kinetically-controlled reaction, the short channel length of Microlith substrates is expected to aid the mass transfer controlled reaction, and the metallic support should improve conductive heat transfer to avoid local hot spots and increase durability to withstand mechanical and thermal shocks.[12,13]

II. Microlith[®] Catalytic Technology

The catalyst and reactor described here are based on PCI's patented Microlith technology (trademarked by PCI).[14] The Microlith substrate consists of a series of ultra-short-channel-length, catalytically coated metal meshes with very small channel diameters (Fig. 1). The mesh-like substrates provide very high heat and mass transfer coefficients, low thermal mass, and extremely high reaction rates. The use of this kind of reactor, where the reacting stream is passed through the catalyst at extremely high space velocity, is generically termed a short contact time (SCT) approach. Whereas in a conventional honeycomb monolith, a fully developed boundary layer is present over a considerable length of the device, the ultra-short-channel-length Microlith substrate minimizes boundary layer buildup, resulting in remarkably high heat and mass transfer coefficients compared to other substrates (e.g., monoliths, foams, and pellets). In catalytic reactors involving exothermic reactions, such as the Sabatier process, enhanced heat transfer properties are necessary to eliminate local hot spots and temperature excursions at the catalyst surface, and to prevent catalyst deactivation due to metal sintering. The Microlith substrate also provides about three times higher geometric surface area over conventional monolith reactors with equivalent volume and open frontal area (i.e., low pressure drop).

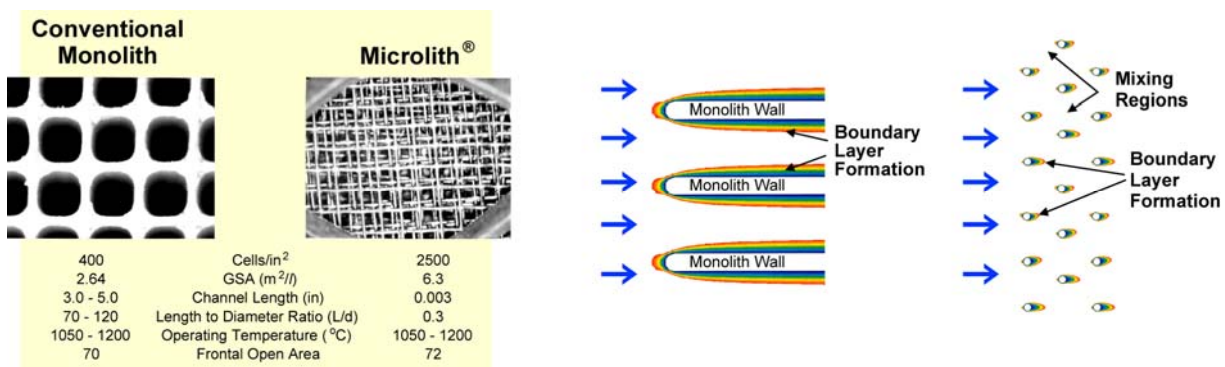| Conventional Monolith		Microlith[®]
400	Cells/in^2	2500
2.64	GSA (m^2/l)	6.3
3.0 - 5.0	Channel Length (in)	0.003
70 - 120	Length to Diameter Ratio (L/d)	0.3
1050 - 1200	Operating Temperature (ºC)	1050 - 1200
70	Frontal Open Area	72

Figure 1. Physical characteristics of conventional, long honeycomb monolith and Microlith substrates, and CFD analysis of boundary layer formation for a conventional monolith and three Microlith screens.

The heat and mass transfer coefficients depend on the boundary layer thickness. For a conventional long channel honeycomb monolith, a fully developed boundary layer is present over a considerable length of the catalytic surface, thus limiting the rate of reactant transport to the surface of active sites. This is avoided when short channel length

catalytic screens are used. A Computational Fluid Dynamics (CFD) analysis (Fig. 1) illustrates the difference in boundary layer formation between a monolith and Microlith screens. Finally, PCI's proprietary catalyst coating formulations and application methods, with high surface area washcoats, allow for very low catalyst usage with rigorously demonstrated long-term mechanical, thermal, and performance durability.

Another advantage of using a Microlith substrate is that it requires neither a completely premixed, completely vaporized, nor completely uniform mixture for stable operation. The high mass transfer rate of the Microlith substrate provides sufficient mixing to remove small-scale inhomogeneities in the reactor feed, but large scale variations still need to be removed upstream of the reactor. Therefore, a simple reactant mixture preparation strategy, using a standard static or quartz mixer, can be employed without risk of damaging the catalytic Microlith substrates. PCI has had considerable experience in providing a highly uniform mixture to the reactor and has identified simple premixing techniques with the design elements necessary for good reactor stability. The results demonstrated by the Microlith-based reactors in water gas shift reaction, partial oxidation of methane, oxidative steam reforming of methanol, and highly exothermic H_2O_2 decomposition offer its potential for effective catalytic CO_2 reduction via the Sabatier process.

The use of catalyst substrates with high heat and mass transfer rates, high surface area, and low pressure drop has a significant impact on reactor performance and size. Current catalytic reactors are generally based on substrates such as pellets, monoliths, foams or microchannels. Work on short contact time substrates has been reported by groups at National Labs, universities, and commercial organizations. Notable among them is Professor Lanny Schmidt at the University of Minnesota.[15,16] However, PCI's Microlith short contact time substrate has shown several benefits over other such substrates on the basis of recent results and developments. The effectiveness of the Microlith technology and long-term durability of PCI's proprietary catalyst coatings have been systematically demonstrated in different applications. These include exhaust

Figure 2. Surface-scan SEM micrograph of the coated Microlith catalytic substrate.

aftertreatment,[17] trace contaminant control,[18,19] catalytic combustion,[20] partial oxidation of methane,[12,21] liquid fuel reforming,[13] CO preferential oxidation, and water gas shift reactors.[22] A scanning electron microscopy (SEM) micrograph of the coated Microlith substrate is shown in Fig. 2. SEM analysis indicates uniform catalyst coatings on the substrate with complete coverage.
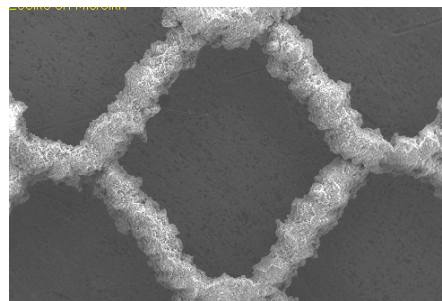
III.   Results and Discussion

A. Design and Fabrication of Sabatier Reactor

Designing a suitable reactor for the exothermic Sabatier reaction is a key challenge. As mentioned before, a low operating temperature is preferred for the Sabatier reaction in order to achieve high reactant conversions and CH_4 selectivity due to the thermodynamic limitations at higher operating temperatures. However, the reaction is severely kinetically limited at low operating temperatures, which will result in reaction quenching due to slow rates of reaction. To remedy this, typical Sabatier reactors are operated with long residence times (i.e., low GHSV) resulting in bulky systems. Additionally, commonly used pellet catalyst beds have low heat transfer coefficients which create another challenge when trying to achieve uniform reactor operating temperatures. Local hot spots are typically encountered in pellet catalyst beds which lead to catalyst deactivation due to metal sintering. TDA Research has developed a prototype consisting of a CO_2 removal bed and a two-bed Sabatier reactor for CO_2 methanation that attempts to mitigate this problem.[23,24] Having two reactor modules, however, negatively impacts the weight and volume of the system.

PCI recently identified and implemented an approach for reactor operation at thermodynamically favored conditions to achieve high CO_2 conversion and high CH_4 selectivity at high space velocities without catalyst degradation. This novel approach was made possible by the use of high-heat-transfer and high-surface-area Microlith catalytic substrates, allowing catalyst operation at conditions favorable for thermodynamic equilibrium of CO_2 methanation.

The Sabatier reactor prototype consisted of an approx. 8" long, 1" diameter stainless steel tube which contained approximately 12 ml (~0.73 in^3) of catalyst bed. A photo of the reactor is shown in Fig. 3. The catalysts, which can be either catalytically coated-Microlith substrates or catalyst pellets, were inserted into the stainless steel tube. The reactor was equipped with multiple thermocouples and two sample ports. The thermocouples were used to monitor catalyst bed temperatures at several radial and axial locations, reactor wall temperatures, and inlet and outlet gas temperatures. Two sample ports were used to monitor the inlet feed and outlet product compositions. A pre-mixing region consisting of quartz beads was inserted upstream of the catalyst bed to enhance the reactants mixing (i.e., pure H_2 and pure CO_2 with known N_2 as internal standard). During the performance testing, the average catalyst bed temperature was maintained at the desired values. The catalyst bed volume was only ~12 ml, and was sized to operate with GHSVs in the range of 30,000 to 60,000 hr^{-1}. This resulted in a total gas flow rate that can represent a system for ~3.5-7 crew members.

Figure 3. Photo of the Sabatier reactor prototype developed at PCI.

B. Sabatier Reactor Performance Testing

A test matrix was developed and finalized in order to evaluate the catalyst performance and to optimize the operating conditions for the Microlith-based Sabatier reactor. Table 1 lists the test plan implemented to develop the performance maps for both Ru-coated and Rh-coated Microlith substrates. In this study, inlet temperature, H_2/CO_2 ratio, GHSV, and operating pressure were varied for each catalyst. CO_2 conversion and CH_4 selectivity were calculated by measuring the product gas composition at these operating conditions. The performance of the two metal catalysts was then compared, and a pellet version of the Ru catalyst was acquired and tested to compare the performance against the Microlith-based

Table 1. Test matrix for developing the performance maps for both Ru-coated and Rh-coated Microlith substrates for the Sabatier reaction.

Parameters	Values
Reactor temperature	250 – 450°C
H_2/CO_2 ratio	Approx. 3.5 – 5.5
GHSV	30,000 – 60,000 hr^{-1}
Pressure	8.3, 11.5, and 13.2 psia
Bench-scale reactor vol.	Approx. 12 ml
Total inlet gas flow	6 – 12 slpm

catalyst. From these tests, the potential benefits of the Microlith substrate were validated, including short contact time kinetics, high heat transfer, and high surface area of catalyst active sites, to achieve a highly efficient, compact, and durable Sabatier reactor.
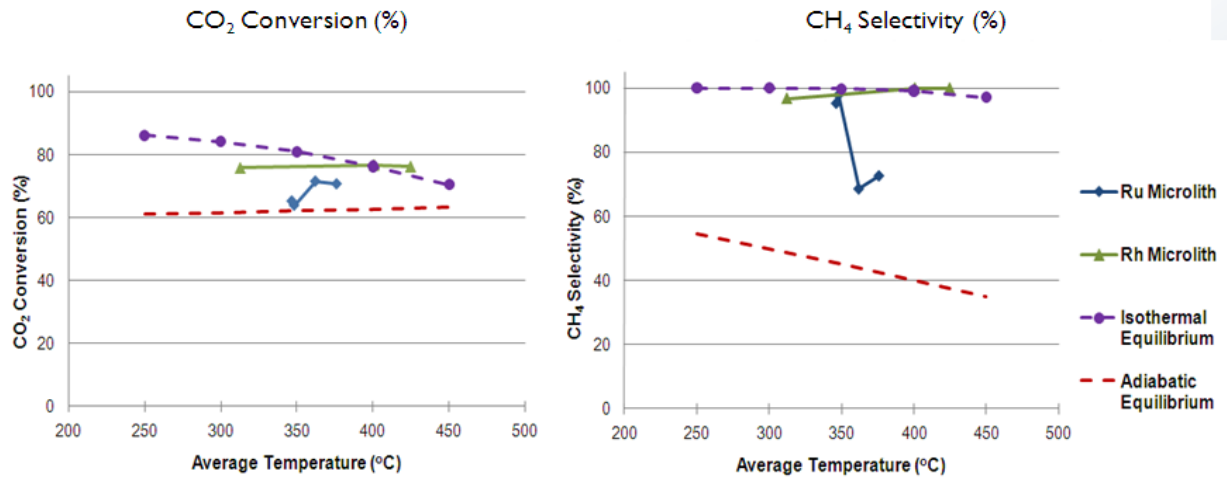
In this study, the Sabatier reactor testing was performed using: (i) Ru catalyst coated on Microlith substrate; (ii) Rh catalyst coated on Microlith substrate; and (iii) Pellet catalyst version of ruthenium (Sigma Aldrich, product # 206199). Performance maps for these catalysts were developed as a function of H_2/CO_2 ratio, operating temperature, space velocity, and pressure according to the test matrix. These catalysts were first reduced under the optimum reduction conditions prior to performance testing. CO_2 conversion and CH_4 selectivity were calculated at each operating condition by measuring the product composition using gas chromatograph with N_2 as the internal standard. These three catalysts were compared based on both GHSV and weight hourly space velocity (WHSV) due to the potential difference in catalyst metal loading of the three substrates within the same reactor volume.

The performance of Ru- and Rh-coated Microlith catalytic substrates were examined by evaluating the CO_2 conversion and CH_4 selectivity at GHSVs from 30,000 to 60,000 hr^{-1}, H_2/CO_2 ratios from 3.5 to 5.5, reactant partial pressures from 8.3 to 13.2 psia, and temperatures from 250 to 450°C. Figure 4 shows the test results from both Ru- and Rh-Microlith catalysts at 30,000 hr^{-1} and different H_2/CO_2 ratios. On average, the CO_2 conversion was found to approach 90-95% of the isothermal equilibrium conversion at the optimum operating conditions. CH_4 selectivity was found to be within 95-100% of the isothermal equilibrium selectivity for both Microlith catalytic substrates regardless of the operating conditions. Rh-Microlith catalyst was found to be slightly more active than the Ru-Microlith catalyst when compared on a GHSV basis, due to its higher metal loading, which resulted in CO_2 conversions of ~7-8% higher than those obtained for the Ru-Microlith (Fig. 4). When compared on a WHSV basis, which accounts for the difference in metal loading, however, the performance was found to be nearly identical.
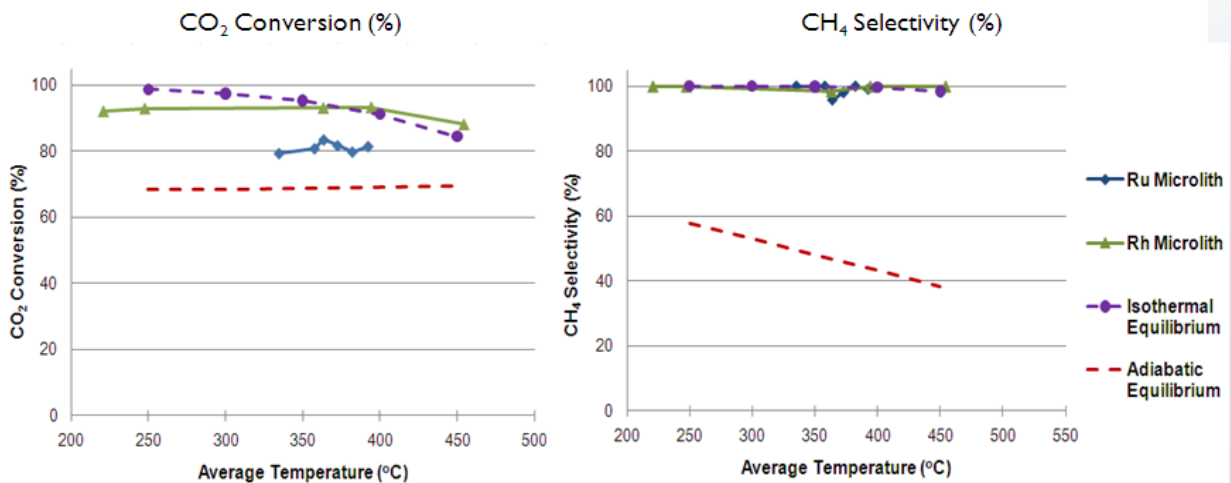
Catalyst Comparison at **GHSV of 30K hr^{-1} and H$_2$/CO$_2$ of ~3.5**: Temperature Sweep

CO$_2$ Conversion (%)   CH$_4$ Selectivity (%)

Catalyst Comparison at **GHSV of 30K hr^{-1} and H$_2$/CO$_2$ of ~4**: Temperature Sweep

CO$_2$ Conversion (%)   CH$_4$ Selectivity (%)

Catalyst Comparison at **GHSV of 30K hr^{-1} and H$_2$/CO$_2$ of ~5.5**: Temperature Sweep

CO$_2$ Conversion (%)   CH$_4$ Selectivity (%)

Figure 4. Comparison between Ru- and Rh-Microlith catalysts at 30,000 hr^{-1} and different H$_2$/CO$_2$.

Both of the catalysts followed the same general trends in regard to GHSV, H_2/CO_2 ratio, partial pressure, and temperature. CO_2 conversion improved at lower space velocities due to longer residence times within the reactor. CO_2 conversion also improved with higher H_2/CO_2 ratios due to the hydrogen rich feed. Operating pressure was found to have minimal effect on the reactor performance, which suggests that the reactor can be operated under vacuum conditions without losses in performance. CO_2 conversion reached a maximum at around 350°C for the Microlith catalytic substrates. The improved heat and mass transfer characteristics inherent in the Microlith substrate enabled cooler and more uniform catalyst temperatures along with higher CO_2 conversions when compared to state-of-the-art pellet catalysts and microchannel reactors. The ability to operate at a much higher GHSV while still exceeding the CO_2 conversion obtained from pellet catalysts, also gives Microlith-based Sabatier reactors an added benefit of a smaller reactor size.

Table 2 lists the optimum CO_2 conversions obtained from the Ru-Microlith, Rh-Microlith, and Ru pellet catalyst testing at different H_2/CO_2 ratios, at ~30,000 hr^{-1} GHSV (~23,500 hr^{-1} for Ru pellets to maintain the same WHSV with Ru-Microlith catalyst), and at a reactant pressure of 13.2 psia. The value obtained from literature for PNNL's microchannel reactor operating at ~30,000 hr^{-1} is also listed for comparison.[7] Test results indicated that short-contact-time kinetics and high-surface-area benefits of the Microlith substrates assisted the Sabatier reaction to achieve high reactant conversions and near 100% CH_4 selectivity at high throughputs (i.e., 30,000-60,000 hr^{-1} vs. 18,000-45,000 hr^{-1} for PNNL's microchannel reactor vs. 1,800 hr^{-1} for state-of-the art pellet-based reactors).

Table 2. Optimum CO_2 conversions for Ru-Microlith, Rh-Microlith, and Ru pellet catalysts at different H_2/CO_2 ratios and 30K hr^{-1} GHSV (23.5K hr^{-1} for Ru pellets to maintain the same WHSV with Ru-Microlith catalyst).

Catalyst	Approx. H_2/CO_2 ratio	Max CO_2 conversion (%)
Ru-Microlith	3.5	71
	4	83.5
	5.5	93
Rh-Microlith	3.5	77
	4	92
	5.5	99.8
Commercially available Ru pellets	3.5	66
	4	76
	5.5	84
PNNL (single microchannel; Ru)[7]	4	78.6

C. Performance Durability of Microlith-based Sabatier Reactor

Durability of the catalyst-coated Microlith substrates was examined by continuously running each Rh-based and Ru-based catalyst for a period of 100 hours while subjecting them to 5 startup/shutdown sequences over the course of the test. CO_2 conversion was monitored throughout the test to determine how much, if any, performance degradation had occurred. Both catalysts were tested at a GHSV of 30,000 hr^{-1}, a H_2/CO_2 ratio of ~3.5 per NASA request (i.e., CO_2-rich condition for spaceflight applications), and a reactant partial pressure of 13.2 psia. This operating condition was chosen to represent a realistic condition in spacecraft and ISS applications. The operating temperature was chosen to achieve the maximum CO_2 conversion at this condition (i.e., at a H_2/CO_2 of 3.5), which were 71% for Ru-Microlith and 77% for Rh-Microlith catalysts (vs. isothermal equilibrium CO_2 conversion of 77-79% at a H_2/CO_2 ratio of 3.5 and at 350-375°C). No performance degradation was observed for either catalyst over the course of the 100 hours of operation with 5 starts/stops as shown in Fig. 5. The lack of catalyst degradation suggested that the high heat transfer rate of the Microlith catalytic substrates permits uniform temperature distribution and avoids local hot spots that can cause metal sintering and catalyst deactivation.

Due to the fact that the cooling system was manually controlled, it could not be adjusted overnight in response to changes in the ambient temperature or other uncontrolled variables that affected the temperature within the reactor. This often led to a slight cooling of the Sabatier reactor and a corresponding slight decrease in the performance overnight. This behavior was not related to the catalyst degradation because performance always returned upon either readjusting the cooling system to maintain the reactor at the optimum operating temperature or restarting the Sabatier reactor. To overcome this challenge in the field, a control system would need to be developed to maintain a constant temperature profile within the reactor. An appropriate control algorithm will be developed and implemented in future development efforts for the long-term, unattended performance testing over 1000 hours. Despite these challenges, no catalyst performance degradation was observed for either of the Microlith catalyst substrates while operating the reactor at a high throughput (i.e., GHSV of 30,000 hr^{-1}). This is an additional potential benefit over pellet catalysts since typical pellet catalysts often suffer from metal sintering due to local hot spots (in the exothermic reactors), which degrades the catalyst and causes the active region to move to different areas of the bed over time. To account for this inevitable degradation, pellet reactors must be oversized to provide longer life

spans without replacing the catalyst. If Microlith catalytic substrates are able to overcome this problem, as is suggested by the durability test data, it will be possible to use smaller reactors and still run for extended periods of time without performance degradation or catalyst replacement.

D. Mechanical Vibration Testing

An in-house mechanical vibration test was performed on Ru-Microlith, Rh-Microlith, and commercially available Ru pellet catalysts to further evaluate the adhesion and durability of catalyst coating on Microlith substrates and to compare it with the catalyst pellets. The test consisted of a 12"×12" vibrating aluminum plate supported on vibration isolation mounts and excited by an industrial-style pneumatic vibrator (recirculating ball style) mounted either in the center or on the edge of the plate to simulate the launch vibration loads. An example of the vibration test setup is shown in Fig. 6. Assembled catalyst beds of Rh-Microlith and Ru-Microlith were placed in a pre-weighed, zip-closed plastic bag to contain the loosened catalyst. The Ru catalyst pellets were placed inside a small, capped stainless steel tube container. Each catalyst was then attached to the plate and was vibrated for a total of ~80 minutes. The amount of catalyst lost was collected and weighed. In this vibration test, the peak force averaged ~50gs and the primary frequency was 250 Hz. The vibration test results indicated that the Microlith-based catalyst coating lost was <~0.2 wt.%, lower than that observed from the Ru pellets (Fig. 7). Here, the coating weight lost for the Microlith catalyst substrates was defined as

a)

b)

Figure 5. CO_2 conversion as a function of time from the 100-hour durability testing of: a) Ru-Microlith catalyst and b) Rh-Microlith catalyst performed at a GHSV of 30,000 hr^{-1}, H_2/CO_2 ratio of ~3.5, and operating pressure of 13.2 psia. The isothermal equilibrium CO_2 conversion at ~77-79% (for 350-375°C temperature) is included for comparison.
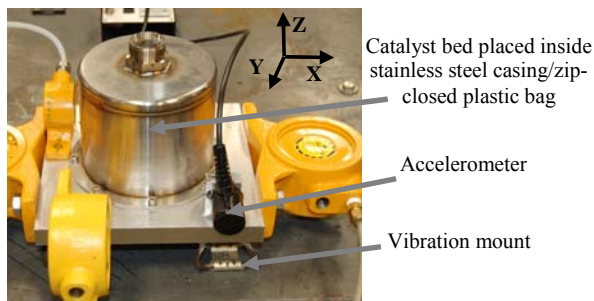

Figure 6. An example of the vibration test setup to evaluate the adhesion and mechanical durability of the Microlith-based catalysts against simulated launch vibration loads.
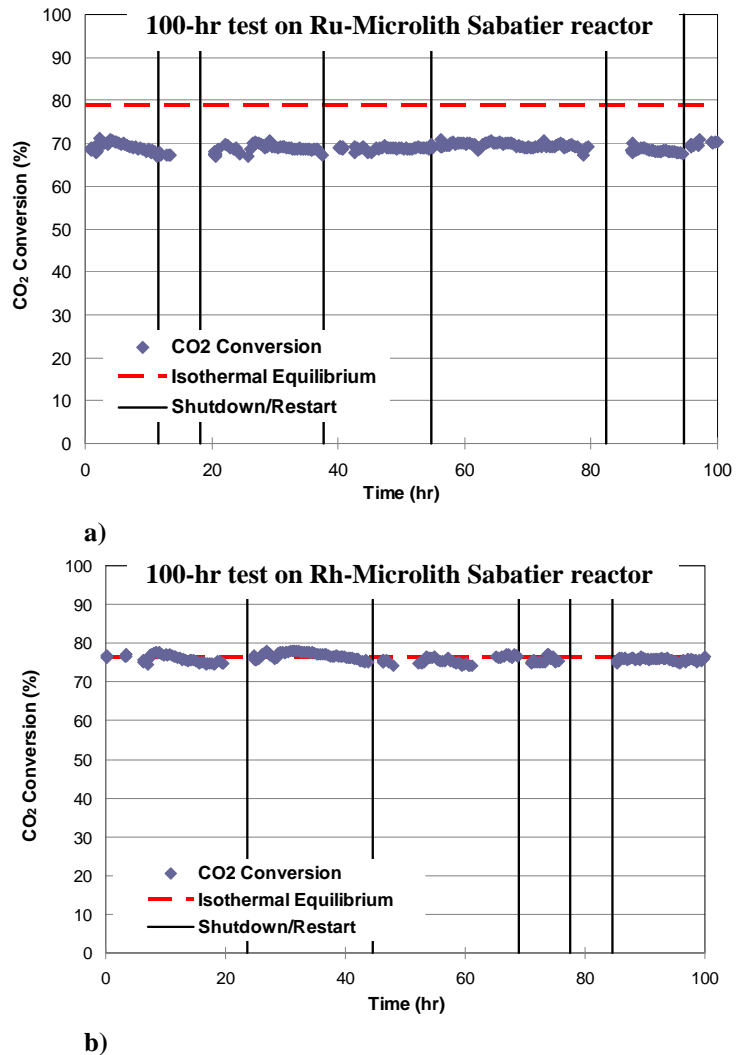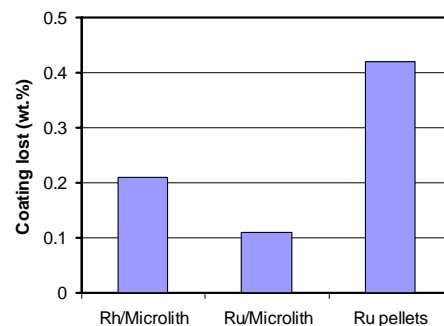

Figure 7. Catalyst lost (i.e., "fines" generated) from the mechanical vibration testing.

American Institute of Aeronautics and Astronautics

the ratio of the amount of "fines" generated to the amount of the catalyst and washcoat only (without taking into account the weight of the Microlith substrate which would not contribute to any losses). On the other hand, the coating weight lost for the catalyst pellets was defined as the ratio of the amount of "fines" generated to the total amount of the pellets since the support material will contribute to losses.

IV.   Conclusion

This paper demonstrates the benefit of the Microlith catalytic substrates for efficient Sabatier reaction. The properties of short contact time kinetics, high heat transfer, and high surface area of catalyst active sites enable the design of a highly efficient, compact, and durable Sabatier reactor. A proof-of-concept Microlith-based Sabatier reactor capable of producing high CO_2 conversion and near 100% CH_4 selectivity (i.e., ≥90% of the thermodynamic equilibrium values) at high space velocities and low operating temperatures was developed and demonstrated. The reactor was operated at GHSVs of 30,000-60,000 hr^{-1}. Additionally, the versatility of the Microlith-based reactor was demonstrated by operating it under H_2-rich (H_2/CO_2 ratio of >4), stoichiometric (ratio of 4), and CO_2-rich (ratio of <4) conditions without affecting its performance.

The ability to operate the Microlith-based reactor at high space velocities results in a compact and lightweight Sabatier reactor that will reduce size and launch costs. Based on the test results, an approximately 14 ml reactor is sufficient for a 4-crew unit, capable of achieving high reactant conversions and high CH_4 selectivity. Additionally, the current estimate of the required Microlith catalytic substrate is only 3.1 grams per crew. Finally, both performance durability and mechanical durability of the Microlith catalytic substrates were demonstrated. The performance durability testing for 100 hours on each rhodium- and ruthenium-Microlith catalytic substrate was completed without any performance degradation. The mechanical durability test was performed using an in-house vibration plate at an average peak force of ~50gs and a primary frequency of ~250 Hz. The resulting "fines" generation was <~0.2 wt.%, which was lower than the "fines" generation observed from the commercially available Ru pellets. Thus, in addition to a reduced weight, the implementation of the Microlith-based Sabatier reactor has potential to increase the catalyst durability and to reduce the issues with "fines" generation in the space shuttle application.

Acknowledgments

References

[1]Sanders, G. B., Peters, T. A., Wegeng, R. S., TeGrotenius, W. E., Rassat, S. D., Brooks, K. P., and Stenkamp, S., "Report on Development of Micro Chemical/Thermal Systems for Mars ISRU-Based Missions," *AIAA Report*, AIAA 2001-0939, 2000.

[2]Chamitoff, G., James, G., Baker, D., and Dershowitz, A., "Martian resource locations: Identification and optimization," *Acta Astronautica*, 56, 756 (2005).

[3]Jeng, F. F., Lewis, J. F., Graf, J. C., and LaFuse, S., "CO_2 Compressor Requirements for Integration of Space Station Carbon Dioxide Removal and Reduction Assemblies," 1999-01-2195, *SAE*, 29th International Conference on Environmental Systems, Denver, Colorado, 1999.

[4]Murdoch, K., Perry, J., and Smith, F., "Sabatier Engineering Development Unit," 2003-01-2496, *SAE*, 33rd International Conference on Environmental Systems, Vancouver, Canada, 2003.

[5]Knox, J. C., Campbell, M., Murdoch, K., Miller, L. A., and Jeng, F., "Integrated Test and Evaluation of a 4-Bed Molecular Sieve (4BMS) Carbon Dioxide removal System (CDRA), Mechanical Compressor Engineering Development Unit (EDU), and Sabatier Engineering Development Unit (EDU)," 2005-01-2864, *SAE*, 35th International Conference on Environmental Systems, Rome, Italy, 2005.

[6]Holladay, J. D., Brooks, K. P., Wegeng, R., Hu, J., Sanders, J., and Baird, S., "Microreactor development for Martian in situ propellant production," *Catalysis Today*, 120, 35 (2007).

[7]Hu, J., Brooks, K. P., Holladay, J. D., Howe, D. T., and Simon, T. M., "Catalyst development for microchannel reactors for martian in situ propellant production," *Catalysis Today*, 125, 103 (2007).

[8]Brooks, K. P., Hu, J., Zhu, H., and Kee, R. J., "Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors," *Chemical Engineering Science*, 62, 1161 (2007).

[9]Du, G., Lim, S., Yang, Y., Wang, C., Pfefferle, L., and Haller, G. L., "Methanation of carbon dioxide on Ni-incorporated MCM-41 catalysts: The influence of catalyst pretreatment and study of steady-state reaction," *Journal of Catalysis*, 249, 370 (2007).

[10]Weatherbee G.D. and C.H. Bartholomew, J. Catal., "Hydrogenation of CO2 on Group VIII Metals, IV. Specific Activities and Selectivities of Silica-Supported Co, Fe, and Ru," 87, 352 (1984).

[11]Perry, J. L., Bagdigian, R. M., and Carrasquillo, R. L., "Trade Spaces in Crewed Spacecraft Atmosphere Revitalization System Development," *AIAA Report*, AIAA 2010-6061, 40th International Conference on Environmental Systems, Barcelona, Spain, 2010.

[12]Lyubovsky, M., Karim, H., Menacherry, P., Boorse, S., LaPierre, R., Pfefferle, W. C., and Roychoudhury, S., "Complete and partial catalytic oxidation of methane over substrates with enhanced transport properties," *Catalysis Today*, 83, 183 (2003).

[13]Roychoudhury, S., Castaldi, M., Lyubovsky, M., LaPierre, R., and Ahmed, S., "Microlith catalytic reactors for reforming iso-octane-based fuels into hydrogen," *Journal of Power Sources*, 152, 75 (2005).

[14]Pfefferle, W. C., "Microlith Catalytic Reaction System," U.S. Patent No. 5,051,241. Sept. 24, 1991.

[15]Bitsch-Larsen, A., Degenstein, N. J., and Schmidt, L. D., "Effect of sulfur in catalytic partial oxidation of methane over Rh-Ce coated foam monoliths," *Applied Catalysis B: Environmental*, 78, 364 (2008).

[16]O'Connor, R. P., Klein, E. J., Henning, D., and Schmidt, L. D., "Tuning millisecond chemical reactors for the catalytic partial oxidation of cyclohexane," *Applied Catalysis A: General*, 238, 29 (2003).

[17]Bianchi, J. F., Gonzales, F., Muench, G., Pfefferle, W. C., and Roychoudhury, S., "Development and Performance of Microlith Light-off Preconverters for LEV/ULEV," 971023, *SAE*, 27th International Conference on Environmental Systems, Lake Tahoe, Nevada, 1997.

[18]Carter, R. N., Bianchi, J. F., Pfefferle, W. C., Roychoudhury, S., and Perry, J. L., "Unique Metal Monolith Catalytic Reactor for Destruction of Airborne Trace Contaminants," 972432, *SAE*, 27th International Conference on Environmental Systems, Lake Tahoe, Nevada, 1997.

[19]Perry, J. L., Carter, R. N., and Roychoudhury, S., "Demonstration of an Ultra-Short Channel Metal Monolith Catalytic Reactor for Trace Contaminant Control Applications," 1999-01-2112, *SAE*, 29th International Conference on Environmental Systems, Denver, Colorado, 1999.

[20]Kraemer, G., Strickland, T., Pfefferle, W. C., and Ritter, J., "A Compact Catalytic Combustor System for Small Turbogenerators," *Proceedings of the International Conference on Joint Power Generation*, ASME (1997).

[21]Lyubovsky, M., Roychoudhury, S., and LaPierre, R., "Catalytic partial ''oxidation of methane to syngas'' at elevated pressures," *Catalysis Letters*, 99, 113 (2005).

[22]Castaldi, M. J., LaPierre, R., Lyubovsky, M., Pfefferle, W., and Roychoudhury, S., "Effect of water on performance and sizing of fuel-processing reactors," *Catalysis Today*, 99, 339 (2005).

[23]Alptekin, G., Copeland, R., DeVoss, S., Lind, J., and Smith, F., "An Advanced CO_2 Removal and Reduction System," 2004-01-2445, *SAE*, 34th International Conference on Environmental Systems, Orlando, Florida, 2004.

[24]Alptekin, G., Hitch, B., Dubovik, M., Lind, J., and Smith, F., "Prototype Demonstration of the Advanced CO_2 Removal and Reduction System," 2005-01-2862, *SAE*, 35th International Conference on Environmental Systems, Rome, Italy, 2005.

American Institute of Aeronautics and Astronautics