Compact, Lightweight Adsorber and Sabatier Reactor for CO$_2$ Capture and Reduction for Consumable and Propellant Production

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The utilization of CO$_2$ to produce (or recycle) life support consumables, such as O$_2$ and H$_2$O, and to generate propellant fuels is an important aspect of NASA’s concept for future, long duration planetary exploration. One potential approach is to capture and use CO$_2$ from the Martian atmosphere to generate the consumables and propellant fuels. Precision Combustion, Inc. (PCI), with support from NASA, continues to develop its regenerable adsorber technology for capturing CO$_2$ from gaseous atmospheres (for cabin atmosphere revitalization and in-situ resource utilization applications) and its Sabatier reactor for converting CO$_2$ to methane and water. Both technologies are based on PCI’s Microlith® substrates and have been demonstrated to reduce size, weight, and power consumption during CO$_2$ capture and methanation process. For adsorber applications, the Microlith substrates offer a unique resistive heating capability that shows potential for short regeneration time and reduced power requirements compared to conventional systems. For the Sabatier applications, the combination of the Microlith substrates and durable catalyst coating permits efficient CO$_2$ methanation that favors high reactant conversion, high selectivity, and durability. Results from performance testing at various operating conditions will be presented. An effort to optimize the Sabatier reactor and to develop a bench-top Sabatier Development Unit (SDU) will be discussed.

Nomenclature

°C = Degree Celsius  
cfm = cubic feet per minute  
cm = centimeter  
ESA = electrothermal swing adsorption  
g = gram

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Efficient production or recycling of life support consumables such as water and oxygen, along with generation of reactants and propellants from in-situ resources is crucial for deep exploration of space where re-supply options are nonexistent. If propellant required for the return to Earth can be produced with native resources, the human/robotic missions will not have the added burden of transporting the return propellant from Earth. The ubiquitous CO₂-rich Martian atmosphere provides the essential at-exploration site resource; therefore, with the proper in-situ resource utilization (ISR-U) system architecture, it can be employed to significantly reduce launch weight, size, and cost. Moreover, the concept of closed-loop cabin Atmosphere Revitalization System (ARS) in the space shuttle, which includes the CO₂ Removal Assembly (CDRA), Oxygen Generator Assembly (OGA), and CO₂ Reduction Assembly (CRA), has become an integral part of NASA mission architectures for future long-duration human space exploration to the Moon and Mars. In the current International Space Station (ISS) and other low orbit missions, the metabolically generated CO₂ is removed from the cabin air via adsorption and vented into space, resulting in a net loss of O₂. This requires a continuous resupply of O₂ via water electrolysis, and thus highlights the need for large water storage. To achieve a complete closure of O₂ and H₂O, the CO₂ produced by metabolic processes is removed from the cabin air by the CDRA and is then reacted with H₂ from the OGA in a Sabatier CO₂ methanation reactor (i.e., part of CRA) to produce methane and water. The basic system design may consist of four main unit operations: (i) a regenerable CO₂ adsorber to separate CO₂ from Ar and N₂ (and then Ar and N₂ will be used as buffer gas); (ii) a CO₂ accumulator and a compressor to store and manage CO₂ flow to the Sabatier reactor; (iii) a CO₂ methanation reactor that reacts CO₂ with H₂ extracted either from in-situ resource or carried from Earth to produce water and methane; and (iv) a solar-powered water electrolyzer that produces O₂ and recycle H₂.

Adsorption processes have important applications in air quality engineering. For example, an adsorption-based approach has been used for cabin air quality control on all crewed spacecraft, and is expected to remain at the forefront of spacecraft cabin air quality control technologies. In addition to the sorption of CO₂, the trace contaminants also need to be removed because these substances can be harmful to the crew if they are allowed to buildup over time. In spacecraft applications, these chemicals can be adsorbed via several options, such as pellet bed canisters and charcoal beds. As mission durations increase and exploration goals reach beyond low Earth orbit, the need for in-situ regenerable adsorption processes for continuous removal of CO₂ and trace chemical contaminants from the cabin air becomes important. Furthermore, the sorption process may have potential for adsorbing and separating the CO₂ from the Mars atmosphere (consisting of 95% CO₂ with 2.7% N₂ and 1.6% Ar) if the resulting system is compact and has low power consumption.

The implementation of zeolites, molecular sieves, and silica gel in the adsorption process is of interest due to their high efficiency to selectively remove chemical contaminants as well as their chemical inertness and non-

I. Introduction

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flammable properties. Furthermore, these sorbent materials can be readily regenerated via either thermal swing adsorption (TSA) or pressure swing adsorption (PSA), and therefore, they are suitable for the removal of CO₂ and trace contaminants. These regenerable adsorbers do not have to be replaced during a mission, and can be smaller and lighter than the disposable adsorber beds. Currently, packed beds of sorbent pellets are mostly used in the adsorption systems; however, recent studies have shown that these materials can be easily fluidized and/or eroded, due to both thermal cycling and mechanical vibration, and can generate fine particulates that bypass the downstream mesh filters.⁹,¹¹ This results in particulates buildup in downstream pumps, blowers, and other components, and has been problematic in some aerospace applications. Furthermore, these packed beds of pellets create a large pressure drop across the adsorption system resulting in high parasitic losses.

In an effort to develop alternative approaches to packed bed systems, NASA-supported research at Precision Combustion, Inc. (PCI) has demonstrated that zeolites and molecular sieves coated on Microlith® metal mesh elements (patented and trademarked by PCI) can effectively adsorb a number of the contaminants of interest, such as CO₂, ethanol, and ammonia.¹² The inert Microlith substrates and the use of a binder during coating of the zeolites and other sorbent materials on them result in volumetric sorbent loadings that are considerably lower than the conventional carbon bed and packed bed systems. Typically, the volumetric sorbent loadings obtained for the Microlith-based sorbent beds are about 30-35% of the loadings reported for the packed bed systems. However, the unique capability for direct resistive heating of the Microlith metal mesh support permits rapid periodic regenerations via direct internal heating with low power requirements, which confers a clear advantage over a packed bed of pellets that can only be regenerated using an external heater. Furthermore, the high heat transfer rate of the Microlith substrate results in relatively uniform temperature distribution across the sorbent bed and fast transient response during the regeneration process, compared to a more sluggish thermal response of the packed bed of pellets. Therefore, the weight and volume of the conventional adsorber subassemblies can potentially be reduced by implementing zeolites supported on the Microlith substrate and by employing periodic sorbent regeneration. Additionally, the implementation of the Microlith substrates, with a large void fraction, reduces the pressure drop across the adsorption system when compared to a similar packed bed unit.

Once the CO₂ is separated and collected, it can be fed to the Sabatier or CO₂ methanation process, where CO₂ reacts with hydrogen in the presence of catalysts to produce methane and water, as shown in Eq. (1) below:

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

A competing reverse water gas shift (RWGS) reaction, Eq. (2), is typically present in the process. Under certain operating conditions, CO₂ reduction via the Bosch reaction may also occur, where CO₂ reacts with hydrogen to form solid carbon and H₂O, as shown in Eq. (3). Both Eqs. (2) and (3) reduce the selectivity towards methane formation. Furthermore, the Bosch process is undesirable 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.

\[
CO_2 + H_2 \rightarrow CO + H_2O \quad (2)
\]

\[
CO_2 + 2H_2 \rightarrow C(s) + 2H_2O \quad (3)
\]

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 O₂ and H₂. Hydrogen can be recycled back to the Sabatier reactor for carrying out more CO₂ reduction and to decrease the H₂ requirements. Depending on the application, methane can be stored and used as a rocket propellant (i.e., Martian ISRU application) or passed through a pyrolysis reactor to recover H₂ for recycle (i.e., CRA in space shuttle).

The Sabatier process is an exothermic reaction and is limited by thermodynamic equilibrium. Lower operating temperatures, typically around 250-400°C, are desirable for higher CO₂ conversion and higher CH₄ selectivity. To date, extensive studies have been performed by others to evaluate and 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 CH₄.¹³,¹⁴

In this paper, we will discuss the development efforts for both the Microlith-based adsorber and the Microlith-based Sabatier reactor. In the first part, we will describe the performance of the adsorber modules for the cabin air quality control and the Martian ISRU applications. The results from testing a pair of adsorber units consisting of a
water removal module and a CO₂ removal module to obtain full-scale (i.e., 4-crew unit) CO₂ removal functionality from cabin air will be presented. We will also present results on the adsorber performance, including sorption capacity, cycle-to-cycle variation, and power consumption, upon exposure to a simulated Martian atmosphere (i.e., 95% CO₂ at low pressure). In the second part of the paper, we will discuss the ongoing effort to characterize and optimize the Microlith-based Sabatier reactor and to develop a bench-top (breadboard) Sabatier Development Unit (SDU) prototype. In general, the high surface area per volume of the catalytic Microlith substrates is expected to improve the reaction kinetics, the short channel length of Microlith substrates is expected to reduce mass transfer limitations, and the metallic support should improve conductive heat transfer to avoid local hot spots and increase durability to withstand mechanical and thermal shocks.15,16

II. Microlith® Substrate and Catalytic Technology

The development efforts described here are based on PCI’s patented Microlith technology (trademarked by PCI).17 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 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, resulting in a lower pressure drop.

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 long honeycomb monolith and Microlith screens. Finally, PCI’s proprietary catalyst coating formulations and application methods, with high surface area washcoats, permit low sorbent and catalyst usage with rigorously demonstrated long-term mechanical, thermal, and performance durability.

The use of Microlith substrates with high heat and mass transfer rates, high surface area, and low pressure drop has a significant impact on adsorber and reactor performance and size as compared to pellet or monolith based units. The effectiveness of the Microlith technology and long-term durability of PCI’s proprietary adsorbent and catalyst coatings have been systematically demonstrated in different applications. These include exhaust aftertreatment,18 trace contaminant control,19,20
catalytic combustion, partial oxidation of methane, liquid fuel reforming, CO preferential oxidation, and water gas shift reactors. A scanning electron microscopy (SEM) micrograph of a coated Microlith substrate is shown in Fig. 2. SEM analysis indicates uniform coatings on the substrate with complete coverage.

III. Results and Discussion

A. Design of Regenerable Adsorber Module

The electrothermal swing adsorption (ESA)-based adsorber design consisted of a “jelly roll” sorbent coil in a radial flow configuration. The radial design was based on a two-layer “sandwich” system consisting of a continuous layer of sorbent-coated Microlith screens and a corresponding insulating layer coated with the same sorbent material. The insulating mesh was utilized to electrically isolate the Microlith metal screens when applying the resistive heating during the ESA regeneration mode. Upon coiling the two-layer system around a centerline feed tube (i.e., a “jelly-roll” coil), the radial flow configuration can be achieved as illustrated in Fig. 3. A preliminary calculation indicated that the radial flow arrangement provided volumetric sorbent loadings that are at least comparable to a linear stack of screen elements. Furthermore, from the electrical and hardware assembly vantage points, a continuous length of coated screens largely mitigated the complicating issues encountered with a stack of screens, such as shorting and reactant channeling. Therefore, direct electrical heating of the metal Microlith substrate to regenerate the sorbent could be implemented more readily in the radial flow arrangement. Figure 4 shows the external and internal cross-sectional views of a Microlith-based radial flow adsorber unit with internal resistive heating capability. To date, PCI has delivered to NASA Marshall a pair of full-scale (i.e., 4-crew load) adsorber units for the removal of CO$_2$ from cabin air atmosphere. CFDesign, a CFD simulation software package available at PCI, was used to study the flow pattern of process air within the adsorber unit. The unit design and sizing were optimized based on the modeling results to obtain a uniform flow distribution in the radial flow configuration and to avoid the presence of recirculation zones while minimizing the total housing volume (i.e., increasing the overall volumetric efficiency).

B. Moisture, CO$_2$, and Trace Contaminant Sorption for NASA Cabin Air Application

We have previously reported the design, development, and testing of sub-scale adsorber modules (5 cfm flow rate) for the removal of moisture, CO$_2$, and trace contaminants for NASA’s cabin air applications. These units were designed to provide the required removal rate of metabolic-generated CO$_2$ for one crew member (i.e., 1 kg CO$_2$/day) and have been characterized by NASA Marshall. Utilizing the sub-scale test data furnished by NASA Marshall, PCI scaled-up and sized the required adsorbent beds for the CO$_2$ removal module and the moisture
removal module for the targeted 4-crew member. The full-scale sorbent bed design was similar to the subscale modules, which was based on the radial flow configuration and “jelly roll” coil sorbent bed. The CO₂ sorbent bed was scaled-up and sized to be able to perform CO₂ sorption for at least 30-min half cycle with an inlet CO₂ partial pressure of 533-667 Pa (4-5 Torr) at a 20-cfm process air flow rate and to provide a target CO₂ removal rate of 4 kg/day (equivalent to the metabolic CO₂ generation rate of 4 crew). The moisture sorbent bed was scaled-up and sized to be able to remove residual water vapor from 570 slpm (20 cfm) of process air at -12°C dew point.

As reported previously, in this full-scale adsorber hardware design, the centerline of these radial flow adsorber modules was occupied by a 6.35 cm (2.5 inches) diameter feed tube; hence, based on the required sorbent bed volumes for the full-scale system, the dimensions of the CO₂ sorbent bed (i.e., “jelly roll” coil coated with MS5A) and the moisture removal bed (i.e., “jelly roll” coil coated with zeolite 13X) were estimated. Then, for each adsorber module, the housing dimension was optimized to achieve maximum overall volumetric efficiency with uniform reactant flow distribution and minimal recirculation zones. A total of four full-scale adsorber modules, consisting of two CO₂ adsorber modules and two moisture removal modules, were delivered to NASA Marshall for performance validation.

As discussed above, the use of the inert Microlith substrate to support the zeolite sorbents resulted in a reduced volumetric sorption capacity compared to a pellet bed. To narrow the gap in sorption capacity, an important goal was to increase the sorbent volumetric loading on the Microlith substrate and the insulating mesh (i.e., “jelly roll” sorbent coil) while maintaining good coating adhesion as well as mechanical and thermal durability. This can be done via several approaches, e.g., modifying coating formulations, optimizing washcoat application parameters, and using different supporting substrates (i.e., new insulating mesh with less open area). To date, effort continues to increase the overall volumetric sorbent loadings on the Microlith substrates while minimizing the effect on the coating adhesion. The results give potential benefits to the overall adsorber performance (e.g., longer adsorption time, less exposure to thermal cycles, lower overall power consumption, and size benefits) due to the higher sorbent density, and thus a higher expected volumetric sorption capacity.

Preliminary performance testing has been completed on these adsorber modules at NASA Marshall to characterize sorption capacity and power consumption. Figure 5 shows the breakthrough profile (i.e., CO₂ removal rate as a function of time) from a single adsorption cycle with one of the CO₂ adsorber modules. Figure 6 presents the corresponding cumulative amount of CO₂ adsorbed as a function of time during the adsorption cycle. As evident from the test results, a pair of these CO₂ adsorber units should be able to continuously remove ~120 g of CO₂ in a 30-minute cycle, which equals to 5.7 kg CO₂/day. This is more than the targeted CO₂ removal rate of 4 kg/day. Thus, the cycle time can be extended to meet the target removal rate, which will result in the reduction of power requirements. Moreover, as can be seen from Fig. 5, the overall sorbent bed utilization for this adsorber unit is still relatively low (i.e., early CO₂ slippage followed by a gradual increase in CO₂ outlet flow rate) despite several modifications implemented during the fabrication and assembly to reduce the flow bypassing and to increase the bed utilization. Currently, we are implementing changes to the existing full-scale adsorber units to reduce flow bypass. Increasing the overall bed utilization will significantly increase the volumetric sorption capacity which will reduce the sorbent bed size and weight in future development.

Figure 5. Breakthrough profile and CO₂ removal rate as a function of time from a single adsorption cycle with one of the CO₂ adsorber modules.

Figure 6. Cumulative amount of CO₂ adsorbed as a function of time corresponding to the adsorption cycle presented in Fig. 5.
C. CO₂ Separation from a Simulated Martian Atmosphere for Mars ISRU Applications

In this preliminary study, proof-of-concept testing was performed for zeolite 13X-coated and MS5A-coated Microlith sorbent beds at different adsorption temperatures in order to develop performance maps for each sorbent and to optimize the operating conditions during separation of CO₂ from the Martian atmosphere. A smaller version of the full-scale adsorber with the same “jelly roll” radial flow configuration (i.e., sorbent bed volume of 500 ml vs. 19,000 ml for the full-scale unit) was developed at PCI to realize this effort (Fig. 7). The adsorption and regeneration cycles of the CO₂ adsorber were initially performed at a sorbent bed temperature of 25°C, followed by 10°C, and concluded with -10°C (limited by the current test setup). At least three adsorption-regeneration cycles were performed at each of the three temperatures for both sorbents and the adsorber performance, including sorption capacity, power consumption, regenerability, and cycle-to-cycle variation, was evaluated. The gas mixture consisted of 95% CO₂ with 2.5% N₂ and 2.5% Ar to simulate the Martian atmosphere. The inlet gas flow rate was varied to maintain the system pressure at the desired value.

The initial target pressure for this effort was ~933 Pa (7 Torr) (i.e., Martian atmospheric pressure). The system pressure, however, was limited to 4000-4670 Pa (30-35 Torr) due to the current limitation of the gas-sampling pump in the Quadrupole Mass Spectrometer used to monitor the CO₂ concentration during the adsorption process. To enable proper sampling at a lower system pressure and to achieve the targeted 933 Pa (7 Torr) CO₂ partial pressure, a modification to the gas acquisition system is required and will be performed in a future effort. Operating the adsorber at 4000-4670 Pa (30-35 Torr) should still be acceptable for evaluating the feasibility and benefits of the Microlith-based regenerable CO₂ adsorber for separating CO₂ from Martian atmosphere. The resulting sorption capacity can still be compared against the sorption capacity of crystal or pellet version of the sorbent at the specific operating pressure and temperature. Additionally, adsorber operation at a lower temperature (<-10°C) will be targeted in a future effort by implementing an external chiller or freezer. In addition to comparing the performance metrics of the Microlith-based sorbent bed with the packed bed of pellets, the test results were also compared against other alternative technologies, such as CO₂ freezers under development at NASA Johnson and NASA Kennedy.

First, the sorbent bed was subjected to an adsorption process by exposing it to a gas mixture consisting of 95% CO₂. The exit CO₂ concentration was monitored using the Mass Spectrometer. Once the sorbent was saturated and CO₂ breakthrough occurred, the adsorption process was stopped and the adsorber was switched to desorption (regeneration) mode by applying electric current directly on the Microlith metal mesh. For CO₂ quantification purposes, a known amount of N₂ was flowed through the CO₂ adsorber during the regeneration process. Prior to heating the Microlith sorbent bed, the adsorber was purged with N₂ to remove the volume of CO₂ contained within the adsorber, but not actually adsorbed to the sorbent. Generally, after purging the bed for about 5 minutes, 27 volts (i.e., 80 W peak power) was applied across the Microlith mesh to resistively heat the sorbent bed to ~150°C. This voltage was determined to safely heat the bed at a rate of ~15°C/min which has been previously determined to minimize potential damage to the sorbent from thermal cycling. Once the bed reached 150°C, the voltage was reduced to 17 V (30 W) and was held there for 15 minutes until the bed reached ~170°C. The heating procedure took a approx. 25 minutes. The power was then discontinued and the sorbent bed was cooled down to the desired temperature prior to starting the next CO₂ adsorption. The regeneration cycle took place for a total of ~90 minutes, and the average power consumption during the 90-min cycle was calculated to be 10-15 W, depending on the sorbent used and the adsorption temperature. This procedure was used consistently for comparison purposes despite the potential for optimization of heating time, regeneration temperature, and power requirement. Also, the maximum ramp rate of 15°C/min was conservatively determined to be a safe operating protocol based on PCI’s previous experience. More tests will need to be performed to determine the effect of faster heating rates on the sorbent morphology and adhesion quality.
Table 1 lists the total amounts of CO₂ captured using the zeolite 13X-coated Microlith sorbent bed for all three different adsorption temperatures. Additionally, the average power consumption (during desorption) and the sorption capacities (weight basis and volume basis) of the sorbent calculated based on the amount of zeolite 13X (~52 grams) and the volume of the sorbent bed (500 ml) are included in the table. The sorption capacities were calculated based on the average of the values obtained from multiple cycles at the same temperature. A higher amount of CO₂ was captured and desorbed from the sorbent bed upon subjecting it to CO₂ adsorption cycle at a lower temperature. This is as expected since the CO₂ adsorption isotherms found in literature for zeolite 13X (as well as MS5A) indicate that the CO₂ sorption capacity increases at lower adsorption temperatures at the same CO₂ partial pressure.²⁷

Table 1. The average power during bed regeneration, the amount of CO₂ desorbed, and the sorption capacity for the zeolite 13X-coated Microlith sorbent bed at different adsorption temperatures. At least three adsorption-regeneration cycles were performed at each of the three temperatures.

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Sorption T (°C)</th>
<th>Average power (W)</th>
<th>CO₂ desorbed (grams)</th>
<th>Wt.% sorption capacity</th>
<th>Vol. sorption (g CO₂/L bed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-6</td>
<td>25</td>
<td>10</td>
<td>1.9 ± 0.3</td>
<td>3.6 ± 0.5</td>
<td>3.7 ± 0.6</td>
</tr>
<tr>
<td>7-9</td>
<td>10</td>
<td>11</td>
<td>5.3 ± 0.6</td>
<td>10.1 ± 1.2</td>
<td>10.6 ± 1.2</td>
</tr>
<tr>
<td>10-12</td>
<td>-10</td>
<td>12.5</td>
<td>8.5 ± 0.4</td>
<td>16.4 ± 0.7</td>
<td>17.1 ± 0.7</td>
</tr>
</tbody>
</table>

Figure 8 compares the average wt. % sorption capacity (i.e., capacity based on the weight of the sorbent material) obtained from the zeolite 13X-coated and the MS5A-coated Microlith sorbent beds at the three different temperatures. The test results indicate that the MS5A sorbent bed gives a higher sorption capacity compared to the 13X sorbent bed at 25°C. Zeolite 13X, however, performs better at the lower operating temperatures and achieves a higher sorption capacity at -10°C. Since the future CO₂ adsorber development will be aimed toward Martian application and will be exposed to Martian temperatures between -87°C and -5°C (186-268 K), the zeolite 13X-coated Microlith sorbent bed appears to give an advantage with its higher CO₂ sorption capacity. Therefore, zeolite 13X is selected for this application, and will be further examined in a future development effort.

The CO₂ sorption capacities obtained from both the zeolite 13X-coated and the MS5A-coated Microlith sorbent beds are comparable with the theoretical capacities found for the crystal (i.e., powder) version of the sorbents. Implementing the powder version of these sorbents for NASA applications, however, is not desirable due to their extremely high pressure drop (i.e., high parasitic losses) and fine particulates issues. A comparison of the performance of the Microlith-based sorbent beds to the packed bed of pellets (pellets tests were performed at NASA Johnson) indicates that the Microlith-based sorbent beds can perform better compared to the pellet counterpart. The tests performed at NASA Johnson on the zeolite 13X pellet bed gave a maximum CO₂ sorption capacity of only 6.6 wt.% (i.e., 6.6 grams of CO₂ uptake per 100 grams of sorbent) when operating the bed at -73.3°C and exposing it to 95.7% CO₂ with 2.7% N₂ and 1.6% Ar at 933 Pa (7 Torr) system pressure.²⁸ This sorption capacity is significantly lower than the 16.4 wt.% capacity obtained from the zeolite 13X Microlith sorbent bed at a higher adsorption temperature (-10°C) and a slightly higher CO₂ partial pressure (4000-4670 Pa). We expect the sorption capacity to be at least the same as we expose the Microlith-based sorbent to a lower temperature and a lower CO₂ partial pressure, which will need to be demonstrated in a future development effort.

Proof-of-concept testing performed on the Microlith-based regenerable CO₂ adsorber indicates two benefits of implementing zeolite-coated Microlith substrates for the separation of CO₂. First, the ability to directly resistively heat the metal mesh support permits a rapid increase in the sorbent bed temperature. In this example, the bed...
temperature was increased from ambient to 150°C in less than 10 minutes (i.e., limited by the safe approach on the heating rate), and can still be optimized. This confers a clear advantage over a packed bed of pellets that can only be regenerated using an external or embedded electric heater. Second, the high heat transfer property of the Microlith metal mesh results in a uniform temperature profile of the sorbent bed during the regeneration. All four thermocouples, which were placed at different axial and radial locations within the sorbent bed, showed similar temperature readouts (i.e., within 10°C) during desorption. This avoids any temperature excursions and local hot spots during heating of the sorbent bed, which can prolong the sorbent life and durability. In contrast, the more sluggish thermal response of a packed bed of pellets requires higher sorbent regeneration temperature and causes issues with local hot spots, which result in the sorbent deactivation.

D. Sabatier Reactor Development: Catalyst Optimization

We have previously reported the development of a proof-of-concept Microlith-based Sabatier reactor capable of producing high CO₂ conversion and near 100% CH₄ selectivity (i.e., ≥90% of the thermodynamic equilibrium values) at high space velocities and low operating temperatures. The reactor was operated at GHSV of 30,000 hr⁻¹. Additionally, the versatility of the Microlith-based reactor was demonstrated by operating it under H₂-rich (H₂/CO₂ ratio of >4), stochiometric (ratio of 4), and CO₂-rich (ratio of <4) conditions without affecting its performance. 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, the implementation of the Microlith-based Sabatier reactor has potential to increase the catalyst durability and to reduce the issues with “fines” generation in both ISRU and spacecraft applications.

Two areas that have been the main focus in the past year are catalyst optimization and heat-exchanger design optimization in order to provide higher conversion at lower catalyst temperatures (i.e., <350°C) and to gain better control of the reactor operating temperature.

Results from the proof-of-concept effort indicated that increasing active metal loading on the Microlith substrates, while maintaining a high catalyst dispersion on the washcoat support, can increase overall catalyst activity and improve the Sabatier reactor performance, including higher reactant conversions and CH₄ selectivity. Additionally, as mentioned previously, the Sabatier reaction is severely kinetically limited at low operating temperatures, which will result in reaction quenching due to slow rates of reaction. Therefore, in order to obtain high reactant conversion at the low temperature range (which is preferred for the reaction due to the thermodynamic limitations at higher operating temperatures), the surface area of the active sites within the Microlith substrates will need to be optimized. Here, therefore, the effect of higher metal loading on metal dispersion (i.e., exposed metal surface area) for Ru-coated and Rh-coated Microlith catalysts was examined. The goal was to achieve an optimum combination of catalyst loading and metal dispersion/active surface area that will enhance catalyst activity for the CO₂ methanation reaction.

The appropriate catalyst and high-surface-area washcoat formulations for operation under Sabatier reaction conditions were chosen based on the results from the earlier work. In this study, a rhodium-based catalyst formulation was chosen due to its high activity and high selectivity towards CO₂ methanation as shown in literature. Several washcoat formulations were evaluated to further increase the surface area of the washcoat support materials which should permit higher catalyst loadings with a high metal dispersion. The effort was also aimed toward maintaining the same adhesion quality with the one achieved in prior work while optimizing the washcoat support coating on the Microlith substrates. After applying the washcoat, the rhodium metal catalyst was coated on the Microlith substrates. The catalyst formulations must retain the desired chemical and physical characteristics of the metal catalysts (e.g., high dispersion). To date, five Rh/Microlith substrates with different catalyst loadings have been fabricated. The loadings were between 20.1 mg/ml (sample from the proof-of-concept effort) and 31.8 mg/ml.

To evaluate the effect of higher metal loading on metal dispersion, a 44.5-cm² (6.9-in²) sample of Rh-Microlith catalyst substrate was cut from each of the coated substrates and was placed into a chemisorption tube. The sample was then degassed at 300°C for 1 hr, followed by reduction in pure H₂ at 500°C for 1 hr. The H₂ chemisorption analysis was then performed at 40°C. Table 2 lists the catalyst loading from five Rh/Microlith catalyst substrates as well as the metal dispersion and corresponding active metal surface area measured by the H₂ chemisorption upon completion of the catalyst reduction process. Table 2 shows that as the Rh catalyst loading was increased from 20.1 mg/ml to 31.8 mg/ml, the Rh dispersion decreased from 22.5% to 16.0%. The optimum metal dispersion occurred at

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a rhodium metal loading of 21.4 mg/ml. The active metal surface area per gram of catalyst was calculated directly from the measured metal dispersion. Ultimately, the reactor performance for the Sabatier reaction should depend on the active metal surface area per unit volume of catalyst bed as a higher active metal area available for reaction within the same bed volume will increase the overall bed activity, resulting in performance improvement. This value was calculated by multiplying the catalyst loading (mg/ml) with the active metal surface area (m²/g metal). Based on the H₂ chemisorption results, the optimum catalyst loading for the Rh/Microlith substrate was determined to be ~27 mg/ml as it gave the highest available active metal surface area per bed volume. Performance testing is currently ongoing to verify this conclusion.

Table 2. Catalyst loading for the Rh/Microlith substrates and the corresponding metal dispersion measured by the H₂ chemisorption. The resulting active metal surface areas both based on the catalyst weight (m²/g of catalyst) and the catalyst bed volume (m²/L) are also included.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Rh loading (mg/ml)</th>
<th>Rh dispersion (%)</th>
<th>Active metal SA (m²/g metal)</th>
<th>Active metal SA (m²/L bed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.1</td>
<td>22.5</td>
<td>99.6</td>
<td>2000</td>
</tr>
<tr>
<td>2</td>
<td>21.4</td>
<td>22.8</td>
<td>100.4</td>
<td>2140</td>
</tr>
<tr>
<td>3</td>
<td>25.3</td>
<td>20.4</td>
<td>89.8</td>
<td>2270</td>
</tr>
<tr>
<td>4</td>
<td>27.0</td>
<td>19.7</td>
<td>86.9</td>
<td>2350</td>
</tr>
<tr>
<td>5</td>
<td>31.8</td>
<td>16.0</td>
<td>70.3</td>
<td>2240</td>
</tr>
</tbody>
</table>

E. Sabatier Reactor Development: Reactor Design Optimization

In the proof-of-concept study previously reported, PCI identified and implemented an approach for reactor operation at thermodynamically favored conditions to achieve high CO₂ conversion and high CH₄ 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 CO₂ methanation. The Sabatier reactor consisted of an approx. 20 cm (8 inches) long, 2.5 cm (1 inch) diameter stainless steel tube (including the reactant mixing section and inlet and outlet tubes) which contained approximately 12 ml (0.73 in³) of catalyst bed. A photo of the reactor is shown in Fig. 9. The catalysts 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 H₂ and pure CO₂ with known N₂ 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.

PCI has continued to develop the Sabatier reactor by performing reactor design optimization for the future SDU prototype. A number of new design features and modifications to the existing proof-of-concept Sabatier reactor were identified and discussed based on the test results. The objective of these design changes was to not only improve the reactant conversion to methane (and water) achieved by the reactor, but to also increase the heat exchange efficiency (i.e., reduced weight and size) and controllability of the catalyst bed temperature. Based on these discussions and further testing on the proof-of-concept reactor, a couple of designs that have the potential to achieve the stated objectives while still remaining relatively easy to manufacture were drafted.
F. Potential Future Work: Integration of Adsorber and Sabatier Reactor

PCI has developed the CO\textsubscript{2} adsorber and the CO\textsubscript{2} methanation/Sabatier reactor based on its patented Microlith technology and has demonstrated their performance for efficient removal (from cabin air or from simulated Martian atmosphere) and conversion of CO\textsubscript{2} to produce methane and water. Each unit shows potential to provide a compact, lightweight, and power efficient process to produce (or recycle) consumables (i.e., water and O\textsubscript{2}) and propellant fuel for both NASA’s ARS and ISRU applications.

Further effort is still required to develop and optimize an integrated Microlith-based regenerable CO\textsubscript{2} adsorber and CO\textsubscript{2} methanation reactor prototype for CO\textsubscript{2} capture and conversion to produce fuel and water/oxygen. The operating window for the integrated system will need to be mapped out per NASA specifications. Efforts toward realization of the CO\textsubscript{2} accumulator and compressor for CO\textsubscript{2} storage and flow management (between the CO\textsubscript{2} adsorber and the CO\textsubscript{2} methanation reactor) will need to be performed. Long-term performance durability with multiple startup/shutdown sequences will need to be validated.

IV. Conclusion

This paper demonstrates and validates proof of concept that the use of a novel Microlith-based CO\textsubscript{2} adsorber and methanation/Sabatier reactor system can be significantly beneficial for producing fuel and oxygen from the Martian atmosphere (for ISRU application) or cabin air (for ARS application) with high CO\textsubscript{2} conversion and high CH\textsubscript{4} selectivity at low system size/weight and low overall power consumption. For the CO\textsubscript{2} adsorber, the benefits include high heat and mass transfer properties, high surface area, and direct resistive heating capability. The unique capability for direct resistive heating of the Microlith metal mesh support permits rapid regeneration of the CO\textsubscript{2} adsorber via direct internal heating with lower power requirement, which confers a clear advantage over a packed bed of pellets that can only be regenerated using an external or embedded electric heater. Also, having high surface area and highly exposed/dispersed sorbent materials on the Microlith substrate assists the adsorption process by increasing the sorbent utilization. Finally, the high heat transfer property of the Microlith metal mesh permits uniform temperature within the sorbent bed during the regeneration process, avoiding temperature excursions and local hot spots that can lead to sorbent deactivation. For the CO\textsubscript{2} methanation reactor, the benefits are short contact time kinetics, high heat transfer, and high surface area of catalyst active sites that enable the creation of a highly efficient, compact, and durable Sabatier reactor.

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References