CERAMIC FOAM CATALYST—Researchers seek ways to reduce the amount of material astronauts must carry into space. Because fuel for the return trip to Earth consumes too much space, producing fuel in extraterritorial resources is a primary goal. Ceramic foam catalysts increase efficiency and improve reactors for the production of methane, a return fuel.

Advanced Catalysts and Reactors for Mars Exploration Sabatier Processors

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Abstract— Future manned missions to Mars plan to use in-situ resource utilization (ISRU) to reduce the mass of imported supplies. For example, by reacting hydrogen (shipped from earth or made from indigenous water) with carbon dioxide in the Martian atmosphere, methane can be produced and used as a fuel for the return journey. The co-product, water, is a source for the oxidant. This reduces the weight of fuel sent from Earth and can reduce overall costs by up to 45 percent.

The process uses $Ru/\gamma\text{-}Al_2O_3$ catalysts in fixed bed reactors and is very exothermic (i.e. liberates heat). Heat must be removed and recovered from the reactor, and doing this can add mass and, if not functioning properly, can cause the system to fail.

This research alleviates these difficulties by using ceramic foam catalyst supports that give lower pressure drop, higher activity, and improved heat transfer from the reactor, resulting in reduced mass, higher energy efficiency, and greater reliability. UH faculty in Chemical Engineering have developed techniques for loading foams with *Ru* catalysts in the correct proportions. Comparison of the performance of these foam catalysts with conventional catalyst pellets shows an improvement by a factor of two in activity and a factor of five to seven in heat transfer. With these results, better catalysts and reactors can be designed for improved systems.

In-situ resource utilization (ISRU) is one of five areas with the highest cost leverage for manned missions to Mars.[1] Specifically, manufacturing the propellant for the return journey from Martian resources reduces earth-to-orbit mass by 20-45 percent, thereby increasing the cost-effectiveness of the mission. NASA plans to establish chemical plants on Mars prior to the arrival of the first astronauts. These chemical plants will process carbon dioxide from the Martian atmosphere to make methane, using the Sabatier reaction,

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \tag{1}$$

with H_2 shipped from Earth or produced from indigenous water. The principal product, CH_4, will be used as fuel for the return journey. In addition, H_2O produced in Reaction (1) can be converted via electrolysis to generate more H_2 (recycled to the process) and O_2 (for use as an oxidant and for life support). System studies show that the cost of Earth launch is reduced by one half, since a unit of CH_4 generates more thrust than the H_2 used to make it, and less cryogenic storage is required.

Reaction (1) occurs in a tubular fixed-bed of catalyst pellets comprising *Ru* dispersed on $\gamma\text{-}Al_2O_3$. The thermodynamics of the reaction indicate high exothermicity and equilibrium limitation. Heat liberated must be removed to prevent temperature increases in the bed that could destroy the catalyst and the reactor.[5] Usually, long, narrow reactor tubes with high surface-to-volume ratios transfer the heat of reaction outside to some heat transfer medium. A problem is the resulting high-pressure drop, usually overcome by using bigger catalyst pellets. This, in turn, leads to mass diffusion restrictions, so that the effectiveness of the catalyst decreases and larger reactor volumes are needed. Since the main objective of ISRU is mass reduction, increasing heat transfer from the tubes will remove these problems and give a more compact, efficient and safer reactor system.

In this ISSO project, we have explored the feasibility of using catalyst beds made of ceramic foam to accomplish better heat removal from NASA's Sabatier reactor.

Technical Plan and Equipment

Ceramic foams are preformed retriculated structures that are positive images of plastic foams.[2,3] They exhibit extremely high porosities (85 to 90 percent), formed by megapores 0.04 to 1.5 mm in diameter, and spherical-like cells connected through windows. Figure 1 demonstrates these features with a micrograph of an α-Al_2O_3 foam with a pore density of 30 pore per inch (PPI). The pore structure has a high degree of interconnectivity and is characterized by a mean pore diameter d_p. High bed porosity is important, since it gives a much lower pressure drop in a reactor filled with a foam "cartridge" rather than packed particles, thus reducing compression requirements.[3] Furthermore, the extensive pore tortuosity enhances turbulence, mixing, and transport. These features result in significant advantages for catalytic processes limited by mass or heat transfer.

We have measured pressure drop over a wide range of foam samples, and the results confirm a pressure drop advantage of over a factor of ten for foam beds compared to an equivalent bed of packed particles.[4] Similarly, heat transfer measurements showed that radial heat transfer out of the tubes increases by a factor of five to seven (Fig. 2).[5]

In this project, we have investigated the use of ceramic foam structures in Sabatier reactors planned for Mars missions. The principal objectives were (1) to demonstrate that ceramic foams could be successfully loaded with catalyst formulations identical to the Sabatier pellets, (2) to measure kinetic rate equations for the foam-Sabatier reactor and compare them to the pellets, and (3) to construct a simulation model for the reactor based on experimentally-determined parameters.

Based on previous experience, the following advantages were expected:

Higher volume activity. The external surface of ceramic foam is equivalent to a bed of small particles, much smaller than could be used in a reactor. Mass transfer and pore diffusional resistances to reaction are reduced, and the bed should exhibit much higher catalytic activity per unit volume, resulting in smaller reactors, i.e. reduced mass.

Greatly enhanced heat transfer. Figure 2 demonstrates the effect of increasing the wall heat transfer coefficients, with a corresponding temperature decrease in the reactor temperature, resulting in improved overall heat control. Operation of the reactor is more stable, and catalyst deactivation, due to sintering at high temperatures, greatly reduced. In addition, reaction heat is more easily recovered for use in other parts of the plant.

Lower pressure drop. Pressure drop is reduced by about a factor of ten, thereby saving mass since smaller pumps will suffice. Energy consumption is also be lowered.

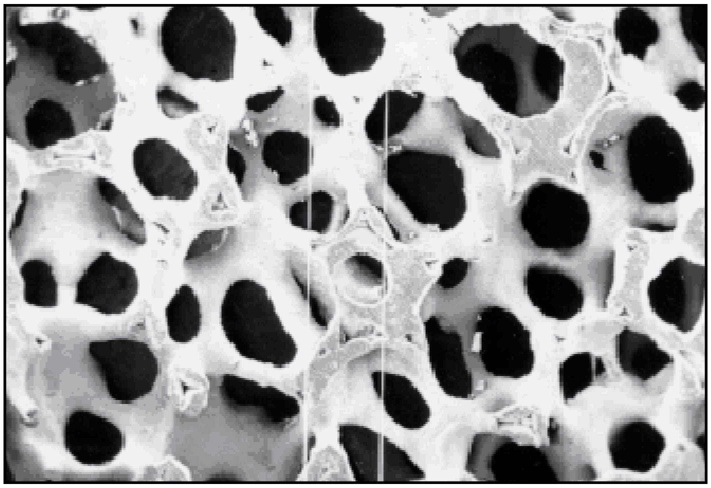

Figure 1. Microstructure of 30 PPI α-Al_2O_3 ceramic foam.

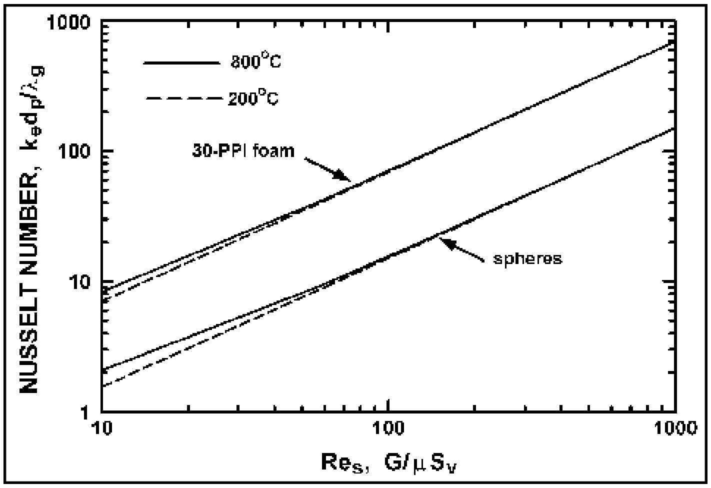

Figure 2. Comparison of radial heat transfer with foam and pellet catalyst beds.

Results and Discussion

Objective No. 1. Loading the foam with the catalyst. Sabatier catalyst particles are 2-3 mm diameter pellets of γ-Al_2O_3 loaded with 0.5-5.0wt% Ru. The γ-Al_2O_3 has a BET surface area of about 100 m^2g^{-1} and the Ru is present as crystallites 5-20 nm in size. The first task was to reproduce these properties in the α-Al_2O_3-foam, which has a low surface area (1-2 m^2g^{-1}). A washcoat of γ-Al_2O_3 was added to increase the area for Ru deposition. Pellets of the foam (1-cm diameter, 2.5 cm in length) were dipped into a 15 percent slurry of high purity boehmite containing 15 percent aluminum nitrate and 0.5 percent glycerol. After one hour, the pellets were removed, drained by shaking and air blowing, and then dried in a microwave oven for three to five hours. This was followed by calcining in an oven for two hours at 550°C. The active component (*Ru*) was added by impregnation with a solution of $RuCl_3 \cdot \times H_2O$, 99.9 percent in ethanol with a concentration calculated to yield a desired 1.0 wt% *Ru* on the finished catalyst. Enough solution was used to just fill the estimated pore volume of the washcoat. The wet pellets were dried in the microwave oven at 105°C for one hour and then calcined at 550°C for four hours to convert

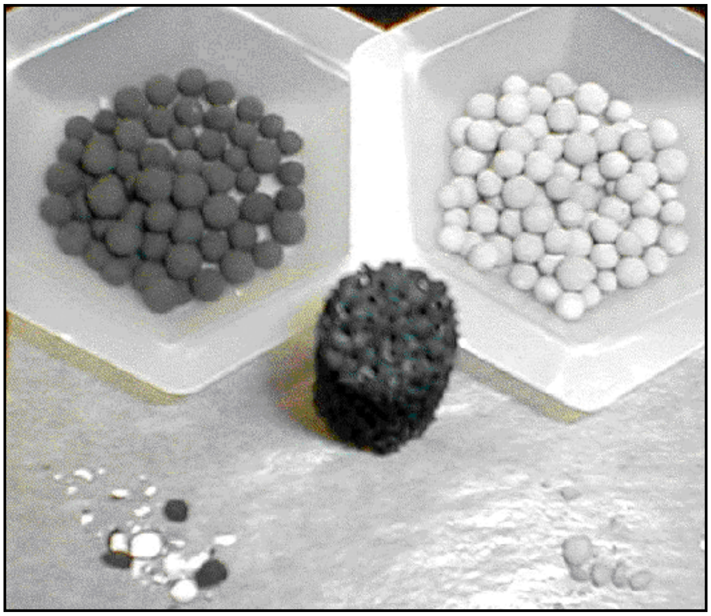

Figure 3. Sabatier catalyst pellets and foams. Upper left: 1.8 mm γ-Al_2O_3 spheres loaded with about 1 wt% *Ru*, metal on the exterior. Upper right: 1.8 mm γ-Al_2O_3 spheres loaded with about 1 wt% *Ru*, uniform metal loading. Center: 30-PPI foam pellet loaded with about 1 wt% *Ru*.

FOAM—Foam cylinders improve catalytic reactors in heat transfer by enhancing turbulence, mixing, and transport.

the salt to the oxide.

These procedures resulted in 30-PPI foam pellets containing 15wt% washcoat as a 50-μm porous layer over the struts of the foam, with an overall surface area of 13.3 m²g⁻¹. After reduction in H_2 at 550°C, X-ray diffraction measurements showed that the washcoat contained 0.85wt% *Ru* metal in the form of crystallites 19.4 nm in size.

Samples of 1.8-mm spherical pellets of γ-Al_2O_3 were treated in a similar manner to produce regular pelleted catalysts for comparison. Typical results are shown in Fig. 3. The spheres in the upper left are black in color and measurements showed that *Ru* was concentrated in the outer layers of the pellet. Since this was undesirable, it was remedied by adding *HCl* to the impregnation solution, resulting in the uniformly loaded pellets in the upper right. Asample of the *Ru*-loaded ceramic foam is shown in the center. The foam pellets is loaded uniformly throughout the structure.

Objective No. 2. Measurement of catalytic kinetics. An existing kinetic apparatus, consisting of a gas metering manifold, a fixed bed reactor, temperature control, and a chromatograph-based analytical system was adapted for studies on Reaction (1). Differential (low conversion) rate measurements were made on the foam, the 1.8-mm pellets and 60-100 mesh (200 μm) powder made by crushing the pellets. Typical results for the foam at 200°C (Fig. 3) show the dependence of the rate on the partial pressure of CO_2 and H_2, the other held constant. This is consistent with a rate equation of the form

$$Rate_{CH_4} = kK_{CO_2} P_{H_2} P_{CO_2} \Big/ \left(1 + KP_{CO_2}\right) \qquad (2)$$

based on an Eley-Rideal mechanism for the reaction. The apparent activation energy is 52 kJ mol⁻¹. Similar rate equations were determined for the pellets and powder. The results of these kinetic studies are summarized in Table 1.

These results show that the pellet has an effectiveness factor of 0.19 when compared to the powder and that the foam is very nearly equivalent to the powder. The critical factor, however, is the difference in the rate per unit volume of the reactor between the pellet and the foam. Table 1 shows an increase by over a factor of two. Possibly, the loading of the foam could be increased to give an even better comparison.

These results imply that the volume of the reactor could be reduced to half the original size with an equivalent saving in space and mass. Alternatively, heat could be removed from the reactor more efficiently, giving better heat recovery, more stable reactor operation, and greater catalyst lifetime.

Objective No 3. Model simulation of the Sabatier reactor. Development of a 2-dimensional model reactor for the Sabatier reactor is in progress. This model generates both axial and radial temperature profiles and is superior to the 1-D model in Fig. 2 that uses only average bed temperatures. The kinetic rate equations measured in this project, together with 2-D heat transfer correlations already found in this laboratory, will be used in this model to accurately predict temperature profiles under a wide range of conditions. Parametric data for process optimization, detailed designs, and system analyses will possibly use this model.

The final step in this project will be testing a prototype reactor under Martian conditions. Although the simulation model will predict many of the results, only pilot testing can validate performance, operability, and long-term stability or reliability.

This project has demonstrated that the NASA Sabatier reactor is a candidate for improved heat removal using ceramic foam as the catalyst bed. The feasibility of loading the foam with a washcoat containing the Sabatier catalyst has been demonstrated. Kinetic rate equations have been measured and compared with a conventional pelleted catalyst. A kinetic advantage of over a factor of two was demonstrated and this could possibly be increased

Table 1. Summary of kinetic differences between powder, pellet and foam catalysts. Temperature = 225°C, P_{CO_2} = 0.100 atm, P_{H_2} = 0.500 atm.

	60-100 mesh powder	1.8 mm pellets	30-PPI foam
wt% *Ru*	0.90	0.90	0.85
surface area, m^2g^{-1}	139	139	13.3
d_{XRD}, nm	16.1	16.1	19.4
bed porosity	0.35	0.45	0.84
bed density, g cm^{-3}	1.67	1.30	0.64
rate × 10^{-5}, mol s^{-1} $g(cat)^{-1}$	9.35	1.76	7.23
rate × 10^{-3}, mol s^{-1} $g(Ru)^{-1}$	10.4	1.96	8.51
rate × 10^{-5}, mol $s^{-1}(cm^3$ bed$)^{-1}$	15.6	2.28	4.63

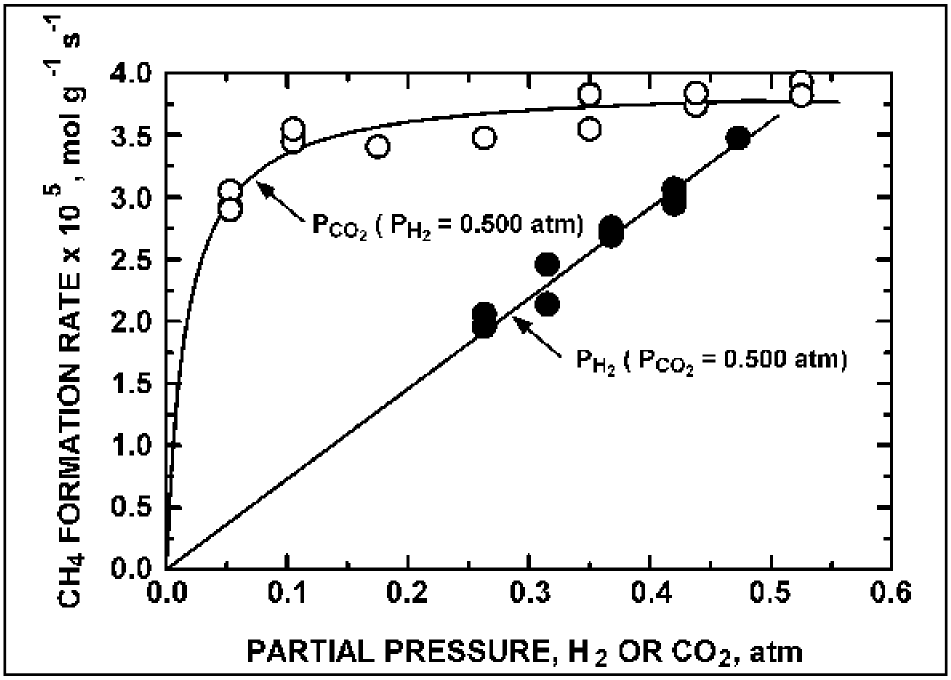

Figure 4. Typical kinetic data with the ceramic foam catalyst in UH experiments

at least a factor of two. This improvement, together with previously proven advantages for enhanced heat transfer, could lead to smaller process equipment (mass savings) and to safer process control and longevity.

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