Improved Sabatier Reactions for In Situ Resource Utilization on Mars Missions

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IN-SITU RESOURCE UTILIZATION (ISRU) IS ONE OF FIVE AREAS with the highest cost leverage for manned missions to Mars.[1] Specifically, ISRU applied to the manufacture of the propellant for the return journey 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 recovered 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 CH_4 generates more thrust per unit mass than H_2.

Reaction (1) takes place in a tubular fixed-bed of catalyst pellets comprising Ru dispersed on γ-Al_2O_3. The thermodynamics of the reaction, shown in Fig. 1, indicate that it is highly exothermic and that equilibrium conversions start to decrease at temperatures above 300°C. Heat liberated must be removed to prevent temperature increases in the bed that could destroy the catalyst and the reactor. The reduction of heat is achieved by using some heat transfer medium on the outside of the tube, but heat transfer rates within the reactor are limited by the convective flow through the bed and are not high enough. Long, narrow reactor tubes with larger heat transfer surfaces are required. The resulting high-pressure drop in the tubes is usually overcome by using larger catalyst pellets. However, larger diameter particles give mass diffusion restrictions, so that the effectiveness of the catalyst decreases and larger reactor volumes are needed. Alleviating the heat transfer problem removes these problems and provides for a more compact, efficient and safer reactor system.

The main concerns in ISRU applications are mass reduction, energy efficiency, and reliability. For the reduction of mass, the catalyst activity should be as high as possible, since this reduces the size of the reactor and allows low reactor temperatures. Energy efficiency relates to the effectiveness of integrating heat recovery with energy demands of the process, and simple heat exchange schemes are desirable. Long-term reliability can only be ensured if catalyst deactivation is minimized. This is best achieved in exothermic beds by avoiding intra-bed temperature gradients and hot spots. Past and current research in the University of Houston's Chemical Engineering Department addresses these issues for a number of important chemical processes. In this ISSO project, we explore the feasibility of using catalyst beds made of ceramic foam to accomplish better heat removal from NASA's Sabatier reactor.

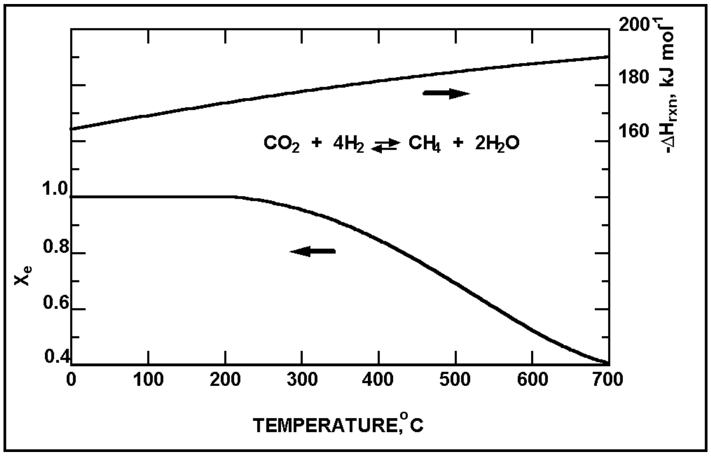


Figure 1. Thermodynamic equilibrium conversion and the enthalpy of reaction for the Sabatier reaction.

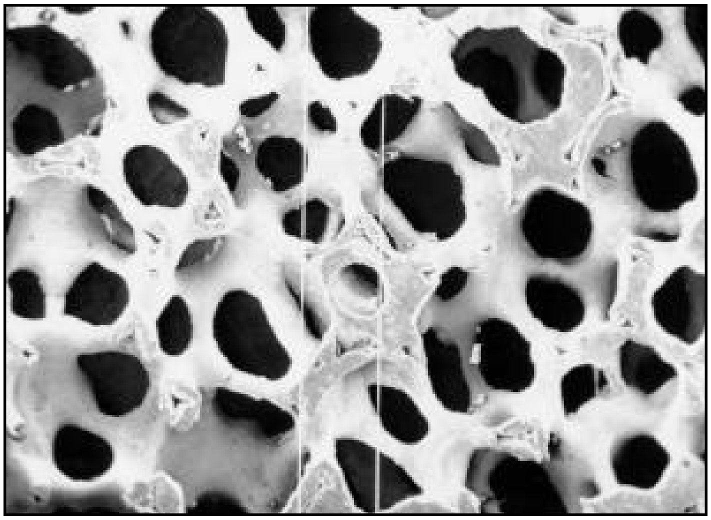


Fig. 2. Microsctructure of 30 PPI α-Al_2O_3 ceramic foam

Methodology

Ceramic foams are preformed reticulated 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 2 shows a micrograph of an α-Al_2O_3 foam that demonstrates these features for a sample 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.

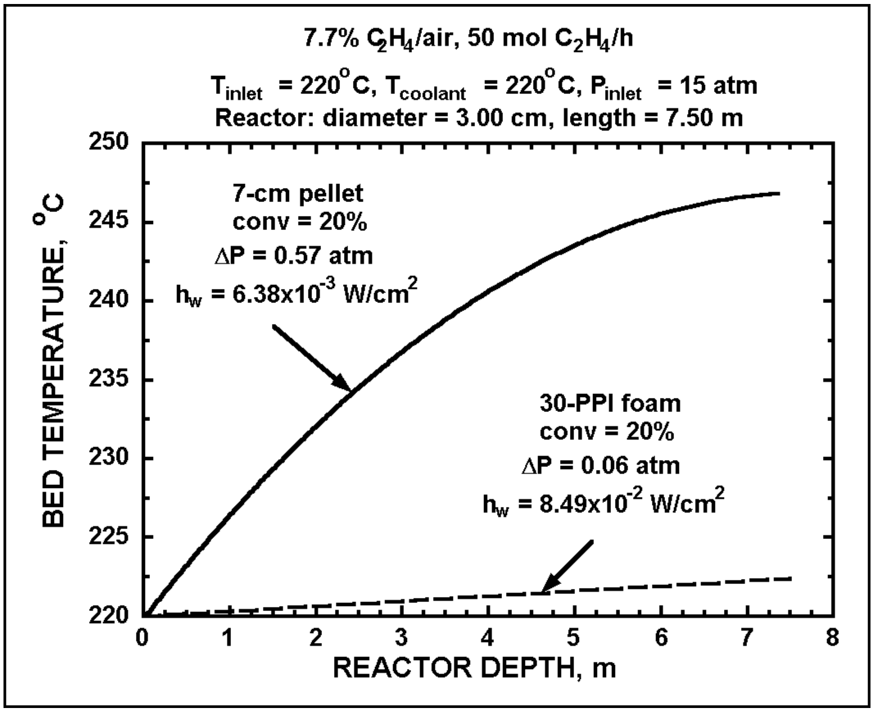
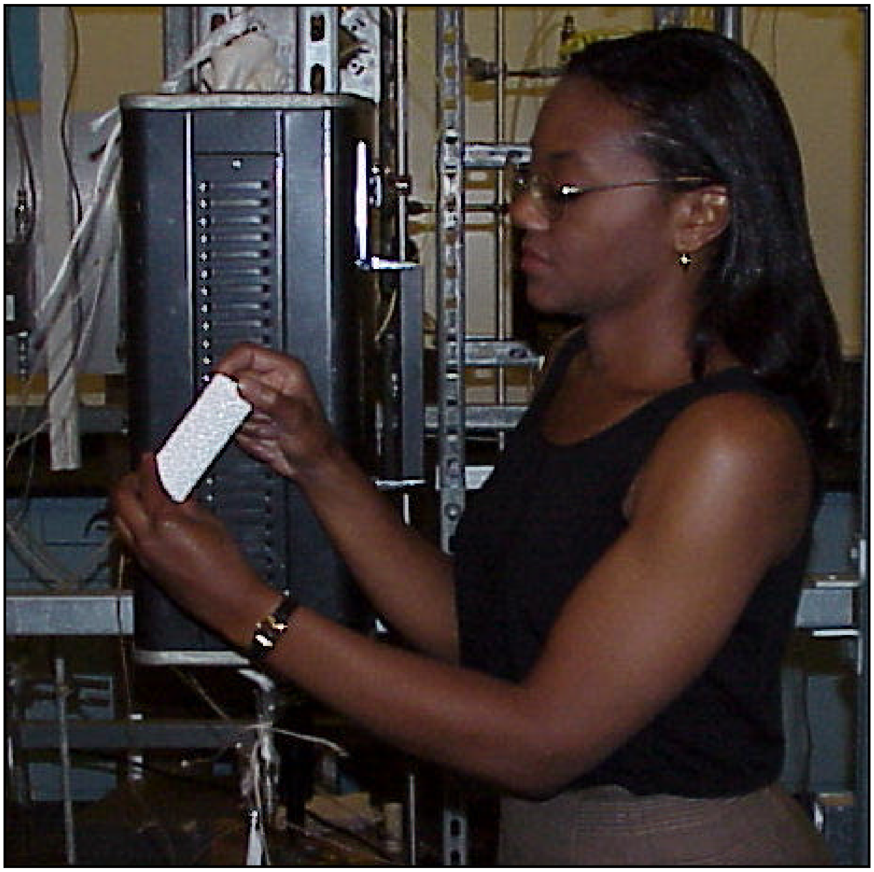


Figure 3. Average axial temperatures for an ethylene oxide reactor containing convention and foam catalyst supports.



CERAMICS—Stefanie Brown, graduate research assistant in chemical engineering, prepares the alumina ceramic foam catalyst for analysis in the laboratory chromatograph.

High bed porosity is the most significant property, since it gives a much lower pressure drop in a reactor filled with a foam "cartridge" rather than packed particles.[3] This is highly desirable in long narrow reactor tubes, where pressure drop results in higher compression requirements. Furthermore, foams have extensive pore tortuosity that enhances turbulence, mixing and transport. These features result in significant advantages for catalytic processes limited by mass or heat transfer.

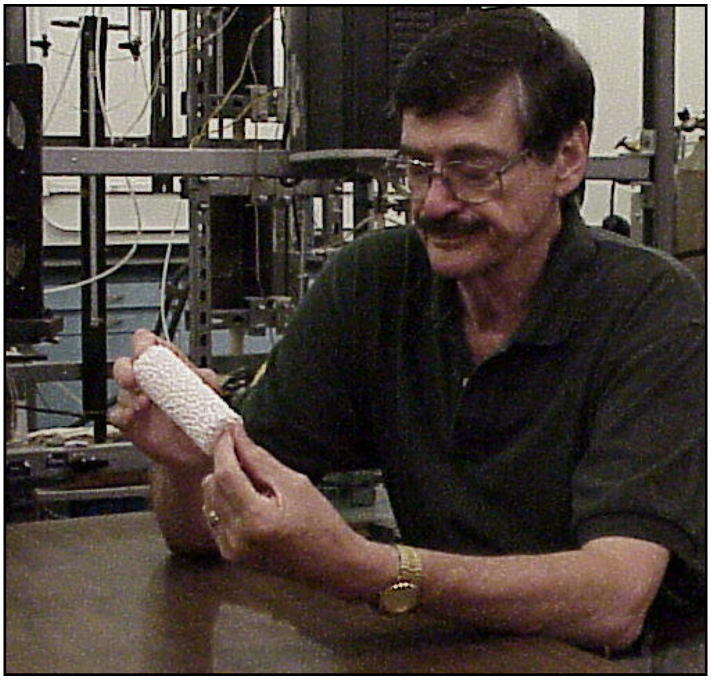
We have previously measured pressure drop over a wide range of foam samples, and the results confirm a pressure drop advantage of over a factor of ten for foam beds compared to an equivalent bed of packed particles.[4]

We also carried out extensive studies on steam reforming, an endothermic process, and showed that reactor tubes could be decreased in size by a factor two due to improved heat transfer.[5]

Recently, our work has involved reactors for ethylene epoxidation to ethylene oxide, a process with many of the same features as the Sabatier reaction. We prepared samples of ceramic foam loaded with appropriate catalysts and found that the usual mass transfer limitations found in commercial catalysts are absent, so that the effectiveness or activity per unit volume is higher. Heat transfer measurements over a wide range of flow rates showed that radial heat transfer out of the tubes increased by a factor of five to seven.[5] A reactor model based on these results indicates a greatly reduced axial temperature profile with a foam bed for an ethylene partial oxidation reactor utilizing a foam catalyst support.

In this project, we apply similar methodology to preliminary studies of Sabatier reactors currently planned for NASA Mars missions. Based on previous experience, the following advantages are expected:

1) 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.
2) Greatly enhanced heat transfer. Figure 3 demonstrates the effect of increasing the wall heat transfer coefficients, with a corresponding temperature decrease in the reactor temperature. This should also be true for the Sabatier reactor, resulting in improved overall heat control. Operation of the reactor will be more stable, and catalyst deactivation due to sintering at high temperatures greatly reduced. In addition, reaction heat will be more easily recovered for



CATALYST EXPERIMENTATION—Dr. James Richardson, professor of chemical engineering, with the alumina ceramic foam catalyst designed to meet Martian reactorspecifications. To reduce mass, catalyst activity should be as high as possible since this reduces the size of the reactor and allows low reactor temperatures. Long-term reliability can only be ensured if catalyst deactivation is minimized.

use in other parts of the plant.

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

Results and discussion

The initial phase of this research has focused on the following three tasks:

Task No. 1. Loading the foam with the catalyst. The pelleted Sabatier catalyst particle consists of 2-3 mm diameter pellets of γ-Al_2O_3 loaded with 0.5-5.0 wt% *Ru*. The γ-Al_2O_3 has a BET surface area of about 100 m^2g^{-1} and the *Ru* is highly dispersed to form crystallites 5-20 nm in size. The first task is to reproduce these properties in the foam. The foam has a low surface area (1-2 m^2g^{-1}), so a washcoat of γ-Al_2O_3 must be added to increase the area for *Ru* deposition. We estimate that the same activity per unit reactor volume could be achieved with a foam surface area of about 20 m^2g^{-1}, since the effectiveness factor is much higher. Experiments were conducted to determine the best conditions to achieve this surface area. Our best achievement to date with 10 wt% loading of γ-Al_2O_3 resulted in 15 m^2g^{-1}. This can be improved, and experiments are continuing.

The washcoated foam was successfully loading with 1 wt% *Ru* using a ruthenium chloride impregnation technique. This catalyst is now being using for preliminary scoping experiments.

Task 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 has been adapted for studies on Reaction 1. Preliminary measurements with pelleted Sabatier catalysts demonstrated good system performance. The next step will be to determine the kinetic rate equation for small foam segments, using differential rate measurements.

Task No 3. Model simulation of the Sabatier reactor. A two-dimensional model reactor for the Sabatier reactor has been developed. This model generates both axial and radial temperature profiles and is superior to the 1-D model in Fig. 3 that uses only average bed temperatures. The rate equations from Task No. 2, together with heat transfer correlations already found previously 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 possible using this model.

Future Research

Future research will initiate a final task:

Task No. 4. Sabatier reactor prototype testing. Based on the results of Task No. 3, a prototype reactor will be constructed to simulate Martian operations. This will be tested for performance, operability, and long-term stability or reliability.

Conclusions

This project has demonstrated that the NASASabatier 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 confirmed.

References

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[4] J. T. Richardson, Y. Peng, and D. Remue, "Properties of Ceramic Foams as Catalyst Supports: Pressure Drop," *Appl. Catal. A: Gen*. (*accepted for publication*).

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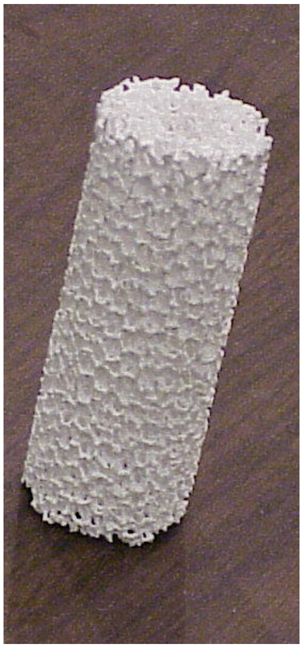

Ceramic Foam Catalyst