Carbon Dioxide Methanation for Human Exploration of Mars: A Look at Catalyst Longevity and Activity Using Supported Ruthenium

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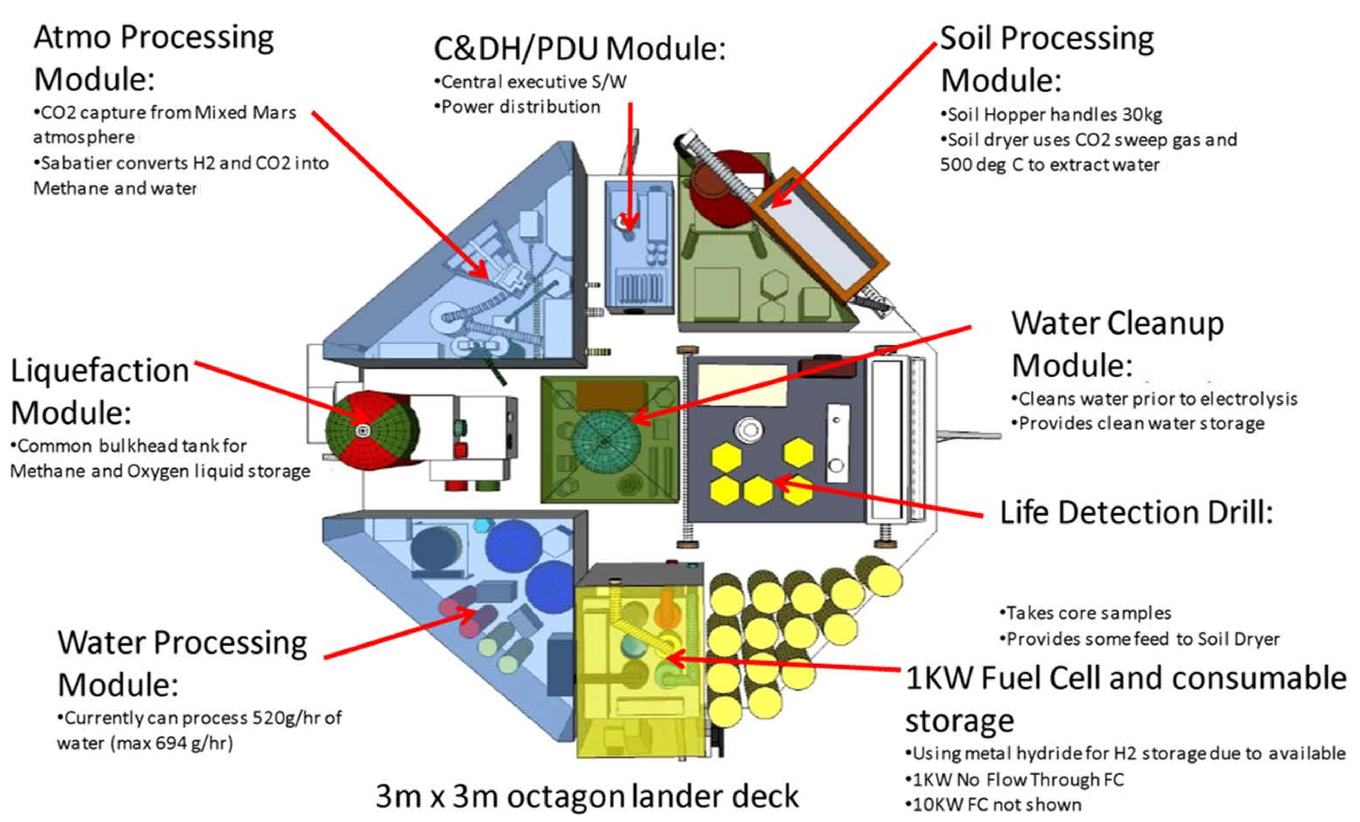
INTRODUCTION



Proposed deck layout for the Mars In-Situ Resource Utilization (ISRU) Lander

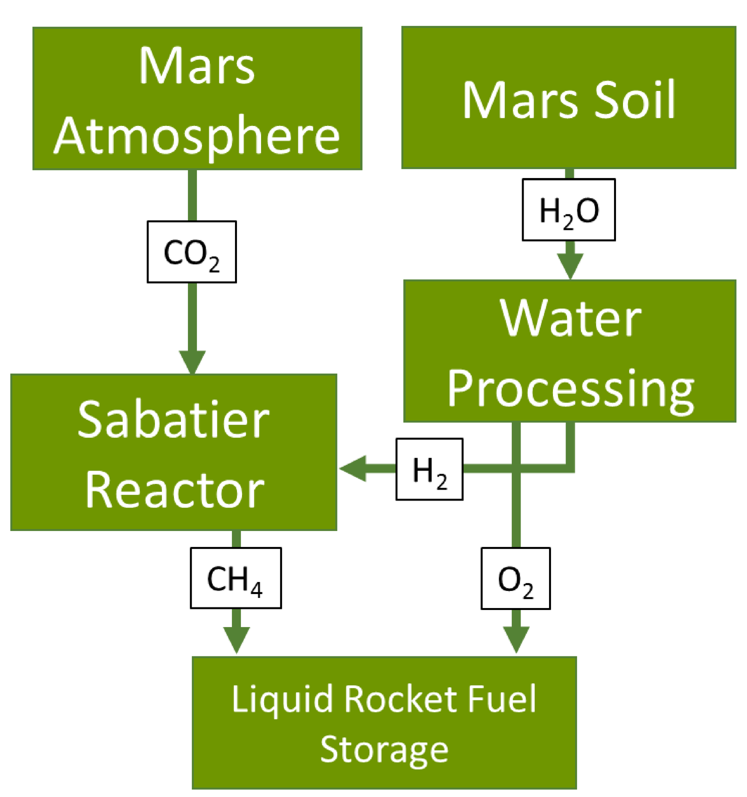
Objective

The remote operation of the Mars ISRU lander to produce rocket fuel prior to crew arrival on the planet to power an ascent vehicle.

Constraints

- Long-term operation (480 days)
- Variable conditions
  - Feed gas flow rates
  - Feed gas flow ratios
  - Reactor bed temperature

Functions of the Mars ISRU Lander



Catalyst Deactivation

- Bed temperature typically >300°C
- Highly exothermic

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$\Delta H = -165 kJ/mol$$

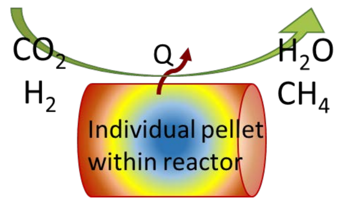
- Steam produced by reaction

Commercial 0.5%Ru/γ-Alumina catalyst

Thermally induced deactivation after ~100 hours on stream and max temp of 560°C

hot spots → elevated surface temperature

- mechanical stress
- carbon monoxide production
  - methane steam reforming
  - reverse water-gas shift
- sintering
- phase transition in the support / pore collapse



OVERARCHING PURPOSE

To design a carbon dioxide methanation/Sabatier reaction catalysts able to withstand variable conditions including fluctuations in bed temperature and feed flow rates for 480 days of remote operation to produce seven tons for methane.

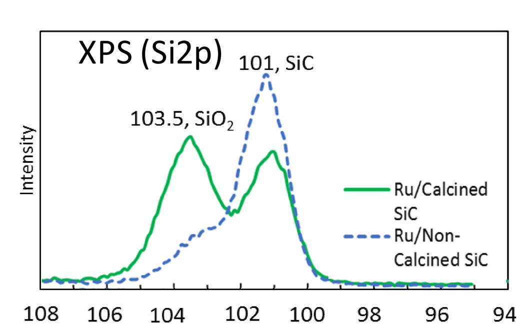
CURRENT STUDY PURPOSE

Examine supported Ruthenium as a carbon dioxide methanation catalyst to determine the effects support properties have on the active phase by studying activity and selectivity.

METHODS

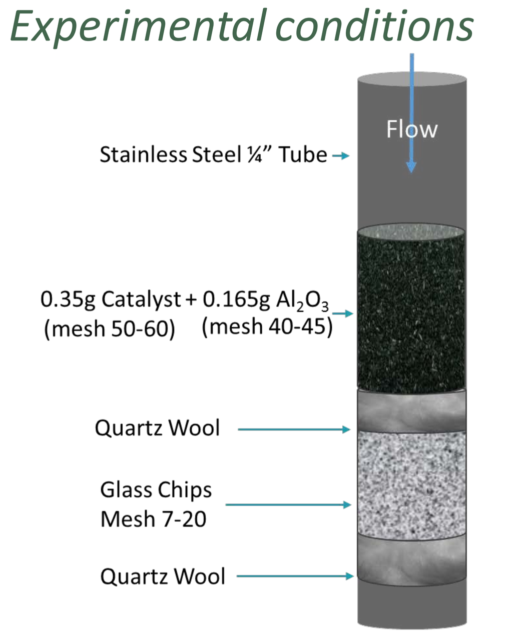
Catalyst Synthesis

- 5wt% Ru/Support
- Incipient wetness impregnation
- Supports used as received
  - TiO_2 – 97%Rutile
  - TiO_2 – 98% Anatase
  - γ-Al_2O_3
  - β-Silicon Carbide (β-SiC)
    - Calcined at 800°C for 2h
    - Non-Calcined



A thin layer of SiO_2 on Calcined β-SiC

Experimental conditions

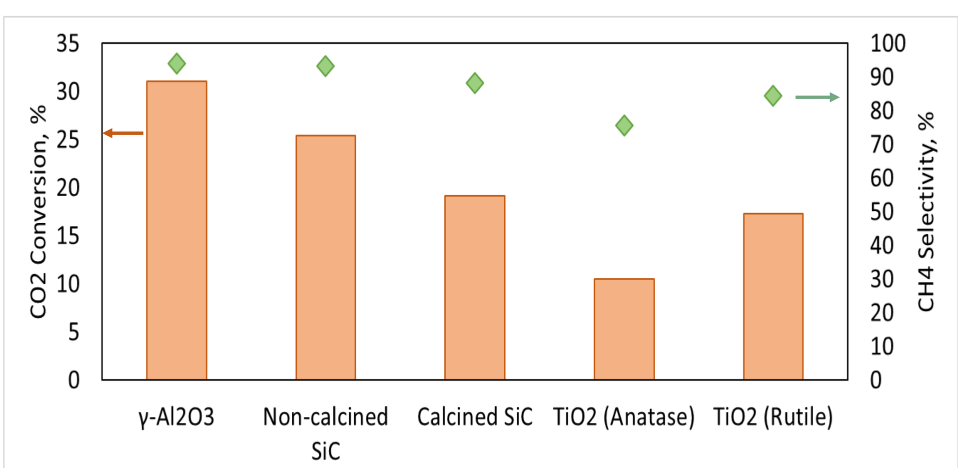


In-Situ Reduction:
30 min, H_2 flow=120mL/min
300°C
Reaction:
325°C ~7hr
Feed Ratio:
4:1 (stoichiometric)
GHSV:
25,000 h^{-1}
Stream Analysis:
Thermal Conductivity Detector (TCD)
He carrier gas

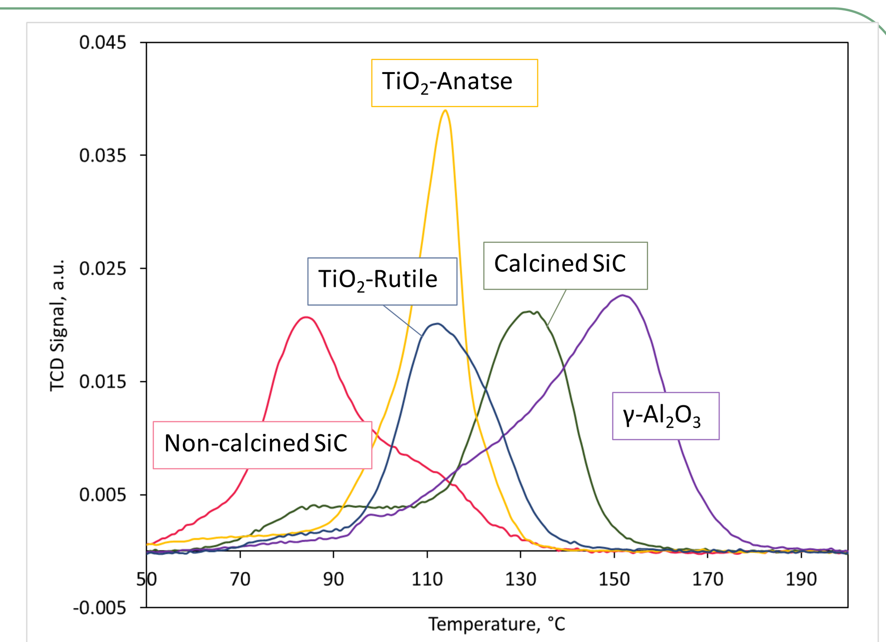
Characterization

- Hydrogen chemisorption
- Nitrogen physisorption (BET)
- Temperature-Programmed Reduction (TPR)

RESULTS



The benchmark catalyst, 5%Ru/Al_2O_3, performed the best with the highest conversion and selectivity as well as the largest temperature of reduction indicating a favorable relationship between this support and the catalyst.



Calcined SiC has a slightly higher dispersion than Non-calcined SiC as expected due to the –OH anchoring sites made available by the SiO_2 layer formation.

Catalyst	Ru Particle Size (nm)		Surface Area $\left(\frac{m^2}{g}\right)$		Thermal Conductivity $\left(\frac{W}{m \cdot K}\right)$	CH_4 Yield (%)
	Pre-reaction	Post-reaction	Pre-reaction	Post-reaction		
5%Ru/γ-Al_2O_3	9.0	10.8	176	150	25	29.2
5%Ru/Non-calcined SiC	10.2	12.1	28	27	150	23.7
5%Ru/Calcined SiC	9.7	10.0	28	28	<150	16.8
5%Ru/TiO_2 (Anatase)	13.8	16.2	134	130	8.3	8.0
5%Ru/TiO_2 (Rutile)	11.9	14.0	15	15	8.3	14.6

CONCLUSIONS

Selectivity improves over time – sintering of the smallest Ru particles

Overall particle size increases and some support sintering is possible but not outside possible error for BET. It is surprising that the rutile titania does not perform better as a support. Its superior performance has been documented in previous work.

REFERENCES

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