Chemical reaction engineering beyond earth: Design study and experimental proof of concept for the Sabatier reaction in a polymeric reactor

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Highlights

- Polymeric reactors can be applied for thermocatalytic reactions.
- CO_2-Hydrogenation can be conducted in a polymeric reactor.
- Proof-of-concept for Martian propellant production.

1. Introduction

In space missions, the role of reaction engineering is crucial due to limited material availability. This necessitates highly integrated major process streams for optimal utilization, even when the destination has its own resources, such as a planet or moon. Efficient material utilization is essential. For instance, in a manned Mars space mission, in-situ resource utilization (ISRU) is employed to produce rocket fuel (methane) for the return to Earth using water and carbon dioxide on Mars [1,2]. This strategy prompts a reevaluation of the reaction engineering aspects of a methanation reactor, given the unique opportunities and constraints of a Mars mission. Previous investigations into CO_x-methanation have indicated promising catalytic activity for a process window that allows for the operation of a polymeric reactor [3].

In our research, we combine theory and experiments to validate the feasibility of a polymeric reactor. We carefully select and analyze design criteria, emphasizing heat management, structural robustness, and gas permeability of chosen materials. An identified catalyst defines the optimal operational range, undergoing detailed experimental scrutiny with a focus on assessing anticipated reactor productivity.

2. Methods

In the initial evaluation, we systematically assessed the merits and drawbacks of polymeric reactors for the design process. Notably, these reactors have limited compatibility with high temperatures and pressures, prompting our focus on addressing thermal management and ensuring mechanical stability. Two polymers, PTFE (polytetrafluoroethylene) and PFA (perfluoroalkoxy alkane), emerged as promising candidates due to their thermal stability and mechanical properties. Subsequent analysis indicated the potential for the Sabatier reaction below 240 °C, contingent on the use of a catalyst with sufficient activity in this temperature range [3,4]. Furthermore, experimental evidence confirmed that polymeric materials inherently exhibit gas permeability, which intensifies with rising temperatures [5].

During catalytic testing, the catalyst and experimental setup were precisely tailored to our key areas of interest. The thermal management was monitored by three thermocouples. Various Ru-based catalysts underwent reduction studies, specifically using temperature-programmed reduction (TPR). The most promising formulations were first assessed in steel reactors. Thereafter, polymeric reactors were equipped and operated over 5 days, incorporating diverse operating conditions. Throughout this period, we introduced variations in temperature (160-220 °C), pressure (1 and 4 bar), and composition (CO_2:H_2 ratios of 1:3, 1:4 and 1:5). Additionally, (de)activation was measured at various intervals under reference conditions.

3. Results and discussion

The TPR measurements revealed excessively high reduction temperatures for Ni/Al_2O_3 catalysts, starting at 260 °C beyond the maximum operating temperature of the polymers. While the Ni catalyst exhibits activity at the target temperature, its pretreatment cannot occur in the polymeric reactor. Alternative Ru-based catalysts could be activated below 200 °C, but their activity heavily depended on the support material. Titania emerged as the most effective support for low-temperature methanation on Ru, surpassing traditional materials like alumina.

The permeability and mechanical integrity of the polymeric material were assessed. In extended experiments at 240 °C and 5 bar (gauge), slight changes in shape were observed due to creep processes during operation. Permeation experiments established a distinct correlation between permeation rate, temperature, and pressure. This relationship allowed us to determine that the anticipated permeation during reaction experiments would be low compared to the feed gas molar flow rate (0.2% at 220 °C).

The reaction experiments in the polymeric reactors were successfully conducted. Throughout the experiments, the emphasis on thermal management paid off, providing detailed insights into the temperature distribution in and around the reactor (Fig. 1). Interestingly, the reactor exhibited ignition behavior attributable to the low thermal conductivity of the polymeric material. Typically, in lab reactors, catalyst beds have lower temperatures than the heaters, but here, the bed displayed a higher temperature. Activity measurements indicated rates of approximately 1 10^{-4} mol $g_{cat}^{-}1$ s^{-1}. With this activity level, the estimated necessary catalyst mass for sufficient propellant production on Mars was estimated to be below 3 kg.

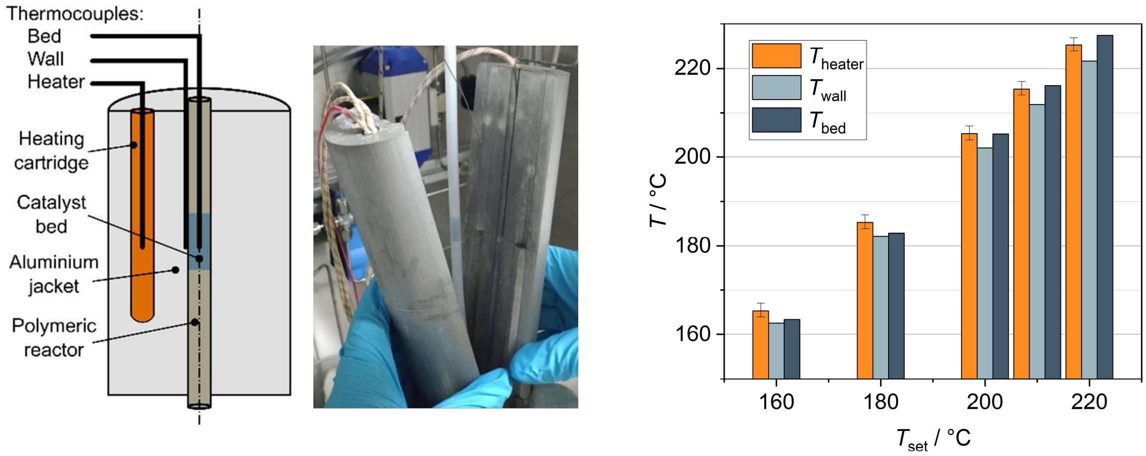

Figure 1. left: Reactor section with temperature measurement and picture of the setup, right: measured temperatures during reaction, change in heat removal regime indicated by the positive gradient between bed and heater for T>210 °C.

4. Conclusions

The investigation demonstrates the potential use of polymeric reactors at the outer limits of their operational capabilities, expanding the material toolkit for reactor design not only for Martian production sites. The systematic assessment of design criteria not only justified the study but also paved the way for identifying promising fields for system improvements. The successful operation over several days serves as a compelling proof of concept for the application of polymeric reactors in thermocatalytic gas-phase reactions.

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Keywords

Methanation; CO_2-Hydrogenation; Fluoropolymer; Space mission