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Catalyst development for microchannel reactors for martian in situ propellant production

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Abstract

Catalytic microchannel reactors were designed for in situ propellant production for Mars exploration. In the reactor system, the Sabatier and the reverse water–gas-shift (RWGS) reactions were carried out for methane and oxygen production using carbon dioxide and hydrogen as feed stock. The focus of the present study was on developing catalysts for these two reactions, aiming at intensifying reactor operation. Demonstrated in this study were the catalyst development pathways and integration methodologies for microchannel reactor system. Initially, near intrinsic kinetic performance was obtained with powder form catalyst. Catalytic performance of the powder form material was therefore used to guide development of structured catalysts which were fabricated on FeCrAlY substrates. In this study, the effects of the noble metals and the properties of their supports on the conversion of CO_2 were evaluated. It was found that 3% Ru/TiO_2 (R/A = 60:40) and 6%Ru/CeO_2-ZrO_2 were very active Sabatier and RWGS catalysts allowing to achieve near equilibrium conversion at high throughputs. In the stability testing under repeated start-up and shut-down cycles, both the Sabatier and the RWGS catalysts were stable, retaining initial activities for sustained period of time.

Keywords: Microchannel reactor; RWGS; Sabatier reaction; Structured catalyst; ISRU; Mars exploration

1. Introduction

The ability to use local resources to ‘‘live off the land’’, commonly referred to as in situ resource utilization (ISRU), is essential in expanding robotic and human extraterrestrial exploration, establishing a long-term human presence beyond low earth orbit, and enabling the commercial development of space. To reduce cost and risk and support human presence on Mars, the Martian atmospheric CO_2 can be converted to useful materials. Catalytic hydrogenation of CO_2 is important for in situ production of building-block hydrocarbons for use on Mars. For example, by reacting hydrogen (either brought from earth or from water electrolysis) with CO_2 in the Martian atmosphere, methane, or C_2^+ hydrocarbons can be produced as fuels for the return journey. The co-product, water, is converted via electrolysis to generate more H_2 for reuse, and O_2 for use as oxidant and for life support. The process flow diagram is illustrated in Fig. 1. The CO_2 hydrogenation reaction to methane is commonly known as Sabatier reaction, which is highly exothermic:

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \quad \Delta H = -165\,\mathrm{kJ/mol} \tag{1}$$

To achieve efficient propulsion operation, the desired O_2/CH_4 mass ratio should be around 3.8 [1]. However, the Sabatier reaction produces oxygen and methane at 2:1 mass ratio. As a result, the RWGS reaction is integrated into the fuel production system to provide the additional oxygen:

$$CO_2 + H_2 = CO + H_2O, \quad \Delta H = +37.2\,\mathrm{kJ/mol} \tag{2}$$

In the RWGS reaction, equal molar H_2O and CO are produced. The H_2O is again condensed and decomposed in the electrolysis process as described above, whereas CO is separated and discarded. One of the challenges encountered in the design of the reactor systems is to select and optimize reaction variables (throughput, conversion, and operating temperatures) for both Sabateir and RWGS reactions. The Sabatier reaction is highly exothermic, and is typically operated at temperatures

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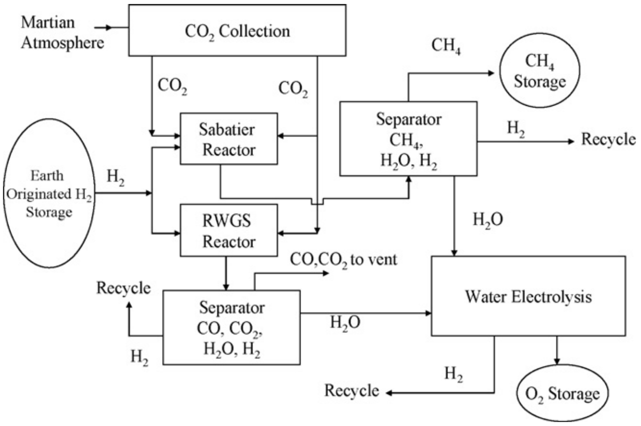

Fig. 1. Process flow diagram of integrated reactor and separator system for CO_2 conversion to CH_4 and O_2 for the Mars ISPP application.

around 250–450 °C. Increasing temperature results in reaction equilibrium limitations while lowering temperature causes kinetic limitations. Conventionally longer residence times are used for near completion conversion at low temperature. In contrast, the RWGS reaction is mildly endothermic and will occur in the presence of an iron-chrome catalyst at temperatures of 400 °C or greater. Unfortunately at 400 °C, the equilibrium constant K_p driving it to the right is only about 0.1. This is a significant problem in driving the RWGS reaction to completion.

Microchannel reactor integrated with structured catalysts was used for these two reactions to improve heat and mass transfer, and allow both to operate at their kinetic limit. These and other advantages of microchanel reactors in highly exothermic and endothermic reactions were addressed elsewhere [2–4]. Essentially, the Sabatier and the RWGS reactions were equally important to the design of the entire reactor system for NASA's ISRU. The focus of the present study was to develop robust Sabatier and RWGS catalysts that can achieve high conversion at high throughput, aiming at intensifying the entire ISRU plant. Among the many choices of catalysts for CO_2 hydrogenations, the literatures reported transition metal oxide catalysts suitable for hydrogenating CO_2 to hydrocarbons and alcohols [5–7]. Certainly, these catalysts could be utilized for CO_2 methanation reactions. However, due to the low turnover rate, we found the transition metal oxide catalysts were not ideal candidates for high throughput CO_2 hydrogenation applications. As a result, the present study was focused on developing supported noble metal catalysts, on which high turnover rate can be achieved.

The specific objectives of this study were to develop highly active and stable catalyst systems for the Sabatier and the RWGS reactor systems, and to fabricate such catalyst systems into structured (engineered) form that can be integrated into microchannel reactors. The system impacts resulting from this investigation were an increase in the efficiency of the reactor systems, a reduction in the energy consumption either from solar panels or a nuclear sources for heating RWGS reactors, and reduction in the size of the radiators for cooling of SR reactor.

2. Experimental

2.1. Synthesis of powder catalyst

All the catalysts used in this study were supported catalysts. Catalyst supports used in this study included TiO_2 (rutile), mixed phase TiO_2 (rutile:anatase = 60:40), and ZrO_2. These catalyst supports were all obtained from Engelhard Corp. Al_2O_3 and Al_2O_3-MgO spinel from SASOL were also evaluated. The catalyst metal precursors studied were Rh and Ru. The Rh nitrite solution (10 wt% Rh) was purchased from Engelhard and Ru nitrate solution was purchased from Colonial. The precursor of catalyst promoter $Ce(NO_3)_2$ was purchased from Aldrich Chemicals.

Synthesis of the Sabatier catalysts was carried out by incipient wetness technique. Solutions containing Ru nitrate or Rh nitrate were prepared and impregnated on different catalyst supports to obtain a range of metal compositions. Typical Rh or Ru loadings varied from 1 to 6 wt%. After introducing metals on catalyst supports, catalyst samples were dried at 110 °C overnight. All the catalyst samples were subjected to final calcination at 450 °C for 3 h using a ramp rate of 2 °C/min.

Synthesis of the RWGS catalyst was slightly different from the method used in making the Sabatier catalyst. First, $Ce(NO_3)_2$ was introduced onto ZrO_2 support by incipient wetness method, then calcined at 350 °C for 3 h. After calcination a thin layer of CeO_2 was formed on the surface of ZrO_2, designated as ZrO_2-CeO_2. A solution of Ru nitrate was then impregnated onto the ZrO_2-CeO_2 support. Final calcination was carried out at 500 °C in air for 3 h using a ramp rate of 2 °C/min.

2.2. Fabrication of structured catalysts

The structured catalysts were prepared using FeCrAlY intermetallic alloy obtained from Porvair. To achieve low pressure drop and improve heat transfer, porous FeCrAlY felt was used as substrate for the Sabatier catalyst. Reaction was carried out in the flow-by mode. While for the RWGS reaction, FeCrAlY foam was selected as substrate. Therefore, reaction was carried at in the flow-through mode. The following is the detailed description on preparing structured RWGS catalysts.

The active components on the RWGS catalyst consist of Ru/ZrO_2-CeO in the powder form, which was prepared as above. The powder catalyst sample was mixed with de-ionized water at ratio of 1:10 by weight, then ball-milled for 24 h before wash coated onto FeCrAlY foam substrates. The porosity of the foam was 65 PPI. Before the catalyst was wash-coated, the foam was cleaned with ethanol and acetone mixture (1:1 by volume) in an ultrasonicated bath for 20 min. After drying 6 h inside a hood at ambient temperature, the foam was dried at 110 °C overnight. The surface of FeCrAlY substrates was thermally treated at 900 °C in air for 2 h. Next, the foam substrate was pre-coated with Al_2O_3 sol–gel to further enhance adhesion and to increase exposed surface area for the subsequent wash coating. Following the surface treatment, these substrates were wash-coated with catalyst slurry prepared from ball milled powder