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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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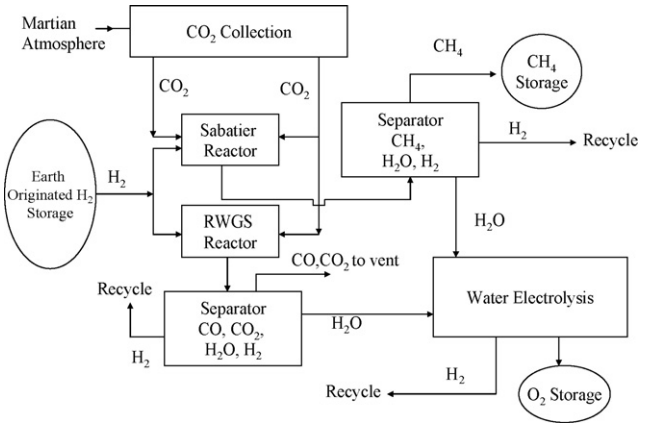

Fig. 1. Process flow diagram of integrated reactor and separator system for CO_2 conversion to CH_4 and O_2 for the Mars ISPP application.

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

catalysts. In order to reach desired catalyst loading on the substrate, wash-coating process was repeated 4 times. Between each coating step, drying was conducted at 110 °C in air. Final calcintion was carried out at 400 °C for 3 h in air.

The structured Sabatier catalyst was prepared in a similar way except that active components consist of Ru/TiO_2 (R/A = 60:40) rather than Ru/ZrO_2-CeO_2 and the substrate was not Al_2O_3 sol–gel pre-coated.

2.3. Catalytic activity testing

The experiments were carried out in a microchannel reactor made of 316 stainless steel, with the channel dimensions of 5.0 cm × 0.90 cm × 0.075 cm. When testing powder catalyst, the catalysts were pelletized, crushed and sieved to 70–100 mesh before placed into the reactor channel. When testing the structured Sabatier catalysts, two pieces of FeCrAlY felt catalyst were installed into a reactor channel, which were separated by stainless steel spacers. Thus, the catalyst felts were pressed against the reactor channel wall. The feed gas then passed through the gap between two felts.

Testing of structured RWGS catalysts was carried out under a flow through configuration. As described above, FeCrAlY foam was used as substrate for RWGS catalyst. The FeCrAlY foam was machined by EDM to match the geometry of reactor channel. Bomite Al_2O_3 was used to seal the gap to minimize bypass between the monolithic catalyst and reactor channel wall. Premixed CO_2 and H_2 were introduced from the top of the reactor. The stream leaving the reactor, consisting of unreacted CO_2, H_2 and hydrocarbon products, was separated into condensed and non-condensable products using a cold trap operated at 0 °C. This was used to capture the majority of condensable products (mainly H_2O, or higher hydrocarbons, such as C_4 and above, if any).

Prior to testing either the Sabatier or the RWGS catalysts, an activation pretreatment was conducted in all of these experiments. During the activation process, catalysts were reduced with 10% H_2 in Helium at 370–380 °C for 12 h. The reduction was carried out using two consecutive heating ramps. After catalyst reduction was completed, reactor temperature was decreased to desired reaction temperature. While the reactor was lined out at desired temperature, reduction gas (10% H_2) was fed continuously. When the catalyst bed temperature reached desired reaction temperatures, the reduction gas was switched to CO_2/H_2 mixture of different H_2/CO ratio. Typically, H_2/CO_2 ratio was varied around stoichiometric ratio of 4:1 for the Sabatier reaction and 1:1 for RWGS reaction.

All the experiments were carried out under isothermal conditions as indicated by the uniform temperature distribution along catalyst bed. The presence of Ar (usually 4%) in the feed stock served as the internal standard for CO_2 conversion and product selectivity calculation purposes. Total feed flow rate was set to achieve a desired gas hourly space velocity (GHSV). The gaseous products were analyzed by gas chromatography to obtain CO_2 conversion and selectivity. Liquid products were periodically drained and analyzed by off-line GC to detect any condensable liquid products other than water.

3. Results and discussion

Although structured catalysts were commonly used in catalysis research, there was no systematic study in the open scientific literature about the use of structured catalyst in high throughput exothermic and endothermic reactions. Experimental data presented in this study were aimed at demonstrating the advantages of structured catalyst in CO_2 hydrogenation to methane and CO via Sabatier and RWGS reactions, respectively.

3.1. Sabatier reaction

In order to compare activities of different catalysts, it was highly desirable to operate the microchannel reactor in isothermal mode. In a single channel test, for each run, it was observed that the operation of the reactor was very steady. A slight temperature gradient along the length of catalyst bed varied within 2 °C was observed. Typically, experiment was started at 250 °C, with the temperature incremented by 25 °C for each condition. Experimental data was taken after steady-state was achieved. Therefore, a temperature profile was generated.

3.1.1. Effect of catalyst reduction conditions

In our previous study on CO_2 hydrogenation, most of catalysts was reduced with 10% H_2. It was believed that mild reduction under low H_2 partial pressure could lead to high metal dispersion which normally resulted in enhanced activity. However, there were only limited experimental data to support such a hypothesis. The study on the effect of reduction feed composition and duration of reduction was important for ISRU. It would not be feasible to transport an inert diluent from Earth to Mars and Martian atmosphere has only low concentrations of such diluents. In addition, shorter catalyst reduction time was preferred to allow longer time for fuel production. In this study, the effects of reduction time and hydrogen concentration on the performance of the Sabatier catalyst were investigated. Two different reduction gas compositions, 10 and 100% were used for the comparison. When 10% H_2 was used as reduction gas, longer reduction time was practiced to ensure fully reduction, whereas when 100% H_2 was used, reduction was carried out for only 2 h. The experimental data are collected from duplicated runs. The experimental error is within ±0.5% conversion. Results are summarized in Table 1. Reduction using 100%

Table 1
Effect of hydrogen concentration and reduction time on the Sabatier catalyst performance (3% Ru/TiO_2 (60:40), $P = 0.1$ MPa, $T = 350$ °C, GHSV = 45,000 h^{-1}, $H_2/CO_2 = 4:1$)

	Catalyst reduction conditions	
	10% H_2 for 12 h at 380 °C	100% H_2 for 2 h at 380 °C
CO_2 conversion (mol%)	81.5	78.0
Selectivity to CH_4 (mol%)	99.4	99.6
Selectivity to CO (mol%)	0.6	0.4

hydrogen causes 3.5% loss in CO_2 conversion. However, selectivity to methane is essentially not affected. The loss of activity might be due to the decrease in Ru dispersion. Compared with the cost of diluting hydrogen to 10% in Martian environment, the use of 100% hydrogen has significant advantages. This is largely because the insignificant loss in CO_2 conversion can be compensated by slight increase in the size of reactor without adding burden on the overall device cost.

3.1.2. Effect of metals

Generally, on supported catalysts, metal loadings and the type of metals affect CO_2 hydrogenation activity. Lower metal loadings can result in higher percentage of metal dispersion and smaller metal particle size, which is translated to higher turn-over-frequency (TOF). However, at lower metal loading, the site density required to achieve certain level of CO_2 conversion may be lower. In contrast, at higher metal loading, the percentage of metal dispersion may be lower; however, the site density could be higher. Initial efforts were focused on optimizing metal loadings. As shown in Fig. 2, starting from 1% Ru, conversion increases with metal loading, and seems to decline after around 3%. This could be because that at higher metal loading, dispersing of metal became difficult, average metal particle size grew larger, therefore ultimately affecting hydrogenation activity.

The impact of using bimetallic catalysts on CO_2 hydrogenation activity was explored. The objective of adding the second metal components was to investigate whether CO_2 hydrogenation activity could be enhanced so that the reactor could be operated at lower temperature or higher throughput. Results shown in Fig. 3 indicate that the combination of Ru-Rh results in the same conversion as Ru catalyst. However, when Ni is incorporated with Ru, an inhibiting effect is observed. With limited data available, we were not able to reveal the advantage of bimetallic catalyst formulations, therefore, this study was focused on monometallic catalyst.

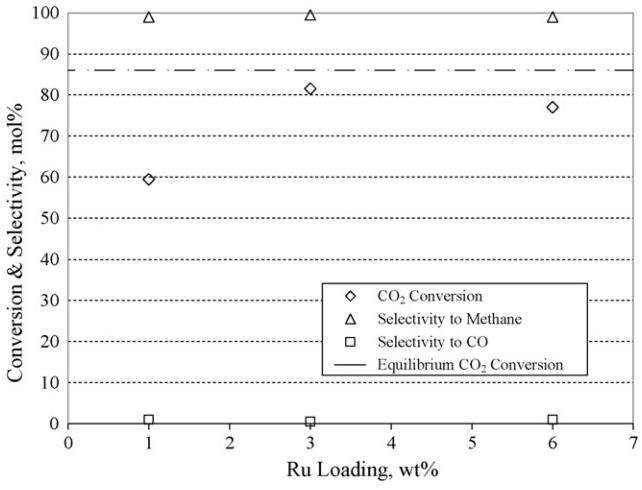

Fig. 2. Effect of Ru metal loading on CO_2 hydrogenation to methane (catalyst = 3% Ru/TiO_2 (R/A = 60:40), P = 0.1 MPa, T = 350 °C, H_2/CO_2 = 4:1, GHSV = 45,000 h^{-1}).

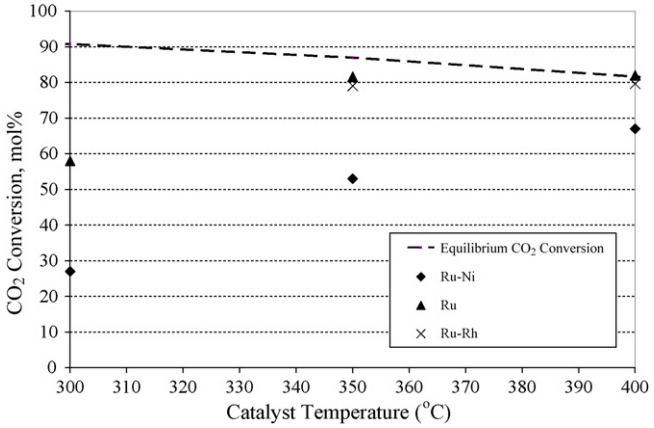

Fig. 3. Effect of metals on CO_2 hydrogenation to methane (each catalyst contains 3% Ru on TiO_2 (R/A = 60/40). The Ru-Ni catalyst contains 5% Ni whereas the Ru-Rh catalyst contains 2% Ru. GHSV = 45,000 h^{-1}, P = 0.1 MPa).

3.1.3. Effect of catalyst support

The original approach was to select high surface area catalysts supports to achieve high dispersion at a given metal loading. It was assumed that the Sabatier catalyst was structural sensitive, which means that small metal particle and high dispersion favor CO_2 conversion. In this study, metal loading was controlled at 3.0 wt%. The activities of the catalysts using different supports were compared for CO_2 hydrogenation reaction. As illustrated in Table 2, for three Ru/TiO_2 catalyst studied, surface area of support plays a significant role in Sabatier reaction because CO_2 conversion is increased with increase in BET surface area. However, when comparing TiO_2 supported catalyst with SiO_2 and Al_2O_3 supported catalysts, the effect of surface area tends to diminish. It seems that not only the surface area of support, but the interaction between metal and support also play an important role in the Sabatier reaction.

3.1.4. Catalytic stability

Catalytic stability is very important in developing the Sabatier catalyst for the NASA's ISRU. In Martian environment, catalyst change out is impossible and regeneration by means of oxidation would be very difficult. Essentially, it is required that catalysts remain active throughout the entire propellant production process of between 70 and 300 days. The approach adopted in this study was to retain support surface area and stabilize metal dispersion by enhancing metal–support

Table 2
Effect of catalyst support material and surface area on Sabatier reaction (350 °C, 0.1 MPa, GHSV = 45,000 h^{-1}, H_2/CO_2 = 4:1)

Catalysts	BET surface area of supports	CO_2 conversion	CH_4 selectivity
3% Ru/TiO_2 (R/A = 60:40)	50.0	81.5	99.4
3% Ru/TiO_2 (P-25)	30.0	64.1	99.0
3% Ru/TiO_2 (rutile)	<5	9.3	28.0
3% Ru/alpha Al_2O_3	<5	16.4	63.7
3% Ru/SiO_2	400	46.0	99.9
3% Ru/MgO-Al_2O_3	168	40.0	96.6

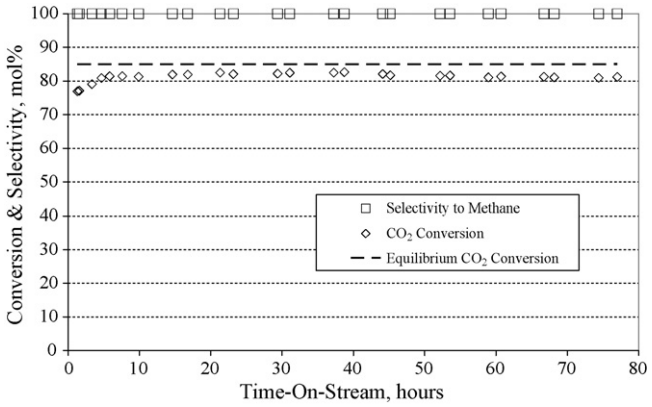

Fig. 4. Catalyst stability testing under repeated shutting down and restart conditions (3% Ru/TiO_2 (R/A = 60:40), CO_2/H_2 = 4:1, T = 369 °C, P = 0.1 MPa).

interactions. A 3% Ru/TiO_2 (R/A = 60:40) catalysts was tested for extended period of time to measure long-term catalytic performance. In catalyst stability testing, the starting CO_2 conversion was established at about 82%, which was less than the equilibrium conversion of 85%. The test was carried out initially for 8 h during the day, then was shut down and restart to operate for another 8 h. The shutdown and restart were repeated for a total of 16 cycles. The total accumulated on-line time was 77 h. It was believed that the catalyst was exposed to the severe conditions that simulate when unexpected shut-down and re-start become inevitable.

As shown in Fig. 4, during the entire catalysts life testing with repeated shutting down and starting up, CO_2 conversion drops by only about less than 2%. It was believed that the high metal dispersion and strong interaction between the metal and support prevented the metal from sintering, resulting in a stable and long-lived catalyst.

3.1.5. Performance of structured catalysts in single channel reactor

Compared with a previous study, Ru/TiO_2 (60:40) catalysts developed in this study were more active than those derived from commercial Ru/TiO_2 catalyst [8]. The catalyst formulations that were most active during powder testing were applied to the fabrication of structured catalysts. It was noteworthy that, for structured catalyst, the method of making and the way of integrating with reactor play a key role in the Sabatier reaction. As described in Section 2, the structured catalyst consisted of FeCrAlY felt, which was wash coated with Sabatier catalyst. Two pieces of felts were installed in each channel, and separated by the spacer made of stainless steel. Essentially, these catalyst felts were pressed against channel wall (see Fig. 5). This was a typical flow-by mode reactor configuration. Heat generated from the reaction was removed by air or oil from the other side of the channel.

In single channel reactor testing, the objective was to achieve same productivity as achieved in powder catalyst testing. The reactor design target was to achieve >80% conversion at GHSV = 10,800 h^{-1} under P = 0.1 MPa and

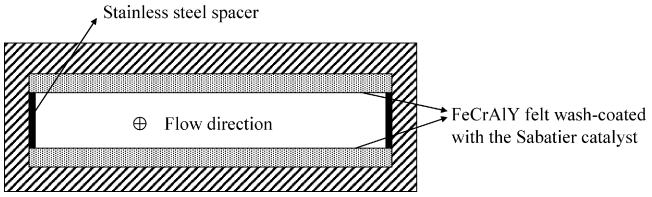

Fig. 5. Top view of reactor channel installed with structured catalyst.

T < 400 °C. The GHSV equals total flow rate divided by the volume of reactor channel. As illustrated in Fig. 6, experiment is started at GHSV = 18,000 h^{-1} and 300 °C. Under those conditions, conversion as high as 78% can be achieved. Raising reaction temperature to 350 °C, conversion is increased to 81%, which is very close to equilibrium limitation. When throughput is further increased to GHSV = 30,500 h^{-1}, conversion of 78.6% is achieved at 365 °C. At this point, the reactor was shut down and cooled to room temperature under pure hydrogen. Two days later, the reactor was restarted by first reducing catalysts with pure hydrogen at 400 °C for 2 h. The Sabatier reaction was resumed. Again as shown in Fig. 6, at the same temperature of 365 °C, conversion of 78.1% is obtained (first repeat). The same CO_2 conversion is achieved during the second repeat test. Overall, in comparing with previously reported catalyst based on commercial Ru/TiO_2 catalyst [8], we can conclude that significant improvements have been made for the structured catalyst.

Powdered bimetallic Ru-Rh/TiO_2 catalyst was also fabricated into structured catalyst form using FeCrAlY as substrate. The use of bimetallic catalyst in this test was to provide flexibility in catalyst formulation selections. As shown in Fig. 7, at 365 °C and 0.1 MPa, the performance of the engineered catalyst exceeds the design target of 80% conversion. About 80% CO_2 conversion can be achieved at GHSV = 10,800 h^{-1}. Under the same conditions, increasing throughput to GHSV = 30,500 h^{-1} only causes slight decrease in CO_2 conversion.

The single channel testing results indicated that it was possible for structured catalyst to achieve the same performance as powder catalyst. The next challenge was the massive

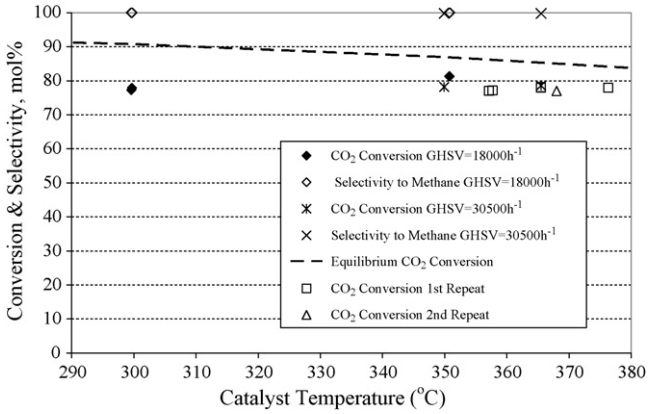

Fig. 6. Performance of the structured catalyst for the Sabatier reaction (catalyst = 3% Ru/TiO_2 (R/A = 60:40) wash coated on FeCrAlY felt, CO_2/H_2 = 4:1, P = 0.1 MPa).

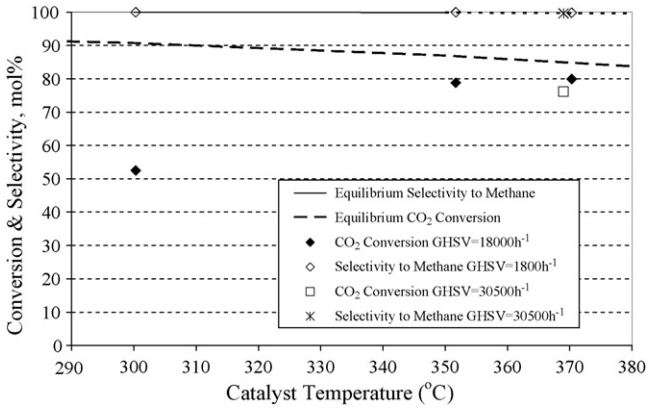

Fig. 7. Performance of the structured catalyst for the Sabatier reaction (catalyst = Ru-Rh/TiO_2 (R/A = 60:40) wash-coated on FeCrAlY felt, CO_2/H_2 = 4:1, P = 0.1 MPa).

production of structured catalysts for multi channel reactors. To improve mass and heat transfer, for each felt catalyst, the catalyst coating thickness and uniformity along the length of FeCrAlY felt had to be nearly identical. Otherwise, the flow distribution and heat transfer characteristics among different reactor channels might be different. Also, the consistent performance of each structured catalyst was important in the catalyst scaling up efforts. A total of 140 strips were prepared as a ''large batch''. The challenge remained in obtaining not only the physical property consistency but also identical catalytic activity. Essentially, it is desirable that structured catalyst manufactured from the ''large batch'' exhibited performance comparable with those prepared as single piece (small batch).

After completion of preparing 140 strips of the Sabatier catalyst, two strips were randomly selected and tested. As shown in Fig. 8, about 81.3% CO_2 conversion at GHSV = 36,000 h^{-1} is obtained, which is identical to those prepared in small batch, indicating that the fabrication of structured catalyst can be scaled up from small batch of few strips to a large batch of 140 strips without any activity deviations. The data obtained from the single channel reactor was used to assist the design of a multichannel reactor. Based on the residence time, CO_2 conversion and methane selectivity, the reactor size could be determined. The design, performance and reactor modeling work are published in Chemical Engineering Science [9].

3.2. The RWGS reaction

Considering the equilibrium constraint of the RWGS reaction, the desired throughput for the RWGS was almost 5–10 times higher than that of Sabatier reaction. The RWGS reaction is endothermic, therefore, thermodynamically the reaction is favored at high temperature. In order to achieve desired conversion at high throughput of about GHSV = 360,000 h^{-1}, in this study, the RWGS reaction was operated at >700 °C. Under such conditions, catalytic material failure and pressure drop across the catalyst bed became issues. As a result, FeCrAlY foam, instead of felt was chosen as substrate for the structured RWGS catalyst. The measurements showed that the foam can stand for temperature up to 1100 °C, and pressure drop across the catalyst was negligible.

3.2.1. Catalyst formulation strategies

It is commonly known that catalyst that can catalyze a forward reaction is able to catalyze the reverse reaction. Among the choice of commercial catalysts, Cu/Zn and Cr/Fe type of catalysts are widely used in water–gas-shift reaction, they could be candidates for RWGS reactions. However, Cu/Zn based catalyst can only be operated at low temperature of <280 °C. Although Fe/Cr based catalyst can be operated at high temperature up to 600 °C, it has very low turn-over frequency. Instead, in the study, noble metal catalysts were explored because they have fast reaction kinetics. The ability of ceria as catalyst support to promote the WGS reaction attracted much attention. The activity of Pt/CeO_2 was shown to exceed that of conventional Cu/ZnO shift catalysts in some circumstances [10]. Other metals could be used included Ru and Rh. However, the challenge was to make high surface area CeO_2 support. High surface area supports, such as SiO_2 and Al_2O_3, were found not stable under high temperature especially in the presence of H_2O (steam). In contrast, ZrO_2 is known not only for its high

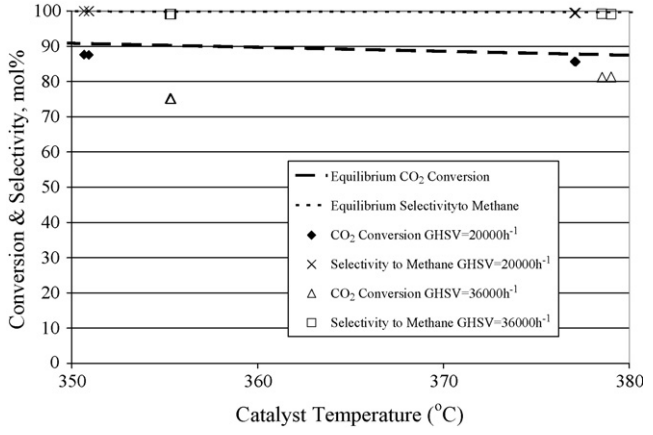

Fig. 8. Performance of the structured Sabatier catalyst prepared from a large batch (catalyst = 3% Ru/TiO_2 wash-coated on FeCrAlY felt, CO_2/H_2 = 4:1, P = 0.1 MPa).

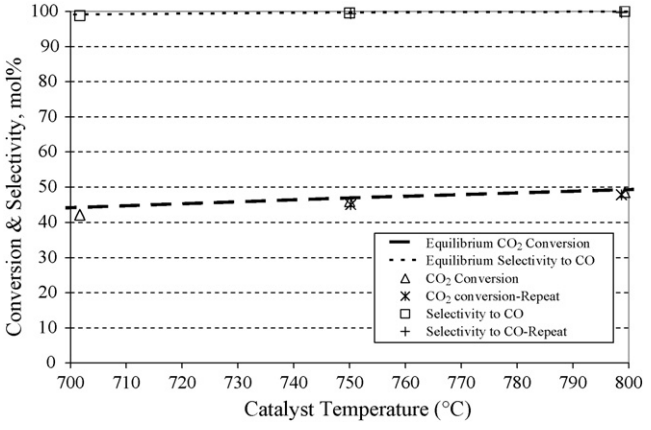

Fig. 9. Performance of the powdered RWGS catalysts with 3% Ru/ZrO_2-CeO (H_2/CO_2 = 1:1, P = 0.1 MPa, GHSV = 240,000 h^{-1}).

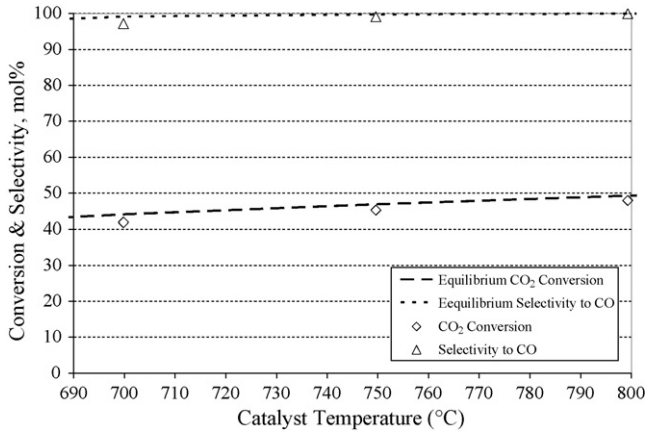

Fig. 10. Performance of the powdered RWGS catalyst with 6% Ru/ZrO_2-CeO (H_2/CO_2 = 1:1, P = 0.1 MPa, GHSV = 360,000 h^{-1}).

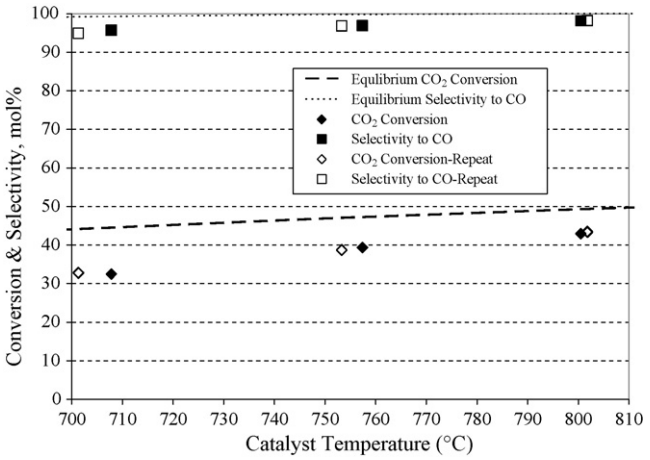

Fig. 12. Performance of the monolith RWGS catalyst (catalyst = 6% Ru/ZrO_2-CeO wash-coated on FeCrAlY foam, H_2/CO_2 = 1:1, GHSV = 330,000 h^{-1}).

surface area, but also for its stability at high temperature in the presence of steam. As a result, in this study, CeO_2 coated ZrO_2 support was developed.

In developing the RWGS catalyst, efforts were focused on synthesizing support material CeO_2-ZrO_2 that ultimately retained high surface area with an exposed CeO_2 outer layer. Two powdered RWGS catalysts were prepared and tested at high temperature up to 800 °C. The performance of 3%Ru/CeO_2-ZrO_2 catalyst is shown in Fig. 9. For an endothermic reaction, temperature has positive effect on CO_2 conversion, an upward curve is observed. Equilibrium conversion can be achieved at high space velocity of 240,000 h^{-1}. Carbon monoxide selectivity near 100% is obtained indicating that side reaction (methanation reaction) would not take place over the catalyst. During the test, startup and shut down procedures were conducted to investigate catalyst degradation. As shown in Fig. 9, data labeled as ''repeat'' indicate the catalyst performance after a shutdown and restart. Apparently, no deactivation is observed. Illustrated in Fig. 10 is the performance of 6% Ru/CeO_2-ZrO_2 catalyst. Near equilibrium conversion is achieved at even high throughput of 360,000 h^{-1}.

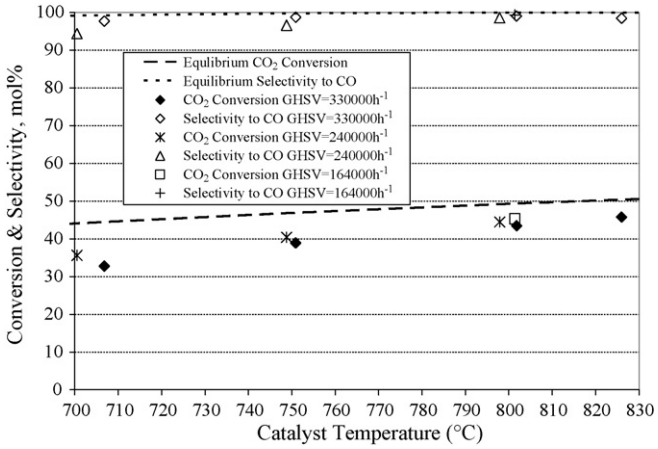

Fig. 11. Performance of the monolith RWGS catalyst with 6% Ru/ZrO_2-CeO wash-coated on FeCrAlY foam (H_2/CO_2 = 1:1, P = 0.1 MPa).

3.2.2. *Performance of monolith RWGS catalyst*

As described earlier, the monolith RWGS catalyst was prepared by wash coating 6% Ru/CeO_2-ZrO_2 catalyst on FeCrAyY foam with dimension of 13 mm × 15 mm × 15 mm. As shown in Fig. 11, under the conditions tested, varying space velocity does not seem to have any effect on CO_2 conversion. This was probably because the RWGS reaction was diffusion controlled at high temperature. Internal diffusion played role in the RWGS reaction.

For the monolith RWGS catalyst, catalytic stability was also tested. As shown in Fig. 12, the RWGS reaction is started, shut down and then restarted for three cycles. Notably, no deactivation is observed as indicated by the overlapping of temperature profile curves.

The effect H_2/CO_2 ratio on CO_2 conversion was studied. Results shown in Table 3 indicate that increasing the concentration of hydrogen results in increasing the conversion of CO_2 beyond stoichiometrical attainable at H_2/CO_2 = 1:1 ratio of H_2 and CO_2. The implications from the findings are the possibility of varying H_2/CO_2 ratio to leverage O_2 production as well as O_2/CH_4 ratio in the combustion fuel. The drawback of using high H_2/CO_2 ratio would be that larger volume off gas must be purified and compressed downstream of the reactor system in order to recover the excess hydrogen. Other approaches have been considered to achieve beyond equilibrium conversion (at stoichiometric ratio) without adding extra hydrogen. One

Table 3
Effect of H_2/CO_2 ratio on the performance of RWGS catalyst (catalyst = 6% Ru/ZrO_2-CeO wash coated on FeCrAlY foam, GHSV = 330,000 h^{-1}, P = 0.1 MPa)

	700 °C	750 °C	800 °C
H_2/CO_2 = 1:1			
CO_2 conversion (%)	33.6	39.2	43.7
Selectivity to CO (%)	94.9	96.4	97.9
CO_2 conversion at equilibrium (%)	44.0	48.0	49.3
Selectivity to CO at equilibrium (%)	99.2	99.8	100
H_2/CO_2 = 1.5:1			
CO_2 conversion (%)	41.7	48.1	53.2
Selectivity to CO (%)	91.7	94.1	96.1

approach is to remove water using membrane during the process. By removing water during the process, the equilibrium conversion of CO_2 can be shifted further towards CO.

4. Conclusion

Experiments consisting of measuring catalyst activity during repeatedly startup and shutdown procedures showed that both the Sabatier and the RWGS catalysts developed in this study were highly stable. For the RWGS catalyst, the presence of CeO_2 on the outer layer of ZrO_2 provided high surface area support with high temperature operability to allow the RWGS reaction to take place at near equilibrium conversion. For the Sabatier catalyst, physicochemical properties such as BET surface area, metal loadings, and metal–support interaction were important during the reaction. For both reactions currently investigated, the H_2/CO_2 ratio affected CO_2 conversion as well as product selectivity. In contrast, GHSV exhibited stronger effect on the performance of the Sabatier catalyst than for the RWGS catalyst. The RWGS catalyst was sensitive to changes of reaction temperatures whereas the performance of the Sabatier catalyst didn't seem to be affected significantly by reaction temperature. This work illustrated that it was possible to transfer the intrinsic kinetic performance obtained at powder catalyst level to structured catalysts. This study also presents a unique catalyst development methodology for microchannel reactors, which is different from those practiced in conventional reactor.

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