Catalysis Today 140 (2009) 142–148

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Fischer–Tropsch synthesis on ceramic monolith-structured catalysts

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ARTICLE INFO

Article history:
Available online 25 November 2008

Keywords:
Fischer–Tropsch synthesis
Monolith
Catalyst
Reactor
Multiphase
Hydrodynamics

ABSTRACT

This paper reports recent research results about the impact of different catalyst bed configurations on Fischer–Tropsch (FT) synthesis product distributions. A powdered CoRe/γ-alumina catalyst with a particle size ranging from 60 to 100 mesh was prepared and tested in a packed bed reactor. The same catalyst was ball milled and coated on a ceramic monolith support structure of channel size about 1 mm. The monolith catalyst module was tested in two different ways, as a whole piece and as well-defined channels. Steady-state reaction conversion was measured at various temperatures under a constant H_2/CO feed ratio of 2 and a reactor pressure of 25 bar. Detailed product analysis was performed. Significant formation of wax was evident with the packed particle bed and with the monolith catalyst that was improperly packed. By contrast, wax formation was not detected in the liquid product by confining the reactions inside the monolith channel. This study presents an important finding about the structured catalyst/reactor system, in that the product distribution highly depends on how the structured reactor is set up. Even if a catalyst is tested under identical reaction conditions (T, P, H_2/CO ratio), hydrodynamics (or flow conditions) inside a structured channel may have a significant impact on the product distribution.

1. Introduction

Fischer–Tropsch (FT) synthesis is a surface catalyzed polymerization process that uses CH_x monomers, formed by hydrogenation of adsorbed CO, in order to produce hydrocarbons with a broad range of chain length and functionality. Methane is the major by-product from this process. Small amounts of alcohols may be produced (<5 wt.%). Liquid hydrocarbon comprises the major reaction product (>90 wt.%). The liquid hydrocarbons with carbon number from 5 up to 80 have a broad range of boiling points. For the production of gasoline or diesel, C5–C18 components are often preferred since the heavy fraction (or wax) has to be cracked in the presence of high-pressure hydrogen using one additional catalytic process. It has long been sought in the FT process technology field to minimize methane formation, while maximizing the liquid fuel portion of hydrocarbons. The product selectivity directly affects the FT process economics.

Since the FT reaction is such an important industrial process, a great amount of research has been conducted for many decades to improve catalyst activity and selectivity by optimizing catalyst compositions and structures. In addition to catalyst improvement, various reactor and process technologies have been explored and developed. Some efforts in the area of shifting the product distribution to a narrow range include conventional upgrading [1], the inter-conversion of alkanes via alkane methathesis [2], and incorporation of membranes and reactive distillation into the design of the FT reactor [3,4].

Physical phase state in an FT reactor is complex, which may include gas, liquid hydrocarbon, water, and solid catalyst. Mass transfer is considered to be a very important factor that affects both activity and selectivity [5]. Even though the syngas feed is in the gas phase, the catalyst pores may be filled with liquid products. Diffusion rate in the liquid phase is typically 4–5 orders of magnitude slower than in the gas phase. Some reactions are even perceived slow due to slow and limited diffusion in the liquid phase [6]. Impact of the mass transport on the reaction activity can be readily understandable. However, impact of the mass transport on the product distribution has not been clearly elucidated due to complex reaction kinetics. Since the FT reaction is highly exothermic, heat transfer is also critical to the product selectivity.

Catalyst pellet-loaded fixed-bed and fine catalyst particle-dispersed slurry reactors are often used to conduct FT reactions. In a fixed bed, catalytic materials can be deposited in a thin outer layer of the catalyst pellet (egg-shell catalysts) to mitigate the pore-diffusion mass transport problem [5]. In a slurry reactor, pore-diffusion mass transfer problem is considered solvable by

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doi:10.1016/j.cattod.2008.10.015

using small catalyst particles. However, separation of waxy FT liquid product from the catalyst fines, potential leaching of metal catalysts into the solution, external mass transfer of the feed gas onto the catalyst surface through the liquid, and product back mixing are other problems with the slurry reactor.

Conducting FT reactions inside small catalyzed reaction channels is a relatively new catalyst and reactor technology for better control of mass and/or heat transfer. FT catalyst can be coated onto the surface of a metallic support that may be made into small channels. It was reported in our earlier research [7] that compared to the 45 μm catalyst particle, coating the same catalyst on a planar aluminum plate and testing in a channel significantly narrows the product distribution to smaller carbon numbers. However, catalyst coating on a metallic support can be difficult and costly, and long-term durability is a concern due to the de-lamination of catalyst layer. Instead, catalyst coating onto porous, ceramic monolith structures is a proven material technology demonstrated in automotive catalytic converters for a few decades.

Using ceramic monolith structures for chemical reaction processing is still a new technology field, particularly for G/L/S multiphase reactions. In principle, the ceramic monolith support structures enable elimination or manipulation of any external and internal mass transfer steps to enhance the reaction activity and selectivity using appropriate material structures and flow conditions [8,9]. A study on the impact of the catalyst coating thickness on the FT reaction activity and liquid product distribution was recently reported [10], which showed that a washcoating thickness around 50 μm is preferred. A thinner coating reduces the catalyst loading while a thicker coating causes pore-diffusion mass transfer problems. Low-pressure drop is another unique feature of the monolith structure. This attribute was explored to control the reaction temperature by circulating a large volume of hydrocarbon liquid through the monolith reactor [11].

Given the encouraging progress with the monolith-structured reactor for multiphase reactions, many catalyst and reactor design issues remain to be understood in order to develop it as a viable FT process technology with a combination of the best activity, selectivity, and scale-up ability. The present study addresses a basic issue about testing of the monolith catalyst and shows the impact of hydrodynamic flow conditions on the product selectivity. Such an understanding provides the guidance to the design, construction and operation of a monolith reactor at an industrial scale.

2. Experimental

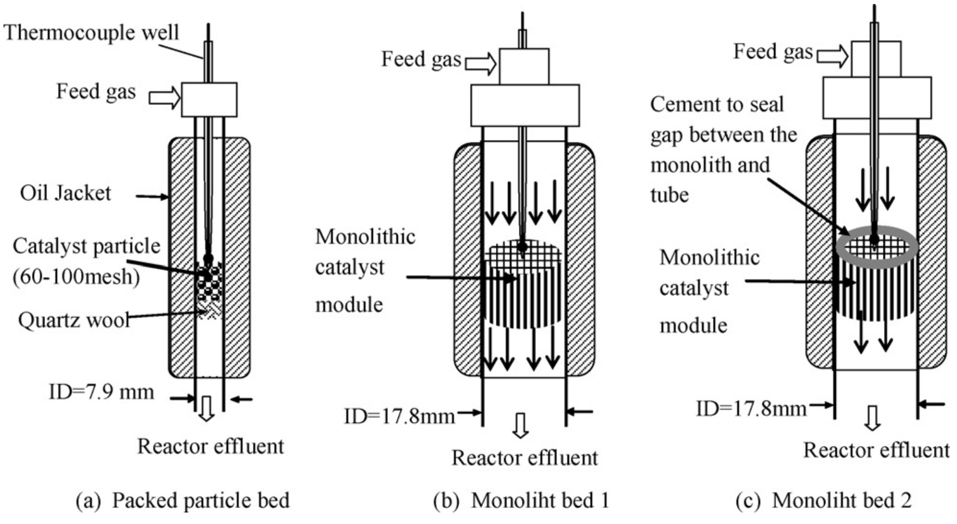
2.1. Catalyst preparation

Acidic γ-Al_2O_3 (Engelhard) was pre-calcined at 500 °C in air for 2 h prior to the impregnation of Co and Re precursors. An aqueous solution of cobalt nitrate hexahydrate (98% purity, Aldrich) and perrhenic acid (Engelhard, 53.29 wt% PM) was co-impregnated onto the γ-Al_2O_3 with a multi-step incipient wetness method. After each impregnation, the catalyst was dried in air at 90 °C for 8 h followed by calcination at 350 °C for 3 h. Three times of sequential impregnation were used to yield a final formulated catalyst with 20 wt% Co and 4.5 wt% Re on Al_2O_3. The catalyst was crushed and sieved to 60–100 mesh for the reaction test in a particle bed.

The monolith support used in this study was cordierite with a cell density of 400 cpsi (#/in^2) of 1 mm square channels. The monolith test pieces in cylindrical shape were core-drilled out of a full-size, oval-shaped monolith block. A catalyst coating slurry was prepared by ball-milling the above Co–Re/Al_2O_3 catalyst particles in de-ionized water for 24 h. The slurry was coated on the channel surface of the monolith support, dried at 110 °C for 6 h, and calcined at 350 °C for 1 h.

2.2. Reactor loading

Fig. 1 shows three types of the reactor setups used in this work. For the testing of particulate catalysts, a reactor tube of small ID (7.9 mm) was used and the catalyst particles were packed in the middle of the reactor tube. A thermocouple well was placed at the top of the catalyst bed. The reactor tube was wrapped by an oil jacket to control the reactor temperature. In the first method employed to test the monolith catalyst, the monolith piece was core-drilled to a size close to the reactor ID, fully loaded with catalyst, wrapped with a thin layer of ceramic wool, and plugged tightly into the reactor tube. In the second method to test the monolith, only 16 well-defined channels in the middle of the monolith piece were loaded with catalyst, while the un-catalyzed channels were plugged at both ends with cement. This monolith piece was placed inside the reactor tube, and the gap between the monolith and reactor tube was plugged with cement on the top so that the feed gas was only allowed to flow through the catalyzed channels. In all the tests, the reactor tube was vertically oriented and a down flow of feed gas was used.



(a) Packed particle bed (b) Monoliht bed 1 (c) Monoliht bed 2

Fig. 1. Catalyst bed configuration used in this work.

2.3. Reaction testing procedure

All the catalysts were activated in hydrogen prior to the introduction of syngas. After the catalyst was reduced at about 400 °C for 12 h at 0.1 MPa of H_2, the reactor temperature was cooled down to 210 °C under flowing hydrogen. Then, the reactor was pressurized to 25 bar with 5% H_2 in helium followed by introducing a syngas feed with H_2/CO ratio of 2. The reaction tests were conducted at temperatures of 210, 220, and 230 °C under constant reactor pressure. Hydrocarbons and water in the reactor effluent were condensed in a chilled vessel under pressure. Non-condensable gases were analyzed using an on-line gas chromatograph (Agilent QUADH G2981A with Molsieve 5A, PoraPlol Q) to determine CO conversion and light hydrocarbon product selectivity. The condensed liquid products were analyzed using a HP 6890 connected with a DB-5 column. The olefinic compounds were identified using a GC–MS (HP 5973C), then quantified using a GC (HP 6890). Conversion and selectivity numbers were calculated based on the product gas analysis for CO, CO_2, and CH_4.

3. Results

3.1. Reaction conversion profiles with time on stream

Figs. 2 and 4 show CO conversion and CH_4 selectivity with time on stream for the particle bed, monolith bed 1, and monolith bed 2, respectively. The respective reactor setups are shown in Fig. 1a–c. The overall reaction testing duration time was from 180 to 300 h.

For the particle bed (Fig. 2), the methane selectivity looks relatively stable, while there are sporadic CO conversion data points during transition of the temperature change. Formation of wax was visible in the liquid product sample throughout the testing. By contrast, wax formation was not observed in the first 48 h with the monolith 1 catalyst (Fig. 3) but was seen subsequently. CO conversion increases with temperature. There is no significant change in methane selectivity with temperature in Fig. 2, but methane selectivity increases with a change in the feed gas flow rate as shown in Fig. 3. Compared to the particle catalyst and monolith catalyst 1, no wax formation was seen in the liquid product from testing of the monolith catalyst 2 (Fig. 4).

Wax formation obtained from the liquid product analysis is consistent with the observation of the spent catalyst sample after the reactor was unloaded for both the particle and monolith catalyst 1 beds. At the end of particle bed test, the catalyst particles were glued together due to the wax formation. Similarly, a thick layer of wax was formed on the exterior of the monolith catalyst 1 shown in Fig. 5, again as a result of wax formation. By contrast, little or no wax formation was seen on the monolith catalyst 2. The 16 catalyst-containing channels in the monolith catalyst 2 look dark in color as compared to the un-catalyzed channels in the picture.

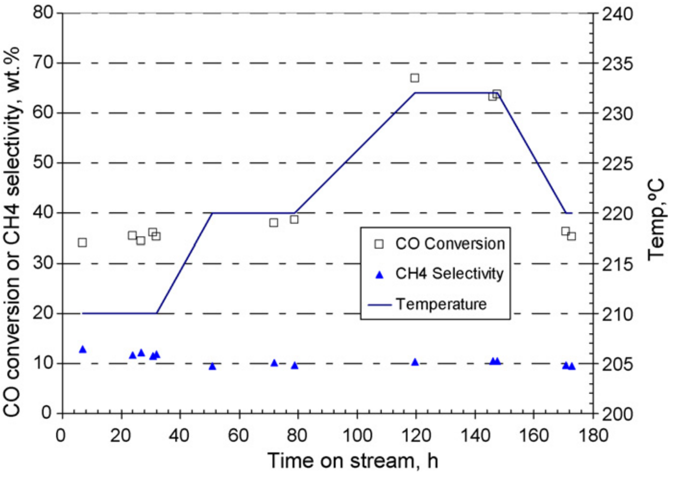


Fig. 2. Variation of reaction temperature and conversion with time on stream (particle bed, feed H_2/CO molar ratio = 2, P = 25 bar).

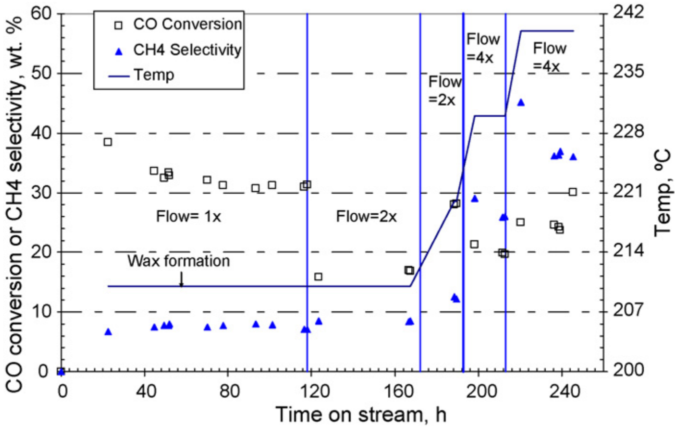


Fig. 3. Variation of reaction temperature and conversion with time on stream (monolith catalyst bed 1, feed H_2/CO molar ratio = 2, P = 25 bar).

3.2. Impact of different catalyst bed configurations on product selectivity

Product selectivity from the catalyst particle bed test is compared to that of the monolith catalysts in Fig. 6. The comparison basis is the same intrinsic reaction kinetics, since the same catalyst, reaction temperature, and reaction pressure are used. At a similar CO conversion level, selectivity to methane, CO_2 and total liquid (C_{5+}) are similar for both the particle catalyst and the monolith catalyst 2. However, the C5–C18 fraction of the total liquid obtained with the monolith catalyst 2 is consistently higher than that of the catalyst particle over a temperature range from 210 to 232 °C. The liquid product collected for the monolith 1 at 210 °C may not be representative since the catalyst did not reach the steady-state (shown in Fig. 3), and therefore, was not included in Fig. 6 for comparisons. The C5–C18 fraction obtained with the monolith 1 at 220 and 232 °C is lower than the monolith 2.

To verify that steady-state product was collected for monolith 2, carbon distribution profiles and olefin-to-paraffin ratios of two samples collected under constant reaction conditions are shown in

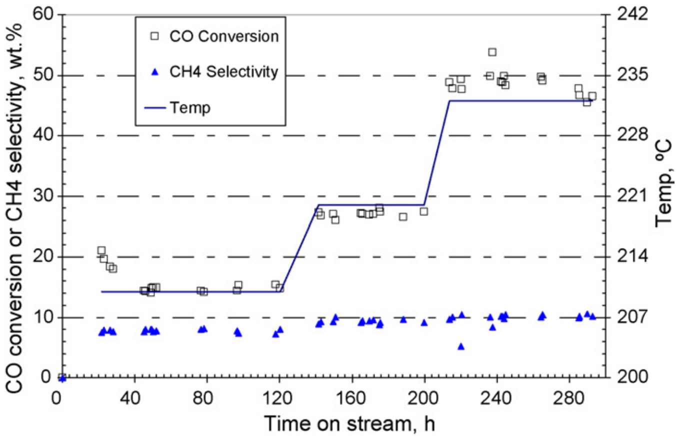


Fig. 4. Variation of reaction temperature and conversion with time on stream (monolith catalyst bed 2, feed H_2/CO molar ratio = 2, P = 25 bar).

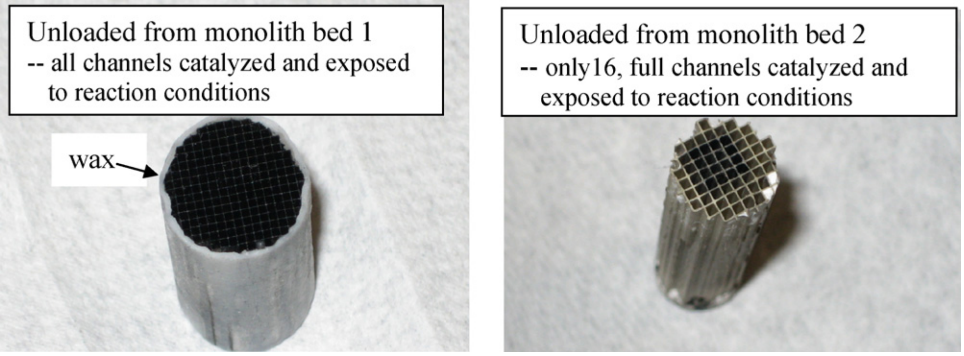


Fig. 5. Spent monolith catalyst samples.

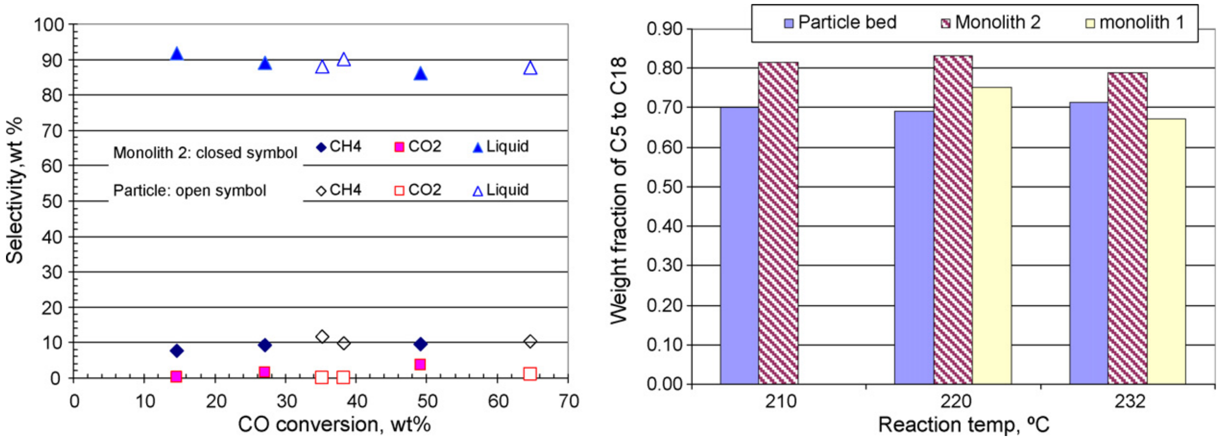


Fig. 6. Comparison of product selectivity over different catalyst bed (feed H_2/CO molar ratio = 2, P = 25 bar).

Fig. 7. Samples #1 and #2 were collected at 48 and 120 h stream time, respectively. The comparison confirms that the product distribution for the monolith 2 reached steady-state over the test period.

Complete product distribution profiles for the catalyst particle, monolith catalyst 1, and monolith catalyst 2, are compared in Fig. 8. The monolith 2 produces a consistently narrower product distribution profile from 210 to 232 °C than the catalyst particle and monolith 1. The latter two catalysts give a long tail in the heavy end at 220 and 232 °C. The olefin-to-paraffin ratio for the monolith 2 is generally higher than that for the particle catalyst and monolith 1.

3.3. Impact of gas flow conditions on methane selectivity

The testing results with either the particle or the monolith catalyst do not show significant change in methane selectivity at different reaction temperatures under a constant flow condition (or WHSV), although the CO conversion changes significantly with the temperature. Fig. 9 shows a large impact of feed gas flow rate

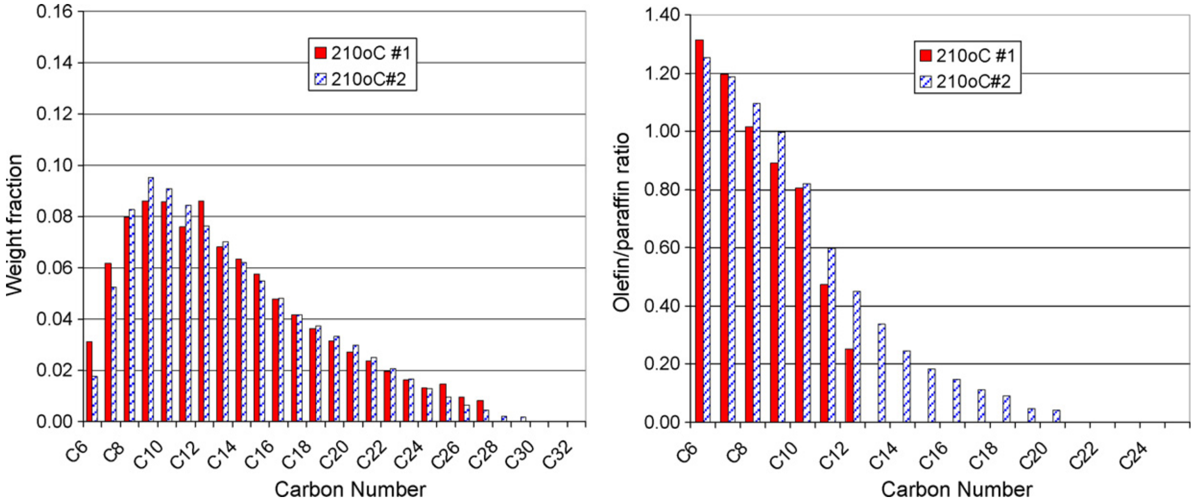
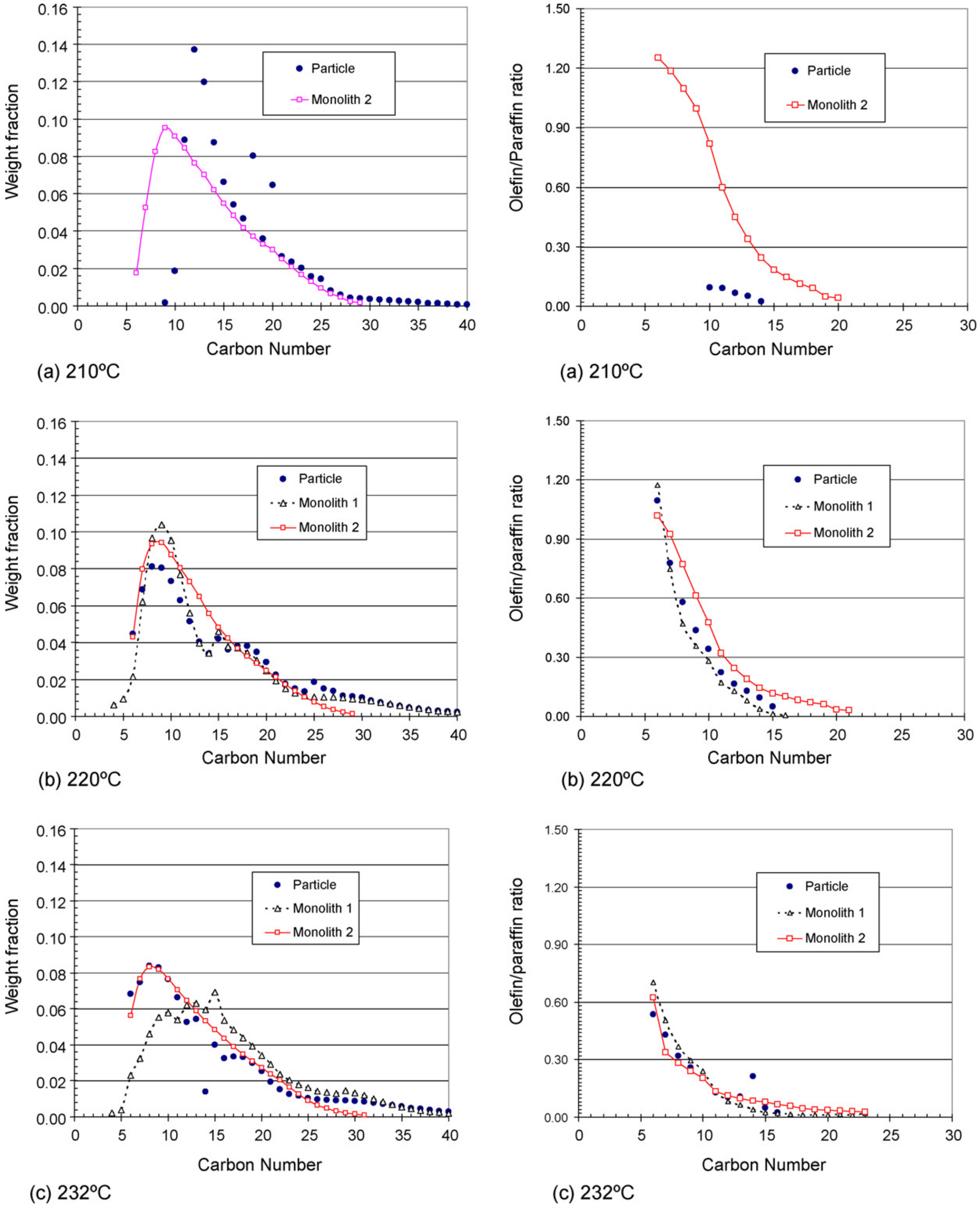


Fig. 7. Product distribution with time on stream (monolith bed 2).



(a) 210°C (a) 210°C

(b) 220°C (b) 220°C

(c) 232°C (c) 232°C

Fig. 8. Carbon number distribution in liquid product.

on the methane selectivity in the monolith catalyst structure. At the same temperature, the methane selectivity increases with the feed gas flow rate. This difference seems to be enlarged at a higher temperature.

4. Discussion

Two important experimental results are revealed in this work. One concerns wax formation and another relates to the impact of feed gas flow rate on methane formation. Experimental results are rationalized by the reaction pathways shown in Fig. 10. Paraffins and olefins are primary products from FT polymerization reactions on the catalyst surface. The olefins are active species and can cause several secondary reactions. The olefin produced from the primary reaction may be hydrogenated into the paraffin, may continue growing into waxy, heavy components, and may form coking. In parallel to the polymerization reaction, CO can react with H_2 to form methane. For a given catalyst composition, relative reaction rates of

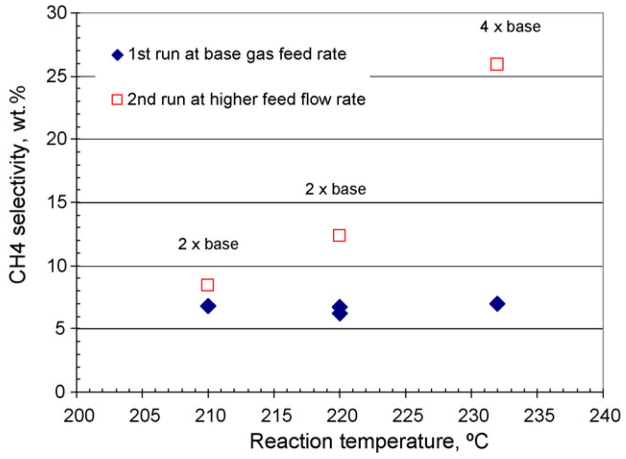


Fig. 9. Impact of feed gas flow rate on methane selectivity (monolith bed 1).

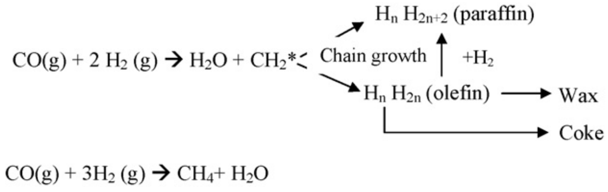


Fig. 10. Reaction pathways.

all those different reactions will be affected by mass transfer and heat transfers inside the catalyst particle and between the bulk fluid and catalyst particle.

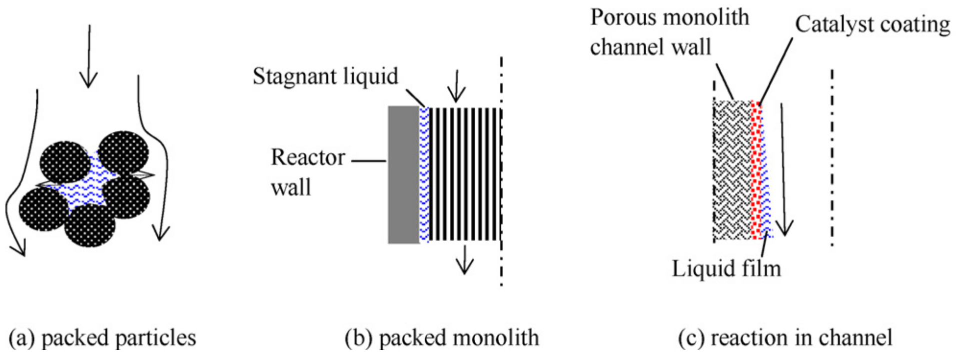
Impacts of catalyst structures on the FT reaction activity and selectivity were well studied in a packed particle bed reactor tube [12], which included uniformly impregnated large pellet, crushed large pellet, eggshell pellet, crushed eggshell pellet, and uniformly impregnated small pellet. The eggshell catalyst structure gave significantly higher Co-based activity and lower methane yield than the uniformly impregnated pellet. The study clearly demonstrates impacts of the mass and heat transfer inside a pellet on the reaction performance.

In the previous catalyst pellet studies, the hydrodynamics, and external mass and heat transfer were controlled by fixing the catalyst particle packing. By contrast, the hydrodynamics, and external heat and mass transfer are changed by using different catalyst bed structures in the present work. The monolith catalyst coating thickness used in this work is less than 50 μm on average. Based on the previous literature studies, pore diffusion mass and heat transfer may be considered negligible at such catalyst thickness. Thus, the present study is related to the catalyst design at the reactor scale. It represents progressive understandings to the FT catalytic process design from intrinsic catalyst site scale, catalyst pellet scale, to reactor scale.

Flow structures inside the present catalyst bed are depicted in Fig. 11. Irregular voids and flow paths are present in a particle-packed bed. The liquid-phase product formed from the FT reaction could be trapped in those voids due to capillary forces and therefore not be flushed away from the catalyst external surface promptly by the convective flow. As a result, molecules in the stagnant liquid phase continue to react and grow into longer chains to form waxes due to secondary reactions.

When a monolith piece is plugged into the reactor tube, some void spaces exist between the monolith exterior and the reactor tube wall since there are many partial channels on the exterior of a core-drilled monolith piece. The liquid-phase reaction product tends to accumulate in those voids and form a stagnant liquid phase because the gas linear velocity near the tube wall surface is very slow. Since the exterior partial channels of the monolith piece are all catalyzed, product molecules in the stagnant liquid can continue to react and form wax. This wax formation mechanism is clearly evidenced by a thick layer of wax formed on the exterior of the monolith body in Fig. 5. This mechanism also explains why it takes a certain time for the wax to emerge in the liquid product, because it takes time for the stagnant liquid phase to reach steady-state. On the other hand, no wax formation was visible inside the monolith channel itself. This could be due to the fact that the liquid phase product can be readily flushed out of the straight channels. The experimental results with the monolith catalyst 2 confirm that wax formation is minimized if the reaction is only confined inside the monolith channel. The present study shows that formation of wax is likely due to secondary chain growth reactions within a stagnant liquid phase inside the catalyst and bed, because of the prolonged residence time of the primary FT reaction products. Minimization of the stagnant liquid phase would reduce the wax formation such as the case with monolith 2 catalyst where more C5–C18 hydrocarbons are formed (Fig. 6).

The impact of the feed gas flow rate on the methane selectivity is explained by the catalyst surface wetting effect. Evolution of the liquid product along the channel surface is illustrated in Fig. 11c. The liquid on the channel surface gradually increases along the channel length. The falling film theory requires a certain amount of liquid flux in order to have the channel surface be fully wetted. Since a dry feed gas is used, the channel entrance region could be dry in all the reaction process. For a given catalyst bed volume, increasing the feed gas flow rate reduces the liquid product conversion due to a shorter residence time and an increased G/L volume ratio inside the channel. As a result, fraction of the dry



(a) packed particles (b) packed monolith (c) reaction in channel

Fig. 11. Hydrodynamic flow structures in different catalyst beds of present study.

channel surface increases with the feed gas flow rate. The fraction of the dry channel surface also increases with the temperature. Thus, the methane formation is considered mainly due to the methanation reaction on the dry catalyst surface. In other words, the selectivity toward methane may be lowered if the channel surface is fully wetted under the reaction conditions. This research subject is under further investigation.

5. Conclusion

It was found that the FT product distributions are significantly affected by the catalyst bed structure and hydrodynamic flow conditions. Higher C5–C18 liquid fractions and olefin/paraffin ratios are obtained by conducting the FT reaction in a monolith catalyst channel rather than a packed catalyst particle bed. Wax formation is mainly caused by secondary reactions in a stagnant liquid. The straight flow channels of a monolith catalyst provide little dead volume and render quick flushing of the liquid product by convective flow so that the wax formation can be minimized or eliminated. Methane formation in the FT reaction is likely due to the dry catalyst surface. The fraction of the dry catalyst surface in a monolith channel is affected by the G/L hydrodynamics inside the channel under the reaction conditions. It is suggested that the methane formation can be decreased by assuring complete wetting of the catalyst surface under the reaction conditions.

Acknowledgments

The authors would like to thank their colleagues at Pacific Northwest National Laboratory (PNNL), Dr. David King, Ms. Shari Li, Mr. Wayne Wilcox, and Mr. Allan Cooper for invaluable technical discussions and assistance. This work is supported by the PNNL Energy Conversion Initiative. The monolith support sample was provided by Corning Incorporated.

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