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Fischer–Tropsch synthesis on monolithic catalysts with oil circulation

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Abstract

Monolithic catalysts made of cordierite and γ-Al_2O_3 have been prepared and tested for the Fischer–Tropsch (FT) synthesis. When operated without oil circulation, washcoated cordierite monoliths have previously been shown to be as active and selective as the corresponding powder catalyst provided that the monoliths have low washcoat loadings. Two-phase operation, i.e. with oil/product circulation during reaction, resulted in improved heat removal and temperature control, in lower apparent activity and faster deactivation, but the C_{5+} selectivity was equal to or even better than without oil circulation. The lower apparent activities obtained with oil circulation seem to be a combination of catalyst deactivation and flow-related problems in the present experimental set-up.

Keywords: Fischer–Tropsch synthesis; Monolithic catalysts; Oil circulation

1. Introduction

Fixed-bed and slurry reactors have been the reactors of choice for low temperature Fischer–Tropsch (FT) synthesis. The large particles in fixed-bed reactors result in poor intraparticle mass transfer characteristics and the space time yield is limited by heat transfer in the catalyst bed. The slurry system gives rise to significant improved mass transfer characteristics within the catalyst particles, but the separation of the catalyst from the product can be troublesome. The backmixing also makes the slurry reactor less efficient in terms of reactor volume than the plug flow reactor.

Mass transfer effects are very important in FT synthesis [1]. Even though the reactants are in the gas phase, the pores of the catalyst are filled with liquid products. The diffusion rates in the liquid phase are typically 3 orders of magnitude slower than in the gas phase and even slow reactions may be diffusion limited in the liquid phase. In a fixed-bed reactor, the selectivity problem can be solved by using catalyst pellets where the catalytic material is deposited in a thin outer layer (egg-shell catalysts) [2]. However, this means that only a fraction of the catalyst present in the reactor is participating in the reaction. In a slurry reactor, the selectivity problem is solved by using small catalyst particles.

Supported cobalt is the preferred catalysts for the FT synthesis of long chain paraffins from natural gas due to their high activity and selectivity, low water–gas shift activity, resistance against deactivation and a comparatively low price.

Slow reactions, which are otherwise conducted in fixed-bed or slurry reactors, have recently been found well suited for monolithic reactors [3–7]. A monolithic reactor/catalyst concept for Fischer–Tropsch synthesis offers several possible advantages compared to other Fischer–Tropsch reactors and could be of great interest especially for offshore installations: high gas–liquid mass transfer rates in two-phase flow, short diffusion distance in monolith walls, plug flow characteristics, high liquid and gas throughputs are possible, low pressure drop, no wax-catalyst separation necessary and direct temperature control by direct cooling of catalyst with the liquid medium and external heat removal.

We have previously used monolithic catalysts [3–5] to study FT synthesis. The previous results have shown that the monolithic substrate without any oil circulation gave about

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Table 1
Comparisons between a conventional powder $CoRe/Al_2O_3$ catalyst and the corresponding monolithic catalysts without oil circulation

Catalyst	Relative activity (HC)[a]	CH_4 selectivity (%)	C_{5+} selectivity (%)	$C_{3=}/C_{3-}$ ratio	CO_2 selectivity (%)
Powder catalyst (53–75 μm)	1.0	8.3	82.3	2.4	0.2
Washcoated cordierite (0.4 g_{cat})[b]	0.92	8.9	82.5	1.9	0.3

Temperature = 483 K, pressure = 20 bar, $H_2/CO = 2:1$. Conversion of CO: 45.5–46.5% [5].

[a] Rate (g_{HC}/g_{cat}, h) relative to the rate for a standard powder catalyst.

[b] Approximate washcoat thickness is 0.04 mm.

the same activity and selectivity as the powdered catalyst (Table 1). It is important and in particular for the selectivity that the monoliths have low washcoat loadings. It has been found that the thickness of the washcoat layer must be lower than approximately 0.05 mm to avoid mass transport restrictions [4]. However, there are heat transfer limitations in the monoliths due to the very exothermic reaction and this causes runaways at high conversions. Circulation of the liquid products could be a proper method to control the temperature and avoid runaways. A recent model study has also shown that a monolithic loop reactor with liquid recycle could be very suitable for the Fischer–Tropsch synthesis [8].

Recently, the use of a monolith loop catalytic membrane reactor for the Fischer–Tropsch synthesis has also been investigated [9]. Microchannel technology has also been proposed and tested for the Fischer–Tropsch synthesis [10].

In the present work, some preliminary results on the use of a monolithic system with oil recirculation for carrying out the Fischer–Tropsch synthesis are reported. The main emphasis has been on demonstrating the concept in the laboratory scale. The same experimental set-up as used for studying powder catalysts has been used putting some restrictions on the conditions that could be used for the oil circulating experiments.

2. Experimental

Cobalt catalysts containing 20 wt% Co, 1 wt% Re on γ-Al_2O_3 were prepared by incipient wetness co-impregnation of the support with aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $HReO_4$. The catalysts were dried in air overnight at 393 K before calcination in air at 573 K for 2 h.

The monoliths used in this work were cordierite (400 cells/in.^{2}) and γ-alumina (400 cells/in.^{2}, test samples) supplied by Corning. The monoliths were cut into cylindrical pieces with a diameter of 9 mm and length of 100 mm. Before washcoating, the monolithic substances were dried at 100 °C for 12 h. The slurry for washcoating was prepared by grinding the Co/Re-Al_2O_3 catalyst together with water in a ball mill. The washcoat was applied by slowly lowering the monolith in the slurry. Due to the nature of alumina monoliths, incipient, wetness impregnation was not possible and the Co/Re was applied by wet impregnation of aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $HReO_4$.

The experiments were carried out in a conventional flow apparatus using a stainless steel reactor surrounded by an electrically heated aluminium jacket. The monolithic catalysts were used as prepared. At the beginning of the run, before production of liquids to any extent, synthetic oil was added to the reactor to wet the catalyst and avoid temperature runaway. The oil used as the circulation liquid was a poly-α-olefin mixture from Mobil Chemical Products International Inc. The oil was introduced by a spray nozzle covering the inlet area (approximately 9 mm diameter) of the monolith. The oil flow at the start of a run was 3 l/h and it was increased to 9 l/h during the run. The experiments were carried out at 20 bar, 210 °C and $H_2/CO = 2.1$. De-ionised water was added to the reactors during a test run. The feed and products were analyzed using an on-line HP 5890 GC equipped with TCD and FID detectors. N_2 (internal standard), CO, CH_4 and CO_2 were separated by a Carbosieve packed column and analyzed on the TCD. The hydrocarbon products were separated by a 0.53 mm i.d. GS-Q capillary column and detected on the FID. Fig. 1 shows an outline of the apparatus. Oil circulation was only applied to one of the two reactors.

Catalyst activities were compared using a relative activity to hydrocarbon products. The relative activity is referred to the reaction rate (g_{HC}/g_{cat}, h) of a standard catalyst. A rate expression of the form $r_{ref} = A\exp(-E_A/RT)P_{H_2}^{x}P_{CO}^{y}$ was used to adjust for temperature and pressure. The relative activity becomes r_{obs}/r_{ref}.

3. Results and discussion

Table 2 shows the results with oil circulation for the washcoated cordierite monolith and for the impregnated γ-alumina monolith. The impregnated γ-alumina monolith could not be used without oil circulation due to temperature runaway. The alumina monolith was made by wet impregnation with aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $HReO_4$. The nominal Co loading of the alumina monoliths in Table 2 was about 30%, but the exact loading is not known. However, the alumina monoliths with Co loading of about 12 wt% could be run without oil circulation.

The results in Table 2 clearly shows that the apparent activity is lower for the impregnated alumina monolith and the washcoated monolith compared to the powdered catalyst when oil is added and more so for the washcoated monolith. It is difficult to compare directly the activity between the washcoated monolith and the impregnated alumina monolith since the amount of exposed Co is not known for the alumina

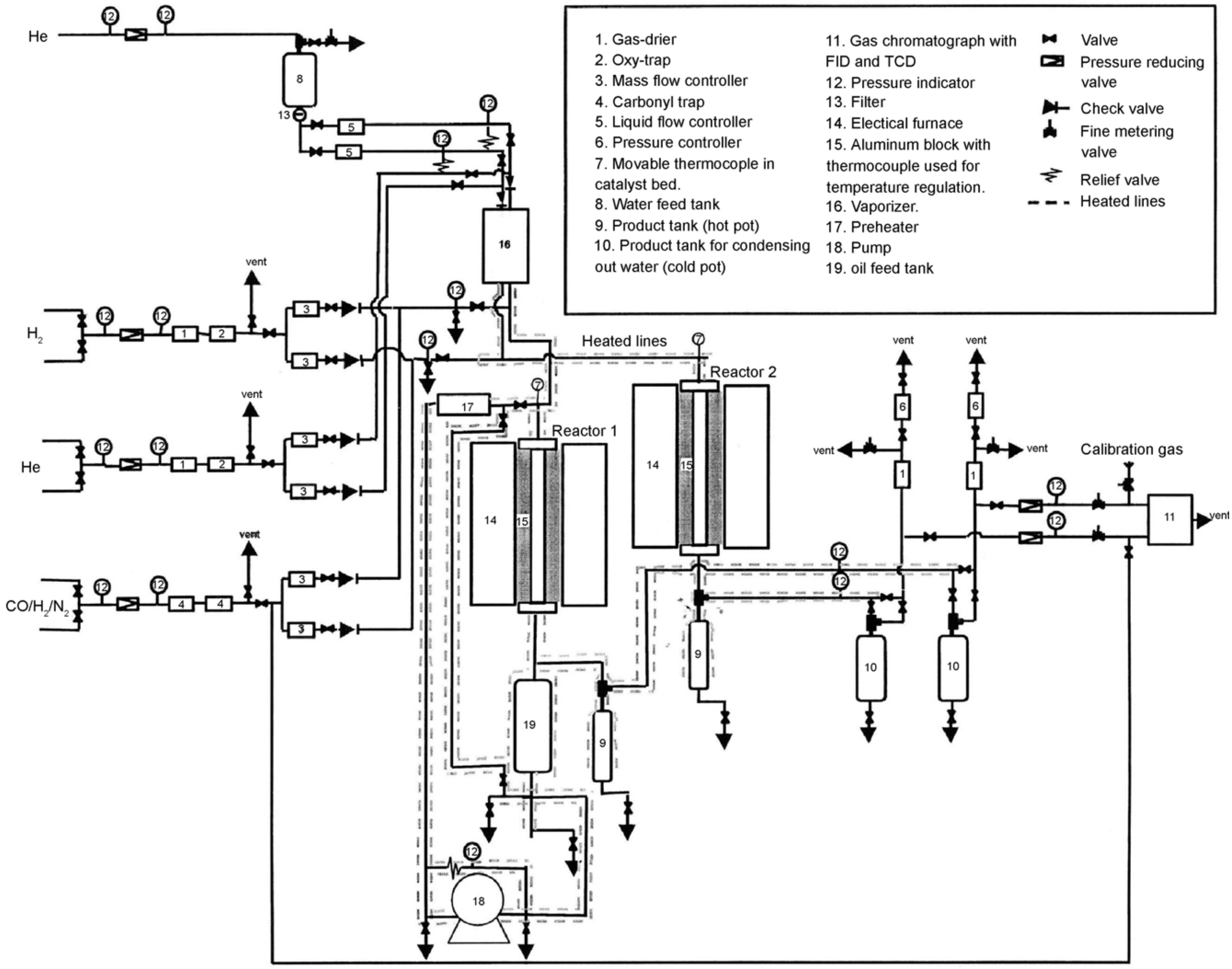

Fig. 1. Experimental apparatus.

monolith. Oil circulation also results in lower olefin selectivity, a somewhat higher paraffin selectivity and a higher CO_2 selectivity, results that are all indications of increased mass transfer restrictions.

Figs. 2 and 3 show how the conversion of CO changes after the space velocity was adjusted to give close to 50% CO conversion and when water was added to the feed stream for monoliths without oil circulation and with oil circulation, respectively. The alumina monolith (with about 11 wt% Co) tested without oil circulation is relatively stable before water is added to the feed, but the CO conversion decreases rapidly when water is added and it looses about 40% of the activity. The alumina monolith (with about 30 wt% Co) tested with oil circulation on the other hand looses more than 40% activity already before water is added and only an additional 20% during water addition.

It has always been observed with powdered Co catalysts that adding water to the feed results in increased C_{5+} selectivity regardless of the support [11]. In contrast to what is normally observed, the C_{5+} selectivity did not increase

Table 2
Comparison between washcoated cordierite monoliths and impregnated alumina monoliths

Catalyst	CO conversion (%)	Relative activity (HC)[a]	C_{5+} selectivity (%)	CH_4 selectivity (%)
Washcoated[b] monolith, no oil added	42.0	0.90	79.7	11.1
Washcoated[b] monolith, with oil circulation	40.8	0.33	82.5	9.1
Co/Re impregnated γ-Al_2O_3 monolith[c], no oil added	N.A. (runaway at startup)			
Co/Re impregnated γ-Al_2O_3 monolith[c], with oil circulation	36.4	0.60	79.3	11.0

Temperature = 483 K, pressure = 20 bar, $H_2/CO = 2.1$.

[a] Rate (g_{HC}/g_{cat}, h) relative to the rate for a standard powder catalyst.

[b] Washcoat containing 20 wt% Co and 1% Re.

[c] Containing about 30 wt% Co and 1.5% Re.

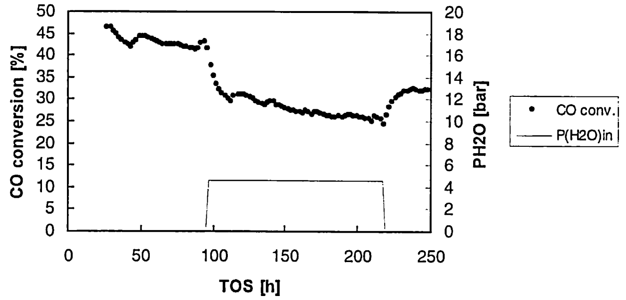

Fig. 2. CO conversion as a function of time on stream for an impregnated γ-alumina monolith tested without oil circulation. $T = 479$ K, $P = 20$ bar, $H_2/CO = 2.1$. Addition of water as indicated. Co loading: approximately 12 wt%; Re loading: approximately 0.5 wt%.

when water was added during oil circulation for the alumina monolith.

When the washcoated monolithic catalyst was run with oil circulation, a decrease in the observed reaction rate was observed compared with the runs with dry synthesis gas without oil circulation. The C_{5+} selectivity, however, was comparable (and even higher) than the values achieved over the monolithic catalyst without oil circulation as indicated in Table 2. For the cordierite monoliths, it was possible to start the run without oil circulation (period A in Fig. 4). The conversion of CO dropped with about 50% when synthetic oil was added (period B in Fig. 4). In order to obtain CO conversions closer to those obtained during dry conditions, the space velocity was increased as shown by period C in Fig. 4 resulting in a higher C_{5+} selectivity than observed at dry conditions. In period D (Fig. 4), the oil circulation was increased from 3 to 6 l/h and apparently the increase in the oil circulation did not change the C_{5+} selectivity. Period E in Fig. 4 represents the behaviour after the oil circulation was removed. The catalyst is deactivating faster during oil circulation than before oil was applied. After the oil was removed, the apparent catalyst activity is in fact slowly increasing again. The C_{5+} selectivity is lower than during oil circulation (the same as before oil was added).

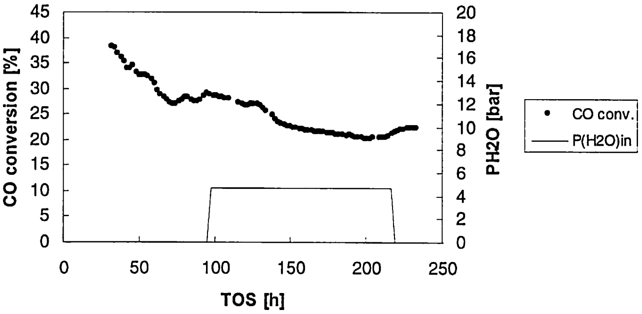

Fig. 3. CO conversion as a function of time on stream for the impregnated γ-alumina monolith tested with oil circulation. $T = 479$ K, $P = 20$ bar, $H_2/CO = 2.1$. Addition of water as indicated. The monolith is impregnated two times giving a Co loading: approximately 30 wt%; Re loading: approximately 1.5 wt%.

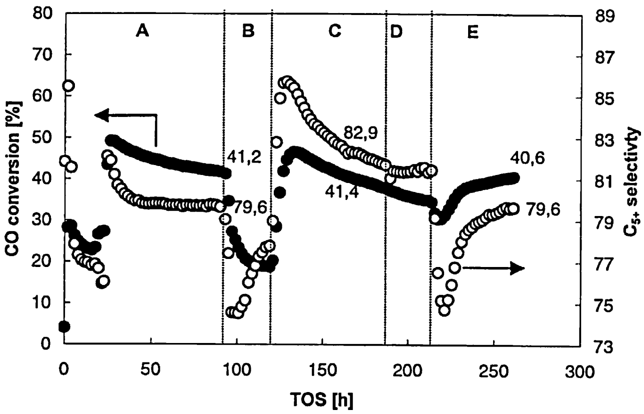

Fig. 4. CO conversion and C_{5+} selectivity as a function of time on stream for the washcoated cordierite monolith; $T = 479$ K, $P = 20$ bar, $H_2/CO = 2.1$. The washcoat consists of 20 wt% Co, 1 wt% Re on alumina. Period A: normal start at dry conditions with reduction of space velocity to adjust the conversion, no oil circulation; period B: oil circulation 3 l/h; period C: oil circulation 3 l/h, reduced space velocity; period D: oil circulation 6 l/h; period E: without oil circulation.

Significant temperature gradients were observed through the washcoated monolith (almost 10 °C) before oil circulation was started. Pumping oil through the reactor improved the heat removal resulting in constant temperature through the monolith.

After introducing oil circulation, the C_{5+} and CO_2 selectivity increased, the CH_4 selectivity decreased, but only small changes in the olefin/paraffin ratio were observed. The activity decreased rapidly with about 50%. The changes in C_{5+} and CH_4 selectivity could be explained by increased water concentrations since water improves the C_{5+} selectivity. Increased concentration of water will also result in increased CO_2 selectivity as observed. Increased water concentration could be explained if some of the water produced remains in the circulating liquid. This could also explain the higher deactivation rate during oil circulation. Normally, increased olefin/paraffin ratios are observed when water is added to the feed as a result of decreased paraffin selectivity [11]. This is, however, not observed during oil circulation.

The effect of oil circulation in this system seems to be a decrease in activity while a somewhat higher C_{5+} selectivity is observed. The low apparent activity suggests that some of the catalyst is inaccessible to the reactants when oil circulation is on. The olefin/paraffin ratio remains essentially unchanged during oil circulation. These observations could be explained by complete blockage of some channels by oil or by a deactivating mechanism rendering some of the Co inactive. It could be possible that some channels become liquid-filled and that the liquid is kept in the channel by capillary forces. Removing oil circulation resulted in only a slight increase in the activity suggesting that some channels remain inaccessible or that some of the Co is permanently deactivated.

In order to study this in some more detail, a powdered catalyst was wetted with synthetic oil for 5 min after about

Table 3
Effect of wetting a powder catalyst with synthetic oil (poly-α-olefin)

TOS[a] (h)	CO conversion	Relative activity[b]	C_{5+} selectivity
Before oil circulation			
86	44.9	1.07	82.2
After oil circulation			
106	38.9	0.92	81.8
134	37.8	0.89	81.5

Temperature = 483 K, pressure = 20 bar, $H_2/CO = 2.1$.

[a] TOS, time on stream.

[b] Rate (g_{HC}/g_{cat}, h) relative to the rate for a standard powder catalyst.

90 h on stream. As shown in Table 3, the selectivity was not affected by wetting of the catalyst with synthetic oil, but the activity decreased even at this short exposure time and more than expected from normal deactivation with time on stream. This suggests that the decrease in activity for the monolith catalyst with oil circulation at least partly may be caused by deactivation of Co sites.

As discussed above, the lower rate (mol/g_{cat}, h) with a monolithic catalyst using oil circulation could be due to unfavourable flow regimes of the gas/liquid mixture through the monolith. Taylor flow is necessary to achieve the predicted benefits of the monolith reactor. According to other studies [12], this flow regime is often achieved at liquid velocities higher than 2 cm/s. In these experiments, the oil velocity at start of a run was lower than 2 cm/s. However, increasing the liquid velocity to 3 cm/s did not result in any improvement of the apparent activity. With the present configuration of the fixed-bed system, the experiments are also carried out at a lower gas than liquid velocity while it has been claimed that an approximate equal flow of liquid and gas are desirable [13].

4. Conclusions

It can be concluded that oil circulation is a convenient way to control the temperature in the reactor. A very stable axial temperature was obtained and no problems with runaways were observed. The apparent activities of the monolith catalysts were lower with oil recirculation than at gas-phase conditions, but the selectivities of C_{5+} were comparable with the ones obtained at gas-phase conditions. The lower activities appear to be a combination of deactivation and flow-related problems at the operating conditions. It is possible that the observed increase in the deactivation rate is a result of increased water concentrations.

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