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Fischer–Tropsch synthesis in a microstructured reactor

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ABSTRACT

A multichannel microstructured packed bed reactor is manufactured. The performance of the microstructured reactor for Fischer–Tropsch synthesis with high activity cobalt/alumina catalysts is studied. For evaluation of the microstructured reactor performance, the results are compared with results obtained in an electrically heated laboratory scale fixed-bed reactor under similar conditions. The catalyst activity and selectivities obtained with undiluted catalyst in the microstructured reactor are similar to results obtained with diluted catalyst in the fixed-bed reactor. The microstructured reactor's capability to operate with high active catalysts at severe conditions without causing temperature runaways and thus increased deactivation of the catalyst is demonstrated.

1. Introduction

Microstructured reactor technology is an emerging technology for the Fischer–Tropsch synthesis. The Fischer–Tropsch synthesis is now a commercial pathway for the conversion of natural gas to transportation fuels. However, many applications such as offshore production and biogas conversion could benefit from compact and modular conversion technology [1–3]. Microstructured reactors have a large number of small, parallel channels with enhanced mass transfer properties and intensified heat transfer [4–7] enabling isothermal operation of the highly exothermic Fischer–Tropsch reactions. Hence, microstructured reactors could be especially suitable for highly active Fischer–Tropsch catalysts [8]. We have previously studied the Fischer–Tropsch synthesis in monoliths washcoated with Fischer–Tropsch catalysts, showing activities and selectivities comparable to the corresponding powder catalyst [9]. One of the concerns in using microstructured reactors for heterogeneously catalysed gas-phase reactions is how the catalytic active phase is introduced in the reactor [10]. Configurations as wall-coated reactors, packed bed reactors and structured catalytic beds are proposed [11]. Pressure drop might limit the use of packed bed reactors and wall-coated reactors could suffer from lower reactor productivity [12].

Supported cobalt is the preferred catalyst for Fischer–Tropsch synthesis of long-chain paraffins from natural gas because of its high activity and selectivity to linear paraffins, high relatively resistance toward deactivation and low water–gas shift activity [13]. Adding Ni to a Co or Co/Re catalysts is reported to increase the catalyst activity significantly without decreasing C_{5+}-selectivity and Ni also have a stabilising effect on the catalyst activity [14]. In the present work, the performance of a multichannel microstructured packed bed reactor with different CoRe/γ-alumina catalysts is compared with results from a lab-scale fixed-bed reactor.

2. Experimental

2.1. Catalyst preparation

Supported catalysts containing 20 and 40 wt.% cobalt promoted with 0.5 and 1.0 wt.% rhenium, respectively on γ-Al_2O_3, were prepared by a one-step incipient wetness co-impregnation method with aqueous solutions of cobalt nitrate hexahydrate and perrhenic acid. In addition the 20 wt.% cobalt catalyst was co-impregnated with nickel nitrate hexahydrate. The composition of the catalysts is given in Table 1. After impregnation, the catalysts were dried in an oven kept at 393 K for 3 h. The catalysts were then calcined in air at 573 K for 16 h. The temperature was increased from ambient to 573 K at a rate of 2 K/min. Further pre-treatment was done *in situ*.

2.2. Microstructured reactor

The stainless steel microstructured reactor is made by the Institute of Micro Process Engineering at Forschungszentrum Karlsruhe. It has a 2 cm^3 reactor volume and consists of eight

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Table 1
Specifications of the γ-Al_2O_3 supported catalysts.

Catalyst	Sieve fraction (μm)	Co (wt.%)	Re (wt.%)	Ni (wt.%)	Dispersion (%)	Cobalt surface area ($m^2\,g^{-1}$)
A	53–90	20	0.5	5	10.3	13.9
B	53–75	40	1.0	0	3.6	9.8

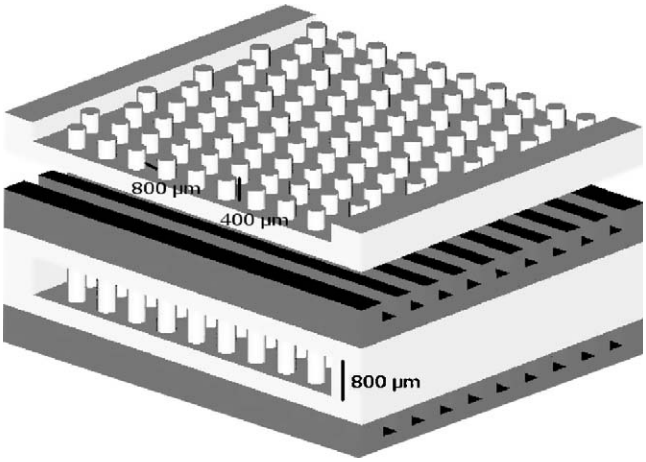

Fig. 1. Illustration of the stacking of the microstructured reactor, showing the pillar structured catalyst foils and the cross-flow rectangular oil channels.

parallel catalyst sections sandwiched between cross-flow oil channels for heat exchange. Each catalyst section consists of two foils with an etched 400 μm deep pillar structure, hexagonally arranged with 800 μm distance between the pillars. The foils are stacked opposite to each other, giving 800 μm channel height. Stacking of the catalyst foils and oil channels is illustrated in Fig. 1. The catalyst foil and the microstructured reactor are shown in Fig. 2. A Julabo HT-30 high temperature oil circulator with Thermal H350 high temperature heat transfer oil was used to maintain the reaction at desired temperature. Three thermocouples in the reactor body measured the reactor wall temperatures and are regulated against temperature in the oil circulator bath during the experiments.

2.3. *Fixed-bed reactor*

The fixed-bed reactor is made of 1/2″ stainless steel tube with 10 mm inner diameter. The fixed-bed reactor is clamped inside an aluminium block and heated by a Kanthal oven. The average reactor temperature is calculated from three temperature measurements inside the reactor and is regulated against the temperature in the aluminium block.

2.4. *Activity and selectivity measurements*

After drying, calcination and sieving, 1.5 g catalyst was filled into the reactors. In the fixed-bed experiments the catalysts were diluted 1:20 with inert silicon carbide particles in order to improve the heat transfer along the catalyst bed. The catalysts were reduced *in situ* with H_2 at 1 bar while the temperature was increased by 1 K/min to 623 K. After 16 h of reduction, the catalysts were cooled to 443 K. The system was then pressurised to 20 bar, and synthesis gas of molar ratio $H_2/CO = 2.1$ was introduced into the reactor. The temperature was then slowly increased to the desired start-up reaction temperature. Conversions and selectivities were measured over a minimum 24 h period before changing parameters. The experimental setup and procedures have been described in detail elsewhere [15].

3. Results and discussion

3.1. *Activities and selectivities*

Tables 2 and 3 show the results obtained with the microstructured reactor and the fixed-bed reactor, respectively. The observed reaction rates and C_{5+}-selectivities vs. time at constant conditions for Catalyst A at 225 and 240 °C in the two reactors shown in Figs. 3 and 4 show similar results for Catalyst B at 20 and 30 bar. The results obtained with undiluted catalyst in the microstructured reactor are similar to the results with the diluted catalyst in the fixed-bed reactor. This verifies the good heat and mass transfer properties of the microstructured reactor. The results obtained in the microstructured reactor are in general promising, considering the modular scalability properties of microstructured reactors.

3.2. *Effect of Co-loading and Ni-promoter*

In the present work, the effect of Ni is not primarily studied and since cobalt loading and dispersion are different, the effect of Ni on the activity cannot be estimated. However, the 20%Co5%Ni/Al_2O_3 catalyst (Catalyst A) is obviously a catalyst with high activity. At 20 bar and 225 °C we obtained 1.7 $g_{C_{5+}}\,g^{-1}\,h^{-1}$ at 72% CO-conversion (Table 2). Compared with, e.g. Cao et al. [8], they reported 1.69 $g_{C_{2+}}\,g^{-1}\,h^{-1}$ at 77% CO-conversion on a 30%Co4.5%Re/γ-Al_2O_3 at 25 bar and 225 °C.

As an attempt to get a catalyst with even higher activity, a catalyst with 40 wt.% cobalt was made (Catalyst B). From Tables 2 and 3 it can be seen that the catalyst activities, expressed as the

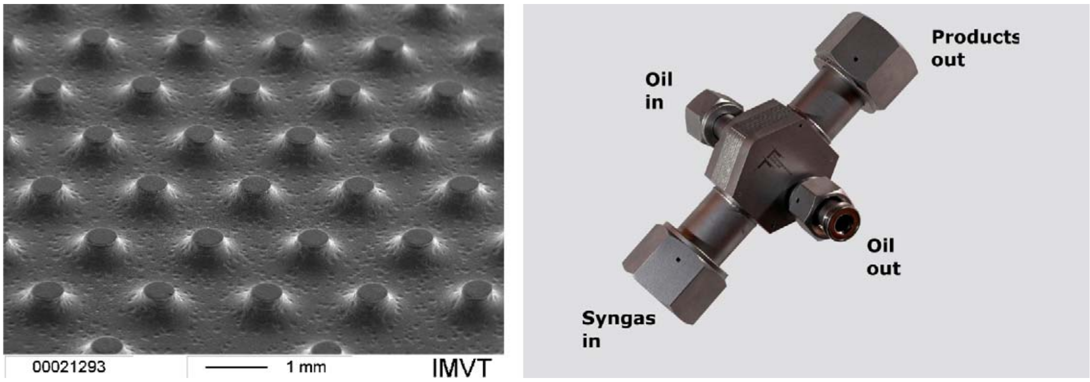

Fig. 2. SEM image of a catalyst foil and picture of the microstructured reactor.

Table 2
Productivities and selectivities in the microstructured reactor.

Catalyst	A			B				
Temperature (°C)	215	225	240	215	225	215	225	225
Pressure (bar)	20	20	20	20	20	30	30	30
GHSV (N ml g_{cat}^{-1} h^{-1})	14400	14400	20500	16200	16200	16200	16200	12500
CO-conversion (%)	51	72	83	46	72	49	80	91
CH_4-selectivity (%)	9	9	12	9	9	9	9	8
r_{CO} (mol CO g_{cat}^{-1} h^{-1})	0.10	0.15	0.24	0.10	0.16	0.11	0.18	0.16
C_{5+}-selectivity (%)	83	84	80	84	84	84	86	87
C_{5+} − productivity($g_{C_{5+}}$ g_{cat}^{-1} h^{-1})	1.2	1.7	2.6	1.2	1.9	1.3	2.1	1.9
Rel. deact. rate[a] ($\times 10^{-3}$)	1.2	2.9	4.9	2.7	0.8	1.1	0.5	0.2
TOS (h)	40	120	140	65	115	165	210	270

[a] Relative deactivation rate at this time on stream, $-\Delta r_{CO}/(r_{CO} \times \Delta t)$.

Table 3
Productivities and selectivities in the fixed-bed reactor.

Catalyst	A				B		
Temperature (°C)	210	215	225	240	218	218	228
Pressure (bar)	20	20	20	20	20	20	20
GHSV(N ml g_{cat}^{-1} h^{-1})	10500	12300	14400	20500	22600	16200	16200
CO-conversion (%)	47	48	69	80	34	48	77
CH_4-selectivity (%)	8	9	9	12	10	9	9
r_{CO}(mol CO g_{cat}^{-1} h^{-1})	0.07	0.08	0.14	0.23	0.11	0.11	0.18
C_{5+}-selectivity (%)	83	83	84	81	82	85	85
C_{5+} − productivity($g_{C_{5+}}$ g_{cat}^{-1} h^{-1})	0.8	1.0	1.6	2.6	1.3	1.3	2.1
Rel. deact. rate[a] ($\times 10^{-3}$)	2.1	1.0	6.4	8.7	–	2.4	1.3
TOS (h)	60	115	130	150	25	70	100

[a] Relative deactivation rate at this time on stream, $-\Delta r_{CO}/(r_{CO} \times \Delta t)$.

observed reaction rate (r_{CO}), are close to identical for the two catalysts in both reactor systems. This could be explained by the cobalt dispersion measurements given in Table 1. Cobalt dispersion is considerably lower for the catalyst with 40 wt.% cobalt compared with the 20 wt.% cobalt catalyst. However, the effect of cobalt loading and promoters was not the topic of the current study.

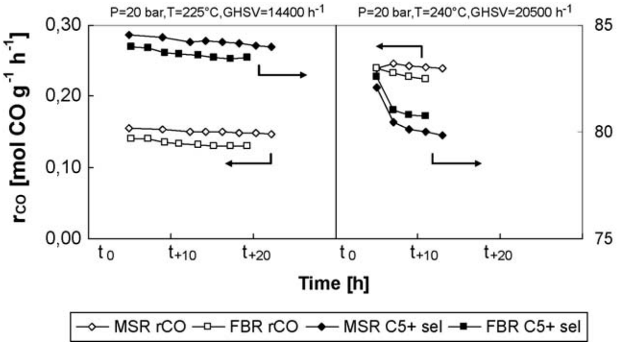

Fig. 3. Reaction rate and C_{5+}-selectivity vs. time at constant conditions for Catalyst A in the microstructured reactor (MSR) and the fixed-bed reactor (FBR).

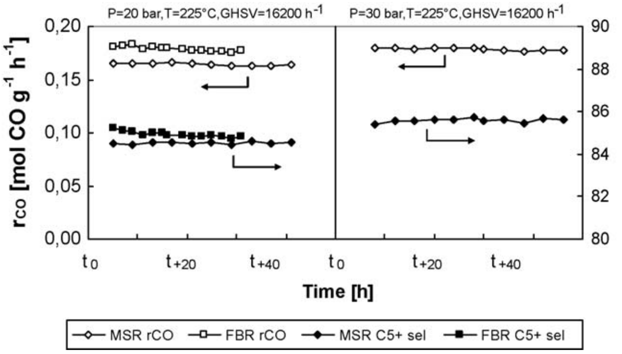

Fig. 4. Reaction rate and C_{5+}-selectivity vs. time at constant conditions for Catalyst B in the microstructured reactor (MSR) and the fixed-bed reactor (FBR).

Fig. 4 compares the performance of Catalyst B in the two reactors at 20 bar. Again it can be seen that the behaviour is close to identical. Fig. 4 also shows the performance at 30 bar and 80% CO-conversion for the microstructured reactor. Also at these conditions the catalyst stability is good. The ability of the microstructured reactor to operate at 91% CO-conversion (and high P_{H_2O}/p_{H_2}) with low deactivation rate is also demonstrated for Catalyst B (Table 2).

3.3. Catalyst deactivation

A lot of attention is recently paid to explaining the deactivation mechanisms for cobalt-based FTS catalysts. Among postulated deactivation mechanisms are cobalt oxidation, cobalt-aluminate formation, poisoning, sintering, cobalt reconstruction, and the formation of inert carbonaceous phases and it is likely that the deactivation results from a combination of several deactivation mechanisms [16,17]. Insufficient heat transfer during FTS causes high temperature gradients and local hot spots which may cause metal sintering and fast catalytic deactivation. Thus, proper heat transfer is important to minimise heat gradients. The microstructured reactor pillar structure in the catalyst foils used in this study ensures good heat transfer from the catalyst bed to the heat transfer oil.

Deactivation rate is calculated from changes in CO-conversion rate over a 10–20 h period with otherwise constant reaction conditions. The short time window makes this a rough estimate and does not necessarily represent the correct long time deactivation behaviour. However, it gives an indication on the catalyst stability. From the comparison of the data obtained with the undiluted catalysts in our microstructured reactor and the diluted catalysts in the fixed-bed reactor, there is no significant difference in the deactivation rates. This can be considered as an

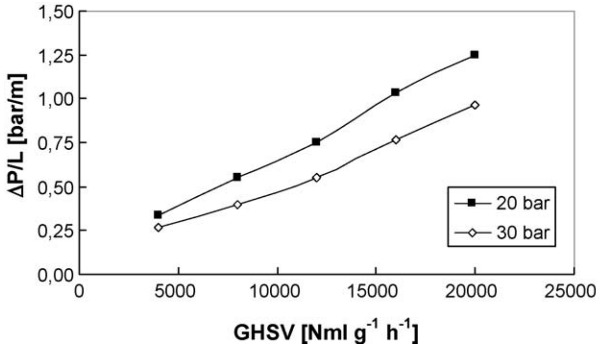

Fig. 5. Pressure drop measured over the microstructured reactor. Catalyst B (d_p = 53–75 μm), H_2/CO = 2.1 at 225 °C.

indication of the excellent heat transfer properties of the microstructured reactor and it is shown that the microstructured reactor can be operated at severe conditions (high temperature, high pressure and high CO-conversions), without temperature runaways in the catalyst.

From the deactivation data in Table 2, the catalyst with 40 wt.% cobalt seems to be more stable, but due to the uncertainties in the calculation of the relative deactivation rates there is no significant difference in catalyst stability for the two catalysts.

3.4. Temperature profiles

In the fixed-bed reactor, the measured temperature gradient along the catalyst bed was always lower than 1 °C. The low temperature gradient is mainly due to the 1:20 dilution with SiC and also the aluminium block.

In the microstructured reactor, the measured wall temperatures were 5–10 °C lower than the reported reactor temperature and with an apparently high temperature gradient along the channels. However, reactor modelling has shown fully isothermal behaviour in more than 97% of channel length and reactor temperature to be identical to inlet oil temperature when an identical reactor is used for methanol synthesis [18]. The selectivities and low deactivation rates also indicates isothermal behaviour. The measured deviations from reactor temperature are believed to be due to insufficient thermal insulations against surroundings and therefore the measured inlet oil temperature is used as reactor temperature.

3.5. Pressure drop

The pressure drop (ΔP) over the microstructured reactor was measured using a differential pressure transmitter from Aplisens. Fig. 5 shows the pressure drop over the microstructured reactor operated at FTS conditions. At these conditions, with the current configuration, $\Delta P/L$ does not exceed 1.5 bar/m even at considerably high GHSV.

4. Conclusions

A multichannel microstructured packed bed reactor with excellent heat and mass transfer properties and low pressure drop is manufactured. Fischer–Tropsch synthesis is performed with high activity Co/Al_2O_3 catalyst and the performance of the microstructured reactor fits well with results obtained with diluted catalysts in a lab-scale fixed-bed reactor. Due to the heat and mass transfer properties of the microstructured reactor, the microstructured reactor can be operated at severe conditions (high temperature, pressure, CO-conversion) without large temperature gradients and increased catalyst deactivation.

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