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Fischer–Tropsch synthesis using a porous catalyst packing: experimental evidence of an efficient use of permeable composite monoliths as a novel type of the Fischer–Tropsch synthesis catalyst

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Abstract

Novel type of the catalytic material: a permeable composite monolith (PCM) is studied in the Fischer–Tropsch synthesis (FTS) at 2.1 MPa. Due to highly intense mass transfer and high density of an active component, it was shown to provide steadily the process productivity of ca. 100–200 mg/(h cm^3) of reactor volume at 483 K. At that the selectivity of the process over PCM is maintained at the highest level ($\alpha = 0.84$; the olefin fraction in the C_3–C_4 fraction above 50%). At the effective mode of the PCM particle operation, the effectiveness factor of ca. 70% is achieved.

Keywords: Permeable composite monolith; Fischer–Tropsch synthesis; Selectivity

1. Introduction

Mass-transfer limitations affect dramatically the performance of many three-phase catalytic processes. The Fischer–Tropsch synthesis (FTS) is one of such processes, even despite it is rather slow. Numerous studies are devoted to the studies on three-phase reactors and aim to weaken the mass- and heat-transfer limitations for the three-phase catalytic processes, in particular, for the FTS (see, e.g. [1–8]). The challenge becomes even more complicated due to the necessity to weaken both the internal diffusion limitations and the gas–liquid mass-transfer restrictions, as well as provide fast heat transfer within the catalyst bed (see, e.g. [9]). A low pressure drop and homogeneity of the catalyst bed must be retained too. Slurry reactors [2–4] and monoliths [5–8] seem to solve the problem. However their disadvantage is high extent of the catalyst dilution (by slurry filling or monolith support). Actually, the catalyst loading for the slurry bed catalytic reactors is not higher than 200–250 kg/m^3 of the reactor volume, since the higher catalyst loading leads to a dramatic decrease in the gas–liquid interface area [3,10].Thus, the productivity of the volume unit of the reactor appears to be quite low. This results in huge sizes of commercial reactors (e.g. 5 m × 22 m for SSBP [11]). When using the monoliths, the catalyst loading can be foreseen to be increased by achieving the cell density above 600 in.$^{-2}$ as well as by extruding monoliths directly from the catalytic material. Therefore in prospective, using the monoliths for the FTS seems more preferable.

Here we present the experimental data on the performance of the FTS using a new type of the composite

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monolith material, which combines the high density of the catalyst bed and the high thermal conductivity at that providing simultaneously low mass-transfer resistance.

2. The concept of a reactor based on a permeable composite monolith

The discussed reactor represents itself as a wetted porous permeable monolith, which is blown through by the gaseous reagents flow. The procedure of the permeable composite monolith (PCM) preparation represents itself the combination of the state-of-the-art methods for preparation of composite materials starting from powders. The catalyst amount in the PCM particle 0.8–1.1 g/cm^3 with respect to the unreduced catalyst, decreasing to 0.7–1.0 g/cm^3 during the catalyst reduction; after reduction the metallic cobalt particles (of 8 nm mean size) comprise ca. 24 wt.% of the catalyst.

Introducing the metallic component to the PCM composition allows one to augment the heat conductivity of the PCM catalyst grain up to 3–5 W/(m K), which is significantly higher in comparison to those of the traditional catalysts, 0.1–0.5 W/(m K), as they are reported in [12,13] or ceramics 0.7–1.6 W/(m K). It is also at least 10 times higher than the radial heat conductivity of the traditional fixed catalyst bed, $\lambda_r = 0.3$–0.5 W/(m K) (here λ_r estimated according to [14] as $\lambda_r = (1-\varepsilon)\lambda_{sc} + 0.15 Re\, Pr\, \lambda_{gas}$ in consideration of (5 mm × 5 mm) cylinder catalyst grain, catalyst bed porosity $\varepsilon = 0.35$, $Re \approx 200$, $Pr \approx 6 \times 10^{-3}$, $\lambda_{sc} \approx \lambda_{cat} = 0.5$ W/(m K), $\lambda_{gas} = 0.2$ W/(m K)). Therefore, it may be supposed that the heat transfer in the single PCM particle could be much more efficient comparing to the traditional fixed catalyst bed.

A detailed study on the porous structure of the PCM material was reported recently in [15]. Assuming that the reported results may be not easy to access, below we present their summary.

The PCM material has the porosity of ca. 60–70%. The porous structure of the PCM is at least tri-modal. First, there are large "transport" pores, which provide the convective motion of the reactive gas through in the annular regime (i.e. with the liquid film covering the walls of a material channel). The size of these pores distributes in the range of 1–20 μm, the distribution maximum is achieved at 2–4 μm depending on the conditions of the PCM preparation. The "transport" pores contribute 4–10% of the PCM volume. The estimated pore-to-pore distance is ca. 20–50 μm. This estimation gives also the surface area of the transport pores as 200–500 cm^2/cm^3 of the PCM, which can be roughly be considered as the gas–liquid interface area.

Secondly, there are more thin liquid filled macropores with the size within the range of 0.1–1 μm. Also, nanoscale pores are present in the PCM. Together these comprise ca. 50–55% of the PCM volume. The rest few percent of the grain volume are pores, which are greater than 1 μm; however, these are not involved into convective mass transfer, since they are oriented almost perpendicular to the flow axis.

The transport pores are responsible for the permeability of the PCM. Typically, it varies from 10^{-14} to 5×10^{-13} m^2 (10–500 mDarcy). (Here we define the permeability, K, as it is recommended by Russian State Standard (GOST 25283-82), $K = hV\eta/S\Delta P$ where h is the PCM height, V the gas space velocity, η the dynamic gas (or liquid) viscosity, ΔP the pressure drop, and S the PCM cross-section area.) It is possible to prepare PCM with higher permeability; however, this leads to a dramatic decrease of the mechanical strength of the PCM grain. It is noteworthy that the quite low permeability of the PCM catalysts puts the certain restrictions on the size of a PCM particle reasonable for the industrial applications. According the laboratory scale FTS catalytic tests data [15], the pressure drop over the PCM particle normally is described by an equation $\Delta P = \{(1.2 \pm 0.5) \times 10^4 + (3 \pm 2) \times 10^{13} h^2 P^{-1} t^{-1}\}$ Pa, where h is expressed in m, P is the characteristic process pressure (Pa) and t the contact time (s). By fixing the parameters $P = 2$ MPa, $t = 0.5$ s, one can estimate the pressure drop to be almost proportional to the squared height of the PCM catalyst particle: $\Delta P = (3 \pm 2) \times 10^7 h^2$. This means that the reasonable pressure drop of ca. 0.5 MPa could be achieved over the PCM particle with a dimension less than 10–20 cm in the direction of the gas flow. Despite this value is not high, it seems to be quite reasonable for supposing the possibility of the PCM industrial application considering the parallel gas flow organization through a number of PCM particles.

The micrometer scale pore structure of the PCM together with the high concentration of the transport pores allowed to expect the mass-transfer restrictions to be rather mild to ensure the high effectiveness of the catalyst use as well as a good process selectivity. Actually, the catalytic tests performed at 0.1 MPa seem to prove our expectations [15].

Below we present our data on the PCM performance in the FTS at 2.1 MPa.

3. Performance of PCM in the FTS at 2.1 MPa

3.1. Experimental procedure

The catalytic tests were performed at $T = 483\,\mathrm{K}$, $P = 2.1\,\mathrm{MPa}$, H_2:CO = 2 (mol). Ten volume percent of N_2 was introduced into the gas flow as an internal standard for gas chromatography.

The PCM samples used in the tests had a cylindrical shape with the diameter of 1.45 cm and height of ca. 6 mm, sealed into a solid ring for insulation of the cylinder element (see Fig. 1). Thus, the volume of the PCM sample varied from 0.95 to 1.0 cm^3. The amount of catalyst loaded to the PCM at the preparation stage varied slightly from 0.9 to 1.03 g of the unreduced matter (i.e. 0.77–0.86 g with respect to the reduced catalyst) per PCM sample. Before starting a test, the PCM samples were pre-activated (reduced) in hydrogen flow and placed into liquid tetradecane (n-$C_{14}H_{30}$) under the protection of the flowing argon in order to avoid contact with air oxygen. Then the sample was moved into the plug-flow reactor with ascending gas flow.

Two series of tests were made in a "dry" mode (i.e. with no additional liquid hydrocarbon introduced into the reactor volume) and in a "wetted" mode (i.e. with having the layer of liquid hydrocarbon of 1–2 cm in height maintained over the top of PCM cylinder). Tetradecane or tetracosane (n-$C_{24}H_{50}$) were used as the liquid hydrocarbon. Note that the PCM sample was initially flooded by n-tetradecane for all the test series.

Reference data for the evaluation of the PCM performance were obtained by testing the Co-containing catalyst used for the PCM preparation in a tubular fixed-bed reactor. The sample size was 1.04 g (0.87 g after the reduction) with the catalyst powder particle size of 0.15–0.25 mm. The catalyst was activated in the fixed-bed reactor directly before the start of the catalytic tests.

3.2. Results of the catalytic tests and discussion

Table 1 summarizes the experimental data on the PCM performance in comparison to that of the initial catalyst powder in the fixed-bed reactor (denoted as "TFB" in the table). The reported catalyst loading values and those of productivities relate to the reduced samples.

One can see from these data that the "wet"-operating PCM materials provide the efficiency of the catalyst usage ranging from 40 (PCM-4 series) to 70% (PCM-3 series) with respect to the powder fixed-bed tests. At the same time, the operation of the PCM at the "dry" mode provides 5–6 times lower productivity of the

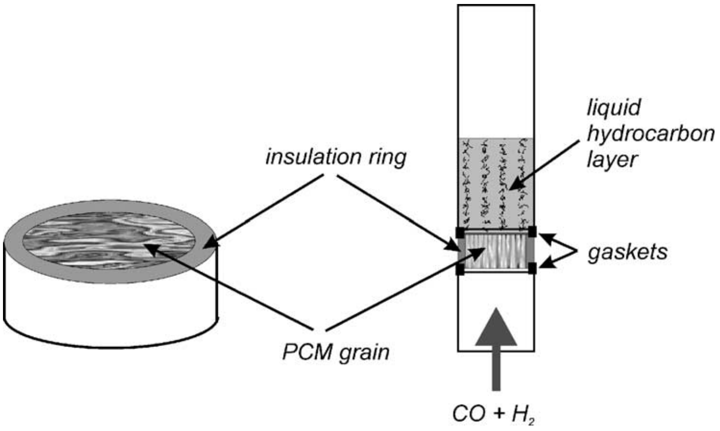

Fig. 1. The principal scheme of a PCM particle and a reactor using PCM catalyst.

Table 1
Summary of the experimental data on the PCM catalytic performance in the FTS at 2.1 MPa

Test series, sample size (g)	Operation mode	Gas feed velocity (N l/h)	CO conversion (%)	Productivity ($mg_{C_xH_y}$/(g_{cat} h))	Selectivity to methane (%)	ASF α parameter[a]			Olefins[b]	
						Paraffins	α-Olefins	β-Olefins	C_3 (%)	C_{12} (%)
TFB, 0.87		0.9	64	132	14	0.74	0.64	0.7	48	13
		2.8	45	275	16	0.81	0.55	0.82	11.5	2.9
PCM 1, 0.79	Dry	3.0	12	82	6.8	0.83	0.62	0.71	65	15
	Dry	2.8	11.5	76	6.7	0.84	0.6	0.75	63	17
PCM 2, 0.85	Dry, 483 K	2.8	12.6	79	7.9	0.83	0.65	0.80	73	23
	Dry, 493 K	2.8	18.5	114	11	0.72	0.61	0.73	60	15
PCM 3, 0.77	Wet	2.8	35	255	5.3	0.76	0.6	0.74	55	3.5
	Dry	5.6	4.2	57	7.9	0.83	0.62	0.78	68	9.7
	Wet	2.8	37	258	3.2	0.86	0.55	0.75	62	13
	Dry	2.8–5.6	3.8–6.8	47–52	8–9	0.82	0.72	0.77	70	16
PCM 4, 0.86	Wet, C_{24}	2.4	32	153	6.1	0.83[c]	0.65	–	70	–
	Wet, C_{14}	5.4	18	171	4.2	0.83	0.62	–	69	–
	Wet, C_{14}	1.6	39	120	5.8	0.84	0.62	–	69	–
	Dry	1.9	10	39	7.0	0.83	0.62	–	69	–

[a] The values of α parameter in Anderson–Schultz–Flory distribution were estimated from C_{11} to C_{20} fraction of hydrocarbons.

[b] Contents of C_n olefins in the corresponding products fraction.

[c] For these experiments, α values were estimated from C_{19} to C_{30} fraction of hydrocarbons.

process. It is quite remarkable that the selectivity with respect to heavy hydrocarbons (the value of parameter α in the Anderson–Schulz–Flory distribution) is retained high. The same should be concluded regarding the selectivity to olefins. Only a small decrease of the α-value could be noticed at the “dry”-mode operation. At the same time, it is well known that the internal mass-transfer limitations result in lower α-values due to a higher diffusion coefficient for hydrogen in comparison with that for CO (see, e.g. [16]). These limitations also should lower the selectivity to α-olefins due to increasing their residence time inside the catalyst grain, which results in a higher probability of the secondary process of the olefin re-adsorption (see [16,17]). Therefore, the retained high selectivity seems to come into an apparent conflict with the low effectiveness factor of the “dry”-operated PCM and force us to conclude that internal diffusion limitations and gas–liquid mass transfer do not affect the selectivity of the process over the PCM grain.

The mentioned contradiction can be explained by assuming, that the transport pores of the PCM grain form several disjoint clusters of pores (in analogy to the independent domain theory [18]). (This assumption is quite natural, since transport pores must contribute at least $\{1 - \exp(-0.33)\} = 28\%$ to the particle volume in order to provide a single joint cluster, as it is predicted by the percolation theory [19]. For PCM, the transport pores contribute less than 20%. Therefore, they plausibly form several pore clusters, which are separate.) In this case, the value of the effectiveness factor indicates the fraction of the pore clusters “in use”, while the high selectivity indicates an efficient mass transfer within each of the operating clusters. Indeed, both these two statements need more detailed discussion.

The efficient mass transfer within each operating cluster implies that the area of the gas–liquid interface is high enough to promote an efficient mass transfer of reactants from gas phase and that narrow channels joining the transport pores are rather short (less than 50 μm) to ensure sufficient diffusion rates. Both these statements seem to be reasonable (the area of the transport pores is above 200 cm^2/cm^3 of the PCM volume, see Section 2) in a supposition that a liquid film covers the walls of the PCM transport pore, which was recently proved in [15]. A general scheme of the pore system can be illustrated by a thicket of ivies, which have disjoint stems (the transport pores) with rather short leaves (narrow pores).

The fraction of pore clusters "in use" differs much for the "dry" and "wet" operation modes. A low efficiency of the "dry"-operated PCM could originate from flooding the most of the transport pores. Actually, in the conditions of "annular" flow of the gas through the wetted pore, the film thickness can fluctuate. Once the film thickness in a selected pore is increased, the hydrodynamic resistance of the pore becomes higher resulting in a smaller gas flow through the pore. This makes a positive feedback to the thickness of the liquid film, which results in total flooding of the pore. Therefore, in the steady state, only few transport pores (the widest ones) remain still opened to the gas flow.

The "wet" mode of the operation differs from the "dry" mode, since the capillary (Laplace) pressure is added to the pressure drop over the PCM sample, since the liquid covers the exit of the pore. The capillary force acts as stabilizing force for preventing irreversible flooding of the channel: even once flooded it can be re-opened for the gas flow, since the pressure drop over the PCM sample is higher than the capillary pressure inside the transport channel. This results in periodic changing the permeability of the PCM sample, which *was visually observed* during a special test series in a glass reactor at the atmospheric pressure. Apparently, the finest fraction of the transport pores (or those, having extremely narrow spots inside) is flooded irreversibly, resulting in lowering the efficiency factor down to 40–70%. The nature of hydrocarbon has only a little effect on the "wet" mode performance (see the PCM-4 series).

The data of the PCM-3 series illustrate that the "dry" mode can be easily shifted to the "wet" mode by simple adding a liquid layer on the top of the PCM grain without any loss of the productivity or selectivity with respect to the initial "wet" mode of the operation.

4. Conclusions

The following conclusions should be made on the base of the present data and our recent data [15]:

1. The PCM material may be prospective for the application in the FTS [20]. Due to a highly intense mass transfer and high density of the active component loading, it can steadily provide the process productivity of ca. 100–200 mg/(cm^3 h) of the reactor volume at 483 K. At that, the selectivity of the process on the base of PCM is maintained at a reasonably high level ($\alpha = 0.84$; olefins content in the C_3–C_4 fraction above 55%).
2. An efficient mode of a PCM grain operation needs the ascending organization of the syn-gas flow as well as a layer of a liquid over the upper base of the PCM grain. In these conditions, the Laplace pressure at the transport pore exits helps to prevent the irreversible flooding of the most of the transport pores. The effectiveness factor of ca. 70% is achievable in this operation mode.
3. Without the stabilizing capillary force, i.e. in the "dry" regime of the PCM operation, the efficiency of the PCM operation is low (less than 10–20%) due to flooding phenomena. However, even in this case the selectivity of the process remains to be high, since the operating clusters of pores and the flooded clusters are disjoint. Moreover, the process can be easily shifted to the effective regime by simply adding a liquid layer on the top of the PCM particle.
4. The better performance can be achieved for the PCM material with a more homogeneous distribution of transport pores by size. This is the challenge for further research activities.

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