



Monolithic, microchannel and carbon nanofibers/carbon felt reactors for syngas conversion by Fischer-Tropsch synthesis



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ABSTRACT

The present contribution summarizes work carried out on different microstructured reactors in the Catalysis Group at the Norwegian University of Science and Technology during the last years. The work has involved co-operation with industry (Statoil) as well as foreign groups (University of Karlsruhe). The experimental work covers monolithic reactors made of different materials, microchannel reactors and some recent work using carbon nanofibers/carbon felt (CNF/CF). The summary is focused on syngas conversion by the Fischer-Tropsch synthesis, but references to work on methanol and DME production in microreactors are also included. Supported Co-based catalysts are used for the Fischer-Tropsch synthesis and the results are compared with experiments carried out in a standard fixed-bed reactor using the same type of catalysts. A monolithic/microreactor/catalyst concept for Fischer-Tropsch synthesis offers several possible advantages compared to other Fischer-Tropsch reactors and could be of interest for offshore installations and distributed small scale production.

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1. Introduction

Natural gas, coal or biomass can be converted to liquid fuels via synthesis gas followed by Fischer-Tropsch synthesis, methanol or DME synthesis. Conventionally, large units are preferred but applications such as offshore production could benefit from compact and modular conversion technology. Limitation in space and weight as well as demanding conditions on site, calls for highly integrated, compact, light-weight and safe technology. Monolithic/microstructured reactors have the potential to meet such requirements. Conversion of synthesis gas made from biomass, could be another area of interest for these types of reactors.

Supported cobalt catalysts are preferred for Fischer-Tropsch synthesis of long chain paraffins from natural gas due to their high activity and selectivity, low water-gas-shift activity and moderate deactivation [1,2]. The active catalyst is cobalt in the reduced state and the performance of the catalyst depends on the degree of reduction as well as the size and shape of the Co particles. Cobalt site-time yields have usually been considered independent of both the particle size for cobalt and the support material [1,3,4] provided that the Co particles are not too small (>6–8 nm). The selectivity of higher hydrocarbons (C₅+), however, depends on the Co particle (size, crystal faces, shape) and on the support [5–7]. The relationship between the catalyst properties and the selectivity is still far

from being established. For reaction conditions where reactant or product diffusion is important, diffusion limitations may also influence the product selectivity heavily [8,9].

Monolithic reactors have usually been applied for fast reactions of gaseous reactants [10–12] in which case only the external catalytic surface participates and low pressure drop is required because of the high gas-flow. It has, however, been shown that monolithic reactors also can be used for slower reactions that are usually carried out in fixed-bed or slurry reactors [13]. Mass transfer effects are very important in Fischer-Tropsch synthesis. Even though the reactants are in the gas phase, the catalyst pores are filled with liquid products, namely wax and water [8]. The diffusion rate in the liquid phase are typically 3 orders of magnitude lower than in the gas phase, and hence even slow reactions may be diffusion limited in the liquid phase [8,13]. The C₅+ selectivity for active Fischer-Tropsch catalysts decreases significantly for diffusion lengths exceeding 0.1–0.3 mm [14]. Slurry reactors with small particles or fixed-bed reactors with large egg-shell catalyst particles are practical solutions to this, each associated with new challenges. In a monolithic reactor the active catalyst is deposited in a thin layer on the channel walls, representing an alternative possibility to control the diffusion length.

Our work on monolithic reactors for the Fischer-Tropsch synthesis dates back to a patent application (Statoil) from 1997 [13] and includes cordierite monoliths [9] as well as monolithic catalysts made of other materials such as alumina and steel [15]. Even monolithic systems with oil circulation for improved heat removal

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were studied [14]. The performance of the monolithic systems was comparable with fixed-bed reference experiments [9,15].

Moulijn and co-workers [16] presented in 2003 a monolithic loop reactor design for Fischer–Tropsch synthesis. Their model indicated that high productivity could be obtained with acceptable pressure drop. They also reported experimental values showing competitive activity and chain growth probability for Fischer–Tropsch synthesis carried out in the monolithic loop reactor using a 17 wt%Co–0.5 wt%Re/Al₂O₃ catalyst [17]. According to Moulijn and co-workers, washcoat layers loaded with the same CoRe catalyst should not be thicker than about 50 μm to avoid internal diffusion limitations [18]. Honeycomb monoliths as supports for cobalt based FT catalysts have also recently been studied by Turek and co-workers [19]. They concluded that compared with the powder catalyst, the monolithic catalysts show a higher reaction rate and activation energy at similar methane selectivities. However, calculations showed that the productivity per unit total reactor volume for the monoliths should be significantly increased in order to make them industrially attractive [20].

Ceramic foams have also been proposed as a catalytic reactor instead of monoliths [21]. A monolith loop catalytic membrane reactor has also been investigated as a possible reactor for the Fischer–Tropsch synthesis [22]. The product yield per unit reactor volume, however, was less than the state-of-the-art industrial reactors.

Fischer–Tropsch synthesis is a strongly exothermic reaction and effective heat transfer is a prerequisite for successful operation. Heat can be removed by circulating the liquid product as described above. It has also been shown by mathematical modelling that extruded aluminium honeycomb monoliths are promising [23,24]. Limited temperature gradients are obtained at extreme process conditions leading to interesting volumetric reactor yields with negligible pressure drop [23].

Microstructured reactors consist of smaller channels than monolithic reactors and are among the most promising technologies in achieving process intensification. Microstructured or microchannel reactors consist of a large number of small, parallel reaction volumes, leading to enhanced mass and heat transfer within each volume [25]. Integration of heat transfer channels and application of highly conducting materials further facilitates isothermal operation of highly exothermic reactions such as the Fischer–Tropsch synthesis. The small volumes/channels enable application of thin catalyst wall-coatings or small catalyst particles; hence minimizing mass transfer limitations without too high penalties from pressure drop [26]. In addition comes the possibility to control residence time and build in inherent safety to open new process windows (temperature, pressure, concentration) [27]. The introduction of the active catalyst in the reactor represents, however, a challenge, since each of the configurations that have been explored, wall-coatings, packed-beds or structured beds have their drawbacks in industrial operation.

Microstructured reactors are well suited for distributed production of fuels via the Fischer–Tropsch synthesis. They have also been proposed as an interesting system for off-shore application. A recent review by Kolb [28] gives an overview of the activities in the field such as reactor design, plant concepts, testing and fabrication techniques. The advantages of microchannel reactors make it possible to obtain attractive economics at much smaller scale than conventional technology [29]. Deshmukh et al. [30] have described the scale-up of microchannel reactors for the Fischer–Tropsch synthesis at multiple scales using four reactors with different lengths and number of channels. In 2013 companies like Velocys [31] and CompactGTL [32] will have pilot plant/demonstration units in operation several places.

We have been involved in the use of microstructured reactors for production of synthesis gas [33] and the use of microstructured

reactors for methanol [34,35] and DME [36] synthesis as well as for the Fischer–Tropsch synthesis [37]. This work has been done in close cooperation with Karlsruhe Institute of Technology (formerly Forschungszentrum Karlsruhe) and the reactors have been produced in Karlsruhe.

A recent development is a compact Fischer–Tropsch reactor based on hierarchically structured and highly thermal conductive Co catalysts based on CNFs [38] or CNF@SiO₂ on carbon felt [39]. Due to somewhat exceptional properties, including high purity, high specific surface area, chemical resistance to acidic and basic environments, as well as good thermal and electric conductivity, the use of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) as catalyst support has been intensively studied [40,41].

The application of non-supported powder CNFs in Fischer–Tropsch synthesis aiming at improving the dispersion and reducibility of cobalt nanoparticles, which could result in high activity and selectivities, has been reported [39,42]. However, CNFs in their nanoscopic form are difficult to handle. A novel microstructured catalyst based on aligned multiwall carbon nanotube arrays on metal surfaces has been reported to remove the reaction heat effectively and to avoid runaway of the FT reaction [42]. Another strategy is to immobilize CNFs on carbon felt (CF) where the interwaved carbon nanofibers not only form a 3-D carbon network providing superior thermal conductivity, but also randomly distributed channels giving low flow resistance [38]. The advantages of such highly conductive structured catalysts have been demonstrated for exothermic gas-phase reactions [43,44]. We have developed hierarchically structured Co/carbon nanofibers/carbon felt composites for the FT synthesis [39]. Carbon materials are light and conductive and it therefore paves a way to provide high productivity per weight [38]. However, the CNF supported Co catalysts deactivate rapidly at industrially relevant conditions. As will be shown below, the stability of these systems can be substantially improved by covering the CNF with a layer of SiO₂.

In the present contribution, the experimental work carried out in the Catalysis Group at the Norwegian University of Science and Technology (NTNU) using different monolithic/microstructured reactors is reviewed and discussed, with particular emphasis on the Fischer–Tropsch synthesis. The work related to monolithic catalysts has been published previously [9,13–15]. Part of the work with microreactors [37] and with hierarchically structured Co catalysts based on CNF@SiO₂ on carbon felt [39] has been published previously, but this is also ongoing research at NTNU. The performance is compared with standard results obtained in a fixed-bed laboratory setup [1,2] and with analogous catalyst particles

2. Experimental

2.1. Fixed-bed reactor experiments

All the supported Co catalysts were tested in a fixed-bed reactor (SS 316, 10 mm ID) described in detail elsewhere [1,2]. The catalyst particles (1.7 g, 53–90 μm) were mixed with silicon carbide (3.3 g, 75–150 μm) to prevent temperature excursions during reaction. Reduction was performed under H₂ for 16 h at 623 (ramping 1 K/min), before cooling to 443 K and flushing with He. The pressure was then increased to 20 bar before synthesis gas was fed to the reactor and the temperature raised slowly to 483 K. Heavy hydrocarbon products were collected in a heated trap (363 K) and further liquid products were removed in a cold trap (298 K). The gaseous products were analyzed for N₂, H₂, CO, CO₂ and C₁ to C₉ hydrocarbons using a GC (HP5890) equipped with FID and TCD detectors.

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