Chemical Engineering Journal 167 (2011) 536–544

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Fischer–Tropsch synthesis in microchannels

L.C. Almeida[a], F.J. Echave[a], O. Sanz[a], M.A. Centeno[b], G. Arzamendi[c], L.M. Gandía[c], E.F. Sousa-Aguiar[d], J.A. Odriozola[b], M. Montes[a,*]

[a] Dept. Appl. Chemistry, University of the Basque Country, San Sebastian, Spain
[b] Inst. of Material Sciences of Seville, CSIC, University of Seville, Seville, Spain
[c] Dept. Appl. Chemistry, Public University of Navarre, Pamplona, Spain
[d] CENPES-PETROBRAS, Rio de Janeiro, Brazil

ARTICLE INFO

Article history:
Received 13 April 2010
Received in revised form
20 September 2010
Accepted 22 September 2010

Keywords:
Microchannels reactor
Structured supports
Washcoating
Fischer–Tropsch (FTS)
Microreactors

ABSTRACT

Different metallic supports (aluminum foams of 40 ppi, honeycomb monolith and micromonolith of 350 and 1180 cpsi, respectively) have been loaded with a 20%Co–0.5%Re/γ-Al_2O_3 catalyst by the washcoating method. Layers of different thicknesses have been deposited onto the metallic supports. The catalytic coatings were characterized measuring their textural properties, adhesion and morphology. These structured catalysts have been tested in the Fischer–Tropsch synthesis (FTS) and compared with a microchannel block presenting perpendicular channels for reaction and cooling. The selectivity depends on the type of support used and mainly on the thickness of the layer deposited. In general, the C_{5+} selectivity decreased at increasing CO conversion for all of the systems (powder, monoliths, foams and microchannels block). On the other hand, the selectivity to methane increased with the thickness of the catalytic layer due to the higher effective H_2/CO ratio over the active sites resulting from the higher diffusivity of H_2 compared with CO in the liquid products filling the pores. The C_{5+} selectivity of the microchannels reactor is higher than that of the structured supports and the powder catalyst.

1. Introduction

The FTS is a well-known catalytic process for the conversion of synthesis gas into liquid fuels. The main product of the process is a mixture of hydrocarbons of variable molecular weight. The reaction mechanism follows a polymerization-like scheme based on sequential –CH_2– additions, that can be described with the Anderson–Schultz–Flory (ASF) product distribution, characterized by the chain growth probability parameter (α) [1]. This parameter, α, and consequently the selectivity significantly depend on the temperature because the activation energy of the termination step is higher than that of the growing step [2–4]. Thus, high temperatures favor the formation of light products, mainly methane.

Taking into account the exothermal character of the FTS, the reactor design to obtain a good selectivity to middle distillates is predominantly guided by the temperature control. Conventional packed-bed and slurry reactors have been used for the FTS. In the case of the packed-bed reactors, the internal mass-transfer limitations can be diminished using small catalyst particles or egg-shell pellets with thin catalytic layer. However, the pressure drop may become prohibitive if too small particles are selected. Furthermore, the use of conventional packed-bed reactors is limited by heat removal [5], making necessary to use diluted catalyst beds. In contrast, slurry reactors can work with very small catalyst particles, which prevent internal diffusional limitations; moreover, the well-mixed reaction mixture results in nearly isothermal operation that allows running the process at higher CO conversion per pass. However, catalyst particles for these reactors have to be optimized to resist to mechanical stress and attrition and an efficient filtrating system has to be developed for the liquid products/catalyst separation [1].

One of the main advantages of using metallic substrates like monoliths to prepare structured catalysts, is the possibility of applying a thin layer of catalyst with controlled thickness in a fixed body of a large-scale reactor with very low pressure-drop [6]. Thin catalyst layers may prevent diffusion limitations. The tuneability of the catalytic layer thickness allows designing the monolithic catalyst for optimal activity and selectivity [7]. Other important advantages of the use of washcoated monoliths are the high gas–liquid mass transfer rates in two-phase flow, the possibility of using high liquid and gas throughputs, and the fact that no separation between liquid products and the catalyst is necessary [1].

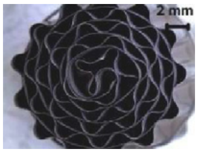
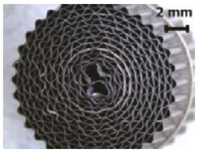
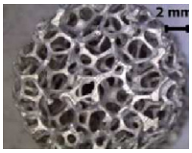
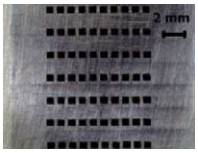
In FTS, carbon monoxide and hydrogen have to be transported from the bulk gas phase to the active sites inside the catalyst pores. Not only is the catalyst effectiveness an important factor but the selectivity of the reaction is also very much dependent on the

---

* Corresponding author at: University of the Basque Country, Department of Applied Chemistry, Paseo Manuel de Lardizabal, 3, ES-20018 San Sebastián, Spain. Tel.: +34 943018183; fax: +34 943015270.
E-mail address: mario.montes@ehu.es (M. Montes).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.09.091

Table 1
Geometric characteristics of the investigated structured supports.

Structured support	Monolith	Micromonolith	Foam	Microchannels block
				
Geometric surf. (cm^2)	258	510	140	56
Hydraulic diameter (μm)	835	373	700	700
Porosity (%)	89	79	95	–
ppi (pores/in.^{2})	–	–	40	–
cpi (cells/in.^{2})	350	1180	–	–
Dimension				
∅ (mm)	16	16	16	–
L (mm)	30	30	25	20

presence of both reactants in about stoichiometric amounts. The effective H_2/CO local ratio changes from the outside of the catalyst particle toward the inside because of the higher hydrogen diffusivity in the liquid products filling the pores. Large diffusion lengths lead to the depletion of carbon monoxide. These local super-stoichiometric amounts of hydrogen result in lower chain-growth probabilities and, therefore, lighter products [8]. Therefore, the relation between diffusion limitations and selectivity is complex. Both the reactants (gases) and the reaction products (gases and liquids including waxes) play an important role. It is clear that diffusion limitations play a crucial role in the activity and selectivity of Fischer–Tropsch synthesis catalysts. On the other hand, the FTS is significantly exothermic, so it is necessary to remove the heat to avoid hot-spots in the catalysts, resulting in the formation of light hydrocarbons. Several secondary reactions of 1-olefins influencing the overall selectivity of the FTS have been described: (i) isomerisation to internal olefins, (ii) cracking and hydrogenolysis, (iii) hydrogenation to paraffins, and (iv) chain ionization [9]. Intraporous diffusional resistance favors olefins readsorption, the first step of all these reactions, and changes the actual H_2/CO ratio over the active sites, modifying their relative importance and consequently the overall FTS selectivity. The decrease in the olefin to paraffin ratio has been related to the increase in the internal mass-transfer limitations [1]

Hilmen et al. [7] investigated the FT activity of different monolithic systems in a comparative study using catalysts with similar composition. It was shown that high washcoat loadings resulted in lower C_{5+} selectivities and olefin/paraffin ratios due to the increased transport limitations. On the other hand, Kapteijn et al. [10] reported an extensive and systematic study on the effect of the catalytic layer thickness (20–110 μm) on the FTS in cordierite monoliths. They showed that washcoat layers thicker than about 50 μm led to internal diffusion limitations.

In this paper an experimental investigation on structured catalysts for FTS using metallic supports of different geometries is reported. The investigated structures include aluminum foams, honeycomb monoliths with different cpsi and a microchannels reactor. The catalytic performance of the supported catalyst was assessed, in terms of both activity and selectivity comparing supports with the same catalytic load per volume unit. Catalytic tests with the catalyst in powder form were also carried out for comparison.

2. Experimental

2.1. Catalyst preparation

A powder catalyst containing 20 wt.% cobalt and 0.5 wt.% rhenium was prepared by one-step incipient wetness co-impregnation of γ-Al_2O_3 support (Spheralite SC505, Procatalyse) with an aqueous solution of cobalt nitrate hexahydrate and perrhenic acid. The support and aqueous metal solution were mixed under ambient temperature and pressure conditions. Before impregnation, the support (<60 μm) was calcined in a muffle at 773 K for 10 h with a heating rate of 1 K/min. After impregnation, the catalyst was dried at 393 K for 3 h and finally calcined at 623 K for 10 h at a heating rate of 2 K/min.

2.2. Structured catalyst supports

2.2.1. Supports pre-treatment and forming

Several types of structured supports were used: parallel channel monoliths, foams and a microchannels block. Homemade parallel channel monoliths consisting of 50 μm Fecralloy sheets (Goodfellow) corrugated using rollers producing different channel sizes were fabricated. Monoliths were made by rolling around a spindle alternate flat and corrugated sheets. DUOCEL aluminum foam from ERG Materials and Aerospace of 40 ppi was used (void fraction 0.927; geometric surface area 235 m^2/m^3). Foams were cut out from slabs using a hollow drill with a diamond saw border. Both monoliths and foams were cylindrical ($D = 16$ mm; $L = 30$ mm). The microchannels (depth: 700 μm; width: 700 μm; length: 20 mm; number of channels per plate: 10) were fabricated on Fecralloy (Goodfellow) by microdrilling. The machined plates were joined together placing metallic sheets (Fe79/B16/2 Goodfellow) between them and further were diffusion bonded. The final block was composed of 100 microchannels for reaction in 10 plates welded intercalated by 10 additional plates presenting 100 microchannels for cooling in cross flow arrangement. The geometric characteristics of the investigated structured supports are compiled in Table 1.

In order to improve the interaction between the washcoat layer and the metallic support, the surface of both monolith and foam was modified. The monoliths and micromonoliths were pretreated in air for 22 h at 1173 K to generate α-alumina whiskers (see Fig. 1A). Aluminum foams were pretreated by anodization in 1.6 M oxalic acid at 323 K, 40 min and 2A/foam for obtaining a rough alumina surface (see Fig. 1B) [11].

2.2.2. Preparation of the slurry

The washcoating method was used to cover the structured substrate with the slurries prepared from previously synthesized catalysts. Preparing stable slurries of the catalyst to be deposited is the first step to washcoat a metallic substrate. The catalyst was ball milled for 5 h to obtain small particles. The particle size ($d_{4,3}$) after ball milling was 3.4 μm. To obtain stable slurries of different solids, particle size distributions below 10 μm are recommended [12]. The catalyst content of the suspension was kept constant at 20 wt.% (beyond this value their viscosity increased significantly).