



Effect of the thermal conductivity and catalyst layer thickness on the Fischer-Tropsch synthesis selectivity using structured catalysts



David Merino, Oihane Sanz*, Mario Montes

Applied Chemistry Department, Chemistry Faculty of the University of the Basque Country (UPV/EHU), Donostia-San Sebastián, Spain

HIGHLIGHTS

- Catalyst layer thickness controls diffusion limitations and so selectivity.
- Corrugated metal monoliths allow good thermal control and high selectivity.
- High cell density monoliths compensate moderate substrate thermal conductivity.
- Aluminum monoliths favor Fischer-Tropsch Synthesis intensification.

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ABSTRACT

Metallic monoliths composed of flat and corrugated foils were prepared in-house using two different alloys (Fecralloy[®] and aluminum) and cell densities (280 and 2300 cps), and different loadings of a (20% Co–0.5% Re)/Al₂O₃ catalyst were deposited on their surface by washcoating, producing a wide range of average catalyst layer thicknesses. The obtained structured catalysts were tested in the Fischer-Tropsch synthesis, exhibiting increased selectivity for methane and decreased selectivity for C₅₊ fraction production with increasing average catalyst layer thickness. This effect was observed for all layer thicknesses in the case of aluminum monoliths with both cell densities and for Fecralloy[®] ones with a high cell density. Conversely, Fecralloy[®] monoliths with a low cell density exhibited a critical maximum catalyst layer thickness of ~50 μm, with diffusional and thermal limitations resulting in temperature and selectivity runaways at higher thicknesses. These results indicated the importance of high effective thermal conductivity of substrates for adequate temperature control in structured Fischer-Tropsch synthesis catalysts, which could be achieved by using highly conductive metallic monoliths (e.g., those made of aluminum) or increasing the cell density of less conductive alloys (e.g., Fecralloy[®]). Finally, the good thermal control observed for aluminum monoliths permitted to enhance the production of C₅₊ at higher temperatures without significantly increasing methane selectivity.

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1. Introduction

Fischer-Tropsch synthesis (FTS) is a well-known industrial process for transforming syngas into liquids hydrocarbons. Pressures of 20–40 bars are usually required in the case of Co-catalyzed FTS, favoring the formation of long-chain hydrocarbons. Other additional features normally associated with FTS are the low specific activity (TOF) of conventional cobalt catalysts (20–50 · 10⁻³ s⁻¹) and high reaction exothermicity ($\Delta H_R = -165 \text{ kJ} \cdot \text{mol}^{-1}$). The former implies that a high Co catalyst loading is needed to achieve the maximal catalyst volumetric density in the reactor for maximizing volumetric productivity. However, this approach is

hindered by the high reaction exothermicity. Consequently, reaction heat dissipation is required to control the process temperature and safety by avoiding hot spots and thermal runaways [1,2]. Furthermore, selectivity is markedly influenced by temperature, with high temperatures favoring the formation of methane and other light hydrocarbons [3]. Currently, extensive efforts are devoted to developing systems with higher heat exchange capabilities, e.g., by using metal additives in catalyst formulation [2] and employing highly thermally conductive catalyst supports such as SiC [4,5] or carbon nanofibers [6]. However, the heat exchange efficiency depends not only on the catalyst formulation but also on the type of reactor used.

Although fixed-bed reactors (FBRs) are traditionally used for FTS, still being employed in the Shell middle distillates plant in Bintulu [7], radial heat transfer in such reactors is fairly inefficient

* Corresponding author.

E-mail address: oihane.sanz@ehu.eus (O. Sanz).

[8]. Randomly packed beds are characterized by few contact points between particles and, importantly, between particles and reactor walls, resulting in insignificant heat transfer by thermal conduction and the dominance of the gas-phase convection pathway. High heat transfer coefficients imply high linear gas velocities, which reduces contact time and requires longer tubes, consequently increasing the pressure drop through the bed [9].

Another disadvantage of packed bed reactors is the necessity of using large catalyst particles to avoid a high pressure drop through the bed. This situation results in the apparition of diffusion limitations through catalyst pores, enhancing the formation of undesired products such as methane and light hydrocarbons [3,10] as a consequence of the long diffusion pathway of reactants and products through catalyst pores. One of the proposed solutions is the use of egg-shell catalysts, which reduces diffusion length but, concomitantly reduces the volumetric active density in the reactor [11].

Thus, heat transfer, pressure drop, and diffusion limitations are the main problems for conducting FTS in FBRs [12]. Other reactor designs have been employed to overcome these problems specific to packed bed reactors, such as the slurry bubble reactor (SBR) [13]. However, the ease of FBR operation and their high catalyst hold-up (~ 0.65) inspire scientists to continuously improve the multitubular FBR technology. Currently, the challenge is to enhance the mass and heat transfer properties of FBRs and thus increase volumetric reactor productivity, achieving an intensification of FTS in FBRs [12,14–16]. Excellent results have been obtained for microfibrillar entrapped catalysts, composed of small catalyst particles entrapped in sintered fiber structures of highly conductive materials such as stainless steel, nickel and copper [17,18]. The use of small catalyst particles avoids diffusion limitations, and the microfibrillar network provides a high heat exchange capability. However, the reduced void fraction of these structures may suppose, in practice, a significant pressure drop increase. Additionally, the catalyst holdup in these systems has to be low to ensure enough void volume through the bed.

Earlier, catalyst structuration using honeycomb monolithic catalysts was proposed, which can be viewed either as an FBR improvement or a new reactor type (monolithic reactor). The main advantage of monolithic reactors is the lower pressure drop attributed to their high void fraction or open frontal area (0.7–0.9) and their longitudinal channel configuration [19]. Furthermore, mass transfer coefficients higher than those of packed beds could be obtained at high gas flows and low catalyst layer thicknesses. At the beginning of the last decade, Hilmen et al. proposed FTS catalyst structuration over ceramic monoliths [20]. Although the ceramic nature of both the catalyst and the substrate resulted in easy deposition, the results were not as good as expected, since the insulating character of ceramic substrates hindered radial heat removal from the monolithic system and thus complicated temperature and selectivity control. However, liquid product recirculation was proposed as a solution, constituting the operation basis of monolithic loop reactors (MLRs) [21–23]. Although MLRs were demonstrated to represent an alternative to FBRs, in practice, the recirculating flow required to achieve good thermal conductivity is usually too high.

Recently, Hooshyar et al. [12] performed simulations to show that FBR productivity could be increased by more than 40% when the heat transfer coefficient was improved by a factor of 2.5 at the same conversion level. Our group previously studied FTS using different metallic substrates, concluding that thermal conductivity was positively correlated with selectivity control [24]. On the other hand, Tronconi et al. studied the possibility of increasing the heat transfer capacity of monolithic reactors by employing a metallic substrate instead of a ceramic one [9,25–29] and thus promoting thermal conduction through the solid matrix of the former substrate. Although gas-phase convection is the main mechanism of

heat removal in packed beds, monolithic catalysts with a metallic substrate enable both conduction and convection pathways. The use of metallic honeycomb monoliths with high thermal conductivity makes thermal conduction more effective than convection in randomly packed beds of particles. Consequently, the effective radial thermal conductivity in metallic substrates is usually an order of magnitude higher than that in randomly packed particle beds ($2\text{--}5\text{ W m}^{-1}\text{ K}^{-1}$). In contrast to monoliths composed of flat and corrugated foils, the extruded aluminum monoliths used by the above authors are difficult to manufacture with a high cell density [30]. This consideration is very important, since the catalyst layer thickness directly depends on the geometric surface area of the monolith, with structured substrates exhibiting low geometric surface areas entailing thick layers. For structured-catalyst-based FTS, catalyst layers thicker than $50\text{ }\mu\text{m}$ are known to suffer from diffusion limitations [20,23,31]. However, this implication has been established for structured catalysts with ceramic substrates, and then, with a limited heat exchange capability. These insulating substrates have demonstrated to be clearly unsuitable for FTS because of the high reaction heat of the process and the thermal gradients observed, and consequently making difficult the discrimination between the effects due to the diffusion in the porosity (associated to the thickness of the catalytic layer) and those due to the non isothermicity of the system.

This work investigates the catalytic behavior of an in-house-made monolithic FTS catalyst composed of flat and corrugated foils of two alloys with different thermal conductivities (Fecralloy[®] and aluminum). Metallic substrates were coated with a Co-Re/Al₂O₃ catalyst to obtain a wide range of catalyst loadings and layer thicknesses, and tested in FTS. The above catalysts were also characterized by N₂ physisorption, H₂ chemisorption, mercury porosimetry, X-ray diffraction (XRD), and an adherence test.

2. Materials and methods

2.1. Preparation of metallic substrates and structured catalysts

In-house-made metallic monoliths with parallel channels and cell densities of ~ 280 (R4-type) and ~ 2300 (R1-type) were prepared using Fecralloy[®] (Goodfellow[®]) and high-purity aluminum (>99 wt%, INASA). Foils of $50\text{-}\mu\text{m}$ thickness were used for Fecralloy[®] monoliths and 63- and $82\text{-}\mu\text{m}$ -thick foils were used for aluminum monoliths, with the increased foil thickness required to increase structural strength. Monoliths were prepared by rolling alternating flat and corrugated sheets into cylinders of 16-mm diameter and 30-mm length, achieving a total monolith volume of 6.03 cm^3 . The geometric parameters of different monoliths are summarized in Table 1. The hydraulic diameter (D_H) was calculated as four times the cross-sectional area (monolith section \times void fraction) divided by the wetted perimeter of the cross-section.

Prior to coating, Fecralloy[®] monoliths were thermally pretreated in air for 22 h at $900\text{ }^\circ\text{C}$, whereas aluminum ones were immersed into an alkaline medium (pH 10.5) for several minutes, dried, and calcined at $500\text{ }^\circ\text{C}$ for 2 h.

Catalyst deposition on metallic substrates was performed by washcoating with a Co-Re/Al₂O₃ slurry to obtain a coating of (20 wt% Co–0.5 wt% Re)/Al₂O₃ [24,32]. The nominal catalytic loading varied from 450 to 2000 mg per monolith, corresponding to average catalyst layer thicknesses (δ) of $5\text{--}90\text{ }\mu\text{m}$, depending on the cell density and the alloy. Later, the washcoated monoliths were calcined at $350\text{ }^\circ\text{C}$ for 6 h in air. Additionally, the catalytic slurry was dried and calcined under the same conditions as those used to prepare monolithic catalysts to obtain the slurried catalyst, which was representative of the solid layer coating the walls of the

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