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Fischer–Tropsch synthesis on monolithic catalysts of different materials

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Abstract

Monolithic structures made of cordierite, γ-Al_2O_3 and steel have been prepared as catalysts and tested for Fischer–Tropsch activity. The monoliths made of cordierite and steel were washcoated with a 20 wt.% Co–1 wt.% Re/γ-Al_2O_3 Fischer–Tropsch catalyst whereas the γ-Al_2O_3 monoliths were made by direct impregnation with an aqueous solution of the Co and Re salts resulting in a loading of 12 wt.% Co and 0.5 wt.% Re. The activity and selectivity of the different monoliths were compared with the corresponding powder catalysts.

Higher washcoat loadings resulted in decreased C_{5+} selectivity and olefin/paraffin ratios due to increased transport limitations. The impregnated γ-Al_2O_3 monoliths also showed similar C_{5+} selectivities as powder catalysts of small particle size (38–53 μm). Lower activities were observed with the steel monoliths probably due to experimental problems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Monolithic catalyst; Fischer–Tropsch synthesis; Co–Re/γ-Al_2O_3

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1. Introduction

The Fischer–Tropsch synthesis is a promising way of converting natural gas to liquid fuels. A key element in improved Fischer–Tropsch technology is the development of active catalysts with high wax selectivity. Supported cobalt is the preferred catalysts for the Fischer–Tropsch synthesis of long chain paraffins from natural gas due to their high activity and selectivity, low water-gas shift activity and a comparatively low price.

Fixed-bed and slurry reactors have been the reactors of choice for low temperature Fischer–Tropsch synthesis. The large support particles in fixed-bed reactors result in poor intraparticle mass transfer characteristics and the space–time yield is limited by heat transfer in the catalyst bed. The slurry system gives rise to significantly improved mass transfer characteristics within the catalyst particles, but the separation of the catalyst from the product can be troublesome. The backmixing also makes the slurry reactor less efficient in terms of reactor volume than the plug flow reactor.

Mass transfer effects are very important in Fischer–Tropsch synthesis [1]. Even though the reactants are in the gas phase, the pores of the catalyst are filled with liquid products. The diffusion rates in the liquid phase are typically three orders of magnitude slower than in the gas phase, and even slow reactions may

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be diffusion limited in the liquid phase. With increasing transport limitations, the selectivity to C_{5+} will go through a maximum. The C_{5+} selectivity will increase as a result of the longer olefin residence times resulting in increased readsorption and consequently decreased chain termination to olefins. On the other hand, increasing transport limitations will eventually result in CO depletion and enhanced hydrogenation reactions resulting in lower selectivities to C_{5+} [1]. A decrease in the olefin/paraffin ratio at a given conversion is therefore an indication of increased transport limitations.

In a fixed-bed reactor, the selectivity problem can be solved by using catalyst pellets where the catalytic material is deposited in a thin outer layer (egg-shell catalysts) [2]. However, this means that only a fraction of the catalyst present in the reactor is participating in the reaction. In a slurry reactor, the selectivity problem is solved by using small catalyst particles.

The present work deals with the use of different monolithic systems for carrying out the Fischer– Tropsch synthesis. In a monolithic reactor, a short diffusion distance can be maintained without having to reduce the fraction of active material since the catalyst is located in the thin walls of the monolithic structure. Other advantages offered by monolithic catalysts are the low pressure drop, the high gas–liquid mass transfer rates in two-phase flow, the possibility of using high liquid and gas throughputs and the good temperature control by direct cooling of the catalyst with a liquid medium and external heat removal. A monolithic reactor may therefore operate with a short diffusion distance and a low pressure drop at the same time. No wax–catalyst separation is necessary as it would be in the slurry reactor.

Reports on the use of monolithic reactors for carrying out the Fischer–Tropsch synthesis are very few. We have previously reported some results by using monolithic structures [3,4]. Recently, modelling of a monolithic reactor for the Fischer–Tropsch synthesis has shown promising results for this type of reactor compared to slurry reactors [5]. A kinetic study involving a Co–Pt/SiO_2/monolith Fischer–Tropsch catalyst has also appeared quite recently [6]. However, the application of monolithic reactors for other three-phase catalytic systems has been reported [7–10]. We have earlier reported the characterisation and deactivation studies of cobalt Fischer–Tropsch catalysts [11–13].

2. Experimental

Cobalt catalysts containing 12–20 wt.% Co, 0.5–1 wt.% Re on γ-Al_2O_3 were prepared by incipient wetness co-impregnation of the support with aqueous solutions of $Co(NO_3)_2\cdot 6H_2O$ and $HReO_4$. The catalysts were dried in air for 3 h at 393 K before calcination in air at 573 K for 16 h.

The monoliths used in this work were: cordierite (400 cells/in.^{2}) and γ-Al_2O_3 (based on Vista Catapal) (400 cells/in.^{2}) supplied by Corning and steel monoliths (i.e. steel sheets) from Emitec. The steel monoliths were prepared from corrugated and flat steel sheets from Emitec and both cylindrical and square-shaped steel monoliths were prepared. The cylindrical monoliths were prepared by attaching a corrugated and flat steel sheet to a wire and turning the wire until the desired diameter was obtained. The roll/twist was placed in a steel casing that was welded to keep the rolled sheets in a cylindrical shape. The square-shaped steel monoliths were prepared by alternately stacking corrugated and flat sheets into a square steel casing which was made cylindrical by thin Al-foils. All the ceramic monoliths were cut into cylindrical pieces with a diameter of 9 mm and a length of 100 mm. The method of washcoating/impregnation depends on the monolith.

A slurry containing the Co–Re/Al_2O_3 catalyst was grinded in a WC-ball mill for 1 h before dipcoating the cordierite substrates. After washcoating, the monoliths were dried in air at 393 K overnight. In some cases, the monoliths were dipped several times (dried at 393 K between dips) in order to increase the amount of catalyst on the monoliths. The steel monoliths were washcoated in the same way as the cordierite monoliths, but longer milling times of the catalyst slurry were also tested. The γ-Al_2O_3 monoliths were prepared by impregnating the monolithic support with aqueous solutions of $Co(NO_3)_2\cdot 6H_2O$ and $HReO_4$. Drying and calcination procedures were the same as for the powder catalysts described above. The nominal Co loading of the alumina monoliths were 12 wt.% Co and 0.5 wt.% Re. The thickness of the washcoat layer was calculated from the weight increase upon washcoating and the density of the layer.

The experiments were carried out in a conventional flow apparatus using a stainless steel reactor surrounded by an electrically heated aluminium jacket.

The powder catalyst was diluted with an inert material (SiC) in a 1:5 weight ratio in order to minimise temperature gradients. The monolithic catalysts were used as prepared. All catalysts were reduced in flowing hydrogen at 1 bar and 623 K for 16 h (1 K/min ramping from ambient to 623 K). After reduction, the catalysts were cooled to 443 K in flowing hydrogen before increasing the pressure to the desired value in a mixture of 50% He and 50% H_2, purging with He for 1 h and then switching to a feed mixture consisting of synthesis gas $H_2/CO = 2:1$ premixed with 3 mol% N_2 as an internal standard. The reaction temperature was then slowly increased to the desired temperature (usually 483 K). The space velocity was varied to give 30–50% CO conversion. The product gas was analysed for N_2, CO, CO_2, and C_{1+} hydrocarbons on a gas chromatograph (GC). The experimental data are averaged over a period of 10 h and are representative of stabilised catalysts, i.e. after about 90 h on stream.

3. Results and discussion

The performance of the powder catalyst (particle size 38–53 μm) is shown in Table 1. It has been shown previously that large particles (425–850 μm) produce unacceptably high selectivities of methane and light gas with a corresponding drop in the C_{5+} selectivity [3].

The performance of the washcoated cordierite compared to the powdered catalyst is also shown in Table 1. Calculation of the relative rate for formation of hydrocarbons shows that the washcoated cordierite substrate is as active as the conventional (powder) catalyst.

The monolithic catalyst in Table 1 also has similar CH_4 and C_{5+} selectivities as the conventional catalyst, but a slightly lower olefin to paraffin ratio for the cordierite-based catalyst indicates higher diffusion resistance than for the powder sample.

The effect of the washcoat layer thickness is shown in Figs. 1 and 2 where the selectivity is given as a function of the structural parameter χ defined by Iglesia et al. [1] as

$$\chi = R_0^2 \Phi \frac{\theta_m}{r_p} \tag{1}$$

The structural parameter χ contains the site density θ_m, the diffusion length R_0, the porosity Φ, and the mean pore diameter r_p.

Increasing the washcoat layer thickness on the cordierite substrate shows that the C_{5+} selectivity and the olefin/paraffin ratio decreases and the CH_4 selectivity increases, while the rate remains relatively unaffected. The CO_2 selectivity is usually somewhat higher than that for small particles. These differences are caused by intraparticle diffusion effects.

Metallic monoliths can be prepared with thinner channel walls and with improved thermal conductivity compared with the cordierite and the alumina structures. It was, therefore, of interest to prepare and test some steel monoliths. Table 2 shows the results for the square-shaped steel monoliths. The relative rate, the C_{5+} selectivity and the $C_3{=}/C_3{-}$ ratio for the steel monoliths were generally lower than that for the corresponding powder catalyst. The CO_2 selectivity was also higher than that for pure powder catalysts.

The steel monoliths are placed in a casing that becomes covered by catalyst powder during preparation. This casing is wrapped in an aluminium foil before it is placed in the reactor and the catalyst on the outside of the casing will, therefore, probably not participate in the reaction. A rough estimate of the amount of catalyst that is on the outside of the casing shows that this should be about 10% of the total amount of catalyst provided that the catalyst is evenly distributed.

Table 1
Comparisons between a conventional powder Co–Re/Al_2O_3 catalyst and the corresponding monolithic (cordierite) catalyst (temperature: 483 K, pressure: 20 bar; $H_2/CO = 2:1$)

Catalyst	Relative rate (HC)[a]	CH_4 selectivity	C_2–C_4 selectivity	C_{5+} selectivity	$C_3{=}/C_3{-}$ selectivity	CO_2 selectivity
Powder catalyst (38–53 μm)	1.00	8.3	9.3	82.3	2.4	0.2
Washcoated cordierite[b]	0.92	8.9	8.7	82.5	1.9	0.3

[a] Rate (g_{HC}/g_{cat} h) relative to the rate for powder catalyst (38–53 μm).
[b] Approximate washcoat thickness is 0.04 mm.

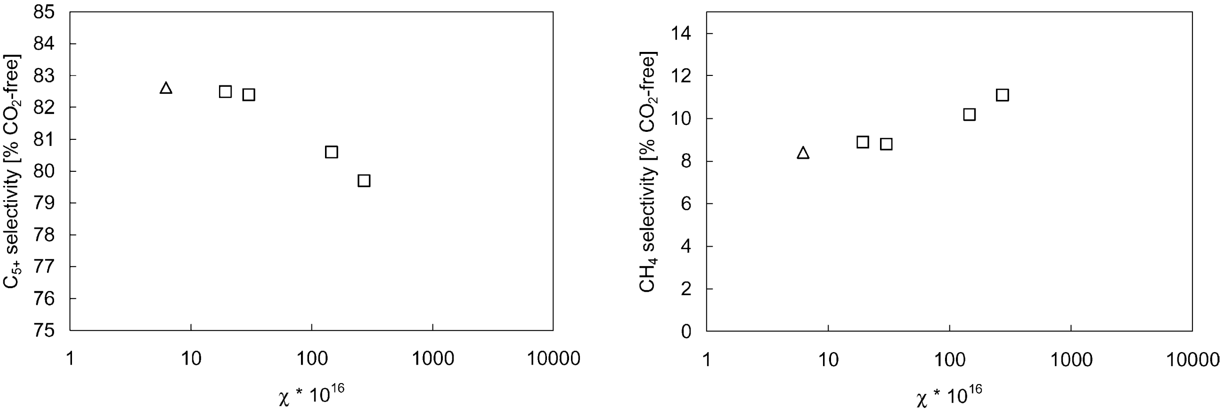

Fig. 1. The C_{5+} selectivity and CH_4 selectivity as a function of the structural parameter χ [1]. χ for the monoliths was calculated using the average washcoat layer thickness as the diffusion distance: (△) powder catalyst (38–53 μm); (☐) washcoated cordierite monoliths (20 bar, 483 K, $H_2/CO = 2{:}1$).

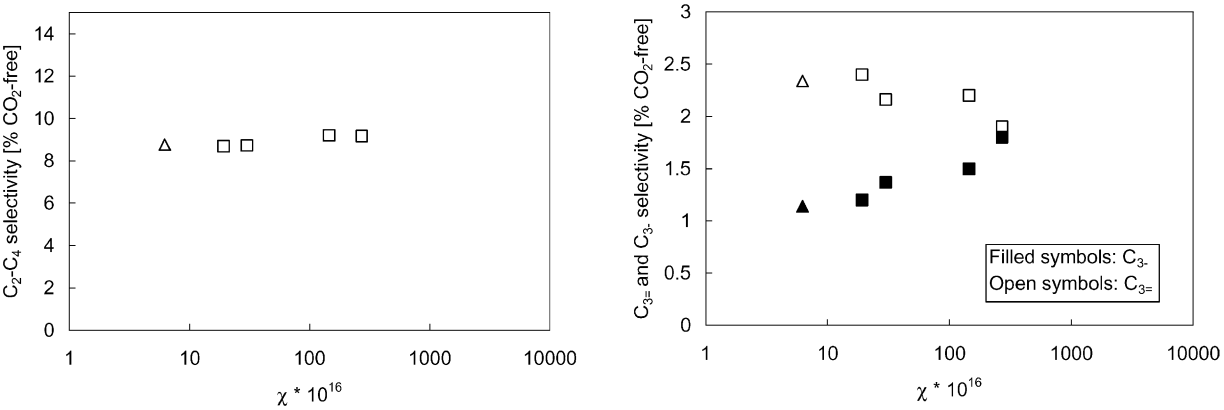

Fig. 2. C_2–C_4 selectivity and C_3 olefin and paraffin selectivity as a function of the structural parameter χ [1]. χ for the monoliths was calculated using the average washcoat layer thickness as the diffusion distance: (△) powder catalyst (38–53 μm); (☐) washcoated cordierite monoliths (20 bar, 483 K, $H_2/CO = 2{:}1$).

Table 2

Comparison between conventional powder Co–Re/Al_2O_3 catalyst and the corresponding washcoated square-shaped steel monoliths ($H_2/CO = 2{:}1$, temperature: 483 K, pressure: 20 bar)

	Approximate diffusion distance (μm)	Relative rate (HC)[a]	CH_4 selectivity	C_2–C_4 selectivity	C_{5+} selectivity	$C_{3=}/C_{3-}$ ratio	$C_{3=}$	C_{3-}
Powder	23	1.00	8.3	9.3	82.3	2.4	2.7	1.1
Steel	52	0.65	10.4	9.5	80.1	1.3	2.2	1.7
Steel	83	0.66	11.0	9.9	79.0	1.3	2.2	1.8

[a] Rate (g_{HC}/g_{cat} h) relative to the rate of powder catalyst (38–53 μm).

Table 3
Selectivity and relative rate of a 12 wt.% Co–0.5 wt.% Re powder catalyst and a 12 wt.% Co–0.5 wt.% Re on γ-Al_2O_3 monolith (pressure: 20 bar; feed: $H_2/CO = 2:1$)

Catalyst	T (K)	Relative rate[a]	CH_4 selectivity	C_{5+} selectivity	C_3=/C_3– ratio	CO_2 selectivity
Powder catalyst (75–90 μm)	483	1.00	8.7	82.3	2.2	0.2
Alumina monolith	479	0.49	8.6	83.2	2.4	0.4

[a] Rate (g_{HC}/g_{cat} h) relative to the rate for the 12 wt.% Co–0.5 wt.% Re powder catalyst (75–90 μm).

However, this is not enough to explain the lower activity observed for the steel monoliths. The calculated approximate washcoat layer thickness for these catalysts were in the same range as for the cordierite monoliths (0.05–0.08 mm), but the washcoat was not as evenly distributed over the steel monolith surface. The steel monoliths are difficult to make at the small diameters used in this study also making the structure inside the monolith uneven. The catalysts should therefore be tested with a larger diameter to eliminate/reduce the influence of irregularities and the casing.

The γ-Al_2O_3 monoliths were provided by Corning as test samples and were not commercially available. The cell density was similar to the cordierite monoliths, but the wall thickness was slightly larger. The alumina monoliths were extremely fragile and the internal cracks made it difficult to cut 10 mm × 100 mm cylinders. Another problem was that the channels were not straight. The lower loading was chosen in order to reduce the risk of temperature runaway.

The impregnated γ-alumina monolith (Table 3) shows a C_{5+} selectivity similar to the selectivity of a powder catalyst with the same nominal Co loading (Table 3). However, the relative rate is only half of the rate of the standard 12 wt.% Co–0.5 wt.% Re powder catalyst. The temperature rise through the monolith was larger for the alumina monolith than normally measured and the mean temperature through the bed was, therefore, somewhat lower than for the other experiments (479 vs. 483 K). The temperature difference can explain some of the difference but not all. A possible explanation may be that the Co dispersion is lower on the alumina monolith.

The results indicate that the monolithic catalysts could be an interesting alternative to conventional powder catalyst for Fischer–Tropsch synthesis. The monolithic structures are presently being tested with oil circulation in order to remove produced heat.

4. Conclusions

Cordierite monoliths have been found to be as active and selective to C_{5+} as comparable powder catalysts of small particle size when loaded with relatively low amounts of catalyst, approximate washcoat layer thickness of 0.04–0.05 mm. Increasing washcoat layer thickness resulted in increased mass transfer restrictions and therefore in decreased C_{5+} selectivity.

Steel monoliths were found to have lower activity and C_{5+} selectivity than powders and cordierite monoliths. Some of the lower activity can be explained by inaccessible catalyst on the monolith casing. It is also believed that there are increased mass transfer limitations for these catalysts due to uneven monolith structure. These problems will probably be solved by using larger monolith diameters.

Alumina monoliths were found to give comparable selectivities to powder catalysts but somewhat lower activity. These catalysts also have a high catalyst loading per reactor volume compared to washcoated monoliths. The main problem with these catalysts at present is that they are fragile and have imperfect channel structure. In addition, testing of these catalysts at gas-phase conditions is difficult due to temperature runaway problems.

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