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PREPARATION, EVALUATION AND CHARACTERIZATION OF MONOLITHIC CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

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Abstract:

Square channel cordierite monolithic catalysts for Fischer-Tropsch synthesis (FTS) have been prepared and evaluated. Two different methods to apply the washcoat layer were used; washcoating the available Co-Ru/γ-Al_2O_3 catalyst and the second method involving washcoating of γ-Al_2O_3 followed by the impregnation of the active phase and promoter. The catalysts have been evaluated in a laboratory reactor and have been characterized using XRF, XRD, TPR, SEM, BET surface area and adhesion measurements. The effect of changing the promoter was studied and Re showed a better performance than Ru. The activity and selectivity of the monolithic catalysts were compared with the corresponding powder catalysts. The monolithic catalysts prepared with the second washcoating method were further examined with reaction conditions have been tested in a temperature range of 210–250 °C and in different feed flow rates (20-50 ml/min) with synthesis gas compositions consisting of H_2/CO ratio of 1 to 3. The effect of these processing conditions on the activity, selectivity and chain growth probability of monolithic catalysts for FTS were investigated.

Keywords: *Monolithic catalyst; Fischer–Tropsch synthesis; Promoter; Selectivity*

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1. Introduction

Fischer–Tropsch synthesis (FTS) is a process to convert synthesis gas (2:1 mixture of H_2 and CO) to water and hydrocarbons that can be used as liquid fuels or base chemicals. Feedstocks for the generation of synthesis gas can be natural gas, coal and biomass. FTS is an old and established process, but in the last decade, the research interest is growing due to an ever increasing demand on converting natural gas from remote sources to liquid fuels and to utilize associated gas from the oil rigs [1].

A key element in the improved Fischer–Tropsch technology is the development of active catalysts with high wax selectivity. Supported cobalt is the preferred catalyst for the Fischer–Tropsch synthesis of long chain paraffins from natural gas due to its high activity and selectivity, low water-gas shift activity and a comparatively low price [2].

In Fischer–Tropsch synthesis a simplified reaction model comprises of the adsorption of CO, the formation of a surface intermediate monomer by reaction with hydrogen, and a chain growth of surface intermediates with this monomeric species. Termination can proceed either by hydrogenation of the surface species yielding an n-alkane or by a reductive abstraction to a 1-alkene. A polymeric growth process can describe the product distribution. In Fischer–Tropsch synthesis the chain growth parameter indicates the chance that a surface intermediate grows further [3]. The selectivity of the process is usually described by the Anderson–Schulz–Flory (ASF) distribution and the characteristic chain growth probability, α. The chain growth probability is determined by both catalyst properties and process conditions. Through readsorption the alkenes can either be hydrogenated at the catalyst or be

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reinserted in the chain growth process. Diffusion limitations inside catalyst particles can strongly affect the final product distribution. Both secondary reactions and diffusion limitations may give rise to deviations from the ASF distribution [3].

Mass transfer effects are very important in Fischer–Tropsch synthesis [4]. 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 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 selectivity to C_{5+} [4]. A decrease in the olefin/paraffin ratio at a given conversion is therefore an indication of increased transport limitations.

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–heat transfer in the catalyst bed limits time yield. 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 [5]. The back-mixing also makes the slurry reactor less efficient in terms of reactor volume than the plug flow reactor.

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) [6]. However, this means that only a fraction of the catalyst present in the reactor is participating in the reaction. In a slurry reactor, using small catalyst particles solves the selectivity problem.

Recently, the use of a monolith loop catalytic membrane reactor for the Fischer–Tropsch synthesis has also been investigated [7]. Microchannel technology has also been proposed and tested for the Fischer–Tropsch synthesis [8]. Modeling of a monolithic reactor for the Fischer–Tropsch synthesis has shown promising results for this type of reactor compared with slurry reactors [9].

Monoliths are ceramic structures with small parallel channels (0.5–2mm internal diameter) separated by thin walls (60–300μm) [10] consisting of cordierite or high surface area catalyst support material such as alumina or silica. Cordierite monoliths can be washcoated with thin layers of catalyst support. Application of the active phase on the monoliths can be done by several methods [11]. Hence, the characteristic diffusion length of the catalyst layer can be tuned by catalyst hold up and cell density.

The present work deals with the use of 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. 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. The main emphasis has been on demonstrating the concept in the laboratory scale. The same experimental set-up as used for studying powder catalysts has been used.

2. Methods and Materials

2.1 Catalyst preparation

The monoliths used in this work were extruded cordierite with a square-channeled shape (400 cells/in.^{2}). All the ceramic monoliths were cut into pieces with a wide of 1cm, length of 1 cm and a height of 4 cm. Two methods were used for preparation of monolithic catalysts as follow:

1. First method: Cobalt catalysts containing 15 wt.% Co, 1 wt.% Ru 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 ruthenium nitrozil nitrate .The catalysts were dried in air for 12 hours at 393 K before calcinations in air at 673 K for 4 hours. The slurry for washcoating was prepared by grinding the Co/Ru-Al_2O_3 catalyst together with water in a ball mill. The washcoat was applied by slowly lowering the monolith in the slurry. 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. Then the excess slurry was blown out of channels with pressurized air. The monolith was dried at 393 K for 12 hours while it was rotated horizontally [12] followed by calcining at 723 K for 4 hours.

2. Second method: at first, the alumina washcoat was prepared using the slurry coating method. Aqueous slurry of 8 grams of γ-Al_2O_3, 2.7 grams of pseudo-bohemite (AlOOH) and 20 ml deionized water were prepared. The slurry was stirred well and its pH was controlled at 3.5 by a pH controller.

The alumina washcoat was applied by slowly lowering the monolith in the slurry. Then the excess slurry was blown out of channels with pressurized air. The monolith was dried at 393 K for 12 hours while it was rotated horizontally and it was calcined at 723 K for 4 hours [13].

The active phase was applied by wet impregnation from a solution of cobalt nitrate and promoter (e.g. perhinic acid $HReO_4$) in water with concentration determined by the weight of washcoated alumina. Then the excess solution was blown out of channels with pressurized air. The monolith was dried and calcined as described previously. Five monolithic catalysts were prepared as described in Table 1.

Table 1. Prepared monolithic catalysts

Catalyst name	Method of preparation	Promoter	%wt of washcoat	%wt Co on Al_20_3
C1	First method	Ru	15	15
C2	First method	Ru	33	15
C3	Second method	Re	17	18
C4	Second method	Re	30	33
C5	Second method	Ru	28	33

2.2 Characterization of catalysts

XRD and TPR tests were recorded for prepared catalysts. The results of XRD tests indicate peaks at 46.1 and 66.5º corresponding to γ-alumina and the other peaks were related to the different crystal planes of Co_3O_4. The size of cobalt clusters in catalyst C3 was larger than catalyst C1.

Figure 1 present the TPR profiles for powder catalyst with and without promoter, as well as C1 and C3 monolithic catalysts. The first peak in the profiles is typically assigned to reduction of Co_3O_4 to CoO, although a fraction of the peak likely comprises the reduction of the larger, bulk-like CoO species to Coº. The second peak is mainly assigned to reduction of CoO to COº. It also includes the reduction of cobalt species that interact with the support; which extends the TPR spectra to higher temperatures. With addition of Ru and Re to the Co/Al_2O_3 powder catalysts (Figure 1-b and 1-c) the high temperature peak shifts to lower temperatures and also causes its tail to get shorter. It seems that washcoating the powdered catalysts on the monolithic substrates (Figure 1-d and 1-e), have no effect on the TPR profiles of catalysts. Catalyst C3 indicated a larger shift in the high temperature peak.

The BET surface of the catalysts was 140 m^2/g. SEM analysis revealed flat washcoat layers on the cordierite monolith channels with rounded corners where the layer is thicker (Figure 2). The calculated layer thicknesses on the various monoliths were in the range of 40 to 55 µm.

The adhesion tests of washcoated catalysts in ultrasonic bath showed that the weight loss of catalysts that were prepared with second method (0.3 wt% for C3) was lower than those prepared with the first method (2.5 wt% for C2). Better adhesion in second method maybe due to the use of bohemite as binder in the slurry of alumina.

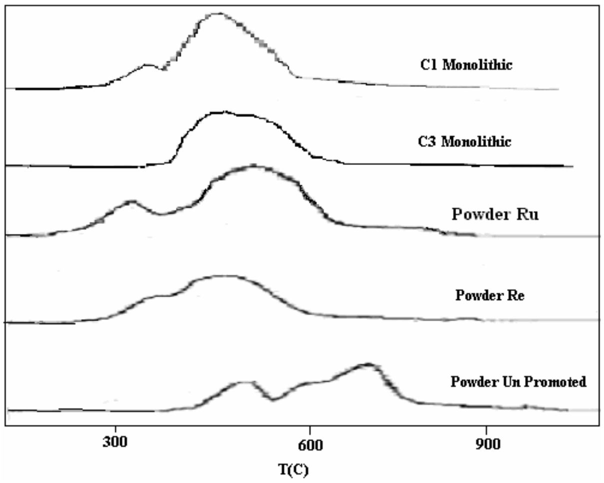

Figure 1. TPR profiles for a) powder catalyst, b) powder catalyst with Re promoter, c) powder catalyst with Ru promoter, d) C1 and e) C3.

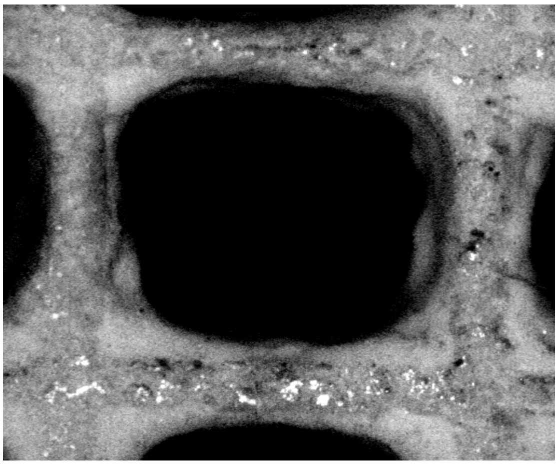

Figure 2. SEM of washcoated monolith

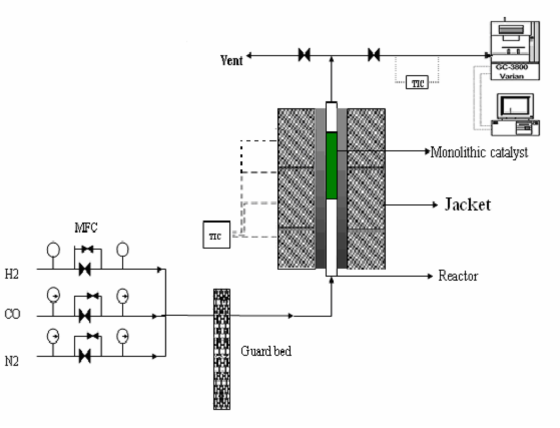

Figure 3. Schematic of reactor set up

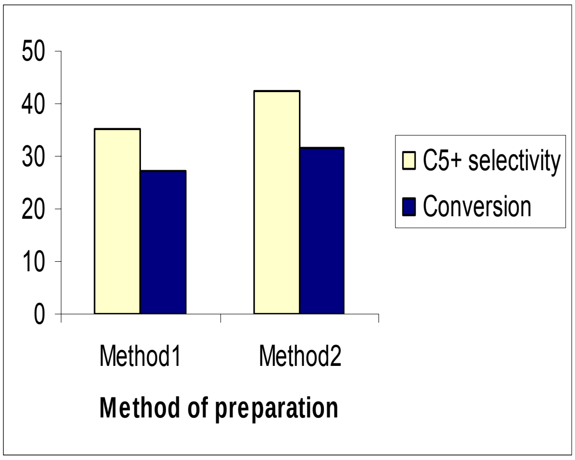

Figure 4. CO conversion and C_{5+} selectivity for different methods of preparation. (T=220ºC, GHSV=30 ml/min, pressure=1 bar; H_2/CO=2:1)

2.3 Reactor tests

Catalytic reaction runs were conducted in a dedicated set-up for Fischer–Tropsch synthesis shown in Figure 3. All catalysts were reduced in flowing hydrogen at 1 bar and 673 K for 14 hours (1 K/min ramping from ambient to 673 K). After reduction, the catalysts were cooled to 493 K (reaction temperature).

The experiments were carried out at atmospheric pressure, temperatures in the range of 210 to 250ºC, GHSV= 20 to 50 ml/min and H_2/CO = 1, 2, 3. The products were analyzed using an on-line HP 5890 GC equipped with TCD and FID detectors.

3. Results and Discussion

The effect of the preparation method on Co conversion and C_{5+} selectivity are shown in Figure 4. The second method of preparation (catalyst C3) shows better result for Co conversion, C_{5+} selectivity and chain growth probability. Figure 5 show the reactor test results for all catalysts. In the second method a previously available catalyst that had already been calcined was washcoated on monolithic substrate and was calcined again with substrate. It seems that in the second calcinations some of the catalytic active phases were sintered.

The effect of increasing washcoat weight or washcoat thickness is illustrated in Figure 6. This increase causes the conversion and C_{5+} selectivity to increase. Increasing the washcoat beyond a certain thickness would result in increased mass transfer restrictions and hence a decreased C_{5+} selectivity [2, 3].

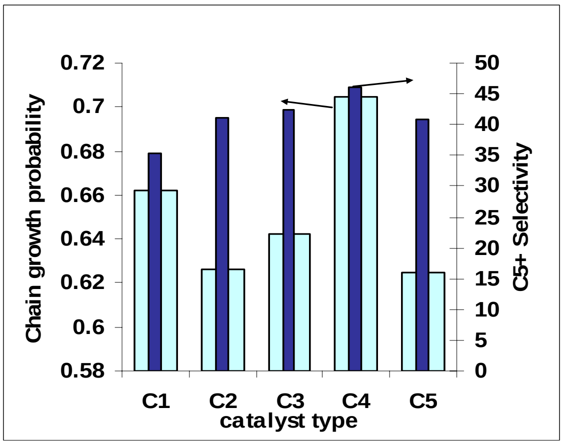

Figure 5. The chain growth probability and C_{5+} selectivity for different catalysts. (T=220ºC, GHSV=30 ml/min, pressure=1 bar; H_2/CO=2:1)

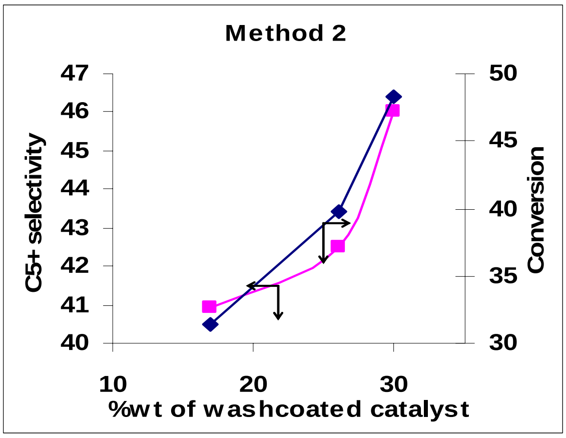

Figure 6. The C_{5+} selectivity and conversion as a function of weight percent of washcoat for second method of preparation. (T=220ºC, GHSV=30 ml/min, pressure=1 bar; H_2/CO=2:1)

Table 2 shows the results of reactor tests for catalyst C4 and C5, the difference between these two catalysts is in their promoters. The TPR profiles showed that catalyst C3, which have Re promoter, causes a more significant shift in the high temperature peak, thus Re as promoter would cause better reduction and higher catalyst activity in comparison with Ru as promoter.

The performance of washcoated cordierite compared with the powdered catalyst is presented in Table 3. Calculation of the relative rate of hydrocarbon formation shows that the washcoated cordierite substrate is as active as the conventional catalyst.

Table 2. Comparison between promoters Ru and Re (temperature=493 K, pressure=1 bar, H_2/CO=2:1)

Catalyst type	C_1 selectivity (%)	$C_{2\text{-}4}$ selectivity (%)	C_{5+} selectivity (%)	CO conversion (%)	α^a
C4-Re	12.1	26.762	46.013	48.25	0.7094
C5-Ru	9.23	24.112	40.306	39.7	0.7026

[a] *Chain growth probability*

Table 3. Comparison between a conventional powder Co–Re/Al_2O_3 catalyst and the corresponding monolithic (cordierite) catalyst (temperature=493 K, pressure=1 bar, H_2/CO=2:1)

Catalyst	C_1 selectivity	C_2-C_4 selectivity	C_{5+} selectivity	CO conversion %	relative rate^a	α
Powder	33	34.5	34	23	1	0.684
MonolithC1	31.9	27.7	35.27	27.4	0.92	0.662

[a] *Rate (g HC/g cat h) relative to the rate for powder catalyst*

Table 4. Selectivity and conversion in different H_2/CO ratios (T=493 K, GHSV=30 ml/min, Pressure=1 bar, catalyst C5)

H_2/CO	C_1 selectivity	C_2-C_4 selectivity	C_{5+} selectivity	CO conversion (%)	α
1	8.71	20.55	46.621	18.31	0.7275
2	9.23	24.112	40.306	39.7	0.703
3	10.215	26.98	28.741	49.84	0.6197

The effects of changing temperature, feed flow rate and H_2 to CO ratio on conversion, selectivity, olefin to paraffin ratio and chain growth probability were examined for catalyst C5. With increasing temperature, the rate of production, methane selectivity and C_2-C_4 selectivity would increase while C_{5+} selectivity and chain growth probability would decrease (Figure 7). Temperature increase would cause an increase in the concentration of hydrogen on the surface of catalyst due to an increase in hydrogen mobility, thus enhancing the rate of termination reactions leading to a decrease in the selectivity for heavier products (Figure 8).

With increasing GHSV, methane selectivity and C_2-C_4 selectivity would increase and conversion, C_{5+} selectivity and chain growth probability would decrease. Increasing GHSV causes reduction in retention time and production of light component. It is obvious that increasing of GHSV causes faster deactivation of the catalyst (Figure 9).

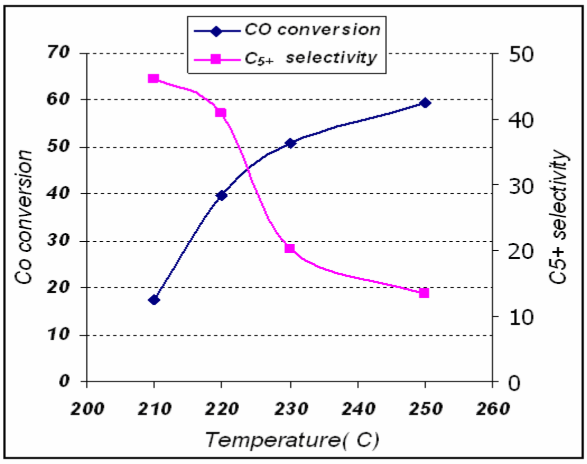

Figure 7. CO conversion and C5+ selectivity as a function of temperature (GHSV=30 ml/min, pressure=1 bar; H_2/CO=2:1 catalyst C5)

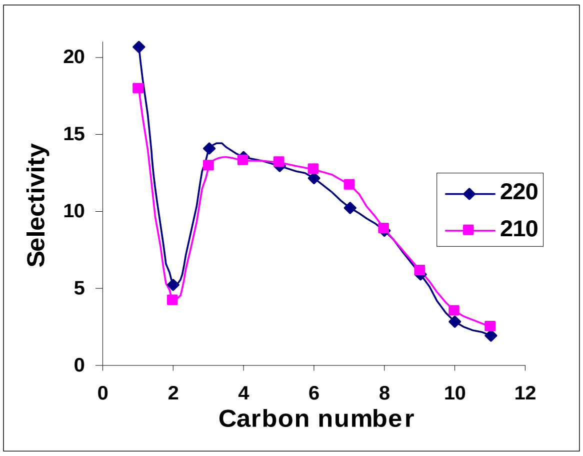

Figure 8. The selectivity as a function of temperature (GHSV=30 ml/min, pressure=1 bar; H_2/CO=2:1, catalyst C5)

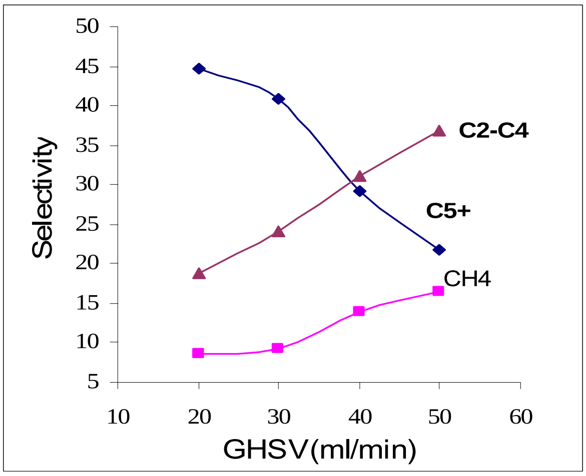

Figure 9. The effect of increasing GHSV on products selectivity (T=220ºC, pressure=1 bar H_2/CO=2:1, catalyst C5)

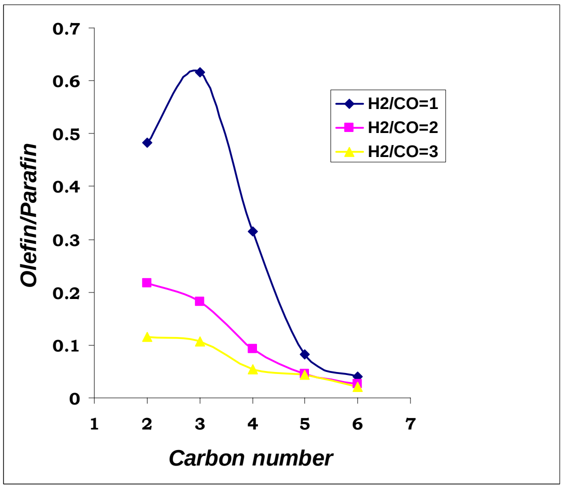

Figure 10. Olefin/Paraffin ratio as a function of H_2/CO ratio (T=220ºC, pressure=1 bar; GHSV=30 ml/min, catalyst C5)

With increasing H_2/CO ratio, conversion, methane selectivity and C_2-C_4 selectivity would increase and C_{5+} selectivity and chain growth probability would decrease (Table 4). Since the syngas molar flow is kept constant in these experiments the CO flow rate decreases with increasing H_2/CO ratio.

The increasing feed H_2/CO ratio increases hydrogen concentration at the surface of catalyst and together with a decrease in CO surface concentration would enhance termination reactions leading to a decrease in selectivity of heavier products. The decreasing feed H_2/CO ratio increases the olefin to paraffin ratio (O/P) ratio considerably as depicted for the washcoat monolith at 220 ºC (Figure 10). The hydrogen concentration appears as a strong factor determining the O/P ratio. By introducing more hydrogen, the paraffin formation is strongly increased at the expense of the olefins in hydrogenation reactions.

4. Conclusion

The experimental results for monolithic catalysts show that coating the alumina and cobalt in separate steps would result in better catalyst performance. Washcoating the powdered catalysts on the monolithic substrates, had no important effect on the TPR profiles of catalysts. Re as promoter caused better reduction and more activity in catalysts in comparison with Ru as promoter. The study shows the feasibility of using monolithic catalysts in Fischer–Tropsch synthesis and indicates that monolithic catalysts may provide an alternative for existing FTS reactors. The effects of various process conditions including temperature, GHSV and feed composition were also examined on a selected monolithic catalyst.

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