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Fischer–Tropsch synthesis in milli-fixed bed reactor: Comparison with centimetric fixed bed and slurry stirred tank reactors

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ABSTRACT

This paper presents a comparative study of Fischer–Tropsch synthesis in single channel milli-fixed bed, conventional centimetric fixed bed and slurry stirred tank reactors. In the three reactors, the catalytic measurements were carried out with the same conventional platinum-promoted alumina supported cobalt catalyst at 493 K and 20 bar using a stoichiometric syngas ratio ($H_2/CO = 2$). The single channel milli-fixed bed reactor displays a higher initial Fischer–Tropsch reaction rate than the conventional centimetric fixed bed reactor. This effect was assigned to a better temperature control and less significant catalyst deactivation during the startup of the single channel milli-fixed bed reactor. The slurry stirred tank reactor shows much lower hydrocarbon productivity than the milli- and centimetric fixed bed reactors, which is probably due to incomplete catalyst reduction. A considerable catalyst deactivation due to the uncontrolled temperature hike can occur during the reactor startup in the conventional centimetric fixed bed reactor. The slurry stirred tank and milli-fixed bed reactors show similar apparent deactivation behavior.

1. Introduction

Indirect conversion of natural syngas into hydrocarbons via Gas-to-Liquids (GTL) technology and Fischer–Tropsch synthesis (FT) is currently one of the most promising and environmentally effective solutions to the problem of finding suitable substitutes for liquid clean fuels. Multi-tubular fixed bed and slurry bubble column reactors have been currently used on industrial scale in South Africa, Malaysia and Qatar for this highly exothermic reaction [1–8]. Both fixed bed and slurry reactor technologies present several serious drawbacks. Wax-catalyst separation, highly demanding scaling-up, catalyst deactivation and attrition are the major barriers inherent to the use of slurry bubble column reactor. The fixed-bed multi-tubular reactor suffers from higher cost, insufficient heat removal, diffusion limitations and pressure drop. A conventional fixed bed reactor with internal tube diameter of several centimeters filled with catalyst pellets exhibits significant axial and radial temperature gradients which may lead to higher production of methane, lower selectivity to long chain hydrocarbons and a shorter catalyst life.

Due to several disadvantages of both reactor systems, new concepts are presently investigated. For intensification of mass transfer properties of multiphase reactors, alternative catalyst geometries like honeycombs, monoliths, structured packings or foams have been proposed [9–13]. In the micro-structured reactor the catalyst can be loaded by coating the reactor walls or by placing small catalyst powder in the micro-fixed bed. It has been shown that coated micro-reactors allow reducing the pressure drop and improving the heat transfer. Holmen et al. [14] previously found that the reactors wash-coated with FT catalysts could have catalytic performance similar to that observed with powdered catalysts. The reactors with layer thicker than about 50 μm suffer however, from diffusion limitations, accompanied by the expected decrease in the apparent activation energy [9,14,15]. The conventional proven FT catalysts cannot be used directly in coated micro-reactors. The mechanical and chemical resistance of catalyst coatings at a wide range of temperatures and in the presence of reagents and reaction products could be a challenge because of the difference in thermal expansion coefficients and catalyst stability. In addition, the catalyst inventory, i.e. ratio of catalyst to reactor volume, in the coated micro-reactor is often insufficient to attain satisfactory hydrocarbon productivity. Thus, to become commercially attractive, the ratio of catalyst and reactor volume in coated micro-reactors and hydrocarbon productivity should be significantly increased [16].

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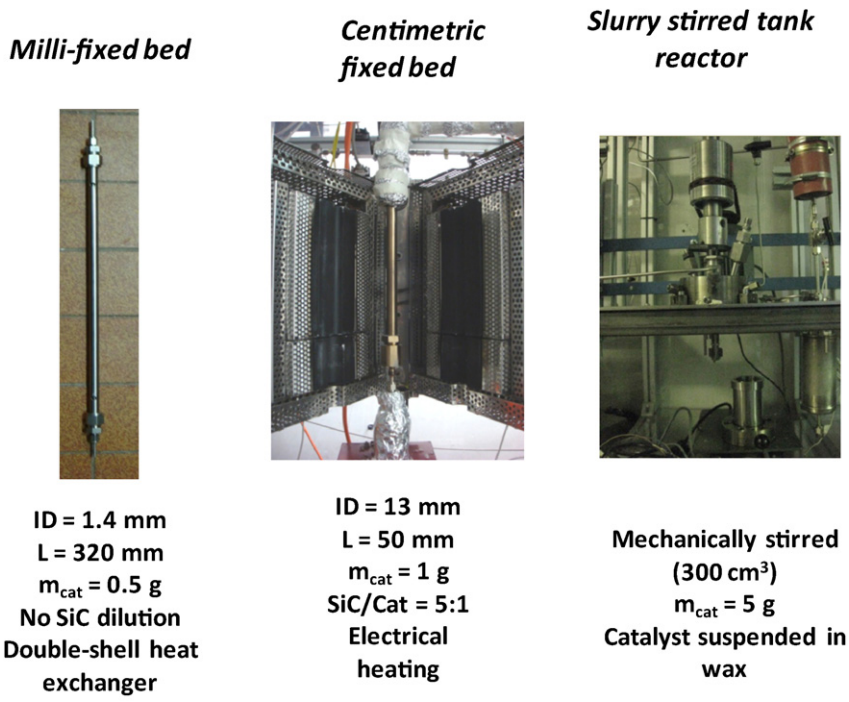

Fig. 1. Principal characteristics of laboratory reactors for FT synthesis.

The micro-fixed bed reactor has a number of advantages relative to the coated micro-reactors, such as higher catalyst inventory, use of proven efficient Fischer–Tropsch catalysts, easier reactor loading and possible catalyst replacement [17]. Note that the coated micro-reactors require specifically designed catalysts. The catalyst deposition on reactor wall can be challenging. On the other hand, micro-fixed bed reactors can show a significant pressure drop especially at higher flow rates and less efficient heat removal than coated micro-reactors. The capability of micro-structured packed bed reactor to operate with a highly active cobalt catalyst under severe conditions has been recently demonstrated by Myrsrad et al. [18]. Encouraging results with micro- and milli-structured fixed bed reactors on the scale of both laboratory and pilot FT units have been repeatedly reported by Velocys, Inc. [19].

Although the enhancement of heat transfer has been usually reported for the reactors with inner diameter smaller than 1 mm, several examples suggest that a sufficient degree of process intensification can be obtained with reactors of characteristic length of a few millimeters. The advantages of a milli-fixed bed reactor relative to micro-fixed bed counterparts are related to a lower pressure drop because of using larger catalyst pellets, simpler design and easier catalyst loading/discharging. Knochen et al. [20] showed that efficient heat removal in FT synthesis is possible even with reactor channel width of 3 mm and the pressure drop can be acceptable with particle sizes of 100 μm. The present work focuses on the particularities of FT synthesis in a single channel milli-fixed bed reactor. An attempt has been made to get new insights into the possible advantages of milli-fixed bed reactors relative to more conventional centimetric fixed bed and slurry stirred tank reactors.

2. Experimental

Carbon monoxide hydrogenation was carried out in three different stainless steel reactors (Fig. 1): a tubular milli-fixed bed reactor (ID = 1.4 mm, L = 320 mm), a centimetric tubular fixed bed reactor (ID = 13 mm, L = 400 mm) and a slurry stirred tank reactor (300 cm^3, radial impeller) [21] under identical operating conditions. The same laboratory-made Co(25%)Pt(0.1%)/Al_2O_3 catalyst was used in milli-fixed bed, centimetric fixed bed and slurry phase reactors. The catalyst was synthesized via incipient wetness co-impregnation; its preparation and characterization details are available elsewhere [22]. To minimize formation of heat spots the catalyst was diluted with SiC (5:1) in the centimetric fixed bed reactor, whereas non diluted catalyst was used in the milli-fixed bed and slurry stirred tank reactors. The validity of chemical regime was checked in all the reactors.

The isothermal regime in milli-fixed bed and centimetric fixed bed reactors was verified using the Mears criterion for neglecting radial temperature gradient [23,24]. When this criterion is fulfilled, the radial temperature profile is assumed to be flat, while the presence of heat spots along the bed cannot be excluded:

$$(1-\varepsilon) r_P \left|\Delta H_R\right| \frac{T_A d_t^2}{4\lambda_{er}^{sf} T_p^2} \left(1 + \frac{8\lambda_{er}^{sf}}{U d_t}\right) < 0,4$$

Calculation for centimetric fixed bed reactor with (5:1) catalyst dilution with SiC gives the Mears criteria of 2.0 assuming 60% carbon monoxide conversion, 60 N cm^3/min carbon monoxide flow rate and using the following parameters [23]: rate of reaction r_p = 3.4 mol s^{-1} $m^{-3}{}_{cat}$ (with catalyst dilution), void fraction of the catalyst ε = 0.4, reaction enthalpy ΔH_R = −165 kJ mol^{-1}, adiabatic temperature T_a = 14,400 K, tube diameter d_t = 0.0125 m, global heat exchange coefficient U = 400 W m^{-2} K^{-1}, effective radial thermal conductivity $\lambda^{sf}{}_{er}$ = 1 W m^{-1} K^{-1} and reactor wall temperature T_p = 493 K. The analogous estimation for the single channel milli-fixed bed reactor (d_t = 0.0014 m, same thermal parameters) yields the Mears criteria of 1.43 (with r_p = 17.7 mol s^{-1} $m^{-3}{}_{cat}$). Calculations suggest the presence of radial temperature gradient of about 0.5 K in both reactors.

The FT operating temperature and pressure in all the three reactors were respectively 493 K and 20 bar. The catalyst loading was 0.5 g and 1.0 g in the milli- and centimetric fixed reactors and 5.0 g in the slurry stirred tank reactor. Before the reaction the catalyst

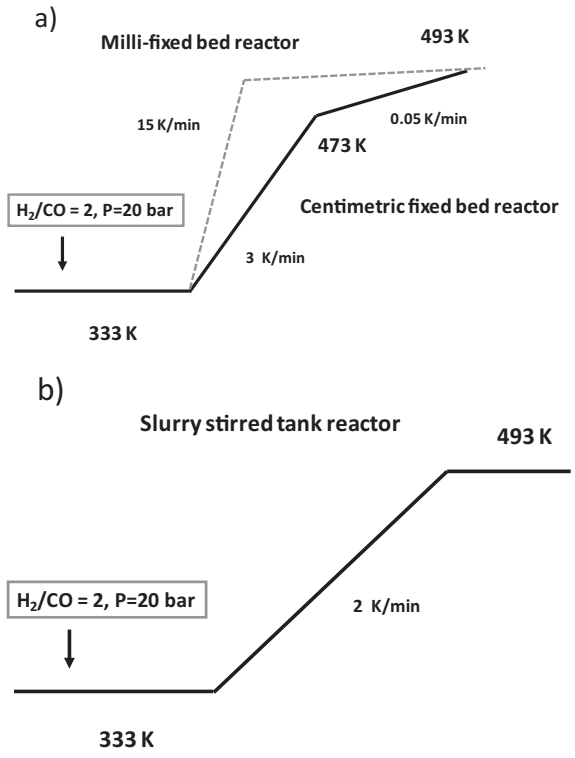

Fig. 2. Optimized startup procedures for fixed bed (a) and slurry stirred tank reactors (b). The dotted line indicates the startup procedure for milli-fixed bed reactor.

was reduced in situ in all the reactors in a flow of hydrogen during 16 h. The SX70 wax (Shell) was used for the startup of slurry reactor. The reduction temperature was 573 K and 603 K in the milli-fixed bed reactor, 623 K in the centimetric fixed bed reactor and 673 K in the slurry stirred tank reactor. The catalyst was then cooled down to 333 K. Hydrogen was replaced by a premixed syngas flow (molar ratio $H_2/CO = 2$) with a desired flow rate adjusted by mass flow controllers. The temperature was then increased to 493 K. The temperature ramping procedure during the reactor startup has been optimized for each reactor (Fig. 2). The gaseous reaction products were analyzed on-line by gas chromatography (GC Varian 3800). Analysis of H_2, CO, CO_2, CH_4 and N_2 was performed every 24 h using a CTR-1 column and a thermal conductivity detector. Hydrocarbons (C1–C7) were separated in a capillary CP-Plot column and analyzed by a flame ionization detector. Carbon monoxide contained 5% nitrogen which was used as an internal standard for calculating carbon monoxide conversion. Liquid reaction products recovered every 2–3 days in hot collector maintained at 423 K (wax phase composed of C_8–C_{75} hydrocarbons) and cold collector held to 288 K (diesel phase composed of C_7–C_{45} hydrocarbons) were analyzed by a flame ionization detector using a capillary CP-SimDist Ultimetal column. Typically at least two weeks are needed in slurry reactor to replace the startup wax and to quantitatively determine the composition of the reaction products.

3. Results and discussion

3.1. Optimization of the startup procedure for different FT reactors

After reduction in hydrogen, the catalyst in the milli-fixed bed, centimetric fixed and slurry stirred tank reactor was exposed to syngas and temperature (Fig. 2). It turns out that the startup procedure has to be adapted to a specific type of reactor. The temperature control during the reactor startup has been found particularly problematic in the centimetric fixed bed reactor. It was observed that rising the temperature in the centimetric reactor with the ramp of 1 K/min, 3 K/min or higher from 463 to 493 K during the exposure to syngas systematically led to reactor runaway. The temperature rose uncontrollably up to 523 K instead of 493 K which is required for smooth FT operation. Significant time has been spent for optimization of the startup procedure. The optimized startup procedure for centimetric fixed bed reactor is shown in Fig. 2a. After purging the reactor with syngas the reactor temperature was ramped with the rate of 3 K/min to 473 K. From 473 to 493 K the temperature was further ramped with the rate of 0.05 K/min. During this startup procedure, no direct evidence of runaway in the centimetric fixed bed reactor was observed using a thermocouple which was in direct contact with the catalyst.

Differently to centimetric fixed bed reactor, no uncontrolled temperature increase was noticed during the startup either in the milli-fixed bed or slurry stirred tank reactors. Moreover, different temperature ramping rates (up to 15 K/min) were tested with the milli-fixed bed reactor. None of them led to the reactor runaway. No significant uncontrollable increase in reactor temperature was also observed in slurry phase reactor. The temperature ramp used for the slurry reactor startup was typically 2 K/min due to the significant temperature inertia of the slurry stirred tank containing about 70 cm^3 of liquid phase.

3.2. Performance of cobalt catalyst in different reactors

3.2.1. Single channel milli-fixed-bed reactor

The variations of CO conversion and CH_4 selectivities with time on stream obtained with $Co(25\%)Pt(0.1\%)/Al_2O_3$ catalyst measured at 493 K, 20 bar and GHSV = 13.2 N L h^{-1} g_{cat}^{-1} in milli-fixed bed reactor are depicted in Fig. 3a. The $Co(25\%)Pt(0.1\%)/Al_2O_3$ catalyst reduced at 603 K exhibits high initial CO conversion (~62%) and low selectivity to methane (~8%). Water–gas shift activity is not significant; <0.3% of CO_2 are produced. The Anderson–Schulz–Flory distribution of hydrocarbons is shown in Fig. 3b. The calculated apparent chain growth probability was 0.92 with C5+ productivity of 1.1–1.4 g h^{-1} g_{cat}^{-1}.

It is noteworthy that some deactivation occurs in milli-fixed bed reactor with a loss of activity of nearly 10% after 300 h of continuous catalytic test. The catalyst activity in milli-fixed bed reactor was affected by catalyst reduction temperature. As expected, decrease in the catalyst reduction temperature from 603 to 573 K leads to a 10% lower carbon monoxide conversion (Fig. 3a). Indeed, in alumina supported catalysts cobalt reducibility is often a challenge [3], and increase in the reduction temperature in the 373–473 K range is usually beneficial for the catalytic performance. However, decrease in carbon monoxide conversion with the reaction time still occurs with the same trend suggesting that reduction at different temperatures does not inhibit catalyst deactivation. Interestingly, the catalytic performance of cobalt catalysts and particularly methane selectivity in milli-fixed bed reactor strongly depend on the ramping rate during the reactor startup. Higher reactor startup ramping rate leads to lower methane selectivity.

3.2.2. Centimetric fixed bed reactor

Typical catalytic performance data observed in centimetric fixed bed reactor are shown in Fig. 4a. To avoid any reactor runaway a very slow temperature ramping (0.05 K/min) from 473 to 493 K was used during the startup (Fig. 2). The carbon monoxide conversion at similar gas space velocity was slightly lower in centimetric fixed bed reactor than in milli-fixed bed reactor. The methane selectivity was nearly the same in both reactors. Because of a larger volume of centimetric fixed bed reactor compared to milli-fixed bed counterpart, the apparent carbon monoxide conversion and hydrocarbon selectivity during the first hours of the operation were affected

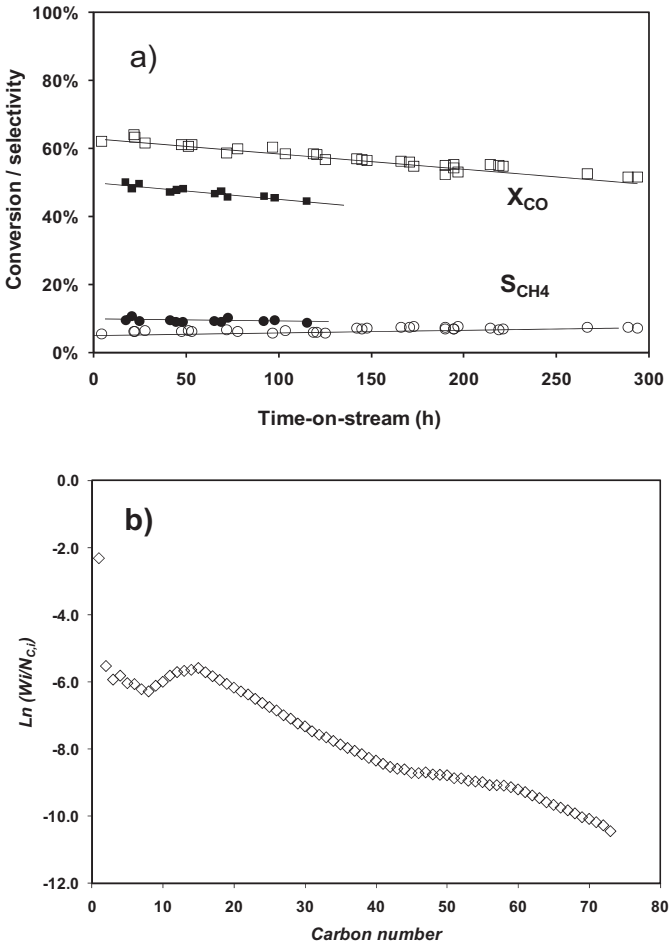

Fig. 3. Performance of single channel milli-fixed bed reactor: (a) variation of conversion and methane selectivity with time on stream after reduction at 573 K (bold symbols) and 603 K (empty symbols), (b) Anderson–Schulz–Flory plot for the catalyst reduced at 603 K (Co(25%)Pt(0.1%)/Al_2O_3 catalyst, P = 20 bar, H_2/CO = 2, T = 493 K, GHSV = 13.2 N L h^{-1} $g^{-1}{}_{cat}$).

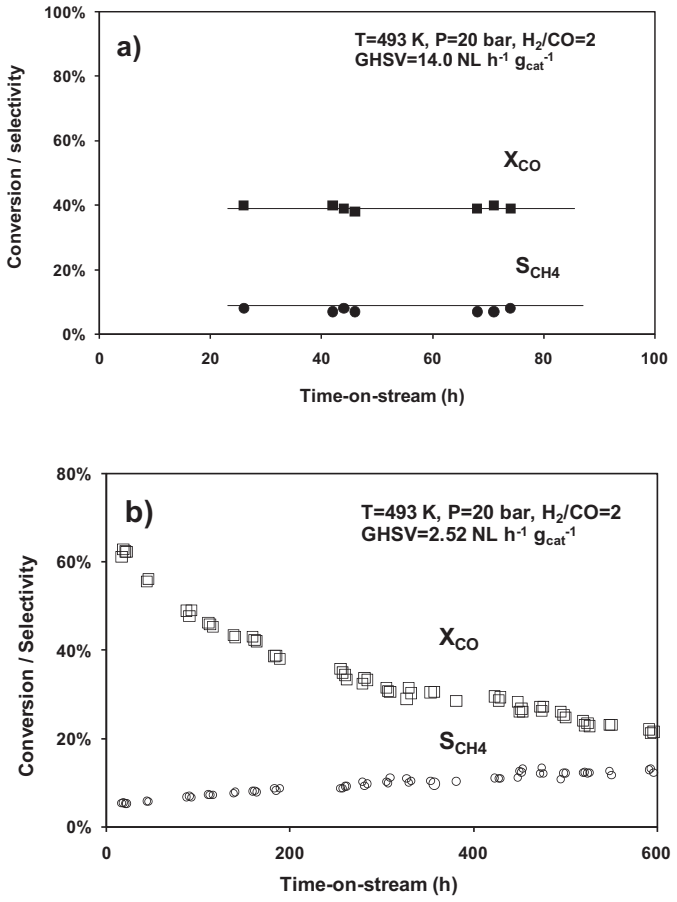

Fig. 4. Variation of conversion and methane selectivity with time on stream in centimetric fixed bed (a) and slurry stirred tank reactors (b).

by the reactor gas transient. In contrast with the milli-fixed bed reactor, at longer time-on-stream, carbon monoxide conversion becomes fairly constant in the centimetric fixed bed reactor. No visible catalysts deactivation was observed after several days of catalytic testing. Our attempts to increase carbon monoxide conversion to more than 50–55% by decreasing the gas space velocity have led to uncontrollable rise of the reactor temperature (up to ~540 K). It appears that reactor runaway could be a common problem of FT synthesis in conventional centimetric fixed bed reactors.

To evaluate the influence of the reactor runaway on the catalyst structure and catalytic performance, the temperature in the centimetric fixed bed reactor was intentionally increased to 533 K for 72 h. This value corresponds to the temperature hike typically observed in centimetric fixed bed reactor during a reactor runaway. After catalyst treatment in syngas at 533 K, the reactor temperature was lowered to 493 K. The variation of carbon monoxide conversion and methane selectivity during this treatment are shown in Fig. 5. The increase in the reactor temperature to 533 K leads to almost 100% carbon monoxide conversion with methane selectivity of about 20%. After the treatment with syngas at 533 K and after switching back to the standard reaction conditions and usual FT reaction temperature (T = 493 K) a major loss of the catalytic activity was observed. Carbon monoxide conversion at GHSV = 14 N L $g_{cat}{}^{-1}$ h^{-1} decreased from 39 to 15%. The catalyst has lost more than a half of its activity. Significant changes were also observed in the catalyst structure. Fig. 6 shows the SEM images of the cobalt catalyst after catalytic test under standard conditions (493 K, without visible runaway) and after exposure to syngas at 533 K. The SEM images display spheres of Puralox alumina in silicon carbide. Silicon carbide was used for catalyst dilution in centimetric fixed bed reactor. Cobalt repartition was nearly uniform (Fig. 6a) after catalytic tests in centimetric fixed reactor under standard conditions (without detectable runaway). After conducting catalytic reaction at 533 K (simulated reactor runaway), significant agglomeration of cobalt was observed; unsupported cobalt clusters of several microns were observed (Fig. 6b). This suggests that uncontrolled rise of temperature and hot spots in the centimetric fixed bed reactor can dramatically modify cobalt distribution over catalyst grains, lead to cobalt sintering and result in mediocre catalytic performance in FT synthesis.

3.2.3. Slurry stirred tank reactor

The slurry stirred tank reactor showed much lower hydrocarbon productivity than the milli-fixed bed or centimetric fixed bed reactors. Indeed, carbon monoxide conversion of 60% was obtained at much lower space velocities (GHSV = 2.52 N L h^{-1} $g_{cat}{}^{-1}$, Fig. 4b). It is known that a CSTR is less efficient than a plug flow fixed bed reactor, however the difference is so pronounced that another phenomenon must be involved. The much lower performances of the slurry reactor are probably due to incomplete reduction of cobalt catalyst prior to catalytic tests. Note that the catalyst in the slurry stirred tank reactor was reduced in situ; it was placed in the bottom of the slurry reactor during the reduction without liquid phase or stirring. The incomplete catalyst reduction could be due to insufficient gas mixing, external diffusion limitations and slow water

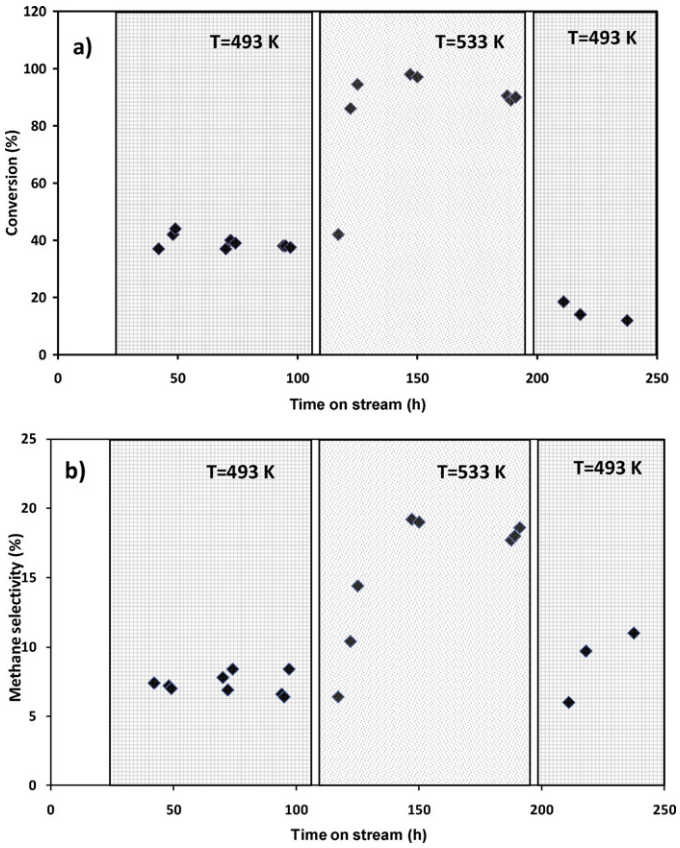

Fig. 5. Effect of exposure of centimetric fixed bed reactor to 533 K on carbon monoxide conversion (a) and methane selectivity (b). Reaction conditions: Co(25%)Pt(0.1%)/Al_2O_3 catalyst, P = 20 bar, H_2/CO = 2, GHSV = 14.0 N L h^{-1} g_{cat}^{-1}.

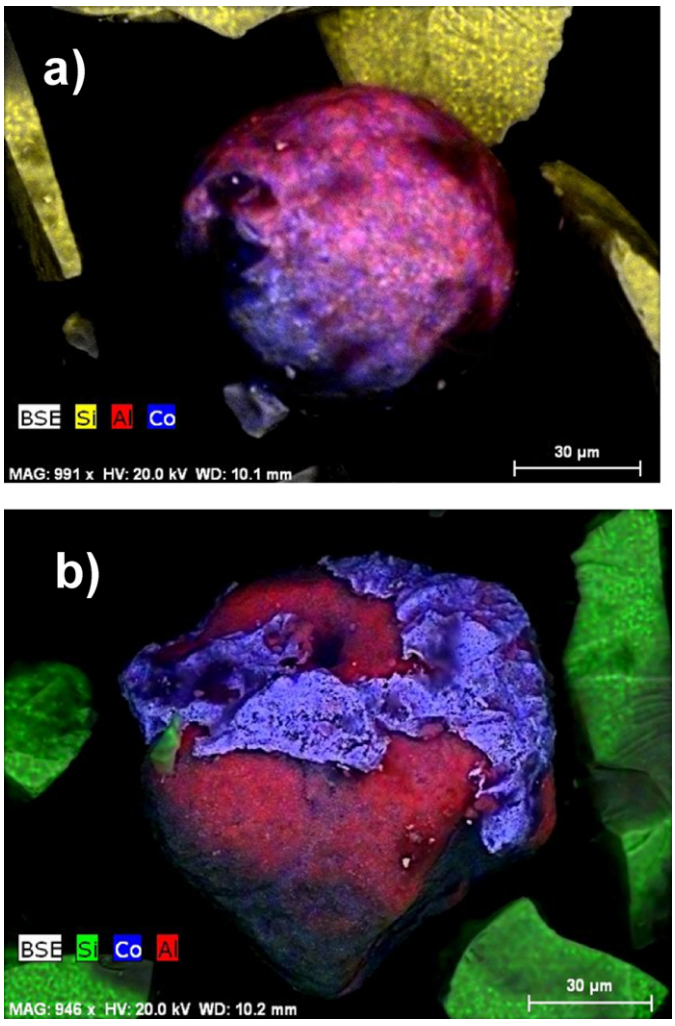

Fig. 6. SEM-EDX images of Co(25%)Pt(0.1%)/Al_2O_3 catalyst after catalyst run in centimetric fixed bed reactor under standard conditions without reactor runaway (a) and after exposure to 533 K (b).

removal. The methane selectivity was about 7% which is similar to methane selectivity values observed in the other reactors. Carbon monoxide conversion in the slurry reactor progressively decreased to a half of its initial value after 300 h on stream. This observation is consistent with previous reports [21,25,26] describing catalyst deactivation in slurry FT reactors. The reactor showed however, good thermal stability even at higher carbon monoxide conversion levels (~80%).

3.3. Comparison of single channel millimetric, centimetric fixed bed and slurry stirred tank reactors

FT synthesis is an exothermic reaction. As expected, our results suggest that the principal advantage of milli-fixed bed reactor relevant to FT reaction can be attributed to a better control of catalyst temperature. However they show that this advantage is particularly important during the reactor startup when a dry and activated catalyst is exposed to syngas at the reaction temperature. Because of slow radial heat transfer in centimetric fixed reactor, the catalyst exposure to syngas can lead to reactor runaway. The runaway of the centimetric reactor and uncontrolled temperature increase could result in a significant modification of the catalyst structure and loss of catalytic performance. Our characterization data are indicative of remarkable cobalt sintering in the cobalt catalyst after the reactor runaway (Fig. 6b). These suggestions are consistent with the report by Marquez et al. [27], showing that the reactor startup procedure and especially catalyst pre-wetting has a remarkable impact of the reactor stability of centimetric fixed bed reactors. In contrast to the centimetric reactors, no significant effect of startup procedures on the bed stability in miniaturized multiphase packed bed reactors was observed in that work [27]. A better radial heat transfer in the milli-fixed bed reactor due to a smaller reactor diameter (1.4 mm versus 13 mm) and higher surface to volume ratio allow efficient temperature control in milli-fixed bed reactor during the reactor startup using temperature ramping rates up to 15 K/min. The hydrodynamics of FT reactor is rather complex because of the simultaneous presence of gaseous and liquid phases. Calculation of Re number in porous medium and assuming only gas flow indicates transitional (laminar-turbulent) regime in both reactors. Because of higher superficial velocity, the hydrodynamic regime is more turbulent in milli-fixed bed reactor which could possibly enhance to some extent the heat and mass transfer.

Lower FT reaction rate in the slurry phase FT reactor is probably due to the incompletely reduced catalyst. Similarly lower activity of iron catalyst in stirred tank slurry reactor than in fixed bed reactor was previously observed by Bukur et al. [28]. It was also attributed to incomplete catalyst reduction. Indeed, the catalyst for FT synthesis can be reduced either *ex situ* in a fixed bed reactor and then in reduced state can be transferred to a slurry reactor. During this transfer however the catalyst re-oxidation cannot be completely excluded. The catalyst can be also reduced in situ in slurry stirred tank reactor. However because of poor gas mixing in the autoclave, the reduction conditions for the catalyst in this case are also not optimal. It appears that optimization of the reduction procedure could lead to higher hydrocarbon productivity in slurry reactors.

Our results show a strong impact of the catalytic reactor on catalyst deactivation behavior. Some deactivation is observed in milli-fixed bed reactor; the conversion decreases from 60 to 50% after 300 h of operation. A more significant catalyst deactivation is observed in slurry phase reactor. On the other hand, after the initial startup episode, no significant loss of activity was observed for the conventional fixed bed reactor. It is known that the deactivation of FT catalysts is interplay of several phenomena: catalyst poisoning with sulfur or nitrogen containing, compounds, cobalt oxidation, carbon deposition, carbidization, cobalt sintering, cobalt loss/leaching during the reaction, surface reconstruction. The progressive decay in hydrocarbon productivity in slurry reactor can be also due to catalyst attrition which leads to formation of fine particles and catalyst loss in the filters. In addition, the start-up liquid can affect the deactivation behavior of Fischer–Tropsch catalysts in slurry reactor. Previously Gormely et al. [29] observed higher FT deactivation rate on iron catalysts in heavier starting media (with average carbon number higher than 48) versus the lighter medium (carbon number 28).

The contribution of these different mechanisms depends on the catalyst, reactor and operating conditions. Recent reports suggest [25,26,30,31] that cobalt sintering/restructuring can be involved in the deactivation of cobalt catalysts which occurs during the first hours/days of the reaction, while a long term catalyst deactivation can be possibly related to other phenomena such carbon deposition and coking [25,32].

In agreement with catalyst characterization data (Fig. 6) it can be suggested that a sharp temperature hike typically observed during the startup of the centimetric fixed bed reactor could significantly accelerate cobalt sintering and restructuring. Consequently, the catalyst in centimetric fixed bed reactor which was exposed to uncontrolled temperature hike would exhibit a lower FT reaction rate than in a milli-fixed bed reactor. In the centimetric fixed bed reactor cobalt sintering occurs during the startup and thus the reactor exhibits a quasi-stable activity during the first several hundred hours of operation. The milli-fixed reactor does not display any temperature hike during the startup procedure. As a result, it shows higher initial FT reaction rate than the centimetric fixed bed reactor. The catalyst performance slightly declines as a function of time on stream in milli-fixed bed reactor due to deactivation. Our recent in situ XRD studies [30,31] performed in the operando reactor (analogous in geometry to the milli-fixed bed reactor) under realistic conditions of FT synthesis were indicative of cobalt sintering during the first several hours of the reaction. Thus, progressive decrease in carbon monoxide conversion in milli-fixed bed reactor during the first several hundred hours can be related to a slower and progressive cobalt sintering. Cobalt sintering can also contribute to the decrease in carbon monoxide conversion with time on-stream in slurry stirred tank reactor. Indeed, cobalt sintering in alumina supported catalysts in slurry reactor was previously observed after several days of operation using *ex situ* characterization [25]. The rate of cobalt sintering however can be dependent on the reactor. Note that the slurry reactor also does not show any uncontrolled temperature variation during the startup procedure which could enhance cobalt sintering in centimetric fixed bed reactor. In addition to cobalt sintering, the decrease in hydrocarbon productivity in slurry reactor can be also due to catalyst attrition, which could be significant at higher water concentrations, catalyst loss with reaction products [33] and other phenomena which should not be confused however, with the deactivation process.

4. Conclusion

Our results show that single channel milli-fixed bed reactor allows higher initial hydrocarbon productivity in FT synthesis than centimetric fixed bed reactor and slurry stirred tank reactors. Uncontrolled temperature increase during the reactor startup seems to be a common problem of FT synthesis in the centimetric fixed bed reactors. This temperature increase during the reactor startup can lead to catalyst deactivation. No temperature overshoot was observed during the startup of the milli-fixed bed reactor despite the higher temperature ramp (15 K/min). The enhanced FT productivity in a single channel milli-fixed reactor could arise from less significant cobalt deactivation during the rector startup due to a better temperature control. Lower productivity of slurry stirred tank reactor seems to be related to difficulties in obtaining highly reduced cobalt catalyst. The three reactors exhibited different initial deactivation behaviors. Slow catalyst deactivation takes place in milli-fixed reactor (1% per day), while deactivation was much more significant in the slurry reactor. After the initial startup period, the carbon monoxide conversion remains unchanged for several days in centimetric fixed bed reactor.

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