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Direct fluorination of carbon monoxide in microreactors

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ABSTRACT

Many attempts to obtain a clean stream of COF_2 have been carried out in the past by means of the direct fluorination of carbon monoxide with elemental fluorine or by electrochemical fluorination. The reaction is highly exothermic, therefore difficult to control. It can easily develop into a thermal runaway with a poor selectivity. We have successfully circumvented these critical issues by using a stainless steel parallel channel microreactor (surface/volume ratio $\approx 1 \times 10^4\ m^{-1}$, residence time $\tau \approx 0.1$ s) for the direct fluorination of carbon monoxide. Its performance in terms of operability and selectivity is compared to that of a standard reactor assembly, namely a fluorine burner reactor coupled with a water cooled heat exchanger. While the microreactor assembly succeeded to control the exothermic reaction, in the same experimental conditions the standard assembly reactor underwent serious corrosion issues that lead to nozzle meltdown lack of selectivity and consequent plant shutdowns.

1. Introduction

High purity COF_2 is required in many applications [1–10]. The usual approach to obtaining this compound is the direct fluorination of carbon monoxide with elemental fluorine. In general the reaction of organic substances with fluorine, in conventional reactors, is difficult to control due to the heat generated by the reaction itself [11]. The fluorination of a hydrogenated compound is a typical example where the exothermicity of the whole reaction is such that any carbon–carbon bond can be easily broken if the reaction is not properly controlled by dilution of reagents and by adopting a low reaction temperature and CH activation [12,13]. The improperly conducted fluorination leads invariably to several byproducts and ultimately to CF_4 and HF [14].

Attempts to obtain a clean stream of COF_2 have been carried out mainly by trying to reduce the flame temperature via massive dilution of the inlet streams or by switching to electrochemical fluorination [15,16]. The introduction of inert gases implies, at a fixed contact time, an increase of the reactor volume or, at a constant volume, a decrease in plant productivity. As a matter of fact, only a massive introduction of a dilution stream results in a lower flame temperature and hence in a higher selectivity [5,9,17].

Recently a *flame-less* approach has been patented [18]. It is reported that the two reactants, fluorine and carbon monoxide are continuously bubbled in a continuous stirred-tank reactor (CSTR) filled with a solvent [19]. This system has clearly some critical points, i.e. solvent stability [20] and operability.

A good practice to obtain pure carbonyl-difluoride is to reduce the flame temperature by increasing the heat exchange surface. Due to the large amount of heat released during the reaction, the surface/volume ratio of the reactor has to be high, thus the use of a microreactor seems to be a suitable option. In fluorine chemistry, there is a large interest in the development of microreactors for chemical processing [21–25] due to the benefits that this technological device could provide: better reaction control, arithmetic scale-up and higher safety. Herein we report the use of a microreactor to test the highly exothermic gas phase reaction $CO + F_2$ with the aim of better controlling the temperature and increase the reaction selectivity.

2. Materials and methods

Pure fluorine (98%, from Solvay Fluor) and pure carbon monoxide (99.8%, from Sapio) were fed in the reactor without any further dilution. The experiments were performed by setting the carbon monoxide flow-rate to 1 NL/h (44.6 mmol/h) and acting on the fluorine flow-rate in order to reproduce three experimental conditions: a lean, a stoichiometric and a rich combustion. The composition measurements of the gas produced were taken

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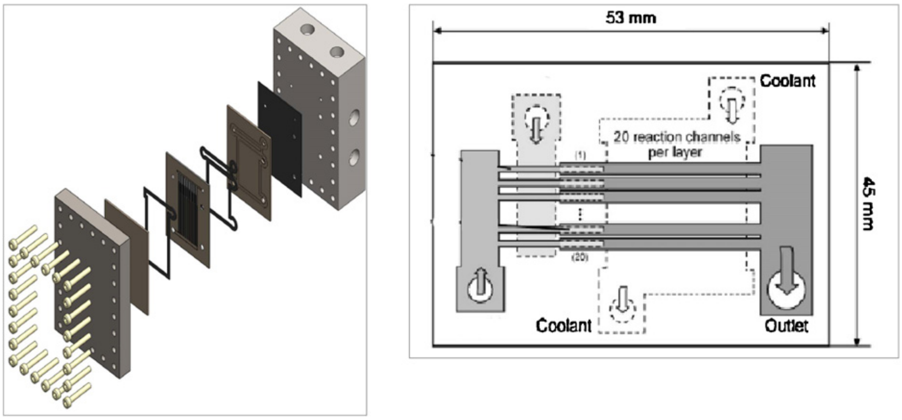

Fig. 1. Left: exploded view of the MIT micro-reactor assembly. Right: simplified scheme of the fluorination micro-reactor plate. The dashed lines refer to structures on the back side whereas the continuous lines indicate structures on the top side.

20 min after the imposed steps giving the system enough time to reach a steady-state, if any.

The construction of a microreactor suitable for direct fluorination reactions has several challenges. The microreactor needs to be accurately designed and dimensioned at a microscale level. It must also be constructed by using corrosion resistant materials able to withstand a hostile environment, at extremely high temperature for a long time. The microreactor used for the experiments (Fig. 1) is based on a design of de Mas et al. [24,26] and has a volume of 65 mm^3 and a surface/volume ratio of $1 \times 10^4\ m^{-1}$. The original microreactor was realized in silicon and nickel coated, but to withstand the corrosion issues associated with pure fluorine and carbonyl-difluoride and to increase the heat transferred via conduction, alloys like AISI 316 and R400 were used in the present version. The reactor plates were machined via electron discharge while the gaskets were water-jet cut from a perfluoro-elastomer (FFKM) sheet.

The microreactor resembled a very small heat exchanger and was constructed by assembling many stacked parts: the enclosure consisted of two thick plates of stainless steel that integrates the temperature sensors, process inlets, outlets, and coolant ports. The internal combined stainless steel reaction and cooling plates machined with gas and coolant distribution systems were inserted between two counter-plates and separated with FFKM gaskets as illustrated in Fig. 1. Each reaction-cooling plate contained on the front side 20 parallel microchannels for reaction and 20 cross flow parallel microchannels for cooling on the back. The coolant channels were embedded using a computer controlled milling machine. The reaction channel dimensions were 25 mm long, 400 μm wide and 400 μm deep. To ensure a uniform distribution of the reactants in all the microchannels a neck was machined at the beginning of each channel.

The thermal energy produced during the reaction was dispersed from the gas phase through the microreactor plates and dissipated into the cooling fluid (Water, Solvay Specialty Polymers Galden® HT 110/HT 55 or $CF_3O–CFCl–CF_2Cl$, depending on the target temperature). The amount of heat removed from the coolant was controlled by setting the cryostat temperature. Cooling the system was critical since the loss of temperature control of the reaction could damage the reactor plates and seals.

The analytic apparatus consists of a Nicolet 380 FT-IR spectrometer equipped with a 10 cm long PTFE cell with calcium fluoride windows (recommended spectrum width 7400–1111 cm^{-1}) and a GC-TCD (Dani 6500) with PFA packed column (Kel-F oil on Hyflon MFA® perfluorinated plastic). The output of the TCD could be sampled and injected into a GC–MS system (Agilent 6850+5975C with PLOT-U column). After the analyses the off-gases coming from the microplant were neutralized through two columns filled with pellets of soda lime (abatement system).

The standard reactor assembly consisted of one 1/8 in. Swagelok tee where the two reactants were fed through two 1/8 in. tubes. In addition 2 m of 1/8 in. tube has been installed after the tee. The standard reactor apparatus was cooled using a stirred bath to dissipate the heat generated by the chemical reaction. The fluid used was Solvay Specialty Polymers Galden® HT 110 for low temperatures and water for tests above room temperature.

A heated safety vessel of 25 cm^3 was installed after both the reactors to provide a dead volume for transient control since a poorly controlled plant could cyclically lead to the formation of lean and rich mixtures. If a fluorine rich mixture would come in contact with carbon monoxide in the same volume an explosion would be expected. If this uncontrolled reaction happened in the IR cell, it could damage the windows and the spectrophotometer. The influence of the safety vessel was negligible on the conversion and selectivity of the two reactors under comparison.

Among the signals coming from the collected IR spectra only one "characteristic absorption peak" for each compound was chosen for the on-line monitoring. The unique non-overlapping signal of carbon monoxide lies at 2120 cm^{-1} whereas carbonyl-difluoride absorbs the IR radiation at 1559 cm^{-1}, 1900 cm^{-1}, 2489 cm^{-1}, 2924 cm^{-1} and 3860 cm^{-1}. The peak at 1900 cm^{-1} is too intense, but the other peaks at 1559 cm^{-1}, 2924 cm^{-1}, 3860 cm^{-1} are too weak and noisy to be used. Thus, the preferred peak for COF_2 is 2489 cm^{-1}. Trifluoromethyl hypofluorite (CF_3OF) has absorption bands at 1378 cm^{-1} and 1489 cm^{-1}. Only the first band was used.

For every IR scan the relative ratio between peak heights belonging to a single substance are calculated as reported in Table 1.

Any scan that did not match the relative peak ratio of the pure substance was discarded. Data collected from the IR spectra were normalized against carbonyl-difluoride peaks to provide an immediate performance comparison of the two systems.

Table 1
Relative ratio of IR peak height.

Substance	Peaks	Ratio
Carbonyl-difluoride	Abs (2489 cm^{-1})/Abs (1559 cm^{-1})	1.62 ± 0.04
	Abs (2924 cm^{-1})/Abs (1559 cm^{-1})	0.502 ± 0.006
Trifluoromethyl hypofluorite	Abs (1489 cm^{-1})/Abs (1378 cm^{-1})	0.71 ± 0.08

2.1. Safety

Reactants and products are toxic [27]. Pure fluorine and carbonyl-difluoride are heavier than air and react quickly with water to form the hydrogen fluoride. Burns caused by fluorine or carbonyl-difluoride require immediate medical treatment with calcium gluconate since the symptoms of poisoning, often become manifest only after some hours. Both compounds have a pungent odor and adequate warning properties, thus a small leak can be quickly detected and subsequent actions can be taken. Localized fluorine leaks can be detected by using a cotton tip wetted with starch iodide solution while carbonyl-difluoride gives acid reaction.

On the contrary, the presence of flammable, toxic and teratogenic carbon monoxide in the environment cannot be promptly detected since it does not have any warning properties.

Working with these gases requires good suction fume hoods and appropriate personal protective equipment like neoprene gloves and a full piece mask.

3. Results and discussion

The synthesis of carbonyl-difluoride (Scheme 1) is recognized as a fast and exothermic radical gas phase reaction [28].

The equilibrium temperature for the reaction with pure fluorine and pure carbon monoxide has been calculated to be around 3700 K at an estimated conversion of 38%. The calculated adiabatic temperature [29] in the presence of a standard 75% nitrogen dilution is 5015 K with a 1.5% conversion. The adiabatic temperature calculation made in the absence of nitrogen, thus with pure fluorine, shows a value that is several orders of magnitude higher than the one calculated in the presence of nitrogen dilution. In the absence of proper temperature control the reaction is also prone to thermal run-away (Scheme 2). If the local reaction temperature exceeds 670 K many byproducts (Scheme 3) are formed.

It is also difficult to separate carbonyl-difluoride from the byproducts formed by the reactions shown in Scheme 3 because of their low concentration and similar boiling points. Moreover, the similar chemical properties of these byproducts make it difficult to separate them by adsorption or chemical neutralization methods.

To overcome these analytical disadvantages a specific online gas analysis system was assembled. The gases produced in the standard reactor systems or in the microreactor were analyzed by an online analytic system allowing a continuous evaluation of the output coming from the FT-IR spectrometer, GC–TCD and GC–MS system. The microreactor performances in terms of operability and selectivity were compared with a standard reactor having a surface/volume ratio (S/V) equal to 700 m^{-1} by adopting a resident time of $\tau \approx 10$ s.

$$CO + F_2 \rightarrow COF_2 \qquad \Delta H°_R = -530 \text{ kJ/mol}$$

Scheme 1. Direct fluorination of carbon monoxide leading to carbonyl-difluoride.

$$CO + 2\,F_2 \rightarrow CF_4 + 0.5\,O_2 \qquad \Delta H°_R = -820 \text{ kJ/mol}$$

Scheme 2. Direct fluorination of carbon monoxide leading to tetrafluoromethane.

a) $2\,CO + O_2 \rightarrow 2\,CO_2$

b) $COF_2 + F_2 \rightarrow CF_3OF$

c) $CF_3OF + COF_2 \rightarrow CF_3\text{-}OO\text{-}CF_3$

d) $CO_2 + F_2 \quad CF_2(OF)_2$

e) $CF_3OF \rightarrow CF_4 + 0.5\,O_2$

e) $CF_3OF + CO \rightarrow CF_3O\text{-}C(O)F$

f) $CF_3O\text{-}C(O)F \rightarrow CO_2 + CF_4$

g) $2\,CO + F_2 + O_2 \rightarrow CF(O)\text{-}OO\text{-}C(O)F$

Scheme 3. Side reactions that might take place in the reaction environment.

Table 2
Operative conditions applied.

Test number	Temperature	F_2/CO ratio	Notes
1	−18 °C	0.96	CO = 1 L/h
2	−18 °C	1.22	CO = 1 L/h
3	−18 °C	0.80	F_2 = 0.96 L/h
4	−18 °C	1.99	CO = 1 L/h
5	−35 °C	1.22	CO = 1 L/h
6	−50 °C	1.22	CO = 1 L/h
7	−62 °C	1.22	CO = 1 L/h
8	−73 °C	1.22	CO = 1 L/h
9	25 °C	1.22	CO = 1 L/h
10	100 °C	1.22	CO = 1 L/h

The operative conditions applied while GC and IR data were recorded are summarized in Table 2.

In Fig. 2, we report the IR spectra recorded in preliminary tests under lean, rich and stoichiometric conditions obtained in the standard reactor. Under rich conditions, the adsorption band due to the excess of carbon monoxide can be noticed along with the signals of the main product COF_2. When the reaction was carried out using an equal reactant flows the carbon monoxide band disappeared. When the reaction was carried out with an excess of fluorine, trifluoromethyl hypofluorite (CF_3OF) bands appeared at 1378 cm^{-1} and 1489 cm^{-1}. GC analyses confirmed that the amount of trifluoromethyl hypofluorite produced was approximately 10% of the COF_2 stream in our experimental conditions (room temperature $F_2/CO = 1.9$ (v/v), standard assembly).

The presence of trifluoromethyl hypofluorite was expected when carbonyl-difluoride and elemental fluorine are simultaneously present in the reactor [4,7,30,31]. When changing the experimental conditions from the rich to the lean tests a mismatch in peak ratio, shown in Table 1, was observed. The explanation of this measure relies on the fact that the weaker signal was noisy, therefore any mathematic operation on his modulus is affected by a significant error.

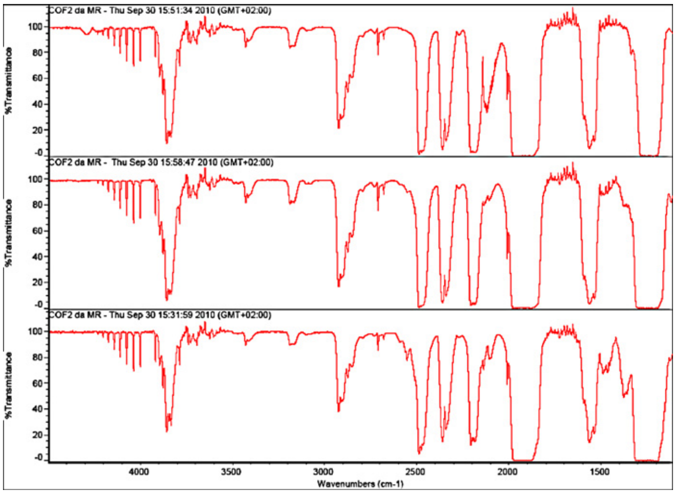

Fig. 2. IR spectra obtained in the standard reactor. Top IR – excess of carbon monoxide ($F_2/CO = 0.93$, v/v) (CO band at 2120 cm^{-1}). Central IR – stoichiometric mixture ($F_2/CO = 1$, v/v) (carbonyl-difluoride bands at 1559 cm^{-1}, 2489 cm^{-1}, 2924 cm^{-1} and 3860 cm^{-1}). Bottom IR – excess of fluorine ($F_2/CO = 1.9$, v/v) (hypofluorite bands at 1378 cm^{-1} and 1489 cm^{-1}).

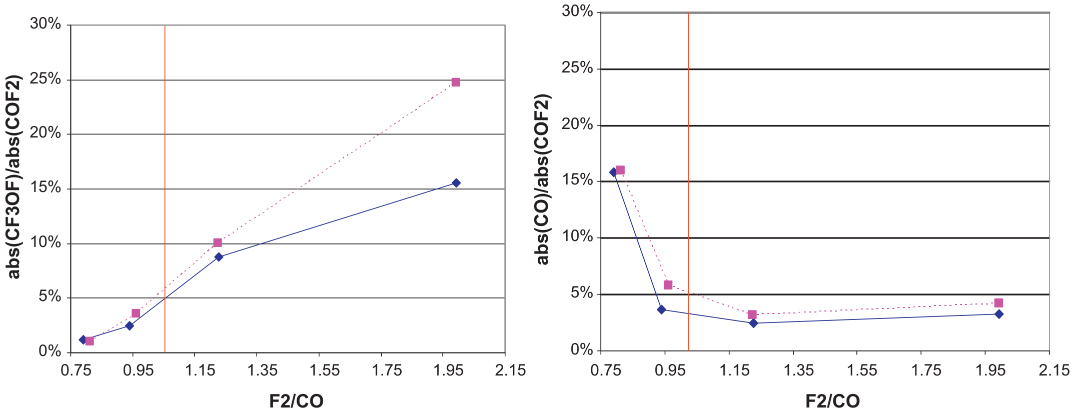

Fig. 3. IR absorbance ratios in the tests performed by varying the stoichiometry at −18 °C for the standard assembly (dashed line) and the microreactor (continuous line). Left: $Abs_{CF_3OF}/Abs_{(COF_2)}$. Right: $Abs_{(CO)}/Abs_{(COF_2)}$. The vertical red line represent the ideal stoichiometric 1:1 ratio between CO and F_2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

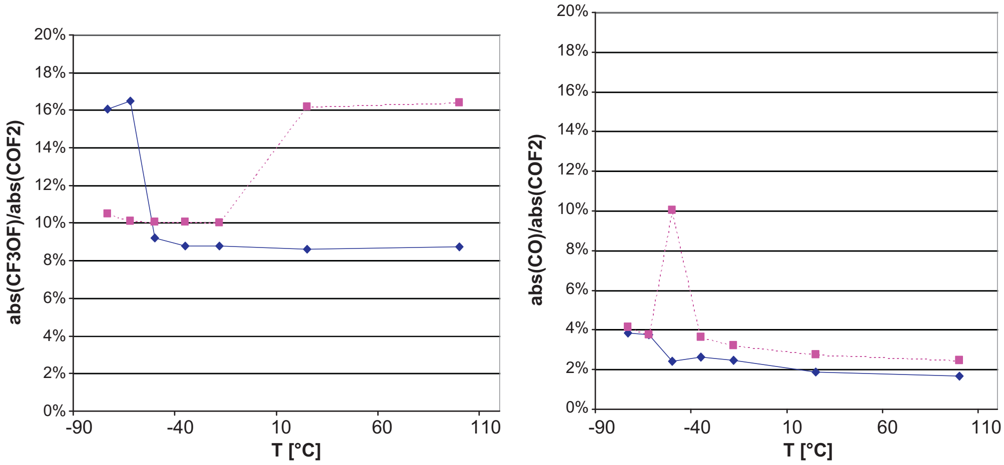

Fig. 4. IR absorbance ratios in the tests performed by varying the temperature at constant stoichiometry (F_2/CO = 1.22) for the standard reactor assembly (dashed line) and the microreactor (continuous line). Left: $Abs_{CF_3OF}/Abs_{(COF_2)}$. Right: $Abs_{(CO)}/Abs_{(COF_2)}$.

Detailed experiments were performed at constant temperature (−18 °C) in both the reactors assembly, standard and microreactor. The carbon monoxide conversion (Fig. 3) is about 30% higher in the microreactor. In both cases the amount of CF_3OF produced is linearly proportional to the amount of pure fluorine introduced in the system. However, the amount of trifluoromethyl hypofluorite produced in the microreactor was up to 40% lower than that in the standard reactor test, even at high F_2/CO ratio.

At stoichiometric flow rates, an unstable operation condition was observed in the standard reactor because at this condition (CF_3OF) and (CO) were simultaneously present in the gas phase. This thermodynamically unstable mixture may eventually burn in the heated safety vessel, but no evidence of this has been found. This unstable condition was less evident in the microreactor because the amount of trifluoromethyl hypofluorite and carbon monoxide produced was much lower compared to the trifluoromethyl hypofluorite and carbon monoxide produced in the standard reactor test (Fig. 4).

At constant F_2/CO ratio (1.22) another unstable operating condition appears. At temperatures lower than −50 °C (Fig. 4) the reaction performed in the microreactor lacks conversion and selectivity. Under those conditions the COF_2 synthesis does not ignite in the microreactor channels, probably also due to the active termination of the radicals on the walls. A mixed stream of fluorine and carbon monoxide then leaves the microreactor and burns without temperature control in the safety vessel, but outside the reactor. This behavior was also confirmed by measuring the temperature increase of the gases in the safety vessel, along with the temperature increase of the tubes connecting the microreactor with the safety vessel. This unstable operative condition was also

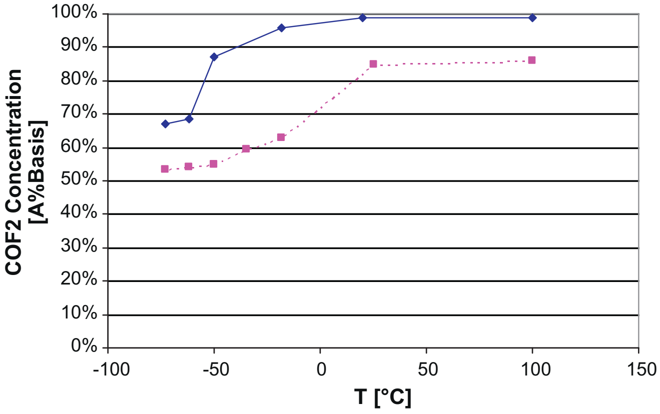

Fig. 5. Concentration of COF_2 (area basis) in the tests performed by varying the temperature at constant stoichiometry (F_2/CO = 1.22) for the standard reactor assembly (dashed line) and the microreactor (continuous line).

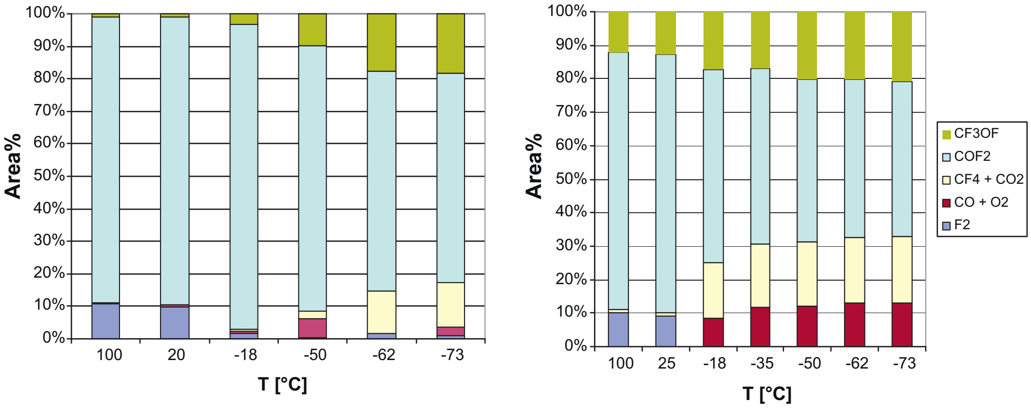

Fig. 6. Product distribution from GC–TCD analyses for the tests at F_2/CO = 1.22 at various temperatures. Left: microreactor. Right: standard reactor.

observed in the standard reactor, but it was less noticeable due to its large volume.

For reaction temperatures higher than −35 °C (Figs. 5 and 6) the microreactor had 15–50% higher selectivity than the standard reactor. GC–TCD, GC–MS and IR data of the effluent produced in low-selectivity tests carried in both reactors revealed that along with CF_3OF many other by products were present: tetrafluoromethane, carbon dioxide and oxygen.

Interestingly in the low selectivity tests carried out with the standard reactor (Fig. 6), even if a fluorine excess was fed some unconverted carbon monoxide was still present in the output gases. In these conditions the reaction mixture become unstable and the overall reaction leading to COF_2 was characterized by low selectivity with clear evidence of byproducts formation as shown in Scheme 3.

Under these conditions 1/10th or more of the carbon monoxide was no longer converted while the whole excess of fluorine reacted with COF_2 giving CF_3OF through reaction (b) of Scheme 3. At high temperature the trifluoromethyl hypofluorite can decompose through reaction (e) of Scheme 3 forming CF_4 and oxygen [14,32], finally CO_2 was formed through the oxidation of carbon monoxide through reaction (a) of Scheme 3. As a result, the final mixture consists of a stream containing COF_2, CF_3OF, CF_4, O_2 and CO_2.

4. Conclusions

Microreactors are an industrial technology already used in pharmaceutical and fine chemistry. With these devices it is possible to carefully control a highly exothermic chemical reaction such as the synthesis of COF_2 from pure CO and F_2 avoiding unsafe conditions, product decomposition and runaways. In our experience the microreactor increased the selectivity of the reaction by a range between 15% and 50% and enhanced the carbon monoxide conversion up to 30%. The trifluoromethyl hypofluorite, an unstable byproduct of the COF_2 synthesis produced also in the microreactor was up to 40% lower than in the common standard reactor. On the laboratory scale, stainless steel microreactors were proven to be safe and reliable for direct fluorination reactions with pure fluorine. The microreactor has the capability to control and dissipate the large amount of heat produced during the reaction, while at the same experimental conditions the standard reactor undergoes serious corrosion issues that lead to nozzle meltdown, lack of selectivity, frequent plant shutdowns, damages and poor operability.

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