



# Catalytic formation of 2,3,3,3-tetrafluoropropene from 2-chloro-3,3,3-trifluoropropene at fluorinated chromia: A study of reaction pathways



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## ABSTRACT

The catalytic gas phase reaction between  $\text{CF}_3\text{-CCl=CH}_2$  with HF yielding  $\text{CF}_3\text{-CF=CH}_2$  was investigated regarding the reaction pathways involved. Different from the reaction under liquid phase (homogenous) conditions, in heterogeneous phase  $\text{CF}_3\text{-CCl=CH}_2$  does not add HF forming the saturated intermediate  $\text{CF}_3\text{-CFCl-CH}_3$  but undergoes direct Cl/F exchange at the starting olefin molecule resulting directly in the formation of  $\text{CF}_3\text{-CF=CH}_2$ . This might be caused mainly by the fact that under heterogeneous gas phase conditions higher temperatures are needed as compared to liquid phase conditions thus suppressing the formation of kinetically less stable  $\text{CF}_3\text{-CFCl-CH}_3$  under these conditions. Since for all the reaction steps involved in this complex reaction system the Gibbs free reaction enthalpy values are close to zero [1], the selectivity towards several reaction products is strongly dependent on the reaction parameters, e.g. temperature, pressure and molar ratio of the reactants. Based on the catalytic data obtained for fluorinated chromia as catalyst, a reaction path distinguishing direct chlorine against fluorine exchange versus hydrofluorination/dehydrochlorination is proposed.

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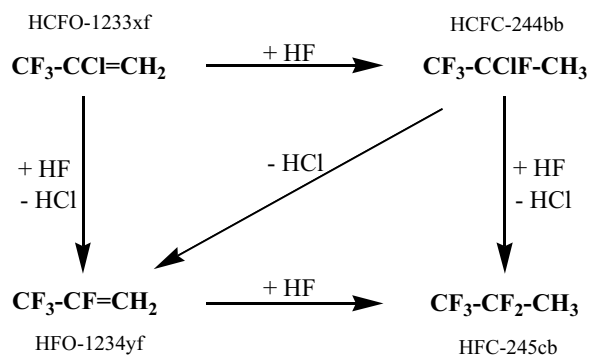
## 1. Introduction

Haloalkenes are very important starting compounds for halogen containing polymers (e.g. PVC, PVdC, PVDF, PTFE). Moreover, the global warming potential (GWP) of 1,1,1,2-tetrafluoroethane (HFC-134a) has caused an intense search for lower GWP alternatives. This prompted the European Community to stop its use as a refrigeration agent for air conditioning devices, e.g. in automobiles.

Hydrofluoroolefins (HFOs) have been considered as favourable replacements for saturated hydrofluorocarbons (HFCs) due to their zero ozone depletion potential (ODP) and a very low GWP respectively [2,3]. Moreover, HFOs exhibit very low toxicity and flammability [4–6] and as a result, 2,3,3,3-tetrafluoropropene,  $\text{CF}_3\text{-CF=CH}_2$ , (HFO-1234yf) has been identified as a promising compound to be used as a replacement as indicated by Wallington et al. and Luecken et al. [7,8].

Several reaction pathways might be designed to end up with the targeted product HFO-1234yf. A straightforward reaction sequence to the desired HFO-1234yf is fluorination of the hydrochloroolefin (HCF) 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) with HF in the presence of a suitable fluorination catalyst as presented by Eq. (1). However, this is an overly simplified reaction path which does not at all reflect the real reactions that might take place depending on the catalyst and the catalytic conditions established. As can be predicted from Scheme 1, the real reaction system is much more complicated and might even be more complex when isomers of the several possible intermediates are taken into account. The most open issue is to identify the reaction pathway that could lead to HFO-1234yf from HCFO-1233xf. This can proceed either *via* direct fluorine replacement of the chlorine atom on the HCFO-1233xf molecule as represented by Eq. (1) or *via* the saturated intermediate 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb). In other words, the main question is whether or not the reaction of HCFO-1233xf with HF to HFO-1234yf proceeds *via* HF addition (with HCFC-244bb as intermediate) followed by loss of HCl, or through direct chlorine/fluorine exchange reaction. It is generally accepted that direct F-for-Cl replacement at an olefinic

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**Scheme 1.** Possible reaction pathways for the reaction of HCFO-1233xf with HF.

C atom is not favourable whereas this is very likely for an  $sp^3$  C atom. Hence, the intermediate formation of the saturated HCFC-244bb as intermediate as it is evidenced in case of the catalytic liquid phase reaction had to be considered for the heterogeneous reaction too. Unfortunately, there is no academic publication on the mechanism of this new but industrially important reaction, just two articles appeared very recently focusing on the characterization of the fluorinated chromia catalyst employed [9,10]. Therein the authors emphasize how synthesis conditions of the fluorinated chromia based catalyst influences the catalytic performance from HCFO-1233xf to HFO-1234yf. The most surprising outcome was that a pre-calcination temperature of about  $550^\circ\text{C}$  causing a crystallization of the catalyst resulted in the best catalytic performance of 63.3% conversion with 59% selectivity for HFO-1234yf and 38% for HFC-245cb. Moreover, carbon deposit at the surface was found to be the major reason for slow deactivation of the catalyst. Thus, the reactivation of the chromia catalyst by oxygen treatment as reported in [10] is logic and in line with many earlier reports on reactivation of chromia based fluorination catalysts (see [11] and references therein). However, information regarding the mechanism/reaction path has not been given. Just from patent literature information regarding the reaction path under catalytic liquid phase conditions is accessible even though this is very limited. Thus, starting from HCFO-1233xf, two different reaction paths have to be taken into account (cf. Scheme 1): (i) preliminary formation of HCFC-244bb followed by further formation of either HFO-1234yf or HFC-245cb and (ii) direct formation of HFO-1234yf which may undergo further consecutive reaction thus forming HFC-245cb. According to the patent literature, it is possible to run a two-step process in which the second step (reaction of HCFO-1233xf) is performed under liquid phase homogeneous catalytic conditions in the presence of antimony pentachloride based catalysts whereupon HFO-1234yf is formed via formation of HCFC-244bb as intermediate [12]. An alternative gas phase process for both reaction steps (formation of HCFO-1233xf and HFO-1234yf) using fluorinated chromia as the heterogeneous catalyst was recently proposed [10]. Unfortunately but expectedly, no information is given regarding the reaction pathway, thus no further input for the work intended in this article could be extracted.

Since the knowledge of the reaction path and the formation of the different possible intermediate compounds are closely related to the dependency of each single reaction step from the reaction conditions, the fundamental understanding of the reaction path is a mandatory basis to control and optimize the reaction conditions. Hence, the present work was intended to elucidate the reaction path of the formation of HFO-1234yf starting from HCFO-1233xf under heterogeneous catalytic gas phase conditions employing a fluorinated chromia catalyst. Therefore, less attention was laid on the optimization of the chromia catalysts since one of us has long time experience with this kind of fluorination catalysts [11].

Therefore a fluorinated chromia catalyst which has shown optimal conditions in the fluorination of C2-haloalkanes was chosen as a standard catalyst. Instead, the main focus was laid on investigating the reactivity and halogen exchange behavior of each possible single intermediate compound by varying the reaction conditions in order to get deeper insights into the mechanism/reaction path of the reactions according to Scheme 1. Fluorinated chromia is by far the most commonly used and most frequently investigated catalyst for this kind of chlorine/fluorine exchange reaction [11,13–16] therefore similar chromia phases were likely to be used for these investigations. Since the main characteristics of these kinds of catalysts have been extensively published many years ago and even the cited publications [9,10] did not add fundamentally new insights, we pretend to repeat these data, and therefore, will just briefly give the details of catalyst preparation and treatment.

## 2. Experimental

### 2.1. Catalyst preparation

The fluorinated chromia catalyst (designated as F-Cr<sub>2</sub>O<sub>3</sub>) was prepared by fluorination of freshly prepared chromia (~5 g) with  $20\text{ ml min}^{-1}$  gaseous HF (Solvay Fluor GmbH) at  $350^\circ\text{C}$  for 16 h in a flow-thru system (Fluorine content 30–40%, determined by fluoride sensitive electrode after soda-potash fusion). To obtain freshly precipitated chromium hydroxide Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Sigma–Aldrich, 99%) was first dissolved in water (0.4 M) followed by addition of ammonia (Acros Organics, 28–30 wt%) until pH=8 was reached. The precipitated solid was separated, washed three times with deionized water and finally calcined at  $400^\circ\text{C}$  for 5 h (previous heating rate  $1^\circ\text{C/min}$ ).

The HS- $\text{AlF}_3$  catalyst (HS=high surface area) was prepared according the fluorolytic sol gel synthesis as described in [17]. In brief, aluminium isopropoxide (Sigma–Aldrich, 98%) was dissolved in isopropanol (Sigma–Aldrich, 98%, dried with standard method) and then a stoichiometric amount anhydrous HF (Solvay Fluor GmbH) dissolved in isopropanol was added. After stirring overnight, the solvent was removed under reduced pressure and elevated temperature ( $80^\circ\text{C}$  in maximum). The dried  $\text{AlF}_3$ -xerogel was directly used and activated under *in situ*-conditions with chlorodifluoromethane (Solvay Fluor GmbH).

Barium and strontium chloride fluoride catalysts (designated BaClF and SrClF) were prepared by *in-situ* chlorination during reaction with HFC-244bb from respective fluorides (Sigma–Aldrich, 99.99%) as shown in [18].

### 2.2. Catalytic reactions

An Inconel tube with a stopper of silver wool was used as steady flow reactor. The organic chlorofluorocarbon compounds (supplied by SynQuest Laboratories: 2-chloro-3,3,3-trifluoropropene (98%), 2,3,3,3-tetrafluoropropene (97%), 2-chloro-1,1,1,2-tetrafluoropropane (98%) and 1,1,1,2,2-pentafluoropropane (99%)) and carrier gases (air and argon) were dosed via mass flow controllers (Quantim Series from Brooks Instruments). HF (Solvay Fluor GmbH) was dosed using a Sonic Nozzle or with a customized mass flow controller from Millipore. The reaction gas mixture leaving the reactor was passed through a sodium hydroxide solution to trap acid gases followed by a calcium chloride column for drying purposes. The detailed reaction conditions for each performed experiment are listed in Table 1. The analysis of the reaction mixtures was performed by gas chromatography either with a Shimadzu GC 17A or Agilent Technologies 7890 gas chromatograph equipped with a GS-GASPRO or ShinCarbon column.

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