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Synthesis of 2,3,3,3-tetrafluoropropene (HFO-1234yf) on chrome-magnesium fluoride catalyst

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Abstract: The analysis of available methods for the production of 2,3,3,3-tetrafluoropropene and laboratory-scale synthesis of this substance using chrome-magnesium fluoride catalyst.

Keywords: 2,3,3,3-tetrafluoropropene, 2-chloro-3,3,3-trifluoropropene, 1,1,1,2,2-pentafluoropropane, gas-phase hydrofluorination, dehydrofluorination.

Introduction

2,3,3,3-tetrafluoropropene ($\text{CF}_3\text{-CF}=\text{CH}_2$; HFO-1234yf) is a forth-generation non-ozone-depleting fluid. HFO-1234yf has got ODP=0 (ozone-depletion-potential), and GWP=4 (global warming potential). EU legislation prohibits the use of refrigerants with GWP>150 in new transport air-conditioners after 2011, and in any transport equipment after 2017 [1]. The performance properties of HFO-1234yf are close to those of R-134a thus making it an eligible drop-in substituent to R-134a refrigerant (GWP=1600) currently used in vehicle air-conditioners.

In this study we made a review of the main methods for HFO-1234yf manufacture, chose the promising route for further investigations and conducted a series of laboratory tests.

Methods for the manufacture of HFO-1234yf

There are a lot of methods for the synthesis of HFO-1234yf, and their drawbacks are well-known: multistep process, low selectivity, environmental hazards, or diseconomy.

Honeywell International Inc patented a method for HFO-1234yf manufacture where trifluorochloroethylene, chloromethane, and hydrogen fluoride are used for raw materials [2]. That is a double-step gas-phase process conducted in two similar reactors. Its first step is a thermal reaction between trifluorochloroethylene and chloromethane (1) resulting in the formation of intermediate 3-chloro-1,1,2-trifluoropropene ($\text{CF}_2=\text{CF-CH}_2\text{Cl}$).



The said intermediate interacts then with hydrogen fluoride following (2), HFO-1234yf being one of the products.



HFO-1234yf is isolated from the product blend by distillation. If fluoromethane (R-41) is used instead of chloromethane the synthesis may be conducted in one reactor, but its selectivity drops dramatically.

Besides of thermal reactions one may apply catalytic interactions [3]. The method is based on the interaction between trifluorochloroethylene (or tetrafluoroethylene) and fluoromethane (R-41) according to (3) or (4), correspondingly. This liquid-phase process uses SbF_5 for catalyst.



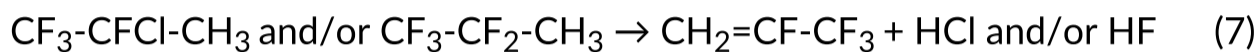
There is a method for HFO-1234yf and 1,3,3,3-tetrafluoropropene (CF₃-CH=CHF; HFO-1234ze) manufacture through the reaction of 3,3,3-trifluoropropyne (CF₃-C≡CH) with hydrogen fluoride according to (5). The process proceeds under heating in gas-phase in the presence of a catalyst containing fluorinated chromium oxide [4].



The chief technology was developed by DuPont and Honeywell that based on it their full-scale production. Their method for HFO-1234yf manufacture is a two-step process that involves two catalytic reactions in two separate reactors [5]. The first step follows (6), i.e. 2-chloro-3,3,3-trifluoropropene (CF₃-CCl=CH₂; HFO-1233xf) interacts in liquid with hydrogen fluoride on SbCl₅ catalyst.



The second step (in the second reactor) involves dehydrochlorination and/or dehydrofluorination of the resulting blend that contains 1,1,1-trifluoro-2-chloropropane (CF₃-CFCl-CH₃) and/or 2,2,3,3,3-pentafluoropropane (CF₃-CF₂-CH₃; HFC-245cb); the reaction follows (7). The second process step is catalyzed by activated carbon (various grades).



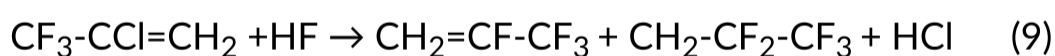
Another method for the manufacture of HFO-1234yf makes use of dehydrofluorination of 1,1,1,2,3-pentafluoropropane (CF₃-CHF-CH₂F; HFC-245eb) following (8) [6].



The process may be operated either in liquid (in an alkaline solution), or in gas, using a catalyst that contains chromium oxide (Cr³⁺) and alkaline metals.

In full-scale production they prefer the methods based on commercially available feedstock, solid catalysts, and gas-phase processes that require the less complicated equipment. In our experimental studies for feedstock we used 2-chloro-3,3,3-trifluoropropene (CF₃-CCl=CH₂; HFO-1233xf), and for catalyst we chose chrome-magnesium fluoride that contained 5-7% of chromium (based on Cr³⁺) developed by RSC «Applied Chemistry». [7]

Our study based on the process patented by Daikin Industries, Ltd, where HFO-1234yf is produced through the interaction between HFO-1233xf and hydrogen fluoride according to (9) [8]. Unlike the method described in [5] the synthesis proceeds in one stage, in gas-phase, using a catalyst that contains fluorinated chromium oxide.



Experimental

Experimental studies on gas-phase hydrofluorination were conducted at laboratory-scale using a 50 cm³ nickel reactor charged with 45g of chrome-magnesium fluoride catalyst that contained 5-7% of chromium (basing on Cr³⁺). Upstream to the reactor there was an over-heater to heat the reaction blend up to 250-270°C. The reactor operation temperature range was 350 - 450°C. HF : HFO-1233xf mole ratio varied from 2:1 to 19:1, while the contact time varied from 16 to 23s. Downstream to the reactor the gas mixture underwent neutralization, then accumulated in a rubber collector, and condensed in a cylinder-receiver cooled to minus 30°C. The synthesis process followed (9), and the resulting products after neutralization were analysed with the help of GC instrument "Tsvet - 800".

In our study we revealed that the reaction resulted in the formation of 1,1,1,2,2-pentafluoropropane (HFC-245eb) in amount nearly equal to that of the target HFO-1234yf, and a number of fluorinated products, their content ranging from ten to below one percent depending on the process conditions. The test results are shown in Table 1. It should be marked that by-produced 1,1,1,2,2-pentafluoropropane may be further dehydrofluorinated to HFO-1234yf according to (7). The method is disclosed in patent [5].

Table 1. HFO-1234yf and HFO-1233xf formation depending on the process temperature.

T (°C)	Conversion, % CF ₃ -CCl=CH ₂	Content in reaction mixture, % CF ₃ -CF=CH ₂	Content in reaction mixture, % CF ₃ -CF ₂ -CH ₃	Content in mixture, % impurities

350	18,5	9,1	8,7	0,7
380	18,2	10,0	7,9	0,3
400	19,2	11,3	7,0	0,9
420	24,4	10,1	10,0	4,3
450	29,3	11,4	7,4	10,5

From Table 1 one may see that the with chrome-magnesium fluoride catalyst the process was selective up to 400°C, and the total content of by-products, except for 1,1,1,2,2-pentafluoropropane, did not exceed 0.3 – 0.9 %. At higher temperature the conversion of original 2-chloro-3,3,3-trifluoropropene was even higher, but its selectivity decreased, and the total content of by-products achieved 10%.

Taking into account the possibility of dehydrofluorination of by-produced 1,1,1,2,2-pentafluoropropane, the total yield of «useful» products may reach 20%. After the separation of reaction blend at a rectification column non-reacted HFO-1233xf may be recycled into the synthesis process.

Conclusions

1. The main HFO-1234yf production methods are reviewed and the focus area is chosen for laboratory studies.
2. Laboratory-scale tests with chrome-magnesium fluoride catalyst (developed by RSC “Applied Chemistry”) has shown that total content of HFO-1234yf and 1,1,1,2,2-pentafluoropropane in the reaction blend at 350 - 420°C achieved 18-20%.

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