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## Chemistry and Technology of Polyfluorinated Organic Compounds Based on New Aggression Resistant Catalysts

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**Abstract:** Scientific principles of selection of effective catalysts of direct gas-phase fluorination of organic compounds have been developed. The use of created catalysts improve existing and allow to develop the new technologies of polyfluorinated organic products.

**Keywords:** Organofluorine compounds, fluorine, cobalt trifluoride, isomerization, heterogeneous catalyst, catalytic fluorination.

### 1. Introduction

As materials possessing a number of findunique properties fluororganic compounds find wide application in different fields of technics. Fluoroplasts, fluorelastomer, special fluorinated lubricants and liquids are irreplaceable while working with aggressive media under conditions вЂ“ using of those materials, particularly, led to revolution in the atomic industry technology, in airspace and reaction (jet) technics, as well as in high-speed aviation.

Special physical and chemical properties of fluorochlororganic liquids (e.g. chladones and freons) provided/provoked rapid development of refrigerating technics.

Compositions using polyfluorinated organic compounds (вЂ“light waterвЂ“) form the base for modern flame extinguishing means.

Aqueous emulsions of a number of fluororganic liquids, in particular perfluorodecaline are the effective carriers of oxygen; this creates perspectives for their usage as blood substituents in medicine. High biological activity of a number of polyfluorinated organic compounds is being used in both medicine (cancer fighting medicines) and agriculture (pesticides). Even that, far from full list of application fields for fluororganic products allows appreciating of their applied meaning. A wide range of perfluorinated products can be obtained by fluorination of polyfluorinated organic compounds using elemental fluorine. At the same timestudies on interaction of fluorine with organic compounds are held by non-selective, explosive nature of that process caused by its high exothermicity.

Application of heterogenic catalysts is one of the ways to increase selectivity of direct fluorination; however, it should be noted, that though the achieved level of catalytic fluorination technique allows singnificant increase of selectivity compare to homogenous gas-phase process, nevertheless it is as a rule characterized by high destruction of substrate, and sometimes by contraversioal, unrepeatabe results. The developed (known) catalysts proved to be not effective enough for usage on enlatrged, industrial scale, and catalytic fluorination method, as a consequence, did not gain practical ground of wide range. We also should note, that high reactivity of fluorine dramatically narrows the range of materials applicable for preparation of stable catalysts. All of that outlines the actuality of studies aimed at creation of effective aggression resostant heterogenic contacts and development of direct fluorination technique based on them, which backs the opportunity of its wide range practical usage. Solving this important task was held in our opinion by the absence of new rational approaches to the selection of direct organic compounds gas-phase fluorination catalysts.

Selectivity and rate/speed of a whole class of practically important thermal transformations of polyfluorinated organic compounds (oxidation, dechlorination with hydrogen, isomerization etc.) also can be increased when using effective catalysts, however, practical application of catalysis for solving the actual tasks of fluorine products technology regarding decreasing the materials consumption and energy capacity, environmental pollution, synthesis of new unique materials is obviously not enough. When creating stable, commercial catalysts of thermal transformations of polyfluorinated organic compounds a high aggressivity of a reaction medium is also one of the problems, that results in premature destruction of heterogenic contacts. All that stipulates the actuality of studies in the field of selection of effective aggression resistant catalysts of thermal transformations of polyfluorinated organic compounds.

In the first part of the present work the scientific principles of selection of effective catalysts of organic compounds direct gas-phase fluorination are developed and for the first time the opportunity of sharp increase of selectivity and rate of fluorination by undiluted fluorine at directed change of nature of catalytic composition is experimentally shown. The selected universal aggression resistant catalytic composition  $\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$  allowed not only carrying out the synthesis of a number of practically important perfluorocarbonic products with quantitative yield (2-perfluoromethylperfluoropentane, 3-perfluoroisopropyl-2-perfluoromethylperfluoropentane, perfluoroethane, perfluorobutane, pentafluorochloroethane etc.), but also for the first time introduce into industrial practice the technology of direct catalytic fluorination (the production of perfluorodimethylperfluorocyclohexane, the purification of perfluorodecaline, B-I, M-I liquids, lubricants, regeneration of fluorocarbonic liquids etc.)

In the second part of the work based on the systematical study of wide class of thermal gas-phase transformations of polyfluorinated organic compounds it has been stated, that  $\text{O}_2\text{-Al}_2\text{O}_3$  is a universal aggression resistant carrier for the catalysts of these processes. A number of new effective heterogeneous contacts Based on  $\text{O}_2\text{-Al}_2\text{O}_3$  especially for the catalysis of 1,2-dichlorohexafluoropropane and 1,2-difluorotetrachloroethane dechlorination using hydrogen, as well as oxidation of tetrafluoroethylene.

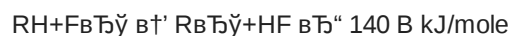
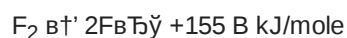
As a result of studying the kinetic particularities of thermal gas-phase reactions of polyfluorinated organic compounds it has been stated, that dehydrated activated carbon is an effective aggression resistant catalyst of nucleophilic type and it can be widely used even in unmodified form, especially, for catalysis of hexafluoropropyleneoxide  $\text{C}_3\text{F}_8$  isomerization, destruction of carbonyldifluoride oligomers, perfluorinated polyperoxides and  $\text{C}_2\text{F}_4$ -chlorperfluoroalkylfluorosulphates, hydrolysis and hydrofluorination of perfluoroisobutylene.

Application of created thermal aggressive resistant catalysts allowed improving existing and developing new resource saving, more ecologically pure technologies of a number of polyfluorinated organic products (hexafluoropropylene, 1,2-difluorodichloroethylene, carbonyldifluoride, perfluoropolyoxamethylenacetylfluorides etc.)

## 2. Direct Catalytic Fluorination Of Polyfluorinated Organic Compounds.

### 2.1. Analytical Review

Chemism of direct fluorination of organic compounds, which according to [1-3] goes along radical type, is to a great extent determined by thermodynamical particularities of its certain stages:



These particularities lie in rather low energy of dissociation of molecular fluorine (155 kJ/mole) and high heat which is isolating during fluorination (more than 420 kJ/mole of fluorine). If we take into account, that the energy of C-C bond in the molecules of hydrocarbons consists approximately 330 kJ/mole it is getting clear, why the branching of chains with destruction of carbon frame of substrate is quite typical for direct fluorination.

The dilution of fluorine with inert gases [4-11], the dissolution of organic substrate in the inert to fluorine solvent [12-18], the cooling of reaction mixtures [19-32], using of reactors with special constructions [33-37] - jet one, with zone heating, as well as controlled fluorination in solid phase [38-51] are applied to increase the selectivity of direct fluorination.

Along with direct fluorination electrical and chemical [52-58] and metal and fluoride methods [59-70] have been developing; the last one is based on using metal fluorides mainly cobalt in the state of their higher valency as fluorinating agents.

Using these milder compare to elemental fluorine fluorinating agents allows providing firm control of fluorination temperature, which is especially important when conducting a process on an enlarged scale. That is why the metal fluoride method inspite of high material and energy consumption as well as low productivity formed the base of existing fluorinating technology for organic compounds.

One of the ways to increase selectivity of fluorination is conducting interaction of elemental fluorine and organic substrate in the layer of catalyst [71]. During WWII that method formed the base for the first production of strategically important fluorocarbons [72]. As it follows from [73-75] the dispersing of heat isolating during fluorination is the main function of catalyst (packing), that allows escaping local overheatings, lowering average mass temperature of reaction gases and then by doing so decrease the input of destruction of initial raw materials, intermediate and end products. Due to that the wide use of metal catalysts  $\text{CoF}_3$  copper, silver, nickel of high thermal conductivity is becoming understandable. [72-79].

For the first time the use of metal catalyst at fluorination according to [2] was described by by Fredenhagen and Kadenbach: fluorine mixed with nitrogen (mole ratio 1: 1) was being introduced into glass reactor (diameter  $\text{D} = 6\text{cm}$ , length  $\text{L} = 40\text{cm}$ ) by perfluorinated copper tube wrapped in a few

layers of copper net. The reactor was being turned at such a rate that the organic liquid in the bottom dispersed in the form of film along its walls.

Later Bigelow used the reactor of analogous construction (diameter -2,8cm, length вЂ“ 75cm, input of fluorine and nitrogen at a mole ratio 1:1, 6 along perfluorinated copper tube wrapped with copper net) for fluorination of tetrachloroethylene and hexachloroethane. The substrate was being put on the bottom of reactor and also closed with the copper net; yield of 1,2-difluorotetrachloroethane вЂ“ the product of selective attachment of fluorine achieved 20% at that.

In [2,73,80] the data on gas-phase direct fluorination of ethane, methane, ethyl chloride, 1,2-dichloropropane, benzole, toluene, benzotrifluoride and acetone in the layer of dense nozzle made of copper net or copper wire rolls is listed. Besides the main product вЂ“ tetrafluoromethane, hexa-, penta-, tetra- and trifluoroethane have been obtained fluorinating ethane; the formation of di- and monofluoromethane was not observed. During fluorination of methane, besides tetra-, tri-, di and monofluoromethane the formation of hexafluoroethane and octafluoropropane has been registered, which shows the association of intermediate radicals [2,73].

During fluorination of ethyl chloride 1,1-dichloroethane and 1,1-dichlorine-2,2-difluoroethane have been found in the reaction products, besides tetrafluoromethane and products of selective substitution of hydrogen atoms for fluorine. This result points out, that during fluorination chlorination occurs; it takes place either due to formation of fluorine chloride which is a strong chlorinating agent or as a consequence of substarte вЂ“s interaction with isolating free chlorine [73].

The same results were obtained during gas-phase fluorination of trichloroethylene over ground copper [2] - tetrachlorodifluoroethane is one of the main products of reaction. According to [80] trichloropentafluoropropane and tetrachlorotetrafluoropropane are one of the main products of reaction of direct fluorination of 1,2-dichloropropane in the layer of nozzle made of copper wire at 429-470 K; the yield of 1,2-dichlorohexafluoropropane вЂ“ the product of selective substitution of hydrogen atoms for fluorine is 15-25% under these conditions.

Destruction of carbon frame and polymerization are rather typical for direct gas-phase fluorination in the layer of copper nozzle; thus,  $CF_4$ ,  $C_2F_6$ ,  $C_3F_8$ ,  $C_4F_{10}$ ,  $C_5F_{12}$ ,  $C_6F_{12}$ ,  $C_6HF_{11}$  and  $C_{12}F_{22}$  [73] have been isolated from benzene fluorination products. The yield of perfluorodecaline during tetralyne (620 вЂ“ 650K) fluorination over silver plated copper filings amounted only 15% [81]. Only insignificant amounts of perfluorodecaline form during fluorination of O±-methylnaphtalene over silverplated copper wire [73]. During fluorination of benzotrifluoride under the same conditions significant amounts of destruction products and partial fluorination products, including perfluorocyclohexane and perfluoromethylmonohydroperfluorocyclohexane are formed besides perfluoromethylperfluorocyclohexane. [73].

At the same time [72] it is being noted, that modifying of copper filings using silver (in rare cases вЂ“ gold) allows achieving significant increase of selective exhaustive fluorination products yield (Table 1).

Also 2,2,3-trimethylbutane, 2,2,4-trimethylpentane, cetane, toluene, mezytylene, reten and christen [72] were subject to direct fluorination using that method. The characteristics of products of their selective fluorination are listed in [82].

In [73] the following conditions are formulated to achieve maximum yield of fluorocarbons at direct fluorination:

- application of catalyst вЂ“ silver on metallic nozzle;
- carrying out the process at the excess of fluorine;
- keeping the temperature within the range of 410-600 K (at temperature below 410 K organic compounds condensate at nozzle and destruct in fluorine, and at temperature over 600 K the nozzle cripples);
- fluorine and organic substarte vapour must mix up in the catalyst вЂ“s layer.

**Table 1. Fluorination of Hydrocarbons Over Silver Plated Copper Nozzle [72].**

Initial Compound	Reaction Temperature, K	Yield of Selective Exhaustive Fluorination Product, % of Theoretical One
$C_6H_6$	538	58
n- $C_7H_{16}$	408	62
$C_6H_5CF_3$	473	85

$C_6H_4(CF_3)_2$	473	87
Antracene	573	43
Naphthenic oil	563	15
Aromatic oil	573	19

According to /2/ the copper fluoride covering copper nozzle is not a fluorinating agent as direct experiments show. In the authors' opinion, this fact reduces the nozzle function to the elimination of local overheatings and excludes the chance of its catalytic influence. On the contrary, silver difluoride is an effective fluorinating agent /2,61/. In this connection the authors think /72/, that silver fluoride is the main fluorinating agent when using copper nozzle modified by silver, and the role of elemental fluorine is reduced to regeneration of that fluoride.

At the same time authors /74, 75/ come to the contrary conclusions and think, that modification of copper nozzle using silver does not have any significant influence on its catalytic properties. Comparative data on benzene fluorination at 538K at different metallic catalysts /74/ are listed below (Table 2).

Analyzing the listed information we can see, that catalytic influence of most metal nozzles is practically the same; it can also be seen, that silver plating does not influence catalytic properties of copper filings.

**Table 2.** Direct Catalytic Fluorination Of Benzene.

Catalyst	Yield of $C_6F_{12}$ , % Of Theoretical One
Copper Filings	29
Silver Plated Copper Filings	26
Gold Plated Copper Filings	35
Nickel Plated Copper Filings	23
Cobalt Covered Copper Filings	28
Brass Filings	24
Amalgamated Copper Filings	10
Copper Wire Plated with Rhodium	17
Chromium Plated Copper Filings	7

In /2/ it is noted, that in some cases modified catalysts proved to be less effective, than unplated copper and nickel fraction, and we make a conclusion, that the main function of metal nozzle is in dispersing of reaction heat, as a consequence of which the fluorination goes at moderate temperatures. It is also being noted /2/, that the form of nozzle (net, filing, fraction) is less important, than the nature of metal surface.

Cobalt trifluoride is also described as a catalyst of direct fluorination of aromatic compounds /83-85/. The processing of  $\alpha$ -methyl naphthalene using elemental fluorine at 633 K in the layer of cobalt trifluoride is mainly accompanied by destruction; the yield of perfluoromethylperfluorodecaline amounted to 11%. The fluorination of perchlorocyclopentadiene under the same conditions results in formation of pentachloropentafluorocyclopentane with the yield of 70% /83/.

We are informed about obtaining of liquid fluorocarbons by exhaustive fluorination of pentane, hexane, toluene, metha-xylol, tetralyne, O±-methylnaphthalene /84, 85/, alkyladamantanes, adamantancarboxylic acids, derivatives of bicycloheptane, bicyclononane /86/; the substrate is evaporated and filtered through fluidized layer of cobalt trifluoride at 600-725 K over elemental fluorine.

Partial fluorination of hydrocarbons by fluorides of silver, manganese, sulphur or antimony precedes the stage of fluorination using elemental fluorine /86/. Electrochemical fluorination of cycloalkenes or their partly substituted fluorine derivatives in anhydrous hydrogen fluoride over cobalt fluorides, nickel and manganese fluorides is described in /56/.

The fluorination of organic compounds on the particles of alkali metal fluoride dispersed in the flow of inert gas is described in /87,88/. Authors /87/ mixed organic substrate with sodium fluoride, carefully triturated it, sprayed in the flow of nitrogen and introduced for fluorination; aromatic compounds (benzene toluene, naphthalene), aliphatic and cycloaliphatic hydrocarbons (for example, hexane, dodecan), polyethylene, substituted hydrocarbons (nitrobenzene, benzoic acid), and also some dibasic acids were used as substrate. A significant input of association of intermediate radicals is noticed at low-temperature fluorination of aromatic compounds on sodium fluoride in /87/. Thus, the mixture of compounds of average molecular weight of 670 was obtained at 253 K using fluorination of benzene by fluorine, diluted nitrogen (rate 1 : 10), products of average molecular weight of about 1000 were obtained under analogous conditions out of toluene.

The authors /88/ prepared spray of sodium fluoride in the flow of helium beforehand, mixed it with the flow of helium saturated with substare vapours вЂ“ pentane, cyclohexane or dioxane, and directed them into precooled fluorinating reactor. Fluorinating cyclohexane, for example, at 210 K at at rate fluorine : substrate equal to 1 : 1 and at tenfold dilution of fluorine with helium monofluorocyclohexane of 26% yield, difluorocyclohexane (20%) as well as other polyfluorinated products were obtained. Authors /88/ have used the reactor equipped with multisection cooling allowing keeping up the certain temperature in each zone of reaction zone for controlling the selectivity of fluorination. Direct fluorination of nitrogen-, oxygen-, and sulphur containing organic compounds at alkali metals fluorides is described in /89-97/.

The catalytic fluorination of 2-hydroperfluoropropane at copper, silver, gold, mercury, cobalt, platinum, their fluorides or alloies with obtaining of octafluoropropane is described in /98-100/. Initially the starting material вЂ“ hexafluoropropylene is being processed with anhydrous hydrogen fluoride at 370-570 K over chrome oxifluoride. 2-hydroperfluoropropane forming at that is put into the layer of catalyst at 370-620 K together with elemental fluorine (fluorine excess is (5-30%), diluted nitrogen (1 : 1). The yield of octafluoropropane at 510-520 K on silver plated copper filings preliminary treated with fluorine amounted to almost 95% of theoretical one (onto hexafluoropropylene reacted).

The obtaining of octafluoropropane using direct fluorination of propane or propylene at 330-510 K over fused porous aluminium oxide is described in /101, 102/. Fluorine is introduced into the inner part of the tube made of fused aluminium oxide, through the pores of which it is migrating into the outer part, where the carbon is introduced to. At that the yield of octafluoropropane amounts to 10-85% of the one possible in theory /101/. Metallic copper and nickel /102, 103/ are described as porous element; porous tube, thourh which fluorine is migrating can be impregnated with catalytically active compounds /104/.

Cobalt /73/, aluminium /105/, antimony and titanium /106/ fluorides as well as chloric iron are used as catalysts of selective substitution of haloid atoms (mainly, fluorine) for fluorine during direct fluorination of organic compounds. Thus, authors /105/ used aluminium trifluoride (in the form of crystals of 5003e size) preliminary contacted with oxygen at 670-730 K /108/ as a catalyst; the fluorination was carried out within the temperature range of 380 K (at the entry of reactor) to 630 K (at the exit of reactor) at mole ratio chlorofluorocarbon : fluorine equal to 1 : 1,7 and contacting period equal to 125 sec. Application of aluminium fluoride allowed obtaining of perfluoropropane of 81% yield out of 1,2,2-trichloroperfluoropropane, and perfluorobutane (yield is 76%) out of 2,3,3-trichloroperfluorobutane.

The work of Bigelow and co-workers, in which acetone was used as a substarte, and copper net вЂ“ as a catalyst is considered a first successful experiment on direct gas-phase fluorination of oxygen containing organic compounds. Reaction gases contained significant amounts of destruction products вЂ“ tetrafluoromethane, carbonyldifluoride and perfluoroacetylfluoride besides perfluoroacetone and products of incomplete fluorination of acetone. The yield of perfluoroacetone amounted to 10% at a rate of fluorine : acetone : nitrogen equal to 6:1:19 and starting temperature in reactor of 333 K. Fluorination of acetone with more concentrated fluorine (fluorine : nitrogen = 1 : 1) at temperature of 473 K in reactor filled with gold plated or platinum plated copper filings is characterized by increasing of yield of destruction products. Octafluorobutanone -2 /2/ is obtained by fluorination of methylethylketone with the yield of 10% under analogous conditions.

According to /73/ Cady and co-workers carried out direct fluorination of alcohols for the first time; carbonyl fluoride and trimethylhypofluorite were the main products of methyl alcohol fluorination with diluted alcohol at 450 K over silver plated cooper band. In /109-120/ you can find information on obtaining trifluoromethylhypofluorite, difluoromethylen-bis-hypofluorite and perfluoroalkylhypofluorites by selective attachment of fluorine along double bond carbon-oxygen; alkali metals fluorides (especially вЂ“ cesium), active at even 195 K and below and silver and nickel fluorides are effective catalysts of this process.

The results on direct fluorination of nitrogen containing organic compounds are listed in /121, 122/. Tetrafluoromethane was the main product of methylamine fluorination at 370 K (rate fluorine : amine was equal to 5 : 1 : 15) in the layer of copper fraction; at that  $CF_3NF_2$ ,  $CF_3CF_2NF_2$  and  $(CF_3)_2NF$  /121/ also

are formed. The composition of reaction products shows significant destruction of raw materials and further partial association of forming radicals.

Fluorination of malononitrile at 523 K in the layer of copper fraction (rate fluorine : malononitrile : nitrogen equaled to 3: 1 : 9) is characterized by formation of tetrafluoromethane (13 mass.%), octafluoropropane (30 mass. %), and also products of destructive fluorination and association of forming radicals /122/.

A number of sulphur-organic compounds had undergone direct catalytic fluorination; thus, in /71/ we are being informed, that interaction of methylmercaptane with elemental fluorine at 437 K in the layer of silver modified copper net is accompanied by forming (with small yield) of hydrogen atoms  $\text{vT}^{\text{TM}}$  selective substitution products -  $\text{CF}_3\text{SF}_5$  (15%)  $\text{P}\ddot{\text{e}}$   $\text{CF}_3\text{SHF}_4$  (15%).

Thus, direct gas-phase fluorination of organic compounds is characterized as a rule, by significant input of destructive fluorination with breakage of C-C bonds in the molecule of substrate, which is due to high energy isolating during elemental stages of that exothermal process. Heterogenic catalysts  $\text{vT}^{\text{TM}}$  mainly metals (copper as a rule), which in a number of cases are being modified (in most cases  $\text{vT}^{\text{TM}}$  using silver) are used for decrease of destruction at gas-phase fluorination. Metallic catalysts are chosen because of their high thermal conductivity, it provides for effective heat removing from the areas of local overheating and thereafter decreasing of destruction.

At the same time it should be noted, that though catalytic fluorination allows significant increasing of process selectivity (compare to homogenous gas-phase fluorination), nevertheless it is characterized as a rule, by relatively high destruction of the raw materials, and sometimes controversial, unrepeatable results. The developed catalysts proved to be insufficiently effective for their use in on enlarged industrial scale, and as a consequence the catalytic fluorination method did not receive wide practical application. This fact outlines the actuality of studies aimed at creation of effective catalysts and development of direct fluorination technology based on them to the level providing the opportunity of its practical use on a large scale. In our opinion, the resolving of this important task was held by the absence of new, rational approaches to the creation of effective catalysts of direct gas-phase fluorination of organic compounds.

## 2.2 Scientific Foundations for Selection of Effective Aggression Resistant Catalysts Of Organic Compounds $\text{vT}^{\text{TM}}$ Direct Gas-Phase Fluorination

The following considerations are laid as a base of developing by us approach for selection of effective catalysts of fluorination of organic compounds.

1. Gas-phase interaction of organic compounds with fluorine leads to formation of intermediate adducts possessing excessive energy. These exited adducts undergo either spontaneous destruction or transfer into main state due to clash with molecules of gas phase or surface.

2. We can suppose, that improving the selectivity of interaction of organic compounds and fluorine will be achieved at localization of elemental acts of fluorination on the surface. In this case the probability of timely removal of excessive energy of exited adducts along the bonds with elements of nozzle surface, which acts as averaging  $\text{vT}^{\text{TM}}$  thermal reservoir  $\text{vT}^{\text{TM}}$  sharply increases. *At that the destruction of exited adducts decreases, but not the thermal destruction (for example, because of strong heating of reaction gases).*

3. To localize the elemental acts on the surface not only has the catalyst to intensively sorbate molecular fluorine, e. g. to possess well-developed related to fluorine surface, but also activate it.

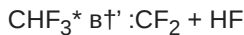
Only in this case kinetic background for localization of the process directly on the surface can appear.

Thus, the preference at choosing the fluorination catalyst must be given to the contacts with developed surface modified using activating fluorine additives. The presence of developed surface leads to improving of selectivity also due to the breakage of chains of radical branching process. According to that the low effectiveness of metallic catalysts is becoming clear, their exterior surface is quite small.

4. High aggression of the medium is a specific feature of direct fluorination; it applies additional requirements to the stability of catalysts.

The main principal feature of this new approach to the creation of effective catalysts of direct fluorination is concluded in the fact, that we can suppose the possibility of sharp increase in selectivity due to localization of fluorination acts on the surface, but not due decreasing or averaging of reaction gases temperature (removing of local overheatings) when using thermal conductive nozzle  $\text{vT}^{\text{TM}}$  catalyst, as it had been done before.

Actually, the destruction of raw materials is often observed /19, 87, 88/ at fluorination under regulated mild conditions (273 K and below), when thermal breakage of molecular bonds is unlikely to happen  $\text{vT}^{\text{TM}}$  this effect can be explained only by the decomposition of energetically exited adducts /123,124/. Energetic branching of chains is quite typical for low-temperature gas-phase fluorination and defines, in particular, kinetic particularities of its passing /125-136/. Thus, authors /125-129/ explain the significant decreasing of fluorination rate at transfer from difluoromethane to trifluoromethane by the possibility of chains branching at fluorination of  $\text{CH}_2\text{F}_2$  at account of decomposition of exited molecule of forming  $\text{CHF}_3$ :



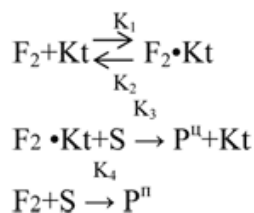
During fluorination of trifluoromethane such an opportunity is absent, that causes abrupt decrease of the process rate. In this connection the observed in /132-133/ high fluorination rate of dichloromethane and fluorochloromethane  $\text{CF}_2$  there is also a chance of energetic branching of chains during decomposition of energy-saturated intermediate adducts.

In this connection it is interesting, that difluoromethane fluorination rate significantly decreases, and the yield of trifluoromethane is increasing at highering of partial pressure of inert gas; this effect can be explained /134/ by deactivation of excited molecules of trifluoromethane forming at clash with molecules of inert gas.

The ratio of energetically excited molecules at fluorination decomposition rate and thermally active molecules decomposition rate is clearly characterized by the data on selectivity of fluorochloromethane fluorination /133/  $\text{CF}_2$  decomposition of difluorochloromethane forming passes only with detaching of anhydrous hydrogen fluoride, but not hydrogen chloride, which is typical for thermally active molecule of difluorochloromethane, for example, at its pyrolysis /137/.

Decomposition rate along excited C-F bond is significantly higher than redistribution rate of excessive energy along non-excited bonds, that causes unusual selectivity of destruction of difluorochloromethane forming /133/. These results speak about/demonstrate/show the impact of decomposition of forming excited adducts on selectivity of fluorination of organic compounds using elemental fluorine.

Below you will find the principal kinetic scheme for the discussed above model of catalytic fluorination, analysis of which clearly illustrates the demands to effective catalyst<sup>1</sup>:



<sup>1</sup>The scheme has got common character and doesn't focus on, for example, elementary stages, their radical mechanism, and describes only main patterns of fluorination characterized by the presence of competing processes in gaseous phase and at the surface.

At that, it is being supposed, that interaction between adsorbed fluorine ( $\text{F}_2 \cdot \text{Kt}$ ) and substrate (S) at the surface of catalyst is accompanied by forming of only target products ( $\text{P}^{\text{C}}$ ) at a rate characterized by effective  $K_3$ ; the fluorination with participation of gasiform fluorine ( $\text{F}_2$ ), which is characterized by  $K_4$  constant leads to forming of only by-products ( $\text{P}^{\text{I}}$ ).

The analysis of this scheme shows, that reciprocal value of fluorination selectivity ( $1/\alpha$ ), is described by the equation:

$$\frac{1}{\alpha} = 1 + \frac{1 - V_{\text{Kt}}}{V_{\text{Kt}}} \cdot \frac{1}{\rho_{\text{Kt}} \cdot S_{\text{vD}} \cdot C_{\text{Kt}}} \left[ \frac{K_4}{K_3} \left( \frac{K_2}{K_1} + C_{\text{F}_2} \right) + \frac{K_4}{K_1} C_{\text{S}} \right]$$

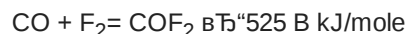
Driving from that it is seen, that selective fluorination is provoked by the increase of share of reaction volume, filled with catalyst ( $V_{\text{Kt}}$ ), the increase of its specific surface ( $S_{\text{vD}}$ ) and surface concentration of active centres ( $C_{\text{Kt}}$ ) as well as increased sorption ability towards molecular fluorine presented at contact ( $K_2/K_1$ ) and its activating influence onto adsorbed fluorine ( $K_3$ ). On the contrary, selectivity is decreasing at gas-phase fluorination input increasing ( $K_4$ ), as well as concentrations of fluorine ( $C_{\text{F}_2}$ ) and substrate (Cs).

It should be noted, that demands to effective catalyst of fluorination ensuing from model under consideration are rather universal; for example, the activation of fluorine may include its dissociation on the surface forming atomic fluorine, which reactivity is increased to a wide range of substrates  $\text{CF}_2$  classes (but not to all of them). The selection of catalyst component activating fluorine most effectively is a first stage in determining the composition of optimal catalytic composition.

Gas-phase interaction of carbon and fluorine oxides forming trifluoromethylhypofluorite (THF)  $\text{CF}_2$  the effective initiator and reagent to synthesize a wide range of fluororganic compounds was studied as a model reaction /138  $\text{CF}_2$  140/.

### Catalytic Fluorination of Carbon Oxide

Gas-phase fluorination of carbonoxide includes two stages:



The rate of second stage of this process is interaction of carbonyl difluoride and fluorine can be significantly increased when using catalyst or initiator [112-118, 141-142].

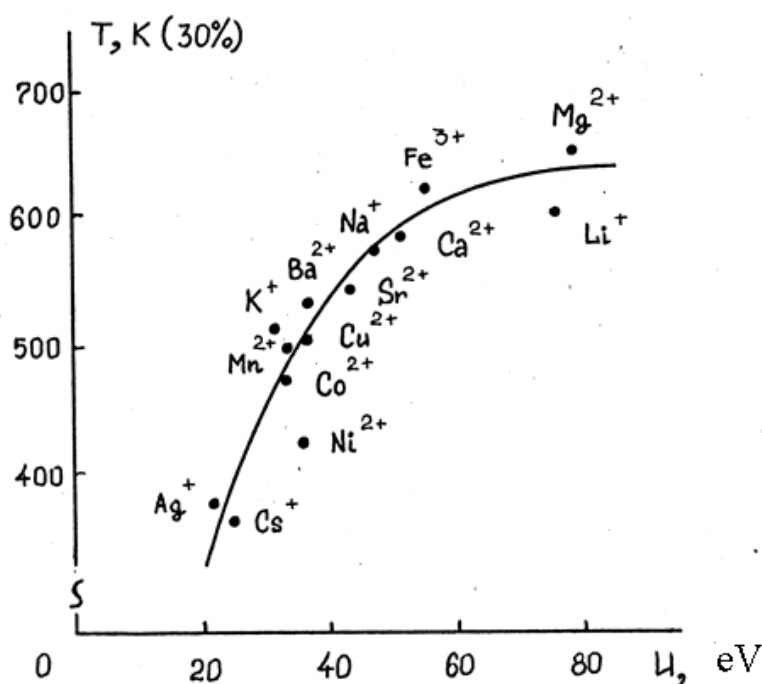
Studying the catalytic properties of silver, nickel, cobalt, copper, manganese, iron, cesium, potassium, lithium, barium, strontium, calcium and magnesium fluorides applied on  $\text{O}_i\text{-Al}_2\text{O}_3$  in equimolar quantities using impregnation method proved, that activity of those catalysts is unequal and it is determined by the nature of metal fluoride applied. As you can see from the Pic. 1 the activity correlates with ionization potential of corresponding cation. This result is understandable if we take into account, that the character of fluorine molecule is pronounced as electron-seeking. Partial transfer of electrons from cation of ionization low potential onto  $\pi$ -loosening orbital of adsorbed fluorine molecule eases the dissociation of halogen forming active atomic fluorine [143], that causes increase of reaction rate.

Applied nickel, silver and cesium fluorides are of most high catalytic activity as it follows from Pic. 1.

In [144-147] it is being noted, that nickel is an effective catalyst of dissociation of molecular fluorine into atoms. Adducts of interaction of nickel and fluorine are described by the formula  $\text{NiF}_x$ , where  $2 \leq x \leq 3$ ; their IR-spectra coincide with spectra of nickel trifluoride [142, 145, 148]. Adducts of interaction of nickel chloride and fluorine are also described by the formula of  $\text{NiF}_{2.5}$  [149].

Obtained in [139] kinetics data on direct fluorination of carbonyl difluoride on nickel difluoride agrees with process scheme including atomization of fluorine on catalyst (reaction order on fluorine equals to 1, 5). According to estimates listed in [139] the rate of fluorine dissociation at nickel difluoride increases by more than 5 times (compare to non-catalytic dissociation). Atomization of fluorine on the surface of lowest fluorides of nickel and silver accompanied by forming of highest fluorides [149] apparently determines their catalytic activity in direct fluorination of carbon oxide.

Catalytic influence of cesium fluoride at fluorination of carbonyl fluoride is the intermediate product in the synthesis of THF is caused as follows from [112-116] by activation of substrate (and not the fluorine) forming corresponding cesium alcoxide; this result was obtained when carrying out the reaction under rather mild conditions is 200 K and below.



**Picture 1.** Correlation of applied (coated) metal fluorides activity in catalytic fluorination of carbon oxide and ionization potentials ( $U$ , eV) of corresponding cations ( $T$  temperature was taken as a measure of activity, at that  $T$  the concentration of trifluoromethylhypofluorite in reaction gases reached 30 volume % at a rate of reagents supply equal to  $1800 \text{ hour}^{-1}$  and mole ratio equal to  $\text{F}_2:\text{CO}=2$ ).

At the same time it is being noted in [150, 151], that alkali metals fluorooxides, in particular cesium, are being destroyed at temperature over 470 K and, thus, are unstable under studied conditions of THF synthesis (up to 650 K). That is why the catalytic influence of cesium fluoride at high-temperature fluorination of carbon oxide till THF can be caused by fluorine activation.

High-temperature catalytic fluorination of carbon oxide, including the one at cesium fluoride applied is characterized, as the analysis of reaction gases proved/showed, by forming of significant amounts of



bistrifluoromethyl peroxide /152/, what, in author's opinion /115/, testifies in favour of fluorination radical mechanism with atomic fluorine participating.

It should be noted, that electrochemical fluorination of carbon oxide, carbonyldichloride and carbonyldifluoride under mild conditions passing with participation of atomic fluorine is characterized by high yield of THF /153-154/. That result points out high activity of fluorine atoms at synthesis of THF and witnesses in favour of offered fluorine activation mechanism at active component of catalyst during fluorination of carbonoxide.

It is typical for the catalysts prepared by mechanical mixing (thorough pestling in agate mortar) of metal fluoride components and  $Oi-Al_2O_3$ , to be significantly less active than the catalysts obtained by method of coating (application) (impregnation). Apparently, that result is caused by different level of dispersity of active component and indicates significant influence of catalyst preparation methods on their efficiency. It is interesting, that coated (applied) catalysts of  $NiF_2/Oi-Al_2O_3$ , obtained using nickel chloride, nitrate and sulfate (at preliminary fluorination of catalysts these salts applied on  $Oi-Al_2O_3$ , transfer to nickel difluoride) are approximately equally active.

We should also note, that known metal catalysts dense nozzle made of thin copper wire and rollers of nickel net were virtually inactive under analogous conditions. Apparently, that is a consequence of their low specific surface. Specific surface of metal catalysts dense nozzle made of copper wire spirales and rollers made of nickel net accounts to  $2,8 \times 10^{-3} m^2$  and  $3,5 \times 10^{-3} m^2$  per 1 ml of catalyst respectively. For comparison the specific surface of waste/used catalysts based on  $Oi-Al_2O_3$  is 15-20  $m^2/ml$ .

Choosing the carrier was the following stage of determining the optimal composition of direct fluorination. The X-ray phase study of used/waste catalysts based on  $Oi-Al_2O_3$  and determining of their chemical composition proved, that total fluorination of contacts occurred during reaction forming phase of aluminium fluoride. That phase transfer is accompanied by decrease of mechanical stability/resistance/ruggness of catalysts, that led to gradual decomposition of their granules and to increase of reactor's resistance.

An interesting observation has been made during studying of catalytic properties of nickel oxide applied on  $O\pm-Al_2O_3$ ; not only was that catalyst of high activity during carbon oxide fluorination obtaining THF, but also has it preserved its initial strength and granulometric composition:

Catalyst	Operating Conditions	Overall fraction weight, % C grains size less than <sup>1</sup> , mm				
		0,5	2,0	3,0	5,0	7,0
$NiO/Oi-Al_2O_3$	553 K, 24 hours	12,6	45,8	73,2	91,9	100,0
$NiO/O\pm-Al_2O_3$	623 K, 200 hours	0,5	0,8	1,0	2,9	100,0

<sup>1</sup>Size of initial grains 5-7 mm.

From the listed data we can see, that only 8,1% of grains of catalyst based on  $Oi-Al_2O_3$  have remained unaltered in their size after operating for 24 hours at 553K; all the others had been destroyed. The catalyst based on  $O\pm-Al_2O_3$ , operated under more severe conditions (623 K, 200 hours) had remained its granulometric composition virtually unaltered.

X-ray-phase analysis of the catalyst  $NiF_2/O\pm-Al_2O_3$  had revealed, that during operation or preliminary fluorination the coated (applied) oxide fully transformed/transferred into nickel fluoride, while the intensity of lines responding to the carrier  $O\pm-Al_2O_3$  stays the same. The presence of saturation lines (of small intensity) in spectra responding to the aluminium fluoride provides a basis for making an assumption, that during preliminary fluorine treatment (using fluorine) and operation the  $O\pm-Al_2O_3$  is being coated with thin aluminium fluoride film, which prevents it from further fluorination and thus, from mechanical decay. Thus, used catalyst is a nickel fluoride applied (coated) onto  $O\pm-Al_2O_3$ , which is coated with aluminium fluoride. To keep it short this contact is referred to as  $NiF_2/O\pm-Al_2O_3$ .

Here we shall note, that exclusively high stability/ resistance of  $O\pm-Al_2O_3$  amid fluorinating media at increased temperatures, that we had discovered during our work, allowed using of that carrier (as will be shown below) to prepare effective catalysts of a wide range of fluoroorganic compounds reactions..

In the reaction of carbonyl difluoride's fluorination the tests of GIAP-3-6H commercial catalyst, which is also a nickel oxide applied on  $O\pm-Al_2O_3$  had confirmed a high efficiency of that catalytic

composition (Table 3) and allowed obtaining of reaction gases containing THF at a point exceeding 95% of volume.

**Table 3.** Direct Fluorination of Carbonyl Difluoride at GIAP-3-6H (volume rate of reagents  $\nu\tau^{\text{TM}}$  input -  $100 \text{ hour}^{-1}$ ; mole ratio substrate:fluorine=1).

#	Temperature, K	Composition <sup>1</sup> of Reaction Gases, % volume			
		F <sub>2</sub> +CO	CF <sub>2</sub> O	(CF <sub>3</sub> O) <sub>2</sub>	CF <sub>3</sub> OF
1	448	2,6	1,7	0,4	95,3
2	473	2,2	1,4	0,2	96,2
3	498	1,8	1,1	<0,1	97,1

<sup>1</sup>Content of tetrafluoromethane and carbon dioxide in the reaction gases below 0,1 volume %.

We shall note, that cesium and silver fluoride applied on O $\pm$ -Al<sub>2</sub>O<sub>3</sub>, are also initially catalytically highly active in THF synthesis based on fluorination of carbon oxide; in this case as well the carrier O $\pm$ -Al<sub>2</sub>O<sub>3</sub> remains its high mechanical stability even after prolonged use under rather severe conditions. At the same time lowering of activity in time is typical for these catalysts, which is caused by gradual layering off and carrying away of active components  $\nu\tau^{\text{TM}}$  metal fluorides; the latter leads to increase of catalysts  $\nu\tau^{\text{TM}}$  layer  $\nu\tau^{\text{TM}}$ s resistance and plugging in reactor.

Besides that, cesium fluorides and especially silver fluorides are expensive and hard to find. Due to that later the main part of our attention was devoted to studying of catalytic properties of active, stable and available NiF<sub>2</sub>/O $\pm$ -Al<sub>2</sub>O<sub>3</sub>, as well as their comparison to the properties of inert nozzles, for example, melted calcium fluoride, non-modified O $\pm$ -Al<sub>2</sub>O<sub>3</sub>) and known metal catalysts.

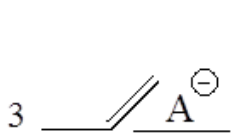
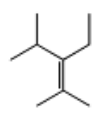
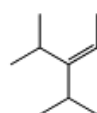
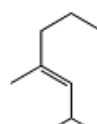
Under fluorinated admixtures are a complex mixture of polyfluorinated unsaturated and hydrogen containing compounds. We have conducted a study of model reactions of direct catalytic fluorination of a wide range of unsaturated and hydrogen containing individual polyfluorinated compounds to select effective catalysts of their direct fluorination. However, in a number of cases studying the model reactions of direct fluorination had been of independent practical interest.

## 2.3 Catalytic Gas-phase Fluorination of Double Bond Polyfluorinated Compounds

### 2.3.1 Perfluorononenes $\nu\tau^{\text{TM}}$ Fluorination

We have studied the gas-phase fluorination of perfluorononenes (PFN) as a model reaction to estimate the effect of fluorine activation by the surface on rate and selectivity of its attachment by double bond.

Perfluorononenes are formed with high yield at anionic oligomerization of hexafluoropropylene (155-162):

		3-perfluoroisopropyl-2-perfluoromethylperfluoropentene-2 (PFEN-1) 60 mass.%
		3-perfluoroisopropyl-4-perfluoromethylperfluoropentene-2 (PFEN-2) 30 mass.%
		2,4-perfluorodimethylperfluoroheptene-3 (PFEN-3) 5 mass.%

Perfluorononanes (PFAN) are the products of selective fluorinations of PFEN, they are perspective dielectrics, coolants and thermal resistant solvent.

Information on direct gas-phase fluorination of PFEN in the layer of metal copper and nickel melted calcium fluoride and  $O\pm-Al_2O_3$ , modified by nickel oxide are listed in Table 4. Here the results on fluorination of PFEN in an empty reactor without catalyst are listed for you to compare.

The nonselective, explosive behavior is a specific feature of direct gas-phase fluorination of PFEN in an empty reactor as well as in the layer of metal copper, nickel and melted calcium fluoride at temperature over 440 K according to the experiments; at that tetrafluoromethane and carbon-black are the main products of reactions.

We have obtained nontrivial results while studying gas-phase interaction of PFEN and fluorine at temperatures below 420 K. A stable radical, 3-perfluoroisopropyl-2-perfluoromethylperfluoropentyl-3 (PFYL) is the main product of reaction in an empty reactor as well as in the layer of metal copper, nickel and melted calcium fluoride (Table 4, # 1-9); we have isolated and characterized it using the method of Electron paramagnetic resonance (EPR). The yield of PFYL at gas-phase fluorination at gas-phase interaction of PFEN and fluorine reaches 85% (per reacted PFEN).

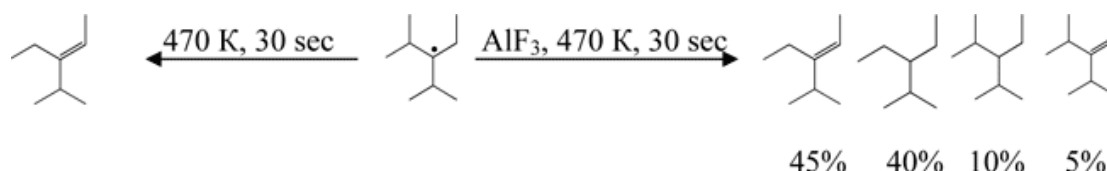
This stable perfluoroalkyl radical was first obtained and characterized using EMR method by the authors [163, 164] when studying liquid-phase direct fluorination of PFEN; liquid-phase selective fluorination of hexafluoropropylene oligomers is also described in [165,166]. We shall also note, formation of stable perfluoroalkyl radicals at radiolysis and photolysis of perfluoroolefines, particularly, hexafluoropropylene oligomers, is described in [167-173].

As the studies have proved the extreme stability of PFYL is its characteristic feature thus, particularly, it is stable during keeping outdoors (6 months). PFYL is stable even in the atmosphere of fluorine up to 420 K (contact period 20sec) at both their homogenous mixing and contacting in the layer of metal copper, nickel and melted calcium fluoride; when putting the temperature over 440 K the interaction of PFYL and  $F_2$  shows explosive behavior forming tetrafluoromethane and carbon-black.

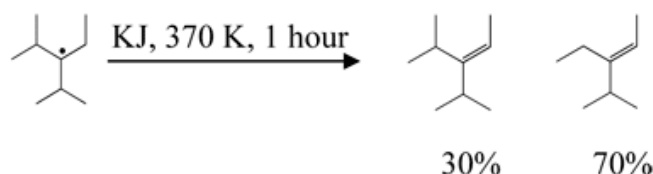
The contacting of PFYL with fluorine in the layer of  $NiF_2/O\pm-Al_2O_3$  at 400 K leads to formation of equimolar quantity of 3-perfluoroisopropyl-2-perfluoromethylperfluoropentane (PFAN), and at 520 K and above to formation of 3-perfluoroethyl-2-trifluoromethylperfluoropentane (PFAO) and tetrafluoromethane.

**Table 4. Direct Fluorination of Perfluorononenes (volume rate of input - 170 hour<sup>-1</sup>; mole flow rate substrate:fluorine:nitrogen = 1:1,25:1,70).**

PFYL is totally decomposing in gas-phase at 470 K in 30 sec forming 3-perfluoroethyl-4-perfluoromethylperfluoropentene-2 (PFEO) and tetrafluoromethane; under these conditions while contacting fluorinated  $O\pm-Al_2O_3$  PFAO and PFEO are formed along with tetrafluoromethane, as well as PFEN and PFAN:



PFYL also reacts to potassium iodide (aqueous solution, 370 K, 1 hour) isolating iodine and forming PFEN and PFEO:




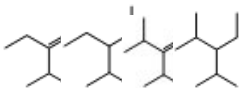
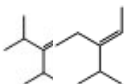


Chemical properties of PFYL are summarized in Table 5.

The principal change of character of direct gas-phase fluorination of PFEN, which is a sharp increase of its rate and total conversion of selectivity was discovered by us when using nickel fluoride as a catalyst applied  $O\pm-Al_2O_3$ . Thus, the rate of conversion of PFEN-1 and fluorine at fluorination in an empty reactor, in a layer of metal copper, nickel and melted calcium fluoride (403 K) is 2-5 and 4-13% at a catalyst  $NiF_2/O\pm-Al_2O_3$  under the same conditions more than 99 and 88% respectively (Table 4, # 1, 3, 5, 7 and 12).




The fluorination in the layer of nickel fluoride applied on  $O\pm-Al_2O_3$  at 393-493 K is accompanied by quantitative formation of PFAN the product of selective attachment of fluorine along the double bond of PFEN (Table 4, # 10-12); PFAN does not virtually form under these conditions at known catalysts such as metal copper and nickel.

**Table 5.** Some Chemical Properties of PFYL

#	Reaction Conditions	Carrying Out	Main Reaction Products
1	Air; 298 K, 6 months		Doesn't react (stable)
2	Fluorine, below 420 K, 20 sec		Doesn't react
3	Fluorine, Cu, Ni (metal.) CaF <sub>2</sub> , <420 K		Doesn't react
4	Fluorine, over 440 K		CF <sub>4</sub> , carbon-black
5	Fluorine, Cu, Ni (metal.) CaF <sub>2</sub> , over 440 K		CF <sub>4</sub> , carbon-black
6	Fluorine, NiF <sub>2</sub> /O±-Al <sub>2</sub> O <sub>3</sub> , 400 K, 20 sec		
7	Fluorine, NiF <sub>2</sub> /O±-Al <sub>2</sub> O <sub>3</sub> , 520 K, 20 sec		
8	470 K, 30 sec		
9	O±-Al <sub>2</sub> O <sub>3</sub> (fluorinated), 470 K, 30 sec		
10	KJ, 370 K, 1 hour		

It is a rather characteristic feature that the reactivity of PFEN-1, as it follows from the listed data is significantly lower than one of PFEN-2, which is caused apparently by steric particularities of configuration of their molecules. The differences of reactivity of isomers of perfluorononen are clearly illustrated by the results obtained at gas-phase fluorination of their mixture at catalysts of NiF<sub>2</sub>/O±-Al<sub>2</sub>O<sub>3</sub> in the insufficient amount of fluorine (Table 6).

**Table 6.** Fluorination of Mixture of PFEN-1 and PFEN-2<sup>1</sup> at Catalyst of NiF<sub>2</sub>/O±-Al<sub>2</sub>O<sub>3</sub> (temperature 403 K, volume rate of input 140 hour<sup>-1</sup>, mole ratio nitrogen : PFEN = 2,6)

##	Mole Rate Fluorine: PFEN	Conversion level, %			Yield  , %
				F <sub>2</sub>	
1	0,25	55,7	6,2	>99,0	98,8



1	Ni, Metal	15,4	6,1	6,4	2,1	3,4	36,8	29,8
2	NiF <sub>2</sub> /O <sub>2</sub> - Al <sub>2</sub> O <sub>3</sub>	6,3	3,2	4,1	1,9	1,6	82,9	<0,1

Looking at data given here it is seen, that direct gas-phase fluorination of perfluorohexenes at catalyst NiF<sub>2</sub>/O<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> goes rather selectively; the yield of perfluorohexane at metal nickel catalyst is significantly lower.

In case of fluorination of perfluorohexenes there are no steric difficulties, that's why data for fluorination at heterogeneous contacts of principally different nature of action differ only in quantitative terms.

WE shall also note, that listed results allow considering direct catalytic fluorination as a promising method to obtain 2-perfluoromethylperfluoropentane based on isomers of 2-perfluoromethylperfluoropentene-2.

### 2.3.3 Perfluorobutenes Fluorination

Data on direct gas-phase fluorination of perfluorobutenes in the mixture with octafluorocyclobutane and perfluoromethylperfluorocyclobutane over melted calcium fluoride, metal copper, as well as nickel fluoride applied on O<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, is listed in Table 8; here the results on fluorination in an empty reactor without catalyst are listed for comparison.

Tetrafluoromethane and carbon-black are the main products of reaction without catalyst; at that the process is prompt to explosion even at 300 K. The selective attachment of fluorine along double bond does not occur; octafluorocyclobutane and perfluoromethylperfluorocyclobutane are subject to destructive fluorination along with perfluorobutenes. The last fact mentioned conforms to data [174], where it is shown that at 550 K and above the fluorine reacts to octafluorocyclobutane under homogeneous conditions forming energetically excited intermediate radical n-C<sub>4</sub>F<sub>9</sub>, which main product of further transformations is tetrafluoromethane.

Using nozzle made of melted calcium fluoride or metal copper leads to some increase of fluorination selectivity

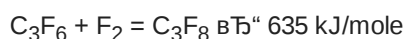
(Experiments 3-6, Table 8) the yield of perfluorobutane reaches 50%. At the same time in this case too the process is characterized by deep destruction of raw materials forming tetrafluoromethane.

The principal increase of fluorination selectivity is observed when carrying out the process in the layer of NiF<sub>2</sub>/O<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> the yield of perfluorobutane increases up to 96-99% at perfluorobutenes degree of conversion exceeding 99%; octafluorocyclobutane and perfluoromethylperfluorocyclobutane virtually do not react during that.

**Table 8. Direct Fluorination of Perfluorobutenes in the Mixture with Perfluorocyclobutane and Perfluoromethylperfluorocyclobutane (volume rate of input is 30 hour<sup>-1</sup>, mole ratio fluorine:perfluorobutenes = 4)**

### 2.3.4 Hexafluoropropylene Fluorination

To estimate the effect of fluorine activation by catalysts surface onto selectivity of its attachment along the double bond gas-phase fluorination of hexafluoropropylene had been studied as a model reaction as well:



Nickel fluoride applied onto O<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> contact asserting the activation of fluorine on the surface had been used as a catalyst and for comparison unmodified O<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, melted calcium fluoride and known metal catalysts copper and nickel. The part of experiments had been conducted in an empty reactor. The information can be found in Table 9.

One can see, that interaction of fluorine and hexafluoropropylene in an empty reactor (even when it is diluted with nitrogen) passes in a non-selective way the tetrafluoromethane is the main product of reaction. The filling of reactor with nozzle/packing results in specific (depending on the nozzle's nature) increase of the input of selective fluorination. When using nickel fluoride applied onto O<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, (# 11,12, Table 9) the hexafluoropropylene fluorination passes in a most selective way; only in that case octafluoropropane is the main product even when using undiluted fluorine. Apparently, that result is a consequence of the increase of the input of selective heterogeneous fluorination at activation of fluorine at dispersed nickel difluoride.

The association of intermediate radicals forming significant quantities of linear and branched perfluorohexanes is a characteristic feature of hexafluoropropylene's direct fluorination.

### Table 9. Hexafluoropropylene Direct Fluorination .

### 2.3.5 Tetrafluoroethylene and Trifluorochloroethylene Fluorination

In Tables 10 and 11 comparative data on composition of products of direct fluorination of tetrafluoroethylene and trifluorochloroethylene at catalyst of  $\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$  and in the layer of dense nozzle/packing made of thin copper. During fluorination of tetrafluoroethylene and trifluoroethylene the volume rate of input was  $220 \text{ hour}^{-1}$ , mole ratio substrate:fluorine: nitrogen = 1:1,1:2,5; temperature of reactor  $\text{B}\bar{\text{T}}^{\text{TM}}$ 's exterior wall was 313 K (at heating off).

**Table 10.** Direct Fluorination of tetrafluoroethylene.

#	Catalyst	Fluorination Product Composition, volume%					
		$\text{CF}_4$	$\text{C}_2\text{F}_6$	$\text{C}_3\text{F}_8$	$\text{C}_4\text{F}_{10}$	$\text{C}_5\text{F}_{12}$	Others
1	$\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$	24,8	34,7	12,8	12,4	4,2	11,1
2	Cu, metal	37,7	22,4	10,7	11,8	4,0	13,4

One can see from the listed data, that direct fluorination of tetrafluoroethylene and trifluorochloroethylene passes nonselectively forming significant quantities of dimerization and destruction products; the yield of selective fluorination products  $\text{B}\bar{\text{T}}^{\text{TM}}$  hexafluoroethane and pentafluorochloroethane at  $\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$ , although, is significantly higher, than when using metal nozzle/ packing.

**Table 11.** Trichloroethylene Direct Fluorination.

#	Catalyst	Fluorination Products Composition, volume. %							
		$\text{CF}_4$	$\text{C}_2\text{F}_6$	$\text{CF}_3\text{Cl}$	$\text{C}_3\text{F}_8$	$\text{C}_2\text{F}_5\text{Cl}$	$\text{C}_4\text{F}_{10}$	$\text{C}_4\text{F}_8\text{Cl}_2$	Others
1	$\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$	10,6	4,2	9,6	5,7	33,6	2,5	17,3	16,5
2	Cu; metal	18,5	4,1	13,4	7,1	20,8	2,8	16,8	16,5

While data on direct gas-phase fluorination of hexafluoropropylene and, particularly, of tetrafluoroethylene and trifluorochloroethylene testifies the increase of input of selective fluorination when using developed catalyst  $\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$  (compare to known metal contacts) it clearly illustrates the limitations of that method.

Low selectivity of fluorination of  $\text{B}\bar{\text{T}}^{\text{TM}}$  small  $\text{B}\bar{\text{T}}^{\text{TM}}$  fluorolefines can be caused by significant heating up of reaction gases during fluorination (due to their low thermal capacity), when thermal decomposition contributes mainly to the destruction, and not the decomposition of energetically excited molecules ( as in case with perfluorononenes and perfluorobutenes).

Due to that the studying of direct catalytic fluorination of fluorolefines diluted with inert, saturated fluororganic compounds was of our interest; such process  $\text{B}\bar{\text{T}}^{\text{TM}}$ 's carrying out would have allowed decreasing the heating up of reaction gases in exothermal fluorination and thus lowering the input of thermal destruction.

### 2.3.6 Two-stage Olefines $\text{B}\bar{\text{T}}^{\text{TM}}$ Fluorination. Olefines Removal from Fluorochlorocarbons

The heating up of reaction gases in direct fluorination can be decreased by carrying out preliminary  $\text{B}\bar{\text{T}}^{\text{TM}}$  soft  $\text{B}\bar{\text{T}}^{\text{TM}}$  fluorination of olefins, for example, using cobalt trifluoride. Thereupon we had studied two-phase fluorination of tetrafluoroethylene, acetylene, hexafluoropropylene and trifluorochloroethylene /175/. We shall note, that the authors /176-179/ had studied in details the fluorination of acetylene and hexafluoropropylene using cobalt trifluoride, where it is shown, that the yield of hexafluoroethane at fluorination of acetylene is small because of forming partial fluorination products in significant quantities  $\text{B}\bar{\text{T}}^{\text{TM}}$  pentafluoroethane and 1,1,2,2-tetrafluoroethen  $\text{B}\bar{\text{T}}^{\text{TM}}$  hydrogen containing adducts, which further fluorination using cobalt trifluoride goes rather slowly. At the same time the obtaining of hexafluoroethane a precious working body for plazmo- chemical processing of elements of electronic systems, out of acetylene would allow carrying out the synthesis with minimum spending of fluorine without using intermediate chloroorganic products. The obtaining technology for tetrafluoroethylene, from which hexafluoroethane can be obtained, includes the use of chloroform, which production is rather labour intensive and is characterized by significant chlorine spending.





Initial Products' Composition		0,3	72,9	<0,1	22,5	0,5	1,1	1,6	B 0,7
1	473	0,3	97,0	<0,1	0,4	<0,1	0,2	1,5	B 0,6
2	523	0,3	97,4	<0,1	<0,1	<0,1	<0,1	1,6	B 0,7
3	573	0,3	97,3	<0,1	<0,1	<0,1	<0,1	1,6	B 0,8
Initial Products' Composition		<0,1	6,0	4,3	46,1	3,8	38,3	<0,1	B 1,5
4	523	25,1	72,0	<0,1	1,4	<0,1	<0,1	<0,1	B 1,5

By the data above we can see, that direct fluorination of acetylene and cobalt trifluoride interaction products at catalyst  $NiF_2/O\pm-Al_2O_3$  is accompanied by selective fluorination of pentafluorochloroethane and allows obtaining of perfluorinated products containing 97,0 вЂ° 97,4 volume % of hexafluoroethane (#s 1 вЂ° 3, Table 13); fluorination of mixtures containing significant amounts of tetrafluoroethane and unreacted acetylene is accompanied by forming of tetrafluoromethane (# 4, Table 13).

We shall note, that tetrafluoroethane, pentafluoroethane and hexafluoroethane can be obtained of virtually quantitative yield as shown in /175/ by such two-phase fluorination of tetrafluoroethylene, trifluorochloroethylene and hexafluoropropylene respectively (at first by cobalt trifluoride, and then by fluorine at  $NiF_2/O\pm-Al_2O_3$ ); at that, the content of haloidolefines in the target products was lower than the level of sensitivity of their discovery (0,01 volume %).

Data on direct fluorination of tetrachloroethylene and fluorotrichloroethylene in the mixture with fluorochlorocarbons of ethane row are listed in Table 14.

**Table 14.** Direct Fluorination of Tetrachloroethylene and Fluorotrichloroethylene in the Mixture With Chladones Of Ethane Row At Catalyst  $NiF_2/O\pm-Al_2O_3$ .\*

#	T, K	Organic Products Composition, mass %					
		$C_2F_4Cl_2$	$C_2F_3Cl_3$	$C_2F_2Cl_4$	$C_2Cl_4$	$C_2Cl_3F$	Others
Initial Products Composition		0,3	91,8	0,3	4,8	2,6	0,2
1	333	0,3	94,3	4,6	0,4	0,1	0,3
2	393	0,4	95,2	4,2	<0,1	<0,1	0,3
3	573	3,3	92,8	3,5	<0,1	<0,1	0,4
Initial Products Composition		<0,1	24,3	60,2	12,2	0,2	0,2
4	453	0,1	27,9	71,8	<0,1	<0,1	0,2
5	473	0,3	28,2	71,4	<0,1	<0,1	0,4
6	523	0,8	31,4	67,5	<0,1	<0,1	0,3

\*Experiments 1-3 were carried out in the reactor of 50 ml volume, input rate of organic products вЂ° 100 g/hour, fluorine вЂ° 2 g/hour. Experiments 4-6 were carried out in the pilot reactor volume 6,2 l, input rate of organic products вЂ° 10 kg/hour, fluorine вЂ° 0,3 kg/hour, nitrogen вЂ° 4m<sup>3</sup>/hour.

From the data above we can see, that fluorination of tetrachloroethylene and fluorotrichloroethane at catalyst  $\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$  goes in a selective way forming 1,2-difluorotetrachloroethane and 1,1,2-trifluorotrichloroethane respectively and within the temperature range 390-570 K and it is characterized by total purification of unwanted haloidolefins; at that the fluorination of saturated fluorochlorocarbons does not occur.

We shall note, that purification of ethane row chlorides from tetrachloroethylene and fluorotrichloroethylene using the method of direct catalytic fluorination had been successfully used at a commercial scale (reactor of 60l volume).

Data on purification of octafluorocyclobutane from unsaturated and hydrogen containing admixtures by direct catalytic fluorination are listed in Table 15.

**Table 15.** Octafluorocyclobutane Purification From Unsaturated And Hydrogen Containing Admixtures by Direct Fluorination At Catalyst (Volume Velocity of Input -  $60 \text{ hour}^{-1}$ , mole ratio octafluorocyclobutane:fluorine= 20).

Admixtures Titles	Admixtures Content in Octafluorocyclobutane, volume %	Admixtures Content volume (%) in octafluorocyclobutane, purified at, K	
		423	473
hexafluoropropylene	0,24	$9 \times 10^{-4}$	$< 10^{-4}$
perfluorobutene-2	$6 \times 10^{-4}$	$< 10^{-4}$	$< 10^{-4}$
2,2-dihydroperfluoropropane	$2 \times 10^{-4}$	$10^{-4}$	$< 10^{-4}$
2-hydroperfluoropropylene	$9 \times 10^{-4}$	$4 \times 10^{-4}$	$< 10^{-4}$
trans-perfluorobutene -2	$9,7 \times 10^{-2}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
cis-perfluorobutene-2	$2,1 \times 10^{-2}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
perfluorocyclobutene	$1,2 \times 10^{-2}$	$< 10^{-4}$	$< 10^{-4}$

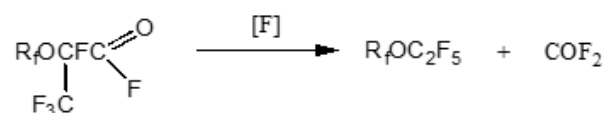
From the data above we can see, that method of direct catalytic fluorination allows carrying out fine purification of octafluorocyclobutane from unsaturated and hydrogen containing admixtures. As experiments proved [181], purified octafluorocyclobutane is an effective solvent for carrying out the copolymerization of perfluoropropylperfluorvinyl ether and tetrafluoroethylene obtaining fluoroplast-50.

Thus listed results show, that developed catalyst  $\text{NiF}_2/\text{O}_2\text{-Al}_2\text{O}_3$  allows carrying out direct selective fluorination of fluorolefines at diluting them with inert saturated fluororganic compounds. These results open new practical perspectives for obtaining pure fluorocarbons based on corresponding olefins: their synthesis can be carried out in two stages and includes preliminary fluorination at cobalt trifluoride and following direct catalytic fluorination.

The developed method can be used for fine purification of fluorocarbons from underfluorinated compounds.

### 2.3.7 Fluorination Of Perfluoropropionylfluoride and Hexafluoropropyleneoxide Lowest Oligomers. Stabilization of Perfluoropolyesters Based on Hexafluoropropylene and Oxygen

The technology of inert perfluoropolyethers oxygen containing fluorocarboxylic liquids based on hexafluoropropylene and oxygen widely used in special fields of technics includes fluorination of mixture of polymolecular products of low-temperature initiated oxidation containing end fluoranhydride group; as a result an elimination of carbonyldifluoride and stabilization of perfluoropolyethers takes place [182-184]:



Highmolecular perfluoropolyethers are stabilized by fluorine in liquid phase, and low-molecular вЂ“ in gaseous phase using cobalt trifluoride; in both cases the fluorination is characterized by high destruction of precious fluorocarbonic raw materials.

Thereupon and for the purpose of establishing the impact of heterogenous contact nature onto selectivity and rate of interaction of fluoroanhydrides and fluorine we have studied model reactions of direct fluorination of perfluoropropionylfluoride and individual perfluoropolyethers containing end fluoroanhydride group вЂ“ lowest oligomers of hexafluoropropylene oxide: 2-perfluoromethyl-3-oxaperfluorohexanoylfluoride (hexafluoropropylene oxide dimer), 2,5-perfluorodimethyl-3,6-dioxaperfluorononylfluoride (hexafluoropropylene oxide trimer) and 2,5,8-perfluorotrimethyl-3,6,9-trioxaperfluorononylfluoride (hexafluoropropylene oxide trimer) and 2,5,8-perfluorotrimethyl-3,6,9-trioxaperfluorododecanoylfluoride (hexafluoropropylene oxide tetramer) вЂ“ low-molecular analogues of perfluoropolyethers based on hexafluoropropylene and oxygen.

Here we shall note, that the direct gas-phase fluorination of perfluoropropionylfluoride and oligomers of hexafluoropropylene oxide in an empty reactor, without catalyst is explosive and uncontrolled вЂ“ tetrafluoromethane, carbonyldifluoride and carbon-black are the main products of reaction. Information on direct gas-phase fluorination of perfluoropropionylfluoride and lowest oligomers of hexafluoropropylene oxide over metal nickel,  $O\pm-Al_2O_3$  and  $NiF_2/O\pm-Al_2O_3$  catalyst can be found in Table 16,17 and at Picture 2.

**Table 16.** Direct Catalytic Fluorination of Perfluoropropionylfluoride (volume rate of input is  $95\text{ hour}^{-1}$ , mole ratio fluorine:substrate=1,2).

#	Catalyst	Temperature, K	Conversion level PF <sup>1</sup> ,%	Neutralized Reaction Gases Composition <sup>2</sup> , Volume %		
				CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	Others
1	Ni, metal.	473	14	45,6	52,3	2,1
2	$O\pm-Al_2O_3$	473	22	39,4	57,1	3,6
3	$NiF_2/O\pm-Al_2O_3$	373	34	35,3	60,8	3,9
4	Same	473	80	20,6	79,0	0,4

<sup>1</sup>The Conversion level of perfluoropropionylfluoride at 373 K at  $O\pm-Al_2O_3$  and metal nickel is lower than 1%.

<sup>2</sup>Composition of neutralized reaction gases is given without taking carbon dioxide into account.

By the information listed in Table 16 one can see, that rate and selectivity of fluorination of perfluoropropionylfluoride significantly depends on the nature of applied catalyst;  $NiF_2/O\pm-Al_2O_3$  catalyst is most active.

Hexafluoroethane and tetrafluoromethane are the main reaction products; it is typical, that when using less active catalysts of  $Al_2O_3$  and metal nickel under comparable conditions the  $O\pm$ - relative yield of product of deep destructive fluorination вЂ“ tetrafluoromethane is significantly higher than at  $NiF_2/O\pm-Al_2O_3$ .

One can see from the data listed in Table 17 and on Picture 2, that the nature of heterogeneous contact impacts significantly the fluorination rate of lowest oligomers of hexafluoropropylene oxide.

Thus, the Conversion level of hexafluoropropylene oxide trimer at  $O\pm-Al_2O_3$ , metallic nickel and  $NiF_2/O\pm-Al_2O_3$  at 473 K is 11, 35 and 90 %, respectively (#s 10,13,16, Table 17). Practically quantitative yield of 5,8-perfluorodimethyl-3,6,9-trioxaperfluorododecane at fluorination of hexafluoropropylene oxide tetramer at catalyst  $NiF_2/O\pm-Al_2O_3$  draws our attention (# 17, Table. 17).

Catalytic gas-phase fluorination of lowest oligomers of hexafluoropropylene oxide can contain the formation of unstable perfluoroalkylhypofluorites, which further destruction in accordance with /185/ passes with elimination of carbonyldifluoride and forming of stable fluoroethers with end perfluoroethoxy

group. This conjection conforms to the pointed earlier higher activity of  $\text{NiF}_2/\text{O}_\pm\text{-Al}_2\text{O}_3$  catalyst during the synthesis of trifluoromethylhypofluorite out of carbon oxide or carbonylfluoride.

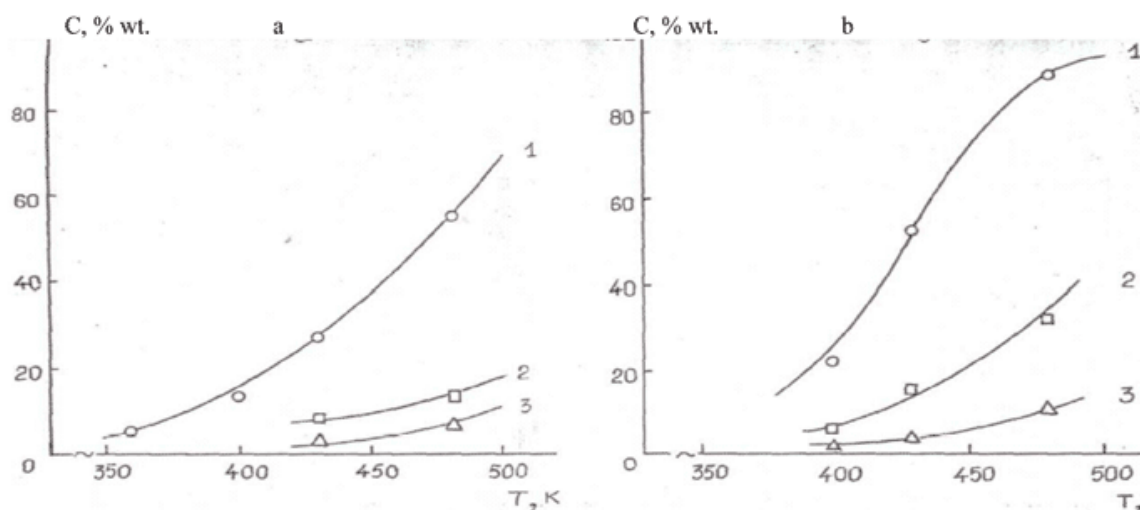
From the listed in Table 17 data one can see, that reactivity of lowest oligomers of hexafluoropropylene oxide is not equal вЂ“ thus, at 473 K the rate of conversion of dimer, trimer and tetramer at  $\text{NiF}_2/\text{O}_\pm\text{-Al}_2\text{O}_3$  catalyst amounted to 52, 90 and 98% respectively. The increasing of reactivity of fluoroanhydrides along with (simultaneously) their molecular mass growth is rather important from the practical point of view and it indicates the higher reactivity of relatively high-molecular perfluoropolyethers forming during low temperature initiated oxidation of hexafluoropropylene. However, gas-phase fluorination of high-molecular perfluoropolyethers is possible only at low pressure or dilution with inert gas.

**Table 17.** Direct Catalytic Fluorination of Lowest Hexafluoropropyleneoxide Oligomers (volume rate of input - 95 hour<sup>-1</sup>, mole ratio fluorine:substrate = 1,2).

#	Catalyst	Reaction Temperature, K	Conversion level of Organic Substrate %	Main Product Yield, %
1. Fluorination of Dimer of HFPO				
1	Ni, metallic	423	9	97
2	Same	473	15	91
3	$\text{O}_\pm\text{-Al}_2\text{O}_3$	423	3	98
4	Same	473	7	98
5	$\text{NiF}_2/\text{O}_\pm\text{-Al}_2\text{O}_3$	393	14	99
6	Same	423	28	99
7	- B«-	473	52	98
2. Fluorination of Trimer of HFPO				
8	Ni, metallic	393	6	98
9	Same	423	16	98
10	-B«-	473	35	92
11	$\text{O}_\pm\text{-Al}_2\text{O}_3$	393	2	99
12	Same	423	4	99
13	-B«-	473	11	98
14	$\text{NiF}_2/\text{O}_\pm\text{-Al}_2\text{O}_3$	393	22	99
15	Same	423	53	99

16	-B«-	473	90	98
3. Fluorination of Tetramer of HFPO				
17	NiF <sub>2</sub> /O±-Al <sub>2</sub> O <sub>3</sub>	473	98	96

<sup>1</sup>3-oxaperfluorohexane, 5-perfluoromethyl-3,6-dioxaperfluorononane and 5,8-perfluorodimethyl-3,6,9-trioxaperfluorododecane are the main products of selective fluorination of dimer, trimer and tetramer of HFPO respectively.



**Picture 2.** Temperature Dependencies of concentrations of 3-oxaperfluorohexane (a) and 5-perfluoromethyl-3,6-oxaperfluorononane (b) in liquid products of direct gas-phase fluorination of hexafluoropropyleneoxide вЂ™s dimer and trimer at catalysts: 1 - NiF<sub>2</sub>/O±-Al<sub>2</sub>O<sub>3</sub>; 2 вЂ™ metal nickel and 3 - O±-Al<sub>2</sub>O<sub>3</sub> respectively.

The effective catalyst NiF<sub>2</sub>/O±-Al<sub>2</sub>O<sub>3</sub> for fluorination of lowest oligomers of hexafluoropropylene oxide had been used for gas-phase stabilization of light fraction of perfluoropolyethers based on hexafluoropropylene and oxygen (boiling out temperature 313-343 K at 133 Pa). Nowadays stabilizing technology of this fraction is based, as it has been mentioned, on fluorination of cobalt trifluoride and is characterized by low productivity, high material and energy consumption. Comparative data on fluorination of perfluoropolyethers using fluorine at NiF<sub>2</sub>/O±-Al<sub>2</sub>O<sub>3</sub> catalyst and using cobalt trifluoride are listed in Table 18.

**Table 18.** Stabilization of Light Fraction of Perfluoropolyethers Based on Hexafluoropropylene and Oxygen.

#	Temperature, K	Raw Materials Loss at Fluorination, mass. %	Residual Concentration of detached Ion Fluorine <sup>1</sup> , mass. %	Degree of Fluorination %
1. Direct Fluorination of Catalyst NiF <sub>2</sub> /O±-Al <sub>2</sub> O <sub>3</sub> <sup>2</sup>				
1	573	7,1	1,0 x 10 <sup>-1</sup>	91,3
2	623	8,5	8,2 x 10 <sup>-3</sup>	99,3
3	643	9,7	4,3 10 <sup>-3</sup>	99,6
4	673	10,6	8,0 x 10 <sup>-4</sup>	>99,9

2. Fluorination using Cobalt Trifluoride <sup>3</sup>				
5	573	16,3	$2,5 \times 10^{-1}$	78,3
6	623	18,7	$1,4 \times 10^{-1}$	87,8
7	673	20,8	$5,5 \times 10^{-2}$	95,2

<sup>1</sup>The content of fluoroanhydride groups was estimated by concentration of ion-fluoride detached during prolonged thermal water-alkali hydrolysis; its content in initial ethers amounted to 1,15 mass. %.

<sup>2</sup>Catalyst amount вЂ“ 50ml, input rate of ethers вЂ“ 50 g/hour, fluorine вЂ“ 4 g/hour, fluorine Conversion level at 573, 623, 643 and 673 K amounted to 44, 51, 58 and 65 %, respectively.

<sup>3</sup>Cobalt trifluoride amount вЂ“ 250 g, content of active fluorine вЂ“ 13,4 mass.%, ethers вЂ“ input rate вЂ“ 50 g/hour.

Listed data clearly illustrate the advantages of catalytic method, which lie in high rate and selectivity of fluorination. Raw materials loss at catalytic fluorination under rather severe conditions (673 K) amounted only to 10,6 mass.% (# # 4, Table 18), which is really lower, than at using cobalt trifluoride under analogous conditions (20,8 mas..% - # 7, Table 18).

The difference in fluorination rates can be estimated by residual content of unreacted fluoroanhydrides (they were determined using concentration of detached ion-fluorine in fluorinated ethers) вЂ“ their number in products of direct catalytic fluorination is more than 50 times lower than at cobalt trifluoride using (# 4,7 Table 18).

**to be continued**

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