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

Vladimir Y. Zakharov

**State Educational Institution of Higher Professional Education "Vyatka State University", 610000, Kirov, Moskovskaya str. 36, Russia
e-mail: zakhar.05@mail.ru**

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, cobolt trifluoride, isomerization, heterogeneous catalyst, catalytic fluorination.*

(Continuation)

2.4. Catalytic Gas-Phase Fluorination of Hydrogen Containing Polyfluorinated Compounds

The replacement of hydrogen at carbon atom for fluorine at direct fluorination is characterized as it has been already noted, by isolation of significant amount of heat and is accompanied as a rule by high input of subsrate destruction. In the present part of the work the results regarding study of direct fluorination of polyfluorinated hydrogen containing compounds are listed. We also studied the opportunity of aimed qualitative increase of its selectivity when using heterogeneous contacts created based on developed principals of selection of direct fluorination effective catalysts.

2.4.1. Fluorination of 2,5,5,9-tetrahydro-2-perfluoromethyl-4-oxaperfluorononane

We have used 2,5,5,9-tetrahydro-2-perfluoromethyl-4-oxaperfluorononane (THN) as a model subsrate to study the impact of catalyst's nature on selectivity and hydrogen replacement rate within the range of composition of polyfluorinated compounds. This substrate contains hydrogen at primary, secondary and tertiary carbon atoms; during its fluorination the following compounds may be formed:

Formula	Substance	Symbolic Representation

$CF_3CF(CF_3)CF_2OCH_2(CF_2)_4H$	5,5,9-trihydro-2-perfluoromethyl-4-oxaperfluorononane	H, F, H, H
$CF_3CH(CF_3)CF_2OCFH(CF_2)_4H$	2,5,9-trihydro-2-perfluoromethyl-4-oxaperfluorononane	F, H, H, H
$CF_3CF(CF_3)CF_2OCFH(CF_2)_4H$	5,9-dihydro-2-perfluoromethyl-4-oxaperfluorononane	F, F, H, H
$CF_3CF(CF_3)CF_2O(CF_2)_5H$	9-monyhydro-2-prefluoromethyl-4-oxaperfluorononane	F, F, H, F
$CF_3CF(CF_3)CF_2O(CF_2)_5F$	2-perfluoromethyl-4-oxaperfluorononane	F, F, F, F
$CF_3CH(CF_3)CF_2OCH_2(CF_2)_4H$ (substrate)	2,5,5,9-tetrahydro-2-perfluoromethyl-4-oxaperfluorononane	H, H, H, H

Quantitive analysis of the composition of forming products in this case allows estimating relative reactivity of hydrogen depending on the nature of fluorocarbonic fragment connected with it.

We shall note, that studying of THN fluorination is of practical interest – this process is one of the stages we developed together with Timoshenko Military Academy of Chemical Defense (Russia) /185,186/ utilization technology of perfluoroisobutylene (in the TFE pyrolysis products composition) obtaining perspective dielectric liquid of 2-perfluoromethyl-4-oxaperfluorononane (PFN).

Data on gas-phase catalytic fluorination of THN using elemental fluorine are listed in Tables 19 and 20; there are also results on homogenous gas-phase fluorination (in empty reactor).

From the listed data one can see, that fluorination in an empty reactor with no catalyst goes in a non-selective way forming mainly tetrafluoromethane, carbonyldifluoride (fixed in the form of CO_2) and carbon-black (experiment 1, Table 20) – at that the grade of raw

materials' destruction exceeds 99% (experiment 1, Table 19).

Fluorination in the layer of known catalysts – metal copper (unmodified and silver coated) and nickel, also goes in a non-selective way – the raw materials' destruction grade is at level of 85-95% (experiments 2-6, Table 19).

At that the composition of products of destruction is somewhat different, than during fluorination in an empty reactor – the main product of destructive fluorination is n-perfluorobutane (experiments 2-6, Table 20). The content of PFN in liquid products of fluorination is not high and occupies the 1-5 mass.% level.

Fluorination in the layer of melted calcium fluoride and aluminum alpha-oxide is characterized by some increase of selectivity – at that, the grade of destruction of raw materials falls to 50-80%, and the content of PFN in liquid products reaches 30 mass.% (experiments 7-10, Table 19). This result can be explained by the increase of specific surface of contact (compare to metal catalysts), that slows the destructive fluorination due to breakage of chains of this branched radical process.

We have mentioned above, that rate and selectivity of direct fluorination can be significantly increased during modification of α-Al_2O_3 using nickel fluoride.The use of this catalyst while fluorinating of THN is accompanied by sharp increase of depth and selectivity of fluorination as experiments proved (experiments 11, 12, Table 19). Thus, the content of PFN in the liquid products of fluorination (523 K) when using NiF_2/α-Al_2O_3 and unmodified α-Al_2O_3 is 70,3 and 31,0 mass. %, and the grade of destruction of raw materials is 53 and 62% respectively.These results clearly illustrate, how big the role of nature of heterogenous contact is during fluorination and demonstrate the opportunity of practical application of NiF_2/α-Al_2O_3 catalyst for obtaining of PFN and THN using method of direct fluorination.

Table 19. *Direct Gas-phase Fluorination of THN (volume rate of input 180 hour[-1], mole rate THN:fluorine:nitrogen = 1:5:3)*.

Table 20. *Composition of Gasiform Products of Destructive Direct Catalytic Fluorination of THN*

# Acc. To Table 19	Composition Of Gasiform Products of Fluorination, volume %							
	CF_4	C_2F_6	CO_2	C_3F_8	n-C_4F_{10}	i-C_4F_{10}	i-C_4F_9H	Oth
1	87,2	3,1	5,6	1,7	0,7	0,4	>0,1	1,3
2	10,5	8,5	20,3	11,0	42,4	1,7	5,2	0,4
3	8,3	7,5	16,7	5,3	49,3	1,2	7,0	4,7
4	2,8	1,8	15,1	7,1	59,1	1,8	6,8	5,5

5	11,3	7,7	11,5	12,8	46,7	2,4	5,1	2,5
6	20,1	7,9	12,7	12,0	38,0	2,0	4,4	2,9
7	24,6	15,9	15,2	5,4	25,0	2,5	10,5	0,9
8	15,8	10,5	11,4	4,4	40,4	2,9	14,0	0,6
9	8,0	13,8	13,8	10,5	28,2	11,0	11,8	2,9
10	0,6	10,0	6,8	8,4	55,7	9,4	7,1	2,0
11	0,6	0,6	18,8	10,9	52,2	9,1	5,0	2,8
12	0,4	1,0	22,8	17,5	42,0	10,6	0,8	4,9

Studying of selective fluorination products has shown, that activity of hydrogen atoms in THN molecule was different. Thus, 5,9-dihydro-2-perfluoromethyl-4-oxaperfluorononane is the only product of substitution of two hydrogen atoms in THN molecule, what indicates, that the activity of hydrogen at carbon tertiary atom and of unsaturated methylene group is significantly higher, than the one at primary carbon atom. The amount of 9-monohydro-2-perfluoromethyl-4-oxaperfluorononane in the reaction products is significantly higher, than the amount of 5-monohydro-2-perfluoromethyl-4-oxaperfluorononane, that indicates higher activity of hydrogen atom at partially substituted methylene group (at secondary carbon atom) compare to hydrogen atom at primary carbon atom.

Later, we have studied an opportunity of increasing the depth and selectivity of THN fluorination at $NiF_2/\alpha-Al_2O_3$ catalyst using two-section reactor with independent heatings. At that, we intended to carry out "soft" fluorination with minimum raw materials destruction at relatively low temperature in the first section of reactor, and to fluorinate polyfluorinated ethers forming at that up to PFN at increased temperature in the second section. Data is listed in Table 21.

Table 21. *Direct Gas-Phase Fluorination of THN at $NiF_2/\alpha-Al_2O_3$ catalyst in a Two-Section Reactor (volume rate of input 50 hour^{-1}, mole rate THN:fluorine:nitrogen =1:5:3) .*

#	Section Temperature, K		Fluorine Conversion Grade, %	Raw Materials Destruction Grade, %	Composition of Liquid Products of Fluori...		
	1st	2nd					

#							
1	443	443	82	28	58,0	40,3	0,4
2	443	493	87	35	79,1	18,6	1,1
3	453	493	89	44	89,6	8,7	0,7
4	453	523	90	46	91,6	6,8	0,7
5	453	623	90	48	91,8	6,0	1,0
6	473	623	92	52	94,1	3,4	1,2
7	493	623	94	53	94,4	2,8	1,0

One can see from the listed data, that using the reactor with two-section heating allows increasing of PFN content in liquid products up to 94% mass. % without increasing the raw materials destruction grade (~ 50%) – the temperature values of first and second zones are 470-490 and 620K respectively.

We have also studied the opportunity of exhausting catalytic fluorination of polyfluorinated ethers containing in isolated by rectification PFN, in big excess of fluorine for the purpose of obtaining pure target product free from partially fluorinated addmixtures. Data is listed in Table 22.

Table 22. *Purification of PFN from partially fluorinated compounds by direct gas-phase fluorination at $NiF_2/\alpha\text{-}Al_2O_3$ catalyst(volume rate of input 30 hour^{-1},mole rate PFN:fluorine:nitrogen = 3:1,5:1)[1].*

#	Temperature K	PFN Destruction Grade, %	Concentration of partially fluorinated Addmixtures, mg/kg[2]	Composition of Organic products, mass. %	

Initial Product			1540	98,8	1,1
1	473	0,2	18	> 99,9	<0,1
2	523	0,3	11	> 99,9	<0,1
3	593	0,4	7	> 99,9	<0,1
4	623	0,4	4	> 99,9	<0,1
5	673	0,6	2	> 99,9	<0,1

[1]*Fluorine conversion grade amounted to 7-15 %.*

[2]*In Recalculation per detached ion-fluorine.*

Judging by the data listed above we can draw a conclusion, that fluorination of polyfluorinated ethers containing in PFN at $NiF_2/\alpha\text{-}Al_2O_3$ catalyst in the large excess of fluorine at 470-670 K allows achieving thin purification of target product from partially fluorinated addmixtures; at that the polyfluorinated ethers are fluorinated forming PFN.

Purification from partially fluorinated compounds grade (their concentration was controlled by the content of detached ion-fluorine) is increasing with fluorination temperature rise and at 670 K it reaches 99,9 %; the residual content of detached ion-fluorine in PFN at that amounts to 2-4 mg/kg (experiment 4, 5, Table 22). Here we should note, that content of detached ion-fluorine in perfluorodecaline used as a basic component of blood substituent is at the level of 6 mg/kg. The low grade of raw materials destruction, which even at 670K doesn't exceed 1% draws attention. It is significant, that dielectiric durability of PFN purified that way is rather high and it exceeds 80 kB (the limit of measurement at AIM-90 detector).

Thus, the conducted study indicates the opportunity of directed qualitative increase of selectivity and rate of catalytic fluorination for the hydrogen polyfluorinated compounds as well.We should note, that data obtained have been checked on a pilot (experimental-industrial) scale and formed a base for developed PFN technology including direct fluorination of THN and purification of target product from hydrogen containing addmixtures by direct fluorination at $NiF_2/\alpha\text{-}Al_2O_3$.

2.4.2. Fluorination of α-hydro-ω-chlorineperfluoroalkanes

$H(CF_2)_2Cl$ Fluorination.

1,1,2,2-Tetrafluorochloroethane (R-124) and octafluorocyclobutane (within the composition of their azeotrope mixture) are unutilizable multitonnage TFE production waste. Pentafluorochloroethane, which can be easily separated from octafluorocyclobutane by rectification can be obtained fluorinating 1,1,2,2-tetrafluorochloroethane; thus, the selective fluorination would allow setting the obtaining (from unutilizable fluoroorganic waste) of pentafluorochloroethane and octafluorocyclobutane – raw materials for HFP (hexafluoropropylene) production.

Information on direct fluorination of azeotrope mixture of 1,1,2,2-tetrafluorochloroethane and octafluorocyclobutane is listed in Table 23. One can see, that gas-phase homogenious fluorination (without catalyst) passes in a non-selective way forming tetrafluoromethane, chlorotrifluoromethane, trifluoromethane – products of destructive fluorination of 1,1,2,2-tetrafluorochloroethane and octafluorocyclobutane. Using of non-modified carriers – melted calcium fluoride and aluminium alpha-oxide results in significant increase pentafluorochloroethane's yield. An interesting fact is, that modifying of α-Al_2O_3 using copper fluoride, which, as it follows from data presented earlier (Look at Pic, 1) activates fluorine rather weakly, doesn't result in significant improvement of catalytic qualities of that contact. Modifying of α-Al_2O_3 using nickel fluoride allowed significant increasing of fluorination selectivity (up to 80-90%); at that, octafluorobutane doesn't react.

Table 23. *Direct Fluorination of 1,1,2,2-tetrafluorochloroethane in the mixture with octafluorocyclobutane (mole rate F_2:C_2F_4HCl = 1,3).*

<u>$H(CF_2)_3Cl$, $H(CF_2)_4Cl$ and $H(CF_2)_8Cl$ Fluorination.</u>

The fluorination of relatively high-boiling (compare to 1,1,2,2-tetrafluorochloroethane) α-hydro-ω-chloroperfluoroalkanes[1] goes, as test showed more selectively (Refer to Table 24).

Table 24. *Direct Catalytic Fluorination of $H(CF_2)_3Cl$, $H(CF_2)_4Cl$ and $H(CF_2)_8Cl$ (volume rate of input - 100 hour^{-1}, mole rate fluorine: substrate = 1,5).*

#	Catalyst	Temperature, K	Substrate			
			H $(CF_2)_3Cl$		H $(CF_2)_4Cl$	
			Conversion,%	Yield C_3F_7Cl, %	Conversion,%	Yield C_4F_9Cl%
1	α-Al_2O_3	413	12	83,7	15	99,1
2	-«-	433	20	82,4	23	97,8
3	-«-	453	35	82,0	48	97,1
4	-«-	473	68	81,5	93	96,0
5	NiF_2/α-Al_2O_3	373	10	98,8	14	99,7

6	-«-	393	20	98,0	24	98,7
7	-«-	413	42	97,7	48	98,2
8	-«-	433	88	97,3	90	97,8
9	-«-	453	97	96,8	98	97,4

[1]*They are also the waste products of TFE production.*

These data clearly illustrate the catalytic influence of coated nickel fluoride; indeed, the conversion grade (e.g. the fluorination rate) of substrate over catalyst of $NiF_2/\alpha\text{-}Al_2O_3$ is much higher under comparable conditions, than over unmodified $\alpha\text{-}Al_2O_3$. Here we shall also note, that interaction of $H(CF_2)nCl$ (n=3÷8) and undiluted fluorine over catalyst of $NiF_2/\alpha\text{-}Al_2O_3$ is characterized by practically quantitive yield of selective fluorination corresponding produts.

Chloroperfluoroalkanes obtained based on TFE production waste can be turned into corresponding perfluoroalkylfluorosulphates (when treating them with chlorine fluorosulphate), and further into fluoroanhydrides and perfluorocarbonic acids /187 – 189/; particularly, perfluoroheptanoic acid – an effective emulsifier used for production of polymers can be synthesized based on chloroperfluoroheptane.

2.5. Unsaturated and Hydrogen Containing Polyfluorinated Compounds Removal From Perfluorocarbon Liquids Using Catalytic Gas-Phase Fluorination

As it has been mentioned before, the treatment of corresponding hydrocarbons using "soft" fluorinating agent – cobalt trifluoride has been laid as a basis of our obtaining technology for a wide class of perfluorocarbonic liquids; fluorocarbonic liquids (raw material) forming at that contain significant amounts of unwanted admixtures – hydrogen containing and unsaturated polyfluorinated compounds. In the present part of work the results on studying the opportunity of fine purification of fluorocarbonic liquids raw materials from polyfluorinated admixtures during their thermal treatment in gaseous phase using "hard" fluorinating agent – elemental fluorine in the layer of $NiF_2/\alpha\text{-}Al_2O_3$ – an effective catalyst of direct fluorination of both hydrogen containing and unsaturated fluororganic compounds.

2.5.1. Fluorination of Raw Perfluorodimethylcyclohexane.

Perfluorodimethylcyclohexane (PFDMCH) is a promising fluorocarbonic liquid in terms of nanotechnologies. Besides that, the liquid is an effective dielectric and is used contemporary aviation technics. In /190,191/ the quality demands for PFDMCH are formulated, which, in particular, suppose a high purity of a finished product – the concentration of partially fluorinated admixtures must not exceed 40 mg/kg (in terms of detached ion-fluorine).

The known technology of PFDMCH contains thermal fluorination of dimethylbenzene (*meta-xylol*) by cobalt trifluoride, purification of raw PFDMCH e.g. removing of partially fluorinated compounds using acetone extraction, isolation of PFDMCH by rectification, which again undergoes multiply washing with acetone for the purpose of final removal of partially fluorinated admixtures from it.

The main disadvantages of this technology are:

- low quality of PFDMCH caused by unfinished removal of partially fluorinated admixtures during acetone extraction – their resudial content exceeds the permissible concentration more than 10 times (40 mg/kg);

- low productivity and high labour intensiveness of the stage of multiply extraction using acetone;

- relatively low yield of target product caused by forming of large quantities of unutilizable partially fluorinated compoinds;

- fire- and explosion safety caused by using of acetone;

- environmental pollution.

All these disadvantages are avoidable if we carry out the purification of raw PFDMCH by selective gas-phase catalytic fluorination using elemental fluorine; indeed, such setting of technology would allow increasing of target product purity due to lowering of residual content of partially fluorinated admixtures and utilizing of polyfluorinated dimethylbenzene derivatives obtaining target product – PFDMCH, as well as saying no to use of inflammable and explosive acetone, thus totally eliminating its dumping.

Information on catalytic fluorination of raw PFDMCH on laboratory and pilot scale is listed in Table 25; here as well, the results obtained during fluorination of raw product in an empty reactor with no catalyst are liste for you to compare.

From the data listed here one can see, that fluorination of raw PFDMCH using diluted fluorine in an empty reactor without catalyst at 570-620 K is characterized by low removal/purification grade from partially fluorinated compounds, which is at the level of 40-50% (experiments 1, 2 Table 25); at that, the process is going in a non-selective way forming large quantities of destruction and carbon-black products. The raw product after being treated with fluorine in an empty reactor gets its characteristic yellow colour.At temperature range over 620 K a sharp increase of destructive fluorination input occurs.Using of undiluted fluorine during fluorination in an empty reactor is rather complicated as in this case the process becomes explosive in a whole studied range of temperatures.

Table 25. *Direct Fluorination of Raw Product of PFDMCH* [1] *(volume rate of input -140 hour⁻¹)*

#	Catalyst	Temperature, K	Fluorine Conversion Grade, %	Substrate Destruction Grade,%	Concentration of partially fluorinated Admixtures, mg/kg	Grade o Purification from partially fluorinated Admixtures %
Laboratory experiment results (mole rate PFDMCH:fluorine = 5,3)						
1	Without catalyst	573	17	4,2	6020	52,8

2	-«-	623	51	5,3	7580	40,6
3	Cu, metall	573	26	0,8	3700	71,0
4	-«-	623	42	2,4	4800	62,4
5	α-Al_2O_3	573	16	0,2	98	99,2
6	-«-	623	21	0,2	62	99,5
7	-«-	673	22	0,4	37	99,7
8	-«-	723	24	0,5	24	99,8
9	NiF_2/α-Al_2O_3	573	24	0,1	50	99,6
10	-«-	623	28	0,1	34	99,7
11	-«-	673	32	0,2	18	99,9
12	-«-	723	35	0,4	12	>99,9
Results of pilot experiments (mole rate PFDMCH:fluorine = 1,4)						
13	NiF_2/α-Al_2O_3	573	-	0,1	70	99,2
14	-«-	573	-	0,2	73	99,2
15	-«-	623	-	0,2	47	99,5
16	-«-	623	-	0,2	48	99,5

17	-«-	673	-	0,3	15	99,8
18	-«-	673	-	0,2	13	99,9

[1]*Initial raw product of PFDMCH contained partially fluorinated compounds in a quantity (in terms of detached ion-fluorine) 12770 mg/kg (experiments 1-12) and 9130 mg/kg (experiments 13-18). In experiments without catalyst fluorine was diluted with nitrogen (up to 25 volume %), in other experiments undiluted fluorine was used.*

Using of known catalyst – metallic copper nozzle allows applying undiluted fluorine; at that, though the purification/removal grade from partially fluorinated admixtures doesn't exceed 75% it somewhat increase compare to fluorination in empty reactor (experiments 3-4, Table 25).

At temperatures above 620 K the fluorination in the layer of metallic copper is characterized by sharp increase of the raw material destruction grade and decrease of the purification/removal totalness from polyfluorinated admixtures.

Studying of raw product of PFDMCH at α-Al$_2$O$_3$ and NiF$_2$/α-Al$_2$O$_3$ revealed significant increase of purification grade(experiments 5-12, Table 25), which significantly grows with temperature increase (99,9% and more).

Fluorination even under rather severe conditions (720 K, undiluted fluorine) goes in a rather selective way – thus, the raw materials destruction grade at NiF$_2$/α-Al$_2$O$_3$ doesn't exceed 0,4 %.

Comparison of data obtained using α-Al$_2$O$_3$ and NiF$_2$/α-Al$_2$O$_3$ (experiments 5-12, Table 25) indicates significant catalytic influence of dispersed nickel fluoride – residual content of partially fluorinated admixtures at this catalyst can be lowered to 10-20 mg/kg; purification grade at that exceeds 99,9 %.

Data on direct fluorination of raw product of PFDMCH in the layer of NiF$_2$/α-Al$_2$O$_3$ at pilot plant (13-18, Table 25) indicates high effectiveness of catalytic method of removal and good reproduction of results at enlargement of fluorination scale.

We shall note, that listed results are laid as a base of developed by us and introduced technology of high purification PFDMCH, which includes thermal processing of dimethylbenzene using cobalt trifluoride, direct catalytic fluorination of formed raw product at NiF$_2$/α-Al$_2$O$_3$and rectification isolation of target product /192/; PFDMCH produced according to that technology meets the claimed demands by all the showings (ТУ-044-13-85).

2.5.2. Fluorination of Perfluorocarbon Liquids and Lubricants (PFCL and L) Raw material.

The technology of perfluorocarbonic liquids of B-1*, M-1*, lubricants UPI*, KS* and KST*, perspective liquids for nanotechnologies as well as PFDMCH technology contains thermal fluorination of corresponding hydrocarbons (in this case – the fraction of transformer/insulating oil) using cobalt trifluoride, purification of forming raw product from partially fluorinated compounds using multiple extraction by acetone and its fraction distillation at lowered pressure isolating target products. PFCL and L obtained in such way are of low chemical resistance caused by the concentration of significant amounts of partially fluorinated admixtures – for example, they are totally destroyed even at short-term contact

with 10-% aqueous solution of sodium hydroxide (350K).

-trademarks of OJSC HaloPolymer (Russia),

The fluorocarbonic liquids quality improvement can be achieved, as it has been mentioned before, if they are purified using method of catalytic fluorination (instead of extraction by acetone); such setting of technology would allow refusing of fire hazardous and explosive acetoneusing, as well as increasing the yield of target products due to utilization of polyfluorinated (so called "acetonesolubale") admixtures, which concentration in the raw product is rather big and amounts to 12-15%.

Information on direct gas-phase fluorination of raw product of PFCL and L is listed in Table 26.

The process carrying out in an empty reactor (without catalyst) is accompanied by non-selective destructive fluorination even at diluting fluorine with nitrogen. Fluorination over metallic copper catalyst also passes in a non-selective way (experiments 1-3, Table 26).

Using unmodified α-Al$_2$O$_3$ allows achieving of raw product's fine purification from partially fluorinated admixtures (the grade of purification reaches 99,2%); at the same time in a number of cases (refer to experiment 5 Table 26) they have observed sharp decrease of the process selectivity when using this contact.

Using nickel fluoride as a catalyst applied onto α-Al$_2$O$_3$, allowed significant increasing of PFCL and L product purification/removal grade from partially fluorinated admixtures (up to 99,9% and above) as well as stabilizing selective fluorination by undiluted fluorine.

Thus, in this case the use of NiF$_2$/α-Al$_2$O$_3$ allows solving the problem of selective fluorination.

Table 26. *Direct Fluorination of Raw Product of PFCL and L[1] (temperature – 673 K, reactor's volume – 50 ml, raw product input rate – 50 g/hour).*

#	Catalyst	Fluorine Input Rate, g/hour	Fluorine Conversion Grade, %	Raw Material destructtion Grade, %	Partially fluorinated Addmixtures Concentration mg/kg	Grade of Purification from partially fluorinated Addmixtures %
1	Without catalyst	3,3	>99	24	15600	-
2	-«-	4,4	>99	22	15000	-
3	Cu, metal	3,7	>99	17	7100	25,3

4	α-Al$_2$O$_3$	3,5	71	6	75	99,2
5	-«-	4,4	>99	14	3700	61,0
6	NiF$_2$/α-Al$_2$O$_3$	3,4	73	4	54	99,4
7	-«-	4,0	68	3	6	>99,9
8	-«-	4,0	64	3	5	>99,9

[1]*Initial raw product contained partially fluorinated compounds in amount of 9500 mg/kg (in recalculation per detached ion-fluorine). In experiment 2 nitrogen was being poured into reactor at a rate of 6 l/h; in all other experiments undiluted fluorine was used.*

It is interesting to note, that carrying out the purification of PFCL and L product using catalytic fluorination allows decreasing of partially fluorinated admixtures residual content by a factor of hundred compare to using of extraction by acetone. That fact indicates significant improvement of quality of target products, which reveals itself, particularly, in increasing of their chemical stability; thus, raw product after catalytic processing with fluorine endures even a prolonged heating up (375 K) with 40 % solution of sodium hydroxide. Improving quality of perfluorocarbonic liquids and lubricants can result in increase of their service life as well as open new fields for their application.

Conducted at industrial reactor experiments (NiF$_2$/α-Al$_2$O$_3$ catalyst's amount - 6,2 dm^3) fully confirmed the results of laboratory experiments.

Method of catalytic fluorination opens wide opportunities for sharp (two times) increase of production of deficit PFCL and L in their existing production. The icrease of productivity can be achieved, as pilot plant experiments proved, due to trivial increase of hydrocarbons input rate at fluorination using cobalt trifluoride at existing agregates of ongoing operation with further utilization of intensively forming partially fluorinated compounds in this case (35-38%) by selective catalytic fluorination using elemental fluorine /193/.

Thus, using of selective gas-phase fluorination when purifying raw product of *PFCL and L* from undrfluorinated compounds (instead of extraction by acetone) allows:

- significant improving of target products quality at account of sharp increase of totalness of their purification;

- increasing of target products yield at account of utilization of partially fluorinated ("acetone solubale") compounds containing in raw product.

- increasing dramaticallythe capacity of existing production;

- solving the problem of waste products regeneration;

- increasing the production fire safety and decreasing the environment due to total exclusion of acetone from technology.

2.5.3. Fluorination of Perfluorodecaline Raw Product

Technology of producing of Perfluorodecaline (PFD) – perspective fluorocarbonic liquid for nanotechnologies and main component of artificial blood substituent includes thermal fluorination using cobalt trifluoride, condensation of PFD raw product, its purification from partially fluorinated compounds by gase phase homogenious fluorination using diluted elemental fluorine, fine purification from partially fluorinated admixtures using processing with aqueous alcoholic solution of potassium hydroxide and rectification /194/.

A relatively low degree of PFD raw product purification from partially fluorinated compounds during its gas-phase fluorination using diluted fluorine and low productivity of fluorination unit are the disadvantages of this technology. In this connection the studying of catalytic fluorination of PFD raw product was of interest; data is presented in Table 27.

Table 27. *Direct Fluorination of PFD Raw Product[1] (temperature – 673 K).*

#	Catalyst	Volume rate of Input[2], hour^{-1}	Mole rate PFD:Fluorine	PFD Destruction Degree, %	Concentration of partially fluorinated Admixtures mg/kg	Purifca Degree from partially fluorinate Admixtu %
1. Laboratory experiments Results						
1	Without Catalyst	65	2,1	0,2	1312	94,2
2	-«-	95	2,1	1,9	1628	92,8
3	α-Al$_2$O$_3$	130	1,9	<0,1	241	98,9
4	NiF$_2$/α-Al$_2$O$_3$	100	7,2	<0,1	15	99,9
5	-«-	110	3,3	<0,1	5	>99,9
2. The Results of Pilot experiments						
6	Without catalyst	40	1,2	0,8	91	99,0
7	-«-	65	1,2	1,4	310	96,7

8	-«-	65	1,2	burning (carbon black, yellow product)		
9	$NiF_2/\alpha\text{-}Al_2O_3$	65	1,2	0,3	6	>99,9
10	-«-	105	1,2	0,4	8	99,9
11	-«-	130	1,5	0,4	17	99,8
12	-«-	200	1,4	0,4	34	99,6

[1]*The initial PFD raw product contained partially fluorinated compounds in amount of (in terms of detached ion-fluorine) 22670 mg/kg (experiments 1-5) and 9450 mg/kg (experiments 6-12). In experiment without catalyst fluorine was diluted with nitrogen to 15 volume % (experiments 1, 2, 6, 7) and to 30 volume % (experiment 8); in other experiments undiluted fluorine was used.*

[2]*Nitrogen input is not taken into account (was put into in experiments with no catalyst).*

It is typical, that homogenious selective fluorination (without catalyst) can be carried out only when fluorine is diluted with nitrogen – otherwise the fluorination is accompanied by raw materials destruction and decrease of purification degree.

The opportunity to use undiluted fluorine is a specific feature of fluorination in the layer of α-Al_2O_3 and nickel fluoride applied onto α-Al_2O_3, at that the process is going selectively and is characterized by sharp drop of residual content of partially fluorinated compounds – approximately by a factor of hundred compare to the homogenious fluorination (experiments 1-5, Table 27). Such a sharp increase of the purification degree is obviously a consequence of both fluorine activation (in case of NiF_2/α-Al_2O_3) and growth of concentrations of reacting components (fluorine and partially fluorinated admixtures) and contact period when excluding the nitrogen input into the reaction zone.

Pilot experiments fully confirmed the results of laboratory studies (experiments 6-12, Table 27) and they show a significant increase of purification degree and reactor's productivity when fluorinating in the layer of catalyst NiF_2/α-Al_2O_3 using undiluted fluorine.

The method of PFD raw product cathalytic fluorination is introduced in its production.

Results listed in the present work totally conform the facts /195 – 209) and allow drawing out a wide range of promising studies in the field of direct fluorination.

Thus, the carried out complex study of fluorination of wide range of unsaturated and hydrogen containing polyfluorinated organic compounds using elemental fluorine allowed creating scientific basics for selection of catalysts for their selective carrying out and selecting a universal catalytic composition - NiF_2/α-Al_2O_3, which is highly active, selective and stable.

3. Catalysis of Polyfluorinated Organic Compounds' Thermal Transformations. Aggression Resistant Catalysts Based on α-Al_2O_3

3.1 New Perspectives for Creating of Aggression Resistant Catalysts of Polyfluorinated Organic Compounds'Thermal Transformations

High reactive activity of medium caused by formation of aggressive products (hydrogen chloride, hydrogen fluoride, carbonyl difluoride etc.) as it has been mentioned before is a specific feature of thermal transformations of fluoroorganic compounds. This fact must be taken into account when developing catalysts of thermal transformations of polyfluorinated compounds (PoFC), which must be stable/resistant to the effect of initial compounds and reaction products even at high temperatures; chemical interaction of catalysts and components of reaction mixtures is as a rule accompanied by phase transfers, which result in sharp decrease of mechanical durability and decomposition of heterogeneous contacts.

Deep fluorination of γ-$Al_2O_3$when using catalysts based on it for direct fluorination of organic compounds is a demosnrative example of such interaction; the corresponding phase transfer as it has been mentioned earlier results in mechanical decomposition of that catalysts.

The analysis of articles regarding creaction of effective catalysts for thermal transformations shows, that applying of compositions chemically inert towards components of reaction mixtures under the conditions of a certain process is the main method providing stability for heterogeneous contacts. The nature of contrion at active centres of catalyst, which as a rule are metals' cations is defined at that by the nature of reagents. Thus metals oxides /210/ are used most often to intensify the oxidation by oxygen, metals sulfides /211/ are used to carry out the transfromations of sulphur organic compounds, metals nitrides and hydrides /212/ are used to activate the molecular nitrogen and hydrogen, metals chlorides and fluorides /213,214/ are used to catalyze thermal transformations of chlorine- and fluororganic compounds respectively.

Catalysts created without taking into account of these particularities are of lowered stability and, as a rule, they have got a limited, narrow operational temperature interval. Thus, the attempts of industrial use of metallic nickel, copper or chrome tp oxidate hydrocarbons or ammonia appeared to fail, particularly, due to oxidation of metals and their gradual decoposition /215/.

In /73/ it is being noticed, that temperature of direct fluorination of organic compounds at metallic catlysts must not exceed 600 K; otherwise, there is a deep fluorination of metals going on as well as their decomposition.

Even more seldom stability of catalysts is provided by their specific resistance to components of reaction mixtures; thus, the metallic platinum, which doesn't form oxides and decompose during exploitation is the most stable catalyst of high temperature (1100-1200K) selective oxidation of ammonia using oxygen /216/.

As we have showed, its exteremely high resistance/stability in fluorinating media (it doesn't decompose in elemental fluorine even at 920K) is a specific feature of α-Al_2O_3. Using of stable catalysts based on α-Al_2O_3allows, as it has been shown above, sharp increasing (compare to known catalysts)of selectivity and rate of direct fluorination of polyfluorinated organic compounds. Besides that, α-Al_2O_3 isquite available, cheap and widely produced (in different modofications) by Russian industry /217/. All this opens up the new perspectives of creation of effective aggressive resistant catalysts of thermal transformations of polyfluorinated organic compounds based on α-Al_2O_3.

In the present section the reslts of studies regarding catalysis of thermal dechlorination of

fluorochlorocarbones using hydrogen and terafluoroethylene oxidation are listed.

3.2 Fluorochlorocarbons' Dechrolorination by Hydrogen.

Fluorocarbones dechlorination is one the main methods of fluorolefines synthesis – raw material to obtain fluoroplastics, fluororubbers and a whole number of other practically important fluororganic products. Fluorochlorocarbones' dechlorination technology is now based on using expensive and deficit metallic zinc and it is characterized by low productivity, high metallic capacity and environmental congestion with toxic zinc chloride. All of these drawbacks can be avoided by using molecular hydrogen as a dechlorinating agent.

At the same time a relatively high temperature (600K and above) is needed for dechlorination of fluorochlorocarbones using hydrogen over catalysts, that leads to side reactions going on. In this connection the development of active and stable catalytic systems providing selective dechlorination of fluorochlorocarbones using hydrogen is actual.

3.2.1 Analytical Review. Fluorolefines' Obtaining by fluorochlorocarbons' hydrogen dechlorination

Catalytic dechlorination of 1,1,2-trifluorotrichloroethane (R-113) using hydrogen is one of the most fully described.

The only example of carrying out this process over the absence of catalyst is listed in /218/, where heated iron tube was used as a reactor. At 820-870 K and contact period of 1-2 sec the conversion degree of R-113 amounted to 24-36%, and the yield of trifluorochloroethylene - 60-84%. Trifluorodichloroethane (R-123) and tetrafluoroethylene are formed as by-products.

For the first time the obtaining of fluorochlorocarbones by catalytic dechlorination using hydrogen was described by the authors /219/; copper (5-10%) applied onto charcoal and silicagel was used as catalyst, and 1,2-dichlotetrafluorethane, 1,1,2-trifluorotrichloroethane, 1,2-difluorotetrachloroethane, 1,1-difluorotetrachloroethane and 1,2-dichlorohexafluorocyclobutane were used as substartes. The conversion degree of 1,1,2-trifluorotrichloroethane and the yield of trifluorochloroethylene over Cu/SiO$_2$ catalyst at 730-750K and contact period of 10 seconds amounted to 50% and 74-79% respectively.

It is also noted, that metallic copper is less active, than the applied one; increasing temperature up to 870K was required here to achieve comparable conversion degrees.

Dechlorination of 1,2-difluorotetrachloroethane passes under milder conditions (640-660K); the yield of 1,2-difluoroethylene is 90% for reacted (72%) substrate /219/. The conversion degree of non-symmetrical isomer – 1,1-difluorotetrachloroethane is significantly lower under the same conditions (only 20%). The using of nickel, cobalt, platinum and palladium 1,1,2-trifluorotrichloroethane applied onto activated carbon is described in /220-222/.

Maximum yield of trifluorochloroethylene (75%) has been reached using nickel containing catalyst at 700-750K, contact period of 2,5 sec and mole ratio hydrogen : R-113 equal to 1,3.

It is being noted /223/, that using of calcium and barium phosphates, chlorides and fluorides as catalytic carriers doesn't result in rising (compare to activated carbon) of catalysts' effectiveness. Thus, when using these carriers modified by nickel the trifluorochloroethylene yield amounted to 20-40% at 670-750K and contact period of 4,5 seconds.

Also the activity decrease of these catalysts is being noted: fast (in 2-3 hours) – due to forming of nickel fluorides and chlorides, and slow (in 30 hours) – as a result of densinty

products forming on the surface.

In /224/ a wide range of catalysts of 1,1,2-trifluorochloroethylene dechlorination using hydrogen is described (active components – copper, cobalt, silver or platinum, carriers – active aluminium oxide, activated carbon, glass necklace or magnesium fluoride). Maximum yield of trifluorochloroethylene – 96,7% has been reached at R-113 conversion degree of 65% using magnesium fluoride modified by copper and cobalt (mole ratio of components Co:Cu:MgF$_2$= 1:30:150) at 734 K, contact period of 2-3 sec and ratio of substrate:hydrogen equal to 1. Using of magnesium oxide as a carrier results in some decrease of selectivity (to 93%); the raw material conversion degree remains the same at that. It is also being noted /224/, that dechlorination of fluorochlorocarbones at temperature above 870K is undesirable due to selectivity decrease and lowering of catalyst run; catalyst can be regenerated by oxygen containing gas, for example, air at 580-950 K.

In /225/ the trifluorochloroethylene obtaining method by dechlorination of 1,1,2-trifluorotrichloroethane at calcium fluoride modified by chromium oxide as well as copper or nickel is described.

At 620-670 K and contact period of 10 seconds the conversion degree of substarte at Cu,Cr$_2$O$_3$/CaF$_2$ catalyst amounted to 35-40%; at that trifluorochloroethylene was virtually the only products of reaction. Optimal mass ratio of Cu:Cr$_2$O$_3$:CaF$_2$ at preparing the catalyst from nitrates amounts to 30:15:55. It is being noted /225/, that catalyst containing only chromium oxide and calcium fluoride is unactive under these conditions.

At the same time the chromium oxide applied onto chips from alundum or melted aluminium oxide can be used as it follows from /226, 227/ as a catalyst of 1,1,2-trifluorotrichloroethane dechlorination; conversion of raw materials and yield of trifluorochloroethylene at 798 K and contact period of 15 seconds amounted to 24,5 and 73%, respectively. Increased time of catalyst operation to regeneration is being noted (from 52 to 200 hours). In case of magnesium fluoride modified by chromium oxide the process is carried out at 750-820 K, contact period of 2-15 seconds and in excess of hydrogen (25% of stechiometric quantity); conversion of raw material (35%-40%) and yield of trifluorochloroethylene (50-55%) do not decrease during 30 hours of continiuos operation of catalyst /226/.

In /228/ the dechlorination of 1,1,2-trifluorotrichloroethane at chromium oxide modified by copper and barium oxide has been described. The catalysts are being prepared by co-precipitation of hydroxide from the nitrates solutions of different mass ratio of metals Ba:Cr:Cu – from 1:1,5:1,5 to 1:8:9. The ratio of Ba:Cr:Cu equal to 1:3:3,1 is the optimal one; the yield of trichloroethylene and the conversion degree at such catalyst amounted to 85 and 60% respectively (temperature 648 K, contact period 9 sec, mole ratio hydrogen:R-113=1,2) It is being noted /228/, that the carrying out the reaction at temperature above 700 K is accompanied by the transfer of chromium oxide into catalytically inactive form.

In /229/ the data on dechlorination of 1,1,2-trifluorotrichloroethane at activated carbone, magnesium fluoride, chamotte and firebrick modified by copper, nickel, cobalt and iron are listed. Maximum yield of trifluorochloroethylene – 60-75% at conversion of R-113 of 54-83% has been achieved at iron containing catalysts (770-800 K, contact period – 4-10 seconds).

In /230/ the results on 1,1,2-trifluorochloroethane using hydrogen at potassium-magnesium fluoride (NaMgF$_3$) are listed – the yield of trifluorochloroethylene and conversion degree of 1,1,2-trifluorotrichloroethane at 773 K amounted to 83,9 and 21,3% respectively.

Modifying of potassium-magnesium fluoride using nickel, copper and iron leads to significant increase of catalytic activity as it is noted in /230/ and allows putting down the process

temperature; thus, during dechlorination in the layer of copper containing contact (6,3 mass.% copper, 748 K) the conversion degree of 1,1,2-trifluorotrichloroethane amounted to 35,6%, and the yield of trifluorochloroethylene - 85,2%.

Modifying of potassium-magnesium fluoride using palladium (0,5 mass.%) leads to sharp increase of catalysts activity /230/, that allows to lower the temperature to 470 K; at that a significant change in activity of dechlorination selectivity takes place – trifluoroethylene is the main reaction product. In /230,231/ they also point out the high catalytic activity of metallic palladium at 470-570 K in dechlorination of trifluorochloroethylene by hydrogen to trifluoroethylene.

In /232/ you can find the detailed description of recipe and method to prepare oxide aluminium molibden catalyst and an opportunity of its use to dechlorinate R-113 using hydrogen obtaining trifluorochloroethylene is noted as well.

The review of works on dechlorination of 1,2-dichlorotetrafluoroethene (R-114) using hydrogen demonstrates, that the same types of catalysts that are used at dechloriantion of R-113 are usedhere. Thus, in /233,234/ the use of mixture of copper, barium and chromium oxides is described; the catalyst is being prepared by co-precipitation of copper and barium hydroxide with ammonium chromate, the forming complex is being heated through at 623 K and processed with hydrogen at temperature up to 698 K. The conversion degree of 1,2-dichlorotetrafluoroethane and the yield of tetrafluoroethylene at such catalysts under optimum conditions (650-720 K, contact period 5-10 seconds, mole ratio substrate:hydrogen – 0,75-1,25) amount to 20-25% and 60-65% respectively.

It is being noted, that alkaline earth metals fluorides, magnesium, aluminium and silicium oxides can be used as carriers for copper-chromium oxide catalysts.

In /235/ the data on degalogenation of fluorohalocarbones containing 2-8 carbon atoms using hydrogen at aluminium fluoride modified by copper, rhodium, platinum and chromium oxide are listed. Ceolites and active aluminium oxide were used as carriers for a number of catalysts. During dechlorination of 1,2-dichloroethane for example at aluminium oxide modified by copper and chromium oxide (673 K, contact period 60 seconds, mole ratio R-114:hydrogen=1), the yield of tetrafluoroethylene amounted to 61% and the subsrate conversion – to 31%.

Also the iron group metals phosphates applied onto γ-Al$_2$O$_3$ /236,237/ are offered as catalysts for dechlorination of fluorochlorocarbones containing 2-10 carbon atoms; the amount of metal is usually no less than 3% of catalyst weight.

The catalyst is treated with mixture of nitrogen and anhydrous hydrogen fluoride (mole ratio N$_2$:HF=1) at 406 K before the reaction. Nickel containing catalysts are most effective; thus, at dechlorination of 2,3- dichlorooctafluorobutane at nickel oxide modified by nickel phosphate (926 K), perfluorobuten-2 of 88% yield had been obtained at the fluorochlorocarbon conversion degree of 92% /236/.

A two-stage catalytic method of degalogenation of fluorohalocarbons containing 2-10 carbon atoms is described in /238/. At first stage of fluorohalogenating the substarte is put into contact with hydrogen at catalyst containing iron group phosphates applied onto fluorinated γ-Al$_2$O$_3$ at 480-700 K pressure ranging from $9,8*10^4$ to $2,0*10^6$ Pa. The amount of metal phosphate in catalyst in terms of metal is 0,1-10,0 mass.%, the amount of fluorine in carrier– 50-68 mass.%.

The reaction mixture forming at first stage is put into contact (at 480-700 K) with catalytic composition containing oxides and chlorides of cobalt, nickel, zinc, chrome and iron as well as

barium chloride at the carrier made of activated carbon or aluminium oxide and fluorolefines of low by-products content are obtained. Thus, during dechlorination of 1,2-ichlorotetrafluoroethane over fluorinated aluminium oxide modified by nickel phosphate (588 K, contact period of 12,5 seconds) and following contacting of reaction gases with barium chloride applied onto activated carbon (673 K, contact period of 180 seconds) tetrafluoroethylene was obtained with the yield of 71,2% (in a one-stage process its yield equaled to 58,9%). The author /238/ supposes, that increasing of yield of target product when using two-stage method is caused by transformation of by-products (1,1,2,2-tetrafluorochloroethane and 1,1,2,2-tetrafluoroethane) at second stage forming tetrafluoroethylene.

The obtaining of hexafluoropropylene by catalytic dehydrochlorination over hydrogen is described in /239/. The process is being conducted inside nickel tube at 650-750 K in the layer of alkaline and alkaline earth metal modified by copper, nickel and chromium oxide. The yield of hexafluoropropylene at a contact period of 2,5 sec and substrate:hydrogen ratio equal to 1 amounted to 94% and the substrate conversion degree – 56%.

In /240/ data on dechlorination of 1,1-difluoro-1,2-dichloroethane on nickel spirals are listed; at 720-870 K, mole ratio substrate:hydrogen equal to 1,25 and contct period of 10 seconds the yirld of 1,1-difluoroethylene exceeded 99%, and the substrate conversion degree was 40-45%.

Thus, applied catalysts are used to intensify the dechlorination of fluorochlorocarbones using hydrogen. As a rule, nickel, cobalt, copper and chromium oxide are their active components, and activated carbon, silica gel, ceolites, active aluminium oxide, aluminium, calcium and magnesium fluorides are their carriers.

Dechlorination selectivity of 1,2-difluorotetrachloroethane, 1,1,2-trifluorotrichloroethane and 1,2-dichlorotetrafluoroethane at these catalysts is at the level of 90, 75-85 and 60-65%, respectively.

3.2.2. 1,2-Dchlorohexafluoropropane dechlorination

1,2-dichlorohexafluoropropane (R-216) is a multitonnage waste product of tetrafluoroethylene production and undergoes thermal elimination or is thrown into the atmosphere.The dechlorination of R-216 using hydrogen obtaining hexafluoropropylene (HFP) – a key deficit raw material for production of a number of fluoroorganic products (fluoropolymers, fluorocaotchuoc, fluoropolyesters) is one of the ways to utilize it:

$$C_3F_6Cl_2 + H_2 \xrightarrow{KT} C_3F_6 + 2HCl + 13 \text{ kJ/mol}$$
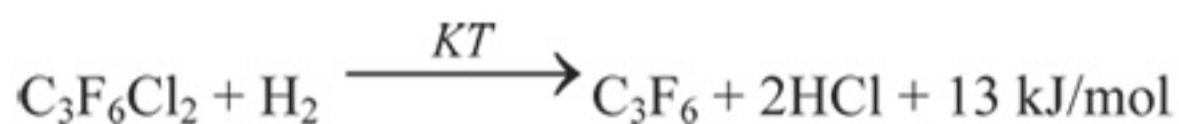
Selecting the catalytic carrier was the first stage of development of effective catalyst for dechlorination of 1,2-dichlorohexafluoropropane.There are no messages on dechlorination of 1,2-dichlorohexafluoropropane; we have tested carriers – activated carbon, active aluminium oxide, aluminium, magnesium and calcium fluorides, which are widely used to prepare catalysts of one type dechlorination processes PoFC /225-240/. Besides that, we have tested α-Al$_2$O$_3$for the first time for this type of reaction, as it has been already mentioned it is highly resistant in agressive fluorinating media.

It's typical, that known carriers containing silicon oxide (silica gel, amorphous aluminium silicate, ceolites), and based on them catalysts are decomposing as well as experiments proved in the first hours of operation, which can be explained by the presence of anhydrous hydrogen fluoride active towards silicon oxide, which is one of the reaction by-products.

Information on catalytic properties of crriers is listed in Table 28 (experiments 2-8); here the results on non-catalytic interaction between 1,2-dichlorohexafluoropropane and hydrogen are listed as well (experiment 1).

Table 28. *Catalytic Dechlorination of 1,2-dichlorohexafluoropropane Using Hydrogen (equimolar reagents mixture input rate - 285 hour^{-1})*

Judging by the listed data one can see, that even in the absence of catalysts the formation of HFP takes place, though the substrate conversion degree is not high and even at 843 K doesn't exceed 10%. It can also be seen, that at activated carbon and γ-Al$_2$O$_3$ significant amounts of byproducts are formed, and target product yield doesn't exceed 15%. It is typical, that the chemistry of formation of virtually all byproducts can be explained by disproportionation of the initial 1,2-dichlorohexafluoropropane and dechlorination of disproportionation products using hydrogen (C$_3$F$_7$Cl, C$_3$F$_5$Cl, C$_3$F$_4$Cl$_2$, C$_3$F$_3$Cl$_3$), as well as hydrohalogenation of HFP (C$_3$F$_7$H, C$_3$F$_6$HCl). We will also note, that γ-Al$_2$O$_3$ is decomposing during thermal contacting with R -216 and hydrogen.

Application alkaline earth metals fluorides allows achieving high (over 90%) yield of HFP (experiments 5,6, Table 28): at the same time practical application of these carriers is rather difficult, because even fresh samples are of low mechanical durability. Though melted calcium fluoride is of high mechanical durability, it is characterized by low selectivity and activity (experiments 7, Table 28).

High yield of target product is typical for α-Al$_2$O$_3$ (experiment 8, Table 28); even the prolong presence of this carrier in the reaction zone under rather severe conditions doesn't influence much its mechanical durability. This result can be explained using data of X-ray phase and chemical analysis of α-Al$_2$O$_3$, and also catalysts based on it after operation, which show the formation only of aluminium fluoride phase trace amounts. On the contrary, its deep fluorination is typical for the catalysts based on γ-Al$_2$O$_3$, and as a consequence loss of mechanical durability.

Thus, testing a wide range of carriers showed, that only α-Al$_2$O$_3$ has got all necessary qualities and it can be used as a carrier for effective catalyst for dechlorination of 1,2-dichlorohexafluoropropane using hydrogen.

Modifying of α-Al$_2$O$_3$ using known active components – chromium oxide, metal cobalt, copper and also nickel results in all cases as it follows from Table 28 (experiments 9-12) and Pic. 3a in increasing (compare to non-modified α-Al$_2$O$_3$) of substarte conversion degree. At that, the catalyst modified using nickel is most active one, and the one modified by chromium oxide is the least active one.

Samples of α-Al$_2$O$_3$,modified by cobalt and copper are of intermediate activity. The yield of HFP within the range of 670-770 K is approximately equal at all the catalysts and is at the level of 90 % (the yield at the sample modified by chromium oxide is somewhat lower). At increasing the temperature up to 840 K the yield of HFP at all the catalysts is going downwards.

α-Al$_2$O$_3$, modified by nickel is a rather active and selective catalyst to obtain HFP using dechlorination of 1,2-dichlorohexafluoropropane, what assumes it can be used in practics; at the same time the application of already ready to use commercial heterogeneous contacts at putting the method into practice would have allowed escaping the difficulties connected to setting up a production of a special catalyst.

Due to that we have tested commercial nickel containing catalyst GIAP-3-6H, which is (after

thermal processing in the hydrogen medium), applied onto α-Al$_2$O$_3$, and for comparison catalyst NKM-1, which is nickel applied onto γ-Al$_2$O$_3$ (experiments 13-16, Table 28).

Judging by the data listed one can see, that using of catalyst GIAP-3-6H allows achiving virtually quantitive yield of HFP – thus, at 793 K and reagents input rate of 285 hour^{-1} the yield of C$_3$F$_6$ amounts to 96,3 %, and conversion degree of 1,2-dichlorohexafluoropropane – 90 % (experiment 16, Table 28).

Analogous to it in terms of chemical composition catalyst NKM-1 prepared based on γ-Al$_2$O$_3$ is characterized by significantly lower yield of HFP (experiment 13, Table 28).

Thus, commercial heterogeneous GIAP-3-6H, is an effective catalyst of dechlorination of 1,2-dichlorohexafluoropropane using hydrogen; high yield of HFP at that is backed by using α-Al$_2$O$_3$as catalytic carrier, on surface of which there are no centres, causing the occurrence of side reactions.

Initial data on desiging pilot plant for utilization of R-216 with obtaining of HFP were issued by the results of work.
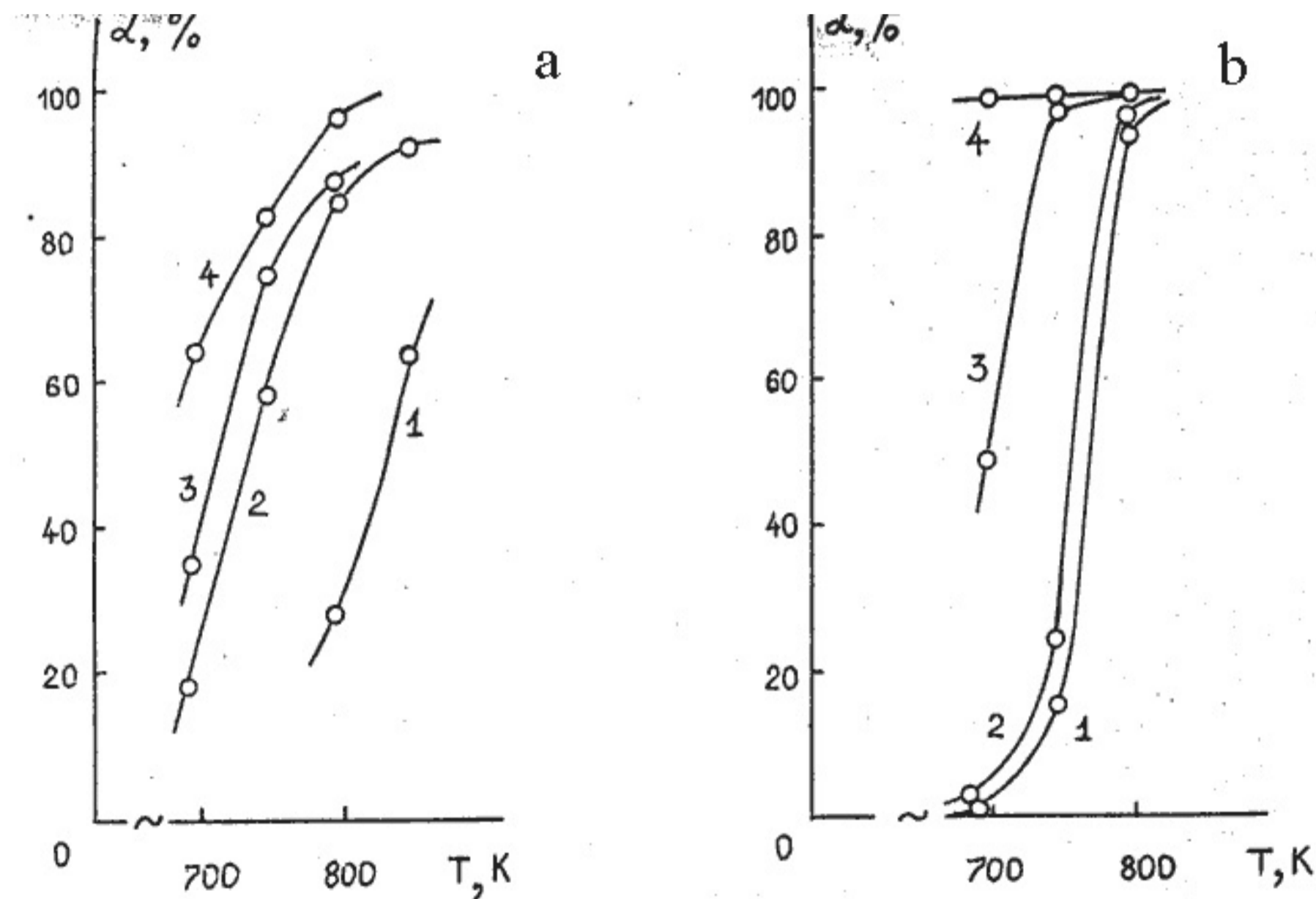
Pic 3. *Temperature dependancies of conversion degrees of (α) 1,2-dichlorohexafluororopane (a) and 1,2-difluorotetrachloroethane (b) while contacting hydrogen at catalysts: 1 – α-Al$_2$O$_3$; 2 – Co /α-Al$_2$O$_3$; 3 – Cu /α-Al$_2$O$_3$; 4 – Ni /α-Al$_2$O$_3$ (volume rate of input of reagents equimolar mixture is 285 hour^{-1}).*

3.2.3. 1,2-Ddifluorotetrachloroethane dechlorination

1,2-difluorodichloroethylene is an initial reagent for the synthesis of perfluoromethylvinyl ether – a raw material for the production of new types of fluororubbers and fluoropolymers. Catalytic dechlorination of 1,2-difluorotetrachloroethane using hydrogen is one of the ways to obtain 1,2-difluorodichloroethylene:

$$C_2F_2Cl_4 \; + \; H_2 \quad \xrightarrow{\;KT\;} \quad C_2F_2Cl_2 \quad + \quad 2HCl \quad - 13 \; кJ/mol$$
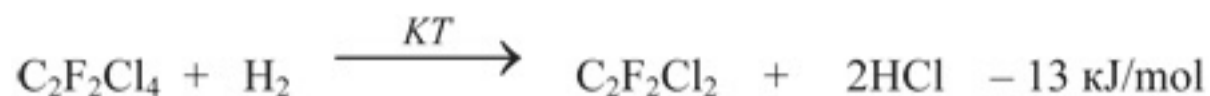
Information on catalytic dechlorination of 1,2-difluorotetrachloroethane using hydrogen is listed in Table 29; here the results on their non-catalytic interaction are listed as well.

It can be seen, that at temperature below 740 K the reaction in the absence of catalyst (tubular quartz reactor) doesn't occur, substarte's conversion doesn't exceed 6% under these conditions. At temperature over 740 K we observe sharp increasing of conversion degree even in the absence of catalyst (experiment 2, Table 29); at that the yield of target product – 1,2-difluorodichloroethylene is not high and is at the level of 60%.

The analysis of data regarding catalytic ptoperties of known carriers (γ-Al_2O_3; AlF_3, activated carbon, MgF_2) proves, that γ-Al_2O_3 is of least selectivity – the yield of 1,2-difluorodichloroethylene in this case doesn't exceed 2%, and R-113, 114 and tetrachloroethylene are the main products of reaction.

Data regarding catalytic properties of aluminium fluoride (obtained by fluorination of γ-Al_2O_3 using elemental fluorine), activated carbon and magnesium fluoride proves, that the yield of target product at these carriers is quite high and amounts to 80-90% at conversion degres of 1,2-difluorotetrachloroethane – 70-99% (experiment 5-10, Table 29).

At the same practical application of these carriers is rather complicated. Aluminium and magnesium fluorides are of low mechanical durability and decompose while operating. Activated carbon gradually looses its activity; at the same time the regeneration by high temperature air treatment, which is effective for mineral carriers /224/, in case of activated carbon is absolutely unacceptable.

Table 29. *Catalytic Dechlorination of 1,2-difluorotetrachloroethane Using Hydrogen (the input rate of equimolar mixture of reagents – 285 hour^{-1})*

While testing the carriers a maximum yield of target product had been reached at α-Al_2O_3 – 94,3 % at full substrate's conversion (experiment 12, Table 29). Experiments proved, that α-Al_2O_3 are of high mechanical durability, which isn't decreasing even at its prolong operation. The absence of forming of products of compacting on its surface which are able of lowering of catalytic activity is a α-Al_2O_3 characteristic feauture. All of that allows us to consider α-$Al_2O_3$the most appropriate carrier for an effective catalyst of 1,2-difluorotetrachloroethane dechlorination, as well as using it as a catalyst in the unmodified form.

It is significant, that the chemistry of forming of practically all of by-products of 1,2-difluorotetrachloroethane and hydrogen interaction, as well as one of 1,2-dichlorohexafluoropropane can be explained by disproportioning of the initial substarte and dechlorination of disproportioning products using hydrogen (C_2F_5Cl, $C_2F_4Cl_2$, $C_2F_3Cl_3$, C_2Cl_4 , C_2FCl_3, C_2FCl_5), as well as hydrohalogenation of halolefines forming at that (C_2F_4ClH, $C_2F_2Cl_3H$). Besides that, during interaction of 1,2-difluorochloroethylene and and hydrogen chlorine substituting products for hydrogen – 1,2-difluorochloroethylene and 1,2-difluoroethylene in the molecule of 1,2-difluorodichloroethylene are formed (for example, the yield of $C_2F_2H_2$, in the experiments 2 amounted to 4,2%).

It might be an interesting fact, that α-Al$_2$O$_3$is quite inert, as experiments proved, in the reactions of disproportioning; thus, the conversion degree of 1,2-difluorotetrachloroethane at this carrier in the medium of nitrogen at high temperatures – 843 and 893 K amounted only to 1,2% and 3,2% respectively. At that, in the reaction products 1,2-difluorodichloroethylene and chlorine have been discovered – this indicates the dechlorinating passing in the inert medium. Thus, the role of hydrogen at dechlorination of fluorochlorocarbones at carriers (especially, at high temperatures) can be included in connecting the forming chlorine in corresponding shift of balance of substrate's dissociation onto fluorolefine and chlorine.

As we can see from the results listed in Table 29 (experiments 13-20) and Pic 3b the modifying of α-Al$_2$O$_3$ using chlorine, cobalt, copper and nickel oxide results in significant growth of activity, which is increasing in the row of Co<Cr$_2$O$_3$<Cu<Ni. For the contacts modified using nickel the total conversion of substrate is observed even at 690 K, copper at 740 K, and cobalt and chromium oxide – only at 790 K.

Contacts modified by chromium oxide are of least selectivity; here 1,1,2-trifluorotrichloroethane and pentafluorochloroethane are the main by-products, which indicates the significant input of substrate's disproportioning.

α-Al$_2$O$_3$, modified by nickel is of most high selectivity; the yield of 1,2-difluorodichloroethylene is reaching 97,1% at full conversion of 1,2-difluorotetrachloroethane (experiment 19, Table 29). Such high activity and selectivity of Ni /α-Al$_2$O$_3$catalyst inpact create prerequisites for commercial implementing of R-112 dechlorination using hydrogen.

Testing of GIAP-3-6H (Ni/α-Al$_2$O$_3$) commercial catalyst revealed its high activity and selectivity (experiments 23-25, Table 29); the yield of 1,2-difluorodichloroethylene at practically total conversion of substrate had reached 98,5%. NKM-1 nickel containing commercial catalyst prepared on the basis of γ-Al$_2$O$_3$ tested for comparison and analogous by chemical composition is of significantly lower impact selectivity (experiment 21, Table 29) and is decomposing in the course of operation.

Forming of significant quantities of 1,2-difluoroethylene, yield of which had reached 24,8% (693 K) is typical for this catalyst besides by-products listed in Table 29. It is an interesting fact, that the preliminary processing of NKM-1 catalyst using fluorine (743 K) results in significant increasing of its impact selectivity (experiment 22, Table 29).

High mechanical durability, which isn't decreasing in the course of operation and regeneration is an distinguishing feature of GIAP-3-6H catalyst. Prolonged use of this catalyst is accompanied by decreasing of its activity, which is caused by formation of products of compacting on its surface; air regeneration (770-820 K) results in full restoration of catalytic activity.

For the purpose of increasing 1,2-difluorotetrachloroethane hydrogen dechlorination stability we have tested a double layer catalyst. Unmodified α-Al$_2$O$_3$(80 mass.%) was the first layer, GIAP-3-6H catalyst (20 масс.%) was the second one. Such double layer catalyst demonstrated high activity and selectivity. Thus, at 740-760 K we have observed full conversion of substarte, and process selectivity had reached 97%. Besides that, double catalyst was of high stability. That effect probably, is caused by the fact, that in the first layers, e.g. in place, where carbon-producing goes more intensively α-Al$_2$O$_3$has been used, at which products of compaction do not form.

According to the results of work the initial data for projecting the 1,2-difluorodichloroethylene obtaining technology using dechlorination of 1,2-difluorotetrachloroethane by hydrogen at double-layer catalyst α-Al$_2$O$_3$ – GIAP-3-6H has been

issued.

3.2.4. 1,1,2-Trifluorochloroethylene dechlorination

Production of trifluorochloroethylene – a raw material for the synthesis of fluoroplastics and fluororubbers is based on dechlorination of 1,1,2-trifluorotrichloroethane by expensive and deficit metallic zinc and it is characterized by low productivity, high materials consumption, as well as polluting the environment with toxic zinc chloride. Carrying out the dechlorination of 1,1,2-trifluorotrichloroethane using hydrogen we can escape all of these drawbacks:

$$C_2F_3Cl_3 + H_2 \xrightarrow{KT} C_2F_3Cl + 2HCl \quad +16 \text{ кJ/mol}$$

Data on catalytic properties of known carriers for catalysts of dechlorination of fluorocarbons using hydrogen – γ-Al$_2$O$_3$, activated carbon, aluminium, magnesium fluorides, as well as melted calcium fluoride are listed in Table 30; the results obtained using α-Al$_2$O$_3$ are listed here too, and for comparison – in an empty reactor, without catalyst.

One can see, that even in the absence of catalyst a significant conversion of 1,1,2-trifluorotrichloroethane can be observed; at that, the selectivity of dechlorination is decreasing while the temperature is rising (experiments 1, 2, Table 30). Thus, at 793 and 843K the substrate's conversion degree was 11 and 88% respectively, and the yield of trifluorochloroethylene – 78,3 and 53,7% respectively. Trifluoroethylene, which yield, for example, at 843 K was 24,8%, was the main by-product at non-catalytic gas-phase interaction of 1,1,2-trifluorotrichloroethane and hydrogen.

The analysis of data obtained using γ-Al$_2$O$_3$ and AlF$_3$ (experiments 3-6, Table 30) shows, that products of disproportioning of initial R-113 – R-115, R-114, R-112 are the main products here, as well as the product of hexachloroethane dechlorination – tetrachloroethylene. The yield of target product doesn't exceed 0,1%. Besides that, R -122, R-123, R-124 and 1,2-difluorodichloroethylene were discovered in the reaction products.

It is worth noting, that the same products are formed during dechlorination of 1,2-difluorotetrachloroethane.

When using activated carbon as a catalyst the yield of target product id significantly higher and is reaching 89,8% (experiments 7,8 Table 30).

Table 30. *Catalytic Dechlorination of 1,1,2-Trifluorotrichloroethane Using Hydrogen (the input rate of equimolar mixtire of reagents -285 hour[-1]). The Yield of Reaction By-Products[1], %.*

The activity of activated carbon dramatically decreases in time and its regeneration by high-temperature processing using air is unacceptable, which is a significant drawback of activated carbon.

In what follows we have tested magnesium and calcium fluorides. Magnesium fluoride was prepared by pressing of high disperse salt (surface – 12,5 m^2/g); that sample was characterized by low mechanical durability. On the contrary, calcium fluoride was rather stable; it was obtained using melting method (surface 0,2 m^2/g).

One can see from the Table 30 (experiments 9 – 11), that substrate's conversion degree is significantly higher at more dispersed magnesium fluoride. Main by-products here are the

same as at non-catalytic interaction of 1,1,2-trifluorotrichloroethane and hydrogen – trifluoroethylene and trifluorodichloroethane isomers (R-123); the yield of target product is rather high and is located at the level of 85 - 90%.

The analysis of data obtained using α-Al_2O_3 shows that application of that carrier allows reaching high yield of trifluorochloroethylene in a wide range of temperatures; thus, a 740-790 K the yield of target product is at the level of 86-91% (experiments 12, 13, Table 30). It is interesting, that the activity of that carrier even in unmodified form is rather high (higher, than one of MgF_2 and CaF_2); we have mentioned earlier, that α-Al_2O_3 is an effective catalyst for dechlorination of 1,2-difluorotetrachloroethane.

Thus, it was discovered by testing of catalytic carriers, that only melted calcium fluoride and α-Al_2O_3 are of sufficient stable mechanical durability. Modifying calcium fluoride using copper, and especially, nickel results in significant increasing of catalytic activity (experiments 14 -17, Table 30), at that, the yield of target product is 87 – 90%.

α-Al_2O_3, modified by chromium oxide is characterized by significant formation of R-114 and difluorodichloroethylene; total yield of those by-products reaches 23% (experiments 18,19, Table 30). Application of α-Al_2O_3 modified using palladium results in significant increasing of trifluoroethylene (experiment 20, Table 30).

α-Al_2O_3 modified by cobalt at temperature below 740 K is characterized by high selectivity (93-95%); at that, substrate's conversion degree is low (below 25%). Temperature increasing up to 793 K is accompanied by (experiment 22, Table 30) significant lowering of selectivity (down to 85,7%).

Modifying of α-Al_2O_3 using nickel results in dramatic increase of catalytic activity at moderate temperatures (690-740 K). Thus, conversion degree of 1,1,2-trifluorotrichloroethane at α-Al_2O_3 after modifying using nickel increases at 693 K from 2 up to 41%, and at 743 K – from 23 up to 70% (experiments 23, 24 Table 30).

The selectivity of dechlorination at Ni/α-Al_2O_3 catalyst, including commercial sample of GIAP-3-6H (experiments 25, 26, Table 30) is 84-90% at conversion degrees of 1,1,2-trifluorotrichloroethane – 40-90%. For comparison, the yield of target product was only 19,5% (experiment 27, Table 30) at catalyst Ni/γ-Al_2O_3 (NKM-1) under analogous conditions.

Abrupt increase of 1,1,2-trifluorotrichloroethane dechlorination selectivity (94%) has been recorded while studying catalytic properties of copper modified α-Al_2O_3 (experiments 28-30, Table 30). The initial activity of that catalyst is also rather moderate– substrate's conversion degree exceeds 99% at fresh samples and temperature over 790 K.

Cu/α-Al_2O_3 particularity is the significant drop of its activity in the course of experiment (compare experiments 29, 30, Table 30). Regeneration using thermal treatment in the air flow, which leads to virtually total recovery of nickel containing catalysts, proved to be low effective for Cu/α-Al_2O_3. The analysis of composition of that catalyst before and after its use for 48 hours (793K) showed a significant decreasing of copper content (from 9,8 down to 2,8 mass.%). Thus, low stability can be caused by its depleted active component, for example, as a consequence of evaporating in the form of volatile copper chloride. The activity of catalyst can also decrease when applied copper dispersion slides down.

Introducing promoting additives – chromium and barium oxides /225, 228, 233-235,237/ is a famous technique to improve stability of copper containing catalysts of fluorochlorocarbones' dechlorination using hydrogen.

The analysis of data obtained using Cu,BaO,Cr_2O_3/α-Al_2O_3 catalyst prepared by us comes as a proof of significant decrease of process selectivity compare to unpromoted Cu/α-Al_2O_3 (experiment 31, Table 30), mainly at account of formation of dichlorotetrafluoromethane and difluorodichloroethylene typical for the Cr_2O_3/α-Al_2O_3catalyst as well.

In what follows we had prepared and tested Cu,BaO/α-Al_2O_3catalyst, where only barium oxide had been used as a promoter (2 mass.%).

One can see (experiments 32-35, Table 30), that even at 793 K that sample is characterized by exclusively high selectivity of action reaching 96,1%. Stable activity is established approximately in 2-4 hours after start of operation and it corresponds to substrate's conversion degree equal to 74-76% at 793 K; using of catalyst during 53 hours did not lead to its activity decrease.

The activity of copper containing catalysts based on melted calcium fluoride, which as well as α-Al_2O_3 is resistant under the conditions of process carrying out is obviously significantly lower due to small carrier's specific surface (0,2m2/g), which as a consequence leads to decreasing yield of target product because of high input of low-selective non-catalytic dechlorination of substrate using hydrogen (for example, between the grains of catalyst).

Thus, using of α-Al_2O_3, which isstable in fluorinating media and has got a rather developed surface(7,5-8,0 м^2/г) allowed us to select an effective catalyst for dechlorination of 1,1,2-trifluorotrichloroethane using hydrogen – Cu,BaO/α-Al_2O_3.

According to the results of work initial data for projecting of semi-industrial plant obtaining trifluoroethylene dechlorinating R-113 using hydrogen have been issued.

3.2.5. Dechlorination of 1,2-dichlorotetrafluoroethane

Catalytic dechlorination of 1,2-dichlorotetrafluoroethane (R-114) using hydrogen is one of promising ways of obtaining tetrafluoroethylene

$$C_2F_4Cl_2 + H_2 \xrightarrow{KT} C_2F_4 + 2HCI \quad +63 \text{ кJ/mol}$$
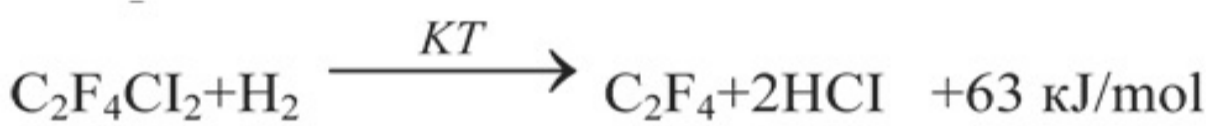
In Table 31 data on dechlorination of 1,2-dichlorotetrafluoroethane using hydrogen over selected by us effective catalysts of same type processes of dechlorination of Rs-216,-112 and -113 are presented; Ni/α-$Al_2O_3$and Cu,BaO/α-Al_2O_3catalysts common feature is that they both are prepared based on α-Al_2O_3. Here you can also find the information obtained using nickel dispersed on the surface of known carrier for the catalyst of dehlorination of fluorocrabones – γ-Al_2O_3/238/.

Table 31. *Catalytic Dechlorination of 1,2-dichlorotetrafluoroethane Using Hydrogen (Equimolar Reagents' Mixture Input Rate – 285 hour^{-1})*

#	Catalyst	Temperature K	Conversion Degree of Fluorochlorocarbon, %	Reaction Products' Yield, %			
				C_2F_6	C_3F_8	C_4F_{10}	C_5F

1	α-Al$_2$O$_3$	823	26	52,5	0,8	3,2	16
2	Same	873	67	48,9	1,5	6,8	17
3	Ni/α-Al$_2$O$_3$	773	33	64,7	1,1	3,9	12
4	Same	823	48	61,8	2,2	5,2	14
5	Cu,BaO/ α-Al$_2$O$_3$	823	43	75,0	1,7	4,4	8,2
6	Same	873	85	65,7	1,7	4,5	8,5
7	NiF$_2$/ γ-Al$_2$O$_3$	773	62	21,5	2,6	8,4	31
8	Same	823	78	14,7	3,5	12,4	30

One can see from the data above, that dechlorination of 1,2-dichlorotetrafluoroethane is characterized by lower yield of target product and passes under significantly tougher conditions (compare to Rs-112,-113 and -216). Maximum yield of tetrafluoroethylene (75%) had been reached over catalyst Cu,BaO/α-Al$_2$O$_3$at 823 K; substrate conversion degree amounted to 43% at that (experiment 5, Table 31). Besides tetrafluoroethylene significant amounts of trifluorochloroethylene and difluorodichloroethylene are formed during interaction of R-114 and hydrogen. Also hexafluoroethane, pentafluorochloroethane and terachloroethylene were discovered in reaction gases.

It is rather characteristic, that using of catalyst based on γ-Al$_2$O$_3$ (experiments 7,8, Table 31) results in sharp increase of input of by-processes corresponding decrease of tetrafluoroethylene yield.

3.2.6. Dechlorination of perfluoromethoxy-1,2-dichlorotrifluoroethane.

Catalytic dechlorination of perfluoromethoxi-1,2-dichlorotrifluoroethane using hydrogen is one of options to obtain perfluoromethylvinyl ether – a monomer for synthesis of new types of fluororubbers and fluoropolymers:

$$CF_3O\text{-}CFCl\text{-}CF_2Cl + H_2 \xrightarrow{KT} CF_3OCF{=}CF_2 + 2HCl$$

Data on catalytic dechlorination of perfluoromethoxi-1,2-dichlorotrifluoroethane can be

found in Table 32.

One can see from the data above, that the selectivity of dechlorination of perfluoromethoxi-1,2-dichlorotrifluroethane using hydrogen is rather low; maximum yield of target product (42,6%) had been reached using catalyst $Ni/\alpha\text{-}Al_2O_3$ at 573K, at that the substrate's conversion rate amounted to 15% (experiment 5, Table 32).

Table 32. *Catalytic Dechlorination of Perfluoromethoxi-1,2-dichlorotrifluoroethane Using Hydrogen (equimolar reagents' mixture input rate – 285 hour^{-1}).*

| #	Catalyst	Temperature K	Conversion Degree,%	Reaction Products Yield, %			
				$CF_3OC_2F_3$	$C_2F_4Cl_2$	CF_3Cl	CF_3H
1	$\alpha\text{-}Al_2O_3$	623	3	24,3	2,5	10,4	16,7
2	Same	673	13	17,0	3,8	18,6	22,4
3	Cu,BaO/ $\alpha\text{-}Al_2O_3$	573	10	36,4	4,0	6,2	11,0
4	Same	623	18	18,9	4,8	7,1	12,4
5	$Ni/\alpha\text{-}Al_2O_3$	573	15	42,6	3,5	9,0	11,7
6	Same	573	57	22,9	4,3	10,3	26,0
7	$Ni/\gamma\text{-}Al_2O_3$	573	34	11,6	36,1	20,5	13,3
8	Same	623	87	7,4	38,5	22,4	14,2

The destruction of the initial fluorochlorocarbon forming 1,2-dichlorotetrafluoroethane, trifluorochloroethylene, trifluoromethane and carbonyldifluoride is the main by-process. Ni/ γ-Al_2O_3 is characterized (experiments 7,8, Table 32) by high input of raw materials destruction (compare to analogous catalysts based on $\alpha\text{-}Al_2O_3$); destruction passes in an intensive way even when there is no hydrogen.

3.2.7. Common Patterns of Relationship, Kinectics and Mechanism of

Fluorochlorocarbones' Catalytic Hydrogen Dechlorination.

The conducted study of fluorochlorocarbones dechlorination using hydrogen showed the defining impact of nature of heterogeneous catalyst (along with substrate's nature) on the selectivity and rate of the process. Selectivity of dechlorination is defined, mainly, by the character of catalytic carrier, and rate – by its specific surface and nature of active metallic component of catalytic composition.

Mechanism of dechlorination of fluorochlorocarbones using hydrogen on applied metallic catalysts can contain two stages: interaction of fluorocarbon (RCl_2) and metal (Me) forming corresponding halgenolefine($R^{\cdot}$), as well as metal chloride ($MeCl_2$) and at second stage reduction of metal by hydrogen with regeneration of metallic catalytic centers and formation of anhydrous hydrogen fluoride:

$$RCl_2 + Me \xrightarrow{K_1} R^{\cdot} + MeCl_2 \qquad (1)$$

$$MeCl_2 + H_2 \xrightarrow{K_2} Me + 2HCl \qquad (2)$$
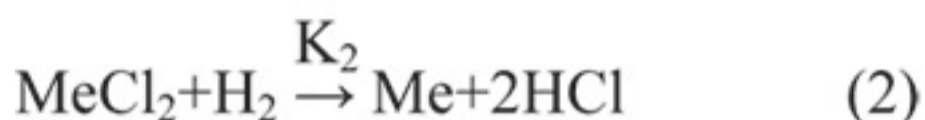
(K_1 and K_2 – constants of corresponding reactions rates).

At a stationary concentration of free metallic centers ($\theta^{??}$) the dechlorination of fluorocarbons by hydrogen for this route is described by the following kinetic equation:

$$-\frac{d[RCl_2]}{d\tau} = \frac{K_1 K_2 [RCl_2][H_2]\theta^{Me}}{K_1[RCl_2] + K_2[H_2]} \qquad (3)$$

Or at small conversion degrees of fluorocarbon (α_{RCl2}) and hydrogenby the equation:

$$\alpha_{RCl_2} = \frac{K_1 K_2 [H_2]^0 \theta_0^{Me} \tau}{K_1[RCl_2]^0 + K_2[H_2]^0} \qquad (4)$$

where $[RCl_2]^\circ$ and $[H_2]^\circ$ - initial concentration of fluorochlorocarbon, and accordingly, hydrogen $\theta_0^{??}$ – initial concentration of metallic active centres of catalyst, t – contact period of reaction gases with catalyst.

Other possible routes of reaction are possible; it was noted above, that dechlorination can contain, for example, catalytic dissociation of fluorocarbon onto halgenolefine, as well as elemental chlorine and following binding of chlorine by hydrogen.

We have studied in details(under comparable conditions)the kinetic patterns of :

- interaction of substrate and metallic nickel applied onto α-Al_2O_3;

- hydrogen reduction of nickel chloride applied onto α-Al_2O_3;

-interaction of substrate and hydrogen in the layer of nickel applied onto α-Al_2O_3 to make the mechanism of fluorochlorocarbones and hydrogen interaction on applied metallic catalysts (using the example of 1,2-dichlorohexafluoropropane and catalyst of Ni/α-Al_2O_3.

Such complex studying allows defining constants K_1 and K_2, characterizing the kinetics of semi-reactions (1) and (2), independently; the comparison of their meanings with ones defined directly at studying the kinetics of substrate's dechlorination by hydrogen makes possible a quantitive estimate of input of the present route. Studying of kinetics of interaction of 1,2-dichlorohexafluoropropane and nickel applied onto α-Al_2O_3 and results of studying the kinetics of nickel chloride applied onto α-Al_2O_3 reduction by hydrogen allowed determining the initial concentration of active nickel and nickel chloride on the surface of α-Al_2O_3 (θ_0^{Ni}, θ_0^{NiCl2}), and studying their temperature dependency allowed determining corresponding meanings of pre-exponential multipliers (Ko) and effective energies of activations (Ea); the results are presented in Table 33 (items 1-4) and at Pic. 4a.

Table 33. *The Meanings of Initial Concentrations of Active Nickels and its Chloride on the Surface of And of Rates' Constants K_1 And K_2 Determined by Direct Measuring (items 1-4) And According to Kinetic Data on Dechlorination of 1,2-dichlorohexafluoropropane by Hydrogen (items 5-6).*

# item	Determined Value	Meanings of Determined Value at Temperature, K					**lg**Ko
		473	493	508	523	543	
1	K_1, l•mole^{-1}•sec^{-1}, x10^2	5,9	7,4	8,9	10,3	12,9	1,4±0,1
2	θ_0^{Ni}, mole• l^{-1}	1,13	1,12	1,15	1,17	1,17	-
3	K_2, l•mole^{-1}•sec^{-1}, x10^2	1,5	3,3	5,9	11,6	22,8	7,4±0,2
4	θ_0^{NiCl2}, mole• l^{-1}	1,24	1,17	1,15	1,13	1,06	-
5	K_1, l•mole^{-1}•sec^{-1}, x10^2	5,7	9,1	11,0	14,5	19,1	2,8±0,2
6	K_2, l•mole^{-1}•sec^{-1}, x10^2	1,3	2,9	5,9	11,3	26,8	8,4±0,3

From data above one can see, that interaction of 1,2-dichlorohexafluoropropane and metallic nickel on the surface of α-Al$_2$O$_3$is characterized by relatively small energy of activation (23,8 kiloloule/mole), which is significantly lower than the activation energy of nickel chloride reduction by hydrogen on the surface α-Al$_2$O$_3$ (84,1 kJ/mole); at the same time pre-exponential multiplier of chloride nickel hydrogen reduction rate constant is significantly higher, than one of constant of substrate's nickel dechlorination.If taking into account, that the initial concentrations of active nickel and nickel chloride in samples of Ni/α-Al$_2$O$_3$and NiCl$_2$/α-Al$_2$O$_3$, are approximately equal (~ 1,15 mole/l of a sample), then in total at temperatures below 520 K the rate of substrate's dechlorination by nickel is higher than the nickel chloride hydrogen reduction rate (Pic. 4a) and, on the contrary, at high temperature according to data on studying the kinetics of model reactions (1) and (2), the dechlorination of 1,2-dichlorohexafluoropropane using nickel is a limiting stage.
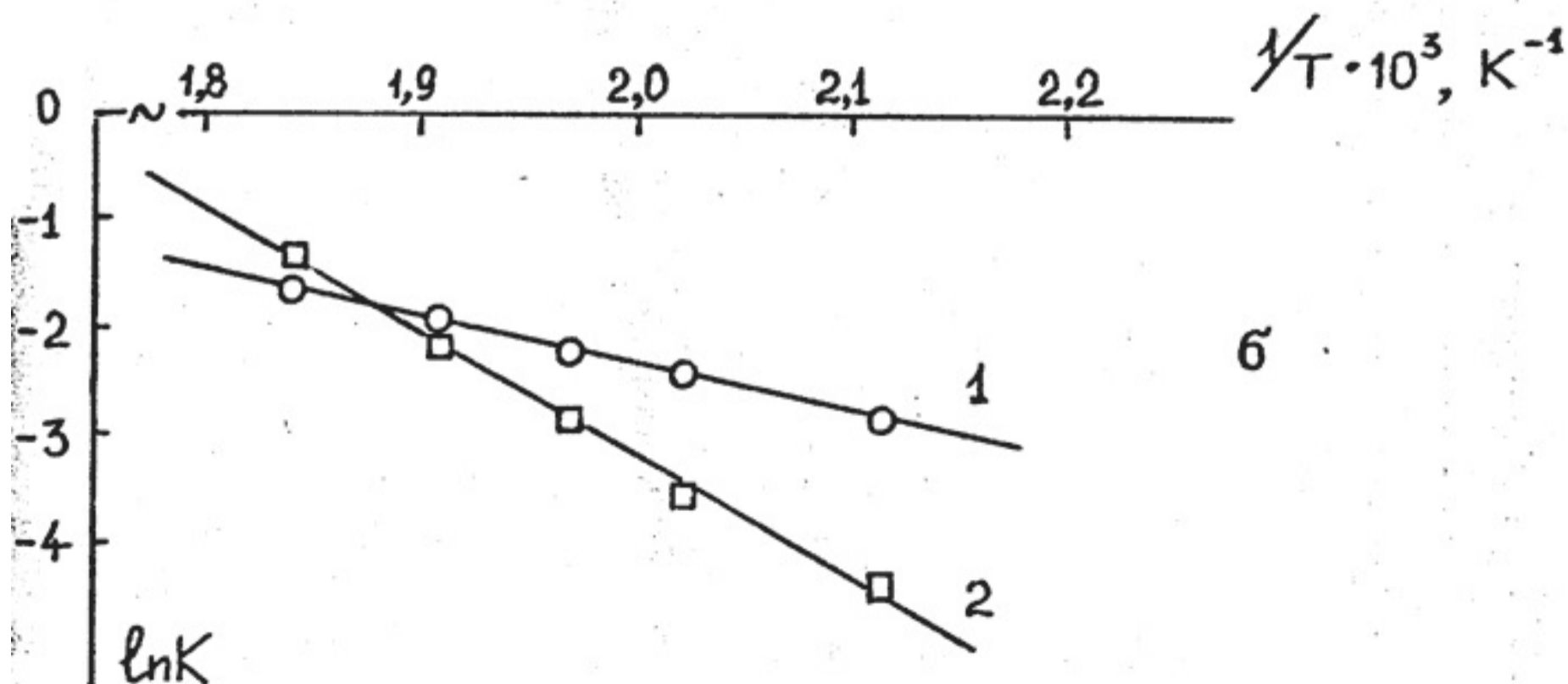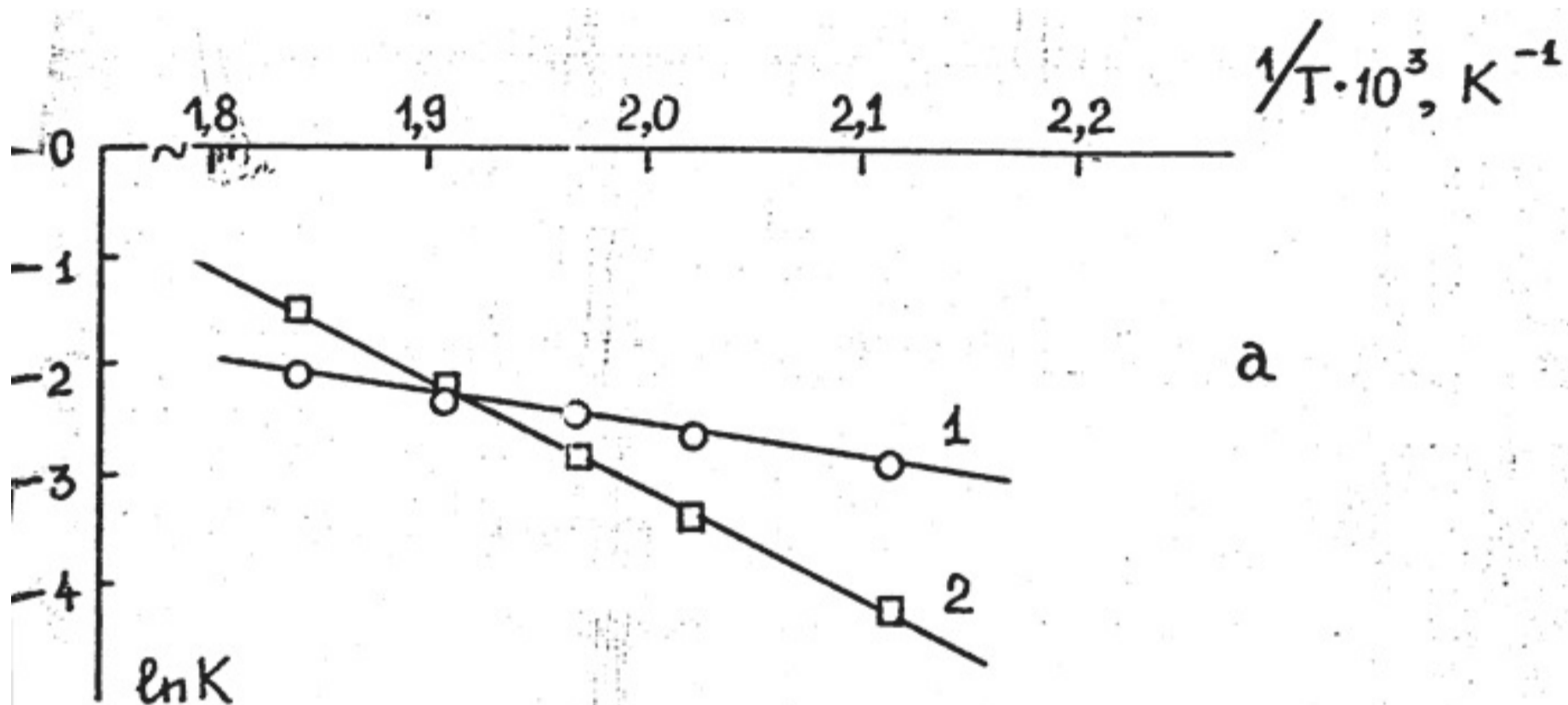
Picture 4.*Temperature dependancies (in coordinates) of constants of 1,2-dichlorohexafluoropropane dechlorination using nickel applied onto α-Al$_2$O$_3$ (1), and reduction of nickel chloride using hydrogen applied onto α-Al$_2$O$_3$ (2), determined by direct measurement (a) and according to kinetic data on catalytic dechlorination of 1,2-dichlorohexafluoropropane by hydrogen at Ni/α-Al$_2$O$_3$ (b).*

Expression (4), characterizing kinetic of fluorocarbons hydrogen dechlorination (at small conversion degrees) according to offered mechanism can be presented in the form of:

$$\frac{1}{\alpha C_3F_6Cl_2} = \frac{l}{K_2\tau 6_0^{Ni}} + \frac{1}{K_1\tau 6_0^{Ni}} \quad (5)$$

where *l* – mole ratio of C$_3$F$_6$Cl$_2$ and H$_2$ in the initial mixture.

Thus, processing the kinetic data on fluorocarbons hydrogen dechlorination in the coordinates 1/α ч *l* and using independently determined meaning θ_0^{Ni} (1,15 mole/l of catalyst) we can directly determine numerical meanings of K$_1$ and K$_2$.

The results of processing of kinetic data on dechlorination of 1,2-dichlorohexane using hydrogen at catalyst Ni/α-Al$_2$O$_3$ are presented at Pic.4, as well as in Table 33 (# items 5,6).

One can see from above data, that the kinetics of dechlorination of 1,2-dichlorohexafluoropropane using hydrogen at Ni/α-Al$_2$O$_3$ is satisfactorily described by kinetic equation (5). It is typical, that temperature dependencies of constants K$_1$ and K$_2$ in this case cross each other (Pic. 4b); at temperature above 520K the stage of dechlorination of substrate using nickel is a limiting one, and on the contrary, at lower temperatures the constant of substrate's nickel dechlorination rate is significantly higher than the constant of forming nickel chloride reduction rate using hydrogen. This result fully complies with patterns discovered during studying the kinetics of model reactions (1,2) and witnesses in favour of mechanism of dechlorination of 1,2-dichlorohexafluoropropane using hydrogen described by us.

At Pic.5 we see an experimentally determined temperature dependency of conversion degree of 1,2-dichlorohexafluoropropane at thermal contacting of hydrogen at catalyst Ni/α-Al$_2$O$_3$; here as well we can see the analogous dependency obtained by calculation method based on meanings of independently determined constants of K$_1$ and K$_2$ of model reactions (1) and (2). One can see from data above, that those constants satisfactorily describe (within the temperature range of 470-550 K) the kinetics of dechlorination of 1,-dichlorohexafluoropropane –deviation of experimental data to calculated ones doesn't exceed 25%. This reslt definitely points out the fact, that the route of dechlorination of 1,2-dichlorohexafluoropropane using hydrogen at Ni/α-Al$_2$O$_3$, described by equations (1) and (2) within the range of 470-550 K, is the main one.
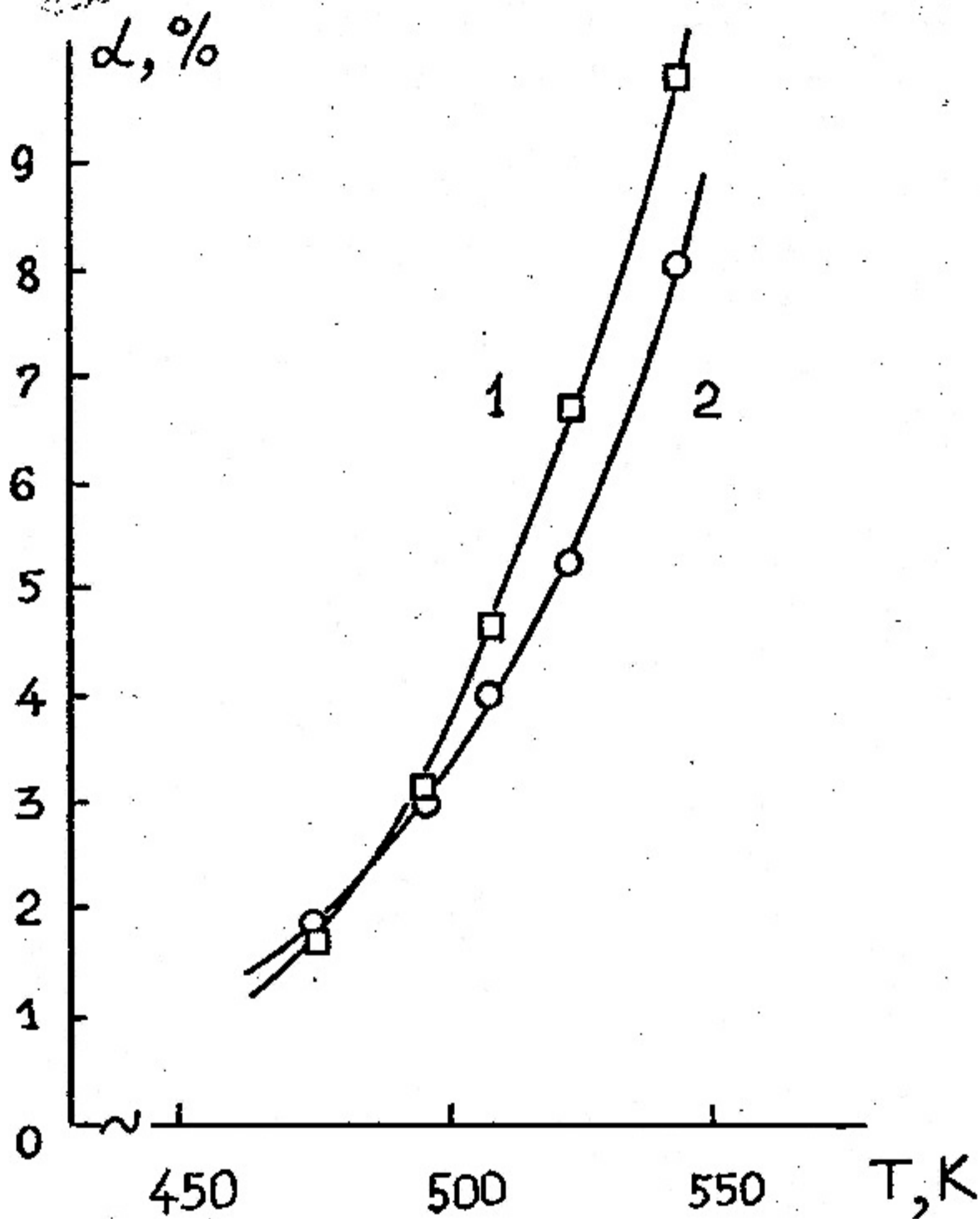
Picture 5.*Temperature Dependancies of Conversion Degree (α) of 1,2-dichlorohexafluoropropane During Interaction With Hydrogen At Ni/α-Al$_2$O$_3$, Obtained Experimentally)1) and by Calculation (2) Based on Meanings of Independently Determined Constants of Dechlorination of 1,2-dichlorohexafluoropropane Using Nickel Applied Onto α-Al$_2$O$_3$, And Nickel Chloride Reduction Using Hydrogen Applied Onto α-Al$_2$O$_3$.*

The model under consideration allows quantitive (based on discovered meanings of constants K1 and K2) estimating the temperature dependency of stationary shares of

metallic centers and metal ($\theta^{Ni} / \theta_0^{Ni}$? $\theta^{NiCl_2}/\theta_0^{Ni}$) on the surface of Ni/α-Al$_2$O$_3$:

$$\frac{\theta^{Ni}}{\theta_0^{Ni}} = \frac{K_2[H_2]}{K_1[C_3F_6Cl_2] + K_2[H_2]} = \frac{K_2}{K_1 l + K_2} \quad (6)$$

$$\frac{\theta^{NiCl_2}}{\theta_0^{Ni}} = \frac{K_1[C_3F_6Cl_2]}{K_1[C_3F_6Cl_2] + K_2[H_2]} = \frac{K_1}{K_1 + K_2/l} \quad (7)$$

where

$$l = [C_3F_6Cl_2]/[H_2]$$

At Pic.6 temperature dependencies of stationary shares of free active metallic centers and centers that formed nickel chloride on the surface of Ni/α-Al$_2$O$_3$ (for mole ratio of substrate : hydrogen equal to 0,32) calculated based on meaninings of K_1 and K_2 determined from data on kinectics of dechlorination of 1,2-dichlorohexafluoropropane are presented.

The character of those dependencies is explained by the alteration of ratio of meanings of K_1 and K_2 with the reaction temperature increase. Thus, in the field of low temperature meanings (400-450 K) the constant of rate of substrate's dechlorination using nickel (K_1) is significantly above the constant of reduction rate of forming at that nickel chloride using hydrogen (K_2) – as a consequence in a stationary state the large share of active surface of catalyst is a nickel chloride. On the contrary, during temperature increase (up to 550-600 K), when the reduction rate of nickel chloride using hydrogen abruptly goes up, the stationary surface of active phase is mainly a metallic nickel.

We shall note, that this conclusion driving from the character of temperature dependencies of rates of separate stages of dechlorination of 1,2-dichlorohexafluoropropane using hydrogen had been confirmed experimentally: X-ray phase analysis of samples Ni/α-Al$_2$O$_3$after contacting the mixture of substrate and hydrogen at 400 and 600 K, respectively, had discovered (besides phases α-Al$_2$O$_3$and AlF$_3$) only nickel chloride in the first case, and in second – only metallic nickel.

Studying the reaction ability of 1,-difluorotetrachloroethane, 1,2-dichlorohexafluoropropane, 1,1,2-trifluorotrichloroethane and 1,2-dichlorotetrafluoroethane under comparable conditions showed, hat it is unequal and correlates with thermal effect of reaction. Thus, thermal effect of dechlorination using hydrogen is – 13, +13, +16 and +63 kJ/mole respectively in this line of substrates; in the same row (Pic. 7) one can observe significant decreasing of fluorochlorocarbons' reactivity.
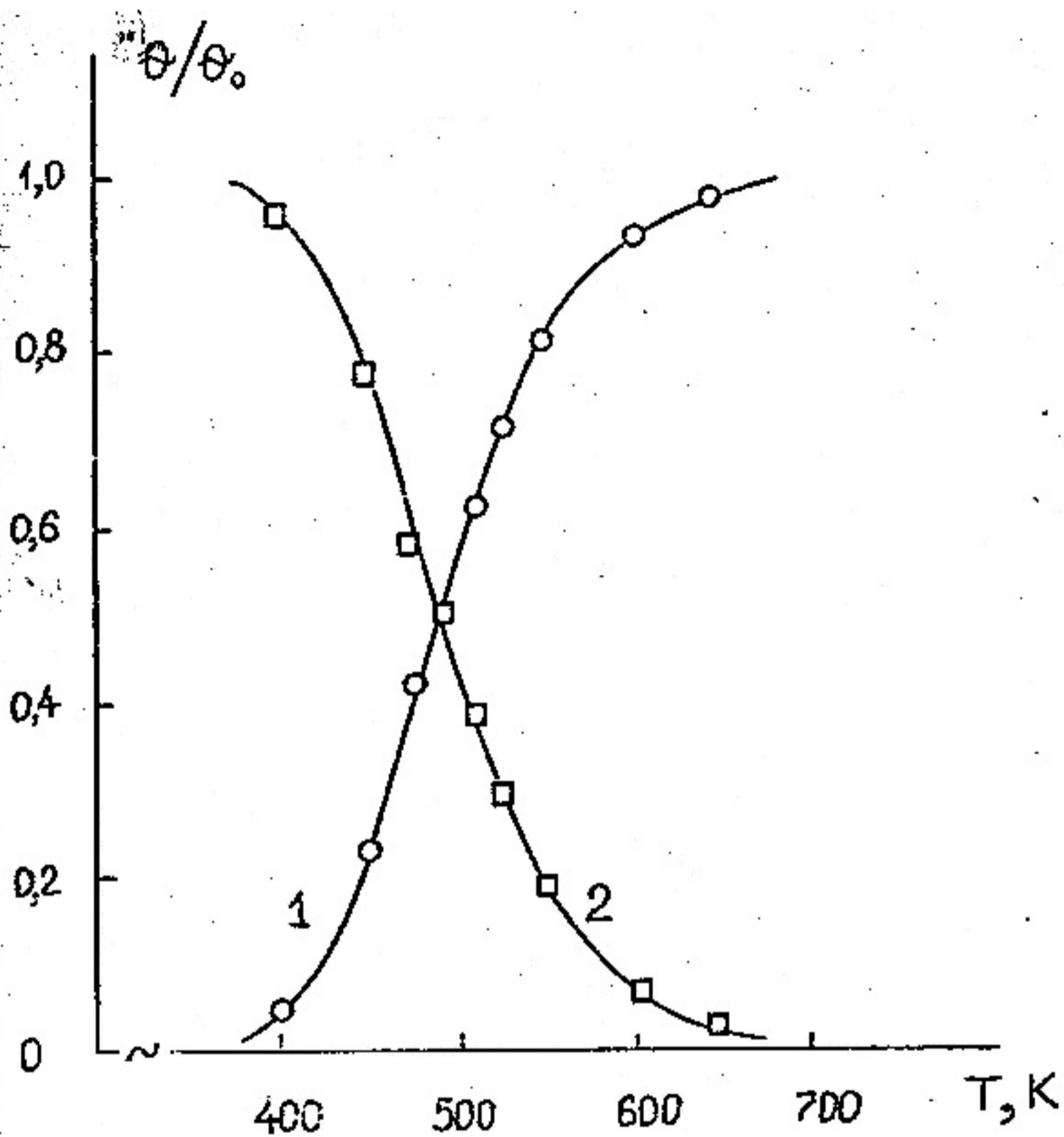
Picture 6. *Temperature dependencies of stationary shares (Θ / Θ$_0$) of Free Radicals of Active Metallic Centres (1) and centres, which formed nickel chloride (2) on the surface of Ni / α-Al$_2$O$_3$during dechlorination of 1,2-dichlorohexafluoropropane using hydrogen.*
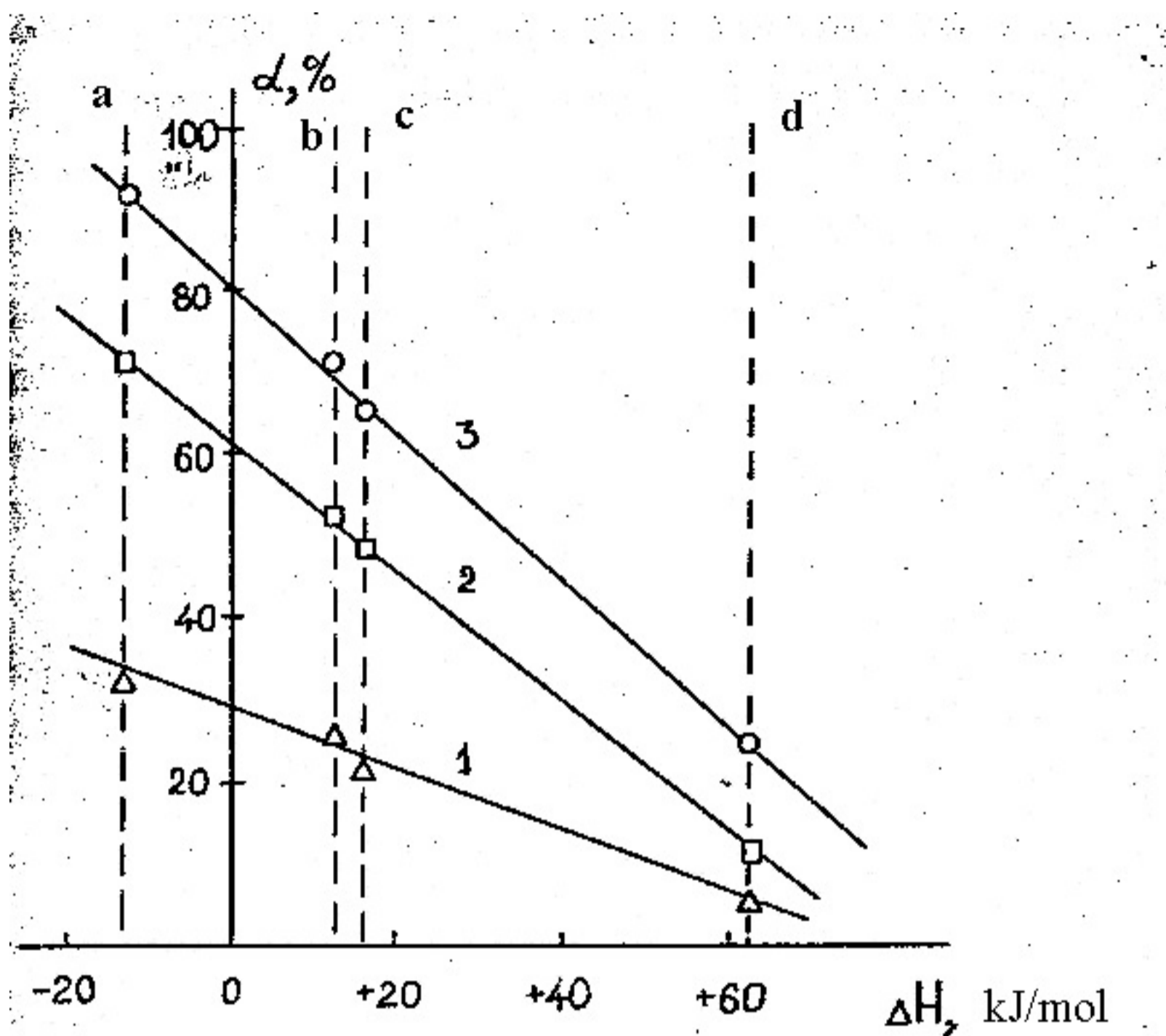
Picture 7.*Correlation of Initial Degrees Of Fluorochlorocarbons Conversion (α) at Interaction with Hydrogen at Ni /α-Al$_2$O$_3$ at 1 – 573; 2 – 623 And 3 – 673 K with Thermal Effects of These Reactions (ΔH) For a – 1,2-difluorotetrachloroethane, b – 1,2-dichlorohexafluoropropane, c – 1,1,2-trifluorotrichloroethane and d– 1,2-dichlorotetrafluoroethane.*

That may be caused by high affinity of double bond with chlorine of halgenolefines containing greater number of fluorine atoms at double bond, that can be explained by positive mesomeric effect of fluorine; thus, according to /319/ the thermal effect of chlorination C_2Cl_4 , C_2FCl_3 , $C_2F_2Cl_2$, C_3F_6 , C_2F_3Cl and C_2F_4 is -127, -158, -171, -197, -200 and -247 kJ/mole respectively.

Obtained data agree with considered two-stage model explaining chemism of dechlorination target products formation; indeed, this model contains stage of fluorochlorocarbon interaction with applied metal, which rate to a great extent should be determined by the reactivity of organic substrate.

Chemism of By-products Formation During Catalytic Hydrogen Dechlorination of Fluorochlorocarbons.

The analysis of composition of reaction mixtures forming during thermal contacting of

fluorochlorocarbons and hydrogen at catalysts (Table 28-32) allowed offering common for all substrates scheme explaining chemism of formation of virtually all main by-products; below you will find the scheme customized for reactions studied.

Dechlorination of 1,2-dichlorohexafluoropropane:
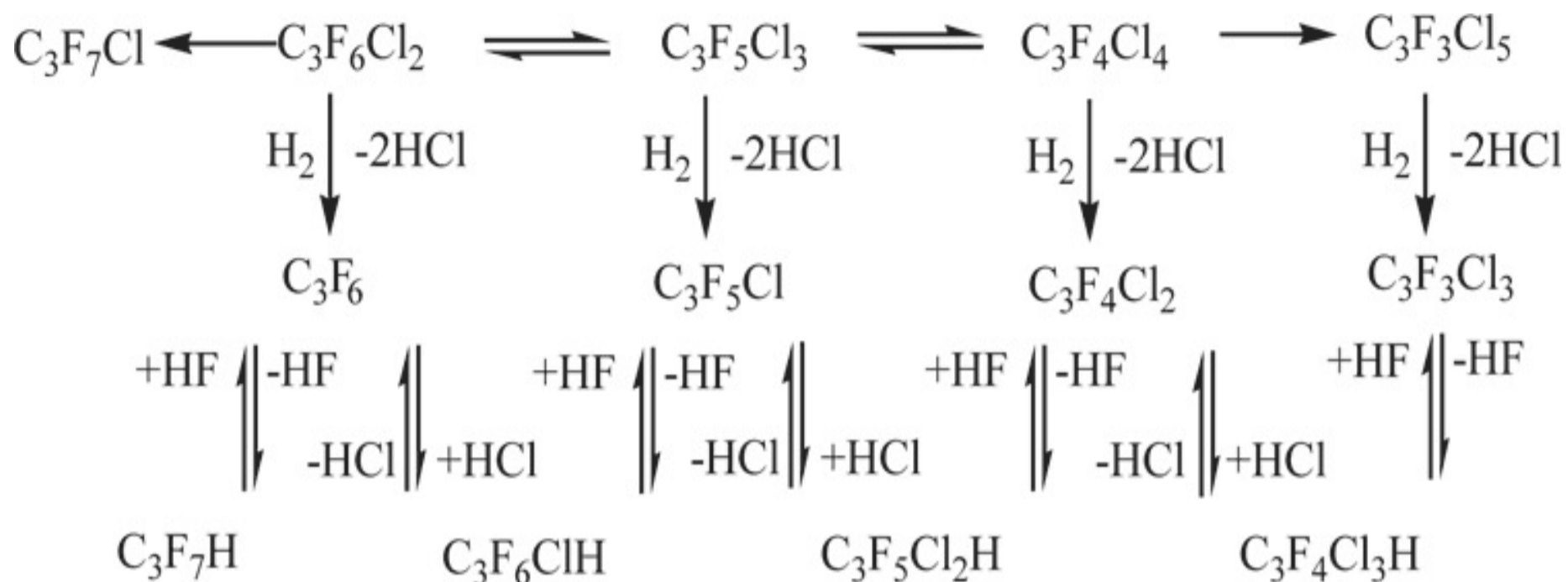
$$C_3F_7Cl \longleftarrow C_3F_6Cl_2 \rightleftharpoons C_3F_5Cl_3 \rightleftharpoons C_3F_4Cl_4 \longrightarrow C_3F_3Cl_5$$

$$H_2 \downarrow -2HCl \qquad H_2 \downarrow -2HCl \qquad H_2 \downarrow -2HCl \qquad H_2 \downarrow -2HCl$$

$$C_3F_6 \qquad C_3F_5Cl \qquad C_3F_4Cl_2 \qquad C_3F_3Cl_3$$

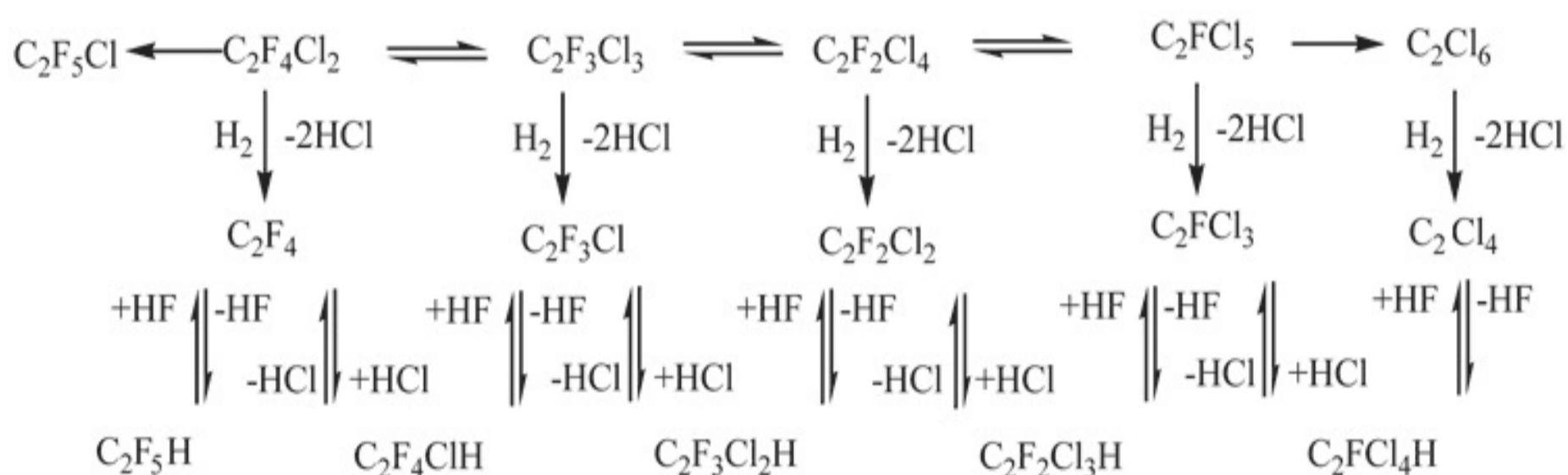$$+HF \updownarrow -HF \qquad +HF \updownarrow -HF \qquad +HF \updownarrow -HF \qquad +HF \updownarrow -HF$$

$$-HCl \updownarrow +HCl \qquad -HCl \updownarrow +HCl \qquad -HCl \updownarrow +HCl$$

$$C_3F_7H \qquad C_3F_6ClH \qquad C_3F_5Cl_2H \qquad C_3F_4Cl_3H$$

Dechlorination of 1,2-difluorotetrachloroethane 1,1,2-trifluorotrichloroethane and 1,2-dichlorotetrafluoroethane:

$$C_2F_5Cl \longleftarrow C_2F_4Cl_2 \rightleftharpoons C_2F_3Cl_3 \rightleftharpoons C_2F_2Cl_4 \rightleftharpoons C_2FCl_5 \longrightarrow C_2Cl_6$$

$$H_2 \downarrow -2HCl \quad H_2 \downarrow -2HCl \quad H_2 \downarrow -2HCl \quad H_2 \downarrow -2HCl \quad H_2 \downarrow -2HCl$$

$$C_2F_4 \qquad C_2F_3Cl \qquad C_2F_2Cl_2 \qquad C_2FCl_3 \qquad C_2Cl_4$$

$$+HF \updownarrow -HF \quad +HF \updownarrow -HF \quad +HF \updownarrow -HF \quad +HF \updownarrow -HF \quad +HF \updownarrow -HF$$

$$-HCl \updownarrow +HCl \quad -HCl \updownarrow +HCl \quad -HCl \updownarrow +HCl \quad -HCl \updownarrow +HCl$$

$$C_2F_5H \qquad C_2F_4ClH \qquad C_2F_3Cl_2H \qquad C_2F_2Cl_3H \qquad C_2FCl_4H$$

As a matter of fact, this scheme is based on two alternative mechanisms of by-products formation. The first one includes disproportioning of the initial fluorochlorocarbon and hydrogen dechlorination of disproportioning products. This mechanism is based on experimentally established fact of fluorochlorocarbons disproportioning in inert medium (nitrogen) at studied catalysts; products of increased chlorine content forming at that (right part of scheme) react even more intensively, as it has been mentioned, to hydrogen, than the initial fluorochlorocarbons.

The second less obvious mechanism of by-products formation includes catalytic interaction of target halgenolefines and chlorine hydride and anhydrous hydrogen fluoride (attachment by double bond), forming at interaction of fluorochlorocarbon and hydrogen and the following chain of reactions of hydrodehydrohalogenation (See Scheme).

To find the basis of this mechanism and estimation of inputs of hydro-dehydrohalogenation and disproportioning we have studied (as a model) the transformations of 1,1,1-difluorochlorethane at γ-Al$_2$O$_3$ in the impulse and running modes. The peculiarity of the process passing in the impulse mode is a chromatographic partition of the initial reactions products (1,1-difluoroethylene, 1,1-fluorochloroethylene, hydrogen fluoride and hydrogen chloride) at

the layer of catalyst. Such partition prevents secondary reactions of hydrohalogenation forming especially 1,1,1-trifluoroethane from occurring and doesn't impact the disproprortioning of initial product. Data on thermal transformations of 1,1,1-difluorochloroethane at γ-Al$_2$O$_3$ in an impulse and running modes are listed in Table 34.

From the listed data one can see, that carrying out of this process in the running mode, e.g. under conditions, when the partition of reaction's products doesn't occur is characterized by high forming of 1,1,1-tifluoroethane – the product of hydrofluorination of 1,1-difluoroethylene; that result indicates the opportunity of catalytic interaction of forming at hydrogen dechlorination of fluorochlorocarbones target halgenolefines and hydrofluoric acid and chlorine hydride.

In what follows, to estimate dehydrohalogenating and in principle of detailed balance and hydrohalogenating activity of catalysts we have studied the model reaction of dehydrochlorination of ethyl chloride. At Picture 8 you can find data showing, that the intensity of by-products formation at catalytic dechlorination of fluorocarbons, in particular, of 1,2-dichlorohexafluoropropane correlates with the activity of the same catalysts in dechlorination of C$_2$H$_5$Cl.

Table 34. *Thermal Transformation of 1,1,1-difluorochloroethane at γ-Al$_2$O$_3$ (substrate's input rate - 7200 hour^{-1}).*

#	Mode	Temperature, K	Conversion Degree, %	Composition of Gaseous Products, volume %		C
				CH$_2$=CF$_2$	CH$_3$-CF$_3$	
1	Impulse	723	>99	26,3	4,1	6
2	Same	773	>99	30,7	1,9	6
3	Running	723	96	20,3	44,7	3
4	Same	773	98	30,0	29,6	4
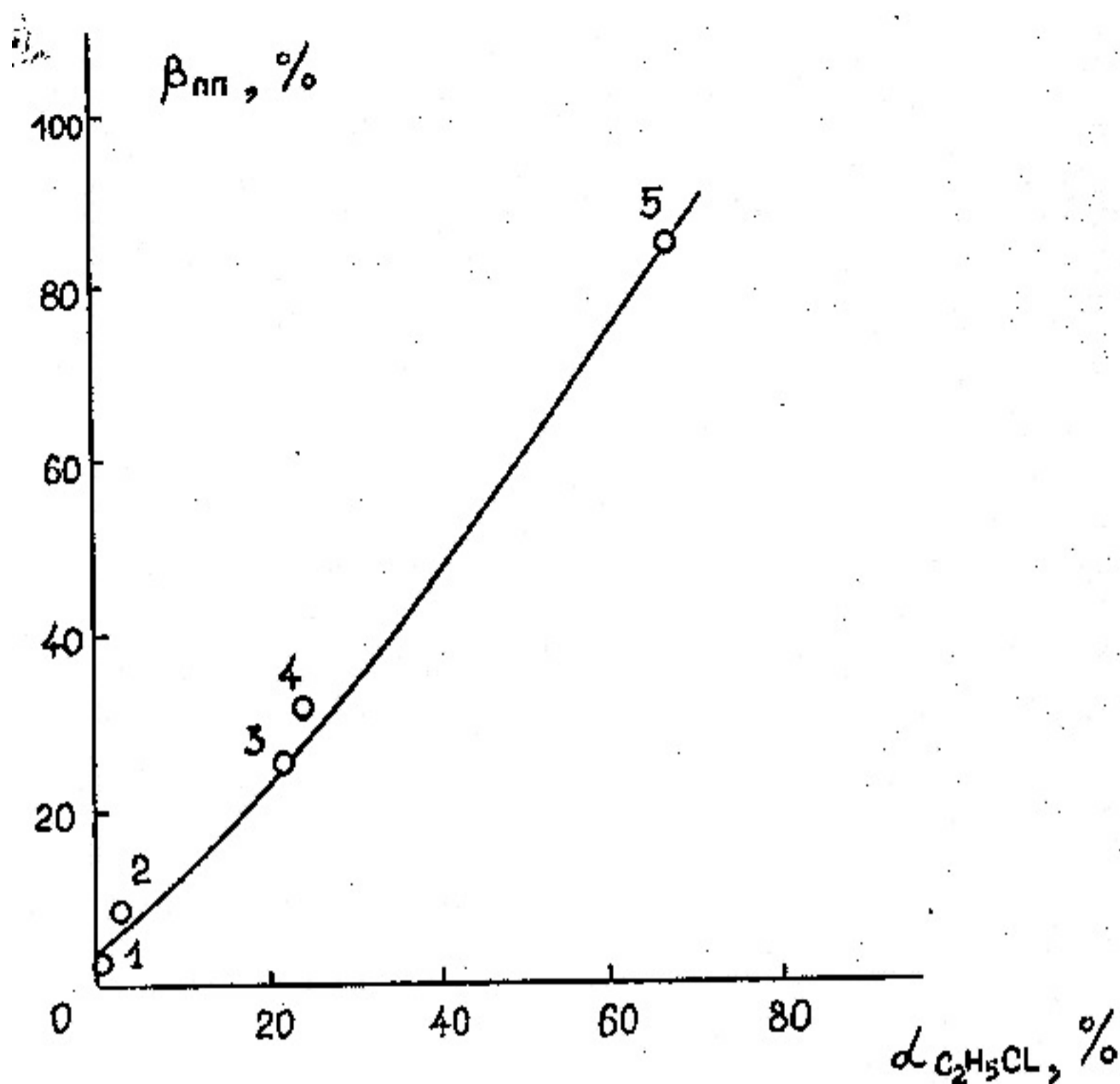
Picture 8.*Correlation of Ethyl Chloride (α $_{C2H5Cl}$) Conversion Degree (673 K) And of By-Products Yield (743 K) at Hydrogen Dechlorination of 1,2-dichlorohexafluoropropane (β) at Catalysts: 1 – Ni/α-Al$_2$O$_3$; 2 – α-Al$_2$O$_3$; 3 – AlF$_3$; 4 – Ni/γ-Al$_2$O$_3$? 5 – γ-Al$_2$O$_3$.*

This result indicates the passing of side reactions during hydrogen dechlorination of fluorochlorocarbons at acidic, electrophilic centers of catalysts, that cause their activity in the model reaction of dehydchlorination of ethyl chloride.

In the course of discussion of the results of catalytic dechlorination of 1,2-difluorotetrachloroethane we have noticed a high formation of 1,2-difluoroethylene at Ni/γ-Al$_2$O$_3$. Taking into account a high activity of nickel in the course of hydrogen hydration, as well as the high electrophilic activity of the carrier – γ-Al$_2$O$_3$,according to the analogous pattern we can offer a following mechanism of the hydrogen input into the halgenolefine's molecule:
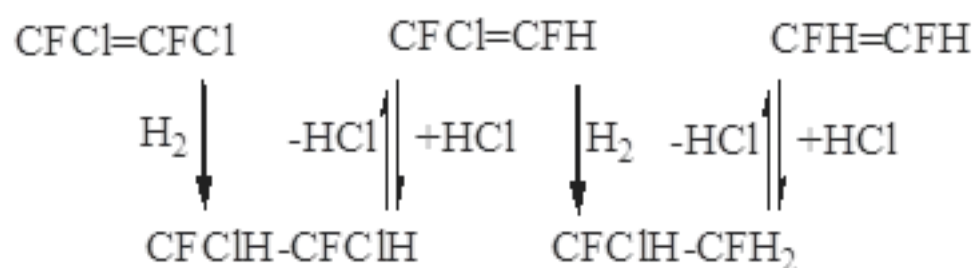
It has been mentioned above, that fluoroolefines are of unequal affinity with chlorine; that circumstance creates thermal and dynamic premises for the interaction of target halgenolefines and initial substrates disproportioning products; such interaction will also lead to decreasing of process selectivity. The results of direct experiments on contacting of halgenolefines and fluorochlorocarbons (Table 35) testify to the effect, that such type of reaction can occur.

The conducted research, thus, allowed discovering common for the all substrates types of side reaction (disproportioning, hydro-dehalogenation, hydrogen attachment by double bond, dechlorination of halgenolefines) and establishing the connection of the intensity of their passing and nature of active centers of catalyst.

Table 35. *Dechlorination of Fluorochlorocarbons Using halgenolefines (Catalyst – Activated Carbon, The Input Rate of Equimolar Mixture of Reagents – 180 hour^{-1}).*

Reaction	Temperature, K	Conversion Degree of Fluorochlorocarbon, %	Ov React
1.$C_2F_4+C_2F_3Cl_3=C_2F_4Cl_2+C_2F_3Cl$	593	20,6	94,
	693	57,1	93,
	793	78,9	70,
2.$C_2F_4+C_2F_2Cl_4=C_2F_4Cl_2+C_2F_2Cl_2$	593	90,3	85,
	693	95,7	94,
3.$C_2F_3Cl+C_2F_2Cl_4=C_2F_3Cl_3+C_2F_2Cl_2$	593	71,8	61,

And as a conclusion we shall note, that the efficiency of catalysts of dechlorination of fluorocarbons using hydrogen (activity, selectivity, stability) is mainly defined by the nature of catalytic carrier; using of α-Al$_2$O$_3$ allowed selecting based on it effective aggression resistant catalysts and developing the technology of synthesis of hexafluorop[ropylene and 1,2-difluorodichloroethylene using dechlorination of corresponding fluorochlorocarbons.

to be continued

References

1. Bigelou L.A., Tompson R.I., Tarrant P. Ftor kak galoid. "Khimiya ftora", № I -M.: IL, 1950,

p. 78-89.

2. Tedder D.M. Ftorirovanie organicheskih soedinenij ehlementarnym ftorom. V kn."Uspekhi himii ftora", t. I-II -M.-L. : Khimiya, 1964, p. 380-423.

3. Orkin V.L., Chajkin A.M. Opredelenie konstant skorosti obrazovaniya atomov v reakciyah molekulyarnogo ftora s okis'yu azota, ehtilenom i tetraftorehtilenom.Kinetika i kataliz, 1982, t.23, v.Z,p.529-533.

4. Anson P.O., Fredricks P.S., Tedder J.M. Free-radical substitutionin aliphatic compounds. Part 1. Halogenation of n-butahe and isobutane in the gas phase. J.Chem.Soc, 1959, March, p.918-922.

5. Fredricks P.S., Tedder. J.M. Free-radical substitution in aliphatic compounds. Part 11. Halogenation of the n-butylhalides. -J.Chem.Soc, 1960, Jan., p. 144-150.

6. Purington S.T., Kagen B.S., Patric T.B. The application of elemental fluorine in organic synthesis. Chem.Rev., 1986, № 86, p.997-1018.

7. Aikman R.E., Lagow E.J. Syhthesis of tetra-cis-(perfluorocyclohexyl)-methane and bis-(perfluorocyclohexyl)-methane by direct fluorination. -J.Org.Chem., 1982, v.47, № 14, p.2789-2790.

8. Eremenko L.T., Oreshko G.V. Ftorirovanie ehlementarnym ftorom labil'nyh polinitrosoedinenij – adduktov reakcii Mihaehlya. -Izv. AN SSSR, Ser. khim, 1969, № 2, p.479.

9. Eremenko L.T., Nacibullin F.Ya., Borovinskaya J.P., Karpova N.D. Sintez perftornitroehtanov. -Izv. AN SSSR. Ser. khim., 1968, № 2, p.429-430.

10. Patent US 4523039. Sposob polucheniya perforirovannyh prostyh ehfirov. /Lagov R.J., Gerhart J.E. -Publ. 11.06.85, RZh Khimiya, 1986, 7N36.

11. Patent US 3242218. Sposob polucheniya ftoruglerodnyh poliehfirov. /Miller V.T. -Publ. 22.03.66, RZh Khimiya, 1967, 12C232.

12. Des Martean D.D, Fluoroperoxytrifluoromethane CF300F. Preparation from trifluoromethyl hydroperoxide and fluorine in the presence of cesium fluoride. -Inorg Chem., 1972, v.11, № 1, p.193-195.

13. Merritt R.F., Johnson F.A. Direct fluorination. Addition of fluorine to indenes and.acenaphthylenes, -J.Org.Chem., 1966, v.31. № 6, p.1859-1863.

14. Merritt R.F, Johnson F.A. Direct fluorination of steroidal olefines to cis-vicinal difluorides. – J.Am.Chem.Soc., 1966, v.88, № 8, p.1822-1823.

15. Patent US 3487093. Ftorirovannye olefiny. Merrit R.F. –Publ. 30.12.69, RZH Khimiya, 1970, 23N29.

16. Grakauskas V. Direct liquid phase fluorination of halogenated aromatic compounds. -J.Org.Chem., 1969, v.34, № 10, p.2835-39.

17. Brooke G.M., Chambers B.D., Heyes J., Musgrave W.K.R. Direct preparation and some reactions ofchlorofluorobenzenes. -J.Chem.Soc., 1964, Febr., p.729-735.

18. Merritt R.F, The polar addition of molecular fluorine to acetylenes. –J.Org.Chem., 1967, v.32, № 12, p.4124-4126.

19. Sheppard U., Sharts K. Organicheskaya Khimiya ftora. -M.: Mir, 1972, p. 52, 89, 112.

20. Miller V., Ehrenfeld J, Felan J., Prober M., Rid Sh, Ftorirovanie polnost'yu galoidirovannyh olefinov. «Khimiya ftora», № 2, -M.: IL, 1950, p. 228-240.

21. Miller W.T. My early days in fluorine chemistry. –J.Fluor.Chem., 1981, v.18, p.305-321.

22. Miller W.T., Stoffer J.O., Fuller G., Currie A.C. The mechanism of fluorination. IV. The effect of temperature and of fluorine concentration on reaction. A new fluorination apparatus. –J.Am.Chem.Soc., 1964, v.86, № 1, p.51–56.

23. Isikava Nobuo, Kitacumeh Tomoya. Novye metody ftorirovaniya aromaticheskih soedinenij. –Yukki gosehj kachaku kyokajsi., 1976, t.34, № 3, p.173-178, RZh Khimiya, 1976, 23ZH360.

24. Patent JP 55-18695. Sposob ftorirovaniya./ Maruo Kehjiti, Misaki Susumu. –Publ. 21.05.80, RZh Khimiya, 1981, 5N122.

25. Sirip L.A., Lagow R.J. Direct fluorination of 2,2,4,4-tetramethyl pentane. Sterically protected residual protons. –J.Org.Chem., 1977, v.42, № 21, p.3437-3438.

26. Kowanko N., Branthaver J.F., Sugihara J.M. Direct liquid-phase fluorination of petroleus. – Fuel, 1978, v.57, № 12, p.769-775.

27. Patent US 40004996. Ftorirovanie organicheskikh soedinenij./ Kollonic J. –Publ. 25.01.77, RZh Khimiya, 1977, 23N57.

28. Patent GB 1077065. Ftorirovanie nitrosoedinenij./ Grakauskas V., Hemel E.E. –Publ. 26.07.67, RZh Khimiya, 1975, 16N84.

29. Merritt R.F. Direct fluorination of 1,1-diphenylethylene. –J.Org.Chem., 1966, v.31, № 11, p.3871-3873.

30. Merritt R.F. The polar fluorination of propenylbenzene. –J.Am.Chem.Soc., 1967, v.89, № 3, p.609-612.

31. Merritt R.F., Johnson F.A. Low-temperature fluorination of Schiff bases. -J.Org.Chem., 1967, v.32, № 2, p.416-419.

32. Misaki S. Direct fluorination of phenol and cresols. –

J.Fluor.Chem., 1981, v.17, № 2, p.159-171.

33. Maxwell A.F., Detoro F.E., Bigelow L.A. The action of elementary fluorine upon organic compounds. XXIII. The jet fluorination of certain aliphatic hydrocarbons as oriented and controlled by operation conditions. -J.Am.Chem.Soc., 1960, v.82, № 22, p.5827-5830.

34. Attaway J.A., Groth R.H., Bigelow L.A. The action of elementary fluorine upon organic compounds. XXIII. The fluorination of some amides, nitriles and of methylthiocyanate. -J.Am.Chem.Soc., 1959, v.81, № 14, p.3599-3603.

35. Robson P., Mc Longhlin V.C.R., Hynes J.B., Bigelow L.A. The action of elementary fluorine upon organic compounds. XXIV. The jet fluorination of hydrogen cyanide, cyanogen, methylamine and ethylenediamine. Pyrolysis and fluorinolysis of selected products. -J.Am.Chem.Soc., 1961, v.83, № 24, p.5010-5015.

36. Boffenberg K. Substitution von benzol durch elementares Fluor in der Gasphase. –

Chem.Ztg.,1972, v.96, № 2, p.84-92.

37. Patent JP 58-41829. Poluchenie oktaftorpropana./ Fukui Siro, Joneda Hadzime. –Publ. 11.03.83, RZh Khimiya, 1984, 5N11.

38. Hayes L.J., Dixon D.D. Direct fluorination of polyester and related compounds. –J.Fluor.Chem., 1977, v.10, № 1, p.1-16.

39. Gerhardt G.E., Lagow R.J. Synthesis of perfluoropolyethers by direct fluorination: a novel preparation for perfluoro (polypropylene oxide) ethers and perfluoro (polymethylene oxide) ethers. –J.Chem.Soc., 1981, part 1, № 5, p.1321-1328.

40. Patent US 4113772. Metod polucheniya oligomerov perftorehfirov s koncevymi karboksil'nymi gruppami. / Lagov R.J. –Publ. 12.09.78, RZh Khimiya, 1979, 15N14.

41. Gerhardt G.E., Lagow R.J. Synthesis of perfluoropoly (ethylene glycol) ethers by direct fluorination. –J.Org.Chem., 1978, v.43, № 23, p.4505-4509.

42. Adcock J.L., Znoue Shoji, Lagow R.J. Simultaneous fluorination and functionalization of hydrocarbon polymers. –J.Amer.Chem., 1978, v.100, № 6, p.1948-1950.

43. Lagow R.J., Margrave J.L. The controlled reaction of hydrocarbopolymers with elemental fluorine. –J.Polym.Sci.: Polym.Lett.Ed., 1974, v.12, № 4, p.177-184.

44. Patent US 3775489. Process for fluorination of aromatic and polynuclear hydrocarbon compounds and fluorocarbons produced thereby. Margrave J.L., Lagow R.J. –Publ. 27.11.73.

45. Lagow R.J., Maraschin N.J. Direct fluorination of cyclic and bicyclic hydrocarbons. –7th Int.Symp.Fluorine Chem., Santa Cruz, Calif., 1973, s.l., s.a., p.1-25.

46. Gerhardt G.E., Dumitru E.T., Lagow R.J. Synthesis of hightbranched perfluoroethers by direct fluorination, promising new materials based on the hexafluoroacetone –ethylene copolymer. –J.Polym.Sci., 1980, v.18, № 1, p.157-169.

47. Robertson G., Liu E.K.S., Lagow R.J. Synthesis of perfluoroadamantane compounds by direct fluorination. –J.Org.Chem., 1978, v.43, № 26, p.4981-4983.

48. Lagow R.J. Large scale synthesis of organofluorine compounds using elemental fluorine; a third Simons cell. –Int.Symp. "Centenary of the discovery of fluorine", Abstr., Paris, 1986, p.2.

49. Adcock J.L., Lagow R.J. The synthesis of the fluorinated ethers "perfluoroglyme" and "perfluorodiglyme" by direct fluorination. –J.Org.Chem., 1973, v.38, № 20, p.3617-3618.

50. Koshar R.J., Hausted D.R., Meiklejohn R.A. Organic fluoronitrogens. V. Bis(difluoroamino)difluoromethane. –

J.Org.Chem., 1966, v.31, № 12, p.4232-4234.

51. Koshar R.J., Hausted D.R., Wright C.D. Organic fluoronitrogens. VII. Tris(difluoroamino)fluoromethane and related compounds. –J.Org.Chem., 1967, v.32, № 12, p.3859-3864.

52. Patent US 3981783. Process ehlektrohimicheskogo ftorirovaniya s dopolnitel'noj podachej vodoroda i uvelicheniem vyhoda po toku. / Chailds V.V. –Publ.21.09.76, RZh Khimiya, 1977, 14L237.

53. Patent DE 2106870. Sposob ehlektrohimicheskogo ftorirovaniya organicheskih soedinenij./Voss P., Niderprum H., Kaul G., Trepp R., -Publ. 24.02.77, RZh Khimiya, 1977, 24N16.

54. Patent DE 2302132, 1976. Sposob polucheniya razvetvlyonnyh perftoralkanov. /Benninger S. -Publ. 23.12.76, RZh Khimiya, 1977, 24L202.

55. Patent US 4035250. Sposob polucheniya perftorgeptana. /Valters H.S., Chailds V.V. -Opubl.12.07.77, RZh Khimiya, 1978, 6N22.

56. Patent JP 53-18488. Sposob polucheniya perftorcikloalkanov. /Sato Dajsuke, Yamamuti Koiti, Murasima Ryoshiro. -Opubl. 15.06.78, RZh Khimiya, 1979, 9N121.

57. Patent US 3662009. Poluchenie nenasyshchennyh ftorsoderzhashchih soedinenij. /Hadchinson V.M. -Publ. 09.05.72, RZh Khimiya, 1973, 9N12.

58. Goldshtejn B.V., Serushkin I.L., Nikonorova N.I. O roli ftorida nikelya v reakciyah ehlektrohimicheskih soedinenij. –Tr. GIPKh, № 39, p. 1, inv. № T-1863., L., 1975, p.43-47.

59. Fauler R.D., Berford N.B., Gamilton J.M., Sweet R.J., Weber K.E., Kasper J.S. Laitain N. Sintez ftoruglerodov. «Himiya ftora», v. № 1 –M.: IL, 1950, p.91-113.

60. Benner R.J., Benning A.F., Downing F.B., Irvin S.F., Jonson K.S., Linch A.L., Parmeli H.M., Wirt W.W. Ftoruglerody, poluchennye ftorirovaniem uglevodorodov trekhftoristym kobal'tom. «Himiya ftora», v. № 1 –M.: IL, 1950, p.114-128.

61. Fauler R.D., Anderson H.S., Gamilton J.N., Berford N.B., Spagetti A., Biterdih S.B., Laitain N. Ftoridy metallov, primenyaemye v sinteze ftoruglerodov. V kn. «Himiya ftora», sb. № 1 –M.:IL, 1950, s.143-153.

62. Patent JP 60-81134. Poluchenie oktaftorpropana. /Katamura Koiti, Kagehyama Yutaka, Nakayama Hidehtosi. –Publ. 09.05.85, RZh Khimiya, 1986, 12N25.

63. Patent JP 60-10933. Poluchenie geksaftorehtana./ Katamura Koiti, Kagehyama Yutaka, Nakayama Hidehtosi. –Publ. 15.06.85, RZh Khimiya, 1986, 11N21.

64. Pak V., Peka J., Cermak V., Sykora F., Petrzila V. Poloprovozni zarizeni pro vyrobu perfluororganickych latek.

–Chem. Prum., 1978, v.28, № 9, p.467-470.

65. Patent FR 2381732. Usovershenstvovannyj sposob perftorirovaniya ciklicheskih uglevodorodov. / Moore R.E. –

Publ. 27.10.78, Izobreteniya v SSSR i za rubezhom, 1979, v.55, № 5, p.67.

66. Patent US 4143079. Sposob polucheniya perftor-1-metil-4-izopropilciklogeksana iz pinena. / Moore R.E. –Publ. 06.03.79, Izobreteniya v SSSR i za rubezhom, 1979, v.55, № 21, p.20.

67. Patent GB 1597914. Sposob perftorirovaniya ciklicheskih uglevodorodov. / Santehch inkorp. –Publ. 16.09.81, Izobreteniya v SSSR i za rubezhom, 1982, v.57, № 12, p.64.

68. Burdon J. The exhaustive fluorination of aliphatic compounds.

–Int. Symp. "Cent. …", Paris, 1936, p.9.

69. Moore R. E., Driscoll G. Perfluorination of bicyclic and tricyclic hydrocarbons. –IV-th Winter Fluorine Conf., Abstr, Daytona Bearen, 1979, p.8.

70. Asovich V.S., Prokudin I.P. Osobennosti ftorirovaniya organicheskih veshchestv chetyrekhftoristym ceriem. –Tr. GIPH, № 40, inv. № T-2117, L., 1976, p.25-31.

71. Isikava N., Kobayasi Yo. Ftor. Himiya i primenenie. –

M.: Mir, 1982, p.91.

72. Keidi J.H., Grosse A.V., Barber E.J., Berger L.L., Sheldon Z.D., Poluchenie ftoruglerodov kataliticheskim ftorirovaniem uglevodorodov. V kn. «Himiya ftora», v. № 1 –M.: IL., 1950, p.129-135.

73. Bigelou L.A. Dejstvie ehlementarnogo ftora na organicheskie soedineniya. «Ftor i ego soedineniya (pod red. J. Saimonsa), t.1 –M.: IL., 1953, p.314-335.

74. Musgrave W. K. R., Smith F. Organic Fluorides. PartII. The effect of metals on the fluorunationof hydrocarbons. –J. Chem. Soc., 1949, p.3026-3028.

75. Brik T. J. Ftoruglerody; ih svojstva i proizvodstvo vo vremya vojny. V kn. «Ftor i ego soedineniya» (pod red. Saimonsa J.), t.I –M.: IL, 1953, p.355-388.

76. Maraschin N. J., Catsikis B. D., Davis L. H., Larvinen J., Lagov R. J. Synthesis of structurally unusual fluorocarbons by direct fluorocarbon. –J.Am. Chem. Soc., 1975, v. 97, № 3, p.513-517.

77. Patent US 4113453. Apparat dlya nizkotemperaturnogo pryamogo ftorirovaniya. / Lagov R.J, Adkok I.L., Marashin N.I. –Publ. 12.09.78, RZh Khimiya, 1979, 19I130.

78. Patent US 4281119. Apparat dlya pryamogo ftorirovaniya s kontroliruemym ohlazhdeniem po zonam. / Lagov R.J., Adkok I.L., Marashin N.I. –Publ. 28.07.81, RZh Khimiya, 1982, 9N225.

79. Rahimov A.I., Himiya i tekhnologiya ftororganicheskih soedinenij. –M.: Khimiya, 1986, p.9-10.

80. Schmeisser M., Ehlers K. P., Sartori P. Dichlorhexafluorpropan durch fluorierung von 1,2-dichlorpropan. –Angew. Chem., 1967, v.79, № 13, p.622.

81. Margrave W. K. R., Smith F. Organic Fluorides. PartI. Fluorination of hydrocarbons. –J. Chem. Soc., November, 1949, p.3021-3026.

82. Grosse A.V., Keidi J. H. Svojstva ftoruglerodov. V kn. «Himiya ftora»: № 1 –M.: IL, 1950, p.35-64.

83. Patent GB 1281822. Improved Fluorination Process. / Kingdom R. J., Bond G. D. –Publ. 19.07.72.

84. Hill M. Process and market development of fluorocarbon fluids. –Chem.and Ind., 1975, № 3, p.118-121.

85. Patent FR 2028457 (V). Sposob ftorirovaniya. / Imperial Smelting Korp. –Publ. 15.01.70, Off. Bull. Francii, Himiya i metallurgiya, 1970, № 45-48, v.I, p.44.

86. Patent US 4220606. Sposob polucheniya perftorproizvodnyh iz ciklichekih uglevodorodov. / Moore R.E. –Publ. 02.09.80, RZh Khimiya, 1981, 9N105.

87. Patent US 3480667. Method of producing fluorinated compounds. / Siegart W. R., Blackley W. D. –Publ. 25.11.69.

88. Patent US 4330475. Aehrozol'nyj sposob pryamogo ftorirovaniya i ustrojstvo dlya ehtoj celi. / Adkok D.L., Renk E.B. –Publ. 18.05.82, RZh Khimiya, 1983,IIN76.

89. Ruff J. K. The catalytic fluorination of perfluorocarbon nitriles and imines. –J. Org. Chem., 1967, v.32, № 5, p.1675-1677.

90. Lusting M., Ruff J. K. Fluorination of some perfluoro alkyliminosulfurdifluorides. –Inorg. Chem., 1965, v.4, № 10, p.1444-1446.

91. Fokin A.V., Stolyarov V.P., Radchenko V.P. Sintezpoliftoramino-iα-ftornitrosoedinenij na osnove reakcij gazoobraznogo ftora. –Izv. AN SSSR, ser. khim., 1982, № 8, p.1853-1861.

92. Fokin A.V., Galahov V.S., Uzun A.T. i dr. Reakciya ftora s solyami shchelochnyh metallov dinitroacetonitrila v prisutstvii ftoridov kaliya ili kal'ciya. –Izv. AN SSSR, ser. khim., 1974, № 2, p.456-458.

93. Fokin A.V., Uzun A.T., Stolyarov V.P. Bis (diftoramino) ftoracetal'degid –novyj predstavitel'α,α-bis (diftoramino) al'degidov. –Izv. AN SSSR, Ser. khim., 1982, № 6, p.1438.

94. Eremenko L.T., Nacibullin F.YA., Borovinskaya I.P., Karpova N.D. Sintez perftornitroehtanov. –Izv.AN SSSR, Ser.khim., 1968, № 3,p.431-432.

95. Sekiya A., Des Martean D. D. Synthesis of 1,1-bis (fluoroxy) –perhaloalkanes by reaction of fluorinated carboxylic acids with fluorine in the presence of cesium fluoride. –Inorg. Chem., 1980, v. 19, № 5, p.1328-1330.

96. Lu S., Des Martean D. D. Direct synthesis of fluorinated peroxides. 7. Perfluoro-tret-butyl-fluoroformyl peroxide. –Inorg. Chem., 1978, v. 17, № 2, p.304-306.

97. Schack C. J. A new synthesis of difluoraminotrifluoromethane. –J. Fluor. Chem., 1981, v. 18, no 4, p.583-586.

98. Patent DE 2712732. Sposob polucheniya oktaftorpropana. /Halaz S.P. –Publ. 28.09.75, RZh Khimiya, 1979, 14N14.

99. Patent US 4158023. Sposob polucheniya oktaftorpropana. / Halaz S.P. –Opubl. 12.06.79. Izobreteniya v SSSR i za rubezhom, 1979, v. 55, № 24, p.121.

100. Patent GB 1568020.Sposob polucheniya oktaftorpropana. / Halaz S.P. –Publ. 21.05.80. Izobreteniya v SSSR i za rubezhom, 1981, v. 55, № 3, p.54.

101. Patent US 4377715. Poluchenie perftorpropana. /Nuchka H.R., Hino I.B., Abek R.E., Robinson N.A. –Publ. 22.03.83, Izobreteniya v SSSR i za rubezhom, 1983, v.57, № 23, p.88.

102. Patent EU 0031519. Sposob ftorirovaniya organicheskih soedinenij ehlementarnym ftorom. / Ellaid Chemical Co. –Publ. 08.07.81, Izobreteniya v SSSR i za rubezhom, 1983, v.57, № 1, p.20.

103. Patent EU 0032210. Sposob ftorirovaniya organicheskih soedinenij ftorom v trubchatom reaktore iz poristogo metalla v prisutstvii perftorirovannogo razbavitelya. / Ellaid Chemical Co. –Publ. 22.07.81, Izobreteniya v SSSR i za rubezhom, 1983, v.57, № 2, p.27.

104. Patent US 4513154. Sposob provedeniya posledovatel'no-konkuriruyushchih gazofaznyh reakcij. / Kurtz B.E. –Publ. 23.04.85, RZh Khimiya, 1986, 4N25.

105. Patent US 2831035. Proizvodstvo ftorirovannyh uglerodov. / Tuchkovskij E.A., Wolf C. – Publ. 15.04.58, RZh Khimiya, 1960, 85740.

106. Patent US 3709800. Poluchenie perftorirovannyh uglevodorodov./ Fox H.M. –Publ. 09.01.73, RZh Khimiya, 1973, 22N23.

107. Патент Японии 5608. Фторсодержащие галоидуглеводороды. / Осиба Такаси. – Опубл. 22.03.65, РЖ Химия, 1968, 5Н35.

108. Patent US 2681267. Process uluchsheniya kataliticheskih svojstv ftoristogo alyuminiya i produktov iz nego. / Kalfee J. D., Miller Ch.B. –Publ. 15.06.54, RZh Khimiya, 1956, № 14, 45553.

109. Hohorst F. A., Shreeve J. M. Bis-(fluoroxy)-difluoromethane,$CF_2(OF)_2$. –J. Am. Chem. Soc., 1967, v.89, № 8, p.1809-1819.

110. Walker N., Des Martean D. D. Direct Synthesis of fluorocarbon peroxides.III. The addition of chloroperoxytrifluoromethane to olefins. –J. Am. Chem.Soc., 1975, v.97, № 1, p.13-17.

111. Patent US 4499024. Nepreryvnyj sposob polucheniya bis (ftoroksi) diftormetana. / Filolt M.G. –Publ. 12.02.85, RZh Khimiya, 1985, 20N14.

112. Lusting M. A., Pitochelli A. R., Ruff J. K. The catalytic addition of fluorine to a carbonyl group. Preparation of fluoroxy compounds. –J. Am. Chem. Soc., 1967, v. 89, № 12, p.2841-2843.

113. Ruff J. K., Pitochelli A. R., Lusting M. A. A simple synthesis of fluoroxyperfluoroalkyl compounds. -J. Am. Chem. Soc., 1966, v.88,№ 19, p.4531-4532.

114. Kennedy R. C., Cady G. H. Reaction of carbonyl fluoride with fluorine in the presence of various fluorides as catalysts. –J. Fluor. Chem., 1973, v.3, № 1, p.141-154.

115. Muhametshin F. M. Uspekhi himii ftororganicheskih gipogalogenitov i rodstvennyh soedinenij. –Uspekhi khimii, 1980, t. 49, № 7, p.1260-1288.

116. Muhametshin F.M. Gipoftority i ih primenenie v organicheskom sinteze. –V kn.«Novye ftoriruyushchie reagenty v organicheskom sinteze». –Novosibirsk: Nauka, 1987,p.140-196.

117. Cady G. H. Proposed mechanisms of catalysis of fluorination of CF_2O. –Anales. Asoc. Quim. Argentina, 1971, v.59, p.3-4, p.125-131.

118. Patent US 3230264. Reaction of carbonyl fluoride with fluorine. –Roger S. P., Cady G.H. –Publ. 18.01.66.

119. Wechsberg M., Cady G.H. Comparative studies of catalytic fluorination of carbon monoxide with elementary fluorine. –J. Am. Chem. Soc., 1969, v.91, p.4432-4435.

120. Kellog K. B., Cady G.H. Trifluoromethyl hypofluorite. –J. Am. Chem. Soc., 1948, v.70,№ 12, p.3986-3988.

121. Gervasi J.A., Brown M., Bigelow L. A. The action of elemental fluorine upon organic compounds. XX. The fluorination of mono-, di-and trimethylamine, ethylenediamine and ethyleneimine. –J. Am. Chem. Soc., 1956, v.78, № 8, p.1679-1682.

122. Avonda F. P., Gervasi J. A., Bigelow L.A. The action of elemental fluorine upon organic compounds. XXI. The fluorination of malononitrile and dimethylformamide. –J. Am. Chem.

Soc., 1956, v.78, № 12, p.2798-2800.

123. Toitelboim M.A., Shoihet A.A., Kaplunov M.G., Vedeneev V.I. Energeticheskie razvetvleniya cepej v reakciyah triftormetilgipoftorita s galoidmetanami. –Kinetika i kataliz, 1981, t. 22, v. 2, p. 298.

124. Toitelboim M.A., Shoihet A.A., Vedeneev V.I. Energeticheskie razvetvleniya cepej v reakciyah triftormetilgipoftorita s galoidmetanami. 2. Mekhanizm otricatel'nogo vzaimodejstviya cepej. –Kinetika i kataliz, 1981, t. 22, v. 3, p. 564-568.

125. Vedeneev V.I., Parijskaya A.V. Mekhanizm ftorirovaniya metana i ego ftorproizvodnyh. I. Sravnenie skorostej ftorirovaniya metana, ftormetana, diftormetana i triftormetana. –Kinetika i kataliz, 1971, t. 12, v. 1, p. 21-26.

126. Parijskaya A.V., Vedeneev V.I. Mekhanizm ftorirovaniya metana i ego proizvodnyh. 2. Diftormetan –Kinetika i kataliz, 1971, t.12, v.2, p.293-298.

127. Parijskaya A.V., Vedeneev V.I. Mekhanizm ftorirovaniya metana i ego ftorproizvodnyh. 3. Ftoristyj metil. –Kinetika i kataliz, 1971, t.12, v.3, p.543-548.

128. Parijskaya A.V., Vedeneev V.I. Mekhanizm ftorirovaniya metana i ego ftorproizvodnyh.4. Metan. –Kinetika i ataliz, 1971, t. 12, v.4,p. 839-842.

129. Nadtochenko V.A., Fedotov N.B., Vedeneev V.I., Sarkisov O.M. O reakcii kolebatel'no vozbuzhdennoj molekuly CH_3F s ftorom. –Dokl. AN SSSR, 1978, t.238, № 6, p.1391-1394.

130. Parijskaya A.V., Vedeneev V.I. O prirode zaderzhek samovosplameneniya v sisteme $CH_3F + F_2 + O_2 + He$. –Kinetika i kataliz, t.14, v.6, p.1365-1369.

131. Vedeneev V.I., Teitelboim M.A., Shoihet A.A. Fotohimicheskoe ftorirovanie ftoroforma v prisutstvii kisloroda. –Izv. AN SSSR, 1976, № 9, p.1968-1970.

132. Medvedev B.A., Teitelboim M.A., Shilov A.E. Himicheskaya aktivaciya molekuly $CHFCl_2$ v reakcii $CHCl_2 + F_2 \rightarrow CHCl_2F + F$. –Kinetika i kataliz, t.12, v.2, p. 269-275.

133. Medvedev B.A., Teitelboim M.A., Shilov A.E. Mekhanizm gazofaznoj reakcii hlorftormetana s molekulyarnym ftorom. –Kinetika i kataliz, 1971, t.12, v.3, p. 49-751.

134. Vedeneev V.I., Medvedev B.A., Teitelboim M.A. Gazofaznoe ftorirovanie diftormetana pri povyshennyh davleniyah inertnogo gaza. –Kinetika i kataliz, t.13, v.1, p.50-53.

135. Obvivalneva A.A., Fedotov V.G. Vozbuzhdennye molekuly v reakcii ftora s acetonom (ftoracetony; sintez; mekhanizm). –Kinetika i kataliz, 1981, t.22, v.5, v.1095-1099.

136. Kapralova G.A., Margolina E.M., Rusin L.Y., Chajkin A.M., Shilov A.E. Rol' kolebatel'no-vozbuzhdennyh molekul v reakciyah ftorirovaniya molekulyarnym ftorom. –V sb. «5 Mezhdunar. simpozium po himii ftora», Tezisy dokl., M., : Nauka, 1969, p.102-104.

137. Knunyats I.L, Gambaryan N.P., Rohlin E.M. Karbeny. (Soedineniya dvuhvalentnogo ugleroda, promezhutochno obrazuyushchiesya v organicheskih reakciyah). –Uspekhi khimii, 1958, t.27, v.12, s.1361-1436.

138. Muhametshin F.M., Zhirnov O.M., Ainagos N.A., Petrov Y.I., Lyapunov M.I. O nekotoryh osobennostyah gipoftoritnogo metoda polucheniya perftormetilvinilovogo ehfira. Soobshch. 2. Sintez triftormetilgipoftorita. –Tr. GIPH, № 69, inv. № T-2769, L., 1980, p.73-78.

139. Muhametshin F.M., Povroznik S.V., Zhirnov O.M. Issledovanie kinetiki i mekhanizma kataliticheskoj reakcii obrazovaniya triftormetilgipoftorita. –Tr. GIPH, № 103, inv. № T-2981, L., 1983, p.75-80.

140. Patent SU 1141707. Sposob polucheniya 1,1-diftor-1-hlorehtana ili 1,1,2,2-tetraftordihlorehtana. /Zaharov V.Y., Goldinov A.L., Borovnev L. M., Golubev A.N., Kalashnikova N.A., Zaharova O.M., Lyubimova L.A.

141. Kapralova G.A., Buben S.N., Chaikin A.M. Kinetika i mekhanizm reakcii ftorirovaniya okisi ugleroda. –Kinetika i kataliz, 1975, t.16, v.3, p.591-595.

142. Povroznik S.V. Razrabotka sposoba i tekhnologii polucheniya ftoroksitriftormetana reakciyami ehlementarnogo ftora s karbonilsoderzhashchimi soedineniyami. Diss. kand. tekhn. nauk, 1987, PF NPO GIPH, 161p.

143. Krasnov K.S. Molekuly i himicheskaya svyaz'. –M.: Vyssh. shkola, 1977, p.117.

144. Bezmelicyn V.N., Legasov V.A., Chaivanov B.B. Sintez diftorida kriptona s primeneniem termicheskoi generacii potokov atomarnogo ftora. –Dokl. AN SSSR. Ser. khim., 1977, t.235, № 1, p.96-98.

145. Bezmelicyn V.N., Legasov V.A., Spirin S.N., Chajvanov B.B. Kinetika kataliticheskoi atomizacii ftora. –Dokl. AN SSSR. Ser.fiz.khimiya, 1982, t.262, № 5, p.1153-1157.

146. Palkina L.A., Spirin S.N., Tishchenko P.P. processy s uchastiem atomarnogo ftora. –Dokl. AN SSSR. Ser.fiz.khimiya, 1982, t.262, p.1428-1433.

147. Bezmelicyn V.N., Vasilev A.A., Sinyanskij V.F., Chajvanov B.B. Kinetika termokataliticheskoj dissociacii ftora na poverhnosti nikelya. –Tezisy dokladov na 8 Vsesoyuzn. simp. po himii neorg. ftoridov, 1987, M.: Nauka, p.59.

148. Nikonorov YU.I. Ftoridy nikelya. Ih kataliticheskaya i okislitel'naya aktivnost'. –Tezisy dokladov na 5 Vsesoyuzn. simp. po himii neorg. ftoridov, 1978, M.: Nauka, p.205.

149. Ryss I.G. Khimiya ftora i ego neorganicheskih soedinenij. –M.: Goskhimizdat, 1956, p.576-579.

150. Redwood M.E., Willis C. J. Fully fluorinated alkoxides. PartI. Trifluoromethoxides of alkali metals. –Canad. J. Chem., 1965, v.43, p.1893-1898.

151. Gubanov V.A., Veretennikov N.V., Troichanskaya P.E., Dolgopol'skij I.M. Sintez perftoralkoksidov metallovI gruppy i termograficheskoe izuchenie ih svojstv. –Zh. Org. khim., 1975, t.II, № 2, p.322-325.

152. Levy J. B., Kennedy R. C. Bis (trifluoromethyl) peroxide.I. Thermodynamics of the equilibrium with carbonyl fluoride and trifluoromethyl hypofluorite. –J. Am. Chem. Soc., 1972, v.94, no 10, p.3302-3305.

153. Patent JP 35888. Sposob polucheniya triftormetilgipoftorita. / Nagase Syundzi, Abe Takasi, Baba Hadzime, Ohira Kadzuo. –Publ. 09.09.72, RZh Khimiya, 1973, 14N120.

154. Patent US 3687825. Sposob polucheniya triftormetilgipoftorita. Nagase Syundzi, Abe Takasi, Baba Nadzime. –Publ. 29.08.72, RZh Khimiya, 1973, 21N26.

155. Patent US 2983764. Sposob polucheniya ftoruglerodnyh soedinenij./ Knak D.F. –Publ. 9.05.61, RZh Khimiya, 1962, 14L53.

156. Patent JP 56-16429. Oligomerizaciya geksaftorpropilena v gazovoj faze. / Osaka Yonosuke, Higasidzuka Takehsi. –Publ. 17.02.81, RZh Khimiya, 1982, 3N10.

157. Patent JP 50-45818. Poluchenie oligomerov geksaftorpropilena. Kadzava Masahiro, Komatsu Tadaaki, Macuoka Kimiaki. –Publ. 08.06.81, RZh Khimiya, 1982, 9NII.

158. Patent US 4296265. Sposob polucheniya oligomerov geksaftorpropilena. / Osaka Yonosuke, Tozuka Takasi. –Publ. 20.10.81, RZh Khimiya, 1982, I3NII.

159. Patent DE 3027229. Sposob polucheniya oligomerov geksaftorpropilena. / Osaka Y., Tozuka T. –Publ. 07.02.81, Izobreteniya v SSSR i za rubezhom, 1981, V.55, № 12, p.30.

160. Patent BE 2055824A. Sposob polucheniya oligomerov geksaftorpropilena. /Osaka Y., Tozuka T. –Publ. 18.07.80, Sbornik referatov NIOKR, obzorov, perevodov i dep. rukopisej. DSP. Khimiya i khimicheskaya tekhnologiya, M., 1986, № 5, p.14.

161. Patent DE 2616733. Sposob polucheniya di- i trimerov geksaftorpropilena. / Okava M., Komatsu T., Matsuoka K. –Publ. 20.03.80, Izobreteniya v SSSR i za rubezhom, 1980, № 15, p.13.

162. Patent JP 57-2697. Sposob polucheniya oligomerov geksaftorpropena. / Neosu K.K. –Publ. 18.01.82, Izobreteniya v SSSR i za rubezhom, 1982, v.57, № 14, p.113.

163. Scherer K. V., Ono T., Jamanouchi K., Fernandez R., Henderson P.B. F-2,4-Dimethyl-3-ethyl-3-pentyl and F-2,4-dimethyl-3-isopropyl-3pentyl: stable tert-perfluoroalkyl radicals prepared by addition of fluorine or trifluoromethyl to a perfluoroalkene. –J. Am. Chem. Soc., 1985, v.107, № 3, p.718-719.

164. Scherer K. V., Fernandez R., Henderson P.B. Long lived perfluoroalkyl radicals: preparation by direct fluorination and alternate routes, properties and rates andmechanisms of disappearance. –Int. Symp. "Centenary of the discovery of fluorine", Abstr., Paris, 1986, p.1.

165. Patent DE 2332097. Sposob polucheniya perftornonanov. /Halaz S.P. –Publ. 16.01. 75, RZh Khimiya, 1975, 18N25.

166. Patent DE 2332088. Sposob polucheniya perftor-2-metilpentana./ Halaz S.P. –Publ. 16.07.81, Izobreteniya v SSSR i zarubezhom, 1981, v.55, № 23, p.21.

167. Allayarov S.R., Barkalov I.M., Gol'danskij V.I., Kiryuhin D.P. Obrazovanie stabil'nyh radikalov iz ftororganicheskih soedinenij. –Izv. AN SSSR. Ser. him., 1983, № 6, p.1225-1228.

168. Allayarov S.R., Barkalov I.M., Gol'danskij V.I., Demidov S.V., Kiryuhin D.P., Mihajlov A.I. Stabil'nye radikaly –rastvorennye perftoralkily. –Izv. AN SSSR. Ser. him., 1983, № 6, p.1448-1449.

169. Allayarov S.R., Mihailov A.I., Barkalov I.M. Novyj stabil'nyj perftoralkil'nyj radikal. –Izv. AN SSSR. Ser. him., 1985, № 7, p.1667-1669.

170. Allayarov S.R., Barkalov I.M., Lebedov M.YU., Loginova N.N., Mihailov A.I. Obrazovanie stabil'nyh radikalov pri radiolize geksaftorpropilena. –Izv.AN SSSR. Ser. him., 1986, № 2,p.462-463.

171. Allayarov S.R., Barkalov I.M., Gol'danskij V.I. Obrazovanie dolgozhivushchih radikalov pri ftorirovanii zhidkih uglevodorodov. – Izv.AN SSSR. Ser. him., 1986, № 10, p.394.

172. Allayarov S.R., Sumina I.V., Barkalov I.M., Mihailov A.I. Obrazovanie stabil'nyh radikalov

pri fotolize perftor-2,4-dimetil-3-ehtilpentena-2. –Izv. AN SSSR, Ser. him., 1986, № 10, p.2359-2361.

173. Krusic P. J., Scherer K. V. An electron spin resonance study of long lived fluoroalkyl radicals generated by photolysis of hindered perfluoroalkenes. Int. Symp. "Centenary of the discovery of fluorine". Abstr., Paris, 1986, p.37.

174. Levy J.B., Kennedy R. C. Homolytic displacement reactions of carbon.I. The fluorine-perfluorocyclobutane reactions. –J.Am.Chem.Soc., 1974, v.96, № 15, p.4791-9795.

175. Gol'dinov A.L., Zaharov V.Y., Baibakov P.Y., ZHukova V.A., Novikova M.D. Novye aspekty pryamogo ftorirovaniya. Kataliticheskoe gazofaznoe ftorirovanie ftorolefinov; poluchenie perftoruglerodov. –Otchet predpriyatiya p/ya A-1619, 1987, inv. № 1288, 87p.

176. Matveev S.A., Prokudin L.P., Timofeev N.V. Ispol'zovanie triftorida kobal'ta dlya ftorirovaniya organicheskih soedinenij po dvojnym svyazyam. –Tr. GIPH, 1975, № 31, inv. № T-1728, p.119-127.

177. Asovich V.S., Prokudin I.P. Ftorirovanie acetilena ftoridami kobal'ta i ceriya. Tr. GIPH, № 55, inv. № T-2552, L., 1978, p.21-24.

178. Asovich V.S., Prokudin I.P., Maksimov B.N., Stepanov V.P. Izuchenie kineticheskih zakonomernostej ftorirovaniya acetilena trekhftoristym kobal'tom. –Tr. GIPH, № 65, inv. № T-2723, L., 1979, p.42-47.

179. Kotikov S.V., Prokudin I.P., Asovich V.S. Izuchenie kineticheskih zakonomernostej ftorirovaniya geksaftorpropilena trekhftoristym kobal'tom. –Tr. GIPH, № 101, inv. № T-2986, L., GIPH, 1985, s.24-27.

180. Burdon J., Knights J.R., Parsons J. W., Tatlow J. C. The fluorination of ethane and ethene over potassium tetrafluorocobaltate (III) and cobalt trifluoride. –Tetrahedron, 1976, v.32, p.1041-1043.

181. Gol'dinov A.L., Borovnev L.M., SHirokova N.S., Kovbasyuk O.G., Tishina V.V. Vliyanie tekhnologicheskih parametrov sinteza i chistoty rastvoritelya na svojstva ftoroplasta-50. – Otchet predpriyatiya p/ya A-1619, 1987, inv. № 1231.

182. Patent DE 2451493. Sposob polucheniya perftorirovannyh ehfirov./ Halaz S.P., Klag F. –Publ. 06.05.76, Izobreteniya v SSSR i za rubezhom,1982, v.57, № 22, p.5.

183. Patent US 3665041. Perfluorinated polyethers and process for their preparation. / Sianesi D., Fontanelli R., -Publ. 23.05.72.

184. Ryabinin N.A., Dolubenov A.E., Shmatov L.E. Ftorpoliehfiry kak antiadgezivy pri pressovanii perhlorata nitroniya. –Tr. GIPH, № 101, inv. № T-2986, L., 1985, p.83-87.

185. Patent SU 1332758. Sposob ochistki geksaftorpropilena, tetraftorehtilena i ih semej ot oktaftorizobutilena. /Fokin A.V., Studnev Y.N., Rapkin A.I. i dr.

186. Gol'dinov A.L., Borovnev L.M., Golubev A.N., Zaharov V.Yu. i dr. Razrabotka tekhnologii polucheniya 2-perftormetil-4-oksaperftornonana na osnove perftorizobutilena i 1,1,5-trigidroperftor pentanola. –Otchet predpriyatiya p/ya A-1619, 1987, inv. № 1229, 39p.

187. Patent SU 1148285. 3-Gidropropilftorsul'fat v kachestve promezhutochnogo produkta dlya sinteza 2,2,3,3-tetraftorpropionovoj kisloty i sposob ee polucheniya. /Fokin A.V., Studnev Y.N., Rapkin A.I. i dr.

188. Patent SU 3966753. Sposob polucheniya 2-gidrotetraftorehtilftorsul'fata. /Fokin A.V., Rapkin A.I., Tatarinov A.S. i dr.

189. Patent SU 1233595. Sposob polucheniya ω-gidroperftorkarbonovyh kislot (ego varianty). / Fokin A.V., Studnev Y.N., Rapkin A.I. i dr.

190. Tekhnicheskie trebovaniya k PFDMCG dlya ispol'zovaniya v radioehlektronike. M.: INEOS AN SSSR. Reg. № 12111-10 DSP ot 18.01.85.

191. Iskhodnye dannye dlya razrabotki zhidkosti-diehlektrika. M.: INEOS AN SSSR. Pril. k vh. № 155 ot 18.02.85.

192. Gol'dinov A.L., Zaharov V.YU., Bajbakov P.YA. i dr. Razrabotka tekhnologii polucheniya perftordimetilciklogeksana povyshennoj chistoty. –Otchet predpriyatiya p/ya A-1619, 1986, inv. № 1218, 24p.

193. Gol'dinov A.L., Maslyakov A.I., Zaharov V.Y. i dr. O vozmozhnosti rezkogo uvelicheniya vypuska deficitnyh ftoruglerodnyh zhidkostej i smazok. –Otchet predpriyatiya p/ya A-1619, 1986, № 1219, 13p.

194. Vremennyj tekhnologicheskij reglament proizvodstva perftordekalina.1981, inv. № 1115.

195. Furin G.G. Synthetic aspects of the fluorination of organic compounds. (Ed.) M.E. Vol'pin./Harwood Academic

Publishers GmbH: United Kingdom, Sov. Sci. Rev., B. Chem., 1991, V.16, Part 1,p.140.

196. Rozen S., Kol M. Olefin epoxidation using elemental fluorine. / J.Org.Chem., 1990. V.55,p.5155-5159.

197. Patent JP 02-131438, (1990). CO719/08. Preparation of hexafluoroethane. /Shimuzu M.C.A. 1990, V.I 13,97031.

198. Patent JP 62-193946, (1989). CO719/08, CO17/04. Sposob polucheniya ftorsoderzhashchih ehtanov. /Faruka Y., Kono H. RZh Kh, 1990, 2N 131.

199. Lagow R.J. Important new developments in direct fluorination technology. /Memorial symposium for Prof. Nobuo Ishikawa, Dec. 9-10, 1991, Nippon Kaiun Club, Japan.

200. Lin W.H., Lagow R.J. Synthesis of perfluorodicyclohexano-crown-6 ether. /J.Chem.Soc., Chem.Commun., 1991,p.13-14.

201. Clark W.D., Lin T.Y., Maleknia S.D., Lagow R.J. Synthesis of perfluorotetralkyl ortocarbonates using elemental fluorine. / J.Org.Chem., 1989. V.54.p.1990-1992.

202. Sievert A.C., Tong W.R., Nappa M.J. Preparation D'analogues fluores de la pheromone d'anthanomus grandis. / J.Fluorine Chem., 1991. V.51.p.397-405.

203. Tonelli C., Tortelli V. Photoinduced fluorination of hexafluoropropene trimers: synthesis of branched perfluoroalkanes. /J.Chem.Soc., Perkin Trans I, 1990, № 1,p.23-26.

204. Patent Application EP 344935, (1989). CO8G65/00. Preparation of prefluoroethers by photo-assisted fluorination. / Nappa M.J., Sievert A. C.A. 1990, V. 112, 216229.

205. Patent US 4960951, (1990). CO743/12. Novel perfluoroalkyl ethers by two-step fluorination of polyols./ Nappa M.J., Sievert A.C. Tong W.R. C.A. 1991, V. 111, 216229.

206. Sievert A.C., Tong W.R., Nappa M.J. Synthesis of perfluorinated ethers by an improved solution phase direct fluorination process. / J.Fluorine Chem. 1991. V. 53,p. 397-417.

207. Mizin G.G., Simakov B.V., Shultezkaya L.V., Moldavsky D.D. Issledovanie sposoba polucheniya perftorehtilciklogeksena. / ZHPH. 1991. t.64 ,v.6. p.293-1296.

208. Moldavsky D.D., Mizin G.G., Shultezkaya L.V., Simakov B.V., Furin G.G. Synthesis of perfluoroethylcyclohexene, its alkoxy and diakylamino derivates and their electrochemical fluorination. / Abstracts of 10-European Symposium on Fluorine Chemistry, Sept. 20-25, 1992, Padua, Italy. Abstracts. B7; J. Fluorine Chem., 1992. v.58.p.185.

209. Moldavsky D. D. Perftororganicheskie soedineniya: Poluchenie pryamym ftorirovaniemuglevodorodov. Diss. dokt. him. nauk, 2002, RNC Prikladnaya himiya, 268p.

210. Suvorov B.V., Bukeihanov N.R. Okislitel'nye reakcii v organicheskom sinteze. 1978g. M., Khimiya, 197p.

211. Semenova G.A., Leites I.L., Aksel'rod Y.V., Markina M.I., Sergeev S.P.,Har'kovskaya E.N. Kataliticheskie i adsorbcionnye metody ochistki gazov ot sernistyh soedinenij. –Ochistka tekhnologicheskih gazov.1977g, M.,Khimiya, 1977,p. 35-37.

212. Panov G.I. Zakonomernosti geterogenno-kataliticheskoj aktivacii dvuhatomnyh molekul (H_2, O_2, N_2). Novye kataliticheskie sistemy aktivacii molekulyarnogo azota. Diss. dokt. him. nauk, 1986, Novosibirsk, 374p.

213. Patent SU 220740. Sposob polucheniya tetrahlortetraftorpropana. –Palleta O., P. Svoboda, L. Stefan, Y. Kvisala. –Publ. 15.12.85. RZhKhimiya, 1986, IIN24.

214. Patent JP 60-116637. Poluchenie ftormetana. –Takayama S., Meiraku F., Takoiti A., Kovasaki H. –Publ. 24.06.85. RZh Khimiya, 1986, 9N16.

215. Margolis L.Y. Okislenie uglevodorodov na geterogennyh katalizatorah. 1977g. M., Khimiya, p. 296.

216. Kavaev M.M., Zaporin A.P., Kleshchev N.F. Kataliticheskoe okislenie ammiaka. 1983g. M., Khimiya, p. 31.

217. Tekhnologiya katalizatorov. 1974g. L., Himiya, p. 138-140.

218. Patent US 2760997. Process for the production of chlorotrifluoroethylene by passing a mixture of trichlorotrifluoroethane and hydrogen through an unobstructed iron tube. / Rucker J. T., Stormon D. B. –Publ. 28.08.56.

219. Patent US 2615925. Preparation of olefinic compounds. / Bordner C.A. –Publ. 28.10.52.

220. Patent US 2704777. Preparation of halogenated olefines / Clark J.W. –Publ. 22.03.55.

221. Patent GB 698386. Improvement in preparation of halogenated olefines / Clark J. W. –Publ. 14.10.53.

222. Patent DE 1044800. Verfahren zur Herstellung von Chlortrifluorathylen / Clark J. W. –Publ. 27.11.58.

223. Patent US 2685606. Preparation of halogenated olefines / Clark J. W. –Publ. 03.08.54 C.A. 48, 127881 (1954).

224. Patent US 2697124. Dehalogenation of fluorohalocarbons / Russel M.M. –Publ. 14.12.54 C. A. 50, 2650 (1956).

225. Patent US 2864873. Production of 1,1,2-trifluoro-2-chloroethylene / Miller C. B., Smith L. B. –Publ. 16.12.58.

226. Patent US 3043889. Poluchenie ftoristogo ehtilena. / Smith L.B., Wolf C. –Publ. 10.07.62. RZh Khimiya, 1964, 3N24.

227. Patent DE 1186847. Poluchenie 1-chlor-1,2,2-triftorehtilena. / Smit L.B., Wolf C. –Publ. 4.10.65, RZh Khimiya, 1966, 13N26.

228. Patent US 3333011. Poluchenie hlortriftorehtilena./Anello L.G., Wolf C. –Publ. 25.07.67 RZh Khimiya, 1969, 14N30.

229. Patent JP 60-185734. Poluchenie triftorhlorehtilena. / Morimoto Takesi, Morikava Sanesuke, Funayama Keidi. –Publ. 21.09.85, 19N37.

230. Patent EU 0053657. Sposob polucheniya hlortriftorehtilena i triftorehtilena. / Kaningham U.D., Plekors R.E., Smith E.M. –Publ. 16.06.82. Izobr. v SSSR i z/r., vyp. 57, № 15, p. 83.

231. Patent JP 43-8454. Sposob polucheniya triftorehtilena. / Sakata Hirosukeh. –Publ. 02.04.68. RZh Khimiya, 1969, 3N36.

232. Patent US 2913400. Katalizator iz okisi molibdena dlya konversii uglevodorodov. / Burton U.P., Lefrenkois F.A., Riblet E.U. –Publ. 17.11.59, RZh Khimiya, 1961, 9K156.

233. Patent US 3354233. Proizvodstvo tetraftorehtilena. / Anello L.G., Wolf C. –Publ. 21.11.67, RZh Khimiya, 1969, 9N32.

234. Patent DE 1270547. Verfahren zur Herstellung von Tetrafluorathylen/ Anello Z. G., Wolf C. –Publ. 30.01.69.

235. Patent US 3505417. Degaloidirovanie ftorgalogenuglerodov. / Gardner L.E. –Publ. 07.04.70, RZh Khimiya, 1971, 11133.

236. Patent US 3636173. Sposob kataliticheskogo degaloidirovaniya./ Gardner L.E. –Publ. 18.01.72, RZh Khimiya, 1972, 21N21.

237. Patent US 3789016. Katalizator gidrodegaloidirovaniya. / Gardner L.E. –Publ. 29.01.74. RZh Khimiya, 1975, 2N217.

238. Patent US 3636172. Degaloidirovanie ftorgaloiduglevodorodov. / Gardner L.E. –Publ. 18.01.72, RZh Khimiya, 1972, 21N20.

239. Patent US 2900423. Proizvodstvo perftorpropilena. / Smith L.B. –Publ. 18.08.59. RZh Khimiya, 1961, 7L44.

240. Patent US 2734090. Poluchenie ftoristogo vinilidena. / Kafi D.D., Miller CH.B. –Publ. 07.02.56, RZh Khimiya, 1957, 12, 42313.

241. Patent US 3404180. Poluchenie carbonilftorida. / K.K. Lester. –Publ. 1.10.68. –RZh Khimiya, 1969, 23N92.

242. Patent FR 1460246. Sposob polucheniya okisi tetraftorehtilena. / Edison. –Publ. 17.10.66. –RZh Khimiya, 1968IINI24.

243. Sokolov L.F. Issledovanie i razrabotka tekhnologii processov okisleniya ftorolefinov. – Diss. dokt. khim. nauk. –Leningrad, VNIISK, 1979.

244. Patent SU 190555. Sposob polucheniya ftoristogo vodoroda. / Gol'dinov A.L., Romanov E.I., Zaharov V.Y. i dr.

245. Gol'dinov A.L., Borovnev L.M., Zaharov V.Y. i dr. Termicheskoe obezvrezhivanie ftororganicheskih othodov v vodorodo-vozdushnom plameni na opytno-promyshlennoj ustanovke. –Otchet predpriyatiya p/ya A-1619, 1982, inv. № 887, 18p.

246. Borovnev L.M., Golubev A.N., Zaharov V.Y. i dr. Kataliz i iniciirovanie destruktivnogo okisleniya, tetraftorehtilena molekulyarnym kislorodom. Poluchenie karbonilftorida. –Otchet predpriyatiya p/ya A-1619, 1983, inv. № 1110, 21p.

247. Patent DE 213342. Sposob polucheniya ftorsoderzhashchih galoiduglevodorodov so srednej stepen'yu ftorirovaniya. / L. Ingehburg, K. Rehjnfred, M. Diter. –Publ. 24.12.85. –RZh Khimiya, 1986, 21N17.

248. Patent DE 203314. Katalizator polucheniya hlorftormetana v gazovoj faze. / I. Lelid, R. Kaden, D. Mross. –Publ. 19.10.83. –RZh Khimiya, 1984, 17N181.

249. Patent US 4504686. Sposob polucheniya 1,1,2-triftor-2-hlorehtildiftormetilovogo ehfira. / S. Takami. –Opubl. 12.03.85. –RZH Himiya, 1986, 8N9.

250. Patent JP 55-85564. Poluchenie β-triftormetilhlorpiridinov./ R.Nishima, K. Rudzikama, I.Jokomiti, Y. Cudzii, S. Nisimura. –Publ. 27.06.80. –RZh Khimiya, 1981, 19N177.

251. Patent US 4139568. Sposob polucheniya metilftorida. / V. Daniehl, M. Libbs. –Publ. 13.02.79. –RZh Khimiya, 1979, 18N18.

252. Patent US 4145368. Poluchenie 1,1,1-triftor-2,2-dihlorehtana. R. Sweney, S. Bernard. –Publ. 20.03.79. –RZh Khimiya, 1979, 20N20.

253. Patent FR 1453510. Sposob ochistki dihlortetraftorehtana. / Corp. Elektrohimiya. – Publ. 16.08.66. –RZh Khimiya, 1968, 11N39.

254. Vilenchik Y.M., Yakurnova G.I., Ostapenko E.A. Sintez triftoracetilftorida na osnove okisi tetraftorehtilena. –Tr. GIPH, 1985, № 101, p. 147-149.

255. Patent JP 58-35978. Sposob polucheniya pentaftorpropionilftorida. / A. Jonotasi, A. Josio. –Publ. 08.05.83.-Izobreteniya v SSSR i za rubezhom, 1984, v. 57, № 8, part 2, p. 130.

256. Patent JP 58-38231. Poluchenie pentaftorpropionilftorida./ I. Jonosuke, A. Josio, S. Hiroyuki. –Publ. 05.03.83.-RZh Khimiya, 1984, 5N46.

257. Patent US 3250808. Ftorsoderzhashchie prostye ehfiry. / E.F. Mur, A. Mil'yan, G. Eleuterio. –Publ. 10.05.66. –RZh Himiya, 1967, 17N82.

258. Patent US 3250807. Ftorsoderzhashchie karbonovye kisloty s ehfirnymi gruppirovkami. / CH.G. Fritz, E.F. Moore. –Publ. 10.05.66. –RZh Khimiya, 1967, 17N84.

259. Patent US 3242218. Sposob polucheniya ftoruglerodnyh poliehfirov. / V.Miller. –Publ. 22.03.66. –RZh Khimiya, 1967, 12S232.

260. Patent DE 78376. Sposob polimerizacii i sopolimerizacii okisi geksaftorpropilena v prisutstvii geksaftorpropilena. / G. Lothar. –Publ. 12.12.70. –RZh Khimiya, 1971, 21S361.

261. Patent US 3125599. Polimery okisej ftoruglerodnyh soedinenij. / D. Vornell. –Publ. 17.03.64. –RZh Khimiya, 1965, 15S277.

262. Patent US 3291843. Fluorinated vinilethers. / Fritz C.G., Selman S., -Publ. 13.12.66.C.A. 1967, 66, 37427 h.

263. Patent US 4377717. Sposob polucheniya perftor-2-metilpentena-2. / L.Anello, R. Sweeny. –Publ. 22.03.83. –RZh Khimiya, 1983, 24N1311.

264. Knunyats I.L., Fokin A.V., Cheburkov Y.A. Chetvertyi mezhdunarodnyj simpozium po himii ftora v Istes-Park (Kolorado, USA) –ZHVHO im. D.I.Mendeleeva, t. 13, № 3, p. 311-321.

265. Patent US 3449389. Pervichnye ftorzameshchennye alkogolyaty. / D. Vornell. –Publ. 10.06.69. –RZh Khimiya, 1970, 18N39.

266. Patent US 3322826. Polimerizaciya geksaftorpropilenehpoksida./ E.F.Moore –Publ. 0.06.67. –RZh Khimiya, 1968, 18S 296.

267. Patent JP 57-45132. Poluchenie perftor-2-metil-3-oksageksanoilftorida. / Y. Masaki, M. Sehjdzi. –Publ. 13.03.82. –RZh Khimiya, 1983, 5N70.

268. Patent US 3274293. Ftorsoderzhashchie prostye ehfiry. / S.Stanley. –Publ. 20.09.66. –RZh Khimiya, 1968, 5N161.

269. Patent DE 2756919. Sposob demerizacii okisi geksaftorpropilena. / G. Kuhne, F. Geller. –Publ. 05.07.79. –RZh Khimiya, 1980, 14N22.

270. Patent DE 2924385. Sposob dimerizacii okisi geksaftorpropilena. / G. Kuhne. –Publ. 07.08.80. –RZh Khimiya, 1981, 23N36.

271. Kinle H., Bader E. Aktivnye ugli i ih promyshlennoe primenenie. –L., Khimiya, 1984, p. 185-192.

272. Patent US 3321515. Sposob polucheniya ftorirovannyh karbonil'nyh soedinenij. / F.Moore, S.Milyan. –Publ. 23.05.67.-RZh Khimiya, 1968, 15N48.

273. Bekker R.A., Asratyan G.V., Dyatkin B.L. O roli prostranstvennyh faktorov v reakciyah poliftorirovannyhα-okisej s aminami. –ZhOrKh, 1973, t. 9, v. 8, p. 1644-1648.

274. Knunyants I.L., Shokina V.V., Tuleneva, V.V., Ceburkov Y.A., Aronov Y.E. Proizvodnye perftorizomaslyanoj kisloty. –Izv. AN SSSR, ser. khim., 1966, № 10, p. 1831-1833.

275. Sianesi D., Passety A., Tarli F., The Chemistry of hexafluoropropene epoxide. –J. Org. Chem., 1966,v. 31, № 7,p. 2312-2316.

276. Borovnev L.M., Golubev A.N., Zaharov V.Y. i dr. Iniciirovanie processa sopolimerizacii tetraftorehtilena i geksaftorpropilena perftorirovannymi diacil'nymi perekisyami, sintezirovannymi na osnove okisi geksaftorpropilena. –Otchet predpriyatiya p/ya A-1619, 1985, inv. № 1154, 28p.

277. Ashmor. Kataliz i iniciirovanie himicheskih reakcij. M.: Mir, 1966, p. 62.

278. Patent US 3213134. Deciklizaciya ftorirovannyh ciklicheskih efirov. / D. Morin. –Publ. 19.10.65. –RZh Khimiya, 1967, 9N60.

279. Patent US 4302608. Sposob izomerizacii okisi geksaftorpropilena do geksaftoracetona. / E.Skuri, D. Milz. –Publ. 24.11.81. –RZh Khimiya, 1982, 20N56.

280. Patent JP 58-62131. Poluchenie geksaftoracetona. / O. Josio, A. Josimasa, M. Makisuke. –Publ. 13.04.83. –RZh Khimiya, 1984, 12N30.

281. Patent JP 58-62130. Poluchenie geksaftoracetona. / A. Josimasa, M. Makisuke, S. Yukio. –Publ. 13.04.83. –RZh Khimiya, 1984, 12N29.

282. Patent SU 740741. Sposob polucheniya geksaftoracetona. / Y.M. Vilenchik, G.I. Yakurnova, G.I. Lekomceva, L.P. Zayakina, A.P. Harchenko. –Publ. 15.06.80. –RZh Khimiya, 1980, 24N67.

283. Patent US 859348. Sposob polucheniya geksaftoracetona. / Y.M. Vilenchik, G.I. Yakurnova. –Publ. v B.I., 1981, № 32, RZh Khimiya, 1982, 21N12.

284. Patent US 4238416. Sposob izomerizacii ftorirovannyh soedinenij. / D. Koduo. –Publ. 09.12.80. –RZh Khimiya, 1981, 17N65.

285. Kiperman S.L. Vvedenie v kinetiku geterogennyh kataliticheskih reakcij. M.: Nauka, 1964, p. 401.

286. Tyul'ga G.M., Gubanov V.A., Popova I.S., Petruhno L.A., Bolhovec B.M., Troichanskaya P.E., Dolgopol'skij I.M. Izuchenie reakcii ftorangidridov perftorkarbonovyh kislot s ftoridami shchelochnyh metallov. –ZhOrKh, 1973, t. 14, v. 11, p. 2339-2346.

287. Konshin A.I., Gubanov V.A. Ob ocenke ehffektivnosti sposoba ochistki hladonovyh rastvorov perftorpolioksametilenacetilftoridov. –Otchet predpriyatiya p/ya V-8415.

288. Patent SU 188404. Ftorsopolimer vinilidenftorida s 3,6,8,10,12-pentaoksaperftortridecenom dlya termomorozoagressivostojkih izdelij. / Grejs A.M., Ershov A.E., Zaharov V.Y. i dr.

289. Karcov S.V., Valov P.I., Sokolov L.F., Sokolov S.V. Rol' poverhnosti reakcionnogo sosuda v processe zhidkofaznogo okisleniya geksaftorpropilena. –Izv. AN SSSR, ser. khim., 1978, № 10. p. 2268-2272.

290. Patent SU 229185. Sposob polucheniya perftorpolioksametilenacetilftoridov. / Zaharov V.Y., Gol'dinov A.L., Borovnev L.M. i dr.

291. Borovnev L.M., Golubev A.N., Zaharov V.Y. i dr. Dinamika izmeneniya sostava gazovoj i zhidkoj faz v promyshlennom reaktore sinteza okisi geksaftorpropilena v hode operacii okisleniya. –Otchet predpriyatiya p/ya A-1619, 1983, inv. № 1089, 10p.

292. Borovnev L.M., Golubev A.N., Zaharov V.Y. i dr. Dinamika obrazovaniya perftorpolioksametilen acetilftoridov v processe zhidkofaznogo okisleniya geksaftorpropilena kislorodom na promyshlennoj ustanovke. –Otchet predpriyatiya p/ya A-1619, 1985, inv. № 1165, 22p.

293. Gol'dinov A.L., Borovnev L.M., Zaharov V.Y. i dr. Okislenie geksaftorpropilena molekulyarnym kislorodom v prisutstvii 1,2-dibromtetraftorehtana (hladona-114V2). Poluchenie okisi geksaftorpropilena. –Otchet predpriyatiya p/ya A-1619, 1982, inv. № 1072, 57p.

294. Patent SU 1128436. Plamyagasyashchaya smes'. / Borovnev L.M., Gusenkov M.V., Zhukova V.A. i dr.

295. Kravchenko N.N., Popov V.A., Ershov Y.A., Pomeranceva E.G. Nekotorye osobennosti fotoliza perftorirovannyh poliehfirov. –VMS, t. 23, № 3, 1981, p. 180-183.

296. Patent SU 3011822. Sposob regeneracii hladona-113. / Panitkova E.S., Berenblit V.V., Senyushov A.N. i dr.

297. Zejfman Y.V., Ter-Gabrielyan E.G., Ganbaryan N.P., Knunyantc I.L. Himiya perftorizobutilena. –Uspekhi khimii, 1984, t. 53, v. 3, p. 431-461.

298. Knunyantc I.L., Shokina V.V., Kuleshova A.D. Prisoedinenie galoidvodorodov k ftorolefinam. –Izv. AN SSSR, ser. khim., 1960, № 9, p.1693-1695.

299. Postovoi S.A., Mysov E.I., Zeifman Y.V., Knunyantc I.L. Nukleofil'naya kondensaciya oktaftorizobutilena s tetraftorehtilenom. –Izv. AN SSSR, ser. khim., 1982, № 7, p. 1586-1590.

300. Patent US 3389187. Dimer perftorizobutilena. / D.L. Miller. –Publ. 18.06.68. –RZh Khimiya, 1969, 17N3211.

301. Knunyantc I.L., German L.S., Dyatkin B.P. Reakcii ftorolefinov. SoobshchenieII. Vzaimodejstvie soedinenij ryada perftorizobutilena s aminami i ammiakom. –Izv. AN SSSR, otd.him.n., 1960, № 2, p. 221-230.

302. Patent JP 53-73504. Udalenie oktaftorizobutilena. / Kuroda Takehsi, Furukava Josiki, Macuoha Nu. –Publ. 30.06.78. RZh Khimiya, 1979, 10N2011.

303. Dorogimskij V.A., Kolomiec A.F., Sokol'skij G.A. O reakcii oktaftorizobutilena s ehtilenglikolem i glicerinom. –ZhOrKh, 1983, t.19, v. 8, p.1762-1763.

304. Patent US 129653. Sposob polucheniya geksaftorizomaslyanoj kisloty. / Knunyantc I.L., Cheburkov Y.A., Krasuskaya M.P. –RZh Khimiya, 1961, 9L75.

305. Borovnev L.M., Golubev A.N., Zaharov V.Y. i dr. Promyshlennye ispytaniya i vnedrenie sposoba ochistki gazov piroliza tetraftorehtilena ot perftorizobutilena. –Otchet predpriyatiya p/ya A-1619, 1981, inv. № 1048, 34p.

306. Gol'dinov A.L., Borovnev L.M., Zaharov V.Y. i dr. Uvelichenie stepeni ispol'zovaniya syr'ya v proizvodstve geksaftorpropilena putem bolee polnogo izvlecheniya oktaftorciklobutana iz kubovoj frakcii. –Otchet predpriyatiya p/ya A-1619, 1982, inv. № 1063, 16p.

307. Patent SU 180854. Sposob polucheniya geksaftorpropilena. / Borovnev L.M., Vinogradova A.P., Golubev A.N. i dr.

308. Borovnev L.M., Golubev A.N., Zaharov V.Y. i dr. Kompleksnaya pererabotka kubovoj frakcii proizvodstva tetraftorehtilena. –Otchet predpriyatiya p/ya A-1619, 1985, inv. № 15/107 DSP, 17p.

309. Patent SU 1336492. Sposob polucheniya 2-hlortetraftorehtilftorsul'fata. / Fokin A.V., Rapkin A.I., Tatarinov A.S. i dr.

310. Patent SU 1184808. Sposob polucheniya monoftorsul'fata broma. / Fokin A.V., Studnev Y.N., Rapkin A.I. i dr.

311. Patent SU 1239092. Sposob polucheniya tris(ftorsul'fata) broma. / Fokin A.V., Studnev Y.N., Rapkin A.I. i dr.

312. Patent SU 3982041. 3-(Poliftorpropionamido) propil-2-oksiehtildimetilammonij hloridy, obladayushchie gipotenzivnym dejstviem. / Fokin A.V., Kovalev G.V., Mazanov L.S. i dr.

313. Patent SU 3982040. N-Poliftoracil'nye proizvodnyeγ-amnomaslyanoj kisloty,

obladayushchie gipertenzivnym dejstviem. / Fokin A.V., Kovalev G.V., Muhina N.V. i dr. Pol. resh. ot 26.09.86.

314. Patent SU 1334655. 3-(ω-Hlorperftoralkanoilamido)propil-dimetil-2-oksiehtilammmonij hloridy v kachestve poverhnostno-aktivnyh veshchestv. /Fokin A.V., Rapkin A.I., Studnev Y.N. i dr.

315. Patent SU 196359. Sposob polucheniyaω-hlorperftorkarbonovyh kislot i ehmul'gator. / Fokin A.V., Studnev Y.N., Rapkin A.I. i dr.

316. Patent DE 3034549. Sposob polucheniya perftorirovannyh ftorangidridov karbonovyh kislot. / Verner S. –Publ. 29.04.82, –RZh Khimiya, 1983, 17N5711.

317. Promyshlennye katalizatory i nositeli. Spravochnik. –Novosibirsk, 1972, p. 246.

318. T. Van der Plas. Tekstura i himiya poverhnosti uglerodnyh tel. V kn.: Stroenie i svojstva adsorbentov i katalizatorov. –M.: Mir, 1973, p. 436-441.

319. Patrik S. Uspekhi khimii ftora. –M., L., Khimiya, 1964, t.1, № 2, p. 336-379

Recommended for publication by prof. S. M. Igoumnov