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Selective hydrogenolysis of CCl_2F_2 into CH_2F_2 over palladium on activated carbon

Kinetic mechanism and process design

J.A. Moulijn, M. Makkee*, A. Wiersma, E.J.A.X. van de Sandt

Department of Chemical Process Technology, Section Industrial Catalysis, Delft University of Technology,
Julianalaan 136, 2628 BL Delft, Netherlands

Abstract

A process-development study is presented aiming at the conversion of CCl_2F_2 into CH_2F_2. The CCl_2F_2 is an undesired compound because of its negative impact on the environment. Palladium on activated carbon is the most appropriate catalyst for this selective hydrogenolysis. During reaction, palladium is present as the carbide ($PdC_{0.15}$). Except for rhenium, all other noble metals show activity but with quite varying selectivities. The kinetic scheme is elucidated and appears to be based on parallel kinetics; one route leads to either $CHClF_2$ or CH_2F_2 and the other to methane. The selectivity for $CHClF_2$ or CH_2F_2 depends on the amount of adsorbed chlorine on the catalytic active surface. The readsorption of the products will not occur. Provided if excess hydrogen is present, the catalyst is sufficiently stable for a commercial process. A conceptual process design is presented. It can be concluded that the process is technically and economically feasible. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: CCl_2F_2; CH_2F_2; Kinetic mechanism; Process design; Hydrogenolysis; Palladium; Activated carbon

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1. Introduction

It is generally accepted that chlorine containing hydrocarbons exhibit unfavourable properties with respect to their environmental impact. This also applies to chlorofluorocarbons (CFCs), which have been used extensively because of their high stability, low toxicity, and favourable price. However, they contribute significantly to the greenhouse effect and ozone depletion. About 95% of the ozone depleting substances are CFCs [1–4]. As a result of this, their production and uses are prohibited and they have to be considered as waste material. A special feature of the CFC waste is that it is rather well defined, nearly pure compounds are in use. For instance in refrigeration, nearly 50% of the CFCs are used, and the major compounds are CCl_3F (CFC-11) and CCl_2F_2 (CFC-12). In fact, these two compounds constitute over 80% of the ozone depleting substances. When a good recovery system would be operative, rather pure streams would be available.

Therefore, a destruction technique such as combustion, in principle, is not a good solution because valuable materials are wasted. More challenging is the conversion of this relatively pure waste material into a valuable product. In that respect, hydrodechlorination might be an option. The simplest would be complete hydrogenolysis:

$$CCl_2F_2 + 4H_2 \rightarrow CH_4 + 2HCl + 2HF$$

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* Corresponding author. Tel.: +31-15-278-1391;
fax: +31-15-278-4452.
E-mail address: m.makkee@tnw.tudelft.nl (M. Makkee)

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Table 1
ODP and GWP of the compounds involved in the process

Compound	Trival name	ODP	GWP
CCl_2F_2	CFC-12	1.0	8500
$CHClF_2$	HCFC-22	0.055	1700
CH_2F_2	HFC-32	0	650

An obvious limitation of such a process is that one the products formed has only fuel value. A more attractive process would be a selective hydrogenolysis:

$$CCl_2F_2 + 2H_2 \rightarrow CF_2H_2 + 2HCl$$

In this case, all products are valuable. CF_2H_2 can be used in refrigeration applications. In fact, it has quite favourable environmental properties: its ozone depletion potential (ODP) is zero and its contribution as greenhouse gas is small, although not completely negligible. The key data are given in Table 1.

The ODP of CF_2H_2 is zero because, it does not contain Cl. The global warming potential (GWP) is among the lowest of the HFCs (Cl-free fluorinated hydrocarbons). So, it is concluded that it constitutes one of the best short-time replacers of CFCs in those applications, where no good alternatives exist. This applies to any case of the refrigerants sector.

The objective of the present study is the development of a conceptual process for the selective conversion of CCl_2F_2 into CH_2F_2.

2. Experimental

2.1. Materials

Sodium hydroxide pellets (>98.5% purity) and 36–38% aqueous hydrochloric acid (Baker grade) were supplied by Baker. CCl_2F_2, $CHClF_2$, and CH_2F_2 were supplied by Uniechemie (Arcton 12, Arcton 22 and Klea 32, respectively, ∼98% purity). Hydrogen, supplied by Air Products (99.95% purity) was used as received. Rhenium chloride, ruthenium chloride, palladium chloride, platinum chloride, iridium chloride, and rhodium chloride (5 mm, BET=1060 m^2/g) were a gift from NORIT N.V. Palladium black, rhodium black, iridium black, and platinum black were a gift from Johnson Matthey Plc. (98.42, 94.09, 94.84, and 97.47% purity, respectively). Ruthenium black, prepared according to the procedure as described by Soede [5], was used (∼90% purity).

2.2. Catalyst preparation

A series of activated carbon supported noble metal catalysts, with different metal loading were prepared. The metals used were ruthenium, rhenium, rhodium, platinum, palladium, and iridium. Fifty grams of activated carbon support was sequentially treated with 5 l 0.5 M aqueous sodium hydroxide, 5 l water, 5 l 0.5 M aqueous hydrochloric acid, and 5 l water in a flow reactor prior to introduction of the metal at a flow rate of approximately 0.28 ml/s. The purified activated carbon support was dried overnight at 373 K. The metals were introduced by incipient wetness impregnation of the activated carbon extrudates with a metal chloride dissolved in aqueous hydrochloric acid. The acid concentration was chosen to give a chlorine to metal ratio of 10 mol/mol. The acid was needed to dissolve the metal chloride. Catalysts were dried overnight at 373 K and subsequently treated with nitrogen to 623 K with a heating rate of 0.033 K/s and kept constant for 1 h. The catalysts were reduced in situ under hydrogen flow from ambient temperature up to the reaction temperature.

2.3. Catalyst performance testing

Reaction conditions such as temperature, pressure, and hydrogen to CCl_2F_2 feed ratio can be automatically varied during a catalytic test. In the experimental sequence used, only the temperature of the reactor and the feed composition were varied. Table 2 shows the experiment sequence used for the catalyst screening experiments. All catalysts were tested in the same experimental sequence and in one run of the multi-microflow-reactor set-up. Therefore, both the performance and modification of the catalysts can be easily compared.

3. Results and discussion

3.1. Selection and development of a satisfactory catalyst

It was anticipated that a supported noble metal catalyst would give the best performance. As support

Table 2
Experiment sequence[a]

Experiment No.	Duration (h)	Temperature (K)	H_2/CCl_2F_2 (mol/mol)
1	7	450	3
2	3	500	3
3	5	500	1.5
4	4	500	6
5	5	500	3
6	5	540	3
7	5	540	6
8	4	540	1.5
9	4	540	3
10	7	500	3
11	8	450	3
12	4	450	6
13	5	450	1.5
14	34	450	3
15	28	500	3

[a] Other conditions: WHSV=1 g/g h, P=0.4 MPa.

material, activated carbon, silica and alumina were considered. Among these three, carbon is expected to be most stable under the corrosive reaction conditions: silica might well be volatilized because of the presence of F, while alumina will be converted into fluorinated and chlorinated alumina or even into bulk AlF_3 and $AlCl_3$ or mixed compounds thereof.

Except rhenium, which did not show any activity, all noble metals were active. The major products were $CHClF_2$, CH_2F_2, and methane. The results are given in Fig. 1. All catalyse hydrodechlorination reactions, but the selectivities are very different. Some give mainly the desired molecule CH_2F_2, while others lead to the partially dechlorinated product $CHClF_2$ [6]. Both the initial activity and the activity after 100 h on stream are given. It is clear that apart from some deactivation, the difference between the two sets of data is modest. Palladium is by far the best for the desired reaction. The sequence in catalytic activity with respect to the formation of CH_2F_2 is

$$\mathrm{Pd} > \mathrm{Pt} > \mathrm{Rh} > \mathrm{Ir} > \mathrm{Ru}$$

It is remarkable that ruthenium is very selective for the undesired $CHClF_2$. So, when this product would have been the desired product, Ru/C has to be selected for further catalyst development. In the present case, it can be concluded that Pd/C is the catalyst of choice. Details on the activated carbon selected are given elsewhere [7]. It appeared that purified NORIT activated carbon was a good support.

3.2. Kinetic mechanism palladium-catalysed selective dehydrochlorination

It might have been expected that the hydrogenolysis would occur according to a serial kinetic network. In Fig. 2 the possible reactants, intermediates and products involved are shown in a triangle. This triangle contains all possible combinations of C, H, Cl, F with the restriction that it is limited to the C_1 group. The arrows represent the Cl/F exchange, the hydrodefluorination, and the hydrodechlorination reactions. The direction of the arrows denote the thermodynamic

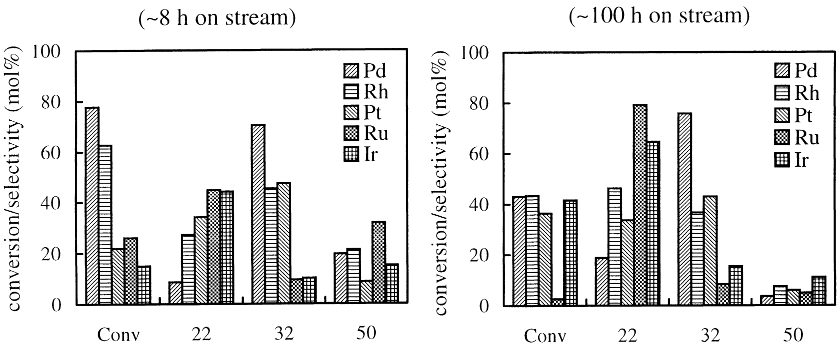

Fig. 1. The initial (~8 h on stream) and final (~100 h on stream) performance of the different catalysts during the experimental sequence (conditions: T=500 K, P=0.4 MPa, WHSV=1 g/g h, and H_2/CCl_2F_2=3; abbreviations — Conv: CCl_2F_2 conversion, 22: selectivity for $CHClF_2$, 32: selectivity for CH_2F_2, and 50: selectivity for CH_4).

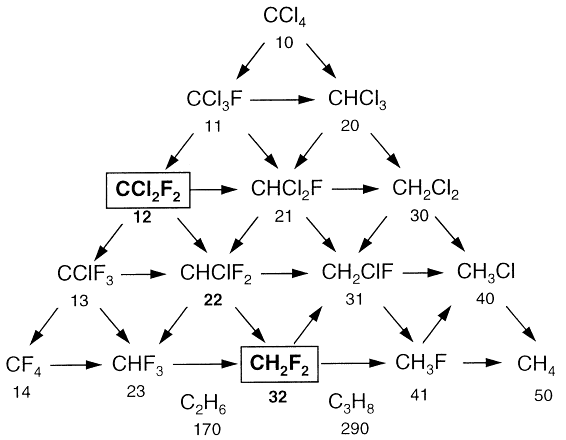

Fig. 2. Thermodynamic relation between chlorinated and fluorinated methanes at 298 K and atmospheric pressure. The direction of the arrows indicates the thermodynamic stability.

driving force. CH_4 is the most stable compound. In agreement with this scheme, under hydrogenation conditions, a serial network of the following type might be anticipated:

$$CCl_2F_2 \rightarrow CHClF_2 \rightarrow CH_2F_2 \rightarrow CH_3F \rightarrow CH_4$$

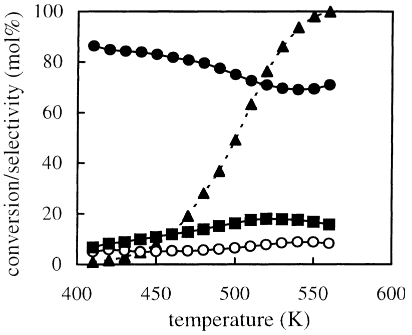

Fig. 3. Conversion (▲) and selectivity in the hydrogenolysis of CCl_2F_2 over 1 wt.% Pd/C as a function of temperature for CH_2F_2 (●), $CHClF_2$ (■), and CH_4 (○). Conditions: WHSV=1 g/g h, $H_2/CCl_2F_2=3$, $P=0.3$ MPa.

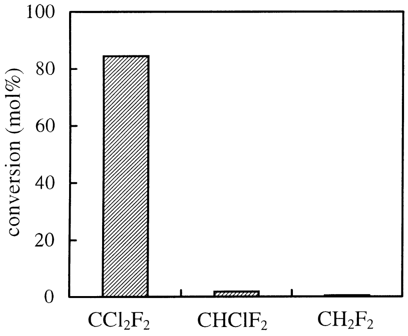

Fig. 4. Comparison of the reactivity of CCl_2F_2, $CHClF_2$, and CH_2F_2 in the catalytic hydrogenolysis over 2 wt.% Pd/C. Conditions: $T=510$ K, $H_2/CFC=3$, $P=0.3$ MPa, feed=8.3 mmol/g h.

It is, however, very clear that this scheme is incorrect. This can be concluded from simple measurements at different conversions while only one parameter is varied. A good example is given in Fig. 3 which shows the performance of the catalyst as a function of the temperature at otherwise constant conditions. The conversion initially increases exponentially with the temperature in accordance with normal Arrhenius behaviour. At higher temperature, a saturation is observed, obviously due to the fact that the reactant concentration decreases. This behaviour is what one would expect from kinetics with a positive order in the reactant and Arrhenius behaviour of the rate constant. However, it is striking that the selectivity is rather constant for all the three compounds, viz., CH_2F_2, $CHClF_2$, and methane. This proves immediately that the scheme of serial kinetics is incorrect. As the conversion is changed over orders of magnitude for serial kinetics, the selectivity also should change profoundly. By comparing the reactivity of the major molecules involved, a direct proof can be obtained. Fig. 4 shows that the reactivities are dramatically different. They decrease in the order

$$CCl_2F_2 \gg CHClF_2 \gg CH_2F_2$$

Clearly, the rule is that the number of Cl atoms is the determining factor: the more Cl, the higher the reactivity. This is in accordance with thermodynamic data. Table 3 shows the relative reactivity measured for relevant compounds of the triangle in relation to the dissociation energy. It is remarkable how well the experimental results correlate with the thermodynamic data for all compounds that were investigated. Apparently, on palladium surfaces the species have a stability related to that of bulk radicals. For the formulation of a kinetic mechanism the major surface species have to be known. From the product distribution, it was tentatively concluded that Cl and F are not major adsorbed species. To check for the impor-

Table 3
Dissociation energy of some halomethanes [8]

Component	Dissociation energy at 298 K (kJ/mol)		Relative reactivity[a]
	C–Cl	C–F	
CCl_4	305		1.0
$CHCl_3$	325		0.009
CH_2Cl_2	339		0.007
CH_3Cl	347		0.005
CCl_2F_2	318	460	1.0
$CHClF_2$	367	n.d.[b]	0.02
CH_2F_2		500	0.005
CH_3F		453	n.d.

[a] Reactivities of $CHCl_3$, CH_2Cl_2, and CH_3Cl with respect to CCl_4; reactivities of $CHClF_2$ and CH_2F_2 with respect to CCl_2F_2.
[b] Not determined.

tance of chlorine, HCl was added during the reaction. Table 4 shows that HCl, indeed, has a large influence. In the presence of HCl, large amounts of $CHClF_2$ are formed. This confirms that Cl should be included as surface species. It should also be noted that the yield of methane is not effected. Therefore, we can conclude that methane is formed by a separate kinetic pathway.

This leads us to the simplified reaction pathway given in Fig. 5. CCl_2F_2 is dissociatively adsorbed at the Pd surface. Either a C–Cl (route 1) or a C–F bond (route 2) breaks. The chance for such a breakage is not statistical. In agreement with thermodynamics, route 1 dominates. It is concluded that the main reaction, route 1, leads via C–Cl bond breaking to the $CClF_2$ radical, that subsequently breaks down to the highly stable CF_2 radical. The major evidence for this is the product distribution observed. Thermodynamic data are again in agreement with this mechanism, as can be seen from Table 5, which lists the enthalpy of

Table 4
Influence of HCl on catalyst performance[a]

Gas	Conversion, CCl_2F_2	Selectivities		
		CH_2F_2	$CHClF_2$	CH_4
H_2	37.3	69.7	21.5	6.9
HCl/H_2	13.5	47.9	42.7	7.2
He/H_2	25.5	78.6	12.5	6.9

[a] Conditions: T=510 K, H_2/CCl_2F_2=3, WHSV=1 g/g h, P=0.2 MPa, HCl/H_2=1 or He/H_2=1 (all values in mol%).

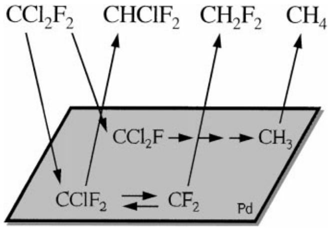

Fig. 5. Simplified reaction mechanism for the selective hydrogenolysis of CCl_2F_2.

Table 5
Enthalpy of formation, entropy, and Gibbs energy of possible intermediates [8]

Compound	ΔH_f^0 (kJ/mol)	S^0 (J/mol K)	ΔG^0 (kJ/mol)
CF_3	−470	265	−549
$CClF_2$	−275	287	−361
CHF_2	−254	259	−331
CCl_2F	−105	299	−194
CH_2F	−32	237	−103
$CHCl_2$	74	278	−9
CCl_3	79	297	−9
CH_2Cl	117	243	44
CH_3	146	194	88
CF_2	−182	241	−254
CClF	26	259	−51
CHF	105	235	35
CCl_2	238	265	159
CHCl	308	235	238
CH_2	386	194	329
CF	255	213	192
CCl	502	224	435
CH	594	183	540
F	79	159	32
Cl	121	165	72
H	218	115	184
C	717	158	670

formation and the entropy and Gibbs free energy of formation for the possible reaction intermediates [8]. It is clear that the intermediates proposed, viz. $CClF_2$ and CF_2 are the most stable ones in the families considered. Both radicals can desorb via reaction with adsorbed H. This might be referred to as 'associative' desorption. The other route, breaking of the C–F bond, does not lead to relatively stable intermediates and it is tentatively concluded that methane, the most stable compound, is formed without the occurrence of intermediate products. The scheme presented here is further supported by the observation that minor amounts of other by-products are formed that support a carbene mechanism. For instance, small amounts of ethane, CH_3F, CH_3Cl, CH_2ClF, and CH_2Cl_2 are found. A detailed study on the reaction mechanism is given elsewhere [8].

The question arises whether the same mechanism applies to all noble metals. Fig. 1 shows large differences between the various noble metals suggesting different kinetic pathways. To check this, a systematic series of experiments was performed at varying H_2/CCl_2F_2 ratio. The results are given in Figs. 6 and 7. It is clear that qualitatively for all noble metals, the behaviour is analogous. The higher the hydrogen partial pressure, the higher the selectivity to CH_2F_2 at the expense of the selectivity to $CHClF_2$. It is concluded that the CF_2-carbene intermediate is the most important reaction intermediate and that the amount of chlorine adsorbed on the catalyst surface governs the selectivities for $CHClF_2$ and CH_2F_2. The differences in behaviour of the noble metals in this respect should be due to differences in Cl-content of the surface. The amount of chlorine present is related to the ease of chlorine removal by means of hydrogen from the catalyst surface. The ease of chlorine removal can be estimated from the TPR profiles and literature data. Newkirk and McKee [9] investigated the decomposition temperatures of several metal chlorides and found, see Table 6, the following order in stability:

$$Ru > Ir > Rh > Pd$$

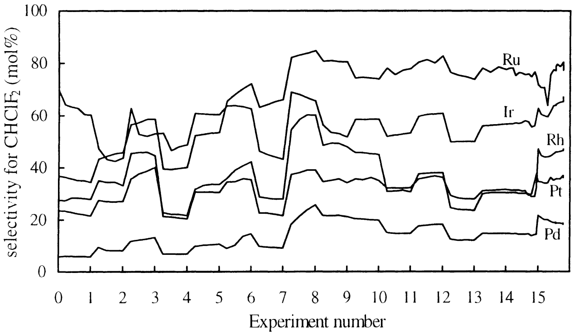

Fig. 6. Selectivity for $CHClF_2$ as a function of experiment number.

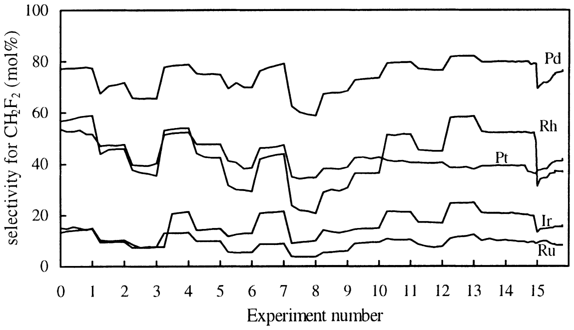

Fig. 7. Selectivity for CH_2F_2 as a function of experiment number.

The same order was found in TPR experiments. So, the removal of chlorine from the surfaces of iridium and ruthenium requires the highest temperatures. These catalysts indeed show a relatively high selectivity for $CHClF_2$. The removal of chlorine from the palladium catalyst on the other hand requires the lowest temperature and as a consequence the highest selectivity is found for CH_2F_2.

The results are in good agreement with the theory of metal–X bond strengths based on the position of the metal in the periodic system. Iridium, ruthenium, and rhodium can all be expected to have a higher metal–chlorine bond strength than palladium [10]. Furthermore, ruthenium can be expected to have the highest metal–chlorine bond strength. In summary, all noble metals operate according to the same kinetic

Table 6
Bulk metalchloride decomposition temperatures in hydrogen [6]

Chloride	Decomposition temperature (K)
$PdCl_2$	300
$PtCl_2$	n.m.
$RhCl_3$	378
$IrCl_3$	463
$RuCl_3$	623

Table 7
Catalyst performance and deactivation after 700 h[a]

H_2/CCl_2F_2	Conversion, CCl_2F_2 (mol%)	Selectivities (mol%)			Deactivation (%)
		CH_2F_2	$CHClF_2$	CH_4	
1.5	50	53	37	7	17
2.2	60	67	24	7	14
3	67	75	16	7	11
6	79	85	7	6	5
10	88	88	4	6	3

[a] Deactivation is given as percentage of initial activity. Conditions: P=0.2 MPa, WHSV=0.5 g/g h, and T=510 K.

network and the differences are only qualitative, in particular the occupancy of Cl differs.

3.3. Optimisation of process conditions and catalyst stability

The conditions to be chosen are the residence time, the pressure, the H_2/CCl_2F_2 ratio and the temperature. For convenience, a high pressure is less attractive. It was decided to limit ourselves in the first instance to a moderately low pressure up to 0.3 MPa. The H_2/CCl_2F_2 ratio was varied over nearly an order of magnitude. Table 7 gives typical results. It is clear that a large excess of hydrogen is very favourable with respect to both activity and selectivity. It was decided that the ratio H_2/CCl_2F_2=12 is a good choice. As important, is, of course, the optimal temperature. Figs. 8 and 9, respectively, give the results of a practical stability test at two different temperatures, i.e. 540/525 and 510 K. At 540 K (Fig. 8), the conversion drops form 80 to 60% over a period of 400 h. Simultaneously, the selectivity to methane increases slightly. At 525 K (Fig. 8), the stability is much better. Over a period of 600 h, the conversion hardly decreases (from 60 to 55%). The selectivity to the desired and the by-products is remarkably constant. The selectivity to the desired product is nearly 90% over the whole period at a temperature of 510 K at a high hydrogen to CFC ratio (Fig. 9). Clearly, the stability is high enough for a practical process. Nevertheless, it was tried to elucidate the deactivation mechanism and at the same time to learn more about the catalyst system under reaction conditions. In particular, a point of concern is the high exothermicity of the process; a significant temperature gradient under practical conditions is unavoidable, in particular during start-up. Therefore, it was considered that a good insight in deactivation is very valuable.

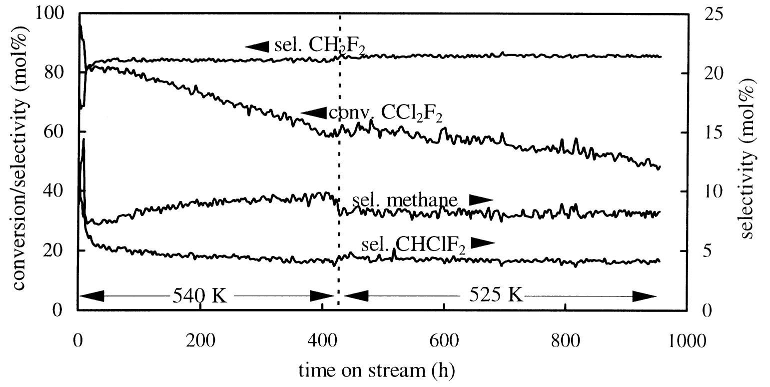

Fig. 8. Catalyst performance at 540 and 525 K (conditions — before 420 h: H_2/CCl_2F_2=12, P=0.2 MPa, T=540 K, WHSV=1.4 g/g h; after 420 h: H_2/CCl_2F_2=12, P=0.2 MPa, T=525 K, WHSV=0.7 g/g h).

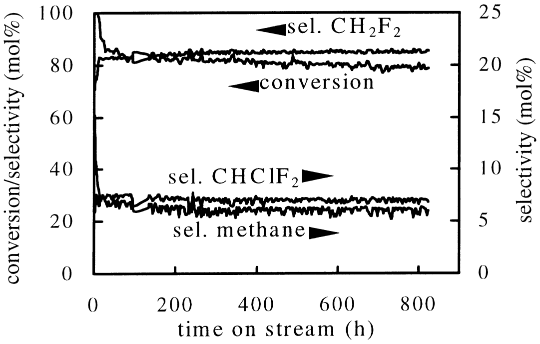

Fig. 9. Catalyst performance at 510 K and H_2/CCl_2F_2 feed ratio of 6 mol/mol (conditions: P=0.2 MPa and WHSV=0.5 g/g h).

Obvious causes of deactivation might be sintering and deposition of poisoning compounds. A TEM study was performed of the fresh catalysts and catalysts after use in the reactor. It was clear that the catalyst are of the egg-shell type [6]. It is striking that during reaction the particle size decreases rather than increases. This effect is stronger and higher with the excess of hydrogen [6]. So, loss of dispersion does not occur and cannot be the cause of deactivation. Another reason might be a change in structure of the active phase. It is well known that palladium can form hydrides and carbides and it was investigated if that could be the case. From an XRD and TPR/TPO study of model catalysts (palladium black) and a 'real' catalyst (although with a higher loading, 2 wt.%), it was concluded that during reaction Pd is present as the carbide, i.e. $PdC_{0.15}$ [11]. However, the formation of a carbide cannot be the cause of the deactivation because the timescales of deactivation and carbide formation are quite different: carbide formation takes place on a scale of minutes, whereas the deactivation takes place at a scale of several hundred hours, which leaves deposition of poisoning material as the main cause for deactivation. In a TPR study described elsewhere it is shown that this might well be the cause. It was found that carbonaceous material, probably polychlorinated large hydrocarbons, are present and that the amounts correlated with the excess of hydrogen; the more hydrogen available the less amounts of carbonaceous material present [6]. So, it is tentatively concluded that the deactivation is caused by the deposition of polychlorinated hydrocarbons on the active phase.

3.4. Process design

A process design was made based on the catalyst found and the optimal conditions set. Moreover, the kinetic mechanism was verified experimentally and explicit equations were formulated, validated and the parameters estimated. Details are given elsewhere (to be published). The model was experimentally tested in a pilot reactor. It was decided to recycle the excess hydrogen and the unconverted feed to avoid the build-up of the other compounds produced.

The schematic diagram is given in Fig. 10. The feed is purified in order to remove oil, water and $CClF_2$–CF_3. The $CHClF_2$ present in the recycle is distilled off and sent to an incinerator, because it is not converted in the reactor and would build-up in the recycle stream. The purge stream is also sent to an incinerator. The reactor section consists of two identical multi-tube reactors in series. Each reactor consists of 6627 parallel tubes, which are cooled by means of boiling water. The dimensions of the tubes are a length of 3.05 m and an inner diameter of 19.3 mm. Length and diameter of the total reactor are 4.1 and 2.8 m, respectively. The temperature in both reactor is controlled within 450 and 510 K. An adiabatic temperature rise of over 600 K was calculated if no effective cooling in the reactor design was applied.

HCl and HF are separated from the product stream, producing saleable products, viz., a 61% hydrofluroboric acid solution and a 30 wt.% HCl solution. The removal of the acids immediately after the reactor section has several advantages. Corrosion of the equipment is minimised, the operation is safer, and possible azeotropes of HF or HCl with CFCs is avoided.

In a vapour–liquid separator, H_2 and methane are separated and recycled to the reactor section. Methane concentration is kept limited by applying a purge stream because in the stability studies it was found that methane gives rise to some catalyst deactivation. Purification of the product stream takes place by distillation.

An economic evaluation was made by comparing the process developed with existing processes. It was concluded that the process is much more economical than existing combustion and hydropyrolysis processes. When the value of the product is included in the evaluation, the process is the only one with a positive profit [12].

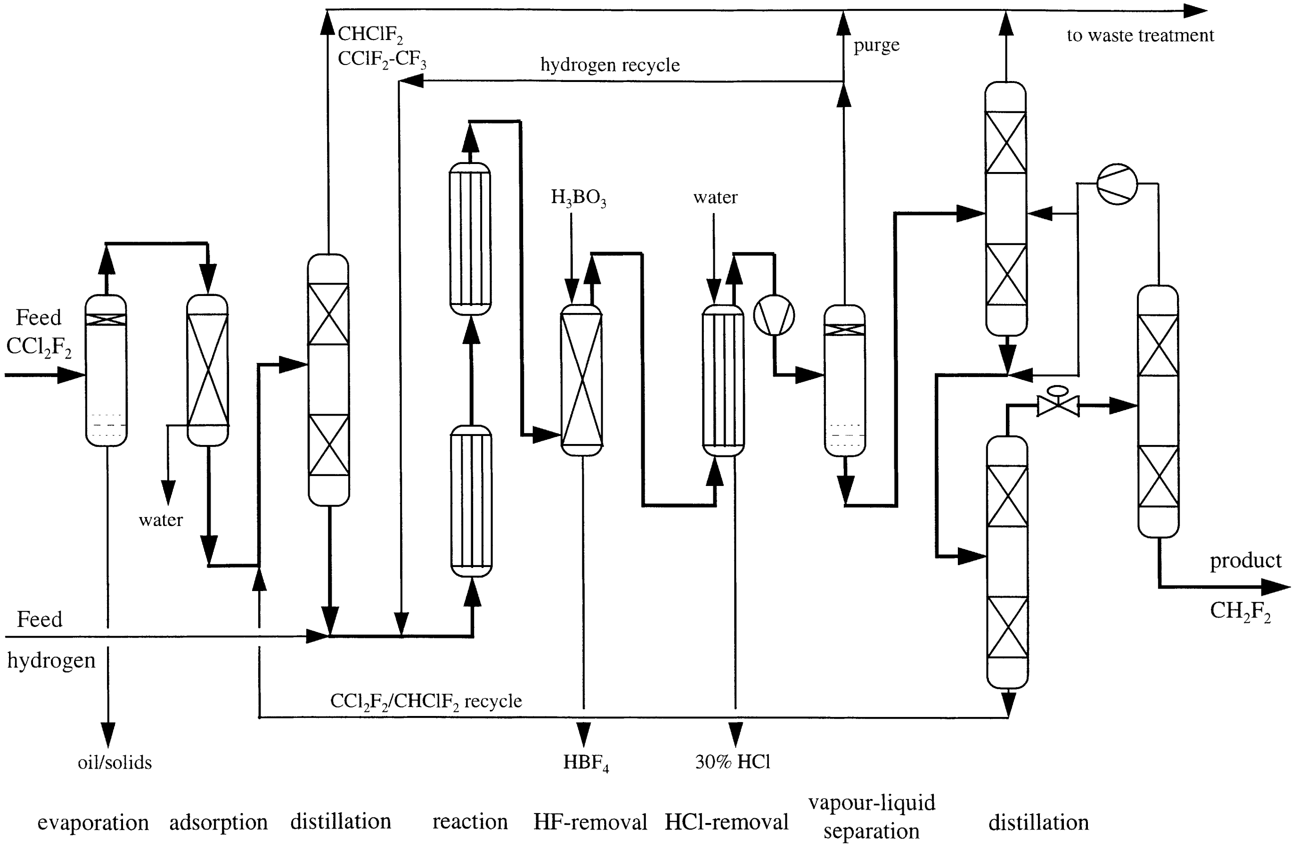

Fig. 10. Scheme of 10 kt per year CCl_2F_2 into CH_2F_2 conversion plant.

4. Conclusions

Pd/C is an excellent catalyst for the conversion of CCl_2F_2 into CH_2F_2. During reaction Pd is present as the carbide, $PdC_{0.15}$.

The hydrogenation does not occur via a serial pathway, readsorption of the products does not take place. The major reaction starts with the breaking of the C–Cl bond. The reactivity of the CFCs positively correlates with the Cl-content. Because CF_2 is the most stable intermediate, a selective process is possible. Adsorbed Cl is kinetically significant and, as a consequence, HCl should not be recycled and an excess of hydrogen is favourable. Alkanes, in particular methane, are formed in a parallel pathway initiated by the breaking of a C–F bond.

The selectivity remarkably parallels thermodynamic stability of intermediates and products. All investigated noble metals on activated carbon follow the same reaction mechanism, where the selectivities to CHClF2 and CH_2F_2 are mainly determined by the amounts of adsorbed chlorine on the catalytic active surface.

A conceptual process has been developed and it is concluded to be technically and economically feasible.

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