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Development of a palladium on activated carbon for a conceptual process in the selective hydrogenolysis of CCl_2F_2 (CFC-12) into CH_2F_2 (HFC-32)

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Abstract

The hydrogenolysis of CCl_2F_2 over 1 wt.% palladium, platinum, rhodium, ruthenium, iridium, and rhenium on activated carbon has been studied in a micro-flow reactor, in a temperature range of 450–540 K, H_2/CCl_2F_2 feed ratios between 1.5 and 20, a pressure up to 0.4 MPa, and a WHSV between 0.5 and 2 g/(g h). The main products of the reaction for all investigated catalysts were $CHClF_2$, CH_2F_2, and methane. Palladium on activated carbon shows the highest selectivity to CH_2F_2 (70–90%) at all conversion levels. The activity, selectivity to CH_2F_2 and stability of the palladium catalyst is a strong function of the hydrogen to CFC ratio, methane recycle ratio and the recycle of $CHClF_2$ is not recommended. The catalyst proves to be stable over a period of 2000 h with simulated recycle streams and an optimum temperature for the catalyst performance was found at 510 K. On the basis of the experimental data and a kinetic network a conceptual process design was made. In this design no hurdles have been encountered and this waste technology looks in economic prospective very promising. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: CFC; Hydrogenolysis; Palladium; Activated carbon; Chlorofluorocarbons; Process development; CCl_2F_2; CH_2F_2

1. Introduction

Fully halogenated chlorofluorocarbons (CFCs) were developed in the 1930’s as refrigerant. Within two decades because of their unique properties, like chemical and thermal stability, low toxicity and non-flammability, they were used in various applications such as blowing agent in foams, refrigerant, aerosol propellant, and solvent.

One of their properties, namely their stability appears to be its main drawback. It has been found [1] that CFCs accumulate in the troposphere and diffuse to the stratosphere [2], where they release chlorine atoms which catalytically destroy ozone. Besides the ozone depletion potential also the emitted CFCs have a relatively large impact on the greenhouse effect. The relative contribution of CFCs to man-induced global warming is estimated to be up to 25% [3].

On the basis of these reports it has been decided that world-wide the production and consumption of CFCs should be terminated 1 January 1996 [4]. The recovery of CFCs in use and the subsequent destruction is a logical step forward. Many destruction techniques have been proposed such as combustion, catalytic oxidation, catalytic hydrogenation, pyrolysis processes, chemical destruction, supercritical water

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oxidation, plasma destruction, ultraviolet destruction and destructive high energy radiation [3]. From these techniques combustion has been demonstrated on a commercial scale and it proves to be expensive destruction technology ($4/kg CFC). Obviously, the conversion of CFCs into valuable chemicals is a better option than the above mentioned destruction.

The long term replacements for CFCs in their application as refrigerant are most probably HFCs. CH_2F_2 (HFC-32) or a mixture thereof are good replacements in heavy duty cooling application, because HFC-32 has excellent cooling properties and in addition a lower global warming potential than HFC-134a. It is clear that the market for CFC-replacements by HFCs is growing and as a consequence a challenging task is to convert the waste CFCs into valuable HFCs. At Delft University, a catalytic process is under development in which CCl_2F_2 (CFC-12) and CCl_3F (CFC-11), which can be converted into CCl_2F_2 (CFC-12) with HF, are converted into CH_2F_2 (HFC-32). This ozone friendly product, HFC-32, in combination with HFC-125 (C_2HF_5) is suggested to be an energy-efficient replacement for R-502 (an azeotropic refrigerant mixture of C_2ClF_5 (CFC-115) and $CHClF_2$ (HCFC-22)) and at the longer term for HCFC-22 itself in refrigerant and air conditioning applications [5].

The catalytic hydrogenolysis can be represented as the reaction of CCl_2F_2 (CFC-12) into CH_2F_2 (HFC-32). A selective conversion to CH_2F_2 can be hoped for because the carbon-fluorine bond is much stronger than the carbon–chlorine bond as has been found in the fifties by Larcher et al. [6]. This earlier work was later confirmed by others [7–10] and in this laboratory [11]. All hydrogenolysis reactions starting from CCl_2F_2 are exothermic irreversible reactions, and the formation of methane is thermodynamically favoured. The reaction enthalpy at 298 K for the selective hydrogenolysis to CH_2F_2 is -150 kJ/mol and for the complete hydrogenolysis to methane -320 kJ/mol. Besides hydrogenolysis also chlorine/fluorine exchange can take place. This can lead to formation of, for example CHF_3, a product which can only be formed via this reaction.

In this study, a comparison of the performance of the noble metal on activated carbon catalysts will be presented. The lifetime of the selected palldium on activated carbon was subsequently studied in detail as function of hydrogen to CFC-12 ratio, of temperature, and of addition of potential recycle components such as HCFC-22 and methane. On basis of these lifetime studies a conceptual design for the waste conversion of CFC-12 into HFC-32 will be made and evaluated.

2. Experimental

2.1. Materials

Sodium hydroxide pellets (>98.5% purity) and 36–38% aqueous hydrochloric acid 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 were supplied by Alfa (99% purity). The activated carbon extrudates (RB1, $d = 1$ mm, $l = 3$–5 mm, BET = 1060 m^2/g) were a gift from Norit N.V. Activated carbon as catalyst support was selected for its inertness under reaction conditions (HCl and HF) and the selection of the carbon extrudates has been made in [12].

2.2. Catalyst preparation

50 g of activated carbon support was sequentially washed 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 at a flow rate of approximately 0.28 ml/s prior to introduction of the metal. 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 the appropriate metal chloride dissolved in aqueous hydrochloric acid. The acid concentration was chosen to give a chlorine to metal ratio of 10. 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 catalyst were reduced in-situ in the flow reactor under hydrogen flow from ambient temperature up to the reaction temperature. This preparation is described in detail in [13]. Almost

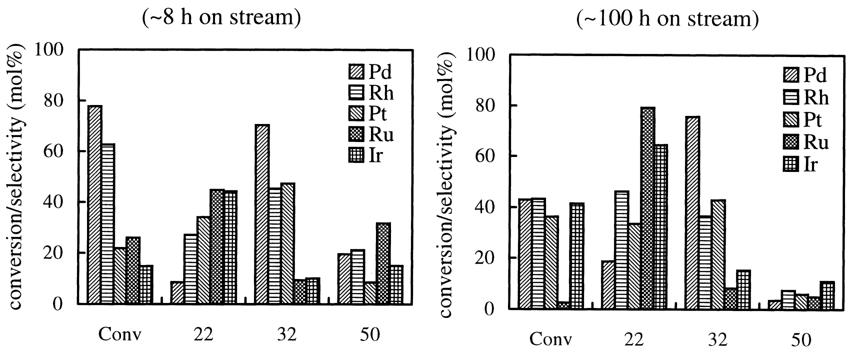

Fig. 1. The initial (∼8 h on stream) and final (∼100 h on stream) performance of the different catalysts during the experimental sequence (conditions: $T=500$ K, $P=0.4$ MPa, WHSV = 1 g/(g h), and $H_2/CCl_2F_2=3$. Abbreviations: Conv.: CCl_2F_2 conversion, 22: selectivity for $CHClF_2$, 32: selectivity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

Table 1
Experiment sequence[a]

Experiment No. (–)	Duration (h)	Temperature (K)	H_2/CCl_2F_2 (–)
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

similar catalyst preparations are reported in the patent literature [14–16].

2.3. Catalyst performance testing

The catalysts have been tested for their activity and selectivity in the hydrogenolysis of CCl_2F_2 at different process conditions in a multi-microflow reactor set-up with six parallel reactors. Temperature, weight hourly space velocity (WHSV, defined as g CCl_2F_2 feed/g catalyst/h), and hydrogen to CCl_2F_2 ratio were varied. The experimental sequence is shown in Table 1. Reference experiments have been included in the sequence in order to check for changes in catalyst performances. The equipment is constructed of monel, whereas the reactors are Hastelloy-C fixed-bed micro-catalytic reactors. The performance of the catalysts was determined by an on-line gaschromatograph, equipped with a 75 m × 0.53 mm Ultimetal Q column (Chrompack), a thermal conductivity detector, and a flame-ionization detector. Conversion and selectivities were calculated on the basis of the products formed.

3. Results and discussion

3.1. Catalyst performance

Because the rhenium catalyst showed no conversion under all investigated conditions, the results of this catalyst will not be discussed in detail. For all other catalysts tested, the main products were $CHClF_2$, CH_2F_2, and methane. The initial performance (∼8 h on stream) and the final performance (∼100 h on stream) are depicted in Fig. 1. This figure shows that the selectivity sequence between the different catalysts did not change profoundly during the experimental sequence. The palladium catalyst has a high selectivity for CH_2F_2 (∼80 mol%). The generally observed selectivity sequences were

$$CHClF_2: \quad Pd \ll Rh < Pt \ll Ir < Ru$$

$$CH_2F_2: \quad Pd \gg Pt > Rh \gg Ir > Ru$$

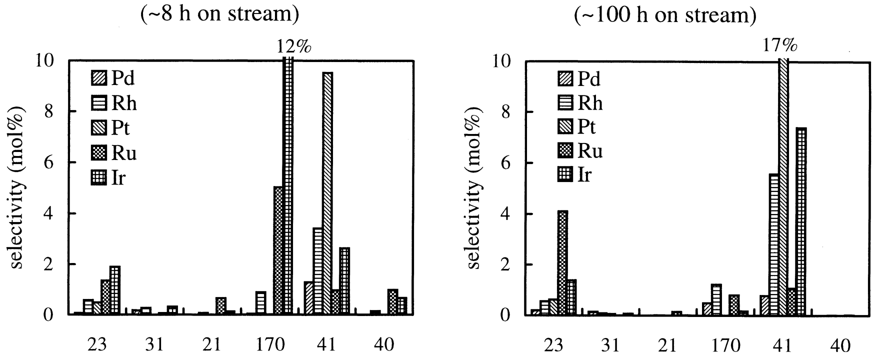

Fig. 2. The initial and final selectivities for by-products (abbreviations: 23: CHF_3, 31: CH_2ClF, 21: $CHCl_2F$, 170: ethane, 41: CH_3F, and 40: CH_3Cl. For conditions, see Fig. 1).

Although the initial selectivities for methane are quite different, the selectivity for methane after 100 h on stream is more or less the same. The most important by-products formed are CH_3F, CHF_3, CH_3Cl, and ethane. Other by-products in a minor extent are $CHCl_2F$, CH_2ClF, CH_2Cl_2, propane, and C_2-CFCs. The amount of by-products formed is generally low. However, in the case of ruthenium and iridium initially a large amount of by-products are formed. This is illustrated in Fig. 2, in which the initial and final selectivities for the most important by-products are depicted. Especially in the case of iridium the total selectivity for by-products is initially over 30 mol%, but this selectivity decreases rapidly after a few hours on stream. During this initial period, especially C_2-compounds are formed. This is illustrated by the initial selectivity for ethane for the iridium catalysts in Fig. 2. The total amount of by products is clearly the lowest for the palladium catalyst. The chlorine/fluorine exchange activity was the lowest for the palladium catalyst, as can be seen in the selectivity for CHF_3, a product, which can only be formed via a chlorine/fluorine exchange reaction. Platinum showed a high selectivity for CH_3F, which increases to 17 mol% after 100 h on stream. A high selectivity for CH_3F was also found for the rhodium and iridium catalyst. In case of platinum, CH_3F can be considered to be one of the main products rather than a by-product.

Figs. 1 and 2 clearly illustrate that the performance of the catalysts changed as a function of time on stream. Although the extent of the change was not the same for all catalysts, some general observations can be made. During the experimental sequence, the rhodium, ruthenium, and palladium catalysts were deactivated, and the iridium and platinum were activated. Wiersma et al. explain this activation by the change of (re)dispersion of the nobel metal as function of reaction conditions applied and the deactivation by adsorption of chlorine and/or deposition of heavy halogenated products [17].

The selectivity for CH_2F_2 is the highest for the palladium catalyst throughout the experimental sequence. In the case of palladium and iridium, the selectivity for CH_2F_2 increased whereas in the case of platinum, rhodium, and ruthenium the selectivity for CH_2F_2 decreased with time on stream. The selectivity for methane decreased for all investigated catalysts and at the end of the experimental sequence the selectivity for methane was more or less the same for all catalysts. On the other hand the selectivity for $CHClF_2$ increased for all catalysts. The changes in the performance of a catalyst mainly occurred in the beginning of the experimental sequence and when the reaction temperature was raised to 540 K.

Since palladium on activated carbon gave the highest selectivity to the desired product HFC-32, this catalyst was studied on its stability in time. Therefore, the performance was studied as function of hydrogen to CFC-12 ratio, of temperature, and of potential recycle components such as HCFC-22 and methane.

3.2. *Stability as function of H_2/CFC ratio at 510 K*

The main product of the hydrogenolysis of CCl_2F_2 with the selected 1 wt.% palladium on activated carbon

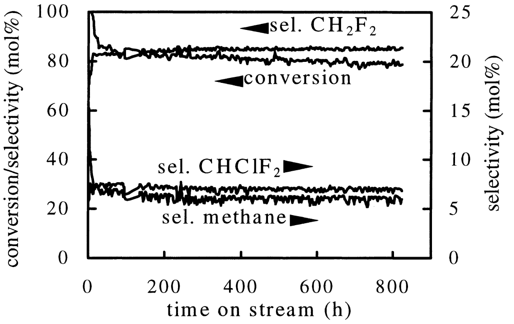

Fig. 3. Catalyst performance at 510 K and H_2/CCl_2F_2 feed ratio of 6 mol/mol (Conditions: $P=0.2$ MPa and WHSV = 0.5 g/(g h).

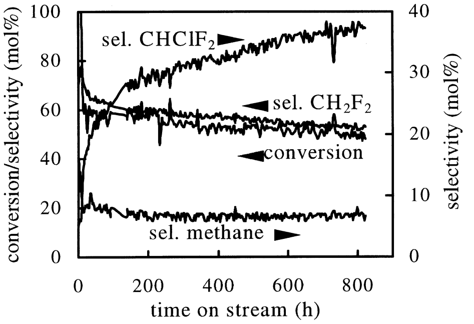

Fig. 4. Catalyst performance at 510 K and H_2/CCl_2F_2 feed ratio of 1.5 mol/mol (conditions: $P=0.2$ MPa and WHSV = 0.5 g/(g h).

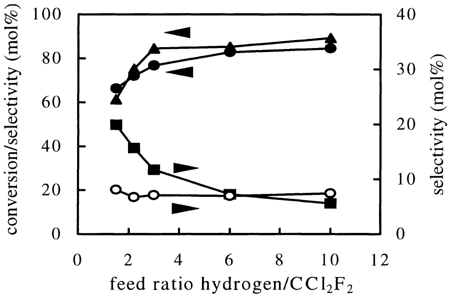

Fig. 5. Initial catalyst performance as a function of H_2/CCl_2F_2feed ratio (conditions: $T=510$ K WHSV = 0.5 g/g(g h), $P=0.2$ MPa, ▲: conversion, ●: selectivity to CH_2F_2, ■: selectivity to $CHClF_2$, ○: selectivity to methane).

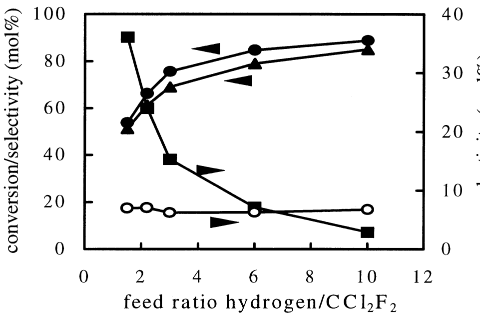

Fig. 6. Catalyst performance after 700 h on stream as a function of H_2/CCl_2F_2feed ratio (conditions: $T=510$ K WHSV = 0.5 g/g(g h), $P=0.2$ MPa, ▲: conversion, ●: selectivity to CH_2F_2, ■: selectivity to $CHClF_2$, ○: selectivity to methane).

catalyst is CH_2F_2. The main by-products are $CHClF_2$ and methane. Other by-products to a minor extent are CH_3F, ethane, propane, CH_3Cl, and CH_2ClF. The main parameters which determine the stability of the selected catalyst are the temperature and the hydrogen to CCl_2F_2 feed ratio. In Figs. 3 and 4 the performance of the catalysts a function of time on stream at 510 K for two different hydrogen to CFC feed ratio is depicted. These figures show that a stable catalyst operation has been obtained after 300 h on stream for a hydrogen to CFC feed ratio of 6. At the lower hydrogen to CFC feed ratio of 1,5→1.5 a continuous deactivation of the catalyst is observed. Not only the activity but also the performance of the catalyst changes as a function of time on stream. The initial performance of the catalyst as a function of the hydrogen to CFC feed ratio is depicted in Fig. 5. At the low hydrogen to CFC feed ratios both the conversion and the selectivity for CH_2F_2 decreases, whereas the selectivity for $CHClF_2$ increases. After 700 h on stream these differences become more pronounced as can be seen in Fig. 6. Figs. 5 and 6 illustrate the catalyst deactivation as a function of the hydrogen to CFC feed ratio (Fig. 5 shows the initial catalyst performance and Fig. 6 that after 700 h on stream). At lower hydrogen to CFC feed ratio the catalyst deactivates. This deactivation leads to a decline in the selectivity to CH_2F_2 in combination with an increase in the selectivity for $CHClF_2$. The strong adsorption of chlorine on the catalyst surface will react with the adsorbed CF_2 carbene on the catalyst surface to a large extent to $CHClF_2$ as been described for the reaction mechanism by Van de Sandt et al. [18]. In this mechanism CF_2 carbene is thought to be the active surface intermediate. Depending on the surface coverage of the adsorbed HCl and hydrogen this coverage will direct the selectivity more to either $CHClF_2$ (high HCl/hydrogen ratio) or CH_2F_2 (low HCl/hydrogen ratio). The selectivity to methane in this proposed mechanism will independently follow a parallel pathway.

Further increase of the hydrogen to CFC feed ratio from 10 to 20 does not lead either to a higher activity or selectivity to CH_2F_2. The results of the stability test at 510 K as a function of hydrogen to CFC feed ratio are summarized in Table 2. Only minor deactivation is observed after 700 h on stream for a hydrogen to CCl_2F_2 above 6. From data presented in Table 2 and data not shown an optimal hydrogen to CCl_2F_2 feed ratio of 12 has been found. At higher hydrogen to CFC feed ratio the palladium catalyst showed a more pronounced deactivation in comparison to the shown deactivation data at ratios between 6 and 12.

3.3. Stability as function of temperature

The catalyst stability at higher temperatures of 520, 525, and 540 K has been tested for high hydrogen to CCl_2F_2 feed ratios (8–16). The results of the stability test at 540 and subsequently 525 K are depicted in Fig. 7 for a hydrogen to CCl_2F_2 feed ratio of 12. Similar behaviour was observed at other hydrogen to CCl_2F_2 feed ratios applied. Both at 540 and 525 K a continuous deactivation of the catalyst is observed. Remarkably, an increase in the selectivity for methane is found at 540 K as a function of time on stream, whereas the selectivity for methane was constant as a function of hydrogen to CCl_2F_2 feed ratio in the experiments at 510 K. At 525 K, the selectivity for methane remains constant again.

In Fig. 8 the catalyst stability at 520 K as a function of time on stream is depicted. A continuous deactivation of the catalyst is observed, although the rate of deactivation is lower than at both 540 and 525 K. The rate of deactivation seems to increase slightly after 500 h on stream. Similar behaviour was observed at H_2/CCl_2F_2 feed ratios of 8 and 16.

A temperature of 510 K was selected for the catalyst activity and stability. At higher temperatures the catalyst starts to deactivate.

3.4. Stability during the addition of recycle components $CHClF_2$ (HCCF-22) and methane

Since a high hydrogen to CFC ratio is required for an optimal catalyst performance in a process design the excess of hydrogen will be recycled. The separation of hydrogen and the by-product methane is expected to be a very energy consuming unit operation and the recycle of methane is anticipated to be present in the hydrogen recycle. Recycling of $CHClF_2$ can be an option, since in a second pass over the catalyst $CHClF_2$ can be converted into CH_2F_2 [19]. Therefore, only the influence of $CHClF_2$ and methane on the catalyst stability is depicted here in Fig. 9 at 510 K. The rate of addition of $CHClF_2$ was not very stable and, therefore, large fluctuations in the GC analysis were unavoidable. However, this figure clearly shows that addition of methane or $CHClF_2$ to the feed leads to additional catalyst deactivation, especially at lower hydrogen to CCl_2F_2 feed ratios. After removal of the recycle components from the feed the catalyst does not restore its original activity completely. At higher temperatures addition of methane to the feed also leads to additional catalyst deactivation. This is illustrated in Table 3, in which the deactivation data of the catalysts, used at 520, 525, and 540 K, are summarized with and without addition of methane to the feed. Especially during the experiments at 520 K a significantly higher catalyst deactivation was observed at the higher methane to CCl_2F_2 feed ratio of 2. In this conceptual process design, therefore, a ratio of 1 is aimed for and the recycle of HCFC-22 is not recommended due to its pronounced catalyst deactivation. Another reason for not recycling HCFC-22 over the reactor is its low reactivity in the presence of CFC-12. Recycling of HCFC-22 will lead then to accumulation in the recycle stream leading to larger reactor dimensions.

4. Conceptual design of a 10 kt/year CCl_2F_2 conversion plant

It has been demonstrated, that palladium on activated carbon is a good candidate catalyst for the selective conversion of CCl_2F_2 into CH_2F_2 (~85 mol% selectivity for CH_2F_2 at all conversion levels of CCl_2F_2). Moreover, the catalyst preparation method proves to be to scale up to a commercial production scale of catalyst (10 kg batches prepared by a catalyst vendor gave identical performance as our laboratory catalyst preparation method).

Although the catalyst and the reactor are obviously very important parts, a CCl_2F_2 conversion plant will

Table 2
Catalyst performance and deactivation after 700 h. (Deactivation is given as percentage of initial activity) (conditions: $P = 0.2$ MPa, WHSV = 0.5 g/(g h), and $T = 510$ K)[a]

H_2/CCl_2F_2	Conv. CCl_2F_2 (mol%)	Sel. CH_2F_2 (mol%)	Sel. $CHClF_2$ (mol%)	Sel. CH_4 (mol%)	Deact. (%)
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
20*	84	88	3	7	–

[a] 10 = after 680 h on stream, 20 = performance after 700 h on stream (20 h after increase of ratio from 10 to 20)

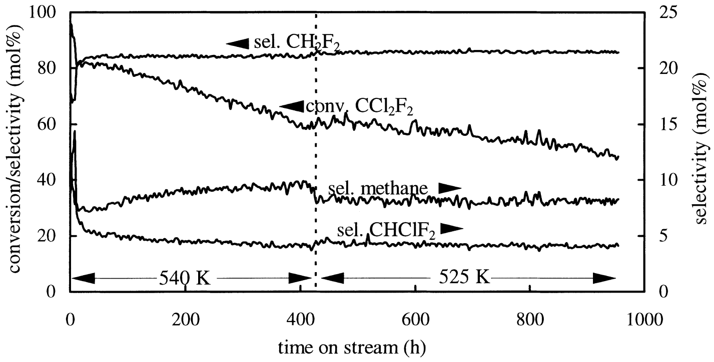

Fig. 7. Catalyst performance at 540 and 525 K. (Conditions: before 420 h: $H_2/CCl_2F_2 = 12$, $P = 0.2$ MPa, $T = 540$ K, WHSV = 1.4 g/(g h), After 420 h: $H_2/CCl_2F_2 = 12$, $P = 0.2$ MPa, $T = 525$ K, WHSV = 0.7 g/(g h)).

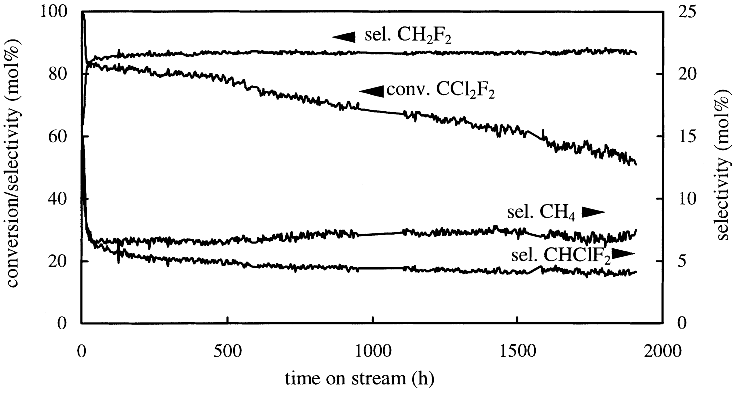

Fig. 8. Catalyst stability at 520 K. (Conditions: $H_2/CCl_2F_2 = 12$, $P = 0.2$ MPa, $T = 520$ K, WHSV = 0.75 g/(g h)).

Table 3
Comparison of deactivation at different temperatures after 400 h on stream

H_2/CCl_2F_2	CH_4/CCl_2F_2	520 K (% deact.)	525 K (% deact.)	540 K (% deact.)
8	–	2.8	21.2	31.4
12	–	4.2	19.6	26.9
16	–	1.7	19.6	28.4
12	1	5.3	33.2	39.8
12	2	15.4	–	43.8

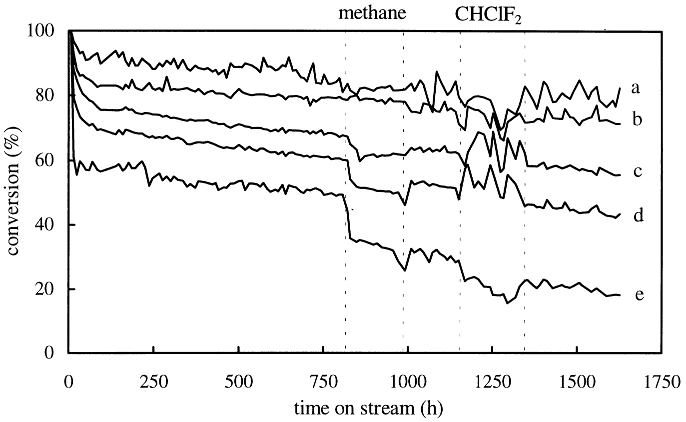

Fig. 9. Catalyst stability with simulated recycle components $CHClF_2$ and methane. (Conditions: $T=510$ K, $P=0.2$ MPa, WHSV = 0.5 g/(g h), H_2/CCl_2F_2: (a) = 10 (20), (b) = 6, (c) = 3, (d) = 2.2, and (e) = 1.5), $CCl_2F_2/CH_4=1$ and $CHClF_2/CCl_2F_2=4$, applied at the indicated time intervals.

Table 4
Composition of CCl_2F_2 feed

Component	Concentration
CCl_2F_2	96 wt.%
$CHClF_2$	2 wt.%
$CClF_2$-CF_3	1 wt.%
Oil	1 wt.%
Water	44 ppm wt.
Solids	40 ppm wt.

include more unit operations. Therefore, the work as described in Section 3 will be used as a basis for a conceptual design of a 10 kt/year CCl_2F_2 conversion plant.

4.1. Base of design

4.1.1. Feed

The main feeds to the process are CCl_2F_2 and hydrogen. The CCl_2F_2 feed can be either recovered CCl_2F_2 or converted CCl_3F. In case of recovered CCl_2F_2 the estimated composition of the feed is depicted in Table 4. Hydrogen is produced on site or supplied by an external supplier. The purity is 99.99%. Furthermore, boric acid is needed for HF removal and water for HCl removal.

4.1.2. Products

The main products are CH_2F_2, a 30 wt.% HCl solution, and a 61 wt.% fluoroboric acid solution. The specification for the CH_2F_2 product is given in Table 5.

Table 5
CH_2F_2 product specification

Minimum purity	99.7 wt.%
Maximum water content	10 ppm wt.
Maximum high boiling impurities	0.01 vol.%
Maximum non-absorbable gases	1.5 vol.% (in vapour phase)

4.1.3. Utilities

Utilities needed in the process are cooling water, process water, electricity, air, and natural gas. The heat balance of the overall process is positive, which means that the process produces more heat than needed in the different units, and no hot utility is needed. However, cold utility is needed at very low temperatures (down to 188 K). This can be done by use of an ethene refrigerant with an estimated duty of 61 kW.

4.1.4. Capacity

The CCl_2F_2 conversion plant capacity is set at 10 kt CCl_2F_2/year. An inventory of CFC-recovery in the Netherlands showed that about 2 kt/year recovered CFCs (CCl_3F and CCl_2F_2) can be expected [20]. Obviously, the CFC recovery is a matter of international interest, and, therefore, a capacity of 10 kt/year is a logical choice for CCl_2F_2 conversion in the European Union.

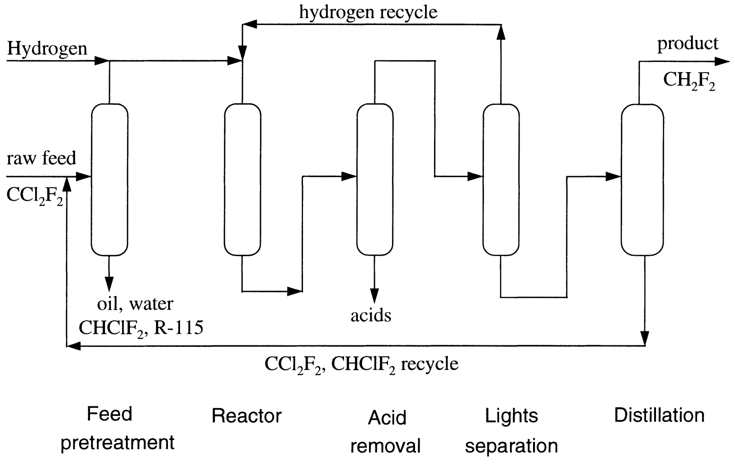

Fig. 10. Simplified scheme of CCl_2F_2 into CH_2F_2 conversion plant.

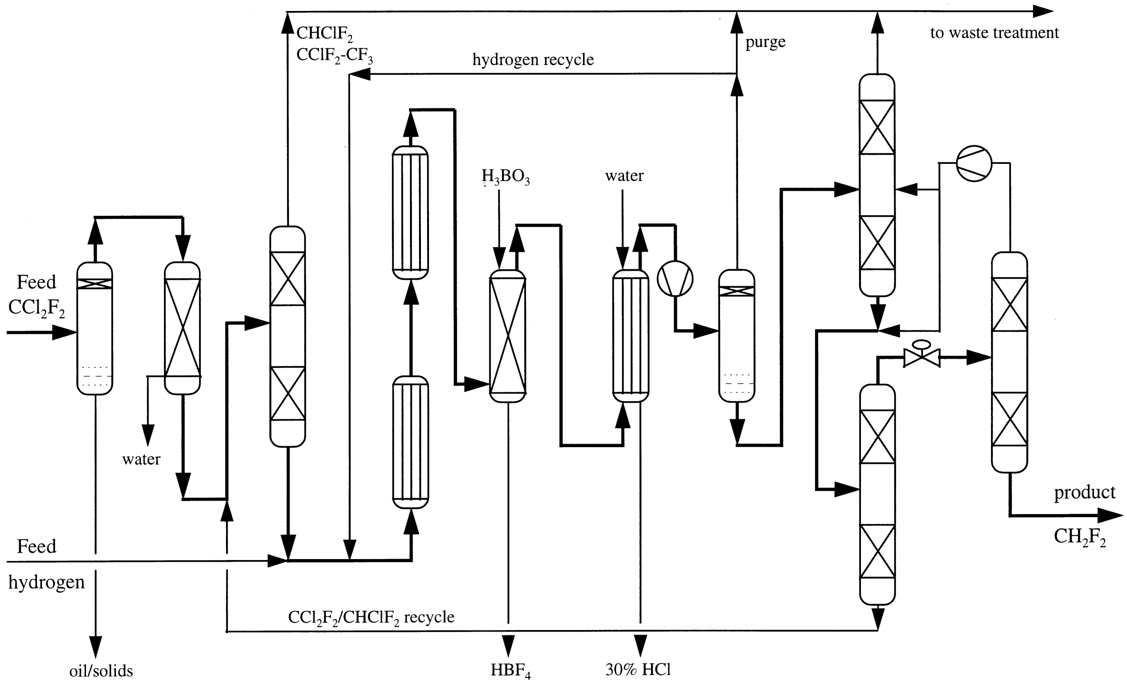

Fig. 11. Scheme of 10 kt/year CCl_2F_2 into CH_2F_2 conversion plant.

4.2. Description of CCl_2F_2 conversion plant

A simplified and detailed schematic representation of the CCl_2F_2 conversion plant is shown in Figs. 10 and 11, respectively. Fig. 10 shows that the CCl_2F_2 conversion process can be divided into four sections

1. Feed pre-treatment section;
2. Reactor section;
3. Acid removal section;
4. Separation.

4.2.1. *Feed pretreatment section*

Recovered waste CCl_2F_2 and recycled CCl_2F_2 and $CHClF_2$ from the separation section are introduced into the feed pretreatment section. The three objectives of the feed pretreatment section are

- Removal of oil, solids, and water from the feed;
- Removal of $CClF_2$-CF_3 from the feed;
- Removal of $CHClF_2$ from the recycle stream.

Oil, solids, water, and $CClF_2$-CF_3 may be introduced into the waste CCl_2F_2 during the use and recovery of the CCl_2F_2. In order to avoid problems with the catalyst or corrosion of process equipment the oil and water have to be removed. $CClF_2$-CF_3 can cause problems in the separation section because azeotropic mixtures with the produced CH_2F_2 can be formed. The removal of $CClF_2$-CF_3 from the feed can be combined with the removal of $CHClF_2$ from the recycle CCl_2F_2 stream. $CHClF_2$ has to be removed, since $CHClF_2$ is not converted in the presence of CCl_2F_2 under the desired reaction conditions.

The feed pretreatment section consists of an evaporation unit, a dryer, and a distillation column as shown in Fig. 11. In the evaporation unit, CCl_2F_2 is evaporated and separated from oil and solids. The evaporated CCl_2F_2 is dried by means of molecular sieves. In the distillation unit 95 wt.% of the introduced $CClF_2$-CF_3 and 100% of the introduced $CHClF_2$ are removed from the CCl_2F_2. The removed $CHClF_2$ and $CClF_2$-CF_3 are sent to the waste treatment section.

4.2.2. *Reactor section*

The reactor section consists of two identical multi-tubular-cooled-fixed bed reactors in series. These reactors consist of 6627 parallel tubes, which are cooled by means of boiling water. The length and inner diameter of the reactor tubes are 3.05 m and 1.93 cm, respectively. The length and diameter of the total reactor are 4.1 m and 2.8 m, respectively. About 80 mol% of the CCl_2F_2 fed to the first reactor is converted in these reactors, whereas about 55 mol% conversion after the first reactor is obtained. The temperature in both reactors can be controlled within the operating window of the catalyst (450–510 K; see also Section 3.3.).

The choice of the reactor type was mainly based on a combination of the exothermic reaction, the selected 1 wt.% palladium on activated carbon catalyst, and the prerequisite of a sure, safe, and quick process development route. At steady-state operation of the catalyst an adiabatic temperature rise of 300–670 K can be expected. This temperature rise is too large in comparison to the allowed operating window of the catalyst of 450–510 K. Therefore, cooling of the reaction mixture is inevitable. Generally, three reactor types can be used for this purpose in case of a gas-phase reaction: (1) fluidized bed reactor; (2) multi-fixed-bed reactor with interstage cooling or cold feed injection; (3) multi-tubular-cooled-fixed bed reactor.

1. Although the produced heat could be sufficiently removed in a fluidized bed reactor, this type of reactor is not attractive in the case of an activated carbon supported catalyst. The strength of activated carbon is in general not sufficient to be used in a fluidized bed and, as a consequence, time consuming catalyst development research would be unavoidable.
2. A multi-bed reactor with interstage cooling is not feasible because an impractical number of beds (>15) would be required to avoid too high temperature rises within the beds.
3. A multi-tubular-cooled-fixed bed reactor is suitable for exothermic reactions. Furthermore, the development of this type of reactor can be expected to be quicker because of the experience with this type of reactor in other processes. Recently, this type of type of reactor has been selected and applied by Shell in the SMDS process for exactly the same reasons [21].

Hence, a multi-tubular-cooled-fixed bed reactor is the most suitable gas-phase reactor type for the selective conversion of CCl_2F_2 into CH_2F_2. It is, however, recommended to check the development of a stable temperature profile and catalyst performance for a long period of time (0.5 year) in a pilot-reactor.

4.2.3. *The acid removal section*

The acids HF and HCl are selectively removed from the reactor effluent. First, HF is removed by means of a hydroboric acid solution. This results in a sellable product: 61 wt.% fluoroboric acid. Second, the hydrochloric acid is removed from the stream by means of water. This results in a sellable 30 wt.% hydrochloric acid solution. Both technologies are commercially applied in the preparation of CFC-12 from CFC-11 by

AlliedSignal in the Netherlands, formerly owned by Akzo–Nobel. This technology is adapted for this process design. After the HF- and HCl removal units the effluent is scrubbed with a lightly alkaline aqueous solution to remove trace of acids. The quick removal of the acids from the reactor effluent ensures a safe operation of the plant. Furthermore, the separation section can be expected to be less complex, because possible azeotropes of HF or HCl with CFCs are avoided.

4.2.4. Separation section

The separation section can be divided into a lights separation and a CFC distillation section. The lights separation section consists of a vapour–liquid separator and a light ends distillation column. In the vapour–liquid separator, the excess hydrogen used in the reactor is separated from the product stream and recycled. A purge stream is needed in the recycle to avoid build up of methane in the recycle stream, which is sent to a waste treatment section. Because a complete separation of methane and hydrogen in the recycle stream is not practical, methane is allowed in the recycle. The maximum methane concentration in the reactor feed is set at $CH_4/CCl_2F_2 = 1$. In a light-ends distillation column, produced light CFCs and methane dissolved in the CFCs are separated from CCl_2F_2, $CHClF_2$, and CH_2F_2, and sent to a waste treatment section. In the CFCs separation section CH_2F_2 is separated from $CHClF_2$ and CCl_2F_2 by means of two distillation columns operated at different pressures. This type of operation is needed due to the azeotrope between CCl_2F_2 and CH_2F_2.

A waste treatment section is included in the design, which ensures a total CFC destruction efficiency of 99.99%. Therefore, the CCl_2F_2 conversion plant is designed to fulfill the destruction efficiency specification of the UNEP [22].

4.3. Technical feasibility of process

A summary of the overall performance of the process is given in Table 6.

Table 6 shows that the conversion 10 kt CCl_2F_2 results in the production of 3 kt CH_2F_2.

This equals a total molecular yield of 70 mol% CH_2F_2. The main by-products of the process are a 30 wt.% hydrochloric acid solution and a 61 wt.% HBF_4 solution. The technical feasibility of the process is very promising, there were no unavoidable barriers encountered. Furthermore, as all unit operations are mainly based on proven technology, the chances for unforeseen problems are minimal.

Table 6
Most important feeds and products of process

Feed	Amount (kt/year)	Products	Amount (kt/year)
CCl_2F_2	10	CH_2F_2	3
H_2	0.4	HCl	5[a]
		HBF_4	0.5[a]
		waste	2

[a] In solution.

Although the combination of an exothermic reaction with the production of hydrofluoric and hydrochloric acid seems dangerous, the process design clearly shows that a safe operation of the plant is possible. In order to minimize the risks the acids can be successfully removed directly after the reactors. However, special additional measures are needed to ensure safe handling and storage of the acids. Furthermore, a dedicated and accurate temperature control system for the reaction is needed. Thus, experienced operators and additional safety measures on site are inevitable. Before implementation of this technology it is recommended to study the catalyst performance in a single tubular-cooled-fixed-bed reactor in conjunction with the start-up procedure of the reactor. Initially, large amounts of methane is produced, which is a highly exothermic reactions and thereby destroying the catalyst.

4.4. Economic evaluation of process

The total investment for the Delft University of Technology CCl_2F_2 into CH_2F_2 conversion process is estimated at $15 000 000. The process can both be regarded as the basis for destruction of CCl_2F_2 as well as for production of CH_2F_2. As a consequence, two different approaches for economic evaluation can be used. The main assumptions that have been made for the economic evaluations are:

- Hydrogen is produced on-site by an external supplier;
- The products prices of HCl and HBF_4 are included in the evaluation;
- Produced additional heat is not included.

Table 7
Comparison of estimated CCl_2F_2 destruction costs for different processes

Process	\$/kg
DUT	1
AVR	2.5–3
Hoechst	4–4.5

Table 8
Comparison of production price of CH_2F_2 compared with market value

Value	\$/kg
DUT production costs	3
Market value	8–16

In the first economic evaluation, the process is compared to other CFC destruction processes. The prices are compared as destruction prices per kilogram CCl_2F_2 destructed. The results of this evaluation are depicted in Table 7. The AVR-process is a simple combustion process in the presence of air (normal waste conversion process) [23]. In the AVR process no valuable by-product is produced. The Hoechst process is specially designed as a CFC-waste treatment process at very high temperatures (oxygen–hydrogen flame) [24]. In the Hoechst process concentrated solutions of HF and HCl as commercially attractive by-products are produced. In the Delft process the production of a valuable product (CH_2F_2) is not taken into account in this evaluation. It should, however, be noted that the Delft process is the only CFC destruction process which produces really a valuable product.

In the second evaluation, which is given in Table 8, the production costs of CH_2F_2 are compared to the current market value of CH_2F_2. Combining these two evaluations it can be seen that the process is economically very promising. It should be noted that the costs for recovery of CCl_2F_2 and CCl_3F from their current applications and the conversion of CCl_3F into CCl_2F_2 are not included in the evaluation. It is advisable to combine the CCl_2F_2 to CH_2F_2 conversion plant with an existing CCl_3F to CCl_2F_2 conversion facility. It can be concluded that the investment for the CCl_2F_2 into CH_2F_2 conversion plant can be earned as a CH_2F_2 production facility in 0.5 years, whereas the estimated lifetime of the plant as a CCl_2F_2 conversion facility is 10 years.

5. Conclusions

From the noble metals tested, Palladium appears to be a good catalyst for the selective conversion of waste CCl_2F_2 (CFC-12) into high added value product CH_2F_2(HCF-32). 1 wt.% palladium on activated carbon shows very high selectivity (70–90%) at al conversion levels.

The palladium on activated carbon proofs to be a stable catalyst for a period over 2000 h on stream with simulated recycle stream. The amount of methane in the recycle stream was to be limited to the ratio of methane/CFC-12 to 1 for catalyst deactivation, whereas the recycle of HCFC-22 is not recommended due to its additional catalyst deactivation under the applied reaction conditions.

The stability appears to be a function of hydrogen to CFC ratio (an optimal ratio was found at 12) and of temperature (an optimum was found at 510 K).

A conceptual design for a 10 kt/year CCl_2F_2 into CH_2F_2 conversion plant has shown that the process is both technically and economically feasible and can be operated safely. The total CFC destruction efficiency is 99.99%, as required by UNEP. The total investment for the plant is estimated to be M\$ 15. This investment can be earned as a CH_2F_2 production facility in 0.5 years, whereas the estimated lifetime of the plant as a CCl_2F_2 conversion facility is 10 years.

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