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Catalyst development for the selective hydrogenolysis of CCl_2F_2 (CFC-12) into CH_2F_2 (HFC-32)

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Abstract

A good catalyst for the selective hydrogenolysis of waste CCl_2F_2 (CFC-12) into the high added value product CH_2F_2 (HFC-32) has been developed. This catalyst is based on palladium on activated carbon and shows a high selectivity (70–90%) at all conversion levels. It is important to purify the activated carbon support prior to impregnation of the palladium salt. A nitrogen heat pretreatment enhances the stability and activity. During reaction, an increase in selectivity to CH_2F_2 has been found. This increase, without loss in activity, can be explained by further lowering the amount of impurities by the produced HF and HCl. These impurities, like iron and aluminium, are responsible for chlorine/fluorine exchange and total hydrogenolysis activities. It was found that during reaction the palladium was converted into palladium carbide.

Keywords: Selective hydrogenolysis; Palladium

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1. Introduction

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

One property, namely their stability, appeared to be the main drawback. In 1971 Lovelock [1] found that CFCs were accumulating in the stratosphere. A few years later Molina and Rowland [2] published an ozone depletion hypothesis in which they claimed that CFCs could diffuse to the stratosphere where they would release chlorine atoms which could catalytically destroy ozone. This destruction could lead to an increase in UV-B radiation at the earth's surface and could affect human health and other biological systems. In the following years, a large number of scientific papers have been reported which are consistent with the above mentioned theory.

On the basis of these reports, it has been decided that world-wide production and consumption of CFCs should be terminated on January 1, 1996. The United Nations [3] have, however, estimated that there are still 2.25 Mton

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Ozone Depleting Substances banked in all kinds of applications (≈45% CCl_2F_2 (CFC-12) as refrigerant and ≈45% CCl_3F (CFC-11) as blowing agent). The recovery of those substances and the subsequent destruction is a logical step forward. Many destruction techniques are proposed, such as combustion, catalytic oxidation, catalytic hydrogenation, pyrolysis processes, chemical destruction, supercritical water oxidation, plasma destruction, ultraviolet destruction and destructive high energy radiation. Among these techniques, only combustion has been demonstrated on a commercial scale.

Obviously the conversion of CFCs into valuable chemicals is a better option than the above mentioned destruction. 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, 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 [4].

2. Background

The catalytic hydrogenolysis can be represented as the reaction of CCl_2F_2 (CFC-12) via $CHClF_2$ (HCFC-22) into CH_2F_2 (HFC-32). A selective conversion to CH_2F_2 can be expected because the carbon–fluorine bond is much stronger than the carbon–chlorine bond, as has been found by Lacher et al. [5]. 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 is −320 kJ/mol. Besides hydrogenolysis chlorine/fluorine exchange can also take place. This can lead to formation of, for example, CHF_3, a product which can only be formed via this reaction. Also, coupled products such as ethane and propane can be formed. The complete scheme of hydrogenolysis and chlorine/fluorine exchange reactions for C_1 derivates is depicted in Fig. 1.

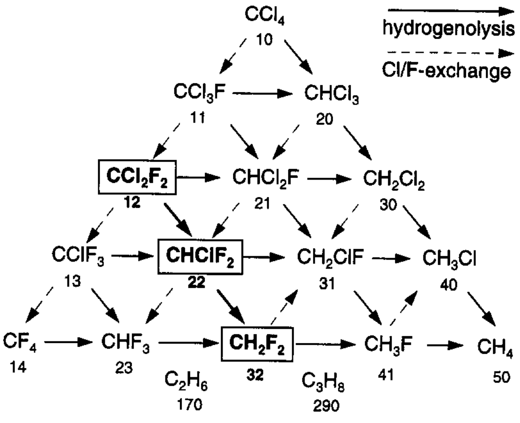

Fig. 1. CFC reaction scheme. The bold formulas and arrows are the reactions aimed at. The direction represents the thermodynamic driving force at 298 K and atmospheric pressure.

Several noble metals on activated carbon support materials have been tested. Palladium from group VIII metals was found to be the most suitable transition metal for this reaction [6]. Activated carbon as a support material is chosen because of its inertness under reaction conditions (HF and HCl).

3. Experimental

3.1. Preparation and testing of catalyst

The support used was gas-activated, peat-based, activated carbon (extrudates with a diameter of 1.0 mm and a length of 3–5 mm; BET = 1060 m^2/g). The carbon was optionally washed at room temperature prior to impregnation consecutively with 0.5 M aqueous sodium hydroxide, water, 0.5 M aqueous hydrochloric acid and water [7]. Catalysts were prepared by pore volume impregnation using palladium chloride as precursor to arrive at a loading of 1 wt%. The acid concentration was chosen to give a molar Cl^-/Pd^{2+} ratio of 10. Subsequently, the extrudates were dried overnight at 373 K; optionally a nitrogen pretreatment was performed at 623 K. The catalyst was treated in-situ under hydrogen flow from ambient temperature up to reaction temperature and CFC was introduced in the gas phase.

As reference, two commercially available 2 wt% Pd on activated carbon (HCl washed prior to impregnation and nonwashed) were included in the investigation. The palladium crystallites are in the order of 10 nm, which makes the characterization more simple.

A Hastelloy-C fixed-bed micro-catalytic reactor was employed to conduct the CFC hydrogenolysis experiments. The performance of the catalyst was determined by an on-line gas chromatograph, equipped with a 75 m × 0.53 mm Poraplot Q column (Chrompack) and a thermal conductivity detector.

3.2. Characterization

X-Ray diffraction (XRD) patterns of 0.05–0.10 g powdered catalyst were recorded on a Siemens D500-B diffractometer with a Cu Kα radiation source. The Bragg relation was used to calculate the lattice distance. The average metal crystallite size was determined with the Scherrer equation and Warren's correction for instrumental line broadening.

Temperature programmed reduction (TPR) was measured on a home-made apparatus. Catalyst samples (ca. 100 mg) diluted with nonporous silicium carbide were heated with 0.167 K/s in a 5% hydrogen-in-argon mixture. The hydrogen consumption/evolution is determined with a calibrated thermal conductivity detector.

The palladium surface area was measured by CO-chemisorption using a pulse technique at room temperature [8]. A stoichiometry of $CO/Pd = 1$ and Pd surface density of 1.27×10^{19} atoms/m^2 were assumed. Prior to pulsing, reduction under hydrogen was performed at 430 K for 2 h.

The impurities in the activated carbon and the palladium loaded activated carbons were determined with a Philips PW1480 X-ray fluorescence (XRF) spectrometer.

The ash-content of the activated carbons was measured by burning off the carbon at 1040 K till constant weight was achieved.

The codes for the catalysts and carbons used are shown in Table 1.

4. Results

4.1. Performance measurements

In Fig. 2, the influence of washing of the activated carbon is depicted for the 2 wt% Pd catalyst. It can be seen that not only does the conversion of CCl_2F_2 (CFC-12) increase, but also the selectivity to CH_2F_2 (HFC-32) increases at the expense of $CHClF_2$ (HCFC-22), and CH_4. The formation of CHF_3 and the formation of coupled products C_2H_6 and C_3H_8 are both strongly suppressed.

This change in selectivities was also found as a function of time on stream. In Fig. 3, the performance for the washed 2 wt% catalyst (Pd2) is depicted at 1 h and at 200 h time on

Table 1
Codes used for catalysts and activated carbons

Code	Description	Code	Description
Pd1	Commercial 2 wt% Pd/C.	C1	Activated carbon.
Pd2	Commercial 2 wt% Pd/HCl washed carbon.	C2	Washed and activated carbon.
Pd3	1 wt% Pd/C2, without N_2 heat treatment.		
Pd4	1 wt% Pd/C2, with N_2 heat treatment.		

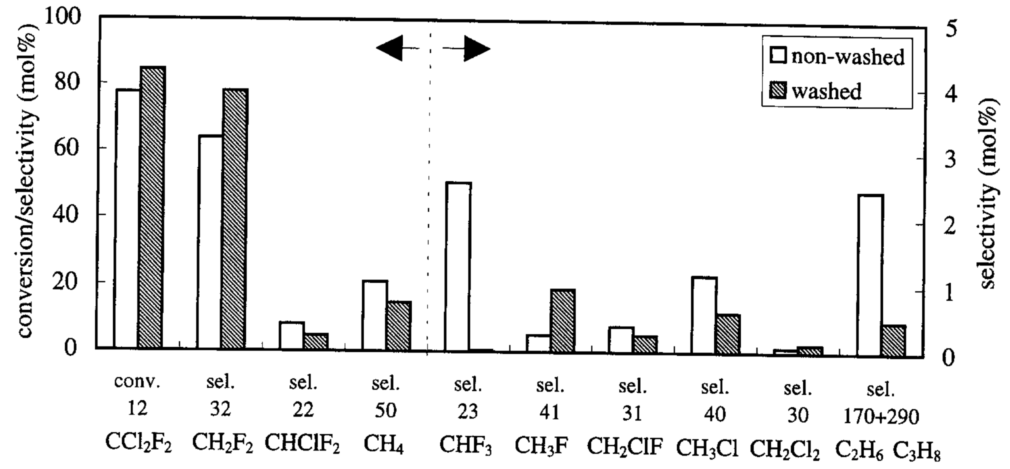

Fig. 2. Performance at 510 K of 2 wt% palladium catalyst on a nonwashed (Pd1) and a washed activated carbon (Pd2) in the hydrogenolysis of CCl_2F_2 (time on stream ≈ 12 h).

stream. The selectivity to CH_2F_2 is increasing at the expense of, in particular CH_4, CH_3F and C_2 and C_3 alkanes. Similar phenomena were observed for the 1 wt% Pd catalyst.

For the 1 wt% Pd catalyst, a nitrogen heat pretreatment at 623 K prior to reaction proves to be beneficial. At 450 K, the activity of the pretreated catalyst increases from 9 to 16% with almost no change in selectivities (see Fig. 4). At the same time, the stability for the pretreated catalyst is significantly improved.

In Table 2, the 1 wt% Pd/C is compared with the 2 wt% commercial catalyst.

In Fig. 5, the performance of the 2 wt% Pd catalyst (Pd2) is plotted when the temperature is stepwise- and cyclic-increased and decreased from 430 to 540 K. All the temperature levels are maintained for 1.5 h and the performance results are averaged. This temperature cycle resulted in an increase in selectivity to CH_2F_2 (HFC-32) at the expense of methane; a minor increase in conversion was observed.

4.2. Characterization

The impurities in the catalysts and in the activated carbons, determined with XRF, are summarized in Table 3. The level of the impuri-

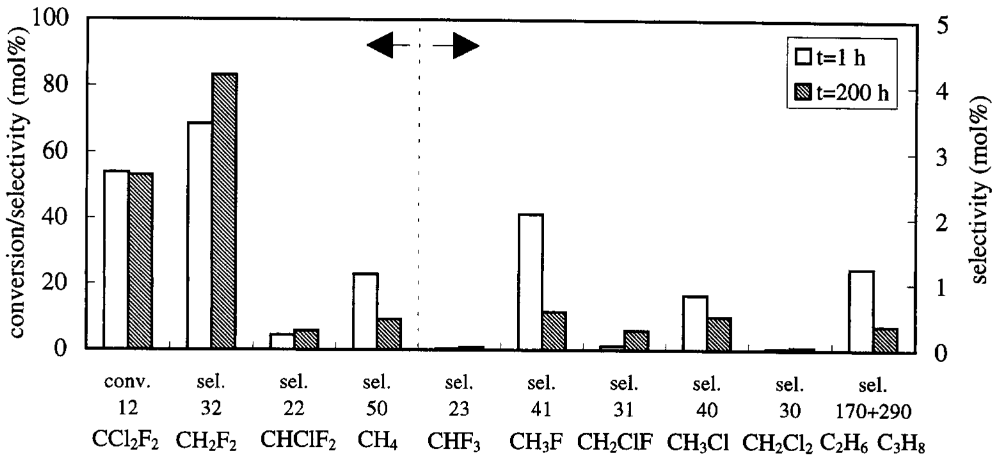

Fig. 3. Performance at 500 K of 2 wt% palladium on washed activated carbon (Pd2) at 1 h and at 200 h in the hydrogenolysis of CCl_2F_2.

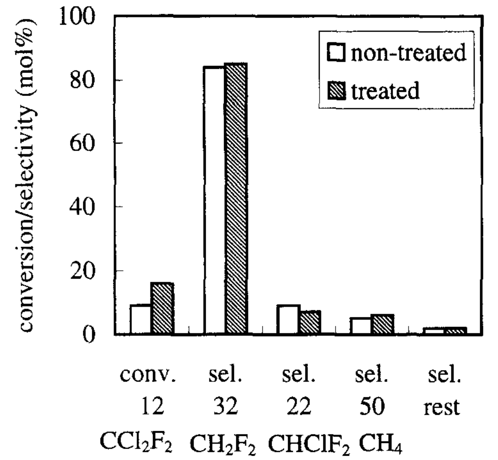

Fig. 4. Performance at 450 K for the 1 wt% Pd catalyst without (Pd3) and with (Pd4) nitrogen heat pretreatment at 623 K.

ties (Mg, Ca, Fe) and the ash content after washing (Pd2, C2, Pd3 and Pd4) are significantly decreased.

The profiles from the XRD and TPR experiments on a fresh and used 2 wt% Pd (Pd2) catalyst are shown in Fig. 6 and Fig. 7, respectively. From XRD, it can be seen that for the used catalyst the peak position is shifted to a lower angle. This shift can be ascribed to the formation of palladium carbide. For the 1 wt% Pd (Pd4) catalyst, no diffraction pattern was found. There is also a difference for the fresh and used catalyst in the TPR-experiments. The fresh catalyst shows an evolution of hydrogen at ≈ 345 K, while for the used catalyst only hydrogen is consumed. This hydrogen evolution was not observed for the fresh 1 wt% (Pd4) catalyst.

The CO-chemisorption and the XRD results are shown in Table 4. Based on the CO-chem-

Table 2

Comparison between 2 wt% Pd (Pd2) and 1 wt% Pd (Pd4) on purified activated carbon catalyst at 470 K (all values are in mol%)

Sample	Conv. CCl_2F_2	Sel. CH_2F_2	Sel. $CHClF_2$	Sel. CH_4	Sel. rest
Pd2 (2 wt%)	27.0	66.9	4.1	26.0	3.0
Pd4 (1 wt%)	39.9	69.4	6.5	19.9	4.2

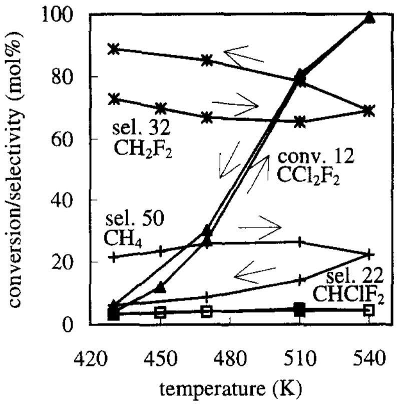

Fig. 5. Performance of washed 2 wt% Pd catalyst (Pd2) as a function of temperature. The temperature is stepwise increased and decreased.

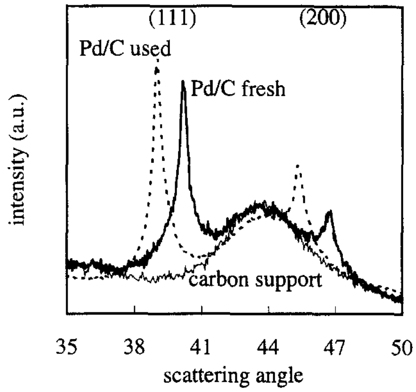

Fig. 6. XRD of fresh and used washed 2% catalyst (Pd2). The carbon support is included.

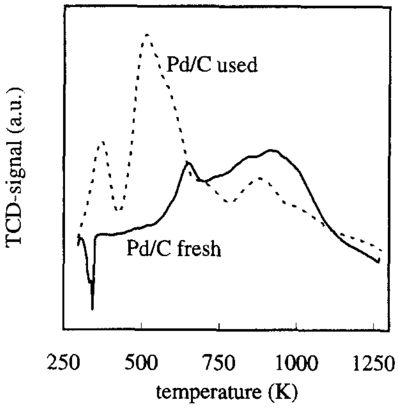

Fig. 7. TPR of fresh and used washed 2% catalyst (Pd2).

Table 3
XRF results

Sample	Na (ppm)	Mg (ppm)	Al (ppm)	Si (ppm)	S (ppm)	K (ppm)	Ca (ppm)	Fe (ppm)	Cl (%)	Pd (%)	Ash (%)
Pd1	0	1190	370	740	1500	21	3000	1240	0	2.02	6.3
Pd2	2100	0	210	750	890	19	2100	260	0.16	1.77	3.7
Pd2 used											2.5
C1	1400	4400	950	2400	1900	730	4000	1190	0	0	5.3
C2	500	400	850	2800	4250	70	350	500	0.94	0	2.4
Pd3	790	340	960	2900	2900	70	310	480	2.54	0.93	3.6
Pd4	320	370	970	2800	3500	70	340	470	1.61	1.00	3.5

Table 4
CO-chemisorption and XRD results

Sample	CO-chemisorption		X-Ray diffraction		
	Adsorbed amount (cm^3 CO/g_{cat})	Av. crystallite size (nm)	Lattice constant (nm)	Phase	Av. crystallite size (nm)
Pd1	0.91	5.2	0.3888	Pd	[a]
Pd2	0.49	9.7	0.3888	Pd	12.2
Pd2 used	0.17	32.1 [b]	0.3996	$PdC_{0.15}$	12.7
Pd3	1.47	1.7	No diffraction pattern		
Pd4	1.73	1.4	No diffraction pattern		
Pd4 used	0.28	8.7	No diffraction pattern		

[a] Not determined because of overlap between signal from impurities and palladium.
[b] Calculated on the assumption of Pd metal.

isorption results, the fresh 1 wt% catalysts (Pd3 and Pd4) have a much higher dispersion than the 2 wt% catalyst (Pd2). There is not much difference in particle size for the 1 wt% catalyst without (Pd3) and with (Pd4) nitrogen heat pretreatment. Also, it can be seen that the amount of adsorbed carbon monoxide is decreased for the used catalysts.

From XRD it can be concluded that the calculated average crystallite size is similar for fresh and used Pd2 catalyst. This is almost identical to the value based on the CO-chemisorption measurements for the fresh one, but the value calculated for the used Pd2 deviates strongly.

5. Discussion

Washing of the activated carbon appears to be an important step in the catalyst preparation. By this procedure, the amount of the impurities is lowered, as found by XRF, and the ash content is decreased. Several impurities like iron and aluminium [9] can act as Friedel–Crafts catalysts and catalyse undesired chlorine/fluorine exchange reactions. The mechanism for this Cl/F-exchange is the Mars and Van Krevelen mechanism [6]. After purification, the formation of CHF_3 (HFC-23) is strongly suppressed. Also, it is found that the amount of methane and coupled products (C_2H_6, C_3H_8) after washing are decreased. This could be explained by the removal of iron which catalyses the formation of these products. It seems that only the accessible impurities are important. Similar results have been reported in a Du Pont patent [10], where a higher selectivity to CF_3CH_2F (HFC-134a) is claimed in the hydrogenolysis of CF_3CCl_2F (CFC-114a) over Pd/C after washing the activated carbon support.

The 1 wt% catalyst (Pd4) gave a higher activity than the 2 wt% catalyst (Pd2). This is possibly caused by the much higher dispersion of the 1 wt% palladium, as found by CO-chemisorption.

The nitrogen heat pretreatment is also a very important parameter in the preparation of the catalyst. The exact reason is not clear, but the nitrogen heat pretreatment gave a more stable and active catalyst. The decrease in the amount of chlorine could play a role.

By increasing the temperature it is possible to obtain complete conversion. It is striking that the selectivity to CH_2F_2 at all conversions is remarkably high and remains unchanged. This supports earlier work [11] in which we concluded that the mechanism for the conversion of CCl_2F_2 proceeds mainly via parallel reaction pathways. The performance of our tested catalysts is significantly better than those in recent literature [12–14].

In Fig. 3 and Fig. 5 it can be seen that the selectivity to CH_2F_2 is remarkably increased as a function of time and after having been used at higher temperatures. Two effects could explain this unexpected behaviour:

(1) *A further lowering of the content of accessible impurities* by the produced HF and HCl takes place and thereby suppresses the chlorine/fluorine exchange and total hydrogenolysis activities. The ash-content of the used 2 wt% (Pd2) catalyst is indeed lowered in comparison to the fresh one (see Table 3).

(2) *A modification of the palladium* takes place which influences the performance. This modification of the palladium is indeed found. The diffraction pattern (Fig. 6) of the used 2 wt% Pd catalyst is shifted to a lower scattering angle compared to the fresh one. From the lattice parameter, it can be concluded that this means that a solid solution of palladium and carbon ($PdC_{0.15}$) has been formed. This phase has also been found by Ziemecki et al. [15], who treated palladium with acetylene, ethylene or carbon monoxide at higher temperatures. The formation of the palladium carbide phase might explain the change in the selectivities. Experiments with palladium black showed [16] that the formation of palladium carbide is a fast process taking place at a time scale in the order of a few hours. The increase in selectivity, however, proceeds over more than 200 h. Therefore, we tentatively conclude that the first explanation is correct, although the second cannot be ruled out completely.

Additional evidence for the formation of palladium carbide stems from the TPR experiments. The fresh 2 wt% catalyst contains rather big palladium particles and, as a consequence, the formation of palladium hydride is possible [17]. When raising the temperature, phase decomposition takes place and palladium and hydrogen are formed (see hydrogen release in Fig. 7). For the used catalyst, no evolution of hydrogen was observed, which indicates that the interfacial spaces are occupied by carbon [18,19].

The particle sizes, calculated from XRD, of the fresh and used 2 wt% catalyst are the same. Also the value for the fresh catalyst, calculated with the CO-chemisorption results, is similar. The used catalyst, however, gives a much larger particle size, which is in contrast with the XRD results. This contradiction may be caused by blocking of the palladium surface for CO by chlorine, which is formed during the reaction, or by carbon, which probably is present due to the formation of palladium carbide.

Similar XRD results were not observed for the 1 wt% catalyst. This can be explained by the fact that the dispersion of the palladium was too high (small particles) to give a diffraction signal and/or that the particles were not crystalline.

In summary, the catalyst is sufficiently active, selective and stable for a practical process. The design of a pilot plant and a commercial plant are currently underway.

6. Conclusions

Purification of the activated carbon by treating with caustic soda and hydrochloric acid is found to be very effective in increasing the selectivity to CH_2F_2 in the hydrogenolysis of CCl_2F_2 over Pd/C. A nitrogen heat pretreatment raised the stability and the activity of the catalyst.

During reaction, the selectivity to the desired product CH_2F_2 increases. Probably, this is due to a removal of impurities by the reaction products HF and HCl.

The overall conclusion is that a very good catalyst has been developed which can convert a waste product CCl_2F_2 (CFC-12) into the high added value product CH_2F_2 (HFC-32).

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