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Journal of Molecular Catalysis A: Chemical 134 (1998) 191–200

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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

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Received 7 October 1997; accepted 11 November 1997

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 accessible impurities by the produced HF and HCl. These impurities, like iron and aluminium are responsible for chlorine/fluorine exchange and total hydrogenolysis activities. The activity, selectivity to CH_2F_2, and the stability of the catalyst is a strong function of the hydrogen to CFC ratio. It was found that during reaction the palladium is converted into palladium carbide. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: CCl_2F_2; CH_2F_2; Hydrogenolysis; Palladium carbide

1. Introduction

Fully halogenated chlorofluorocarbons (CFCs) were developed in the 1930s as refrigerant. Because of their unique properties, like chemical and thermal stability, low toxicity and nonflammability, within two decades they were used in various applications such as blowing agent in foams, 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, the emitted CFCs also 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%.

On the basis of these reports it has been decided that the world-wide production and consumption of CFCs should be terminated by January 1, 1996 [3]. The recovery of CFCs in use and the subsequent destruction is a logical step forward. Many destruction techniques have

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PII: S1381-1169(98)00035-1

been proposed such as combustion, catalytic oxidation, catalytic hydrogenation, pyrolysis processes, chemical destruction, supercritical water oxidation, plasma destruction, ultraviolet destruction and destructive high energy radiation. From these techniques, combustion has been demonstrated on a commercial scale and it proves to be an expensive destruction technology (US$4 per kg CFC).

The long term replacements for CFCs in their application as refrigerant are most probably HFCs. Especially $C_2H_2F_4$ (HFC-134a) is often mentioned, but the total number of possible replacements still increase. 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. 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, 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 [4].

2. Background

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 by Larcher 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 -320 kJ/mol. Besides hydrogenolysis, chlorine/fluorine exchange can also take place. This can lead to the 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 derivatives is depicted in Fig. 1.

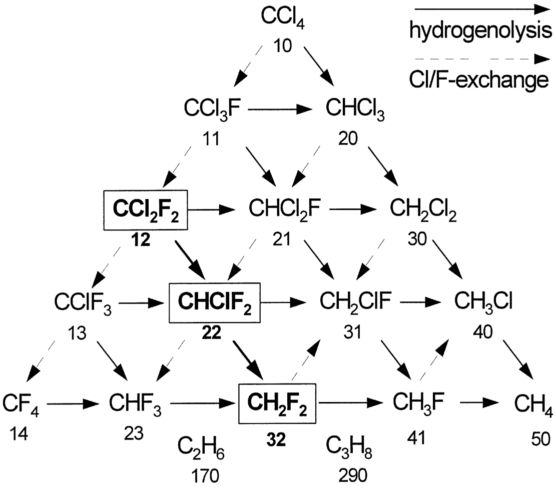

Fig. 1. CFC reaction scheme. The bold formulas and arrows are the reactions aimed at. The direction represents the thermodynamic driving force at 298 K and atmospheric pressure.

Several noble metals on activated carbon support materials have been tested. Palladium

Table 1
Codes used for catalysts and activated carbons

Code	Description
Pd2/C	commercial 2 wt.% Pd/C
Pd2/C-W	commercial 2 wt.% Pd/C-W
Pd1/C-W	1 wt.% Pd/C-W, without N_2 heat treatment
Pd1/C-W/N_2	1 wt.% Pd/C-W, with N_2 heat treatment
C	activated carbon
C-W	washed activated carbon

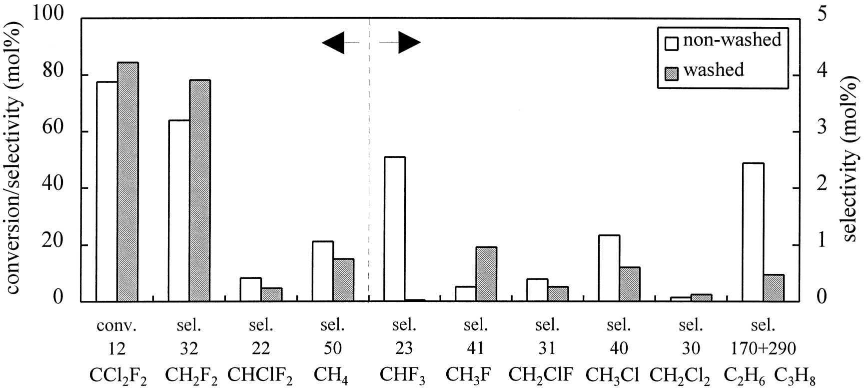

Fig. 2. Performance at 510 K of 2 wt.% Pd catalyst on a non-washed activated carbon (Pd2/C) and a washed activated carbon (Pd2/C-W) in the hydrogenolysis of CCl_2F_2.

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, a commercially available 2 wt.% Pd on activated carbon was included in the investigation. The palladium crystallites are

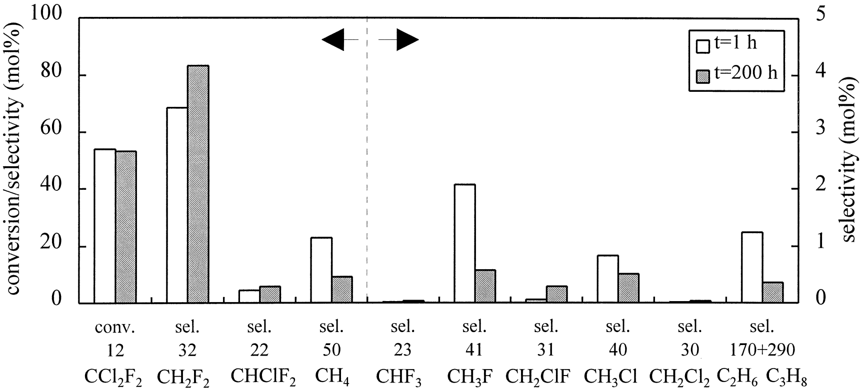

Fig. 3. Performance at 500 K of 2 wt.% palladium on washed activated carbon (Pd2/C-W) at 1 h and at 200 h in the hydrogenolysis of CCl_2F_2.

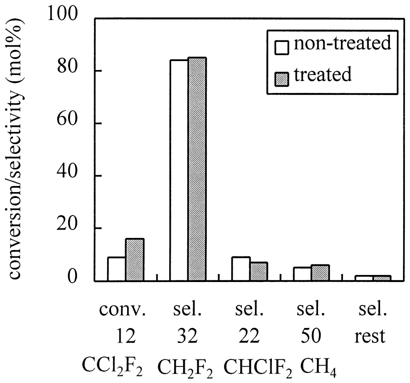

Fig. 4. Performance at 450 K for the 1 wt.% Pd catalyst without (Pd1/C-W) and with (Pd1/C-W/N_2) nitrogen heat pretreatment at 623 K.

in the order of 10 nm, which makes the characterization relatively simple.

A Hastelloy-C fixed-bed micro-catalytic reactor was employed to conduct the 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 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 K_α 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 (≈ 100 mg) diluted with non-porous 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 ones 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. The codes for the catalysts and carbons used are shown in Table 1.

4. Results

4.1. Performance measurements

4.1.1. Washing of the catalyst support (activated carbon)

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 the conversion of CCl_2F_2 (CFC-12) increases, but also the selectivity to CH_2F_2 (HFC-32) 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 selectivity was also found as a function of time on stream. In Fig. 3, the perfor-

Table 2
Comparison between 2 wt.% Pd (Pd2/C-W) and 1 wt.% Pd (Pd1/C-W/N_2) 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/C-W	27.0	66.9	4.1	26.0	3.0
Pd1/C-W/N_2	39.9	69.4	6.5	19.9	4.2

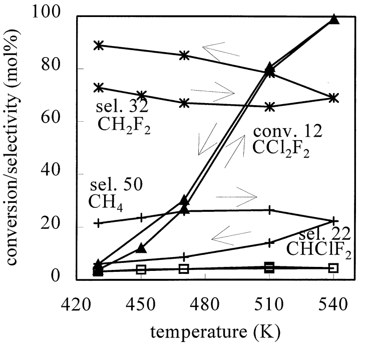

Fig. 5. Performance of washed 2 wt.% Pd catalyst (Pd2/C-W) as a function of temperature. The temperature is stepwise increased and decreased.

mance for the washed 2 wt.% catalyst (Pd2/C-W) is depicted at 1 h and at 200 h time on 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.

4.1.2. Catalyst pretreatment procedure

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 selectivity (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.

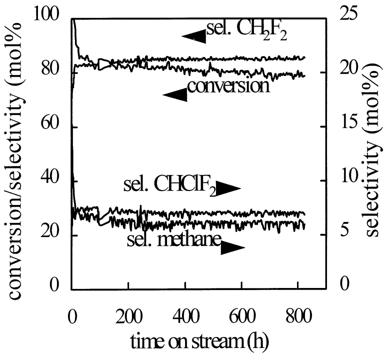

Fig. 6. Performance of 1 wt.% Pd catalyst (Pd1/C-W/N_2) at 510 K and H_2/CCl_2F_2 feed ratio of 6 mol/mol (Conditions: $P = 0.2$ MPa and WHSV = 0.5 g/(g h)).

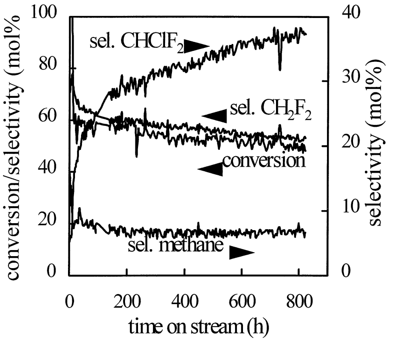

Fig. 7. Performance of 1 wt.% Pd catalyst (Pd1/C-W/N_2) at 510 K and H_2/CCl_2F_2 feed ratio of 1.5 mol/mol (Conditions: $P = 0.2$ MPa and WHSV = 0.5 g/(g h)).

In Fig. 5, the performance of the 2 wt.% Pd catalyst (Pd2/C-W) 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. At the same time, the stability of the catalyst, pretreated in this cyclic temperature procedure, is improved once again.

4.2. Stability as function of H_2/CFC ratio

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

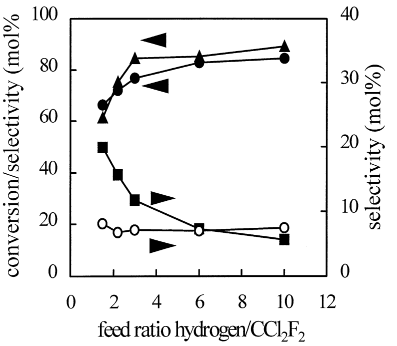

Fig. 8. Initial performance of 1 wt.% Pd catalyst (Pd1/C-W/N_2) as a function of molar H_2/CCl_2F_2 feed ratio (Conditions: $T =$ 510 K, WHSV = 0.5 g/(g h), $P = 0.2$ MPa, ▲ = conversion, ● = selectivity for CH_2F_2, ■ = selectivity for $CHClF_2$, ○ = selectivity for methane).

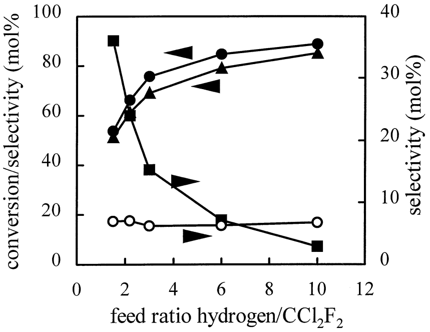

Fig. 9. Performance of 1 wt.% Pd catalyst (Pd1/C-W/N_2) after 700 h on stream as a function of H_2/CCl_2F_2. (For symbols and conditions see the legends of Fig. 8).

activated carbon 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. 6 and 7, the performance of the catalysts as 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, 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. 8. At the low hydrogen to CFC feed ratios, both the conversion and the selectivity for $CHClF_2$ increases. After 700 h on stream, these differences become more pronounced as can be seen in Fig. 9. Figs. 8 and 9 illustrate the catalyst deactivation as a function of the hydrogen to CFC feed ratio (Fig. 8 shows the initial catalyst performance and Fig. 9 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 $CHClF_2$. 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 3. Only minor deactivation is observed after 700 h on stream for a hydrogen to CCl_2F_2 ratio above 6. From data presented in Table 3 and data not shown an optimum hydrogen to CCl_2F_2 feed ratio of 12 has been found. At higher hydrogen to CFC feed ratio the palladium catalyst showed a pronounced deactivation in comparison to the shown deactivation data at ratios between 6 and 10.

4.3. Characterization

The impurities in the catalysts and in the activated carbons, determined with XRF, are summarized in Table 4. The level of the impurities (Mg, Ca, Fe) and the ash content after

Table 3
Performance and deactivation of 1 wt.% Pd catalyst (Pd1/C-W/N_2) 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)

H_2/CCl_2F_2 (mol/mol)	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

Table 4
XRF results

Sample	Na (ppm)	Mg (ppm)	Al (ppm)	Si (ppm)	S (ppm)	K (ppm)	Ca (ppm)	Fe (ppm)	Cl (%)	Pd (%)	Ash (%)
Pd2/C	0	1190	370	740	1500	21	3000	1240	0	2.02	6.3
Pd2/C-W	2100	0	210	750	890	19	2100	260	0.16	1.77	3.7
Pd2/C-W used	–	–	–	–	–	–	–	–	–	–	2.5
C	1400	4400	950	2400	1900	730	4000	1190	0	0	5.3
C-W	500	400	850	2800	4250	70	350	500	0.94	0	2.4
Pd1/C-W	790	340	960	2900	2900	70	310	480	2.54	0.93	3.6
Pd1/C-W/N_2	320	370	970	2800	3500	70	340	470	1.61	1.00	3.5

washing (Pd2/C-W, C-W, Pd1/C-W and Pd1/C-W/N_2) are significantly lower.

The profiles from the XRD and TPR experiments on a fresh and used 2 wt.% Pd (Pd2/C-W) catalyst are shown in Figs. 10 and 11, respectively. From XRD, it can be seen that for the used catalyst the peak position is shifted to a lower angle. For the 1 wt.% Pd (Pd1/C-W/N_2) 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.% (Pd1/C-W/N_2) catalyst.

The CO-chemisorption and the XRD results are shown in Table 5. Based on the CO-chemisorption results the fresh 1 wt.% catalysts (Pd1/C-W and Pd1/C-W/N_2) have a much higher dispersion than the 2 wt.% catalyst (Pd2/C-W). There is not much difference in particle size for the 1 wt.% catalyst without (Pd1/C-W) and with (Pd1/C-W/N_2) nitrogen heat pre-treatment. 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 the same for the fresh and the used 2 wt.% Pd catalyst (Pd2/C-W). This is almost identical to the value based on the CO-chemisorption measurements for the fresh one, but the value calculated for

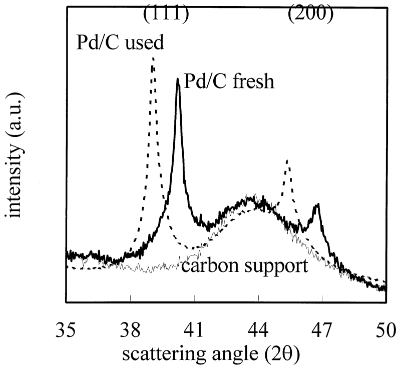

Fig. 10. XRD of fresh and used washed 2 wt.% Pd catalyst (Pd2/C-W). Also the carbon support is included.

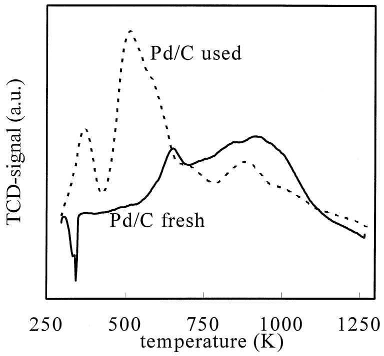

Fig. 11. TPR of fresh and used washed 2 wt.% Pd catalyst (Pd2/C-W).

Table 5
CO-chemisorption and XRD results

Sample	CO-chemisorption		X-ray diffraction		
	Adsorbed amount (cm^3 CO/g_{cat})	Av. crystallite size (nm)	Lattice diameter (nm)	Phase	Av. crystallite size (nm)[aa]
Pd2/C	0.91	5.2	0.3888	Pd	
Pd2/C-W	0.49	9.7	0.3888	Pd	12.2
Pd2/C-W/used	0.17	32.1	0.3996	$PdC_{0.15}$	12.7
Pd1/C-W	1.47	1.7	no diffraction pattern		
Pd1/C-W/N_2	1.73	1.4	no diffraction pattern		
Pd1/C-W/N_2/used	0.28	8.7	no diffraction pattern		

[a] Not determined because of overlap between signal from impurities and palladium.

the used 2 wt.% Pd catalyst (Pd2/C-W) deviates strongly.

5. Discussion

5.1. Catalyst preparation

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 catalyze the 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 catalyzes 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_3CClF_2 (CFC-114a) over Pd/C after washing the activated carbon support.

The 1 wt.% Pd catalyst (Pd1/C-W/N_2) gave a higher activity than the 2 wt.% Pd catalyst (Pd2/C-W). This is probably caused by the much higher dispersion of the 1 wt.% palladium, as found by CO-chemisorption.

The nitrogen heat pre-treatment is also a very important parameter in the preparation of the catalyst. The exact reason is not clear but the nitrogen heat pre-treatment 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 [11,12] 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 [13–15].

5.2. Catalyst stability

The catalyst activity, selectivity, and stability are simultaneously influenced by the hydrogen to CFC feed ratio. Also the time on stream needed to reach a steady-state catalyst performance depends on this ratio. Apparently, it takes some time before the adsorption/desorption equilibria have been established. The catalyst deactivation at lower hydrogen to CFC feed ratio can be tentatively explained by coke formation on the catalyst surface. As the hydrogen concentration is increased, coke precursors are hydrogenated from the catalyst surface. The amount of ethane and propane, which can be an indication for the coke formation, is proportional to the deactivation and to the hydrogen to CFC feed ratio. It can, however, be expected that the hydrogen concentration cannot be increased infinitely, because palladium is expected to sinter easily at 100% hydrogen atmosphere at reaction conditions. On the other hand CFCs can be expected to regenerate a deactivated palladium on an activated carbon support [10]. Therefore, catalyst stability can be obtained when the hydrogen concentration is high enough to prevent coke formation and the CFC concentration is high enough for in-situ stabilization of the palladium dispersion. This explains the stable operation at the optimal hydrogen to CFC feed ratio of 12. At hydrogen to CFC feed ratio lower than 6 coke formation is probably the main cause of deactivation, whereas at hydrogen to CFC feed ratio higher than 12 sintering of the palladium is expected to be the main cause of deactivation. In other words, the presence of an optimum in activity and selectivity as a function of the palladium dispersion could explain the observed phenomena.

5.3. Catalyst characterization

In Figs. 3 and 5, it can be seen that the selectivity to CH_2F_2 is remarkably increased as a function of time on stream and after having been at higher temperatures. This unexpected behaviour could be explained by two effects.

(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/C-W) catalyst is indeed lowered in comparison to the fresh one (see Table 4).

(2) A modification of the palladium takes place which influences the performance. This modification of the palladium is found indeed. The diffraction pattern (Fig. 10) of the used 2 wt.% Pd catalyst (Pd2/C-W) 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. [16] 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 selectivity. Experiments with palladium black showed [6] 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. 11). For the used catalyst, no evolution of hydrogen was observed, which indicates that the interstitial spaces are occupied by carbon [18,19].

The particle size, calculated from XRD, of the fresh and used 2 wt.% catalyst is the same. Also the value for the fresh catalyst, calculated with the CO-chemisorption results, is similar. The used catalyst, however, gives a much higher 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 which can be explained by the limited accuracy of the measurement.

In summary, the catalyst is sufficiently active, selective and stable for a practical process.

The design of a pilot plant and a commercial plant is currently being made.

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 pre-treatment in the combination with a cyclic temperature procedure in the presence of hydrogen and CFC 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 stability of the catalyst proves to be a function of the hydrogen to CFC feed ratio. An optimum ratio of 12 was found.

It was found that during the reaction the palladium on activated carbon was converted into palladium carbide on activated carbon.

The overall conclusion is that a very selective and stable catalyst, namely: 1 wt.% palladium on purified activated carbon, 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).

Acknowledgements

The authors would like to thank Herman van Bekkum for his scientific contributions and his very stimulating discussions. Norit, Amersfoort, The Netherlands and Engelhard de Meern, The Netherlands are greatfully acknowledged for their gift of the activated carbon and the palladium catalyst, respectively. The authors also acknowledge AKZO-Nobel, the Dutch Ministry of Housing and Environmental Affairs, AlliedSignal Fluorocarbon Europe, Johnson Matthey, KTI, and the European Union for the financial support.

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