

Comparison of the Performance of Activated Carbon-Supported Noble Metal Catalysts in the Hydrogenolysis of CCl_2F_2

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Received February 12, 1997; revised March 23, 1998; accepted March 25, 1998

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, $\text{H}_2/\text{CCl}_2\text{F}_2$ feed ratios between 1.5 and 6, a pressure of 0.4 MPa, and a WHSV of 1 g/(g·h). The main products of the reaction for all investigated catalysts were CHClF_2 , CH_2F_2 , and methane. According to their performance, the catalysts could be divided into four groups: rhenium showing no conversion of CCl_2F_2 , palladium with a high selectivity for CH_2F_2 , iridium and ruthenium with a high selectivity for CHClF_2 , and platinum and rhodium with moderate selectivity for CHClF_2 and CH_2F_2 . The adsorption of chlorine on the metal surface plays an important role in the selectivity. Strong chlorine adsorption leads to a higher selectivity for CHClF_2 . These results are consistent with a reaction mechanism in which difluorocarbene is the key intermediate. Apparently, the same kinetic network applies to all metals studied. The performance of the catalysts changed as a function of time on stream. Palladium, rhodium, and especially ruthenium deactivated during reaction, whereas the activity of iridium and platinum increased. This can be explained by two opposite effects. On the one hand, the dispersion of all catalysts increased during reaction, which can explain an increase in activity as a function of time on stream. Apparently, CCl_2F_2 hydrogenolysis conditions are suitable for dispersing noble metal catalysts on activated carbon. On the other hand, deactivation takes place by the adsorption of chlorine and deposits of heavy halogenated products. © 1998 Academic Press

INTRODUCTION

It is accepted that fully halogenated chlorofluorocarbons (CFCs) are partly responsible for depletion of the ozone layer (1). World-wide production and consumption of new CFCs has, therefore, been terminated, but considerable amounts are still present in all kinds of applications (2) (estimated 2.25 Mton; ~45% CCl_2F_2 and ~45% CCl_3F). The recovery and subsequent destruction of these substances is an on-going process. Obviously, the conversion of CFCs into valuable chemicals is a better option than destruction.

At Delft University of Technology, a catalytic process is under development for the conversion of CCl_2F_2 into CH_2F_2 , which can be used in refrigerant applications (3). There is no systematic study available with a comparison of the performance of activated carbon-supported noble metal catalysts in the hydrogenolysis of CCl_2F_2 will be presented. Activated carbon is selected as a readily available support material, which is stable under the corrosive reaction conditions.

Ohnishi *et al.* reported the activity and selectivity of 5 wt% Rh, Pt, Pd, and Ru on $\gamma\text{-Al}_2\text{O}_3$ in the hydrogenolysis of the related compound $\text{CCl}_2\text{F}-\text{CClF}_2$ (CFC-113) (4). They showed that especially Pd is active and selective in the removal of only chlorine atoms.

Supported palladium catalysts have been reported as suitable catalysts for the selective hydrogenolysis of CCl_2F_2 into CH_2F_2 (5–10) and are also claimed to be applicable for the selective hydrogenolysis of CHClF_2 into CH_2F_2 (11). In the patent literature on the hydrogenolysis of $\text{C}_2\text{-CFCs}$, palladium on activated carbon is claimed to be an excellent catalyst for the selective conversion of $\text{CCl}_2\text{F}-\text{CF}_3$ and $\text{CHClF}-\text{CF}_3$ into $\text{CH}_2\text{F}-\text{CF}_3$ (12, 13), but also other supported metal catalysts have been reported (14–16). Generally, supported noble metal catalysts, such as palladium, ruthenium, rhodium, iridium, rhenium, and platinum can be expected to catalyze hydrogenolysis of carbon-halogen bonds. Palladium seems to be of interest for the selective removal of all chlorine atoms, whereas iridium is especially claimed for the selective removal of one chlorine atom (8). The performance of platinum on Al_2O_3 has been studied in several reactions. Depending on the reaction conditions and reactant used different results were obtained. Weiss *et al.* reported the main product ratio $\text{CHCl}_3/\text{CH}_4 = 4$ for the catalytic hydrogenolysis of CCl_4 with a 0.5 wt% Pt on $\eta\text{-Al}_2\text{O}_3$ catalyst (17). Ohnishi *et al.* found a high selectivity for $\text{CHClF}-\text{CClF}_2$ (61 mol% at 17 mol% conversion) in the hydrogenolysis of $\text{CCl}_2\text{F}-\text{CClF}_2$ over a 5 wt% Pt on Al_2O_3 catalyst (4). On the other hand, Bell *et al.* (18) reported a high selectivity for methane (62–80 mol% at 25–40 mol% conversion) for a 2 wt% Pt on $\gamma\text{-Al}_2\text{O}_3$ catalyst

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in the catalytic hydrogenolysis of CCl_2F_2 . Other catalysts comprising of nickel, molybdenum, aluminum, titanium, or iron have been claimed as possible catalysts (19), but these catalysts generally require higher temperature and pressure and their performance is worse since unwanted side reactions such as chlorine/fluorine exchange reactions can also be catalyzed by some of these metals (e.g., aluminum and iron) (20). The performance of claimed homogeneous catalysts, such as ZnCl_2 or LiAlH_4 , for the reaction seems not to be of practical importance (21, 22).

Ahn *et al.* reported that the adsorption of CFCs on the surface of a 3.45 wt% Pd/ AlF_3 catalyst is very important for the kinetics of the hydrogenolysis of CCl_2F_2 (10). It can be anticipated that the adsorption of chlorine or fluorine on the catalyst surface can play an important role. This has been suggested by Coq *et al.* for the hydrogenolysis of chlorobenzene over palladium (23) and by Campbell and Kemball for both the hydrogenolysis of ethyl chloride (24) and *tert*-butyl chloride (25). Therefore, not only the adsorption of the CFCs has to be taken into account, but also the adsorption behaviour of the intermediate species, chlorine and fluorine, should be considered.

In this study a comparison of the performance of the noble metal on activated carbon catalysts will be presented in combination with results of catalyst characterization techniques such as X-ray fluorescence (XRF), temperature programmed reduction (TPR), and high resolution transmission electron microscopy (HTREM). Furthermore, adsorption measurements of CCl_2F_2 , CHClF_2 , and CH_2F_2 on the metals applied will be discussed.

EXPERIMENTAL

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. 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 (26) was used (~90% purity).

Catalyst Preparation

Fifty grams of activated carbon support was sequentially washed with 5 liters 0.5 M aqueous sodium hydroxide,

5 liters water, 5 liters 0.5 M aqueous hydrochloric acid, and 5 liters 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.

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 multimicroflow-reactor setup with six parallel reactors. Temperature, weight hourly space velocity (WHSV, defined as g CCl_2F_2 feed per 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 microcatalytic reactors. The performance of the catalysts was determined by an on-line gaschromatograph, equipped with a 75 m \times 0.53 mm Ultimet Q column (Chrompack), a thermal conductivity detector, and a flame-ionization detector. Conversion and selectivities were calculated on the basis of the products formed.

TABLE 1
Experiment Sequence

Experiment no. (–)	Duration (h)	Temperature (K)	$\text{H}_2/\text{CCl}_2\text{F}_2$ (–)
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

Note. Other conditions: WHSV = 1 g/(g · h); P = 0.4 MPa.

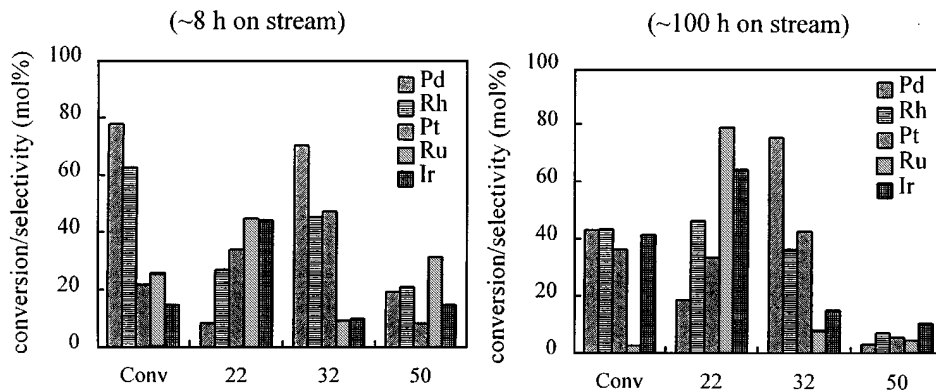


FIG. 1. The initial (~ 8 h on stream) and final (~ 100 h on stream) performance of the different catalysts during the experimental sequence (conditions: $T = 500$ K; $P = 0.4$ Mpa; $WHSV = 1\text{g}/(\text{g}\cdot\text{h})$, and $\text{H}_2/\text{CCl}_2\text{F}_2 = 3$. Abbreviations: Conv = CCl_2F_2 conversion; 22 = selectivity for CHClF_2 ; 32 = selectivity for CH_2F_2 ; and 50 = selectivity for CH_4).

Catalyst Characterization

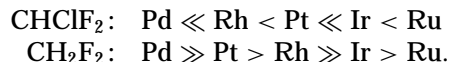
Temperature programmed reduction (TPR) was performed with a home-made TPR apparatus. Catalyst samples (100 to 200 mg) diluted with nonporous SiC were heated with 0.167 K/s in a flow of 0.208 ml/s of 5 vol% hydrogen in argon. The hydrogen consumption was determined by a calibrated thermal conductivity detector (TCD), comparing the thermal conductivity of reactor gas feed and dried reactor effluent. Adsorption isotherms of CCl_2F_2 , CHClF_2 , and CH_2F_2 on palladium black, ruthenium black, rhodium black, iridium black, and platinum black were measured on a NOVA 1200 apparatus from Quantachrome at 300 and 373 K. Prior to adsorption the sample was reduced with hydrogen at 300 K and evacuated at 423 K for 1 h. Pore size distributions and BET surface areas were determined using nitrogen adsorption isotherms measured at 77 K on an Autosorb 6b apparatus from Quantachrome. The samples have been evacuated at 423 K for 16 h prior to the measurement. X-ray fluorescence (XRF) measurements were performed for semiquantitative determination of the impurities and metal loading using a Philips PW 1480 apparatus. High resolution transmission electron microscopy (HTREM) has been executed using a Philips CM 30 ST microscope with a field emission gun (FEG) as source of electrons, operated at 300 kV. Samples were deposited on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

RESULTS

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:



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, although initially a high selectivity for ethane is found (not shown). 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.

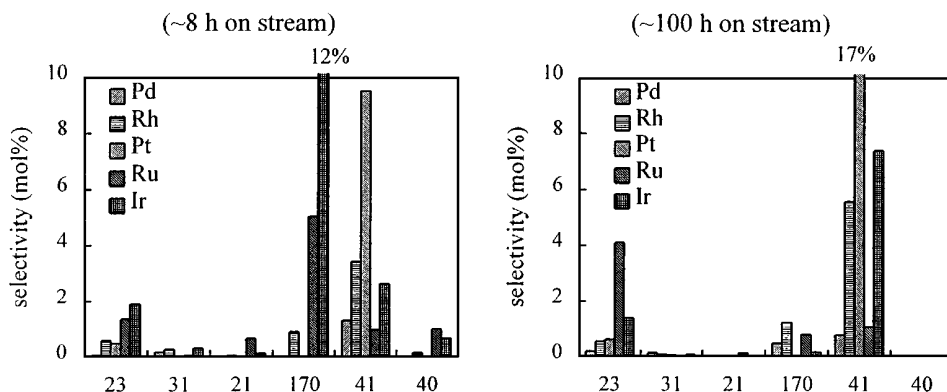


FIG. 2. The initial and final selectivities for by-products (abbreviations: 23 = CHF_3 ; 31 = CH_2ClF ; 21 = CHCl_2F ; 170 = ethane; 41 = CH_3F ; and 40 = CH_3Cl . For conditions, see Fig. 5).

Figures 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. These effects are shown in Table 2, in which the conversion of the catalysts at the reference experiment numbers 2, 5, 10, and 15 are given.

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.

Catalyst Characterization

The impurities in the catalysts, determined with XRF, are summarized in Table 3. Fresh and purified activated

TABLE 2

CCl_2F_2 Conversion (in mol%) for the Different Metal Catalysts at the Reference Experiment Numbers

Experiment	Pd	Rh	Pt	Ru	Ir
2	77.7	47.6	21.8	26.0	14.8
5	65.2	57.4	30.6	21.7	20.3
10	43.0	44.8	37.2	3.5	44.9
15	42.9	43.9	37.8	3.0	41.3

Note. Conditions: $T = 500$ K; $P = 0.4$ MPa; $\text{H}_2/\text{CCl}_2\text{F}_2 = 3$; $\text{WHSV} = 1$ g/(g · h).

carbon are given as reference. It should be noted, that XRF is a semiquantitative analysis method for determination of the bulk composition of a catalyst. It can be seen that the total amount of impurities except chlorine has decreased slightly after use of the catalyst. Especially the silicon content decreases. The decrease of the impurities present in the catalyst is similar for all investigated catalysts. Generally the amount of chlorine of used catalysts is higher than that of fresh catalysts. The amount of chlorine is too high for the chlorine to be present on the metal surface only and it can be concluded, that a substantial fraction of the chlorine is present on the carbon support. The main difference in the TPR profiles between fresh and used catalysts, shown in Fig. 3, is the peak which appears around 600 K for used catalysts. Generally, fresh catalysts show one or more peaks at temperatures between 300 and 550 K and a broad peak around 800 K. Used catalysts, however, give a distinct peak above 600 K and a broad peak around 900 K. The area, temperature of the onset and maximum of the peak above 600 K are summarized in Table 4. The area, reported as atomic hydrogen to metal ratio has been calculated using the assumption that only hydrogen consumption occurs during the TPR measurement. In the discussion it will be shown that the reactions, which occur during the TPR measurement, are more complex. The value, reported as H/metal, is an indication for the area of the peak around 600 K, and should not be used to estimate the stoichiometry of the reaction between hydrogen and metal species. Table 4 shows that the temperature of the onset and the maximum of the peak around 600 K are in the order of $\text{Pd} < \text{Pt} \sim \text{Rh} < \text{Ir} < \text{Ru}$. Furthermore, the peak at higher temperatures (800–900 K) is significantly smaller for the used catalyst than for the fresh catalysts.

Since CO chemisorption is not a feasible method for determination of the dispersion of used catalysts, and, therefore, the size of the metal particles had determined by high resolution transmission electron microscopy (HTREM). The HTREM micrographs of the fresh and used palladium and iridium catalysts are depicted in Fig. 4. These

TABLE 3
XRF Analysis of Fresh (f) and Used (u) Catalysts and Fresh (f) and Purified (p) Activated Carbon (AC)

Sample	Na	Mg	Al	Si	S	Cl	Ca	Cu	Fe	M
AC (f)	0.11	0.57	0.13	0.37	0.55	0.00	0.45	—	0.14	—
AC (p)	0.08	0.03	0.08	0.28	0.43	0.83	0.04	0.004	0.04	—
Pd (f)	0.05	0.04	0.16	0.27	0.37	2.12	0.03	0.005	0.04	0.89
Pd (u)	0.08	0.03	0.11	0.03	0.34	4.60	0.02	0.006	0.03	0.96
Rh (f)	0.02	0.03	0.10	0.26	0.35	2.14	0.03	0.005	0.04	0.85
Rh (u)	0.11	0.02	0.08	0.10	0.34	2.83	0.03	0.004	0.04	0.92
Pt (f)	0.11	0.04	0.14	0.29	0.34	1.96	0.03	0.005	0.04	1.01
Pt (u)	0.14	0.05	0.09	0.23	0.16	5.00	0.03	0.004	0.03	0.85
Ru (f)	0.09	0.04	0.09	0.25	0.34	2.52	0.03	0.004	0.04	0.92
Ru (u)	0.09	0.03	0.07	0.04	0.29	2.44	0.03	0.003	0.03	0.79
Ir (f)	0.09	0.03	0.08	0.26	0.23	1.49	0.03	0.005	0.04	0.85
Ir (u)	0.04	0.02	0.07	0.04	0.27	3.48	0.03	0.004	0.03	0.73

Note. M = metal loading; values are in wt%.

micrographs clearly illustrate the trend in increased dispersion of the catalysts after reaction. The metal particles are more homogeneously distributed over the used catalysts, and the absolute number of particles found on the fresh catalysts are lower, as shown in Table 5. The particles are mainly found in clusters on all investigated catalysts. Figure 4A shows a palladium particle on a fresh catalyst of about 20 nm in diameter, whereas in Fig. 4B, which shows the used palladium catalyst, more palladium particles of smaller size (3 to 10 nm) are observed. For the fresh and

used iridium catalyst, shown in Figs. 4C and D, respectively, a similar behaviour is observed. Figure 4C shows two particles of 5 and 10 nm for the iridium catalyst, whereas the particles size of the used iridium catalyst, as depicted in Fig. 4D, is about 1 nm. The trend in the results of the estimated particle sizes by means of analysis of the HTREM micrographs for all catalysts are summarized in Table 5. This table shows that the mean particle sizes of the all metals are smaller for used catalysts. As illustrated by the number of particles found, the metals are more homogeneously

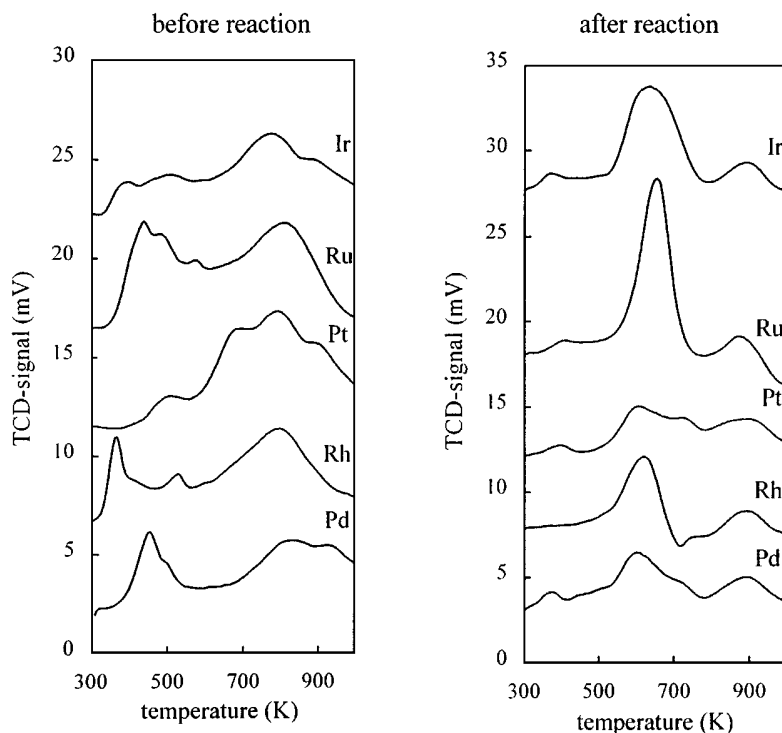


FIG. 3. TPR profiles of 100 mg of fresh and used 1 wt% metal catalysts.

TABLE 4

Area, Reported as H/Metal, Onset and Peak Maxima Temperatures in TPR Profiles for the Used 1 wt% Catalysts

Metal	H/metal (mol/mol)	Temperature onset (K)	Temperature max (K)
Pd	6.1	520	600
Rh	8.5	525	620
Pt	8.3	526	606
Ru	13.7	571	652
Ir	20.6	536	632

distributed on the used catalysts than on the fresh catalysts. Especially for the used platinum and rhodium catalysts the absolute number of particles found is larger. Energy dispersive analysis X-ray (EDX) measurements showed that no extremely disperse Pt or Rh phases, invisible in the micro-

scope, are present on the surface of the activated carbon, neither in the fresh nor in the used catalysts.

CFC Adsorption Measurements on Pure Metals

In order to determine the adsorption behaviour of the CFCs on the metal surfaces the adsorption isotherms of CCl_2F_2 , CHClF_2 , and CH_2F_2 were measured. In order to avoid adsorption on the activated carbon, unsupported metals with a high surface area were used (metal blacks). Before and after the adsorption measurement the BET-surface area was determined in order to check for agglomeration. The results of these measurements are given in Table 6. Palladium and platinum have sintered during the adsorption measurement. This is most probably caused by the reduction step prior to adsorption which could not be sufficiently controlled. Apparently palladium and platinum are more sensitive for sintering than the other metals applied. Thus, the results of the adsorption measurement

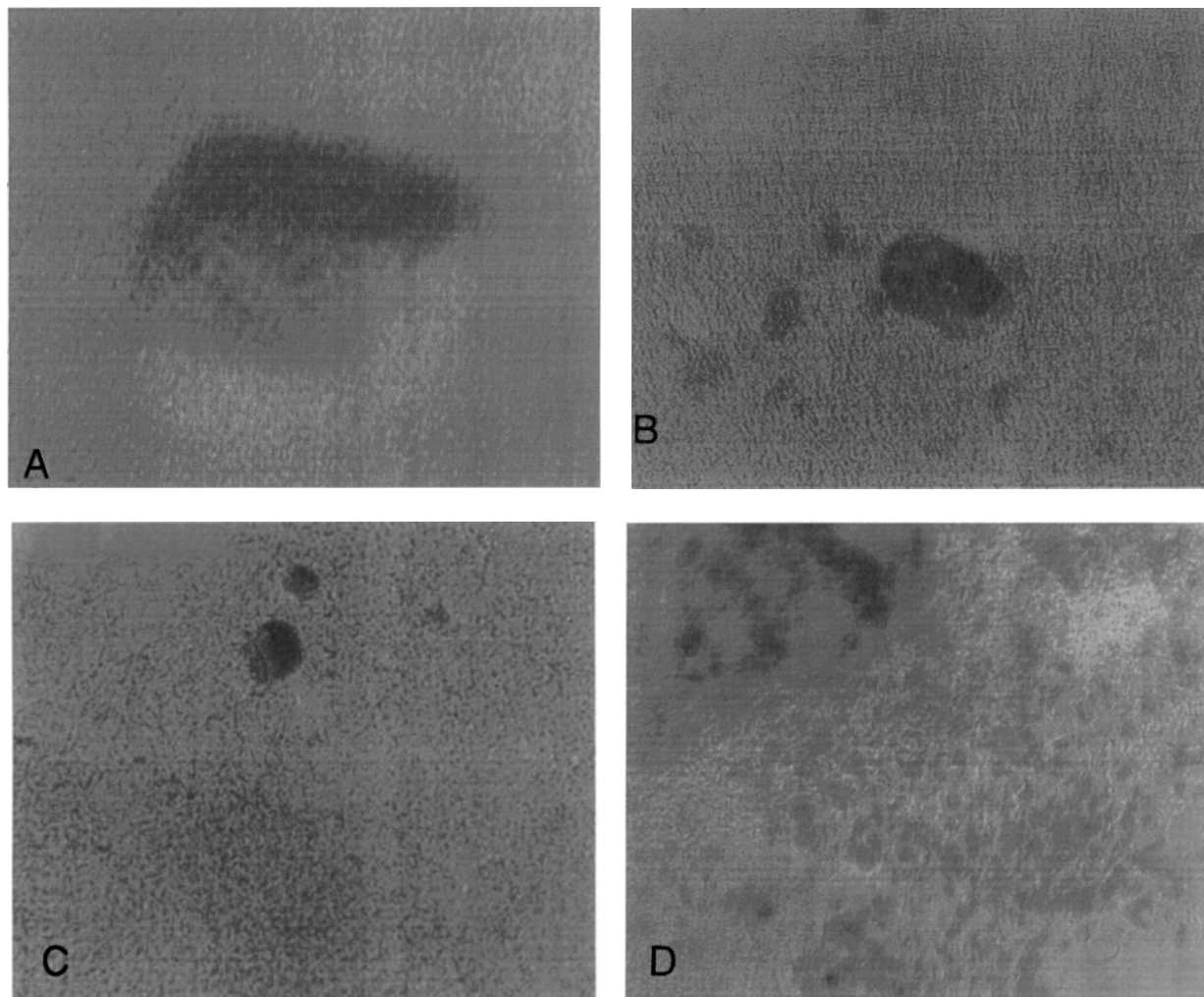


FIG. 4. HREM micrographs of fresh and used catalysts (10 nm each): A, 1 wt% palladium on activated carbon fresh; B, 1 wt% palladium on activated carbon used; C, 1 wt% iridium on activated carbon fresh; D, 1 wt% iridium on activated carbon used.

TABLE 5

Particles Sizes from HTREM Results

Metal	Largest (nm)	Smallest (nm)	Number of particles found	Mean (nm)
Pd (f)	43	6	22	18
Pd (u)	17	1	102	6
Ir (f)	37	1	103	7
Ir (u)	8	0.5	263	3
Pt (f)	9	—	1	9
Pt (u)	12	0.5	225	4
Rh (f)	39	22	4	28
Rh (u)	14	1	64	5
Ru (f)	89	29	10	30
Ru (u)	19	1	14	3

can best be interpreted using the surface area of the used catalysts. The behaviour of all metals in the adsorption of CCl_2F_2 , CHClF_2 , and CH_2F_2 was similar. In Table 7 the adsorbed amounts of the different CFCs at 100 kPa are given. We conclude from the shape of the adsorption isotherms that the type of adsorption represents unrestricted multi-layer adsorption of CCl_2F_2 , CHClF_2 , and CH_2F_2 , both at 300 and 373 K, and only physisorption is observed.

DISCUSSION

In separate experiments, it was shown that mass transfer limitation was not important and that plug flow behaviour was approached (27). Therefore, mass transfer limitations will not be included in the discussion.

The interpretations of the experimental results are complicated because of the changing behaviour of the catalysts as a function of time on-stream. Other authors (5, 10) used a severe pretreatment procedure for palladium to obtain a steady-state catalyst. We, however, prefer to include the initial differences and the changes in catalyst performance as a function of time on-stream in the interpretation of the results. Several explanations for the changing catalyst performance as a function of time on-stream are possible:

1. Further removal of impurities from the activated carbon support, responsible for formation of by-products;

TABLE 6

BET Surface Area of Some Noble Metals

Metal black	S_{BET} fresh (m^2/g)	S_{BET} spent (m^2/g)
Pd	12.5	5.6
Pt	30.5	8.9
Ir	19.5	19.2
Rh	56.5	43.4
Ru	41.2	38.4

Note. See text for experimental details.

TABLE 7

Adsorbed Amount of CFC (ml vapour/g) on Different Metals at 100 kPa at 300 and 373 K

CFC	T (K)	Pd	Pt	Ir	Rh	Ru
CCl_2F_2	300	5.7	10.0	4.9	6.9	10.2
CHClF_2	300	8.5	8.4	4.5	10.7	8.9
CH_2F_2	300	2.5	4.1	3.7	6.6	6.2
CCl_2F_2	373	5.7	3.9	3.9	7.1	4.5
CHClF_2	373	5.8	6.7	2.9	6.3	6.2
CH_2F_2	373	2.2	3.6	2.5	3.0	3.9

2. Modification of the active metal phase;
3. Changing metal dispersion;
4. Strong adsorption of one of the products on the metal surface;
5. Carbonaceous deposits on the metal surface.

Ad. 1. Impurities could be removed from the activated carbon support by the produced acid gases, HCl and HF. However, the major part of the impurities is already removed prior to the reaction by the washing procedure of the activated carbon (15). The additional removal of impurities during reaction, as shown by the XRF measurements, is small. The remarkable high removal of the remains of silicium from the activated carbon is probably caused by leaching by the produced HF, which was not applied in the purification procedure. In our opinion this does not fully explain the different behaviour of the catalysts as a function of time on-stream. Less impurities would lead to a change in selectivity, especially to lower amounts of chlorine/fluorine exchanged products and total hydrogenolysis products such as methane, would be expected (28).

Ad. 2. Characterization of palladium catalysts in the hydrogenolysis of CCl_2F_2 has shown that a phase transformation occurs during reaction, viz., $\text{PdC}_{0.15}$ is formed. However, this phase is rapidly formed in comparison with the time needed for changes in performance (29). Moreover, to our knowledge, the carbide phase is not formed for all metals studied here, e.g., iridium carbide has never been reported. It is concluded that a change in structure is not responsible for the different modification behaviour of the catalysts.

Ad. 3. In principle, a changing metal dispersion during reaction could either lead to an increase or a decrease of the catalytic activity. Furthermore, it could lead to a change in the observed selectivities. Noble metals can be expected to suffer from sintering at higher temperatures in a reducing atmosphere (30). On the other hand, chlorine or chlorine containing compounds such as CCl_4 and CHCl_3 could disperse a noble metal catalyst. These components are well known for their role in redispersion and reactivation of reforming catalysts (31). CFCs are also claimed to disperse noble metal catalysts (32). Foger and Jaeger found

redispersion of Pt/Al₂O₃ after treatment with chlorine at temperatures between 320 and 500 K for 12 h (33). D'Aniello *et al.* found that the redispersion for Pt and Rh on alumina after treatment with chlorine at 773 K for 1 h was similar (34). Iridium is difficult to redisperse by means of chlorine or hydrochloric acid alone. However, when CO or NO is added, also redispersion of iridium on alumina catalysts has been found by Foger *et al.* (35). Based on these results, it can be concluded that dispersing of Pt, Rh, and Ir could be possible under our reaction conditions, because a high concentration of CCl₂F₂ is continuously supplied to the catalysts. For palladium on activated carbon, we observed redispersion of palladium catalysts at a temperature of 540 K using a pure CCl₂F₂ feed (36). The trend that the mean particle sizes determined from an analysis of the HTREM micrographs have decreased after reaction also demonstrates that under reaction conditions dispersing takes place for all catalysts. In other studies dispersing of the palladium was also observed: both a 2 wt% palladium on activated carbon catalyst at T = 430–540 K, P = 0.3 MPa, H₂/CCl₂F₂ = 3, and WHSV = 1 g/(g · h) (36) and a 1 wt% palladium on activated carbon at 510 K after 1600 h on-stream (37) had a higher dispersion after use.

Ad. 4. Differences in adsorption of the products on the metal surface could also explain the observed differences in selectivity or activity. Ahn *et al.* concluded from adsorption measurements at 423 K using an AlF₃ supported Pd catalyst that the order in adsorption strength was: H₂ > CCl₂F₂ > CHClF₂ > CH₂F₂ > CH₃F (10). We, however, conclude from our adsorption measurements that the CCl₂F₂, CHClF₂, and CH₂F₂ adsorption on each metal surface is low and that only minor differences in adsorption are observed. At the low temperature (373 K) at which the adsorption was measured apparently only physisorption of the CFCs occurred. Chemisorption of chlorine on the metal surface, on the other hand, can be expected to be high, as has been reported by Erley (38, 39). Erley reported surface coverages (θ) of 0.3 to 0.6 at a chlorine partial pressure of 1.3×10^{-6} Pa. In this study a surface coverage of approximately 0.3 was obtained at CFC-pressures between 10 and 30 kPa. Measurements of the chlorine and fluorine content of a used palladium-black catalysts showed that chlorine and fluorine are present on the catalyst after reaction in significant amounts (29). The presence of fluorine had no influence on the kinetic network. It can be concluded that the adsorption of chlorine on the catalyst surface is important for interpretation of the results.

Ad. 5. Formation of carbonaceous deposits can also be expected to occur. Carbonaceous deposits cannot only be formed on the metal surface, but also heavy halogenated products could be adsorbed on the activated carbon support. In both cases coupled products should be formed on the metal surface. Indeed, formation of C–C bonds takes place, as is illustrated by the formation of ethane and

propane during the reaction. Furthermore, the formation of a palladium carbide phase, which was found in a separate study (29), also indicates the possibility of formation of carbonaceous deposits on the catalyst surface. The rate of ethane (and propane) formation can be used to estimate the tendency to form carbonaceous deposits on each catalyst. The order is:

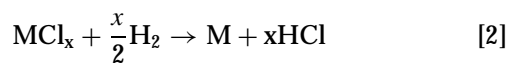
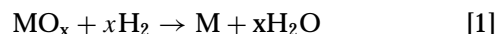


From the observation that the selectivity for ethane is low for all catalysts at the end of the experimental sequence, it is concluded that the sites, most active in C–C coupling, deactivate relatively fast.

Hence, two opposite effects occur. Chlorine adsorption and formation of carbonaceous deposits lead to a decrease in catalysts activity as a function of time on stream, whereas dispersing of the metal leads to an increase in catalyst activity. The amount of deposits and heavy halogenated products present on the catalyst can be estimated from the TPR profiles. The extent of dispersing can be estimated from the HTREM results.

TPR Profiles

The interpretation of the TPR profiles is difficult. Determination of the hydrogen consumption by quantification of the TCD-signals was not possible because not only reduction of the metal, but also removal of chlorine from the surface and gasification of carbonaceous deposits and the activated carbon was observed. This can be described by the following reactions:



Reaction [1] represents reduction of the metal oxide, reaction [2] represents removal of chlorine from the metal surface, reaction [3] represents gasification of carbonaceous deposits or of carbon support, and reaction [4] represents removal of adsorbed chlorine either from the carbon support or the metal surface. Besides these reactions, also heavy halogenated products, adsorbed in the micropores of the activated carbon during reaction, can desorb during a TPR measurement.

Thermogravimetric reduction experiments, combined with mass spectrometry (TPR-MS), showed that for the used catalyst production of HCl and methane occurred simultaneously in the peak above 600 K, whereas for a fresh palladium catalyst HCl was found in the first peak (13). The peaks could not be assigned to a specific reaction. It is,

however, clear from the TPR profiles that components have been formed under reaction conditions which are present on the catalyst after reaction and desorb or react with hydrogen above 600 K. Based on the area of the peak these products have at least partly been transferred to the activated carbon support, especially in the case of iridium and ruthenium.

A tentative explanation for the observed peak at 600 K with used catalysts is that during reaction carbonaceous deposits are formed on the surface of the metal and are adsorbed on the activated carbon support. The simultaneous production of HCl and methane, as found with TPR-MS, suggests that the deposits contain chlorine. This interpretation is consistent with the low CO-chemisorption capacity of used catalysts. Extraction experiments have been performed with a used 1 wt% iridium on activated carbon catalyst in order to remove the formed heavy products and the TPR results showed that, after this extraction with acetone at room temperature for 16 h, the area of the peak at 632 K is significantly lower. Similar results were obtained with a 2 wt% palladium on activated carbon catalyst used in the hydrogenolysis of CCl₄ (40). Furthermore, it can be concluded from TPD-TPR experiments that the peak around 600 K is mainly caused by desorption of heavy halogenated products, rather than reduction (37). Hence, the peak area above 600 K can be used as an indication for the amounts of carbonaceous deposits formed on the metal surfaces and of adsorbed heavy chlorinated products present on the activated carbon support. Thus, the amount of carbonaceous deposits present on the catalysts is in the order of:



This order can be related to the selectivity for ethane and propane.

The high temperature peak (800–900 K) area in the TPR-profiles of used catalysts is significantly smaller than that of the fresh catalysts. This indicates that the amount of functional groups present on the activated carbon support is lower after reaction.

Dispersing

Trends in dispersing under reaction conditions have been directly demonstrated by HTREM. At the end of the experiments all metals show average metal particle sizes between 6 nm (Pd) and 3 nm (Ir), whereas initially the range of particle sizes is 30 nm (Ru) to 7 nm (Ir). To the best of our knowledge, the dispersion of iridium with a chlorine compound has not been reported at these low temperatures before. Foger *et al.* (33, 35) showed that the dispersion of iridium on SiO₂ did not occur below a temperature of 750 K with a chlorine compound alone, whereas the dispersion of platinum was observed at a temperature of 320 K. These au-

thors have formulated criteria for successful redispersion:

1. Formation of a volatile metal halide;
2. Redistribution of the formed compound on the catalyst surface;
3. Anchoring the compound on the support surface.

The authors attributed the redispersion of iridium with NO or CO and Cl₂ to the formation of anionic iridium carbonyl chloride and iridium nitrosyl chloride, which species are strongly bound to the Al₂O₃, based on the claimed redispersion of Pt/Ir catalyst by Fung *et al.* (41) and Landolt *et al.* (42). Foger *et al.* (35, 37) suggest that successful redispersion could also occur with a chlorine compound when the support surface is highly chlorinated. Our results are consistent with this interpretation. Furthermore, during reaction not only a volatile metal chloride, but also a metal fluoride could be formed. This could explain the redistribution of the iridium at relatively low temperatures. Because the activated carbon support is highly chlorinated, as shown by the XRF results depicted in Table 3, the iridium can also be expected to be strongly bound to the support after redistribution. Apparently, CCl₂F₂ hydrogenolysis is a very suitable way to redisperse activated carbon-supported noble metal catalysts at relatively low temperatures. In a next paper we will deal with this dispersion phenomenon in more detail.

Catalyst Performance

A comparison of the catalysts is complicated by the different changes in performance as a function of time on-stream. At first sight a comparison at the end of the experimental sequence would be the best way to compare the metals. However, because the changes in catalyst performance are likely to depend on the process conditions applied, such a comparison is not always satisfactory.

Because of the minor differences in the conversion of the catalysts, except for the ruthenium catalyst with a rapid deactivation, this comparison can best be made by comparing the selectivities. At moderate temperature the selectivity changes as a function of time on-stream are similar for all catalysts, in particular with respect to the formation of CH₄ and coupled products (C²⁺). However, after the temperature is increased, for platinum and ruthenium the selectivities are more or less independent of the reaction parameters. The palladium catalyst has a high selectivity for CH₂F₂ (80–85 mol% at all conversion levels) and a low selectivity for CHClF₂. Its performance of palladium is independent of the hydrogen to CCl₂F₂ feed ratios applied. Generally, the catalysts can be divided into four groups: ruthenium, which has no conversion of CCl₂F₂; palladium, which has a high selectivity for the desired product CH₂F₂; ruthenium and iridium, which mainly form CHClF₂; and platinum and rhodium, which form about equal amounts of CHClF₂ and CH₂F₂.

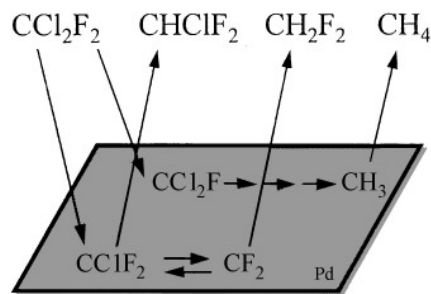


FIG. 5. Mechanism of the CCl_2F_2 hydrogenolysis over palladium.

In a separate study we have postulated a reaction mechanism for the hydrogenolysis of CCl_2F_2 over activated carbon-supported palladium (43). A simplified version of this mechanism is depicted in Fig. 5. The reaction mechanism consists of two parallel pathways on the palladium surface. One route leads to the formation of methane; the other route leads to CHClF_2 or CH_2F_2 . An adsorbed CF_2 -carbene intermediate is the most important intermediate in the reaction. The amount of chlorine adsorbed on the catalyst surface determines the selectivities for CHClF_2 and CH_2F_2 . This mechanism is consistent with the observed differences between the catalysts. The initial differences in the selectivity for methane, ethane, and propane can be understood by a varying contribution of the breakage of the carbon-fluorine bond. As a result, the most active sites become blocked by carbonaceous deposits; the hydrogenolysis of the carbon-fluorine bond diminishes; and the total hydrogenolysis to methane, ethane, and propane is suppressed. The catalyst, which exhibits the highest initial activity for CH_4 and C_2^+ formation, shows the largest peak in the TPR profiles. In agreement with this analysis, in the steady state similar selectivities for methane are observed for all investigated catalysts.

The selectivity for CHClF_2 and CH_2F_2 is determined by the amount of chlorine present on the catalyst surface and on the ease of chlorine removal from the catalyst surface by means of hydrogen. The latter can be estimated from the TPR profiles and literature data. Newkirk and McKee (45) showed that thermal decomposition temperatures of the metal chlorides in air cannot be used since the opposite behaviour in the decomposition temperatures of rhodium, iridium, and ruthenium chlorides in air and hydrogen was observed. These results, illustrated in Table 8, indicate the same order in the ease of chlorine removal from the metal surface in a hydrogen atmosphere as we have found in TPR experiments. 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, occurs at a relatively lower temperature, and as a consequence, a high selectivity for CH_2F_2 is found.

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 are all expected to have a higher metal-chlorine bond strength than palladium (46). Furthermore, ruthenium can be expected to have the highest metal-chlorine bond strength.

The lowest metal-chlorine bond strength of the investigated catalysts is expected for platinum. However, in this case probably the metal- CF_2 bond strength is weak and, therefore, the carbene reacts to CH_2 on the surface, which explains the large amounts of CH_3F and methane formed. Thus, the differences between the metals studied in the selectivities for CHClF_2 and CH_2F_2 observed are consistent with the mechanism we proposed earlier (43). When the removal of chlorine from the surface by hydrogen is difficult, high selectivities for CHClF_2 are observed. If, on the other hand, the removal of chlorine by hydrogen is easy, a high selectivity for CH_2F_2 is observed. Apparently, the same kinetic network applies to all metals studied, viz. Pd, Rh, Pt, Ru, Ir, and Re.

Besides its high selectivity for CH_2F_2 , palladium also shows a remarkably low selectivity for by-products (less than 3 mol% at the end of the experimental sequence); especially the selectivity for CHF_3 is very low. Thus, palladium is not only very selective for the hydrogenolysis of the carbon-chlorine bond, but also it has a very low reactivity for the chlorine/fluorine exchange. Based on our results the chlorine/fluorine exchange activity of the different catalysts is in the order:



For the formation of CHF_3 , a reaction with an adsorbed fluorine has to take place. Therefore, CHF_3 formation is an indication of the influence of fluorine presence on the metal surface on the kinetic network. This influence is low for a palladium surface, whereas fluorine has a larger influence in the case of ruthenium or iridium. It may be noted that the order of metal-chlorine and metal-fluorine bond strengths are in good agreement with the observed differences in selectivity.

TABLE 8

Bulk Metalchloride Decomposition Temperatures in Hydrogen

Chloride	Decomposition temperature (K)	Reference
PdCl_2	300	[41]
PtCl_2	n.m.	
RhCl_3	378	[45]
IrCl_3	463	[45]
RuCl_3	623	[45]

CONCLUSIONS

From the noble metals tested, palladium appears to be a good catalyst for the selective conversion of CCl_2F_2 into CH_2F_2 . The amount of by-products in the case of palladium is low (<3 mol%) at steady-state conditions.

The changing catalyst behaviour, as a function of time on-stream, is due to a dispersing of the metal during reaction, on the one hand, and inhibition of chlorine adsorbed on the catalyst surface and carbonaceous deposits on the metal surface, on the other hand. The noble metals can be divided into four groups: palladium with a high selectivity for CH_2F_2 ; iridium and ruthenium with a high selectivity for CHClF_2 ; platinum and rhodium with intermediate behaviour; and rhenium with no conversion of CCl_2F_2 . Initially, also, large differences in the selectivity for methane are observed, whereas at the end of the experiment the selectivity for methane is more or less the same for all metals investigated.

Adsorption of CCl_2F_2 , CHClF_2 , and CH_2F_2 is weak on all metals and no chemisorption of the CFCs was observed at 300 and 373 K. The amount of chlorine adsorbed on the metal surface is the key factor for understanding the selectivity for CHClF_2 and CH_2F_2 . These results are consistent with the proposed reaction mechanism for palladium and with the formation of a relatively stable CF_2 -carbene intermediate on the catalytically active surface. This CF_2 -carbene can react either with chlorine to give CHClF_2 or with hydrogen to give CH_2F_2 . Apparently, the same kinetic network applies to all metals studied.

The results show that CCl_2F_2 hydrogenolysis can be advantageously used for the redispersion of palladium, rhodium, ruthenium, iridium, and platinum at low temperatures (450–540 K).

ACKNOWLEDGMENT

Dr. P. J. Kooijman of the National Centre for High Resolution Electron Microscopy, Delft University of Technology, Delft, The Netherlands, is acknowledged for the electron microscopy work.

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