

## Article

# Hydrodechlorination of CHClF<sub>2</sub> (HCFC-22) over Pd–Pt Catalysts Supported on Thermally Modified Activated Carbon

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**Abstract:** Commercial activated carbon, pretreated in helium at 1600 °C and largely free of micropores, was used as a support for two series of 2 wt.% Pd–Pt catalysts, prepared by impregnating the support with metal acetylacetonates or metal chlorides. The catalysts were characterized by temperature-programmed methods, H<sub>2</sub> chemisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy (STEM) with energy dispersive spectroscopy (EDS). Overall, the results confirmed the existence of well-dispersed Pd–Pt nanoparticles in the bimetallic catalysts, ranging in size from 2 to 3 nm. The catalysts were investigated in the gas phase hydrodechlorination of chlorodifluoromethane (HCFC-22). In this environmentally relevant reaction, both the ex-chloride and ex-acetylacetonate Pd–Pt/C catalysts exhibited better hydrodechlorination for other chlorine-containing compounds. This synergistic effect can be attributed to the electron charge transfer from platinum to palladium. In general, product selectivity changes regularly with Pd–Pt alloy composition, from high in CH<sub>2</sub>F<sub>2</sub> for Pd/C (70–80%) to the selective formation of CH<sub>4</sub> for Pt/C (60–70%).

Keywords: hydrodechlorination; CHClF<sub>2</sub>; Pd–Pt/C; thermally modified carbon; synergistic effect

### 1. Introduction

The widespread interest in bimetallic systems in catalytic research is motivated by the superiority of many alloy catalysts in several technological processes (better activity/product selectivity/stability). Among these catalysts, carbon-supported bimetallic Pd–Pt catalysts play an important role. Pd–Pt catalysts are commonly used for hydrogenation reactions in the fine chemical industry [1]. They also demonstrate high performance in the oxygen reduction reactions (ORRs) in fuel cells [2], the catalytic hydrodechlorination of toxic Cl-containing compounds [3], catalytic hydrodesulfurization [4], hydrogen peroxide production [5], the hydrogenation of aromatics [6], and the catalytic oxidation of sulfur dioxide [7]. Carbon-supported monometallic palladium/platinum and bimetallic Pd–Pt nanoparticles are typically prepared using impregnation [3]. Other more complex



techniques, including molecular-capping-based colloidal synthesis [8], electrochemical methods [9], the microemulsion method [10], the sonochemical method [11], the polyol process [2], electroless deposition [12], laser vaporization of bulk Pd–Pt alloys [13,14], the controlled surface reaction technique [15], and the supercritical CO<sub>2</sub> deposition method [16] generally resulted in the preparation of well-dispersed and alloyed Pd–Pt particles.

The catalytic properties of such materials depend strongly on the preparation method. In addition to special cases, such as core/shell formulations, ideal bimetallic catalysts should consist of well-mixed nanoparticles of nearly equal size and composition, as only then can significant beneficial synergistic effects be expected. Commercially employed catalysts are typically produced via impregnation, i.e., a technique that generally does not provide the same fine control of alloy nanoparticle formation as the above-cited, more complex, techniques [17]. However, there are several noted cases where simple impregnation leads to reasonably well-alloyed supported metal particles. Such a possibility is expected when strong interactions between the precursors of both metals are already present in a solution used for the impregnation of a carrier, e.g., in the case of dissolved intermetallic compounds. In a previous study, the deposition of mixed Rh-Co carbonyl clusters on typical carriers led to the preparation of well-mixed alloy particles [18]. Similarly, the preparation of mixed compounds composed of palladium and copper acetylacetonate molecules allowed for their smooth deposition on silica, producing metallic alloys upon heating in helium, with a particle size of 2-4 nm and a rather uniform composition [19]. The extension of this "mixed metal acetylacetonate" method to the preparation of palladium–platinum catalysts appears promising, as shown in several previous studies, where proper Pd–Pt alloying was achieved [20–22]. This was also confirmed in our recent study, where the incipient wetness co-impregnation of  $\gamma$ -alumina with a solution of Pd(acac)<sub>2</sub> and Pt(acac)<sub>2</sub> resulted in better Pd–Pt alloying than a similar preparation with the use of metal chlorides [23]. The inhomogeneous distribution of both metals deposited by chloride impregnation on the surface of alumina was also observed and discussed in [17].

In this work, we assess the suitability of the impregnation method for the preparation of carbon-supported palladium-platinum catalysts. Two series of Pd-Pt/C catalysts (ex-metal acetylacetonates and ex-metal chlorides) were characterized by a number of physical and chemical methods. They were then investigated in CHClF<sub>2</sub> hydrodechlorination, an ecologically important reaction. Today,  $CHClF_2$  (HCFC-22) is by far the most abundant HCFC in the atmosphere, so it is imperative to continue to monitor the evolution of its atmospheric concentration [24–27]. Huge stocks of HCFC-22 remaining in refrigeration systems should be converted to other valuable chemicals. Catalytic hydrodechlorination (HdCl) appears to be one of the most promising technologies for the beneficial utilization of harmful chlorine-containing wastes by transforming them into useful, nontoxic products [3,28–41]. Thus, the search for new, efficient catalysts for this process continues [42]. It is well-known that, in this reaction, palladium presents respectable catalytic activity and selectivity to  $CH_2F_2$  [28–37]. However, because of the low reactivity of  $CHClF_2$ , much higher reaction temperatures must be used than in the case of  $CCl_2F_2$  hydrodechlorination. The above-mentioned works also report on the considerable deactivation of palladium catalysts during CHClF<sub>2</sub> hydrodechlorination. It is thought that the introduction of platinum, a metal generally regarded as less active than palladium, to CFC hydrodechlorination reactions [30,36,38], would increase the stability of a palladium-active phase. Platinum is a more noble metal than palladium, so one can expect that both the reactants and the reaction intermediates would be less strongly bonded to the surface of the platinum than in the case of palladium catalysts.

The choice of CHClF<sub>2</sub> hydrodechlorination was also motivated by our desire to use this reaction as a chemical probe to estimate the quality of Pd–Pt alloying. Finding synergy in the catalytic action of alloys (for Pd–Pt) rather than a linear cumulative effect (for Pd + Pt) would be considered evidence for mixed bimetallic systems deposited on the support. In this respect, several previous works reported on the occurrence of a synergistic effect in hydrodechlorination reactions on Pd–Pt catalysts. A 2–2.5-fold increase in  $CCl_2F_2$  hydrodechlorination activity and a considerable enhancement of the selectivity to  $CH_2F_2$  was achieved upon alloying palladium with the less active platinum [38]. An analogous increase of the catalytic activity was reported for the hydrodechlorination of 1,2-dichloroethane [38]. Similar synergistic effects were found in the reaction of  $CH_2Cl_2$  hydrodechlorination on supported Pd–Pt catalysts [3,39,40]. Moreover, Garcia et al. [41] found that the bimetallic Pd–Pt catalysts supported on alumina and alumina/titania are better than their monometallic counterparts in the reaction of 1,2-dichloroethane hydrodechlorination. Therefore, we assumed that a similar effect would occur in  $CHClF_2$  hydrodechlorination, a reaction in which palladium catalysts were previously found to be more active than platinum ones [32,36].

To redisperse the catalytically active phase composed of Pd and Pt, we chose commercial active carbon treated in helium at 1600 °C, the highest temperature obtainable in our laboratory. This heat treatment significantly reduced the microporosity of activated carbon [43,44], leading to metal deposition in places more accessible to reactants and the elimination of possible diffusional limitations [45]. In addition, such serious treatment led to a significant improvement in surface purity by removing sulfur, oxygen-containing functional groups, and trace amounts of metals that, due to Lewis acidity, can sometimes lead to unwanted side reactions, such as Cl/F exchanges or dismutation, as observed in the hydrodechlorination of  $CCl_2F_2$  [46,47] and  $CHClF_2$  [36].

#### 2. Results

#### 2.1. Catalyst Characterization by Temperature Programmed Methods

Figure 1 presents the temperature-programmed reduction (TPR) profiles of two series of carbon-supported Pd-Pt catalysts. The TPR profiles of the 'acac' series did not show any H2 uptake (Figure 1A), indicating a complete reduction of the metal precursor before starting the temperature ramping. This result is not surprising because precalcination in the O<sub>2</sub>/Ar of supported Pd acetylacetonate (a step included in catalyst preparation; see Section 3.1.) should lead to the formation of palladium oxide, which is easily reducible, even at sub-ambient temperatures [48–50]. The TPR profile of the 2 wt.% Pd(acac)/C catalyst showed only a negative peak (with the minimum at 86.5 °C) ascribed to  $H_2$  evolution from  $\beta$ -Pd hydride decomposition. This also indicates the presence of the metallic state of palladium at the beginning of the TPR run. A shallow minimum observed for Pd80Pt20(acac) is a sign of certain solubility of  $H_2$  in this catalyst. Another situation occurred for the TPR of the 'chloride' series of Pd–Pt/C catalysts. Figure 1B shows that the TPR profiles of all these series exhibit single positive peaks, with their maxima shifted towards higher temperatures with increasing Pt content and their amounts of consumed hydrogen (as the areas of TPR peaks) roughly proportional to the number of metal (Pd + Pt) moles in the catalysts of the same metal loading (2 wt.%). The latter suggests that, during the impregnation of  $H_2PtCl_6$  on carbon, a considerable part (if not all) of the Pt(IV) precursor must be reduced to Pt(II), which is consistent with [51]. The reduction of all the catalysts takes place in a temperature range between 145 °C (for Pd100) and 193 °C, (for Pt100), i.e., well above the temperature usually observed for hydride decomposition in hydrogen-assisted temperature-programmed experiments. This sequence of the reduction temperature with a Pd-Pt alloy composition is at variance with that reported for the reduction of Pd-Pt chloride precursors deposited on commercial amorphous activated carbon [3]; however, this result is reminiscent of the situation found for the same precursors supported on oxidic carriers [40]. As the cited authors suggest [3], the interaction of PdCl<sub>2</sub> with commercial activated carbon would be stronger than the interaction with other supports. Our results suggest that the carbon-PdCl<sub>2</sub> precursor interaction is weaker in the case of highly pretreated, partly graphitized carbon than for amorphous carbons, which, apart from considerable microporosity, possess a variety of oxygen-containing functional groups. The effect of carbon pretreatment on the course of the TPR profiles of the PdCl<sub>2</sub>/C catalysts was reported earlier (Figure 1 in [52]).

Overall, a smooth correlation between the peak maximum in the TPR profiles and the Pd–Pt alloy composition (Figure 1B) cannot be considered ultimate proof for good bimetal intermixing in the

precursor state. Nevertheless, if this correlation results from hydrogen spill-over from a Pd that is more easily reduced to Pt, then the proximity of both metal centers can be assumed. The TPR of the physical mixture of Pd100(Cl)/C and Pt100(Cl)/C showed the presence of two independent peaks, separated by a temperature gap somewhat smaller than that observed in Figure 1B (results not shown).



**Figure 1.** Temperature-programmed reduction (TPR) profiles of Pd–Pt/C, (**A**) ex-acac series, (**B**) ex-chloride series.

The Temperature-Programmed (Pd) Hydride Decomposition (TPHD) of prereduced Pd alloy catalysts yields useful information on the degree of homogeneity of bimetallic particles [53]. In the case of the Pd–Pt system, it is known that alloying Pd with Pt foil leads to an increase in plateau hydrogen pressures, which is characteristic of  $\beta$ -hydride phase formation. More specifically, at a temperature of 30 °C (which is close to RT, a convenient starting temperature in temperature-programmed studies), an alloy with only 5 at.% Pt would not form the  $\beta$ -hydride phase at a hydrogen pressure below 12 kPa (Figure 7 in Ref. [54]). Because the H<sub>2</sub>/Ar mixture used in our TPHD studies contained ~10 kPa of hydrogen, a preparation of perfectly mixed Pd–Pt catalysts possessing more than 5 at% Pt should lead to featureless TPHD profiles, i.e., profiles without any peaks demonstrating hydrogen release during hydride decomposition. However, the use of nanoparticles instead of bulky materials extends

the stability of the hydride features for Pd–Pt alloys with a Pt content of 8–21 at% (Figure 6 in [55]). In this respect, the practically flat TPDH profiles recorded for Pd60Pt40(acac), Pd40Pt60(acac) catalysts (Figure 2) indicate a reasonable degree of Pd–Pt alloying, but only with the understanding that these catalysts do not contain very rich palladium phases.



Figure 2. Temperature-programmed hydride decomposition profiles of Pd–Pt/C catalysts.

2.2. X-ray Diffraction, Transmission Electron Microscopy, H<sub>2</sub> Chemisorption, and X-ray Photoelectron Spectroscopy

The XRD profile of the support (Norit1600, preheated at 1600 °C in He) shows that the support's structure results from a mixture of turbostratic carbon, hexagonal carbon, and graphite (Supplementary Material, SET S2, Figures S3 and S4).

Figures 3–5 and Table 1 collectively show the results of XRD, TEM, and chemisorption studies performed on both series of Pd-Pt/C catalysts. More diffuse and less developed XRD reflections from the metal phase are characteristic of the ex-chloride series of Pd–Pt/C (Figure 3B), indicating their higher metal dispersions compared to the ex-acac series (Figure 3A). A more detailed analysis of the XRD results can be found in the Supplementary Material (SET S3, Figures S5–S10). Reasonable agreement was observed for the metal particle sizes obtained from TEM (as  $d_V$  and XRD for the monometallic catalysts of both series (Table 1). However, small differences are observable for the bimetallic catalysts. For the ex-chloride series, the crystallite sizes from XRD do not differ much from the  $d_V$  values, whereas for the 'acac' series, the crystallite sizes from XRD are somewhat smaller than the  $d_V$  values. This difference occurs because the broadening of the XRD reflection used in the Scherrer equation may also result from inadequate alloying between Pd and Pt ( $a_{Pd} = 0.3890 \text{ nm}, a_{Pt} = 0.3924 \text{ nm}$ ). If so, then it can be concluded that the preparation of Pd-Pt/carbon catalysts from the chloride precursors provides better alloy homogeneity than preparation from metal acetylacetonates. However, such a conclusion should be drawn with caution because the crystallite sizes of our bimetallic catalysts were determined to be less than 3 nm, i.e., below the generally accepted lower limit of metal particles sizes measured by XRD (with a typically accepted range of 3–50 nm [56]).

Figures 4 and 5 present the results of (S)TEM studies showing respective images with selected EDS areas for evaluating the relative amounts of both supported metals. The number of spots probed by EDS was rather small (5–10), forming a data set that was not statistically significant. In addition, our EDS analysis did not allow us to propose a single parameter, which would be regarded as the degree of alloying. It appears, however, that in both series, the extent of metal alloying was reasonable but not perfect. The caption in Figure 4 reports a platinum deficiency in the analyzed areas of the 'acac' catalysts. In this respect, the situation for the ex-chloride catalysts appears to be slightly better (caption to Figure 5). The distributions of metal particle size (the right sides of Figures 4 and 5) indicate

the presence of a large variety of differently sized metal particles. Therefore, the average metal particle sizes are subject to a large margin of error (Table 1).



**Figure 3.** XRD spectra of prereduced Pd–Pt/C catalysts. (**A**) ex-metal acetylacetonates, (**B**) ex-metal chlorides. Only the area with the most important XRD reflections from the metallic fcc phase (Pd/Pt) is shown.



**Figure 4.** TEM images and size distributions of Pd–Pt(ex-acac)/C catalysts. Selected EDS areas: for Pd80Pt20(acac): 1—Pd87Pt13, 2—Pd69Pt33; for Pd60Pt40(acac): 1—Pd81Pt19, 2—Pd91Pt9, 3—Pd71Pt29; for Pd40Pt60(acac): 1—Pd62Pt38, 2—Pd67Pt33.



**Figure 5.** TEM images and size distributions of Pd–Pt(Cl)/C catalysts. EDS areas: for Pd80Pt20(Cl): 1—Pd75Pt25, 2—Pd89Pt11; for Pd60Pt40(Cl): 1—Pd80Pt20, 2—Pd63Pt38; for Pd40Pt60(Cl): 1—Pd40Pt60, 2—Pd39Pt61, 3—Pd51Pt49.

Catalyst <sup>a</sup>	Particle Size from TEM (nm) <sup>b</sup>				) <sup>b</sup>	Crystallite Size,	MFE from	H/(Pd + Pt) from
	$\overline{d}_N$	SD <sup>e</sup>	SE <sup>e</sup>	$\overline{d}_S$	$\overline{d}_V$	from XRD <sup>c</sup> (nm)	TEM <sup>d</sup>	Chemisorption
Pd100(acac)	4.75	1.66	0.19	5.91	6.47	7.5	0.19	0.097
Pd80Pt20(acac)	2.87	1.23	0.14	3.97	4.57	2.8	0.28	0.155
Pd60Pt40(acac)	2.69	0.9	0.10	3.28	3.58	2.5	0.34	0.222
Pd40Pt60(acac)	2.24	0.79	0.09	2.87	3.35	2.1	0.39	0.276
Pt100(acac)	2.59	0.80	0.09	3.06	3.28	3.0	0.37	0.416
Pd100(Cl)	2.84	0.73	0.09	3.24	3.43	3.9	0.35	0.229
Pd80Pt20(Cl)	2.31	0.75	0.08	2.79	3.01	~2	0.40	0.214
Pd60Pt40(Cl)	1.36	0.40	0.05	1.63	1.85	~2	0.70	0.235
Pd40Pt60(Cl)	1.45	0.42	0.05	1.70	1.83	~2	0.66	0.339
Pt100(Cl)	1.93	0.52	0.06	2.19	2.31	<2	0.59	0.596

**Table 1.** Metal particle size (from TEM), crystallite size from XRD, and metal dispersion in two series of carbon-supported Pd–Pt catalysts subjected to reduction in  $H_2/Ar$  at 400 °C.

<sup>a</sup> For the catalyst designation, see Section 3.1. <sup>b</sup>  $\overline{d}_N$ ,  $\overline{d}_S$ ,  $\overline{d}_V$  stand for the number-, surface- and volume-weighted average diameters. <sup>c</sup> From XRD line broadening (Scherrer equation). <sup>d</sup> Metal fraction exposed (MFE = dispersion) =  $1.12/\overline{d}_S$  for Pd (Ichikawa et al. [57]) and  $1.13/\overline{d}_S$  for Pt (Rioux and Vannice [58]). <sup>e</sup> SD = Standard deviation of  $\overline{d}_N$ , SE = standard error of  $\overline{d}_N$ .

As mentioned in the Methods section, attempts to determine metal dispersion by means of the pulse chemisorption of H<sub>2</sub> failed. For Pd-rich samples, H/Pd ratios of 0.01 or even less were obtained, indicating a very small amount of irreversibly bonded hydrogen. For Pt-rich samples, the situation was somewhat better, e.g., for Pt100(Cl), the H/Pt ratio was found to be ~0.2, which still does not reflect the very small sizes of the platinum particles determined by physical methods (<2 nm, Table 1). Therefore, the amount of desorbed hydrogen after sample saturation with H<sub>2</sub> at 70 °C (and the removal of weakly bonded hydrogen) was taken to determine the metal dispersions. However, even in this case, the metal dispersions, i.e., the H<sub>ad</sub>/metal ratios, were lower than the values expected from the XRD and TEM studies, especially for the Pd-rich samples (Table 1). Similar disagreement has often been reported for carbon-supported palladium catalysts ([59,60] and references cited therein). In any case, the inability to use the pulse method, which works efficiently for determining the dispersion of Pd and Pt, suggests the activated nature of hydrogen chemisorption, which must be due to the difficulty in accessing the clean surface of the metal.

Nevertheless, the H/Pd ratio from chemisorption studies (Table 1) and the particle sizes of the Pd or Pd-rich phases determined via XRD and TEM for the reduced Pd–Pt/C catalysts indicate that the introduction of Pt to Pd/C leads to an appreciable increase in metal dispersion, which agrees with [40]. This is particularly visible for the 'chloride' series, which must be due to the stronger interaction of carbon with ionic than inert precursors [61,62].

The surveyed XPS spectra of all catalysts are provided in the Supplementary Material (SET S4, Figures S11 and S12). The XPS spectrum of the reduced Pd–Pt(Cl) catalysts showed a low level of surface chlorine (~0.1%), whereas the Cl 2p signal was not seen in the spectra of the ex-acac samples. In addition, in one sample (Pd80Pt20(Cl)), the signal from Ca 2p was detected. A small amount of calcium in Norit1600 was confirmed by chemical analysis, as well as the presence of a few small reflections in the 2theta range between 30 and 40 degrees in the XRD profiles, suggesting the presence of dolomite (remarks in Supplementary Material, SET S1 and SET S2). For the bimetallic catalysts in the 'chloride' series, the XPS method showed some surface enrichment in platinum (~10%, on average), while for the 'acac' catalysts, a slight enrichment in palladium (~5 at%, on average) was observed.

The XPS spectra (Figures 6 and 7) indicate the existence of two different metallic species in the catalysts: zerovalent  $(Pd/Pt)^0$  and cationic  $(Pd/Pt)^{2+}$ , whose relative occurrence depends on the nature of the precursor (Table 2).

This fact appears to be at variance with the TPR results, which showed that the Pd–Pt/C catalysts should be fully reduced at 400 °C. However, our XPS results are in agreement with the results of numerous reports, in which the presence of these dual active sites in carbon-supported metal

catalysts has been documented [3,39–41,63–66]. The existence of electrodeficient metal species was also confirmed after PdPt/C catalyst reduction at 400 °C (Table 2 in [40]).

For all Pd containing catalysts, we recorded two main bands centered at binding energy values of ~335.5 and ~336.7 eV observed for Pd  $3d_{5/2}$ , which can be attributed to metallic palladium (Pd<sup>0</sup>) and electrodeficient palladium (Pd<sup>2+</sup>). The corresponding peaks for Pd  $3d_{3/2}$  are located at ~340.9 eV and ~341.7 eV (left sides of Figures 6 and 7). The Pt4f region of the XPS spectra (right sides of Figures 6 and 7) shows the existence of a doublet in most cases, corresponding to the Pt  $4f_{5/2}$  and Pt  $4f_{7/2}$  bands for zerovalent and cationic platinum. However, in two cases, (Pd80Pd20(acac) and Pd60Pt40(acac)), only zerovalent Pt species were identified. Table 2 shows the relative distribution of zerovalent and ionic species. These variations are rather moderate, especially for the 'chloride' series of Pd–Pt/C catalysts.



**Figure 6.** XPS profiles in the Pt 4*f* region (right) and the Pd 3*d* region (left) of the Pd–Pt(ex-acac) catalysts. Thin black lines—deconvoluted spectra, red lines—fitted overall profiles, thick black lines—envelope spectra.



**Figure 7.** XPS profiles in the Pt 4*f* region (right) and the Pd 3*d* region (left) of the Pd–Pt(ex-Cl) catalysts. Thin black lines—deconvoluted spectra, red lines—fitted overall profiles, thick black lines—envelope spectra.

Table 2. Relative distribution of zerovalent and electrodeficient species on the surfaces of two serie
(acac and Cl) of Pd–Pt/carbon catalysts. For catalyst designation, see Section 3.1.

Catalyst	Pt <sup>0</sup>	Pt <sup>2+</sup>	Pd <sup>0</sup>	Pd <sup>2+</sup>
Pd100(acac)			67.2	32.8
Pd80Pt20(acac)	100	0	66.6	33.4
Pd60Pt40(acac)	100	0	60.6	39.4
Pd40Pt60(acac)	50.5	49.5	59.2	40.8
Pt100(acac)	42.2	57.8		
Pd100(Cl)			55.5	44.5
Pd80Pt20(Cl)	74.6	25.4	61.3	38.7
Pd60Pt40(Cl)	54.9	45.1	76.0	24.0
Pd40Pt60(Cl)	42.8	57.2	70.8	29.2
Pt100(Cl)	52.7	47.3		

# 2.3. Hydrodechlorination of CHClF<sub>2</sub>, Environmentally Relevant Utilization of a Catalytic Probe for the Characterization of Pd–Pt/C Catalysts

Catalytic screening of both series of Pd–Pt/C catalysts in CHClF<sub>2</sub> hydrodechlorination showed that stable conversions, always <3%, were achieved after a relatively long time-on-stream (~16 h), as illustrated in Figure S13 (SET S5). The bimetallic catalysts showed higher conversion than the monometallic catalysts (Figure S14). Considering the differences between the reaction conditions used in our studies and those used by Yu et al. [35] (especially the very different GHSV values), our Pd100/C catalysts presented nearly two times lower catalytic activity than the 0.5, 1, and 3 wt.% Pd/C catalysts investigated in [35]. Unfortunately, this assessment is still uncertain due to the lack of knowledge about palladium dispersion in [35]. On the other hand, our Pd100/C catalysts appeared more selective than the catalysts investigated by Yu et al., where, together with CH<sub>4</sub> and CH<sub>2</sub>F<sub>2</sub>, significant amounts of C<sub>2</sub> hydrocarbons and CH<sub>3</sub>F were found in the reaction products. For comparison purposes, the reader is referred to the compilation of published data on the catalytic behaviors of differently supported Pd catalysts in CHClF<sub>2</sub> hydrodechlorination (SET S5, Table S2).

A comparison of the catalytic activity of the two series of Pd–Pt/Norit1600 catalysts showed that the catalysts prepared from metal acetylacetones were ca. two times less active than the ex-chloride catalysts (Figure S14). Another problem was that, in the acetylacetone series, platinum was ultimately a more active catalyst than palladium. This is not consistent with the published data (see the Introduction) or the sequence of activity in the 'chloride' series. Both of these findings indicate that the oxidative pretreatment of the 'acac' catalysts during their preparation may not have been sufficient to fully remove organic acetylacetonate residues. Therefore, we decided to include an additional oxidation step for these catalysts in a flow of 1%  $O_2$ /Ar at 300 °C for 1 h. This operation was beneficial for improving the activity of ex-acac samples, and the Pd100 catalyst became more active than Pt100, as a result. Nevertheless, these catalysts remained less active than the ex-chloride ones by ca. 30%. The reasons for such disagreement will be considered later.

For the Pd-rich samples, methane and difluoromethane (HFC-32) were found to be the most predominant products, comprising more than 90% of all products (Tables 3 and 4 and Figure 8). A noticeable exception was the monometallic Pt samples, where  $CH_3F$  and  $CHF_3$  made up more than ~30% of all products. During stabilization, changes in product selectivity were relatively small, and  $CH_2F_2$  formation was often increased at the expense of methane.

Calculation of the TOF values (columns #2 in Tables 3 and 4) considered the metal dispersion data from  $H_2$  chemisorption which, as per our understanding, should reflect the number of available active metal sites. The visible maximum at 40 at. % Pt indicated the expected synergy in the catalytic action of the mixed Pd–Pt centers (Figure 9).

The product selectivity presented in Figure 8A–C shows the best selectivity to  $CH_2F_2$  for both Pd100 catalysts (70–80%, for a reaction temperature of 251 °C) and a smooth decrease in the selectivity with platinum addition. Apart from a parallel smooth increase in  $CH_4$  selectivity, the catalysts richer in platinum presented the formation of  $CH_3F$  and even  $CHF_3$ . Regular changes in product selectivity would suggest no synergy in the behavior of the bimetallic system but rather a linear cumulative effect in the catalytic action of alloys (for Pd–Pt). However, the calculated TOF values for the formation of individual products ( $CH_2F_2$  and  $CH_4$ ), as a result of multiplying the overall TOFs by the selectivities, showed respective maxima over the courses of the respective TOF-alloy composition relations (SET S5, Figure S15). Thus, this also provide evidence for the synergistic action of Pd–Pt alloys in CHClF<sub>2</sub> hydrodechlorination.

Catalyst <sup>a</sup>	Reaction	TOF <sup>b</sup>	Р	roduct S	Activation		
Catalyst	°C	$s^{-1}$	CH <sub>4</sub>	CH <sub>3</sub> F	CHF <sub>3</sub>	$CH_2F_2$	kJ/mol
	272	$4.1  imes 10^{-4}$	28.5	1.9	-	66.3	
Pd100(acac)	262	$2.85\times10^{-4}$	25	4	-	69.9	$100.7 \pm 13.4$
	252	$1.7\times10^{-4}$	28	-	-	72	
	272	$9.2  imes 10^{-4}$	30.3	8.2	7.7	53.8	
Pd80Pt20(acac)	262	$5.25 \times 10^{-4}$	22.3	4.9	21.2	51.5	$110.1\pm8.5$
	251	$3.6 \times 10^{-3}$	19	5	25	51	
	272	$1.32\times10^{-3}$	41	14	-	45	
Pd60Pt40(acac)	261	$9.4  imes 10^{-4}$	36.7	14.5	-	48.8	$83.1 \pm 4.6$
	251	$6.3  imes 10^{-4}$	33.5	14.5	-	52.0	
-	272	$1.46 \times 10^{-3}$	45.6	16.7	-	37.7	
Pd40Pt60(acac)	262	$1.09 \times 10^{-3}$	42.0	14.9	-	44.6	$77.1 \pm 5.2$
	252	$7.44\times10^{-4}$	37.5	17.7	-	44.8	
	271	$3.5  imes 10^{-4}$	58.8	20.5	5.0	15.7	
Pt100(acac)	262	$2.5  imes 10^{-4}$	56.5	20.6	-	22.9	$87.8 \pm 6.6$
	251	$1.65\times10^{-4}$	53.5	18.6	11.0	16.9	
-	271	$1.3 \times 10^{-3}$	36.8	1.2	-	62.0	
Pd100(Cl)	261	$9.2  imes 10^{-4}$	33.6	1.2	-	65.2	$88.8 \pm 2.9$
	251	$6.15\times10^{-4}$	30.1	-	-	69.9	
	271	$2.2 \times 10^{-3}$	47.6	4.0	-	48.4	
Pd80Pt20(Cl)	262	$1.6 \times 10^{-3}$	44.1	4.1	-	51.8	$84.7 \pm 4.2$
	252	$1.08\times10^{-3}$	39.8	4.2	-	56.0	
	271	$2.5 \times 10^{-3}$	53.4	5.6	-	41.0	
Pd60Pt40(Cl)	262	$1.87 \times 10^{-3}$	50.9	5.9	-	43.2	$76.1 \pm 1.1$
	252	$1.35\times10^{-3}$	47.4	6.3	-	46.2	
	272	$2.17 \times 10^{-3}$	59.4	7.0	-	33.5	
Pd40Pt60(Cl)	262	$1.5 \times 10^{-3}$	55.6	7.6	-	36.8	$92.2 \pm 1.5$
	252	$1 \times 10^{-3}$	44.5	7.6	6.4	41.4	
	272	$6.8\times10^{-4}$	71.9	11.9	0.3	15.8	
Pt100(Cl)	262	$4.9\times10^{-4}$	68.8	12.6	-	18.5	$75.7 \pm 2.1$
	252	$3.6  imes 10^{-4}$	66.5	13.7	-	19.8	

**Table 3.**  $CHClF_2$  hydrodechlorination on two series of Pd–Pt/C catalysts. Turnover frequencies, product selectivities, and activation energies.

<sup>a</sup> As in Tables 1 and 2.	<sup>o</sup> Based on metal dispersi-	ons measured by H <sub>2</sub>	chemisorption (	Table 1). GH	$SV 5760 h^{-1}$ ,
catalyst weight 0.20 g. A	weraged values from a fev	v measurements.			

Table 4. CHClF2 hydrodechlorination on two series of Pd-Pt/C catalysts. Turnover frequencies, production
selectivities, and activation energies, acac series after additional calcination at 300 °C, 1 h.

Catalyst <sup>a,b</sup>	Reaction Temperature	TOF s <sup>-1</sup>	Product Selectivity, %				Activation Energy
Cuturyst	°C		CH <sub>4</sub>	CH <sub>3</sub> F	CHF <sub>3</sub>	CH <sub>2</sub> F <sub>2</sub>	kJ/mol
Rd100(acac)	272	$7.0  imes 10^{-4}$	27.4	-	-	72.6	
IUDJ 0110	262	$4.5  imes 10^{-4}$	24.4	4	-	75.6	$89.4 \pm 10.0$
H/Pd = 0.110	252	$3.3\times10^{-4}$	21.5	-	-	78.5	
Dd80D+20(acac)	272	$1.20\times 10^{-3}$	26.8	4.6	-	68.6	
FUOUF (20)(acac)	262	$8.0  imes 10^{-4}$	24.7	5.2	-	70.1	$88.1 \pm 5.4$
H/(Fu + Ft) = 0.162	251	$5.5  imes 10^{-4}$	24.9	6.0	-	69.1	
Pd(0Pt/0(acac))	272	$1.80\times10^{-3}$	42.4	4.5	-	53.0	
FU00F140(acac)	261	$1.2 \times 10^{-3}$	35.9	9.1	-	55.0	$85.1 \pm 4.6$
H/(Fu + Ft) = 0.210	251	$8.9\times10^{-4}$	32.6	9.8	-	57.6	
$\mathbf{D}$ 140 $\mathbf{D}$ (0()	272	$1.6 \times 10^{-3}$	44.4	13.5	-	42.1	
FU40F100(acac)	262	$1.05 \times 10^{-3}$	14.0	14.9	-	45.7	$77.1 \pm 5.2$
$r_{1}(r_{u} + r_{t}) = 0.282$	252	$7.2  imes 10^{-4}$	14.9	17.7	-	49.1	
<b>D</b> +100(acac)	271	$3.0  imes 10^{-4}$	58.9	14.9	12.6	13.6	
$\Gamma U = 0.251$	262	$2.0  imes 10^{-4}$	59.2	16.8	9.0	15.0	$86.2 \pm 12.0$
11/1 t = 0.331	251	$1.5\times10^{-4}$	80.3	19.7	-	-	

 $^{\rm a}$  As in Tables 1 and 2.  $^{\rm b}$  Metal dispersion data under catalyst designation.



**Figure 8.** Product selectivity as a function of the Pd–Pt alloy composition for the ex-acac series (**A**,**B**) after additional calcination at 300 °C and the ex-chloride series (**C**). Reaction temperature 272 °C. GHSV = 5760 h<sup>-1</sup>.



Figure 9. Catalytic activity (TOFs) of the Pd–Pt/Norit1600 catalysts vs. nominal Pd–Pt alloy composition.

Our interpretation of the synergy in the catalytic action of Pd–Pt alloys in  $CHClF_2$ hydrodechlorination considers an earlier finding that the rate of HdCl correlates well with the C–Cl bond energy, suggesting that the scission of this bond is rate-determining [66]. As mentioned in the Introduction, palladium is more active than platinum in HdCl. Therefore, we assume that the rupture of the C-Cl bond occurs mainly on Pd sites. If that is true, then the synergy in the Pd-Pt system would result from a beneficial modification of the Pd sites by introducing platinum via electronic interactions between both metals. The electron deficiency of Pt after alloying with Pd has been documented by others [67–69], and the formation of  $Pt^{x\delta+}-xPd^{\delta-}$  ionic bonds has also been suggested [69]. As mentioned in the previous subsection, such changes were found to be consistent with observations of the hydrogen storage capacity of Pt-Pd nanoparticles. The broadening of the valence band width and downshift of the d-band center away from the Fermi level upon Pt substitution also provided evidence for the enhanced stability of the hydride features of the  $Pd_{1-x}Pt_x$ solid-solution nanoparticles with a Pt content of 8–21 atomic percent [55]. If one assumes-in line with Matsubayashi et al. [69]-that the presence of electrodeficient Pt species is associated with an electron transfer from platinum to palladium, then the extra negative charge on palladium atoms could make those atoms superior active centers in HdCl reactions. A number of earlier reports adopted this possibility. The presence of electron rich palladium species was obtained as a result of Pd-MgO support interactions [70-72]. Dal Santo et al. [72] found that the high hydrodechlorination (of CCl<sub>4</sub>) activity of Pd/MgO catalysts leading to the complete cleavage of C-Cl bonds can be ascribed to the strong hydridic character of hydrogen atoms chemisorbed on the electron-rich Pd particles in strong contact with O<sup>2-</sup> sites of MgO. A similar enhancement of HdCl activity was reported by other researchers who modified palladium properties using alkaline supports or additives [73–75]. As mentioned earlier, the reaction mechanism of catalytic hydrodechlorination generally considers the rupture of the carbon–chlorine bond to be the rate-determining step. In the  $CHClF_2$  molecule, this bond is usually stronger than that in other hydrochlorinated organic compounds, including CCl<sub>2</sub>F<sub>2</sub>. The much lower reactivity of CHClF<sub>2</sub> compared to that of CCl<sub>2</sub>F<sub>2</sub> leads not only to a significantly lower catalytic activity exhibited by the same catalysts in the former reaction but also implies a higher activation

energy, which can be correlated with the C–Cl bond strength [66]. The available data on  $CCl_2F_2$  hydrodechlorination by palladium catalysts can help to estimate the apparent energy of activation at the 50–70 kJ/mol level [28,38,76–79], whereas our present data, despite being varied over a wide range, indicate much higher values (80–110 kJ/mol, Tables 3 and 4). Mechanistic indications for the beneficial role of electron-rich palladium atoms also originate from homogeneous catalysis. It was found that Pd complexes containing basic phosphines efficiently catalyze the reductive dechlorination of aryl chlorides via the oxidative addition step [80].

As mentioned earlier, the ex-acac catalysts appeared to be less active than the ex-chloride ones. The reasons for this difference cannot be rationalized in terms of possible contamination with carbon-containing species because the ex-acac catalysts were subjected to intensive oxidation at 300 °C. Such treatment appears sufficient not only for eliminating organic residuals of acetylacetonate precursors [48] but also for removing superficial carbon from palladium particles [59,60]. The differences in metal dispersion between both series were also not considered due to our knowledge about the structural sensitivity of the catalytic hydrodechlorination of CFCs on palladium catalysts. Less metal-dispersed ex-acac catalysts should show higher TOFs than the 'acac' ones [28,78,79], which is not the case here. The differences in the relative distribution of zerovalent and electrodeficient species on the surfaces of the two series of Pd–Pt/carbon catalysts (Table 2) may contribute to the catalytic behavior [3,39–41,64–66].

#### 3. Methods

#### 3.1. Catalyst Preparation

The catalyst support was Norit RO 0.8 (activated charcoal Norit, CAS # 7440-44-0) obtained from Sigma-Aldrich, Saint Louis, MO, USA (product #22875), pretreated in helium at 1600 °C for 2 h (henceforth referred to as Norit1600) in the form of cylindrical extrudes ~1 mm diameter. The catalyst's nitrogen BET surface area measured with an ASAP 2020 instrument (Micromeritics Instrument Corporation, Norcross, GA, USA) was 173 m<sup>2</sup>/g, the BJH pore volume (from the desorption branch) was 0.264 cm<sup>3</sup>/g, and the cumulative micropore volume (t-Plot) was 0.005 cm<sup>3</sup>/g. The pore size distribution shows that the porosity of this carbon material is predominantly shaped by mesopores in the 2–43.5 nm range (Supplementary Material, SET S1, Table S1 and Figures S1 and S2).

Two series of Pd–Pt/Norit1600 catalysts with 2 wt.% overall metal loading were prepared by incipient wetness co-impregnation of Norit1600 with appropriate amounts of dissolved metal salts. During impregnation and drying, good mixing was assured through the rotary motion of a beaker containing catalyst precursor components. After 5 h of stirring, the resulting slurry was evaporated to an apparent dryness using infrared lamps. Finally, the obtained solid was further dried in an air oven at 120 °C overnight. One Pd–Pt/C series was prepared through impregnation of the Norit1600 with mixtures of Pd and Pt bis-acetylacetonate precursors (Pd(acac)<sub>2</sub> and Pt(acac)<sub>2</sub> from Sigma-Aldrich, 99%) dissolved in toluene (analytical reagent from Chempur, Piekary Śląskie, Poland). To remove the organic part of the acetylacetonates, dried powders were calcined in flowing 1% O<sub>2</sub>/Ar (50 cm<sup>3</sup>/min, at STP) at 300 °C for 1 h. The precalcined materials were purged with Ar, cooled to RT, and stored in a desiccator. To prepare the other series, slightly acidified acetone solutions of palladium(II) chloride and chloroplatinic acid hexahydrate (both 99.9% from Fluorochem (Hadfield, UK) were used. The introduction of a few drops of HCl was needed for the complete dissolution of PdCl<sub>2</sub>. In the text, both catalyst series are referred as to the 'acac' and the 'chloride' (or 'Cl') series, whereas particular catalysts are designated as PdXPtY(acac) or PdXPtY(Cl), respectively. X and Y stand for the atomic percentages of Pd and Pt in the metal phase. Catalysts with the following metal phase compositions were prepared, Pd100, Pd80Pt20, Pd60Pt40, Pd40Pt60, and Pt100, thereby more densely covering the area of palladium-rich catalysts, which, according to the literature, should exhibit higher catalytic activity in the test reaction.

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Prior to the catalytic activity tests and characterization studies, the catalyst samples were reduced in the flow of the  $H_2/Ar$  mixture (20 cm<sup>3</sup>/min, STP) at 400 °C.

#### 3.2. Catalytic Tests

The hydrodechlorination of chlorodifluoromethane was conducted in a glass flow system equipped with a gradientless reactor, operating under atmospheric pressure. Prior to each reaction run, the catalyst (0.20 g sample) was subjected to reduction in 10% H<sub>2</sub>/Ar (20 cm<sup>3</sup>/min, STP) at 400 °C (1 h for the 'acac' and 3 h for the 'chloride' series). After reduction, the catalysts were cooled in an  $H_2/Ar$  flow to the desired initial reaction temperature, i.e., 270 °C. For a typical reaction run, the total flow of the reactant mixture was 48 cm<sup>3</sup>/min and consisted of CHClF<sub>2</sub> (1 cm<sup>3</sup>/min), H<sub>2</sub> (8 cm<sup>3</sup>/min), and Ar (39 cm<sup>3</sup>/min). These flows (at STP) were controlled by Bronkhorst HI-TEC (AK Ruurlo, The Netherlands) mass controllers, fixing the GHSV at 5760 h<sup>-1</sup>. This high value allowed us to maintain low conversions, usually <3%, and minimized secondary reactions. The reaction was carried out until a steady state was achieved at 270 °C (~16 h). Then, the reaction temperature was gradually decreased to 260 °C and 250 °C, and new experimental points were collected. A typical run lasted ~20 h. The post-reaction gas was analyzed by gas chromatography (Bruker SCION456-GC, with FID, from Bruker-Poland, Poznań) using a 5% Fluorocol/carbosieve column (20 ft) from Sigma-Aldrich (Saint Louis, MO, USA). Kinetic runs with an increasingly crushed Pd100(acac)/C catalyst showed a very negligible effect of the catalyst grain size on the percent conversion and selectivity (both within the reproducibility level), which suggested the lack of an effect from the internal diffusion process.

# 3.3. Catalyst Characterization by $H_2$ Chemisorption, Temperature Programmed Techniques, XRD, TEM and XPS

A 10% H<sub>2</sub>/Ar mixture (20 cm<sup>3</sup>/min, at STP) was also used in the temperature-programmed reduction (TPR) study of the Pd–Pt/C catalysts. The catalyst temperature was increased from RT to 400 °C at 8 °C/min. The effluent gas was passed through a moisture trap (to remove H<sub>2</sub>O released from precalcined metal acetylacetonates) or a bath with an ethanol–liquid nitrogen slurry (to remove the HCl released from non-calcined 'chloride' catalyst precursors) and detected on-line using a Gow-Mac thermal conductivity detector (Bethlehem, PA, USA) kept in a water bath.

After TPR and further reduction in 10% H<sub>2</sub>/Ar at 400 °C, the Pd-rich (Pd100, Pd80Pt20, and Pd60Pt40) samples were cooled to RT in the H<sub>2</sub>/Ar flow to allow them to transform into their respective  $\beta$ -hydride phases. Next, the samples were heated to ~400 °C under a temperature ramp of 8 °C/min. These runs, called temperature-programmed hydride decomposition (TPHD) and carried out in 10% H<sub>2</sub>/Ar flowing mixture, reveal how the stability and composition of the  $\beta$ -hydride phase is dependent on Pt's introduction to Pd/C [53].

Hydrogen chemisorption carried out via the pulse method was attempted to measure the metal dispersion. However, this method failed. Extremely small hydrogen uptakes were accompanied by the release of very diffuse outgoing hydrogen pulses, suggesting that hydrogen only weakly/reversibly bonded to the surfaces of the tested metals. The irreversible form of hydrogen adsorption, which was characteristic for Pd and Pt, supported on nonreducible metal oxides, and crucial for using the pulse-flow method, was not marked. This finding is consistent with the understanding that the metal surface is blocked with carbon, resulting in kinetic limitations associated with an increase in the activation energy of H<sub>2</sub> chemisorption. Therefore, as an alternative, we adopted the method recommended by Bartholomew for Fe, Co, and Ni catalysts [81], through which the desorption of hydrogen, irreversibly adsorbed at a higher temperature (here at 70 °C), was measured. After H<sub>2</sub> adsorption at 70 °C, the reactor was shortly flushed with an Ar stream to remove the weakly adsorbed hydrogen, and the chemisorbed hydrogen was determined by the temperature programmed desorption, ramping the temperature at 20 °C/min in the Ar flow.

XRD (X-Ray Diffraction) studies of reduced and, in a few cases, post-reaction samples of Pd–Pt/C catalysts were performed on a standard Rigaku–Denki (Tokyo, Japan) diffractometer using Ni-filtered

Cu*K* $\alpha$  radiation. The samples were scanned by a step-by-step technique at 2 $\theta$  intervals of 0.05° and a recording time of 10 s for each step.

TEM (Transmission Electron Microscopy) investigations of Pd–Pt/C samples prereduced at 400 °C were performed in a probe Cs-corrected S/TEM Titan 80e300 FEI microscope equipped with EDAX EDS (FEI Europe B.V., Einhoven, The Netherlands). The images were recorded in STEM mode, using the high angle annular dark field (HAADF) detector. A 300 keV electron beam with a convergence semi-angle of 17 and 27 mrad was used. The condensed beam analyzed using the X-ray energy-dispersive spectrometer in TEM mode and EDS, scanning at an energy resolution of 134 eV in HAADF-STEM mode using a EDAX detector, facilitated the estimation of the local concentration of chemical elements. Moreover, the surface-weighted average diameter of metal particles, determined as  $\overline{d}_S = \sum n_i d_i^3 / \sum n_i d_i^2$ , where  $n_i$  is the amount of counted particles of an average diameter  $d_i$ , made it possible to compare the particle sizes determined by hydrogen chemisorption (Table 1). Similarly, the volume-weighted average diameter of the metal particles, determined as  $\overline{d}_V = \sum n_i d_i^4 / \sum n_i d_i^3$ , enabled a comparison with the crystallite sizes obtained from the XRD analysis.

X-ray photoelectron spectroscopic (XPS) measurements were performed using a PHI 5000 VersaProbe (ULVAC-PHI, Kanagawa, Japan) spectrometer with monochromatic AlK<sub> $\alpha$ </sub> radiation (h $\nu$  = 1486.6 eV) from an X-ray source operating with a 100 µm spot size and at 25 W and 15 kV. After being pre-reduced in the H<sub>2</sub>/Ar flow (at 400 °C in another system), the catalyst samples were transferred through the air, mounted in the XPS instrument, and re-reduced in hydrogen at 325 °C for 1 h. Prior to the XPS analysis, residual pressure of less than  $1 \times 10^{-8}$  mbar was reached. The high-resolution (HR) XPS spectra were collected with the hemispherical analyzer at a pass energy of 117.4 and an energy step size of 0.1 eV. The X-ray beam was incident at the sample surface at an angle of 45° with respect to the surface normal, and the analyzer axis was located at 45° with respect to the surface. The CasaXPS software (2.3.23 version) was used to evaluate the XPS data. Deconvolutions of all HR XPS spectra were performed using a Shirley background and a Gaussian peak shape with 30% Lorentzian character. The binding energies (BE) of all detected spectra were calibrated with respect to the BE of C 1 s at 284.6 eV. Atomic concentrations of palladium and platinum were successfully quantified using the intensities of the most intense peak characteristics of both metals (Pd 3d and Pt 4f) and the relevant databases [82,83].

#### 4. Conclusions

Commercial activated carbon pretreated in helium at 1600 °C, largely free of micropores and impurities, was used as a support for Pd–Pt catalysts, prepared by impregnating the support with metal acetylacetonates or metal chlorides. Through the use of physical (XRD, TEM) and chemical (temperature programmed,  $H_2$  chemisorption, and catalytic reaction) probes, it was found that this simple preparation method can obtain well-alloyed Pd–Pt nanoparticles, ca. 2–3 nm in size. The presence of zerovalent and electron-deficient metal species in the reduced catalysts was confirmed by XPS. In addition, the bimetallic Pd–Pt/C catalysts tested in the reaction of CHClF<sub>2</sub> hydrodechlorination showed higher catalytic activity than the monometallic ones. This synergistic effect is attributed to the electron charge transfer from platinum to palladium. Overall, the monometallic Pd/carbon catalysts demonstrated the best selectivity to difluoromethane, whereas Pt/carbon was selective to methane formation. Further, the ex-chloride Pd–Pt/carbon samples were more active than their ex-acetylacetonates counterparts.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/11/1291/s1, SET S1: Characterization of Norit 1600: Table S1: Basic characteristics of Norit RO 08, Figure S1: Isotherm of N<sub>2</sub> adsorption (at –196 °C) on Norit RO 08 carbon pretreated at 1600 °C (Norit1600), Figure S2: Pore size distribution in Norit1600; SET S2: XRD analysis of Norit heated in He at 1600 °C for 2 h: Figure S3: Identification of different forms of carbon in Norit 1600, Figure S4: PDF cards: #752078 for graphite (A) and #751621for hexagonal carbon (B), Figure S5: XRD of Norit1600. Intense C(002) reflection, characteristic for graphitized carbons is shown; SET S3: XRD analysis of Norit supported bimetallic Pd-Pt catalysts: Figure S6: Refined diffractograms of ex-chloride samples, Figure S7: XRD profiles of ex-chloride samples after subtracting the background from Norit, Figure S10: The 2 theta region of 220 reflection; SET S4: XPS survey spectra

of Pd-Pt/Norit1600 catalysts: Figure S11: Survey spectra of Pd-Pt/Norit1600 catalysts, Figure S12: C1s peak; SET S5. Catalytic data: Figure S13: Hydrodechlorination of CHClF<sub>2</sub> at 270 °C. Time-on-stream behavior of Pt100(Cl) and Pd100(acac) catalysts, Figure S14: Steady state conversion as a function of the Pd-Pt alloy composition at two reaction temperatures: 251 and 272 °C. A – for ex-methyl acetylacetonates, B- for ex-metal chlorides. GHSV = 5760 h<sup>-1</sup>, Figure S15: Catalytic activity of Pd-Pt/Norit1600 catalysts for CH<sub>2</sub>F<sub>2</sub> (left side) and CH<sub>4</sub> (right side) formation at different reaction temperatures. GHSV = 5760 h<sup>-1</sup>, Table S2: Compilation of published data on catalytic activity of palladium in the hydrodechlorination of chlorodifluoromethane (HCFC-22).

**Author Contributions:** M.R. was responsible for the conceptual work, catalyst synthesis, and characterization by chemisorption, the temperature-programmed and reaction studies, experimental planning, and manuscript writing; W.J. was responsible for catalyst characterization by X.R.D.; K.M. was responsible for catalyst characterization by TEM; W.R.-P. was responsible for the preparation and characterization of the catalyst support; Z.K. was responsible for the conceptual work, experimental planning, and overall care for the manuscript writing. All authors have read and agreed to the published version of the manuscript.

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