Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 88 (2004) 93–101

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Hydrodechlorination of dichlorodifluoromethane (CFC-12) on Pd–Pt/Al_2O_3 catalysts

Marta Legawiec-Jarzyna [a], Anna Śrębowata [a], Wojciech Juszczyk [a], Zbigniew Karpiński [a,b,*]

[a] Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01224 Warsaw, Poland
[b] Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University, ul. Dewajtis 5, PL-01815 Warsaw, Poland

---

Abstract

A series of alumina-supported palladium–platinum catalysts of 1–2.8 wt.% overall metal loading were prepared by incipient wetness impregnation and investigated in the reaction of dichlorodifluoromethane with dihydrogen at 160–180 °C. All samples had high metal dispersion, what, in combination with a low metal loading, made physical characterization of catalysts difficult. Temperature-programmed hydride decomposition (TPHD) study, the technique which appeared to be a promising technique for diagnosing the quality of alloying palladium-containing systems, appeared less informative, because, due to high metal dispersion, all tested samples did not show a β-PdH phase formation.

A 2–2.5-fold increase in hydrodechlorination activity and a considerable enhancement of the selectivity towards difluoromethane (from 46 to ∼60%, at 180 °C) are obtained upon introducing small amounts (up to 20 at.%) of platinum to palladium. Further increase of platinum content lowers both the activity as well as the selectivity. This synergistic effect must follow from a considerable effect of interaction between palladium (active component) and platinum (much less active component). $CHClF_2$ is produced in larger amounts on monometallic 1 wt.% Pt/Al_2O_3 catalyst (selectivity 28% at 180 °C and higher at lower temperatures), whereas Pd and Pd–Pt samples form only small amounts of this product. This suggests that the catalytic behavior of palladium is largely preserved in the bimetallic samples. As after reaction the most active and selective Pd–Pt catalysts (with 10 and 20 at.% Pt) contained lesser amounts of carbon than the other (less active) catalysts, it is considered that small amounts of platinum introduced (to palladium) are beneficial for maintaining the catalyst surface less blocked by carbon species, and in effect, more active.

Keywords: CCl_2F_2 (CFC-12) hydrodechlorination; Alumina-supported Pd–Pt catalysts; Selectivity to CH_2F_2 (HFC-32); Effect of alloying

---

1. Introduction

Catalytic removal of chlorine from organic compounds has recently attracted increasing interest. A particular case of this important environmental issue is the hydrodechlorination of chlorofluorocarbons (CFCs). The necessity to replace these detrimental, ozone-depleting compounds by less harmful hydrochlorofluorocarbons (HCFCs) or, more preferably, by benign hydrofluorocarbons (HFCs) launched a more extensive work on hydrodechlorination of CFCs [1,2]. Palladium was found unique among the catalytic metals for its activity and especially, selectivity (towards hydrodechlorination, without undesired deflu-

---

* Corresponding author. Present address: Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01224 Warsaw, Poland. Tel.: +48-22-6324593/6323221x3356; fax: +48-22-6325276.
E-mail address: zk@ichf.edu.pl (Z. Karpiński).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.11.002

orination) in this process, and as a consequence most fundamental work was done with this metal [3–18]. Nevertheless, in search for still better catalysts of CFCs hydrodechlorination, a considerable work has already been dedicated to bimetallic catalysts containing palladium. Coq et al. [19] studied the conversion of CCl_2F_2 over K, Ag, Fe, and Co-doped palladium catalysts. Considerable amounts of coupling products (C_2) were found in case of Fe- and Co-modified Pd/C catalysts. Other additives to Pd were also tested: Re (in CCl_2F_2 hydrodechlorination [20]), and a greater number of various elements (Ag, Bi, Cd, Cu, Hg, In, Pb, Sn and Tl) in the study of Ohnishi et al. [21] on hydrodechlorination of CCl_2FCClF_2 (CFC-113). In the latter case, thallium and bismuth-modified palladium catalysts occurred the best. Similarly, recent patents [22–24] and scientific literature [25–29] deal with supported palladium catalysts greatly improved by gold introduction.

It appeared interesting to us to investigate the effect of added platinum on the catalytic behavior of Pd/Al_2O_3 catalysts. Platinum itself does not seem to be regarded as a catalytic metal as good as palladium in CFCs hydrodechlorination. Bell et al. [30] reported a high selectivity towards methane (∼70%) on a 2 wt.% $Pt/\gamma\text{-}Al_2O_3$ in the reaction of CCl_2F_2 with hydrogen. It means that a desired CH_2F_2 constitutes a minor product. Somewhat higher selectivity toward CH_2F_2 (>40%, thus not as good as in case of Pd, up to ∼80% and higher, [3–18]) was found by Wiersma et al. [8] in their study of CCl_2F_2 hydrodechlorination on Pt/C. Larger amounts of formed $CHClF_2$ were also found in case of Pt/C (selectivity >30%). In a long-term study (100 h on stream), the Dutch group [8] demonstrated the formation of vast amounts of CH_3F (17%).

In this study we report on the performance of Pd–Pt/Al_2O_3 catalysts in CCl_2F_2 hydrodechlorination. The catalytic behavior will be presented and discussed in combination with results of catalyst characterization by temperature-programmed hydrogenation of deposits left on catalysts after reaction.

2. Experimental

The monometallic, 1 wt.% metal-loaded, palladium and platinum catalysts were prepared by incipient wetness impregnation of alumina (Alumina Catalyst Shell S618, 240 m^2/g, pore volume 0.8 cm^3/g, 75–120 mesh, acid washed and precalcined at 550 °C). Before each impregnation, the support was dried in an air oven at 100 °C for 20 h. The Pd/Al_2O_3 was prepared from an aqueous solution of palladium dichloride (analytical reagent from POCh, Gliwice, Poland). For preparation of the Pt/Al_2O_3, chloroplatinic acid was used. It was prepared by dissolving Pt wire (Johnson Matthey Grade 1) in a hot mixture of hydrochloric and nitric acids (volume ratio 1:10, both of analytical purity from POCh, Gliwice, Poland). During impregnation and preliminary drying with infrared lamps, a good mixing was assured by the rotary motion of a beaker containing catalyst precursor components. Then, the solids were further dried in an air oven overnight at 90 °C.

A series of bimetallic Pd–Pt/Al_2O_3 catalysts were prepared by incipient wetness coimpregnation of alumina with appropriate amounts of dissolved palladium dichloride and chloroplatinic acid. After impregnation and preliminary drying in a rotating beaker, the Pd–Pt catalyst precursors were dried overnight at 90 °C and stored in a desiccator. All the catalysts prepared in this work are listed in Table 1.

The prepared catalysts were reduced in flowing 85% H_2/Ar (25 cm^3/min), ramping the temperature from 20 to 400 °C (at 8 °C/min) and kept at 400 °C for 3 h. After a subsequent purge in argon flow at 400 °C for 1 h, the catalysts were characterized by H_2 chemisorption (results in Table 1), temperature-programmed (palladium) hydride decomposition (TPHD) and, only to a very limited extent, by XRD.

Hydrogen chemisorption experiments were performed in a pulse-flow system, as described elsewhere [29]. The thermal conductivity detector (TCD, Gow-Mac) was kept at 0 °C, providing constant response during each run. All the gases used (H_2, Ar and 85% H_2/Ar mixture) were purified by passing through drying traps with final purification over MnO/SiO_2. Hydrogen chemisorption was carried out at 70 °C. After H_2 chemisorption, the samples were cooled to ∼20 °C in H_2/Ar flow (to be transformed into a respective PdH phase). Next, they were heated to ∼150 °C, at the temperature ramp of 8 °C/min.

Prior to reaction, all catalysts were reduced in flowing 10% H_2/Ar (25 cm^3/min), ramping the temperature from 20 to 400 °C (at 8 °C/min) and kept at 400 °C for 3 h.

Table 1
Alumina-supported Pd–Pt catalysts used in this work

Catalyst designation[a]	Overall metal loading (wt.% Pd + Pt)	Metal fraction exposed[b]	Metal particle size[c] (nm)
Pd100	1.0	0.77	1.5
Pd95Pt5	1.1	0.63	1.8
Pd90Pt10	1.2	0.44	2.5
Pd80Pt20	1.45	0.60	1.9
Pd50Pt50	2.8	0.49	2.3
Pt100	1.0	0.54	2.1

[a] In the notation PdXPtY, X and Y denote atomic percentages of Pd and Pt ($X + Y = 100\%$).

[b] From hydrogen chemisorption as H/M_{total}, where $M_{total} = Pd_{total} + Pt_{total}$.

[c] Based on H/M_{total} from H_2 chemisorption ($d_{nm} = 1.12/(H/M_{total})$), [32].

The reaction of dichlorodifluoromethane (CFC-12 from Galco S.A., Belgium; purity 99.9%) with hydrogen (purified over MnO/SiO_2) was conducted in a glass flow system under atmospheric pressure at 160, 170, and 180 °C. Feed partial pressures were 2 and 20 kPa of dichlorodifluoromethane and hydrogen, respectively, in an argon carrier (also purified by MnO/SiO_2). The flow of all gases was metered by MKS mass flow controllers and the overall flow rate of the reactant gas mixture was 100 cm^3/min. The reaction mixture leaving the reactor was introduced via stainless steel tubing onto a gas chromatograph (HP 5890 series II with FID) and analyzed using a 5% Fluorcol/Carbopack B column (3 m) from Supelco. The results of GC analysis were elaborated using HP Chemstation.

In order to adequately establish changes in the catalytic behavior, a typical kinetic run lasted ~24 h. The first stage of the reaction involved a 17–18 h period at 180 °C. During this time, the catalyst performance stabilized in a flow of the reaction mixture, as established by analyzing the reacting gas at 30 min intervals. Next, the reaction temperature was lowered, in 10° steps, and the next experimental points were collected. After catalyst screening at the lowest reaction temperature (160 °C) the catalyst performance was tested again at 180 °C, giving, in most cases, a good return to the initial behavior at this temperature. To avoid secondary reactions, the overall conversion was kept low, i.e. below 5% (at steady state), at the highest temperature of catalyst screening. Blank experiments with γ-alumina showed some, although very low, initial activity (conversion ~0.1%) at 180 °C, i.e. the highest reaction temperature used in testing $Pd–Pt/Al_2O_3$ catalysts. The only products were $CHClF_2$ and $CClF_3$ (at ~4:1 ratio). After 10 h of time-on-stream (TOS), the activity of alumina turned out to be immeasurably low. In fact, a non-negligible activity of γ-alumina in CCl_2F_2 hydrodechlorination is expected at much higher reaction temperature, e.g. ~300 °C [31].

After kinetic runs, the catalysts were investigated by a temperature-programmed hydrogenation (TPH) to detect species which can be removed by hydrogen from used catalysts. Progress of TPH runs, using a 10% H_2/He flow (25 cm^3/min) at a 10 °C/min ramp, was followed by mass spectrometry (MA200, Dycor-Ametek, Pittsburgh). Several masses were monitored during the experiment, but major changes were seen only for m/z 15 and 16 (methane evolution). Attention was also focused at changes in m/z 20, which is suggestive of HF liberation from used catalysts.

3. Results and discussion

Prepared $Pd–Pt/Al_2O_3$ catalysts appeared quite highly dispersed (fraction exposed (FE) = 0.44–0.77, Table 1). The monometallic Pd100 showed the highest metal dispersion (FE = 0.77), whereas the rest of samples exhibited roughly similar metal dispersion, FE = 0.54 ± 0.1. It means that the monometallic Pd100 catalyst would be characterized by mean metal particle size of ~1.5 nm (≈1.12/FE, [32]), whereas the other samples should contain ca. 2 nm metal particles in size (Table 1). This fact, in combination with low metal loading and high background from γ-alumina, precluded use of X-ray diffraction for characterizing the metal phase. In addition, very small difference in the lattice parameter of Pd (0.389 nm) and Pt

(0.392 nm) excluded diffraction methods for diagnosing the composition of bimetallic Pd–Pt phases.

Temperature-programmed hydride decomposition (TPHD) has already been proposed as a suitable method for diagnosing the degree of alloying of bimetallic Pd-based catalysts (Pd–Re [20], Pd–Au [28,33]). In a majority of cases, introduction of another element to palladium lattice (alloying) brings about more or less serious decrease of hydrogen dissolution (i.e. a lower H/Pd ratio in respective β-hydride phase). Application of TPHD technique in present work appeared less successful. Very small, practically negligible, hydrogen evolution after saturating catalysts with hydrogen at lower temperatures resulted from very small metal particles (~2 nm) of Pd-based phase. It is known that for highly dispersed palladium, the formation of a β-palladium hydride phase is considerably suppressed (H/Pd$_{bulk}$ close to 0 [33–35]).

Catalytic screening of Pd–Pt/Al_2O_3 catalysts in CCl_2F_2 hydrodechlorination showed that stable conversions are achieved in a longer time-on-stream (~6–10 h). This is especially the case for the catalysts with somewhat higher platinum content (Fig. 1(b) and (c)). Only monometallic Pd100 almost instantaneously showed a stable conversion (Fig. 1(a)) and after ~3 h, stable selectivity (product distribution, Fig. 1(d)). The Pt100 catalyst appeared much less active (roughly an order of magnitude at 180 °C, i.e. the highest screening temperature) than palladium-containing samples (Table 2 and Fig. 2). Therefore, one is tempted to consider the effect of Pt addition to Pd/Al_2O_3 catalysts as the one followed from diluting active palladium species in an inert matrix. The question arises as to what extent platinum makes mixed ensembles with palladium. Our data analysis (vide infra) indicates that this is actually the case. If platinum were not located in a closest vicinity of palladium material, then the very low activity of Pt would not practically contribute to the overall behavior of Pd–Pt catalysts. In such a case, the catalytic properties have to be determined by unalloyed palladium particles. In other words, one would not observe any possible synergistic catalytic effects associated with Pt–Pd alloying.

First, let us consider the time-on-stream behavior of the Pd–Pt/Al_2O_3 catalysts. As it has already been mentioned, the activity of monometallic Pd100 is stabilized

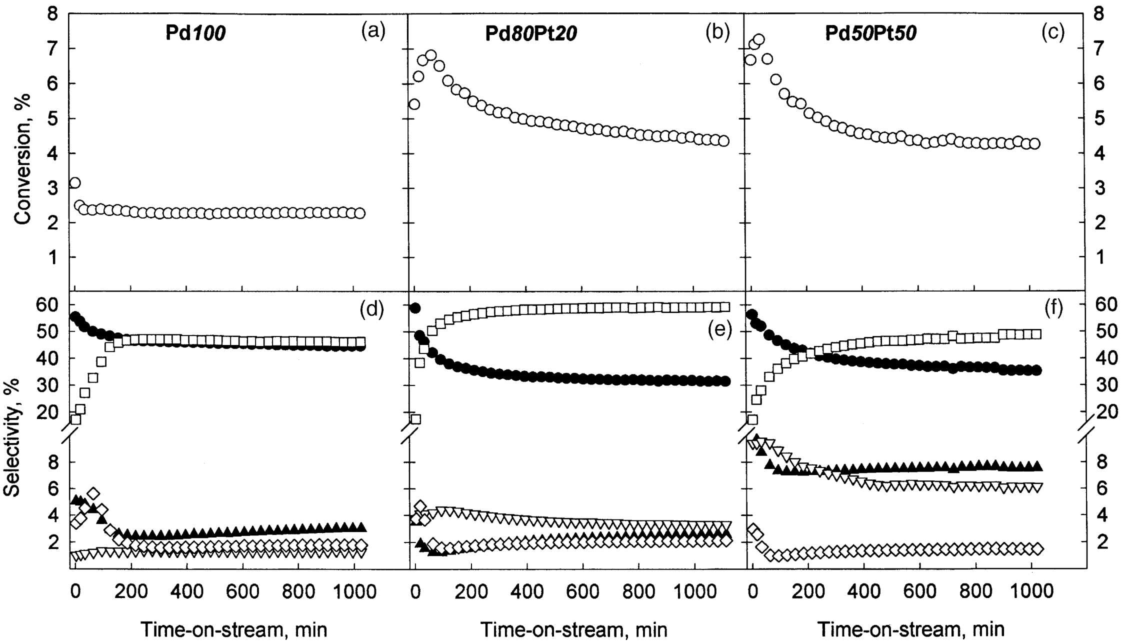

Fig. 1. Time-on-stream behavior in CCl_2F_2 hydrodechlorination at 180 °C: left section—1 wt.% Pd/Al_2O_3; medium section—1.45 wt.% Pd80Pt20/Al_2O_3; right section—2.8 wt.% Pd50Pt50/Al_2O_3. Top figures—overall conversion (○); bottom figures—selectivities to: CH_4 (●), CH_2F_2 (□), CH_3Cl (▲), $CHClF_2$ (▽), CH_2FCl (◇).

Table 2
Hydrodechlorination of CCl_2F_2 on Pd–Pt/Al_2O_3 catalysts: conversions, product selectivities and turnover frequencies

Catalyst[a]	Reaction temperature (°C)	Conversion (%)	Product selectivity (%)[b]						Turnover frequency (s^{-1})[c]
			CH_4	CH_2F_2	$CClF_3$	CH_3Cl	$CHClF_2$	CH_2ClF	
Pd100	180	2.27	44.7	46.2	2.8	3.0	1.3	1.8	0.0040
	170	1.55	41.3	49.6	2.9	2.9	1.7	1.6	0.0027
	160	1.02	37.4	53.0	5.2	3.8	–	–	0.0018
Pd95Pt5	180	2.48	32.1	53.9	3.4	6.3	0.5	2.4	0.0053
	170	1.73	29.1	58.2	3.2	5.9	0.5	2.0	0.0037
	160	1.18	26.3	62.6	2.8	5.3	0.6	1.6	0.0025
Pd90Pt10	180	3.72	34.1	57.5	1.0	2.5	3.0	1.9	0.0107
	170	2.50	30.5	61.1	1.0	2.5	3.4	1.6	0.0072
	160	1.67	27.5	64.6	0.7	2.1	3.8	1.2	0.0048
Pd80Pt20	180	4.51	31.5	59.2	1.3	2.6	3.3	2.1	0.0083
	170	2.99	27.6	63.5	1.0	2.4	3.7	1.8	0.0055
	160	1.94	23.5	68.3	0.6	2.2	4.0	1.4	0.0036
Pd50Pt50	180	4.27	35.4	48.8	0.6	7.5	6.2	1.5	0.0061
	170	2.89	31.0	52.8	0.5	7.5	7.1	1.2	0.0041
	160	1.85	27.2	57.8	0.2	7.0	7.7	–	0.0026
Pt100	180	0.16	56	9	0.5	7	28	–	0.0007
	170	0.12	52	10	–	6	32	–	0.0005
	160	0.10	49	10	–	–	41	–	0.0004

[a] For catalyst designation see Table 1.

[b] Other minor products: CHF_3, C_2H_6, CH_2Cl_2.

[c] Based on metal dispersion data shown in Table 1.

after a relatively short time-on-stream (Fig. 1(a) and (d)). A similar TOS behavior was found for Pd95Pt5 (not shown in Fig. 1). Further Pd doping gradually changes the situation: stable conversions and selectivities are obtained at much higher TOS values (Fig. 1(b), (c), (e) and (f)). The Pt100 shows very low activity at 180 °C (Table 2). Accordingly, the changes in TOS behavior of platinum are subjected to a greater error and can hardly be interpreted. Therefore, we speculate that platinum must modify palladium particles in tested catalysts. It is accepted that platinum exhibits weaker metal-chlorine and metal-carbon bonds, than palladium [8]. Therefore, development of a carbonaceous or/and chloride overlayer on Pt-modified Pd/Al_2O_3 catalysts should take more time than for the surface of monometallic palladium, which binds those species more strongly.

The next issue to be emphasized here is the course of the catalytic activity (TOF at steady state) versus Pd–Pt composition (Fig. 2). A maximum in turnover frequency at 10 at.% Pt suggests that the introduced

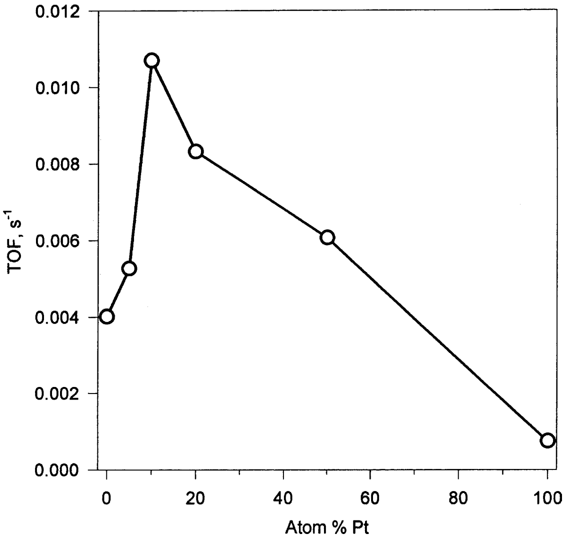

Fig. 2. The effect of Pd–Pt alloying on overall activity in CCl_2F_2 hydrodechlorination at 180 °C.

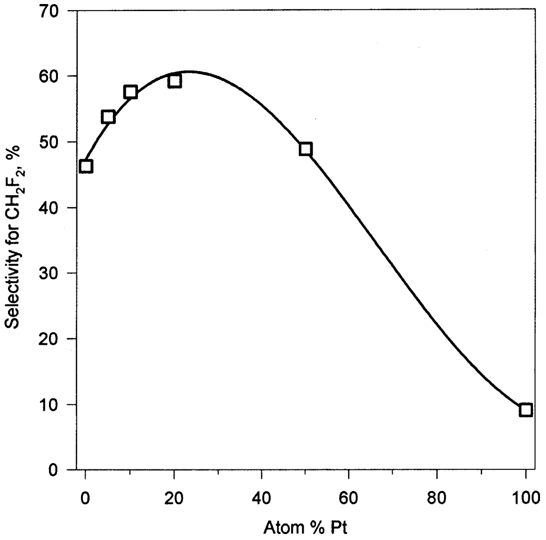

Fig. 3. The effect of Pd–Pt alloying on CH_2F_2 selectivity in CCl_2F_2 hydrodechlorination at 180 °C. The relation was drawn using polynomial regression (third order, regression coefficient = 0.9973).

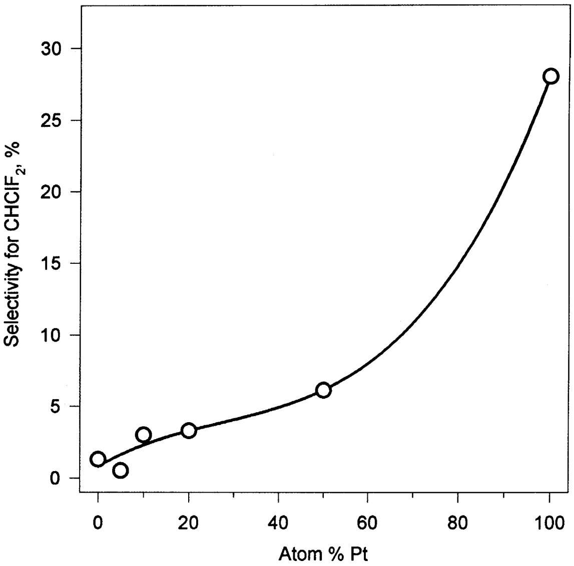

Fig. 4. The effect of Pd–Pt alloying on $CHClF_2$ selectivity in CCl_2F_2 hydrodechlorination at 180 °C.

platinum must interact with palladium in the catalysts. In an opposite case, i.e. without a pronounced Pd–Pt alloying one should not expect any special synergistic effect. It is proposed that, like in the case of Pd–Au catalysts, mixed Pd–Pt sites are beneficial for this reaction because they bind reaction products less strongly than monometallic Pd–Pd ensembles.

Similarly, for Pd–Pt/Al_2O_3 catalysts a gentle maximum of CH_2F_2 selectivity versus alloy composition is observed (Fig. 3). This effect seen at 10–20 at.% Pt suggests that introduction of small amount of platinum onto palladium surface is beneficial for a certain weakening of a metal-reactant (product) bond. It is possible that CF_2 adcarbenes (generally accepted intermediates leading to CH_2F_2) are less strongly bound to Pd–Pt than to Pd, and in excess hydrogen, they can be more efficiently hydrogenated off to CH_2F_2. Too strongly bound CF_2 adspecies would further dehalogenate and, finally, lead either to liberated methane or carbon deposited on the surface of catalysts. However, excessive amounts of platinum are not useful. This is due to the fact that platinum itself is so poorly active in this reaction that further increase of platinum content in the catalysts leads to a significant decrease of catalytic activity.

It must be stressed that, due to low activity of platinum in CCl_2F_2 hydrodechlorination, the catalytic behavior of all palladium-containing Pd–Pt/Al_2O_3 samples is largely shaped due to the presence of palladium, which is the most active component. This is best seen in Fig. 4 which shows, that the selectivity to $CHClF_2$ is low and roughly similar for Pd and Pd-rich bimetallic catalysts. Platinum gives much higher selectivity toward partial hydrodechlorination (∼28%), in agreement with Wiersma et al. [8]. Also the activation energies (not indicated in Table 2) show an analogous tendency: all Pd-containing samples show similar E_a values (between 60 and 67 kJ/mol, without any special trend with Pd–Pt bimetal composition), whereas for Pt100 the activation energy was found much lower, ∼40 kJ/mol.

Interesting information follows from the temperature programmed hydrogenation of deposit retained by the Pd–Pt catalysts after hydrodechlorination (Fig. 5). First observation is that the most active and selective (toward CH_2F_2) catalysts contain much less carbon than the other samples. Especially, the first TPH peak (∼300–350 °C) is decreased when Pd is alloyed with Pt. Secondly, all TPH profiles show a high temperature peak placed at 400–450 °C. Our tentative interpretation of such profiles is that the first methane peak is due to hydrogenation of carbon deposited on metal, whereas the high temperature peak is due to hydrogenation of coke from alumina.

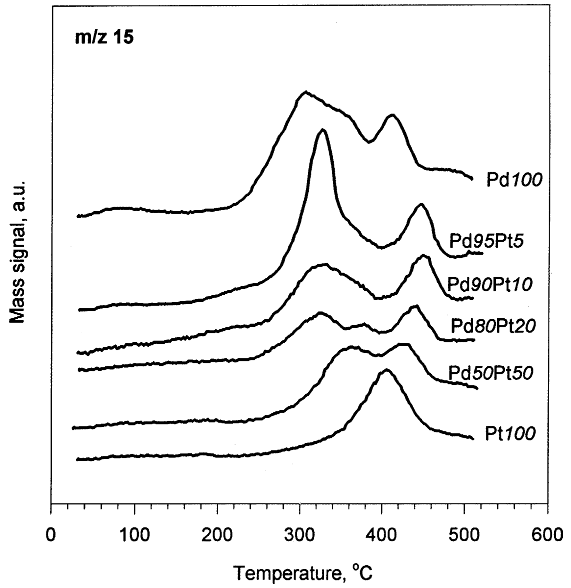

Fig. 5. Methane evolution during temperature-programmed hydrogenation of spent Pd–Pt/Al_2O_3 catalysts. Mass 15 was selected for presentation because CH_4 liberation observed by monitoring mass 16 is somewhat misinterpreted due to evolution of water (especially around 100 °C). Comparable catalyst weights (0.09 ± 0.01 g) were used.

In this respect, the presence of only one TPH peak for Pt100 (at ~400 °C) suggests no deposition of carbon on platinum during reaction but large amounts of carbon are held by alumina. It should be stressed that the hydrogenation of carbon from alumina of the Pt100 catalyst starts earlier than for the other catalysts. This shift toward lower temperature should be expected if a “cleaner” surface of platinum almost immediately furnishes dissociated hydrogen species for carbon hydrogenation from alumina. For other catalysts, hydrogenation of coke from alumina is slowed down by the need of preceding removal of

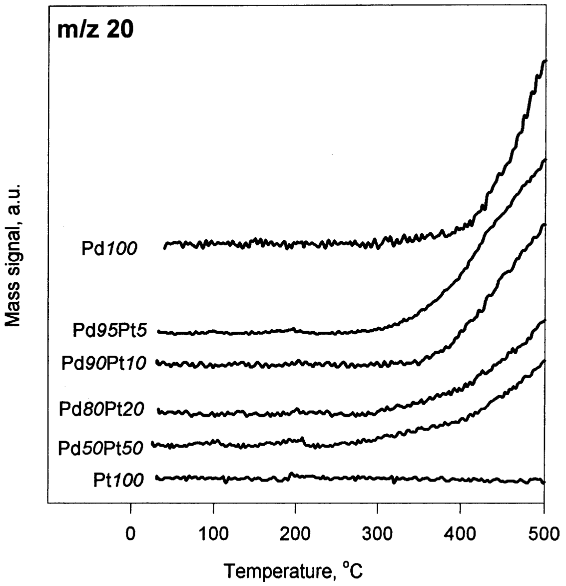

Fig. 7. HF evolution during temperature-programmed hydrogenation of spent Pd–Pt/Al_2O_3 catalysts. Comparable catalyst weights (0.09 ± 0.01 g) were used.

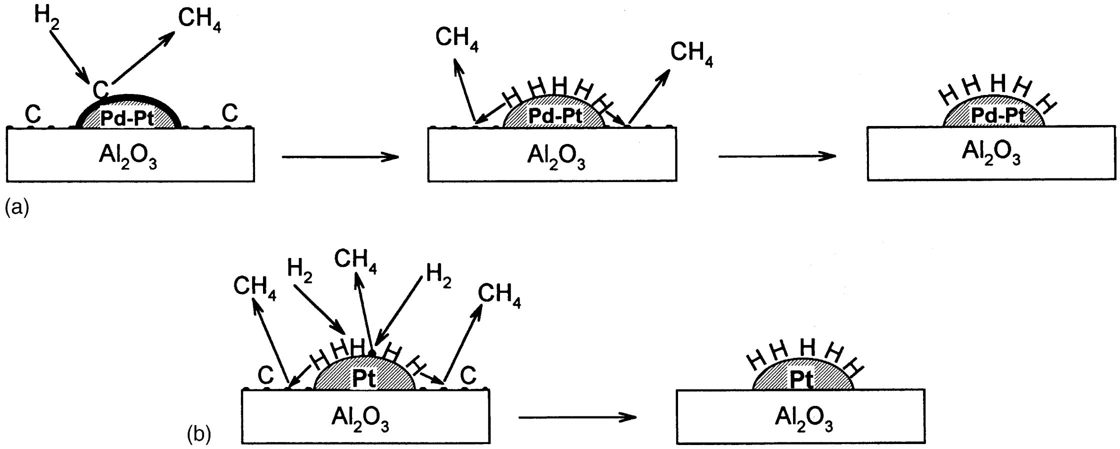

Fig. 6. Carbon removal from Pd–Pt/Al_2O_3 catalysts used in CCl_2F_2 hydrodechlorination: (a) from bimetallic Pd–Pt samples; (b) from monometallic Pt/Al_2O_3.

carbon from the surface of metal. A simplified graphic representation of the difference in carbon removal from Pt100 and all Pd-containing catalysts is given in Fig. 6.

Fig. 7 shows changes in HF evolution (as *m*/*z* 20) during TPH runs from used Pd–Pt/Al_2O_3 catalysts. This evolution starts at >300 °C and is not finished by end of the run (at 500 °C). It suggests that fluorine is firmly bonded to alumina. Fluorination of alumina with fluoromethanes at elevated temperatures is a known practice [36] and takes place during CCl_2F_2 hydrodehalogenation on Pd/Al_2O_3 catalysts [3,4]. Fig. 7 shows, however, that fluorination of alumina does not practically occur in the case of Pt100, which shows much lower activity in CCl_2F_2 hydrodehalogenation than all remaining (i.e. Pd-containing) catalysts. These results suggest that the extent of alumina fluorination is associated with the spillover of fluorine (stripped off from CCl_2F_2) from the surface of metal onto the support.

4. Conclusions

Highly-dispersed alumina-supported Pd–Pt catalysts of low metal loading were investigated in hydrodechlorination of dichlorodifluoromethane. A synergistic effect was found. The bimetallic Pd-rich samples, with 10–20 at.% Pt, appeared the best catalysts, because both the overall activity (TOF) as well as the selectivity toward difluoromethane (desired reaction product) are higher than for the remaining catalysts. $CHClF_2$ is produced in larger amounts on the monometallic alumina-supported platinum catalyst (selectivity 28% at 180 °C), whereas Pd and Pd–Pt samples form only small amounts of this product. This result, in combination with very minor changes in the activation energy for Pd and Pd–Pt catalysts, suggests that the catalytic behavior of palladium is largely preserved in bimetallic samples. Because after reaction the most active and selective Pd–Pt catalysts contained lesser amounts of carbon than the other (less active) catalysts, it is considered that small amounts of introduced platinum (to palladium) are beneficial for maintaining the catalyst surface less blocked by carbon species, and in effect, more active.

Acknowledgements

The authors gratefully acknowledge financial support from the State Committee for Scientific Research of Poland (KBN) within Grant No. 4 T09B 098 24.

References

[1] L.E. Manzer, Catal. Today 13 (1992) 13–22.

[2] L.E. Manzer, V.N.M. Rao, Adv. Catal. 39 (1993) 329–350.

[3] B. Coq, J.M. Cognion, F. Figuéras, D. Tournigant, J. Catal. 141 (1993) 21–33.

[4] B. Coq, F. Figuéras, S. Hub, D. Tournigant, J. Phys. Chem. 99 (1995) 11159–11166.

[5] Z. Karpiński, K. Early, J.L. d'Itri, J. Catal. 164 (1996) 378–386.

[6] E.J.A.X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum, J.A. Moulijn, Catal. Today 35 (1997) 163–170.

[7] E.J.A.X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum, J.A. Moulijn, Appl. Catal. A 155 (1997) 59–73.

[8] A. Wiersma, E.J.A.X. van de Sandt, M.A. den Hollander, H. van Bekkum, M. Makkee, J.A. Moulijn, J. Catal. 177 (1998) 29–39.

[9] M. Makkee, A. Wiersma, E.J.A.X. van de Sandt, H. van Bekkum, J.A. Moulijn, Catal. Today 55 (2000) 125–137.

[10] J.A. Moulijn, M. Makkee, A. Wiersma, E.J.A.X. van de Sandt, Catal. Today 59 (2000) 221–230.

[11] M. Öcal, M. Maciejewski, A. Baiker, Appl. Catal. B 21 (1999) 279–289.

[12] A.L. Ramos, M. Schmal, D.A.G. Aranda, G.A. Somorjai, J. Catal. 192 (2000) 423–431.

[13] S. Deshmukh, J.L. d'Itri, Catal. Today 40 (1998) 377–385.

[14] K. Early, V.I. Kovalchuk, F. Lonyi, S. Deshmukh, J.L. d'Itri, J. Catal. 182 (1999) 219–227.

[15] Z. Karpiński, J.L. d'Itri, Catal. Lett. 77 (2001) 135–140.

[16] Y.C. Cao, X.Z. Jiang, W.H. Song, Z.Q. Bai, X.Q. Fang, Catal. Lett. 76 (2001) 53–57.

[17] A. Morato, C. Alonso, F. Medina, J.L. Garreta, J.E. Sueiras, Y. Cesteras, P. Salagre, D. Tichit, B. Coq, Catal. Lett. 77 (2001) 141–146.

[18] W. Juszczyk, A. Malinowski, Z. Karpiński, Appl. Catal. A 166 (1998) 311–319.

[19] B. Coq, S. Hub, F. Figuéras, D. Tournigant, Appl. Catal. A 101 (1993) 41–50.

[20] A. Malinowski, W. Juszczyk, M. Bonarowska, J. Pielaszek, Z. Karpiński, J. Catal. 177 (1998) 153–163.

[21] R. Ohnishi, W.-L. Wang, M. Ichikawa, Appl. Catal. A 113 (1994) 29–41.

[22] S. Morikawa, S. Samejima, M. Yositake, S. Tatsematsu, Eur. Patent 0,347,830, A2 (1989), to Asahi Glass Co.

[23] V.N.M. Rao, US Patent 5,447,896 (1995), to du Pont de Nemours.

[24] V.N.M. Rao, US Patent 5,629,462 (1997), to du Pont de Nemours.

[25] A. Malinowski, W. Juszczyk, J. Pielaszek, M. Bonarowska, M. Wojciechowska, Z. Karpiński, Chem. Commun. (1999) 685–686.

[26] A. Malinowski, W. Juszczyk, J. Pielaszek, M. Bonarowska, M. Wojciechowska, Z. Karpiński, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), Studies in Surface Sciences and Catalysis, vol. 130, 2000, pp. 1991–1996.

[27] M. Bonarowska, A. Malinowski, W. Juszczyk, Z. Karpiński, Appl. Catal. B 30 (2001) 187–193.

[28] M. Bonarowska, B. Burda, W. Juszczyk, J. Pielaszek, Z. Kowalczyk, Z. Karpiński, Appl. Catal. B 35 (2001) 13–20.

[29] M. Bonarowska, J. Pielaszek, V.A. Semikolenov, Z. Karpiński, J. Catal. 209 (2002) 528–538.

[30] T.N. Bell, P. Kirszensztejn, B. Czajka, React. Kinet. Catal. Lett. 56 (1995) 221–229.

[31] T.N. Bell, P. Kirszensztejn, B. Czajka, Catal. Lett. 30 (1995) 305–312.

[32] S. Ichikawa, H. Poppa, M. Boudart, J. Catal. 91 (1985) 1–10.

[33] M. Bonarowska, J. Pielaszek, W. Juszczyk, Z. Karpiński, J. Catal. 195 (2000) 304–314.

[34] M. Boudart, H.S. Hwang, J. Catal. 39 (1975) 44–52.

[35] N.K. Nag, J. Phys. Chem. B 105 (2001) 5945–5949.

[36] G.B. Mc Vicker, C.J. Kim, J.J. Eggert, J. Catal. 80 (1983) 315–327.