Hydrodechlorination of 1,1-dichlorotetrafluoroethane on supported palladium catalysts. A static-circulation reactor study

Zbigniew Karpiński[a] and Julie L. d'Itri[b]

[a] *Department of Catalysis on Metals, Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01224 Warszawa, Poland*
E-mail: zk@ichf.edu.pl
[b] *Department of Chemical and Petroleum Engineering, University of Pittsburgh, Materials Research Center, PA 15261, USA*
E-mail: jditri@pitt.edu

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Supported palladium catalysts were studied in CF_3CFCl_2 hydrodechlorination at 100 °C using a static-circulation system. In order to minimize catalyst's deactivation a large excess of hydrogen was employed (H_2/CF_3CFCl_2 ratio 54/1). In spite of this precaution significant inhibition of the process occurred, associated with blocking palladium surface by hydrogen chloride species. Differences in the catalytic behavior of alumina-supported and unsupported palladium are discussed. A mild dependence between the catalytic activity and Pd dispersion was found. The Pd/Al_2O_3 catalyst characterized by low metal dispersion was more active than highly dispersed catalysts, showing the overall activity and selectivity to CF_3CFH_2 comparable with those observed by other authors for palladium single crystals. It is speculated that the most active sites for hydrodechlorination are plane atoms, whereas low coordination sites (on edges and corners of metal crystallites) are less suitable.

KEY WORDS: CF_3CFCl_2 hydrodechlorination; supported palladium catalysts; correlation with Pd single crystals

1. Introduction

Recent interest in chlorine removal from chlorofluorocarbons (CFCs) launched extensive research on the reaction of hydrodechlorination (HdCl) catalysed by supported [1–10] and unsupported palladium [11–13]. It was established that both catalytic activity and selectivity (*e.g.,* toward partly dehalogenated products) depend on the type of support [2,3,7,8,10]. Generally, several studies concerning the detailed reaction mechanism were made [2,3,5,8].

One interesting albeit arguable issue associated with the behavior of palladium catalysts concerns the problem of structure sensitivity in CFCs hydrodechlorination. A number of investigations carried out with supported palladium catalysts showed that both the overall activity as well as product selectivity are influenced by palladium dispersion [2,4,9]. The results indicated that CFCs hydrodechlorination on palladium catalysts was a structure-sensitive reaction. On the other hand, examination of the catalytic behavior of unsupported palladium brought about a contradictory conclusion, because Pd(111), Pd(100) and a Pd foil showed comparable catalytic properties (TOF, selectivity) in CF_3CFCl_2 hydrodechlorination [11,13]. The difference in behavior of the two types of catalytic systems may be associated with some effect of the support. Changes in the surface structure and composition of Pd/γ-Al_2O_3 observed during HdCl suggest that the support plays a role of halogen-containing sink [10]. The presence of halogen-containing species probably enhances acidic properties of alumina [14–17] leading to increased formation of carbonaceous residues, which may migrate to palladium and deactivate it in the course of reaction [10].

It should be mentioned that the Pd single crystal studies [11–13] were performed in a batch reactor, whereas the supported catalysts are usually studied in flow reactors. In the flow systems one tends to interpret a steady-state regime, achieved after the initial catalyst deactivation (which may proceed even for hours and be very significant), whereas in batch reactors usually the initial period is analyzed as well. In order to compare more closely the catalytic behavior of supported Pd catalysts with the reported performance of Pd single crystals [13], we decided to test variously dispersed supported palladium catalysts in a static-circulation reactor system.

2. Experimental

2.1. Catalyst preparation and characterization

The preparation of 2 wt% Pd/γ-Al_2O_3 by incipient wetness impregnation was described previously [4]. Other alumina-supported Pd catalysts had metal loadings: 0.39, 1 and 1.45 wt%. In addition, our study included one Davison 62 silica-supported 1.6 wt% Pd/SiO_2. The basic characteristics of all investigated catalysts along with preparation details are shown in table 1.

2.2. Catalytic experiments

The hydrodechlorination of 1,1-dichlorotetrafluoroethane was conducted in a static-circulation system. The apparatus was made of Pyrex and greaseless high vacuum stopcocks and was equipped with a turbomolecular pump backed by a mechanical pump. The essential parts of the circulation system were: a circulation pump (MICROPUMP from Cole-Parmer), a reactor and a rotameter. Both the pump and the reactor had bypasses. The Pyrex (or fused silica) U-tube reactor, equipped with a fritted disc and a thermocouple well, was connected to the system *via* two Cajon Ultra-Torr fittings. Total volume of the circulation system was ~1200 ml.

After precalcination (in 5% O_2/He preblended by Liquid Carbonic or oxygen, 25 ml/min) and reduction in flowing H_2 (25 ml/min) the catalysts (0.02–0.1 g samples) were cooled in H_2 to 100 °C, which was the chosen reaction temperature. This was the lowest reaction temperature used in our previous flow reactor study [4]. The reaction mixture consisted of hydrogen and 1,1-dichlorotetrafluoroethane (purity >99%, courtesy Du Pont). The 99.999% pure (Liquid Carbonic) hydrogen and helium (used for system purging) were further purified by passing them through MnO/SiO_2 traps. The total pressure of the reaction mixture was ~868 Torr, in which the partial pressure of 1,1-dichlorotetrafluoroethane was ~15.7 Torr and the rest was hydrogen. Consequently, the ratio of H_2-to-CF_3CFCl_2 was ~54/1. The reaction mixture was carefully premixed by circulating it for 10–15 min when one or more blank samplings (GC) were performed. Next, the reaction mixture was introduced into the reactor, the reaction run being started. The reaction mixture was analyzed in time by GC. The samples were collected by means of an evacuable sampling valve and injected into a gas chromatograph (Varian 3300 with FID detector and 5% Fluorocol/carbosieve column from Supelco). By each sampling, the pressure in the reaction system was decreased by less than 0.2%, so in a typical run (10–13 samplings), the overall loss of reaction mixture was ~2%. The reaction was studied until a 7–8% conversion level was achieved. A typical course of the experiment is shown in figure 1.

Table 1
Characteristics of supported Pd catalysts used in this work.

Support[a]	Pd loading (wt%)	Pd precursor	Metal dispersion H/Pd[b]
γ-Al_2O_3[c]	2	$Pd(NO_3)_2$	0.1[d]
γ-Al_2O_3	0.39	$Pd(NH_3)_4(NO_3)_2$	0.506
γ-Al_2O_3	1	$PdCl_2$	0.38
γ-Al_2O_3	1.45	$Pd(acac)_2$	0.546
SiO_2[e]	1.6	$PdCl_2$	0.5

[a] PHF γ-Al_2O_3 (American Cyanamid), unless indicated otherwise.

[b] After precalcination in O_2/He stream up to 500 °C (4 °C/min) and reduction in H_2 at 300 °C, unless indicated otherwise. Metal dispersion measured by pulse chemisorption of hydrogen at 70 °C.

[c] Vista-B γ-Al_2O_3.

[d] After reduction in 300 °C for 10 h. Metal dispersion measured by H_2 chemisorption using a double-isotherm method (at 20 °C) in a static system.

[e] Davison 62 silica gel.

Turnover frequencies (TOFs) were calculated on the basis of metal dispersion values, H/Pd, known from hydrogen chemisorption (table 1). To assess possible changes in metal dispersion caused by hydrodechlorination comparable X-ray diffraction studies with freshly reduced and used 1 and 2 wt% Pd/Al_2O_3 catalysts were performed (results not shown). Although a more detailed analysis of the obtained XRD profiles is somewhat complicated by overlapping reflections from Pd and γ-Al_2O_3, it is concluded that neither phase changes (such as C incorporation into Pd, [8,9]) nor

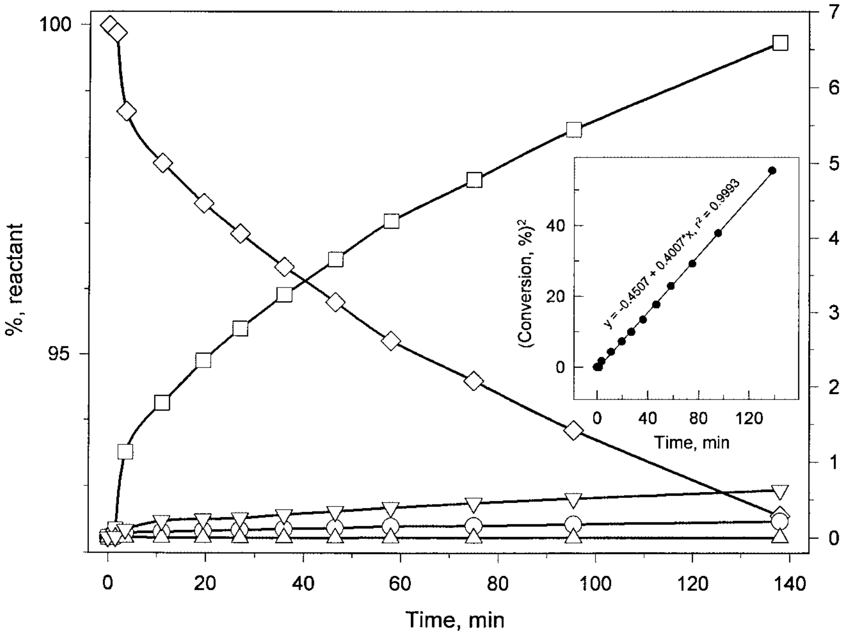

Figure 1. Time course of CF_3CFCl_2 hydrodechlorination over 0.0337 g of 2 wt% Pd/γ-Al_2O_3 at 100 °C. (◇) CF_3CFCl_2, (□) CF_3CFH_2, (○) CF_3CH_3, (▽) CF_3CFHCl, and (△) hydrocarbons ($CH_4 + C_2H_4 + C_2H_6$). Inset: linear dependence of squared conversion *vs.* time.

crystallite size modifications are caused by the reaction. It is possible that the applied screening conditions (low reaction temperature, short reaction time) were too mild to make marked changes in our catalysts.

3. Results and discussion

As shown in figure 1, the overall course of the reaction can be roughly divided into two parts. Preliminary separation of an initial period from the "steady-state" one was adopted from an earlier study of *tert*-butyl chloride hydrodechlorination over Pt and Pd films [18]. All catalysts were tested until an identical conversion level (7–8%) was attained, so preliminary examination of the two reaction periods appears reasonable without any detailed analysis of the origin of catalyst deactivation (by HCl formed, *vide infra*). The reaction rate in the initial period could not be measured very accurately, because the frequency of sampling was limited by the length of GC analysis (~8 min). Anyway, the rate of accumulation of each product accumulation (*e.g.*, $d[CF_3CFH_2]/dt$) at different reaction time was analysed indicating no significant variations in the product distribution within the overall reaction time. The initial and the "steady-state" rates and selectivities are shown in table 2. The selectivity for CF_3CFH_2 was always high and changed from 70 to 90%, depending on the catalyst.

The experiments with two differently loaded $Pd/\gamma\text{-}Al_2O_3$ catalysts of comparable metal dispersions (figure 2 and table 2) clearly show that γ-alumina participated in the reaction in the initial period. Comparison of two charges which had identical amounts of (surface) palladium, but different quantities of alumina, showed that the low Pd-loaded catalyst (0.39 wt%, 0.104 g sample) was much more active in the initial period than the 1.45 wt% Pd/Al_2O_3 (0.0275 g sam-

Table 2
Hydrodechlorination of CF_3CFCl_2 on supported palladium catalysts at 100 °C.

Initial TOF	Initial selectivity (%)				"Steady-state" TOF	"Steady-state" selectivity (%)			
(s^{-1})	CF_3CFH_2	CF_3CH_3	CF_3CFHCl	C_xH_y	(s^{-1})	CF_3CFH_2	CF_3CH_3	CF_3CFHCl	C_xH_y
2 wt% Pd/Al_2O_3 (0.0337 g)									
2.60×10^{-1}	88.1	1.7	9.6	0.6	1.00×10^{-2}	88.1	3.2	8.5	0.2
1.45 wt% Pd/Al_2O_3 (0.0275 g)									
2.07×10^{-2}	74.8	20.1	4.9	0.2	2.96×10^{-3}	76.8	18.0	4.9	0.3
0.39 wt% Pd/Al_2O_3 (0.1040 g)									
8.00×10^{-2}	74.0	19.4	6.0	0.6	4.04×10^{-3}	69.6	25.5	4.7	0.2
1.45 wt% Pd/Al_2O_3 (0.1027 g)									
1.94×10^{-2}	74.1	18.8	4.8	2.3	2.56×10^{-3}	74.9	20.1	4.8	0.2
1 wt% Pd/Al_2O_3 (0.0408 g)									
9.68×10^{-3}	74.2	19.2	6.0	0.6	3.23×10^{-3}	76.7	18.6	4.3	0.4
1.6 wt% Pd/SiO_2 (0.0444 g)									
6.12×10^{-3}	80.0	12.2	7.8	0.1	2.07×10^{-3}	81.8	11.9	6.2	0.1

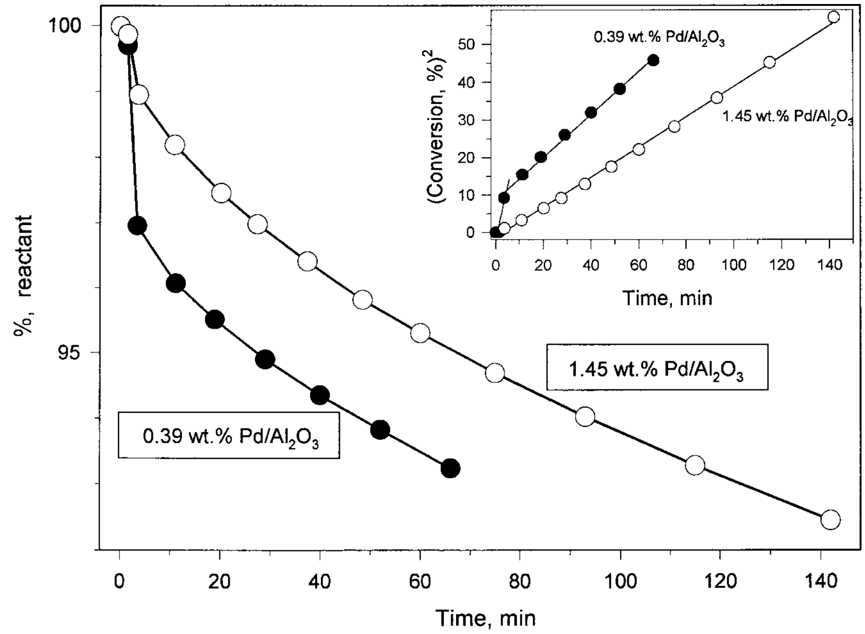

Figure 2. Time course of CF_3CFCl_2 hydrodechlorination over 1.45 wt% $Pd/\gamma\text{-}Al_2O_3$ (0.0275 g (○)) and 0.39 wt% $Pd/\gamma\text{-}Al_2O_3$ (0.1040 g (●)) at 100 °C. Inset: linearisation of $(\text{conversion})^2$–time relations for these catalysts.

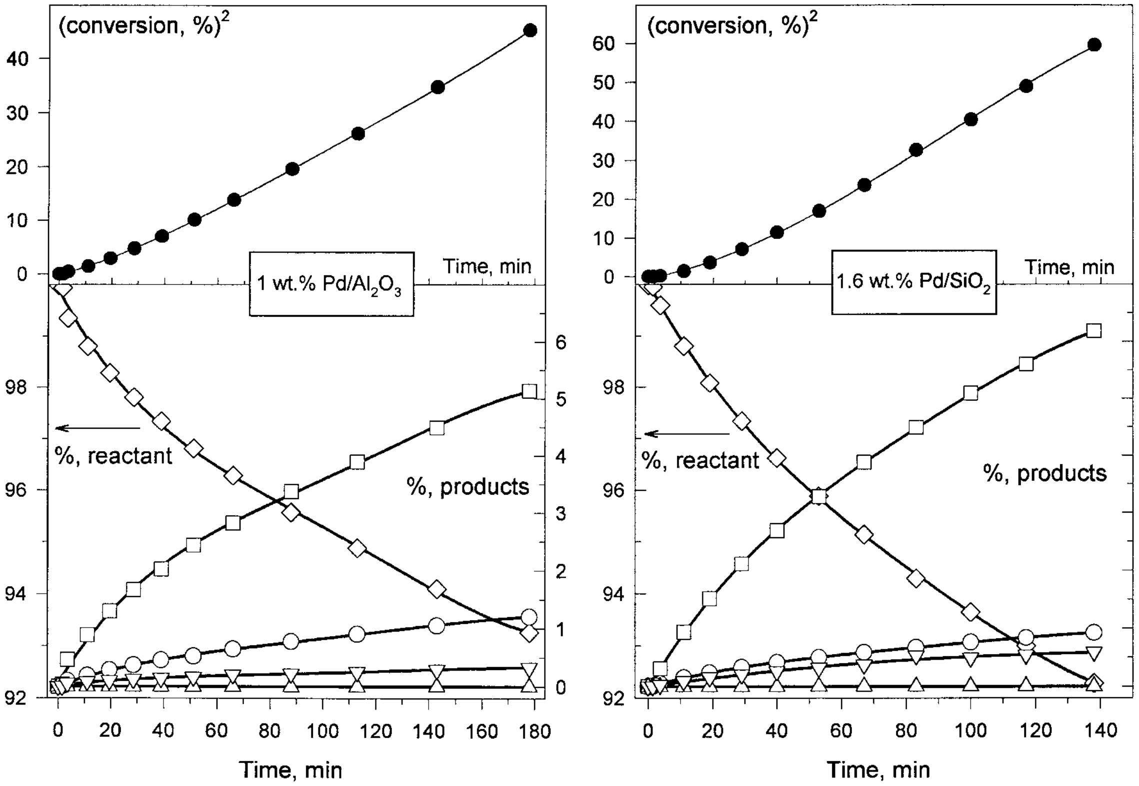

Figure 3. Time course of CF_3CFCl_2 hydrodechlorination over 0.0408 g of 1 wt% Pd/γ-Al_2O_3 (left part) and 0.0444 g of 1.6 wt% Pd/SiO_2 (right part). Reaction temperature 100 °C, symbols as in figure 1. Upper segments display (conversion)^2–time relation for these catalysts.

ple). However, this activity change was based on the molar composition of the reaction mixture. A closer inspection of the overall FID signal corresponding to the organic part of the reaction mixture revealed that the decrease of activity at the initial stage of reaction for 0.39 wt% Pd/Al_2O_3 was larger by a few percent. In addition, after introducing the reaction mixture onto the 0.39 wt% Pd/γ-Al_2O_3, we observed an instantaneous increase of temperature of the catalyst bed by $\sim$5 °C, an effect that was not detected in the case of the 1.45 wt% Pd/γ-Al_2O_3. It is known that interaction of γ-Al_2O_3 with halogenated ethane species leads to extensive binding of these organic molecules [14–17,19] and to substantial modification of alumina [10]. Insignificant changes in product selectivity during the reaction suggest that although alumina binds some nonnegligible amounts of CF_3CFCl_2, it contributes only very little to the formation of products released to the gas phase [10]. After a short initial period, the reaction proceeded similarly on 0.39 and 1.45 wt% Pd-loaded catalysts, as shown by two almost parallel descending curves in figure 2. At this stage the reaction rate did not depend on the amount of alumina in the Pd/Al_2O_3 samples. The catalytic behavior (TOF, selectivity) of a larger sample of 1.45 wt% Pd/Al_2O_3 (0.1027 g) was found similar to that exhibited by the smaller sample of 1.45 wt% Pd/Al_2O_3 (0.0275 g, table 2). So, the catalytic effect of alumina in Pd/Al_2O_3 catalysts at the initial period of reaction is better manifested for catalysts of very low Pd loading. Thus, we speculate that the reaction takes place predominantly on the palladium surface.

In order to compare our data on supported Pd catalysts with the literature data for Pd single crystals [13] we followed their approach to analyse our kinetic data. It was found that CF_3CFCl_2 hydrodechlorination on Pd single crystals was strongly inhibited by forming HCl species. Accordingly, integration of an expected kinetic equation (rate $\propto$ $[HCl]^{-1}$) implied a linear relation between squared conversion (α^2) and time [12,13]. We checked if this relation holds in our case, *i.e.*, for the Al_2O_3- and SiO_2-supported palladium catalysts. In fact, the inset in figure 1 shows that, the kinetic data for 2 wt% Pd/Al_2O_3 (of low metal dispersion, $H/Pd = 0.1$), can be presented as an excellent linear plot in the relation α^2 *vs.* time. It seems that low metal dispersed Pd catalysts exhibit similar catalytic properties as palladium single crystal surfaces in CF_3CFCl_2 hydrodechlorination.

Similar analysis of our results for other supported Pd catalysts did not produce superior linear plots α^2 *vs.* time (figure 2 and, especially, figure 3). Two different cases were distinguished. For the 0.39 wt% Pd/Al_2O_3, a very high initial reaction rate with further deactivation was observed with a relatively good linear fit (α^2 *vs.* time) for the later part of the reaction ($r^2 = 0.9963$, figure 2, inset). On the other hand, for the 1.45 wt% Pd/Al_2O_3 catalyst, characterized by a similar metal dispersion, a good linear plot α^2 *vs.* time ($r^2 = 0.9982$, figure 2, inset) holds for the whole reaction time, including the initial period. As concluded before, the initial period of reaction on 0.39 wt% Pd/Al_2O_3 was "distorted" by a considerable uptake of the CFC reactant by γ-alumina.

Figure 3 shows similar plots for 1 wt% Pd/Al_2O_3 and 1.6 wt% Pd/SiO_2 prepared from palladium chloride. These catalysts (as well as 0.39 and 1.45 wt% Pd/Al_2O_3) are less active than the 2 wt% Pd/Al_2O_3 (table 2). In addition, plotting the kinetic data as α^2 *vs.* time did not produce so good straight lines as for other catalysts (figure 3), indicating that the reaction rate was not proportional to $[HCl]^{-1}$. This result, although in apparent disagreement with kinetic data on Pd single crystals [13], is not unexpected, since the departure from the linear α^2 *vs.* time relation is caused by the presence of big excess of hydrogen in the reaction system (H_2/CF_3CFCl_2 ratio = 54/1). Although hydrogen seems to be less strongly adsorbed by palladium than chlorine species, surface coverage by hydrogen may not be negligible at very high hydrogen partial pressure in the system. In fact, the irreversible hydrogen chemisorption on palladium at 100 °C (or 70 °C) often serves as a measure of palladium dispersion (H/Pd). Application of lower temperatures for H_2 adsorption either is avoided or requires additional measurement of hydrogen dissolved in the palladium bulk. Competition between chlorine and hydrogen species on palladium has already been appreciated by other workers. Coq *et al.* regarded the halogenation/dehalogenation (by hydrogen) as a crucial step in their reaction mechanism [2,3]. Ribeiro *et al.* saturated the Pd foil with Cl_2 and found that heating of the chlorine saturated the Pd surface at 100 °C and 1 Torr of H_2 was sufficient to remove all the chlorine [13]. At large excess of H_2 in a gas phase, the denominator of the Langmuir-type expressions for surface coverages of all reacting species depends very much on hydrogen pressure, so the effect of other species on reaction kinetics becomes less marked. On the other hand, it is known that the rate of chlorination of Pd particles decreases when the dispersion increases [19]. Therefore, the competition between hydrogen and HCl on the palladium surface may depend significantly on the Pd dispersion. Apparently, at comparable conversions (*i.e.*, at similar partial pressures of HCl), massive Pd samples (of 2 wt% Pd/Al_2O_3 or single crystals) show higher surface coverage with chlorine species than the highly dispersed palladium catalysts.

Table 2 shows reaction rates and product selectivities obtained for a "steady-state" period of hydrodechlorination of 1,1-dichlorotetrafluoroethane over several supported palladium catalysts. The low dispersed catalyst (2 wt% Pd/γ-Al_2O_3 prepared from $Pd(NO_3)_2$) shows the highest selectivity toward CF_3CFH_2 formation, namely ~88%. This value is comparable with the selectivity exhibited by palladium single crystal surfaces [13]. Somewhat lower selectivities are obtained for other alumina-supported catalysts.

Figure 4 presents the "steady-state" TOF values as a function of Pd dispersion for all investigated catalysts. Although silica-supported palladium is somewhat less active than similarly dispersed alumina-supported samples, it is clear that more dispersed palladium catalysts show lower TOF values. Similar TOF–Pd dispersion relations were reported in other works for CCl_2F_2 hydrodechlorination [2,9] and also for CF_3CFCl_2 reaction on Pd/Al_2O_3 [4]. It should be stressed that such dependencies are usually not very pronounced, with all TOF variations falling within an order of magnitude for a whole range of metal dispersion [2,9]. Nevertheless, the question arises as to how to reconcile these results with structure-insensitivity of CF_3CFCl_2 hydrodechlorination over Pd single crystal surfaces reported by Ribeiro *et al.* [13]. It seems that a dominant role in catalyzing CFCs hydrodechlorination is played by plane palladium atoms. The difference in covalent unsaturation of surface Pd atoms in Pd(111) (coordination number $Z = 9$) and Pd(100) ($Z = 8$) surfaces is not as large as in the case when one compares plane and corner (or edge) atoms in Pd crystallites, where Z may be even as low as 3. The statistics of differently coordinated surface atoms on fcc metal crystallites determined by their shape and size, shows that for large palladium octahedral or cubooctahedral particles (*e.g.*, ~12 nm in size) plane atoms are the most abundant surface sites [20]. Our 2 wt% Pd/Al_2O_3 catalyst, characterized by metal dispersion 0.1 ($d_{Pd} \approx 11.2$ nm [21]) should actually manifest a predominant presence of such sites, and, in effect, show similar catalytic properties as Pd single crystal surfaces. Simple extrapolation of the data for Pd(111) (TOF = 1.66 s^{-1} at 150 °C and 50 Torr CF_3CFCl_2, 100 Torr H_2, 0.1 Torr HCl, table 2 in [13]) to 100 °C, using $E_A = 100$ kJ/mol (table 3 in [13]) gives the TOF value of 3.6×10^{-2} s^{-1}. This estimate can be compared with the "steady-state" TOF value for 2 wt% Pd/Al_2O_3 (1.00×10^{-2} s^{-1}, table 2). Since partial pressure of CF_3CFCl_2 was ~3 times higher in the single crystal study, and the reaction rate was proportional to the CF_3CFCl_2 partial pressure [4], the comparison of catalytic activity of Pd single crystals and 2 wt% Pd/γ-Al_2O_3 appears very satisfactory.

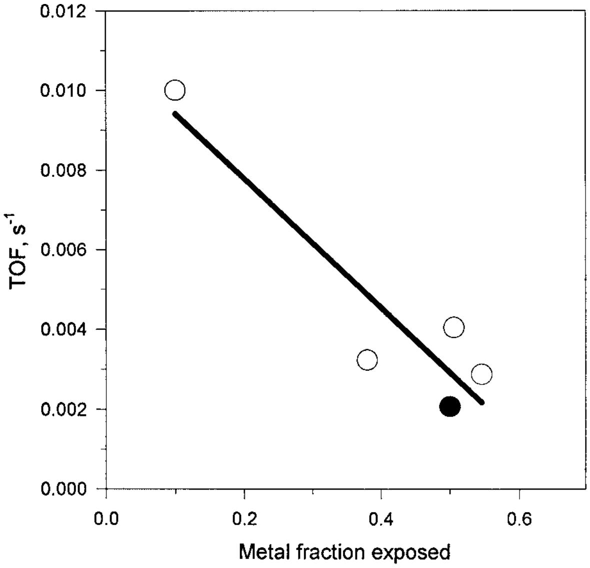

Figure 4. Effect of palladium dispersion (fraction exposed) on catalytic activity of supported palladium catalysts in CF_3CFCl_2 hydrodechlorination. Symbols: (○) stand for alumina-supported catalysts, and (●) for 1.6 wt% Pd/SiO_2.

The structure sensitivity of the hydrodechlorination reaction would be explained by the suggestion that this reaction, like alkane hydrogenolysis, requires large surface ensembles, the number of which should increase with increasing palladium particle size. It is also possible that the increased activity of larger Pd particles is due to the fact that the low levels of site blocking (*e.g.*, by chlorine species) will have less influence on the number of active ensembles present on large particles than on the small particles.

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