

Liquid-Phase Hydrodechlorination of CCl_4 to CHCl_3 on Pd/Carbon Catalysts: Nature and Role of Pd Active Species

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1. INTRODUCTION

This study examines the influence of the preparation variables on the physicochemical properties of Pd/C catalyst and its performance in the hydrodechlorination of carbon tetrachloride and proposes a model of a palladium active site and its catalytic “modus operandi” which satisfactorily describes the chloroform formation from carbon tetrachloride. Several carbon-supported Pd (0.2–1.6 wt%) catalysts were prepared by incipient wetness impregnation of the support with H_2PdCl_4 aqueous solutions and reduced at 523 K (CPd series). Additionally, five portions of the 1.0 wt% CPd precursor were reduced at 423, 473, 623, 723, and 823 K. Another two catalysts containing 1.0 wt% Pd were prepared in similarly to $\text{Pd}(\text{NO}_3)_2$ and reduced at 523 K (NPd series). One of these last samples was calcined at 573 K prior to the reduction. The TPR results indicate that reduction of the CPd precursors is more difficult than that of NPd, which are reduced at subambient temperature. As shown by CO chemisorption, metal dispersion in NPd is lower than in CPd catalysts, in which dispersion decreases as the reduction temperature increases. X-ray photoelectron spectroscopy shows that Pd^0 and Pd^{n+} species are present on the catalysts surface and that their proportion depends on the reduction temperature and the nature of the palladium precursor. All the catalysts containing both Pd^0 and Pd^{n+} were active and highly selective in the hydrodechlorination of carbon tetrachloride to chloroform, whereas samples having only one of these species were inactive. The results indicate that both Pd^0 and Pd^{n+} are required for the catalytic hydrodechlorination reaction and, consequently, it is proposed that the active Pd site is dual in nature and is constituted by the association of the two species: electron-deficient and metallic palladium [$\text{Pd}^{n+}\text{-Pd}^0$]. The hydrodechlorination activity is related to the $\text{Pd}^{n+}/\text{Pd}^0$ ratio and the maximum activity corresponds to $\text{Pd}^{n+}/\text{Pd}^0 \approx 1$. We propose that H_2 chemisorbs and dissociates on Pd^0 to give the covalent adatom Pd–H, whereas CCl_4 chemisorbs dissociatively on the same Pd^{n+} site by abstraction of the slightly nucleophilic chloride anion (Cl^-), leading to the formation of the highly reactive activated complex [$\text{Cl-Pd}^0: \rightarrow \text{CCl}_3$] $^{n+}$. Interaction between the two surface species leads to chloroform and hydrogen chloride and to the regeneration of the active site. © 2002 Elsevier Science (USA)

Key Words: Pd/C catalysts; carbon tetrachloride hydrodechlorination; chloroform manufacture; electron-deficient Pd; XPS.

The use of carbon tetrachloride (TTCM) has been banned, as it was classified as a group IV material at the London Conference in 1990, due to its potential impact on ozone-layer depletion. Since this compound is a by-product in several chlorine industrial processes, such as the manufacture of tetrachlorethylene from propylene, a surplus of CCl_4 is continuously created. At present, carbon tetrachloride is eliminated by combustion, which is an expensive and polluting technique. A more promising way to eliminate CCl_4 is by catalytic hydrodechlorination to chloroform (TCM), which is a valuable intermediate product in organic synthesis. In the past years, numerous works have been published concerning the hydrodehalogenation of chlorofluorocarbons (CFCs) on several Pd catalysts: CCl_2F_2 (1), CF_3CFCl_2 (2, 3), CF_3CFCl_2 and CF_3CCl_3 (4), $\text{CClF}=\text{CF}_2$ (5), chlorobenzenes (6–8), and $\text{Cl}_2\text{FCClF}_2$ (9–11).

Gas-phase conversion of CCl_2F_2 to CH_2F_2 and CH_4 was studied by Coq *et al.* (12) over Pd black and several Pd-supported catalyst. The highest selectivity reached with a Pd/ AlF_3 catalyst (81% in CH_2F_2) was ascribed by the authors to a cooperative effect between Pd and AlF_3 that prevents the diffusion of the halide species into bulk palladium. The reaction is produced by the interaction of CCl_2F_2 with H_2 , which are competitively adsorbed on the active sites. More recently, Ramos *et al.* (13) studied the hydrodechlorination of CCl_2F_2 over nonsupported palladium catalyst. The use of model catalysts allowed these authors to determine the intrinsic activity of palladium and to discriminate the reaction products formed on Pd foil from those produced by the existence of a metal–support interface.

In contrast with CFCs, works related to hydrodechlorination of carbon tetrachloride are rather scarce and most of them were performed in gas phase and using supported platinum catalysts. In addition to several patents (14–16), it should be mentioned that the early work by Weiss *et al.* (17) on Pt/ $\eta\text{-Al}_2\text{O}_3$, essentially focused on elucidating the reaction pathway. In the 1990s, this reaction attracted more attention (18–22). According to the work of Kim *et al.* (18), carried out in a fixed-bed reactor over platinum catalysts,

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longer catalytic life and higher selectivity to chloroform are achieved when the support basicity increases; they found that MgO and Al₂O₃ appeared to be the best carriers. Thus, selectivity of 76.1% at 45.2% conversion was obtained after 8 h onstream on a Pt/MgO catalyst, while over Pt/NaY it was only 4.4% for a conversion of 8.6% after 1.5 h onstream. Zhang and Beard (23) reported the preparation of a remarkably durable catalyst for the hydrodechlorination of CCl₄ in gas phase, by treating Pt/Al₂O₃ catalyst with a solution of NH₄Cl. Prati and Rossi (19) reported that Pt deposited on porous glass (Vycor) is a promising catalyst for the selective gas-phase dechlorination of CCl₄ to CHCl₃. In contrast, alumina-supported palladium catalysts showed the best performances in the deep dehalogenation to CH₄ and HCl.

To our knowledge, with the only exception being a patent by Morikawa *et al.* (24), studies on the catalytic hydrodechlorination of carbon tetrachloride in the liquid phase are not available, despite the fact that this system appears to have some advantages over the gas-phase process, such better thermal control and improved catalyst stability and selectivity. An overview of the principles that govern the rate of liquid-phase hydrodechlorination of substituted chlorobenzenes on Pd/C catalysts was provided by Simakova and Semikolenov (25). In previous papers (26, 27), our group reported the high activity of Pd/C catalysts to selectively hydrodechlorinate CCl₄ to CHCl₃ in the liquid phase in a slurry reactor. Selectivities to chloroform higher than 85% at 95–100% conversion were achieved at 513 K and 1.5 MPa, with a 0.5 wt% Pd/C catalyst. Catalytic performances, however, may greatly change as a function of physicochemical properties of the catalyst, which in turn depend on the preparation procedure. In the present work, the effect of palladium content and reduction temperature on the electronic state of the metal and the hydrodechlorination activity of Pd/C catalysts, prepared from PdCl₂, has been studied. In order to evaluate the effect of the Pd precursor, additional samples prepared from Pd(NO₃)₂ were also examined. From the catalytic performances and the TPR and XPS results it is proposed that the catalytic active site is dual in nature, constituted by the association of two Pd species: electron-deficient and metallic palladium. Carbon tetrachloride is adsorbed and activated on Pdⁿ⁺ while H₂ is adsorbed and dissociated on Pd⁰. Interaction between these two surface species leads to chloroform and hydrogen chloride.

2. EXPERIMENTAL AND METHODS

2.1. Catalyst Preparation

Five catalysts of palladium supported on a cation-free carbon (Erkimia S.A. CF-IV; $S_{\text{BET}} = 1200 \text{ m}^2 \text{ g}^{-1}$, pore volume = $0.62 \text{ cm}^3 \text{ g}^{-1}$, average particle size = $75 \text{ }\mu\text{m}$, and

pH of an aqueous suspension of 6.4) were prepared by incipient wetness impregnation of the support with aqueous solutions of H₂PdCl₄ (prepared from anhydrous PdCl₂) of appropriate concentrations to obtain 0.2, 0.3, 0.5, 1.0, and 1.6 wt% Pd. After drying at 393 K for 16 h, the samples were reduced at 523 K under H₂ stream (99.995%) for 2 h. The catalysts were labeled 0.2CPd, 0.3CPd, 0.5CPd, 1.0CPd, and 1.6CPd. In order to analyze the effect of the reduction temperature, aliquots of the 1.0CPd precursor were reduced at 423, 473, 523, 623, 723, and 823 K. These catalysts are named 1.0CPd-423, 1.0CPd-473, 1.0CPd-523, 1.0CPd-623, 1.0CPd-723, and 1.0CPd-823, respectively. Another sample of this series named 1.0CPd(u) was not reduced. Two samples containing 1.0 wt% Pd on carbon, 1.0NPd-523(c) and 1.0NPd-523, were prepared following the same procedure but using Pd(NO₃)₂ · 2H₂O as precursor and reduced at 523 K for 2 h. Sample 1.0NPd-523(c) was previously calcined at 573 K for 3 h.

2.2. Catalyst Characterization

The actual content of palladium (Pd_t) was determined by inductive coupled plasma (ICP). The reducibility of the catalyst precursors was determined by temperature-programmed reduction in a flow system provided with a thermal conductivity detector. Samples of 0.5 g of the precursors were outgassed at 373 K for 1 h in Ar stream (99.9995%). After cooling to 273 K, the samples were stabilized under a flow of $30 \text{ cm}^3 \text{ min}^{-1}$ of 5% H₂ in Ar and the TPR profiles were recorded upon heating at a rate of 10 K min^{-1} from 273 to 773 K. The number of exposed metal atoms (Pd_s) on the catalysts was determined by CO chemisorption using the dynamic pulse technique with Micromeritics Chemisorb 2700 equipment. Reduced samples of 0.5 g were evacuated under an Ar flow of $30 \text{ cm}^3 \text{ min}^{-1}$ at 573 K for 2 h. After cooling to RT, pulses of 50 μl of CO (99.97%) were introduced in the argon stream until saturation of the sample. Prior to use, each gas was carefully purified. From the volume of CO chemisorbed, Pd_s was calculated assuming a molar stoichiometry of Pd_s/CO = 1.15/1. The dispersion of palladium is defined as $D = 100 \text{ Pd}_s/\text{Pd}_t$.

The surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) with a VG Escalab 200R system, using MgK α radiation ($h\nu = 1253.6 \text{ eV}$). The binding energies (BE) of the Pd 3d_{5/2} and Cl 2p_{3/2} core levels and FWHM values were used to reveal the chemical state of Pd and Cl species. Correction for binding energies due to sample charging was effected by taking the C 1s peak 284.6 eV as an internal standard. The accuracy of the BE values was $\pm 0.1 \text{ eV}$. Surface atomic ratios of Pd/C, Cl/C, and Cl/Pd were determined by comparing the area of the peaks after background subtraction and corrections due to differences in escape depths (28) and photoionization cross

section given by Scofield (29), using the equation

$$\frac{n_i}{n_j} = \frac{I_i/S_i}{I_j/S_j}, \quad [1]$$

where n_i/n_j is the atomic ratio between i and j species, I_i and I_j are the intensities of the corresponding peaks for the i and j atoms, and S is the atomic sensitivity factors given by Wagner *et al.* (30): $S_{\text{Pd}} = 4.6$ (3d level), $S_{\text{Cl}} = 0.73$ (2p level), and $S_{\text{C}} = 0.25$ (1s level). The ratios $\text{Pd}^{n+}/\text{Pd}^0$ were calculated by comparing the intensity of the two components of Pd 3d_{5/2} core-level once the experimental spectrum was deconvoluted.

After reduction, the catalysts were introduced into the sample holder under isooctane and protected from exposure to air by a meniscus of this liquid. Isooctane was removed during pumping in the preparation chamber of the XPS equipment. Prior to the measurement the samples were treated with a hydrogen flow at 373 K for 1 h. This operating procedure ensures that there is no modification of the chemical state of palladium, which is fairly stable (31). In order to confirm that eventual air exposure is not a concern, a fraction of each catalyst to be loaded in the reactor was exposed, after being reduced, to the atmosphere for 24 h. No significant changes in the Pd BE were observed after this period, thus indicating that there were no electronic modifications of Pd. Similar results were also found by other authors (32–34).

2.3. Catalytic Activity Measurements

The catalytic activity measurements in the hydrodechlorination of carbon tetrachloride were carried out in a three-phase bubble column slurry reactor, operated in a semi-batch mode. Liquid CCl₄ with the powdered catalyst in suspension was charged in the reactor and hydrogen was continuously fed upstream at a flow rate of 400 cm³ min⁻¹. In these conditions H₂ acts as both reactant and stirrer. At the same time, the reaction temperature and pressure were adjusted to the required values. When the reaction temperature was reached, a sample of the reacting mixture was taken and this was considered time zero for the run.

The gaseous effluent of the reactor (hydrogen, hydrogen chloride, methane, and chlorinated hydrocarbons) was successively passed through a water absorption column to remove HCl and a cold trap at 193 K to retain volatile chlorinated products. The volume of the exit gas was measured by a flowmeter. To follow the change of carbon tetrachloride concentration with time, samples of the reactor liquid were periodically collected, weighed, and analyzed by GC in a SE-30 (30%)/Chromosorb column. The organic condensate at 193 K was also weighed and analyzed. Samples of the exit gas were analyzed in an active-carbon-packed column to quantify the methane content. The HCl recovered in the absorption column was titrated with NaOH and taken into

account in the mass balance. The reaction conditions were temperature = 373 K, pressure = 3 MPa, hydrogen flow rate ($F(\text{H}_2)$) = 400 cm³ min⁻¹, catalyst/CCl₄ = 1.2 wt%, CCl₄ volume = 0.220 L, and average catalyst particle size (ϕ) = 75 μm.

Using the overall rate equation for a first-order reaction in a slurry reactor (35),

$$-R_{\text{H}} = \frac{C_i}{(1/k_{\text{g},1} a_{\text{g},1}) + (1/k_{1,\text{c}} a_{\text{c}} m) + (1/k_{\text{s}} m \eta)}, \quad [2]$$

where C_i is the solubility of H₂ in CCl₄, k is the mass transfer coefficient at the interfaces, a is the interfacial contact area, m is the catalyst concentration (cat/CCl₄), and η is the effectiveness factor of the catalyst particle, we analyzed the effect of mass transfer resistances at the gas–liquid and liquid–solid interfaces and pore diffusion on the overall rate of the process, under the following ranges of the experimental variables: catalyst/CCl₄ = 0.5–4.0 wt%, $F(\text{H}_2)$ = 50–500 cm³ min⁻¹, and ϕ = 25–130 μm. The results indicated that (i) $-R_{\text{H}}$ is not affected by the H₂ transfer from the liquid phase to the external surface of the catalyst, at least up to a catalyst concentration of 2.5 wt%; (ii) for $F(\text{H}_2) \geq 400$ cm³ min⁻¹, the gas–liquid resistance is lower than 5% of the total resistance and, therefore, does not control the overall rate of the process; and (iii) for $\phi \leq 75$ μm, the process is essentially controlled by the surface chemical reaction. Thus, under the conditions employed in the present work a perfect gas–liquid–solid mixing was attained and the process was essentially controlled by the surface chemical reaction. A complete study of the mass transfer steps for this catalytic system will be published in the near future (36).

3. EXPERIMENTAL RESULTS

3.1. Catalyst Characterization

Catalyst reducibility. A TPR profile of the 1.0CPd precursor presents a well-defined and broad peak at 513 K (Fig. 1). This temperature is higher than that found for PdCl₂ deposited over other supports (10, 31, 37), indicating that the palladium precursor strongly interacts with the carbon surface. Catalysts with different Pd concentrations show similar TPR profiles and H₂ uptake proportional to the Pd loading. In all cases, the H₂ consumption corresponds to the complete reduction $\text{Pd}^{2+} \rightarrow \text{Pd}^0$, assuming that palladium is present as Pd^{2+} ($\text{H}_2/\text{Pd}^{2+} = 1$), which is the expected state for the preparation conditions of the catalysts.

A TPR profile of the 1.0NPd sample (Fig. 2) shows a negative peak at 348 K and two broad positive peaks, at 433 and 553 K. The negative one corresponds to the decomposition of palladium hydride (β -PdH), formed upon absorption of hydrogen in metallic palladium, showing that these catalysts are reduced at subambient temperature. The positive peaks are assigned to the reduction of the oxygenated-nitrogen

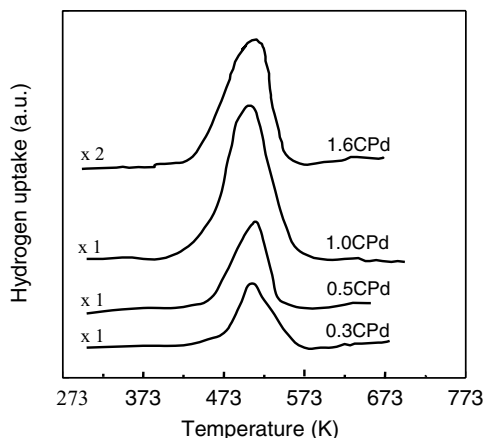


FIG. 1. TPR profiles of the CPd catalyst precursors with different Pd content.

species adsorbed on carbon, as is suggested by the lower intensity of the calcined sample peaks. In fact, similar peaks were also present in the TPR profile of a carbon impregnated with HNO_3 , but they are absent in the TPR of the catalysts 1.0NPd and 1.0NPd(c), reduced at 523 K, which only show the Pd-hydride peak (Fig. 2). This last observation means that during the reduction step at 523 K, the N species were practically removed.

In order to find out the reduction degree of the catalysts reduced at different temperatures, TPR profiles of 1.0CPd catalysts were recorded following the same procedure used for the precursors. The results show that there is no consumption of H_2 , indicating that these samples were completely reduced during the preparation. It must be noted that on these samples β -PdH is not formed. Similar results have already been reported in the literature (38). Since formation of the hydride depends on the nature of the Pd-support interface (39), this behavior may be related to the presence of HCl adsorbed on the catalysts surface.

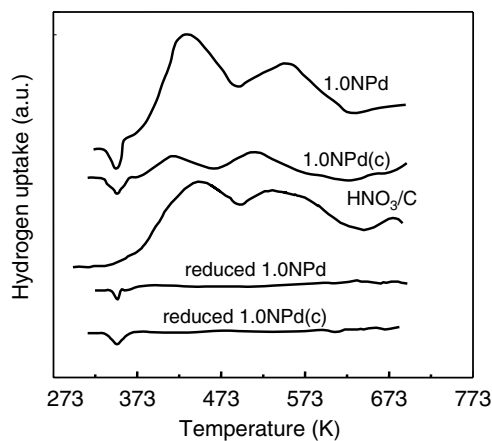


FIG. 2. TPR profiles of the NPd catalyst precursors, HNO_3/C sample, and reduced NPd catalysts.

TABLE 1

Metal Content and Pd Dispersion of the Catalysts

Catalyst	T_{red} (K)	Me_t (wt%)	D (%)
0.2CPd	523	0.19	23.4
0.3CPd	523	0.28	22.0
0.5CPd	523	0.48	20.0
1.0CPd	523	0.99	18.1
1.6CPd	523	1.57	17.7
1.0CPd(u)	—	1.00	—
1.0CPd-423	423	0.98	29.6
1.0CPd-473	473	0.97	26.0
1.0CPd-523	523	1.00	18.1
1.0CPd-623	623	0.99	15.4
1.0CPd-723	723	0.96	10.3
1.0CPd-823	823	0.97	7.9
1.0NPd	523	0.98	10.7
1.0NPd(c)	523	1.02	9.3

Note. T_{red} , reduction temperature; Me_t , metal loading calculated from chemical analysis; D , Pd dispersion.

Palladium dispersion. The catalysts studied were moderately well dispersed (Table 1) and fall in the range reported in the literature for Pd/C prepared in similar conditions (40). Additionally, dispersion slightly decreases when palladium content increases, in spite of the relatively low concentration of palladium. More significant, however, is the negative effect of the reduction temperature on palladium dispersion, which decreases from 29.6 to 7.9% when the temperature increases from 423 to 823 K. According to Ryndin *et al.* (41), this effect is probably due to the high mobility of palladium particles on the carbon surface, which leads to sintering.

Photoelectron spectroscopy. The original Pd 3d core-level spectra for two representative catalysts and the fit of the curves are shown in Fig. 3. Data of the XPS parameters for Pd 3d_{5/2} and Cl 2p_{3/2} core levels of all the analyzed catalysts and some reference compounds are summarized in Table 2. The binding energy of Cl 2p_{3/2} (198.6–198.8 eV)

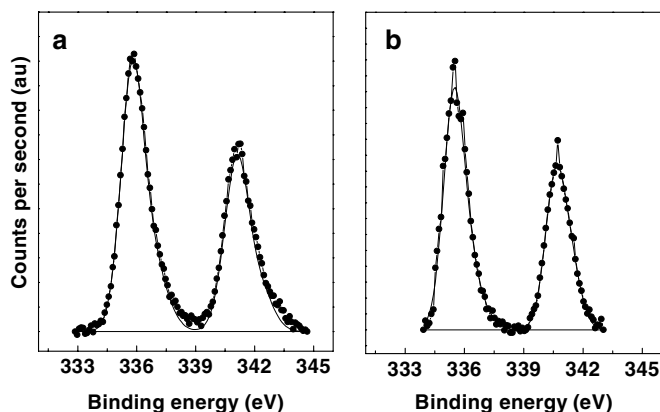


FIG. 3. Pd 3d core-level spectra of (a) 1.0CPd-723 and (b) 1.0NPd.

TABLE 2
XPS Data on Catalysts and Standards

Catalyst	Pd 3d _{5/2}						Pd ⁿ⁺ /Pd ⁰	Cl 2p _{3/2}
	Common peak		Deconvoluted peaks					
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)		
Pd	335.1							
PdCl ₂	337.7							
H ₂ PdCl ₄	338.1							
Pd/SiO ₂ ^a	335.2	2.2						
Pd/C	335.8	2.1						
1.0CPd(u)	338.0	2.2						198.4
1.0CPd-423	337.6		335.8	1.8	337.7	2.1	2.50	198.7
1.0CPd-473			335.9	1.5	337.9	2.3	2.23	198.6
1.0CPd-523			335.8	1.8	337.9	2.0	1.04	198.7
1.0CPd-623			335.7	1.8	337.9	2.5	1.17	198.8
1.0CPd-723	336.0	1.7					0.33	198.8
1.0CPd-823	335.3	2.0					0.00	
1.0CPd-523(p.d.)	335.8		335.9	1.5	337.0	2.4	0.41	200.1
1.0CPd-523(d)	335.7	2.0					0.00	200.3
1.0NPd	335.8		335.7	1.5	337.0	2.4	0.33	
1.0NPd(c)	335.8	1.80					0.00	

^a Prepared from PdCl₂ and reduced at 723 K. No Cl₂ p_{3/2} peak is detected.

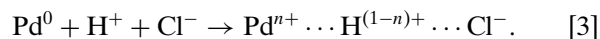
for the fresh samples corresponds to that of a Cl⁻ anion, indicating that, except for 1.0CPd-823, HCl was not completely removed during the reduction step. In contrast, the values BE = 200.1–200.3 eV found for the partially deactivated 1.0CPd-523 sample (1.0CPd-523(p.d.)) and the deactivated 1.0CPd-523 sample (1.0CPd-523(d)) indicate that in the surface of these samples the chlorine species are mainly covalent chlorocarbon (C–Cl bond) compounds.

The spectrum of the unreduced sample (1.0CPd (u)) shows a peak at 338.0 eV with FWHM = 2.2 eV. The spectrum of 1.0CPd-423 exhibits a broad and asymmetric peak, with a maximum at ca. 337.6 eV. As expected for Pd catalysts prepared from PdCl₂ acid solutions and reduced at not very high temperature, deconvolution of the experimental spectrum showed the presence of two components, with BE values of 335.8 and 337.7 eV, corresponding to metal and oxidized palladium species, respectively (42).

The spectra of 1.0CPd-473, 1.0CPd-523, and 1.0CPd-623 samples present two peaks fairly well resolved. Deconvolution gives again the two component peaks corresponding to metal and oxidized palladium. Spectra for 1.0CPd-723 and 1.0CPd-823 samples display a Pd 3d_{5/2} single peak at ca. 336.0 eV (FWHM = 1.7 eV) and 335.3 eV (FWHM = 2.0 eV), respectively, corresponding to Pd⁰. The small shift in the peak together with the slight asymmetry of the curve toward higher BE values observed for 1.0CPd-723 indicates that this sample possibly contains a small fraction of oxidized Pd.

The values of 335.7–335.9 eV for the Pd 3d_{5/2} level are somewhat higher than for the metallic palladium reference

and also for the Pd/SiO₂ catalyst (see Table 2) but are consistent with the value of 335.8 eV reported for the Pd⁰/C catalyst (43). The BE values (337.0–337.9 eV) of the second peak could be assigned to Pd²⁺, as in PdCl₂, although they are lower than the value for Pd²⁺ in H₂[PdCl₄], which in fact is the precursor of the catalysts. However, since TPR results showed that all the catalysts were completely reduced, such values should rather be assigned to *electron-deficient palladium species* Pdⁿ⁺, using the terminology of Dalla Betta and Boudart (44). A well-documented revision about the formation of such species in palladium catalysts was published by Karpinski some years ago (45). In accordance with the mechanism discussed elsewhere (31, 46), Pdⁿ⁺ species can be formed in the catalysts prepared from H₂PdCl₄, even after careful reduction at about 723 K, by interaction of electron-donor Pd⁰ atoms with the electrophilic neighboring protons, arising from both the tetrachloropalladium acid and the Pd²⁺ reduction. The resulting structure is stabilized by the Cl⁻ ions present in the catalyst. This mechanism may be depicted in a simple manner as



Here, the partition of the positive charge between Pd and H is rather a simplified representation of the true structure, which indicates an asymmetric distribution of the charge, since actually the positive charge is smeared out over the palladium and the proton: [Pd–H]⁺. In fact, in this process an ensemble of *x* palladium atoms sharing the positive charge of *y* protons may participate, in a way similar to that proposed by Bai and Sachtler (47). So, the amount of

TABLE 3
Surface Atomic Ratios of the Catalysts

Sample	Pd/C		Cl/C		Cl/Pd	
	Bulk	XPS	Bulk	XPS	Bulk	XPS
1.0CPd-423	0.0011	0.0016	0.0044	0.0030	4	1.9
1.0CPd-473	0.0011	0.0013	0.0044	0.0017	4	1.3
1.0CPd-523	0.0011	0.0014	0.0044	0.0014	4	1.0
1.0CPd-623	0.0011	0.0011	0.0044	0.0010	4	0.9
1.0CPd-723	0.0011	0.0012	0.0044	0.0008	4	0.6
1.0CPd-823	0.0011	0.0010	0.0044	0.0000	4	0.0
1.0CPd-523(p.d.)	0.0011	0.0012	0.0044	0.0570	4	47.5
1.0CPd-523(d.)	0.0011	0.0013	0.0044	0.0720	4	63.1
1.0NPd	0.0011	0.0267				
1.0NPd(c)	0.0011	0.0260				

Pd^{n+} formed and, therefore, the $\text{Pd}^{n+}/\text{Pd}^0$ ratio will depend on the amount of HCl retained on the support surface (31), which in turn is a function of the reduction temperature (Table 2) (46, 48).

The peaks for Pd^0 are sharp, as they correspond to electronically well-defined species, while for Pd^{n+} they are broader, indicating that the binding energy of the electron-deficient species falls in a wider range. The BE values for the Pd^{n+} peak are similar for all the samples, suggesting that these species are chemically alike, while the surface atomic ratio of $\text{Pd}^{n+}/\text{Pd}^0$ decreases from 2.5 to 0 when the reduction temperature increases from 423 to 823 K (Table 2).

The Pd/C external surface atomic ratio for 1.0CPd samples determined by XPS is similar to that of the bulk obtained by chemical analysis (Table 3), indicating that Pd is homogeneously distributed on the support. The XPS surface atomic ratio Cl/Pd decreases from 1.9 to 0.6 when the reduction temperature increases from 423 to 723 K, while for the fresh impregnated carbon this ratio is 4. Only in the sample reduced at 823 K was no signal of the Cl $2p_{3/2}$ peak detected, which shows the difficulty of desorbing the HCl retained on the carbon surface. Note that not all the residual HCl modifies the electronic density of Pd atoms. For example, according to Eq. [3], a ratio of Cl/Pd = 0.6 ($\text{Pd} = \text{Pd}^{n+} + \text{Pd}^0$) would correspond to $\text{Pd}^{n+}/\text{Pd}^0 = 1.5$, while the XPS value found for this sample (1.0CPd-723) was 0.33 (Table 2). This means that only a part of the surface HCl is found in the vicinity of the Pd atoms and, therefore, can form Pd^{n+} , as was also observed by Bozon-Verduraz *et al.* (49). The ratio of $\text{Pd}^{n+}/\text{Pd}^0$ for the partially deactivated catalyst, 1.0CPd-523(p.d.), is lower than for the fresh one, 1.0CPd-523, and it is zero for the deactivated sample, 1.0CPd-523(d) (Table 3). The feature of XP spectra of the CPd catalysts containing varying concentrations of palladium is similar to that of 1.0CPd-523.

The Pd $3d_{5/2}$ core-level spectrum of the 1.0NPd catalyst displays an asymmetric curve which can be deconvoluted into two peaks, with maxima at 335.7 and 337.0 eV,

ascribed to Pd^0 and Pd^{n+} , respectively, with an atomic ratio of $\text{Pd}^{n+}/\text{Pd}^0 = 0.33$ (Table 2). Despite of the fact that palladium is completely reduced at subambient temperature, as shown by TPR, the presence of electron-deficient palladium in this sample is at least surprising. Possibly, in this case, Pd^{n+} can be formed by interaction of Pd^0 with an electron-acceptor species present on the carbon surface. For example, small amounts of NO_x entities, produced through the reduction–decomposition steps of the nitrate counterion, may remain strongly adsorbed and not be completely removed by the reduction treatment. In fact, XPS of this sample showed a N 1s signal at a BE = 401.9 eV, which is assigned to decomposition products of nitrates. In contrast, sample 1.0NPd(c), which was calcined at 573 K before reduction, exhibits a symmetric and sharp peak (FWHM = 1.8 eV) at 335.8 eV, characteristic of Pd^0 . In contrast with 1.0CPd samples, the high values of the ratio of Pd/C for NPd samples indicate that in these samples most of the Pd is mainly deposited on the external surface of the carrier.

3.2. Catalyst Activity

Catalyst performance is expressed in terms of conversion of CCl_4 (X), defined as the percentage of CCl_4 charged in the reactor which is transformed, and selectivity to a product i (S_i), which is the number of CCl_4 molecules transformed into i per 100 molecules of CCl_4 converted. The turnover frequency (TOF) is the number of CCl_4 molecules transformed per exposed palladium atom per minute, while the reaction rate ($-r$) is expressed as micromoles of TTCM per minute per gram of catalyst. Plots in Fig. 4 show conversion of carbon tetrachloride as a function of time of reaction for CPd catalysts containing different Pd loadings. In all cases, conversion grows proportionally with time, indicating that, at least in the range of conversion explored, the reaction rate fits an overall zero-order law. For all the catalysts

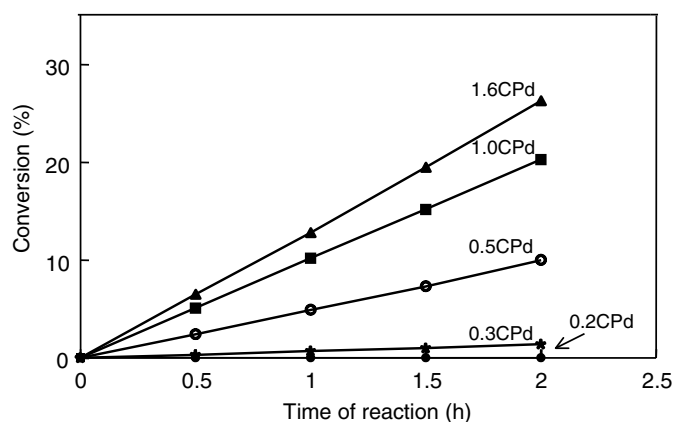


FIG. 4. Effect of the Pd loading on the carbon tetrachloride conversion as a function of the time of reaction at 373 K, 3 MPa, cat/ CCl_4 = 1.2 wt%, H_2 flow = $400 \text{ cm}^3 \text{ min}^{-1}$, and CCl_4 volume = 0.220 L.

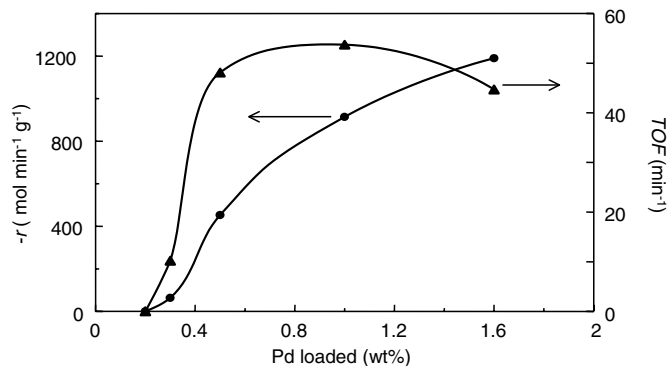


FIG. 5. Effect of the Pd loading on the reaction rate and TOF for CPd catalysts at 373 K, 3 MPa, cat/ $\text{CCl}_4 = 1.2$ wt%, H_2 flow = $400 \text{ cm}^3 \text{ min}^{-1}$, and CCl_4 volume = 0.220 L.

the main reaction product was chloroform ($S_{\text{TCM}} \geq 95\%$), with hexachloroethane being the major by-product. Traces of methane were also detected. The values of TOF and reaction rate, these last calculated from the slopes of this graph, vs the percentage of Pd is plotted in Fig. 5. It is observed that the reaction occurs at a measurable rate if the Pd concentration is above 0.3 wt%. In addition, there is a profitable effect of the Pd content on the reaction rate, while the TOF seems to have an optimum value around 1.0 wt% Pd.

The results obtained after 2 h of reaction with the 1.0CPd catalysts reduced at different temperatures are given in Table 4. Also included in this table are those for NPd catalysts. The hydrodechlorination activity of 1.0CPd catalysts is strongly dependent on reduction temperature, while their selectivity is only slightly modified, in spite of the fact that conversion changes from 0.8 to 20.2%. The highest conversion and reaction rate is obtained with the catalyst reduced

TABLE 4

Effect of the Reduction Temperature on the Hydrodechlorination Activity of the 1.0CPd Catalysts and Catalytic Performance of NPd Samples

Catalyst	X (%)	$-r$	TOF	S_{TCM}	S_{HCA}
1.0CPd(n.r.)	0.0	0.0	0.0		
1.0CPd-423	4.2	190.0	7.2	100.0	0.0
1.0CPd-473	13.0	588.1	24.8	98.3	1.7
1.0CPd-523	20.2	913.8	53.7	95.5	4.5
1.0CPd-623	17.3	782.6	54.6	97.1	2.9
1.0CPd-723	7.8	352.8	37.9	98.7	1.3
1.0CPd-823	0.2	33.9	4.7	99.2	0.8
1.0CPd-523(p.d.)	10.6	479.5	28.2	98.6	1.4
1.0CPd-523(d)	0.0	0.0	0.0		
1.0NPd	5.8	262.4	26.6	85.6	14.4
1.0NPd(c)	0.0	0.0	0.0		

Note. ($T = 373 \text{ K}$; $P = 3 \text{ MPa}$; $\text{H}_2/\text{CCl}_4 = 1.2 \text{ wt}\%$; H_2 flow = $400 \text{ cm}^3 \text{ min}^{-1}$; CCl_4 volume = 0.220 L; $t = 2 \text{ h}$. X , conversion of TTCM; $-r$, reaction rate ($\mu\text{mol TTCM min}^{-1} \text{ g}_{\text{cat}}^{-1}$); TOF, turn-over frequency (min^{-1}); S_{TCM} , selectivity toward TCM; S_{HCA} , selectivity toward HCA.

at 523 K, while the maximum TOF is reached when the reduction is carried out in the range 523–623 K. Samples reduced either at 423 or 723 K are much less active and the unreduced sample and that reduced at 823 K are practically inactive.

The selectivity toward chloroform obtained in the present work with CPd catalysts ($>95\%$) is higher than that reported in the literature for this reaction carried out in gas phase (17, 20), but it is similar to that found by Morikawa *et al.* (24) working in liquid phase. One of the advantages of our catalytic system in liquid phase is the very low production of methane ($<1\%$) compared with that obtained in the gas-phase processes (15–25%).

The 1.0CPd-523 catalyst exhibits a carbon tetrachloride conversion and selectivity toward chloroform higher than its 1.0NPd counterpart. It must be noted that the overall hydrodechlorination activity of this last sample (reduced at 523 K) is similar to that of 1.0CPd-723, although its selectivity to chloroform is lower. Probably, this different behavior is a consequence of the unlike distribution of Pd on the surface of NPd and CPd catalysts, as evidenced by XPS (27). Finally, the sample 1.0NPd(c) is inactive.

4. DISCUSSION

The results presented in this work show that all the catalysts having palladium on the surface as two different species, Pd^0 and Pd^{n+} , are active for the hydrodechlorination of carbon tetrachloride, whereas samples having only one species (either Pd^0 or Pd^{n+}) are inactive. In addition, data in Tables 2 and 4 indicate that the catalytic activity changes with the electronic structure of the palladium. It is noticeable, for example, that the reaction rate with 1.0CPd-523 is about sevenfold higher than with 1.0CPd-423, in spite of the fact that this last catalyst exhibits 1.7 times more exposed Pd atoms. Indeed, the two catalysts have different $\text{Pd}^{n+}/\text{Pd}^0$ atomic ratios.

These facts seem to account for an electronic effect. Figure 6 presents the plots of reaction rate and TOF for CPd catalysts vs $\text{Pd}^{n+}/\text{Pd}^0$ ratio, which go through a maximum. The best catalysts to hydrodechlorinate carbon tetrachloride are those in which the $\text{Pd}^{n+}/\text{Pd}^0$ ratio approaches 1, while samples having most of the palladium either as electron-deficient or metallic species are less active. The XPS results together with those of catalytic activity of samples having a different source, which are consistent with those of 1.0CPd samples, strengthened this proposal. Again, samples with $\text{Pd}^{n+}/\text{Pd}^0$ higher (1.0CP(u)) or lower (1.0NPd-523, 1.0NPd-523(c), 1.0CPd-523(p.d.), 1.0CPd-523(d)) than 1 (Table 4) exhibit a low or null hydrodechlorination activity.

Since the early work in catalysis, the high activity of metal palladium in hydrogenation reactions is well established. In contrast, the activity of oxidized metal species in this type of

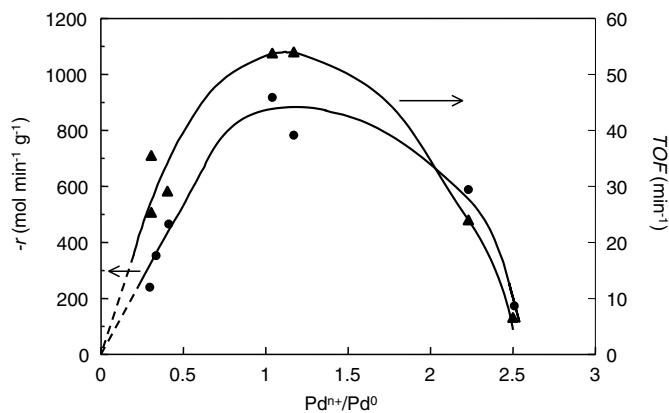


FIG. 6. Reaction rate and TOF as a function of the $\text{Pd}^{n+}/\text{Pd}^0$ mole ratio.

reaction was seldom invoked in the past (44). More recently, however, the catalytic activity of electron-deficient palladium species was experimentally demonstrated in several reactions (45). Sachtler and Stakeev (50) observed mono- and bifunctional activity of the electron-deficient adduct $[\text{Pd}_x\text{-H}_z]^{z+}$ in the hydrogenolysis of neo-pentane and proposed this species as a unique active site. For Choi *et al.* (20), the active phase of Pt during carbon tetrachloride hydrodechlorination over Pt/MgO catalyst is a surface Pt(II) species with Cl ligands, while the bulk remained as Pt metal. When these authors used Pt/ Al_2O_3 in the same reaction they concluded that the different activity between catalysts prepared from Pt(II) and Pt(IV) is due to the different oxidation states of Pt (21). The activity of palladium to hydrodechlorinate chlorobenzenes was associated by Krauss and Banzat (51) to the formation of electron-deficient Pd species.

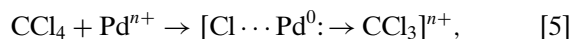
Our findings, however, indicate that both Pd^0 and Pd^{n+} species are required for the catalytic hydrodechlorination to take place and, therefore, that they participate in its elemental mechanism. On the other hand, within the range of metal dispersion of our catalysts, no clear relationship between activity and dispersion is found. In fact, while the dispersion decreases monotonically with the increase in reduction temperature, the activity goes through a maximum. Therefore, although it cannot be completely ruled out that crystal size may have some influence on the catalyst activity, our results show that the electronic effect is by far the most important factor controlling reactivity. On this basis, it appears that the *active site is dual in nature*, constituted by the association of the two species: electron-deficient and metallic palladium $[\text{Pd}^{n+}\text{-Pd}^0]$.

Another argument in favor of the dual-site hypothesis comes from kinetic considerations. The rate of catalytic reactions occurring on sites constituted by two physically or chemically different species are, usually, proportional to the product of the concentrations of such species. Thus, in our

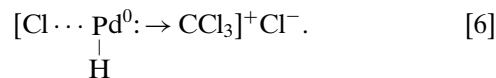
particular case, the equation rate would be written

$$(-r) = kf [\text{Pd}^{n+}][\text{Pd}^0], \quad [4]$$

where k is the reaction rate constant, f is a function of the reactants concentration, and $[\text{Pd}^{n+}] + [\text{Pd}^0] = 1$. Mathematically, Eq. [4] presents a maximum for $[\text{Pd}^{n+}] = [\text{Pd}^0] = 0.5$, as was experimentally found (see Fig. 6). Therefore, it is tempting to explain the hydrodechlorination of carbon tetrachloride via activation of CCl_4 and H_2 on each one of the Pd species in such a way that both site components play a different but complementary role. Thus, a plausible possible *modus operandi* of the dual active site can be visualized as follows: molecular H_2 chemisorbs and homolytically dissociates on Pd^0 to give the covalent adatom Pd-H, whereas CCl_4 chemisorbs on Pd^{n+} by abstraction of the slightly nucleophilic chloride anion (Cl^-), thanks to the high Lewis acid character of Pd^{n+} , leading to the formation of an intermediate Pd(0) complex,



which is highly reactive due to its particular electronic structure. It should be remembered that for the sake of simplicity, in Eq. [5] and throughout the text the symbol Pd^{n+} is used, while keeping in mind that it is associated with the H^+ (i.e., $[\text{Pd-H}]^+$) and that the overall positive charge of the complex is compensated for by the anion Cl^- . Thus, the complex would be more appropriately written as



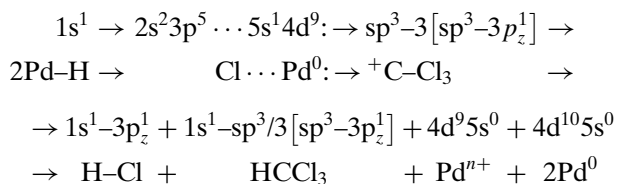
A very similar mechanistic model was proposed by Bai and Sachtler (47) to explain the methylcyclopentane conversion over Pd/HY catalysts, in which the electron-deficient $[\text{Pd}_n\text{H}]^+$ adduct was postulated as the active site. Formally, the process depicted by Eq. [5] may be assimilated to a “dissociative-type adsorption” of the carbon tetrachloride on a single Pd^{n+} adsorption site, by insertion of Pd^{n+} in the CCl_4 molecule with the heterolytic rupture of a Cl-C bond and formation of the $^+\text{CCl}_3$ ion. The high density of unoccupied states of Pd^{n+} (27, 52) enables it to accommodate one electron in its external orbital without an excessive increase in energy.

A dual mechanism was proposed by Driessen *et al.* (53) to explain the synthesis of CH_3OH from $\text{CO} + \text{H}_2$ on Pd/ SiO_2 catalysts, in which Pd^0 species supply hydrogen atoms and the Pd^{n+} species are the centers for activation of CO toward methanol. Chou and Vannice (54) used a similar model to describe benzene hydrogenation over supported Pd catalysts. Concerning carbon tetrachloride, Yakov *et al.* (22) tested the hydrodechlorination of CCl_4 over several silica-supported PdCl_2 -containing molten salts catalysts, promoted by CoCl_2 and CuCl_2 . The authors proposed that

CCl_4 is activated at Lewis acidic sites, with generation of carbeniumlike species, and reaction occurs by the nucleophilic attack on carbon by hydrogen activated by elemental Pd(0) or Pd(II) complexes. Despite the apparent complexity of this system, the nature of the active center can be related to a dual center.

According to the ideas exposed by Tolbert *et al.* (55) in a work devoted to the activation of CH_4 by Pd^+ , the Pd(0) complex $[\text{H}-\text{Pd}^0-\text{CH}_3]$ is formed on Pd^+ thanks to the unique electronic structure of palladium. The configuration $4d^{10}5s^0$ of Pd^0 is unable to make any covalent bonds, but the promotion of one electron, $4d \rightarrow 5s$, requires only 0.8 eV, leading to the configuration $4d^95s^1$, which can form covalent bonds through the $5s^1$ orbital. In addition, the uniquely high Lewis acidity of Pd^+ ions allows initiation of the process via insertion of Pd^+ between the H and CH_3 fragments of the methane molecule. These properties of Pd^+ were also taken into account by Juszczyk *et al.* (56) in order to explain the hydrogenolysis of neopentane by electron-deficient Pd^{n+} sites.

We believe that the ideas of Tolbert *et al.* are valid in explaining the behavior of our catalytic system, substituting CH_4 with CCl_4 and attributing as a reasonable approach the role played by the Pd^+ ion to the Pd^{n+} species. Thus, the activated intermediate complex $[\text{Cl}-\text{Pd}^0: \rightarrow \text{CCl}_3]^{n+}$ will contain a covalent bond $\text{Cl}-\text{Pd}$, by transfer of a 3p-electron from the one Cl^- anion of the CCl_4 molecule to the $5s^0$ orbital of Pd^{n+} , while the electrophilic $^+\text{CCl}_3$ cation (similar to a strong acid carbenium species) is bonded to Pd^0 through a donor-acceptor bond, involving partial donation of a Pd 4d- electron pair to the empty hybridized sp^3 orbital of the $^+\text{CCl}_3$, as illustrated in the scheme



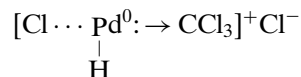
Both complex bonds are readily hydrogenolyzed by atomic hydrogen chemisorbed on neighboring metal palladium atoms (Pd^0-H), leading to hydrogen chloride and chloroform and the regeneration of the active site.

It is assumed that the rate of these steps is strongly enhanced by the high capability of carbon support to spillover atomic hydrogen through the surface from the Pd^0-H sites, thus ensuring the presence of active hydrogen also on the more far $[\text{Cl}-\text{Pd}^0-\text{CCl}_3]^{n+}$ sites (27), a phenomenon widely invoked in hydroprocessing reactions on metal/carbon catalysts (57, 58).

5. CONCLUSIONS

Pd/C catalysts containing both Pd^0 and Pd^{n+} species are active in the liquid-phase hydrodechlorination of carbon

tetrachloride to chloroform. The activity is related to the ratio of $\text{Pd}^{n+}/\text{Pd}^0$, and a maximum is found for $\text{Pd}^{n+}/\text{Pd}^0 \cong 1$. Electron-deficient species, Pd^{n+} , are formed by the interaction of reduced palladium atoms with neighboring electron-acceptor entities, such as protons in catalysts prepared from H_2PdCl_4 . The proportion of Pd^{n+} depends on the residual HCl concentration and, therefore, on the reduction temperature, as verified by XPS analysis. It is proposed that the active centers of the catalyst are constituted by palladium species dual in nature $[\text{Pd}^{n+}-\text{Pd}^0]$. Carbon tetrachloride is adsorbed and activated on Pd^{n+} by abstraction of the slightly nucleophilic chloride anion (Cl^-), leading to the complex



while H_2 is adsorbed and dissociated on Pd^0 . Interaction between these two adsorbed species gives CHCl_3 and HCl .

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