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Chemical State and Reactivity of Supported Palladium

I. Characterization by XPS and uv-Visible Spectroscopy

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The chemical state and environment of palladium supported on silica, titania, and alumina have been studied by uv-visible and X-ray photoelectron spectroscopy. This investigation has concerned the interaction between the supports and the precursor solution, and the nature of the surface complexes produced upon impregnation and drying, in relation to the state of the active phase after reducing pretreatments. Evidence is given that, even when the exchange ability of the support is negligible, a chemical interaction occurs during impregnation and drying, and the nature of the species involved ($PdCl_4^{2-}$, aquocomplexes) depends on the nature of the support. The XPS data obtained on reduced samples show the presence of surface complexes involving a part of the Pd atoms and containing chlorine. The influence of various preparation factors on the photoelectron spectra is also discussed.

INTRODUCTION

While the factors influencing the dispersion of the active phase in supported transition metals have received much attention, investigations concerning their actual chemical state and their local environment are still much needed. The behavior of palladium catalysts in the oxidation of ethylene offers a clear illustration of this view. First known as yielding only total oxidation products or small amounts of acetic acid (*1*), palladium, pure or supported, was recently proved to have a significant selectivity to acetic acid at low conversion (*2*); however, little has been reported concerning the characterization of the surface before or after the reaction runs and the role of the support (carrier). In addition, when using palladium (II) salts deposited on active charcoal without any reducing pretreatment, important amounts of acetaldehyde are obtained (*3*). This situation led us to try to correlate the chemical state and environment of palladium with its activity in ethylene oxidation and its selectivity to partial oxidation products. Concerning the preparation and the characterization of catalysts, it was kept in mind that (i) a broad knowledge must be available about the properties and reactivity of the carriers used (aluminas, titania, and silica were chosen here), and (ii) the different reagents and steps involved in the experimental procedure have to be controlled. The present paper reports the results obtained by electronic (uv-visible) spectroscopy and X-ray photoelectron spectroscopy (XPS), which were employed, conjointly when possible, to study the precursor solution, the nature of the surface complexes after impregnating the carrier, and the chemical state of palladium when submitted to

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various pretreatments. The activity patterns in the oxidation of ethylene and the infrared observations concerning either the adsorption of carbon monoxide, used as a surface probe, or the interaction of reagents and products with the catalysts will be presented separately.

EXPERIMENTAL METHODS

X-ray photoelectron spectroscopy (XPS). The photoelectron spectra were recorded on a Varian IEE spectrometer; using Mg$K\alpha$ radiation ($E = 1253.6$ eV) as a source. The pressure in the spectrometer was about 10^{-6} Torr. The contamination C 1s line was taken as an internal standard at 285.0 eV (*4*), and reference to the Au $4f_{7/2}$ peak (84.0 eV) was used to estimate the contribution of the charge effect. Two criteria have been chosen: (i) the shift of the pollution C 1s line referred to the Au standard, and (ii) the full width at half maximum (FWHM) of this line. In the cases presented below, no correlation could be found between the values of these parameters and the FWHM of Pd 3d lines. Hence the observed variations of the Pd 3d spectrum are accounted for by differences in the chemical state and environment of palladium atoms in the various samples.

Electronic (uv-visible) spectroscopy. Diffuse reflectance and transmission spectra were recorded at room temperature with a Beckman DK-2A spectrophotometer. For reflectance spectra the sample powder was packed in a quartz cell which also allowed control of the atmosphere surrounding the solid at the desired temperature; in this case the "absorbance" represents the function $\log(R_{\text{standard}}/R_{\text{sample}})$ where R is the reflectance and $BaSO_4$ the standard.

MATERIALS

The support materials used in this investigation are described in Table 1.

TABLE 1

Some Characteristics of the Carriers

Support	Phase	Surface area (m^2/g)	Chloride content (%)
Silica "Aerosil" (Degussa)	Amorphous	200	<0.02
Titania "P 25" (Degussa)	Anatase (80%) + rutile	50	0.30
Alumina "110 Cl" (Degussa)	δ	100	0.50
Alumina "Macroporous gel" (Rhône-Poulenc)	η	250	<0.02

Palladium metal and compounds were supplied by the Compagnie des Métaux Précieux. Most of the catalysts were prepared by impregnating the carriers with 2 M HCl aqueous solutions of $PdCl_2$ of the proper concentration. By uv-Visible spectroscopy of these solutions, it was shown that palladium is present as $PdCl_4^{2-}$ ions. [For HCl < 0.5 M, the aquochlorocomplex $Pd(H_2O)_2Cl_2$ was also detected.] Some 2 M HNO_3 aqueous solutions of palladium nitrate were occasionally used. The impregnated samples were dried at 120°C for 3 hr; reduction under flowing hydrogen was performed first at 200°C for 1 hr to preclude $AlCl_3$ formation (*5*) and then at 300°C for 6 hr. Some alumina- and silica-supported catalysts were obtained by cationic exchange from a $Pd(NH_3)_4Cl_2$ aqueous solution; in these cases the reduction was carried out at 100°C for 2 hr.

RESULTS AND DISCUSSION

1. *Unreduced Samples*

"Unreduced" refers to samples which have been only impregnated and dried. Most of the experiments have been performed with $PdCl_2$ as a precursor; the corresponding samples will be called $PdCl_2$/carrier, irrespective of the actual chemical state of palladium.

uv-Visible spectroscopy. The spectra of unreduced catalysts appear to depend

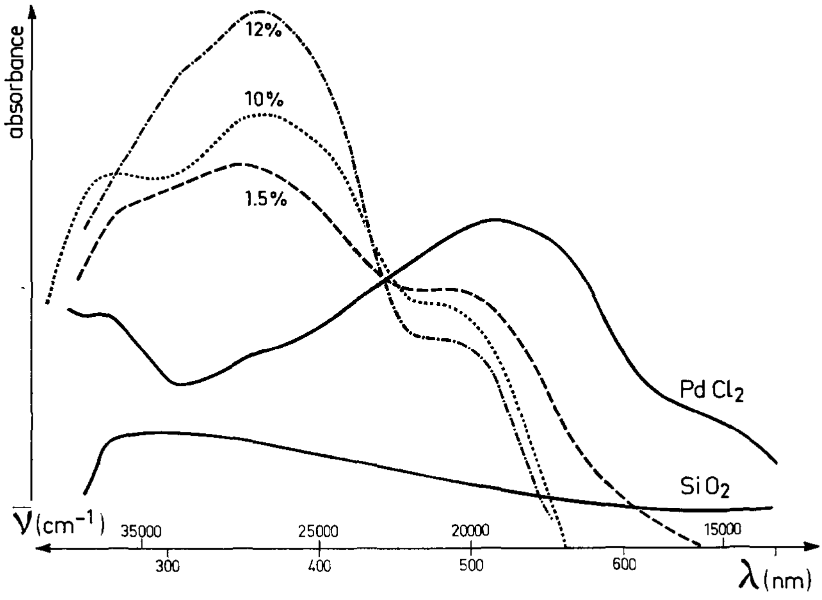

FIG. 1. The uv-visible spectra of pure palladium chloride and of $PdCl_2$/silica samples of various Pd contents.

on the nature of the carrier. For silica-supported samples, two bands near 370 and 500 nm (27 000 and 20 000 cm^{-1}) are observed (Fig. 1). According to Rasmussen and Jørgensen (*6*) and to Companys (*7*), the former may be ascribed to a complex which does not contain any chloride ion in its coordination sphere, i.e., $Pd(H_2O)_4^{2+}$. The presence of the other band indicates that the surface is also covered with palladium chloride.

The spectrum of $PdCl_2/\eta\text{-}Al_2O_3$ (Fig. 2) shows a set of three bands located around 280, 335, and 475 nm which have to be assigned to the tetrachloropalladate ion $PdCl_4^{2-}$ (*8*). For δ-alumina-supported $PdCl_2$, although the observation of the bands is more delicate in the uv range because of the absorption of the carrier, it can be concluded that $PdCl_4^{2-}$ is the predominant species.

Examination of the $PdCl_2/TiO_2$ system is also difficult because of the strong absorption of the support in the uv range, due to transitions across the forbidden energy gap. However, reliable information is obtained in the visible region. For small Pd loadings (<2%) a band is observed at 475 nm. If the Pd content is greater than 2%, the band is shifted toward 500 nm. It may then be inferred that $PdCl_4^{2-}$ is the predominant species for low palladium content, $PdCl_2$ being the main entity at higher loadings. The above results are summarized in Table 2.

The mechanism of the interaction between the carrier and the precursor solution has now to be considered. The reactions usually considered are: (i) the formation of a layer of $PdCl_2$, the carrier acting just as an inert surface; evaporation of aqueous hydrochloric solutions of $PdCl_2$ gives rise to $PdCl_2$ and not to H_2PdCl_4 [Eq. (2) below]; and (ii) ion-exchange between $PdCl_4^{2-}$ ions in the solution and the surface anions (OH groups or Cl^- ions).

The first mechanism partly takes into account the results obtained on SiO_2 and TiO_2 (deposit of $PdCl_2$). On the other hand, the presence of $PdCl_4^{2-}$ on TiO_2 and Al_2O_3 could arise from a rapid anionic exchange reaction; however, this explanation is not valid. When, indeed, TiO_2 and Al_2O_3 carriers are immersed in an excess of precursor solution, no variation of the Pd concentration is detected even after 3 days, this lack of exchange arising from the high concentration of Cl^- ions which are competing with $PdCl_4^{2-}$ (*9*). It must then be recalled that the stability of species like $PdCl_4^{2-}$ or $Pd(H_2O)_4^{2+}$ *in aqueous solution* is strongly dependent upon the Cl^- concentration and the ionic strength of the medium (*6*). Hence the retention of such species by some carriers may be accounted for by considering the surface concentration of Cl^- and the surface ionic strength. Upon impregnating alumina, surface OH groups are replaced by Cl^- ions and a deposit of $PdCl_2$ is formed; however, drying may lead the Cl^- ions to enter the coordination sphere of Pd and to give $PdCl_4^{2-}$ ions.

$$\text{Al–OH} + H^+Cl^- \rightarrow \text{Al–Cl} + H_2O \quad (1)$$

$$PdCl_4{}^{2-}{}_{\text{solution}} + 2H^+{}_{\text{solution}} \rightarrow PdCl_{2\,\text{solid}} + 2HCl\uparrow \quad (2)$$

$$PdCl_{2\,\text{solid}} + 2\ \text{Al–Cl} \rightarrow PdCl_4^{2-}(2Al^+) \quad (3)$$

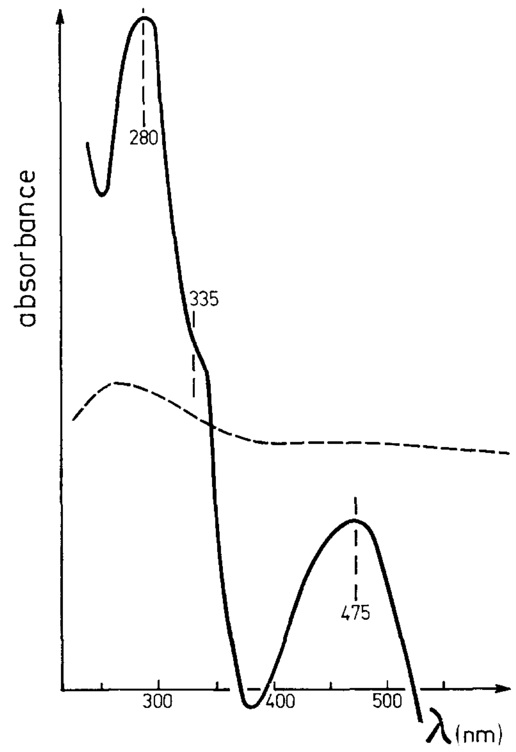

FIG. 2. The uv-visible spectrum of $PdCl_2$/η-alumina (10% Pd). Dotted line: η-alumina impregnated by a 2 *M* HCl solution.

TABLE 2

Summary of the uv-Visible Reflectance Data

Support	Pd content (%)	Band position (nm)	Assignment (predominant species)
η-Al_2O_3	10	280, 335, 475	$PdCl_4^{2-}$
δ-Al_2O_3	Up to 10	280, 335, 475	$PdCl_4^{2-}$
SiO_2	1.5 to 12	370, 500	$Pd(H_2O)_4^{2+}$, $PdCl_2$
TiO_2	0.4 to 1.6	475–480	$PdCl_4^{2-}$
	2 to 10	500	$PdCl_2$

This mechanism differs from an ion-exchange process because the tetrachloropalladate ions are generated upon drying [Eq. (3)] from a deposit of $PdCl_2$.

The validity of Eq. (3) has been checked by grinding $PdCl_2$ with either chlorinated or non-chlorinated alumina. The typical bands of $PdCl_4^{2-}$ are observed only when chlorinated alumina is used. It is also of interest to try to estimate the maximum amount of Pd which could be present as $PdCl_4^{2-}$ ions. After impregnating δ-alumina with 2 *M* HCl and drying at 120°C for 3 hr, the quantity of Cl^- retained by the solid is 1.1×10^{-3} to 1.2×10^{-3} mol of Cl^-/g of alumina (depending on the volume of HCl used). According to Eq. (3), this corresponds to a Pd loading of 5 to 6%. For higher Pd contents, a deposit of $PdCl_2$ should be formed, leading to a shift of the absorption maximum from 475 toward 500 nm. In fact, as the apparent absorption coefficient of $PdCl_2$ is much smaller than that of $PdCl_4^{2-}$ (*10*), a shift is noticeable only for Pd loadings >10%.

On titania the substitution of OH groups occurs to a lesser extent; hence the ability of this carrier to stabilize $PdCl_4^{2-}$ ions is more limited, and except at low Pd content, $PdCl_2$ is the predominant species.

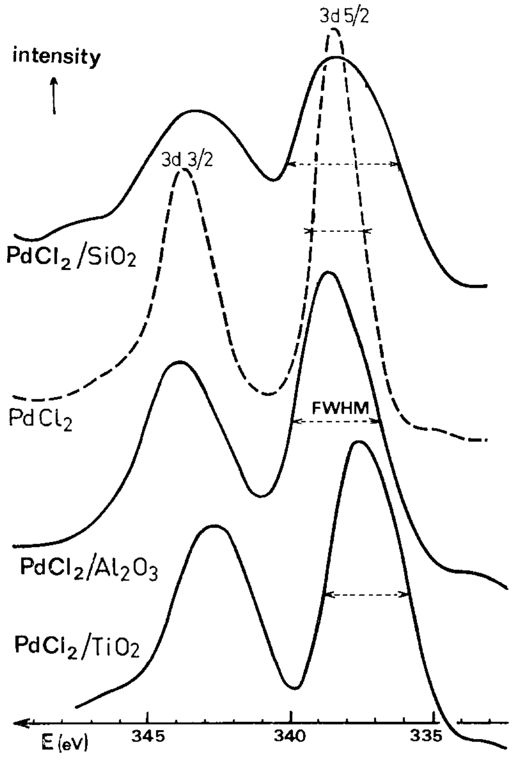

FIG. 3. X-ray photoelectron spectra of nonreduced samples (10% Pd).

When the OH groups are not reactive, HCl is evolved on drying and $PdCl_2$ is either deposited as such (titania, silica) or transformed according to:

$$PdCl_2 + 4H_2O \rightarrow Pd(H_2O)_4Cl_2 \text{ (silica).}$$

Finally, some experiments were carried out on samples prepared by catonic exchange from $Pd(NH_3)_4Cl_2$ aqueous solutions and silica or alumina (no exchange was detected on titania). First, the spectrum of the precursor solution reveals that $Pd(NH_3)_4{}^{2+}$ is the main entity (band maximum at 298 nm) (*6*). Second, the reflectance spectra of the solids show a band located in the 330- to 380-nm range, depending on the washing and drying conditions. These results indicate the presence of $Pd(NH_3)_{4-m}(H_2O)_m$ surface complexes, with $m \geqslant 2$ (*6*), which means that a ligand exchange has occurred during washing and drying.

Photoelectron spectroscopy. Figure 3 shows the Pd 3d electron spectra of $PdCl_2$/δ-Al_2O_3, $PdCl_2/TiO_2$, $PdCl_2/SiO_2$, and $PdCl_2$ alone. For the dichloride, maxima are observed at 338.2 and 343.1 eV; the full width at half maximum intensity (FWHM) is about 2.0 eV for each peak. These results are in good agreement with those of Kumar *et al.* (337.9 ± 0.3 and 343.2 ± 0.3 eV) (*11*). We shall now compare the Pd $3d_{5/2}$ peaks of the three catalysts (the Pd $3d_{3/2}$ line gives similar information). On $PdCl_2/Al_2O_3$, the maximum is observed at 338.5 eV and the FWHM is about 3.2 eV; this binding energy is very close to that measured by Kumar *et al.* (*11*) on $PdCl_4{}^{2-}$ (338.4 ± 0.2 eV), but the FWHM value suggests that a second species may be present, which could be identified with $PdCl_2$. On the $PdCl_2/SiO_2$ spectrum, the position of the maximum is the same as in $PdCl_2$ but the FWHM is much more important (4.0 eV) and the peak exhibits a marked asymmetry toward low binding energies. Graphical resolution allows a second peak to be discerned near 336.5 eV. It may then be inferred that two palladium species are present, in agreement with the conclusions drawn from the uv-visible spectra. If the first peak has to be assigned to $PdCl_2$, the attribution of the second one (336.5 eV) requires further examination. A partial reduction to Pd metal may be first envisaged; recent work, indeed, has indicated that palladium chloride is partly reduced to the metal by X-rays during XPS measurements after hours of irradiation (*12*). However, we did not observe such a reduction in our experimental conditions (less than 60 min of irradiation); in addition, comparison with spectrum c of Fig. 5 shows that the contribution of Pd metal should be rather weak. Considering that, besides the electronegativity of the ligand atom, other parameters are involved such as the nephelauxetic effect (*13*), we then propose that the aquocomplex itself is responsible for the shoulder near 336.5 eV; such an assignment is supported by the fact that in PdO the Pd $3d_{\frac{5}{2}}$ line is observed between 336.3 and 336.9 eV (*15*).

In the spectrum of $PdCl_2/TiO_2$, the Pd $3d_{\frac{5}{2}}$ maximum is shifted toward lower binding energies (337.4 eV) and the FWHM is about 3.0 eV. On the other hand, the obtaining of low binding energies by XPS seems to be related to the presence of surface aquo- or aquochloro complexes. When indeed the formation of such complexes is favored by decreasing the HCl concentration in the impregnating solution, the Pd 3d maxima are shifted toward lower energies; as a matter of fact, with a 0.1 *N* HCl solution, the Pd $3d_{\frac{5}{2}}$ peak maximum is observed at 336.3 eV in $PdCl_2/TiO_2$ and 337.5 eV in $PdCl_2/SiO_2$. Then the value measured on the standard $PdCl_2/TiO_2$ sample (337.4 eV) may be accounted for by the presence of two surface entities; namely, $PdCl_2$ and an aquo- or aquochlorocomplex.

Going back to the uv-visible data, we notice that no aquocomplex was detected on $PdCl_2/TiO_2$. This disagreement is only apparent because (i) the XPS data concern a layer of about 20-Å depth while analysis by uv-visible reflectance spectroscopy goes far beyond it (up to several thousand angstroms) and may fail to detect surface species when the dispersion of active phase is poor, as it is in this case (*14*), and (ii) the sensitivity of uv-visible spectroscopy on TiO_2-supported samples is poor below 400 nm because of the strong absorption of this carrier.

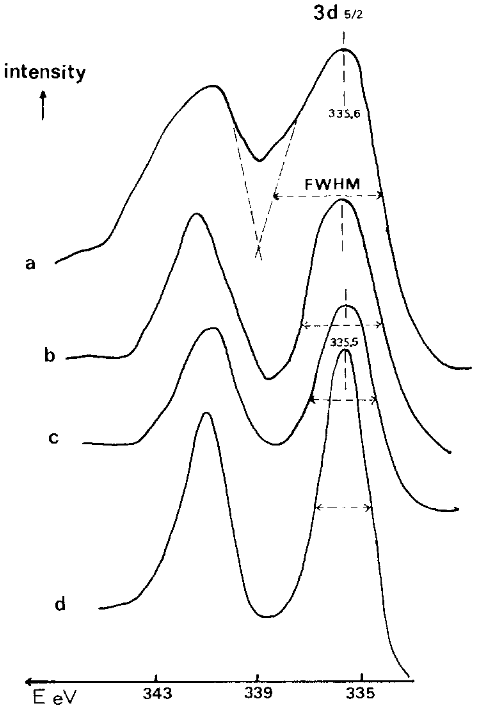

FIG. 4. Photoelectron spectra of reduced samples (10% Pd) prepared through impregnation by $PdCl_2$ solutions. (a) $Pd/\delta\text{-}Al_2O_3$, (b) Pd/TiO_2, (c) Pd/SiO_2, (d) pure Pd powder.

The uv-visible and XPS measurements have then shown that the carriers used cannot be considered as inert although the exchange ability of these supports is negligible in the conditions of impregnation employed here; a chemical interaction occurs during impregnation and drying, which involves at least a fraction of the palladium deposited on the carrier. The strength of this interaction, i.e., the stability of the surface complexes in nonreduced samples, depends on the nature of the carrier, and a similar dependence has to be expected for the reducibility of these samples. As a matter of fact, impregnation of silica with palladium chloride solution promotes the formation of labile complexes (aquocomplexes) which should be more easily reduced to the metal than the palladium(II)–alumina complex. This type of observation has to be born in mind when discussing the existence of any support effect.

2. Reduced Samples

Reflectance spectroscopy. Reflectance spectroscopy can only give information about the presence of Pd(I) or Pd(II); i.e.

TABLE 3

XPS Data, Chloride Content, and Average Particle Size of Various Samples[a]

XPS and related data	Catalysts			
	10% Pd/SiO_2	10% Pd/TiO_2	10% $Pd/\delta\text{-}Al_2O_3$	4% Pd/SiO_2 prepared by exchange
FWHM of Pd $3d_{\frac{5}{2}}$ (eV)	2.7	3.3	4.2	4.5
Total Cl content (%)	<0.02	0.29	0.74	0.22
$I(Cl)/I(Pd)$	0	0.22–0.25	0.32–0.40	0.25
Average particle size (Å[a])	80–100	110	110	30

[a] Determined by X-ray line broadening, electron microscopy, and CO adsorption. Details in Ref. (*14*).

can only detect incomplete reduction. For catalysts prepared by impregnation and reduction in the standard conditions (300°C) or for samples obtained by cationic exchange and reduction at 110°C, no band corresponding to any of these ions was observed.

Photoelectron spectroscopy. As no preparation chamber was available on the Varian spectrometer, a possible modification of reduced samples during their transfer into the spectrometer could be envisaged. For this reason, a series of control experiments was carried out on a AEI 200 spectrometer using a preparation chamber: The spectra recorded before and after heating the samples at 200°C under hydrogen showed no noticeable difference. It was then concluded that the procedure used on the Varian apparatus does not lead to a significant modification of the reduced samples.

The photoelectron spectra of pure palladium powder and of reduced supported palladium are presented in Fig. 4. The binding energy measured for pure palladium (335.5 eV) is in good agreement with previous results (*11*, *15*). For supported Pd, no significant shift of the peak maximum is noticed, but large differences in the FWHM are observed. To obtain more information about the surface composition of the catalysts, the XPS lines of N and Cl, elements involved in residual precursor anions (or native impurities), were also recorded. While no N 1s signal was detected, the Cl 2p line had a significant intensity for several samples. The surface chloride content was expressed by $I(Cl)/I(Pd)$, ratio of the areas of the Cl 2p and Pd $3d_{\frac{5}{2}}$ peaks. This parameter is of great interest despite the fact that a part of the Cl^- ions could be not linked to Pd atoms (especially at low Pd content). Rather than a quantitative analysis (*16*, *17*), the data obtained in this way allow a comparative estimation to be done if the dispersion of the palladium atoms is taken into account.[1] The intensity of XPS lines of supported metals, indeed, has been shown to increase with the metal dispersion (*18*). Hence the $I(Cl)/I(Pd)$ values should not be compared without considering the Pd particle size (Table 3). The peak intensity of the supported metal also depends upon the porosity of the carrier (*19*), but this parameter need not be considered here because the catalysts examined were nonporous (Table 3).

For catalysts prepared by impregnation with $PdCl_2$ (Table 3), the FWHM is greater than for unsupported Pd and decreases in the following order:

$$Pd/Al_2O_3 > Pd/TiO_2 > Pd/SiO_2.$$

The same order is found (i) for the *total* chloride content (ii) for the *surface* chloride estimation. The broadening of the Pd 3d peaks may then be related to the presence of chloride ions in the vicinity of a part of the Pd atoms: In Pd/Al_2O_3, e.g., the *total* atomic Cl/Pd ratio is about $\frac{1}{5}$. Even if one assumes that only a part of these chloride ions has a direct influence on the electronic density on Pd atoms, such

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[1] The Cl^- ions may be considered as monatomically dispersed on all samples; i.e., no $AlCl_3$ is present.

a value seems to be high enough to account for the above spectral data. Other results support this assumption: (i) Heating Pd/Al_2O_3 at 300°C under wet flowing argon led to a significant decrease of both the FWHM (Fig. 5) and of the chloride content of the catalyst (two-thirds of the initial value). (ii) When the alumina (η-Al_2O_3) and the precursor (palladium nitrate) used do not contain Cl^- in detectable amounts ($<0.02\%$), the FWHM is weakened (to 3.3 eV) (Table 4).

Examination of Table 4 shows that the nature of the precursor has an influence on the Pd peak width only in the case of alumina-supported catalysts. Once again the ability of alumina to retain Cl^- ions is evidenced. In this respect, it is interesting to note that the Al 2p (or 2s) lines are moved toward higher energies upon impregnation and that, even after reduction, a shift of about 0.5 eV is noticed: On the other hand, in the case of Si and Ti, when comparing the binding energies measured on the reduced samples and on the carriers alone, no significant difference is observed. The final comment on Table 4 concerns the alumina-supported sample prepared from $PdCl_2$. After only 3 hr of reduction (instead of 6 hr in the standard procedure, Table 3), the binding energy of Pd $3d_{\frac{5}{2}}$ is significantly higher than for the other samples, which is still indicative of an incomplete reduction.

TABLE 4

Influence of the Nature of the Precursor upon XPS Data

Catalysts[a]	Precursor	Binding energy (eV)	FWHM (eV)	Chloride content (%)
10% Pd/Al_2O_3	$Pd(NO_3)_2$	335.7	3.3	<0.02
	$Pd(NH_3)_4Cl_2$	335.6	4.5	1.34
	$PdCl_2$	336.3	4.2	1.25
10% Pd/SiO_2	$Pd(NO_3)_2$	335.6	2.7	<0.02
	$Pd(NH_3)_4Cl_2$	335.6	2.7	<0.02
	$PdCl_2$	335.9	2.9	<0.02

[a] Reduction under flowing H_2 at 300°C, 3 hr.

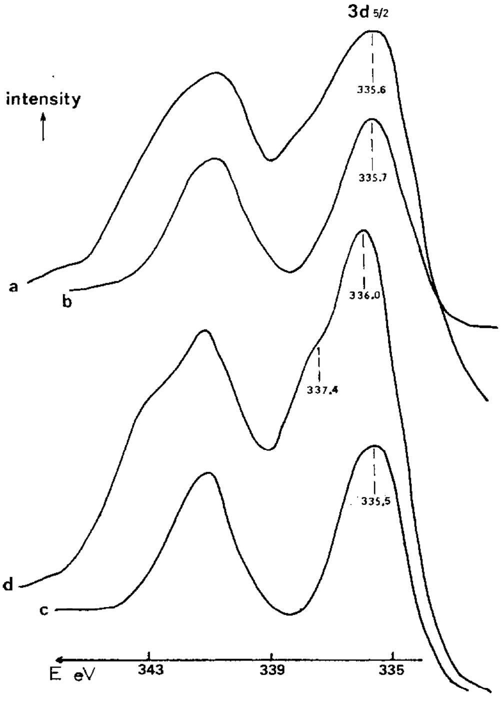

Fig. 5. Photoelectron spectra of reduced samples: influence of the preparation conditions. (a) 10% Pd/δ-alumina, (b) sample (a) after heating at 300°C under wet flowing argon, (c) 10% Pd/silica (impregnated), (d) 4% Pd/silica (ion-exchanged).

Let us now consider the Pd/SiO_2 sample prepared by ion exchange and reduced at 110°C (Table 3; Fig. 5, spectrum d); the Pd $3d_{\frac{5}{2}}$ maximum is slightly higher (336.0 eV) than in Pd metal and a shoulder is observed toward higher energies (337.4 ± 0.3 eV), the FWHM being about 4.5 eV (Fig. 5). This result shows that the reduction of the precursor has not been completely achieved, as also indicated by the high value of the *total* atomic Cl/Pd ratio (about 1/4). On the other hand, the peak intensity at its maximum is higher than that observed for the impregnated sample (spectrum c) although the metal content is 2.5 times lower. This is explained by the better dispersion (about three times higher) of the metal on the sample prepared by ion-exchange; such an effect accounts for the relatively low value of the $I(Cl)/I(Pd)$ ratio measured on this sample, compared to that estimated on Pd/Al_2O_3 (Table 3).

To sum up, examination of reduced samples by XPS has allowed the detection of surface complexes involving a part of the palladium atoms and containing chloride ions. It is especially interesting to note that the samples containing these complexes have the lowest catalytic activity in ethylene oxidation (*14*). These results draw attention to the role of residual chlorine, already suspected by other investigators such as Dorling, *et al.* (*20*), and more generally, emphasize the importance of improving the surface chemical characterization of catalysts. Correlations between dispersion and activity (or selectivity) data can be of little significance if the elemental surface composition has not been investigated.

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