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Active Sites in Polymer-Bound Palladium–Phosphine Coordination Catalysts. Chemical and XPS Investigations

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The nature of the catalytically activated state for polymer-bound Pd catalysts has been studied. The methods used are X-ray diffraction, X-ray photoelectron spectroscopy (XPS), and a chemical technique based on the redox couple benzoquinone/hydroquinone. The chemical method shows that the activation is caused by reduction of part of the Pd(II) present in the resin. This method also gives a quantitative measure of the ratio Pd(II)/Pd^0 in the activated catalyst. The XPS investigation also shows that the activation is due to reduction of part of the Pd(II) in the resin. This method, however, is not as sensitive and conclusive as the chemical one, due to formation of PdO_{ads} on the activated catalyst. The X-ray diffraction study complements the other two methods in that it shows that the reduced Pd in the activated catalyst is Pd metal and not a low-valent Pd complex. The way in which the three methods are influenced by the formation of PdO_{ads} under the action of molecular oxygen is briefly discussed.

INTRODUCTION

The attachment of coordination catalysts to porous polymers has attained increasing interest in recent years (*1*). One of the first systems studied was $PdCl_2$ bound to phosphinated polystyrene (*2, 3*). This catalyst was used for the hydrogenation of methyl esters of fatty oils (*2, 3*). The same system has also been used as catalyst in the oligomerization of butadiene (*4*) and for hydrogenation of olefins other than fatty oil methyl esters (*5*). We have also been studying this system and have found it to be a good catalyst for the hydrogenation of soybean oil (*6*). A common observation in all these studies is a change in catalyst color, from yellow to green, after one or more catalytic runs. This color change also appears after such treatments of the polymer-bound catalyst that makes it active under low pressure (1 atm). For the homogeneous counterpart no such activation can be achieved and it requires high pressures for operation. Different proposals as to the cause of this color change of the catalyst have been made. Bruner (*9*) suggested the yellow to green change was caused by isomerization reactions inside the polymer, resulting in bonding of the metal ion to nonadjacent phosphine groups. This in turn is supposed to cause a weaker interaction between filled metal d_{z^2}, d_{xz}, and d_{yz} orbitals with the electron-rich benzene rings in the polymer. Terasawa *et al.* (*5*) have discussed "the irreversible yellow to green color change" in terms of solvent coordination. Oxygen-containing solvents like dimethyl formamide, ethanol, tetrahydrofuran, and acetone gave the highest reaction rates in their study. Pittman *et al.* (*4*) claimed the deposition of metallic Pd to be responsible for the color change. We (*6*) have suggested that the activation is due to reduction of part of the Pd^{2+} ions in the resin. In further studies we were able to show (*7, 8*) that the resin contains both the expected bisphosphine complex $Cl_2Pd(P\text{-}PS)_2$ as well as other species (P-PS = phosphinated styrene–divinylbenzene polymer). Depending on metal loading and synthetic route the relative proportions of these constituents vary. This situation is depicted in Fig. 1. The ratio X/Y is related to polymer properties such as surface area and phosphorus content and also to metal loading.

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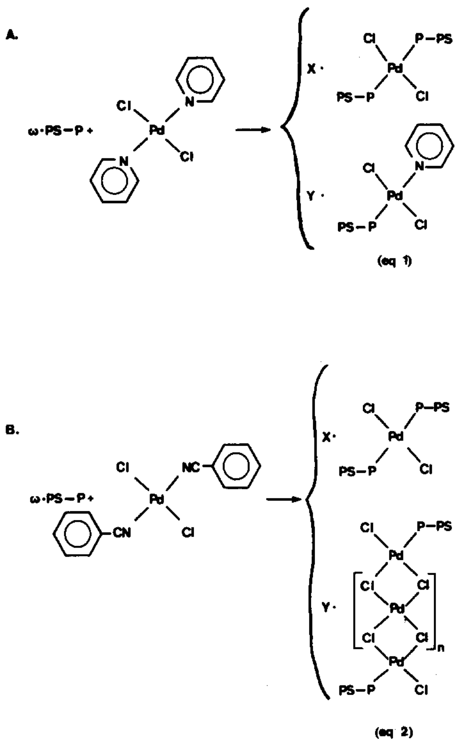


FIG. 1. The complexes formed in the phosphinated polystyrene resin: (a) the pyridine complex as starting material; (b) the benzonitrile complex as starting material.

Accepting the existence of these species in the resin, it is easy to understand that the heterogenized system behaves differently from the homogeneous system having $Cl_2Pd(PR_3)_2$ as the sole component. However, from the catalytic point of view the important questions are: How do these species behave under reaction conditions? Do they decompose or rearrange or stay intact? Do they influence the catalytic reaction at all? In the present study these questions are applied to the catalysts prepared from Cl_2Pd(benzonitrile)$_2$, with different metal loadings as these systems are more easily activated, i.e., they demand a lower temperature for the activation compared to the complexes prepared from Cl_2Pd(pyridine)$_2$. The "green activated catalysts" have been prepared by using different reducing agents such as H_2, CO. We were especially interested in determining whether the "activation" is due to reduction of Pd(II) or not. X-Ray photoelectron spectroscopy (XPS, ESCA) is a technique well suited for this purpose which has been utilized before to study polymer-bound palladium–phosphine complexes (*5, 10*). However, the difference in binding energy between used and fresh catalyst was found (*5*) to be very small, indicating only minor changes on activation. In addition to XPS studies we have designed and applied another method, based on the redox couple quinone/hydroquinone, with the intention to check and perhaps extend the results obtained in the XPS investigations.

EXPERIMENTAL

Preparations. The polymer-bound palladium catalysts studied were prepared by ligand exchange (Eq. (2), Fig. 1). A detailed description of this procedure has been given elsewhere (*8*). The analytical data for the three preparations are given in Table 1.

Activation. To convert these catalysts into the "green" form they were treated with CO or with H_2 according to the following procedure. The catalyst samples (200 mg) were placed in a glass vessel. This was evacuated to ca. 1 Torr and then filled with the appropriate gas to 750 Torr. Acetone (10 ml) was then injected through a membrane. With H_2 the catalyst samples changed their color within 5 min, whereas CO treatment required several hours to achieve the same color change.

Reoxidation. An acetone suspension of a weighed amount of the activated catalyst was acidified with HCl and treated with

TABLE 1

Analytical Data of the Catalyst Samples Studied

Preparation number	Pd (%)	mmol Pd/g catalyst	P (%)	mmol P/g catalyst	Ratio P/Pd
034	2.58	0.24	2.41	0.78	3.22
035	3.64	0.34	2.35	0.76	2.20
036	6.64	0.62	2.22	0.72	1.15

benzoquinone. The amount of benzoquinone added was equimolar to the total amount of Pd in the sample. This mixture was then stirred at room temperature until the catalyst had become yellow (ca. 2 hr). The catalyst was separated and the solution analyzed for hydroquinone. To analyze the amount of hydroquinone formed on benzoquinone treatment the procedure of Joseph and Andrzejczak (*12*) was followed.

Instrumental. XPS spectra were recorded with an AEI ES200 spectrometer using Al K_α radiation. Various sampling techniques were examined. The best spectra were obtained with powdered samples pressed into lead foils and this was used throughout this study.

The C 1s peak, mainly arising from the polymeric resin (phenyl and alkyl groups in the polymer), was used as an internal reference. To determine the binding energy of this reference the procedure of Larsson and Folkesson (*11*), viz., infrared absorption intensity measurements of the C–H stretching vibration in the aromatic ring, was used.

The type of resin we have used in this study (crosslinked polystyrene) cannot be dissolved in any solvent. We have therefore used noncrosslinked polystyrene, which can be dissolved in, e.g., $CDCl_3$, to determine the integrated absorption intensity. This intensity was found to be 1880 M^{-1} cm^{-2}. Thus a value of 284.7 eV for the C 1s binding energy can be calculated, using the correlation graph of Folkesson and Larsson (*11*). Accordingly all binding energies reported in this study are corrected and referred to a C 1s binding energy of 284.7 eV.

GLC analysis was carried out with a PE F17 gas chromatograph equipped with a flame ionization detector.

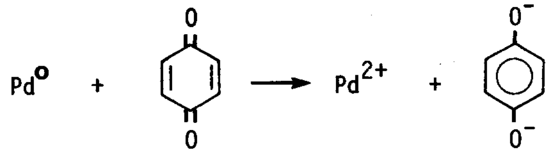
The X-ray diffraction analysis was performed with a Philips PW 1050/25 diffractometer (CuK_α radiation, 45 kV and 24 mA).

Computer resolution programs for the XPS results were those developed by Lykvist in this laboratory (*13*). In all resolution procedures performed in this study a Gaussian peak form and a straight background were applied. The number of component peaks in the Pd 3d peaks observed was chosen on the basis of the chemical and the X-ray diffraction analysis. To reduce the number of independent parameters defining each component peak, i.e., its position, its half-value peak width and its height, the half-value peak widths were chosen corresponding to those which our instrument normally gives for Pd(II) complexes (1.8 ± 0.2 eV) and Pd metal (1.6 ± 0.2 eV). The other two variables were then calcuated by the computer program to give the overall best fit to the experimental curve.

RESULTS AND DISCUSSION

The various conditions described in the literature under which the yellow to green color change and catalyst activation occurs (H_2 or ethylene in methanol (*9*), butadiene in THF (*4*), H_2 in different solvent (*5*)) can all be described as reductive. From Wacker chemistry, however, it is known that the reduced Pd can easily be reoxidized with oxidizing agents like $CuCl_2$ or benzoquinone.

$$Pd^{0} + 2Cu^{2+} \longrightarrow Pd^{2+} + 2Cu^{1+} \qquad (3)$$



(4)

TABLE 2

Analyzed Amount of Pd^0 in the Activated Catalysts

Sample	Activated by	Pd^0 percent of total Pd	mmol Pd^0/g catalyst
034	H_2	6.0	0.014
035	H_2	11.0	0.037
	CO	6.5	0.022
036	H_2	25.9	0.160
	CO	26.7	0.165

On reaction of the green H_2-treated catalyst with $CuCl_2$ in THF this substance reverted to the original yellow color. The same also occurred when benzoquinone was used. This means that the activation of the catalyst is probably a reduction process and that the color change is not irreversible as has been claimed (*9*). The question then arises as to whether previous investigators have been mistaken. The XPS measurements of Terasawa *et al.* (*5*) did not reveal any low-valent Pd, nor did the CN^- test for Pd^0 by Bruner (*9*) or our earlier investigation (*6*) give any evidence for Pd metal. If, however, only very limited amounts of Pd^0 are formed on activation, the methods referred to would probably not be sensitive enough.

Chemical Investigations

Equation (4) states that the amount of hydroquinone formed equals the amount of Pd^0 in the sample. Hence an analysis of the amount of hydroquinone formed after reaction of the activated catalyst with benzoquinone would give the amount of Pd^0 originally present. We have accordingly treated our samples with benzoquinone in an acetone suspension and determined the amount of hydroquinone formed. The reason for choosing the couple benzoquinone/hydroquinone instead of Cu^{2+}/Cu^{1+} lies in the easier means by which hydroquinone can be determined. The results of this investigation are given in Table 2. From these data one can emphasize the following.

(1) At the lowest metal loading the ratio Pd^0/Pd_{tot} is very low indeed (0.06). This is also reflected in the color change of this catalyst. This had only a shade of green, while the other two preparations changed their color completely.

(2) Not only does the absolute amount of Pd^0 increase on increased metal loading, but so does the ratio Pd^0/Pd_{tot}. This fact indicates that the metal content influences the reducibility.

(3) The increase in the ratio Pd^0/Pd_{tot} parallels the increase in the ratio Y/X (Eq. (2)). Hence one can suggest that the reduction of Pd(II) is not a reduction of the palladium in the bisphosphine complex $Cl_2Pd(P\text{-}PS)_2$ but that it is the bridged specimen that is reacting. This is not surprising since palladium coordinated to two phosphine groups in complexes like $Cl_2Pd(PPh_3)_2$ are known to withstand reducing conditions. The bridged complex, on the other hand, is very similar to solid $PdCl_2$, which is built up by chloride-bridged $PdCl_2$ units (*13*), and solid $PdCl_2$ is easily reduced by H_2.

(4) For preparation 034 the existence of the species PS-P–$(PdCl_2)_n$–P-PS in the resin could not be proved in our earlier investigation of this system (*8*), neither from analytical data nor from spectroscopic studies, e.g., ir studies in the metal–chlorine stretching region. However, the fact that even for this preparation, with a low metal content, some Pd^0 is formed on treatment with reducing agents indicates that it probably also contains the bridged complex.

(5) In the discussion above, reduced Pd has been termed Pd^0. This does not however have to stand for palladium metal. The reoxidizing procedure described does not discern whether it is Pd-metal or Pd^0 complexes that act as the electron donor toward benzoquinone. All we can say is that a redox process has taken place. This then makes it necessary to use other methods to further elucidate the system.

Since much of the research in our laboratory is directed toward applications of XPS to catalyst problems we have used this method for further studies.

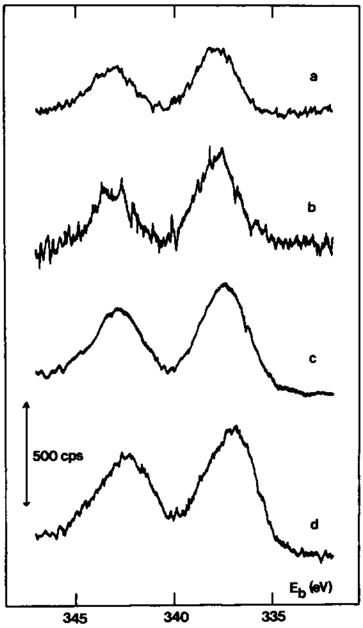


FIG. 2. Pd 3d XPS spectra: (a) Untreated sample 035; (b) sample 035 treated with H_2; (c) sample 036 treated with CO, stored in air; (d) sample 036 treated with CO, direct after treatment.

XPS Studies

The procedure outlined in the preceding section, i.e., treatment of the samples with a reducing agent and reoxidizing with benzoquinone, ought, at least in theory, be easily followed by XPS measurements. This statement is based upon the energy difference between the Pd 3d bands in Pd(II) phosphine complexes (e.g., $Cl_2Pd(PPh_3)_2$, E_b $3d_{5/2}$ = 337.9 eV (*14*)) and Pd metal (E_b $3d_{5/2}$ = 335.2 eV (*15*)). This energy difference of 2.7 eV is so large that with normal FWHM of around 2 eV these bands should be well separated (*16*).

For our three samples (034, 035, 036), differing in metal content we first examined the untreated ones (A), then the same samples treated with reducing agent (B), and finally the latter ones treated with benzoquinone (C). For the sake of clarity we will discuss the XPS measurements under the categories A, B, and C.

A. Untreated samples. All untreated samples gave the same band shape and Pd 3d binding energy independent of metal content (337.9 ± 0.2 eV). A typical spectrum is shown in Fig. 2a. The measured Pd binding energy corresponds to what is normally found for Pd(II) complexes with monomeric phosphine ligands (*14*). Except for the preparation with the highest metal content (036) which gives a slightly higher binding energy (Fig. 4) the difference in composition (different Y/X ratios, Eq. (2)) is not reflected in our measured binding energies. This indicates that the difference in Pd 3d binding energy for $Cl_2Pd(P\text{-}PS)_2$ and PS-P–$(PdCl_2)_n$–P–PS is small (within experimental errors) and hence XPS cannot be used to determine the Y/X ratio. Terasawa *et al.* (*10*) have also observed that the Pd 3d energy binding for polymerbound complexes is relatively insensitive to the type of species in the resin.

B. Samples treated with reducing agents. For the samples with the lowest (034) and the intermediate (035) metal content no shift in binding energy relative to the binding energy of the same untreated samples could be observed (Fig. 2b), nor was the line broadening significant. Hence the very small part of low-valent Pd that the chemical investigation had shown was not revealed in the spectra of these preparations. This is the same general pattern as that found earlier (*5*) for polymer-bound palladium catalysts after they had been used in hydrogenation experiments.

However, for the sample with the highest metal content (036) the situation was different. If this sample was treated with CO and then stored in air the spectrum in Fig. 2c was obtained. Compared to the spectrum of the same untreated sample, the bands are 0.3 eV broader and shifted 0.5 eV toward lower binding energy. Two things can be stated from this observation. First, since lowered binding energy means lowered oxidation state, XPS indicates that the activation is caused by a reduction of Pd(II). Second, as no extra peak or shoulder corresponding to the binding energy of Pd metal can be observed, these bands do not

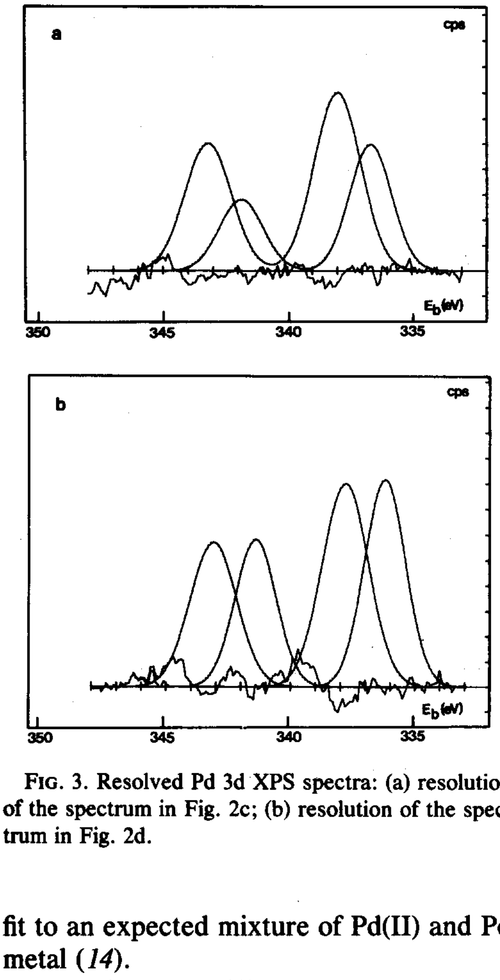


FIG. 3. Resolved Pd 3d XPS spectra: (a) resolution of the spectrum in Fig. 2c; (b) resolution of the spectrum in Fig. 2d.

fit to an expected mixture of Pd(II) and Pd metal (*14*).

A slightly different pretreatment, namely, no storage in air but direct spectrum uptake after the CO treatment, was used to obtain the spectrum shown in Fig. 2d. If this spectrum is compared to the one in Fig. 2c the band maxima have moved 0.6 eV further toward lower binding energy and in addition the $3d_{5/2}$ band in Fig. 2d now shows a skewness indicating a peak at around 337.7 eV.

For the two spectra shown in Figs. 2c and d we have applied the spectrum resolution procedures described in the experimental section. The results of these calculations are shown in Figs. 3a and b. As can be seen in Fig. 3a the spectrum in Fig. 2c can be resolved into a two-component spectrum, the binding energies being Pd $3d_{3/2}$ 343.3 eV, $3d_{5/2}$ 338.0 eV, Pd $3d_{3/2}$ 342.0 eV, and $3d_{5/2}$ 336.7 eV, respectively. The high binding energy component (E_b $3d_{5/2}$ = 338.0 eV) has a binding energy comparable to what is normally found for Pd(II) compounds, so this is most likely unreduced Pd(II). The binding energy of the other component in Fig. 3a (Pd $3d_{5/2}$ = 336.7 eV) is, however, about 1.5 eV higher than that expected for Pd metal and consequently cannot be assigned to Pd metal. For the time being we can leave the assignment of this component and treat the resolution of the spectrum in Fig. 2d.

As can be seen in Fig. 3b even this spectrum is best resolved into a two-component spectrum. Comparing this resolved spectrum with that in Fig. 3a reveals that the high-energy component remains at the same binding energy (E_b $3d_{5/2}$ = 338.0 eV). The low-energy component (E_b $3d_{5/2}$ = 336.1 eV) has, however, moved 0.6 eV toward lower binding energy. This is the same energy difference as that found for Pd metal and PdO_{ads} (*17*), although at a different position on the energy scale. At the same time it is noticeable that the position of the low-energy component (Pd $3d_{5/2}$ = 336.7 eV) in Fig. 3a corresponds to what has been found for the bulk oxide PdO (*17*). Hence, based on the difference in pretreatment and on the binding energies observed, the low energy components in Figs. 3a and b can be assigned to Pd-oxide of some form and Pd metal, respectively.

That the observed difference between the spectra in Figs. 2c and d is caused by an air oxidation of Pd metal was confirmed by the following experiment. The spectrum of the second sample was registered at different time intervals. Between the registrations the sample was kept outside the spectrometer in open air. Changes in the registered spectrum took place and a state of equilibrium was reached after 1 day. This "equilibrium spectrum" was identical to that obtained in Fig. 2c. Whether it is bulk oxide or surface oxide that forms during storage in open air cannot be concluded from our observed binding energy (E_b Pd $3d_{5/2}$ = 336.7

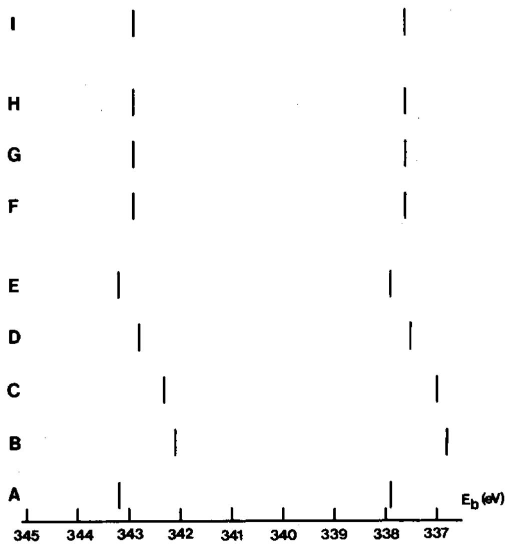


FIG. 4. Measured Pd 3d binding energies: (A) untreated 036; (B) 036 treated with CO, direct after treatment; (C) 036 treated with CO 2 hr after treatment; (D) 036 "equilibrium spectrum"; (E) 036 treated with CO and reoxidized with benzoquinone; (F) untreated 035; (G) 035 treated with H_2; (H) 035 treated with CO reoxidized with benzoquinone; (I) 034 untreated.

eV). This problem will, however, be treated below.

To avoid the influence of molecular oxygen we have tried to perform the gas treatment (CO or H_2) in the sample preparation chamber of our spectrometer. After such treatments, no color change of the sample was found and the spectrum registered was unchanged relative to that of an untreated sample. Hence no reaction had taken place. The reason for this is unknown, but as solvent effects on the catalytic activity have been noted (*5*), solvent assistance might be necessary in the reduction.

C. Sample treated with benzoquinone. When our three different samples after reduction were subjected to the benzoquinone treatment they all reverted to a yellow color. For the sample with the highest metal content this reaction was also reflected in the XPS spectrum, which showed the same Pd $3d_{3/2}$ and $3d_{5/2}$ binding energies as for the untreated sample. Thus the benzoquinone treatment does oxidize the sample back to its original oxidation state, but it is unlikely that the original structure is restored. However, as we have used the benzoquinone treatment only as an aid to determine the amount of Pd^0 in the resin, the structure is unimportant.

Figure 4 summarizes binding energies for all the samples. For the sample with the highest metal content this gives a rather clear-cut illustration of the redox process, both the intended one, with catalyst activation and reoxidation, and the unintended air oxidation. It also illustrates the limits of the XPS method, in this special case, since for the two other samples with low metal content no changes are observable. In this connection we may mention that since the XPS method and the chemical method both give the same qualitative result for the sample with the high metal content it can be concluded that the chemical method devised can be used to detect Pd^0. As to the quantitative results of the two methods used, these are not the same (compare band height 336.1 eV/337.8 eV with Table 2). This is understandable as XPS gives the surface composition but the chemical method gives bulk composition and these are probably not the same.

The Formation of Pd-Oxide

In the preceding section it was suggested that the time-dependent changes in the Pd $3d_{3/2}$ and $3d_{5/2}$ bands observed was caused by an oxidation of Pd metal to palladium oxide of some form. In the resolved spectra this showed up as a change in one of the components from 336.1 to 336.7 eV, while the other remained at its original position. The oxidation of metallic Pd by molecular oxygen is however known to proceed first at higher temperatures. Lam and Boudart (*18*) observed an increased dioxygen uptake at 538 K in their study of small palladium particles. Paryjczak *et al.* (*19*) observed three different temperature ranges for the reaction of dioxygen with Pd supported on alumina or silica, including range I (300–470 K) in which surface chemisorp-

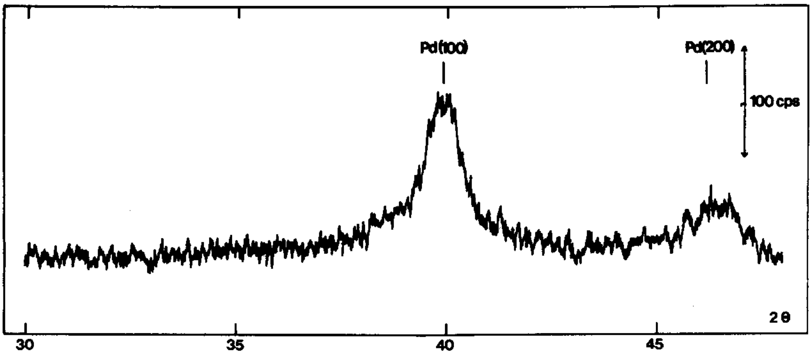


FIG. 5. X-Ray diffraction pattern of the sample 036 treated with CO and exposed to air.

tion occurs and range II (470–770 K) in which bulk metal oxidation occurs. As we have kept our samples only in air at room temperature, it is likely that the band we observe at 336.7 eV can be assigned to PdO_{ads}.

We have, however, also used the X-ray powder method to study the sample (036 treated with CO) for which the change in the XPS spectrum was observed. The diffraction pattern (Fig. 5) shows exclusively diffraction peaks of Pd metal. The fact that no trace of Pd oxide can be detected even though this sample had been kept in air for several weeks supports the interpretation that it is surface oxide that is formed. As X-ray diffraction is a bulk method giving information on the whole sample, the surface oxide is probably too small a part of the total Pd to be observed with this method. XPS on the other hand is a surface method penetrating the sample to a depth of ca. 20 Å (*23*), and will thus probably sense only the oxide. Consequently the results obtained by the two methods do not have to be the same.

In the X-ray diffraction study by Lam and Boudart (*18*) it was shown that palladium oxide can be easily reduced by reacting with dihydrogen at room temperature. This then gives another possibility to check if it is palladium oxide we observe in our XPS investigation. By allowing the same sample as used in the X-ray diffraction experiment to react with dihydrogen (1 atm) in the ESCA sample preparation chamber we obtained a spectrum almost identical to that obtained directly after the CO treatment (Fig. 2d). That the changes in XPS spectra that result from air exposure of the sample can be reversed by treatment with dihydrogen shows that we are dealing with an oxide.

This oxidation of Pd metal by air does not only influence the XPS investigations. It also interferes with the chemical method used in this study, since the amount of hydroquinone formed will not correspond to the amount of Pd metal originally present. The figures in Table 2 should therefore be interpreted with this in mind. However, the amount of Pd oxidized by air in our analysis is presumably very small since no oxide could be detected in the X-ray diffraction investigation. Also the CN^- treatment for the qualitative determination of Pd metal devised by Bruner (*9*) must be sensitive to air oxidation of Pd. The fact that no Pd metal was found in his work might be due to this phenomenon.

The Position of the Bands Assigned to Pd(Metal) and PdO_{ads}

In our resolved spectra in Figs. 3a and b the bands at 336.7 (3a) and 336.1 (3b) were assigned to PdO_{ads} and Pd metal, respectively. These values are, however, about 1 eV higher than what is normally found for Pd $3d_{5/2}$ (Pd metal E_b = 335.2 (*15*) E_b = 335.0 (*17*), PdO_{ads} E_b = 335.6 (*17*)). Other investigators (*14, 21*) have, however, found E_b values of 335.8 eV, i.e., closer to that in Fig. 3b. We have recorded the spectrum for a Pd foil and for a commercial Pd on carbon catalyst from Engelhard and found binding energies for Pd $3d_{5/2}$ of 335.2 and 335.8 eV, respectively. Several reasons for the high value in Fig. 3b can be suggested. One obvious explanation concerns the problem of sample charging and the calibration method. For the Pd foil which is a conductor no charging will interfere but for the Pd on carbon catalyst as well as with our Pd bound to the polymer resin, sample charging might cause problems. The usual manner to compensate for sample charging is to refer measured binding energies to the binding energy of C 1s in pump-oil deposits (285.0 eV). One then assumes that the charging of the pump-oil carbonaceous deposits and the sample is the same. In this study we have used a more elaborate method (*11*) to compensate for sample charging. This method uses an internal standard (the phenyl rings in the polymer) and the binding energy of this standard is indirectly determined by an infrared technique. This method has proved useful in several investigations (*20*) and for the Pd(II) part in our samples it gives results in accordance to what is found for monomeric Pd(II) phosphine complexes. The Pd(II) part in our samples is bound to the resin and is thus contained in the resin phase. Hence the potential sensed by the Pd(II) ion is most likely the same as that sensed by the phenyl groups of the resin. The small metallic particles in the resin, on the other hand, can be regarded as a separate phase, and thus their potential does not have to be the same as that of the resin. So the method of calibration might be the reason for the high value found for Pd metal and PdO_{ads}, the binding energies found for these two items being really ~1.0 eV lower than those recorded here.

CONCLUSION

Different methods have been used to elucidate the composition of the catalytically active state for a palladium complex bound to phosphinated polystyrene resin. X-Ray diffraction shows that metallic palladium is formed on activation of the catalyst. However, from both the chemical and the XPS investigation it can be concluded that the reduction to the metallic state involves only a part of the Pd(II) originally present in the resin. This holds for the catalyst with the highest metal loading. For the other two catalysts investigated, the concentration of the metallic phase is too low to be clearly shown by methods other than the chemical one. Since the chemical method does not specify what type of low-valent palladium is formed, however, the three methods used complement each other.

The disturbing action of molecular oxygen in oxidizing Pd to PdO_{ads} must also be stressed. This is perhaps most relevant in the XPS investigations, since XPS is the surface sensitive method, and consequently the oxidation to PdO_{ads} will make an identification of Pd metal in the XPS spectrum more difficult or even impossible. This reaction with O_2 is most probably one of the reasons for the somewhat limited results we have obtained by the XPS investigation. Even the chemical method is sensitive to oxidation by O_2 in the air, but to a more limited extent. This is because this method gives bulk composition and Pd oxidation is probably important only at the catalyst surface.

From the catalyst composition derived in this study the catalyst can be said to possess two different active sites in the same catalyst particle, viz. metallic Pd, which is known to activate molecular hydrogen easily and to function as a hydrogenation catalyst, and in addition the hydrogenation catalyst $Cl_2Pd(P\text{-}PS)_2$. A natural question to ask is how this situation influences the catalytic activity and selectivity. To obtain activity and selectivity data one must perform detailed hydrogenation experiments. In order to discuss the results, however, a mapping of the components of the catalytic system as described in this investigation is needed. Referring to the present system, detailed knowledge of the variation of kinetic parameters with the ratio Pd metal/Pd(II) would be of great interest. It is not very likely that $Cl_2Pd(P\text{-}PS)_2$ alone would be the active component under the mild conditions often used for this catalyst. Its homogeneous counterpart needs high pressures to operate (*22*) and we have shown in another study (*7*) that the polymer-linked Pd catalyst with $Cl_2Pd(P\text{-}PS)_2$ as the sole component is inactive for the hydrogenation of soybean oil. Instead much of the information available at present indicates that it is the combination of the two components that gives this catalyst its characteristics, but the question is by no means settled.

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