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THERMOANALYTICAL AND SPECTROSCOPIC STUDIES OF THE SYNTHESIS OF SUPPORTED PALLADIUM CATALYST IN A $H_2/PdCl_2/SiO_2$ PARENT SYSTEM

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Abstract

A 5 wt% Pd/SiO_2 catalyst was synthesized by heating $PdCl_2$-impregnated SiO_2 in H_2 at 300°C for 2 h. It was found that the metal particle dispersion is improved when the reduction step is preceded by calcination at 300°C for 2 h. Thermogravimetry of the impregnated support in air, N_2 and H_2 atmospheres was used to monitor the interactions occurring during the various preparative steps (i.e. drying, calcination and reduction) of the catalyst. The solid product of each preparative step was characterized by X-ray diffractometry and UV/Vis diffuse reflectance spectroscopy. The results indicate that following the drying step (at 110°C in air) the palladium occurs in two detectable forms: $PdCl_2$ particles and $Si{-}O{-}Pd^{n+}$ surface species. The calcination appears to transform the $PdCl_2$ particles into the latter surface species. The H_2-reduction eventually converts the surface species into finely-dispersed Pd° metal particles (average size = 8–14 nm). No other reduction products, such as Pd_ySi_x, were detected.

Keywords: catalysts, Pd/SiO_2 catalyst, TG, UV/Vis, X-ray

Introduction

Silica-supported Pd (Pd/SiO_2) actively and selectively catalyzes a number of hydrogenation processes of industrial importance. The most prominent of them are the selective reduction of alkynes to alkenes [1], the reductive cracking and isomerization of saturated hydrocarbons [2], and Syngas (CO, H_2) conversion into methanol [2, 3]. The correlation between the catalyst performance and the surface properties has made obvious the governing role of the chemical state and the environment of the palladium sites [2, 4, 5]. These parameters are intimately related to the catalyst preparation variables and routes [6].

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For instance, the selectivity toward the isomerization of neopentane to isopentane *vs.* the cracking of the latter into CH_4, C_2H_6, C_3H_8 and i-C_4H_{10} has been implemented as a convenient, diagnostic criterion for determining whether Pd interacts with the support [5]. Accordingly, a high isomerization selectivity was related to strong Pd–SiO_2 interactions and the formation of palladium silicide (Pd_xSi_y), rather than to H_2 retained by the catalyst [5].

Moreover, Syngas (CO, H_2) is converted moderately on Pd/SiO_2 to CH_3OH, rather than to CH_4 (and higher hydrocarbons) [2]. The overall activity is promoted by alkali metal additives [3], and the high methanol selectivity has been related to the presence of incompletely reduced palladium (Pd^{n+}) [7]. Driessen *et al.* [7] proposed a mechanism in which Pd° is seen to activate the hydrogen, while Pd^{n+} provides a coordination site for the oxygen-containing intermediate (presumably formyl) species.

The above correlation, and alike, has motivated a number of characterization studies of the synthesis and properties of supported Pd [8, 12]. A few of these studies conducted fundamental research tackling the preparation variables and routes [12].

However, most of these studies were focused on the alumina-supported catalyst [8–10, and references therein]. Therefore, the present investigation is concerned with the silica-supported catalyst. It was designed to explore the interactions involved in the course of genesis of a 5wt% Pd/SiO_2 catalyst from a parent system consisting of H_2/$PdCl_2$/SiO_2.

Experimental

Materials

Silica Aerosil-200 ($S_{BET}=200\ m^2 \cdot g^{-1}$; $V_p=1.3\ ml \cdot g^{-1}$) of DEGUSSA (Germany) and 99.9% pure $PdCl_2$ of Johnson-Matthey Chemicals Ltd (UK) were the support and the metal precursor compound employed, respectively. $PdCl_2$ dissolved in HCl-acidified aqueous medium ($pH=1.12$) was impregnated onto the support ($pH_{zpc}=1$–2 [13, 14]; pH_{zpc} denotes the pH value at which the surface is zero-charged [14]) to provide 5wt% Pd. The impregnation was carried out by adopting the incipient wetness technique [15]. The resulting paste was dried at 110°C for 17 h in air. The material (denoted Pd/Si(D)) was then either reduced in H_2 (Pd/Si(R)) or subjected to calcination (Pd/Si(C)) prior to the reduction (Pd/Si(CR)). The calcination was conducted at 300°C for 17 h in a still atmosphere of air, whereas the reduction was performed by heating at 10 $deg \cdot min^{-1}$ up to 300°C (for 2 h) in a dynamic atmosphere of H_2 (40 $ml \cdot min^{-1}$).

Gases of H_2 (99.9% pure), N_2 (99.5% pure) and compressed air were products of the Egyptian Company for Industrial Gases (Helwan/Cairo). The H_2 and

N_2 were further dried and purified, prior to application, by passing them through appropriate molecular sieve and Oxisorb traps. The HCl was an AR-grade product of El-Nasr Pharmaceutical Chemicals Co. (Egypt).

Thermogravimetry

TG analysis was carried out on heating at 10 deg·min^{-1} up to 900°C in a dynamic atmosphere (40 ml·min^{-1}), using a model 30 H automatically recording Shimadzu analyzer (Japan). Typically, a 10–15 mg portion of test sample was used. The change in mass was measured at a sensitivity of ±0.1 mg.

X-ray diffractometry

XRD was performed on a model JSX-60 JEOL powder diffractometer (Japan) equipped with Ni-filtered CuK_α radiation (λ=1.5418 Å). The generator was operated at 40 kV and 30 mA, and the diffractometer was run with 1° diverging and receiving slits. The diffractograms were recorded in steps of 0.02°·sec^{-1} at ambient temperature and in the 2θ range between 5° and 80°. Test samples were packed into shallow-welled holders and mounted in a horizontal position.

A semiquantitative determination of the average size of the metal crystallites in the Pd/Si(R) and Pd/Si(CR) of the catalyst was conducted by means of the X-ray line-broadening technique [16]. Accordingly, the size could be estimated by using the simple Sherrer equation: $2r = [K\lambda]/[\beta_{1/2} \cos \theta]$; where, r is the average crystallite diameter (nm), K is the Sherrer constant (0.9) in radians, $\beta_{1/2}$ is the corrected line width at half maximum, θ is the angle of incidence, and λ is the radiation wavelength (=0.15418 nm). This equation is approximately valid when applied to particles having a size between 4 and 100 nm [16].

UV/Vis diffuse reflectance spectroscopy

DR spectra were recorded over the wavelength range from 900 to 200 nm on a model UV-2100 double-beam Shimadzu UV/Vis spectrophotometer (Japan) equipped with a diffuse reflectance attachment. Specpure $BaSO_4$ (Shimadzu Corp.) was the reference used. The DR spectra were not used for quantitative measurements; therefore, they are not represented in units of the Kubelka-Munk function [17].

Results and discussion

Thermal behaviour

(A) Unsupported $PdCl_2$ in various atmospheres

The high-temperature behaviour of unsupported $PdCl_2$ in oxidative (air), non-oxidative (N_2) and reductive (H_2) atmospheres was monitored via the TG curves compared in Fig. 1. In air, the material suffers a total weight loss (*WL*) of ca. 42% in two steps: I, ca. 30% at 600–800°C, T_{max}=700°C; and II, ca. 12% at 800–900°C, T_{max}=850°C. Step I accounts for the conversion of $PdCl_2$ into PdO (calc. *WL*=31%), whereas step II monitors the dissociation of PdO and formation of a solid residue of Pd° (calc. *WL*=13%). Reportedly [18], PdO is stable in air up to 800°C, and dissociates detectably to the elements at 870°C.

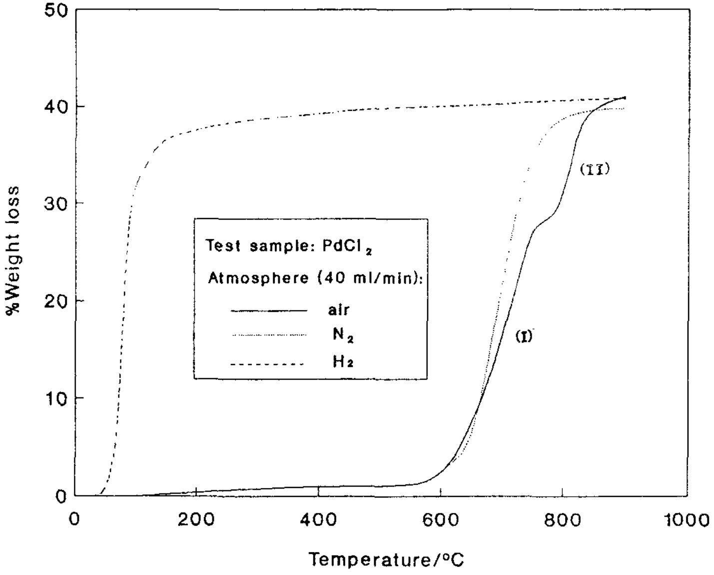

Fig. 1 Thermogravimetry curves for unsupported $PdCl_2$, measured on heating at 10 deg·min^{-1} and at a flow rate of 40 ml·min^{-1} of the various atmospheres indicated

In N_2, the material experiences a total *WL* of ca. 40% in a single step at 600–800°C (Fig. 1). Thus, $PdCl_2$ decomposes directly to its elements (Pd° and Cl_2), without formation of an intermediate oxide species (calc. *WL*=40%). The absence of oxide intermediates may be attributed, therefore, to the absence of oxygen in the reaction atmosphere.

In H_2, however, the decomposition is very much enhanced, to commence near 50°C (Fig. 1). The total *WL* determined at 900°C is 42%. Most of this loss

(35%) is achieved in an early very rapid step, at 50–110°C. The remainder (7%) follows in a subsequent, but much slower step at 110–900°C. Thus, the reductive impact of H_2 drastically destabilizes the otherwise stable (up to 550°C, in air) $PdCl_2$, and leads to the formation of Pd^0 at a temperature as low as 110°C. This was confirmed by a preliminary XRD examination.

(B) Pd/Si(D) in air and hydrogen

TG curves obtained for Pd/Si(D) in air and H_2 are compared in Fig. 2, along with that exhibited by unloaded SiO_2 in air. The TG curve of SiO_2 determines a total *WL* of 5.5% at 900°C. Most of this loss (5%) is effected at 350°C via two different dehydration mechanisms [19]: (i) elimination of physisorbed water molecules (2% at < 200°C), and (ii) condensation of surface hydroxyl groups (3.5% at >200°C). The total *WL* occurring at the expense of surface hydroxyls (3.5%) is very close to that (3.1%) determined previously for a similar sample of silica [19]. According to Fouad *et al.* [19], a 3.5% *WL* corresponds to a surface-OH content of ca. 2.1 mmoles OH/g SiO_2, and consequently to a population of 6.2 OH/nm^2. This result is very close to a result (6 OH/nm^2) reported elsewhere [20].

When measured similarly in air, the TG curve of Pd/Si(D) displays significantly different behaviour from that of SiO_2 (Fig. 2). The difference lies mainly in a considerable decrease in the *WL* due to the condensation of silica surface-OH groups at 200°C (from ca. 3% for SiO_2 to ca. 0.5% for Pd/Si(D)). It may

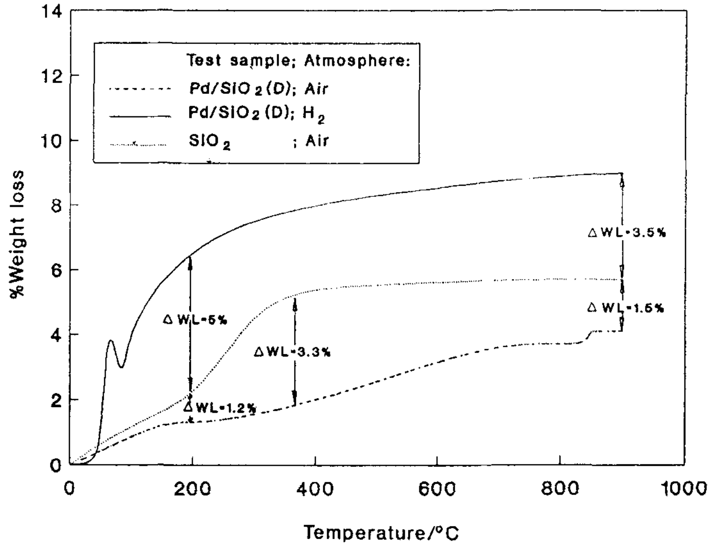

Fig. 2 Thermogravimetry curves for Pd/Si(D) and the silica support, measured on heating at 10 deg·min^{-1} and at a flow rate of 40 ml·min^{-1} of the different atmosphere indicated

be associated with indications of a possible enhancement in the commencement of the $PdCl_2 \rightarrow PdO$ conversion on silica, viz. from 600°C for unsupported $PdCl_2$ (Fig. 1) to ca. 400°C for $PdCl_2/SiO_2$ (Fig. 2). The production of PdO in Pd/Si(D) can be well monitored via the minute (0.34%), but distinct *WL* step at 850°C (Fig. 2). The accompanying *WL* (0.34%) corresponds to 3.8wt% Pd, which is in good agreement with that anticipated (5wt% Pd). The decrease in the dehydroxylation *WL* (ca. 3.3%) at 350°C may suggest that, during the preparation of Pd/Si(D) by drying of $PdCl_2/SiO_2$ at 110°C (17 h), a major proportion (70–80%) of the surface hydroxyls has been used up. This may be considered a consequence of formation of Pd^{n+}-surface complexes.

In H_2, Pd/Si(D) is shown (Fig. 2) to commence losing weight near 50°C, i.e. similarly to unsupported $PdCl_2$ (Fig. 1). It concedes a total *WL* of 9% at 900°C, which is achieved in an initial steep step (ca. 7% at 200°C) and a subsequent slow step (ca. 2% at>200°C). Thus, the initial step, which is intersected by a minute weight gain near 100°C, causes a larger *WL* (ca. 7%) than those (2%) exhibited by SiO_2 and Pd/Si(D) at 200°C in air. Compatibly, it must involve the hydrogen-enhanced decomposition of $PdCl_2$ into Pd^o metal. The weight gain near 100°C is associated accordingly with the tendency of metallic Pd^o to absorb H_2 [5].

However, a comparison of the thermal behaviours of unsupported (Fig. 1) and supported $PdCl_2$ (Fig. 2) at 200°C in H_2 reveals the following effects of the support: (i) a slight retardation of the kinetics of reduction to Pd^o on silica (compare the steepness of the respective *WL* steps), and (ii) a better dispersion of the supported metal particles thus formed. The latter effect may be implied by the weight gain (hydrogen absorption) observed only on Pd/Si(D). The higher *WL* exhibited by Pd/Si(D) in H_2 than in air, over the whole range of temperature examined, can be related to the elimination of the absorbed hydrogen and volatile reduction products. It has been established that Pd/SiO_2 has a strong tendency toward hydrogen retention [5]. Hydrogen is retained not only by the metal particles (absorption and adsorption), but also by the support (formation of O–H and Si–H bonds near 300°C) [5]. The hydrogen retention by silica is enhanced by precedent dissociation of H_2 molecules on metallic surfaces and migration of the atoms onto the support [21].

(C) Pd/Si(C) and Pd/Si(R) in hydrogen

TG results in H_2 for the supported $PdCl_2$ samples produced following drying at 110°C (Pd/Si(D)), calcination at 300°C (Pd/Si(C)) and reduction at 300°C (Pd/Si(R)) are compared in Fig. 3. The comparison discloses that the *WL* determined at a given temperature decreases in the following sequence: Pd/Si(D) > Pd/Si(C) > Pd/Si(R). The minimal *WL* (2.2%) exhibited at 200°C (to 900°C) by Pd/Si(R) is very close to that (2%) due to the elimination of physisorbed water from the support (Fig. 2). Thus, the ex-situ reduction of the material was rather complete and the exposure to air during the TG sampling seems to cause insignificant re-oxidation of the metal particles at room temperature [5].

On the other hand, the decrease in *WL* at 200°C on going from Pd/Si(D) (7%) to Pd/Si(C) (4.5%) indicates that the calcination of supported $PdCl_2$ results in a weight-variant chemical change. This is associated most probably with the exchange of Cl for oxygen ligands. In other words, the precursor is converted into Pd(O)Cl and/or PdO_x species, which should lead, on reduction, to lesser weight losses than for $PdCl_x$ species. Moreover, the results (Fig. 3) may suggest that the support markedly reduces the thermal stability of $PdCl_2$ in air (Fig. 1). Thus, the oxidation of $PdCl_2/SiO_2$ could take place, completely or partially, at 300°C instead of 600°C for the unsupported precursor (Fig. 1).

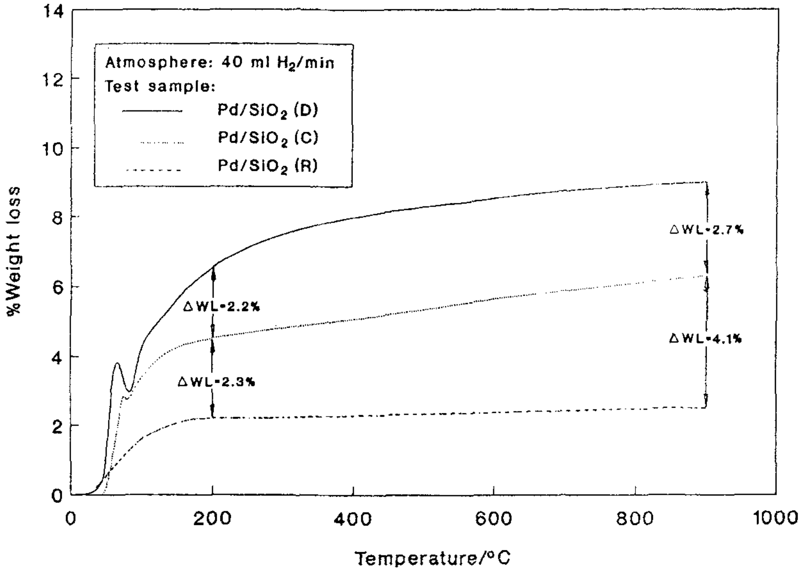

Fig. 3 Thermogravimetry curves measured on heating at 10 deg·min^{-1} in H_2 flowing at a rate of 40 ml·min^{-1} for the variously treated samples of $PdCl_2$-impregnated silica indicated

The comparison in Fig. 3 also reveals that the reduction of Pd(O)Cl and PdO_x species is kinetically slightly slower than the reduction of $PdCl_x$ species. This can be realized from the varied steepness of the initial *WL* steps for Pd/Si(D) and Pd/Si(C). It may explain why the hydrogen retention, which is monitored by a weight gain near 100°C, is more obvious for Pd/Si(D) than for Pd/Si(C).

X-ray diffraction patterns

XRD powder diffractograms of Pd/Si(D), Pd/Si(R), Pd/Si(C) and Pd/Si(CR) are shown in Fig. 4. The diffractogram (a) Pd/Si(D) displays, in addition to the broad peak of the largely non-crystalline silica component [19], tiny peaks due to $PdCl_2$ particles. Accordingly, a part of the precursor loading, at least, aggregates on drying into three-dimensional formations of $PdCl_2$ on the support. A similar conclusion was reached previously [5, 12]; it was attributed to weak interactions at the $PdCl_2/SiO_2$ interfaces. Upon hydrogen-reduction at 300°C (2 h), the weak peaks of $PdCl_2$ are replaced by strong peaks assignable to Pd^0 metal particles (average size=14 nm) (pattern b, Fig. 4). No other crystalline phases were detected. This result is consistent with TG results (Fig. 2), in showing $PdCl_2$ to be completely reduced on silica near 300°C.

The pattern of Pd/Si(C) (c, Fig. 4) shows only an ill-defined peak that might be due to traces of $PdCl_2$ crystallites. Hence, the calcination of Pd/Si(D) at 300°C for 17 h converts $PdCl_2$ into a highly-dispersed phase. In view of the conclusions drawn from the TG results (Figs 1 and 3), the calcination product may contain Pd(O)Cl and/or PdO_x surface species. It is possible therefore, that the genesis of oxide species facilitates the dispersion of metal compounds, by lowering the interfacial tension with the support [22].

The hydrogen-reduction of Pd/Si(C) at 300°C for 2 h results in the formation of Pd/Si(CR), which shows a diffraction pattern (d, Fig. 4) monitoring the for-

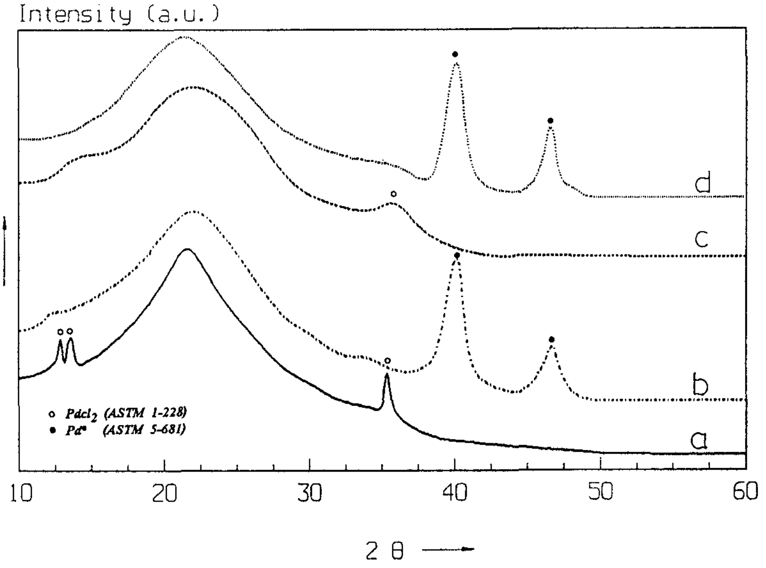

Fig. 4 X-ray powder diffractograms (CuK_α radiation) of (a) Pd/Si(D), (b) Pd/Si(R), (c) Pd/Si(C), and (d) Pd/Si(CR)

mation of finer Pd° metal particles (average size = 8 nm) than those observed in Pd/Si(R). This may stress the likelihood that the pre-calcination step improves the dispersion of the precursor and, consequently, the metal particles in the reduction product (i.e. the catalyst). It is worth mentioning that no surface Pd–Si compounds, such as Pd_xSi_y [5], were XRD-detected in either Pd/Si(R) or Pd/Si(CR). Pd_xSi_y surface compounds, which have been claimed to be responsible for a critical modification of the catalyst hydrogenation activity [5], were observed only after hydrogen-reduction at 600°C.

Optical diffuse reflectance spectra

(A) Impregnating solution

Day *et al.* [23] have shown that the DR spectra exhibited by $PdCl_x$ compounds in the solid state and in solution are quite similar. Therefore, DR spectra were taken of aqueous HCl solutions of $PdCl_2$ as a function of *pH* (= 1–3). The results showed that the present impregnating solution (*pH* = 1.12) gave rise to two *d–d* transition bands at 605 and 480 nm, and three charge-transfer (CT) bands at 200–350 nm. Similar *d–d* bands at 606 and 474 nm were assigned [24], respectively, to $\{d^*(x^2-y^2) \leftarrow d^*xy\}$ and $\{d^*(x^2-y^2) \leftarrow d^*xz, d^*(x^2-y^2) \leftarrow d^*yz, d^*(x^2-y^2) \leftarrow d^*z^2\}$ of $PdCl_4^{2-}$ species. The *d–d* bands suffered low-wavelength (blue) shifts with *pH* increase, e.g. down to 580 and 430 nm, respectively, at *pH* 3. Similar behaviour was observed previously [24], and explained on the basis of a composition change from $PdCl_4^{2-}$ to $Pd(H_2O)Cl_3^-$. A further lowering in the Cl^- content, namely to $Pd(H_2O)_2Cl_2$, $Pd(H_2O)_3Cl^+$ and $Pd(H_2O)_4^{2+}$, was found [24] to be mirrored by the following blue shifts of the two *d–d* bands: to 571 and 420 nm, 555 and 407 nm, and 538 and 379 nm, respectively. This general trend has been attributed [12] to a parallel increase in the metal *d*-orbital splitting [24], as the Cl^- is substituted by H_2O (or other oxygen-containing) ligands.

(B) Impregnated silicas

Figure 5 exhibits DR spectra of Pd/Si(D), Pd/Si(R), Pd/Si(CR), and insets a spectrum of solid-phase $PdCl_2$. The latter spectrum (a) displays two broad *d–d* bands centred at around 570 and 435 nm, along with two CT bands at 285 and 350 nm. The *d–d* bands are similar to those shown at 571 and 420 nm by $Pd(H_2O)_2Cl_2$ in solution [24]. The spectrum (b, Fig. 5) of Pd/Si(D) also displays two *d–d* bands, but at significantly lower wavelengths (520 and 380 nm) than those exhibited by unsupported $PdCl_2$ (at 570 and 435 nm, respectively). However, the spectrum (b) may still be seen to receive contributions from the latter $PdCl_2$ bands. The existence of $PdCl_2$ particles in Pd/Si(D) is XRD-verified (Fig. 4). According to Elding *et al.* [24], the blue shifts experienced by the *d–d* bands may account for the formation of $Pd(H_2O))_4^{2+}$ species, or $Si–O–Pd^{n+}$ species.

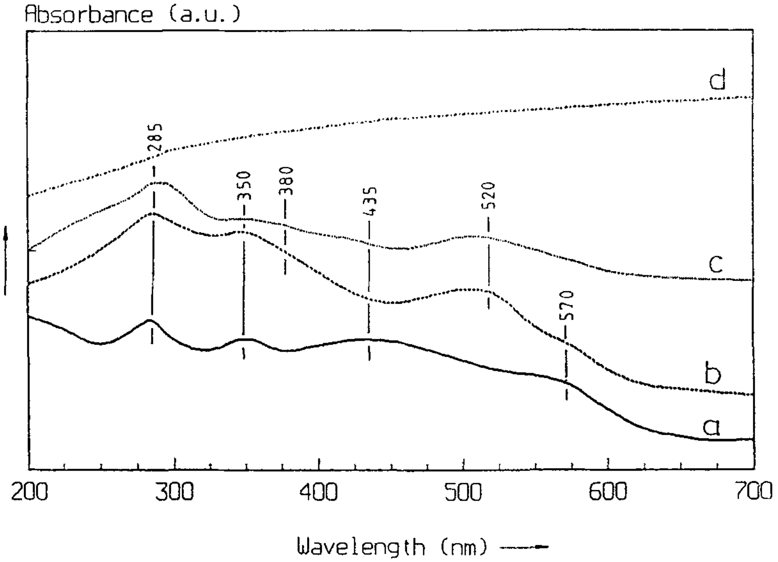

Fig. 5 UV/Vis diffuse reflectance spectra ($BaSO_4$-referenced) of (a) unsupported $PdCl_2$, (b) Pd/Si(D), (c) Pd/Si(C), (d) Pd/Si(R) and Pd/Si(CR)

On the support surface, oxygen-containing groups (Si–OH and $Si–O^-$) [25] could also contribute to the inner coordination sphere of Pd^{n+}. The resulting species may still be electrically neutralized, fully or partially, by Cl^- ligands. It has been reported [24] that the square planar ($Pd(H_2O)_2Cl_2$) and octahedral ($Pd(H_2O)_4Cl_2$) geometries of palladium complexes are equally favourable energetically.

Bozon-Verduraz *et al.* [4] have also interpreted DR spectra as being indicative of the conversion of $PdCl_4^{2-}$ into $Pd(H_2O)_4^{2+}$ upon impregnation onto silica. These authors have even attributed [4] the facile reduction of Pd^{2+} on silica, as compared with the difficult one on alumina, to the formation of labile (aquo) complexes. As a matter of fact, the $PdCl_4^{2-}$ precursor species are weakly adsorbed on silica surfaces, due to the irreactive surface-OH groups of the support ($pK_a = 9$) [26]. Another reason is the impregnation routine (incipient wetness) adopted, since it does not facilitate the occurrence of adsorptive interactions in the real sense [15].

Silanol groups (Si–OH) are weak acids that are not deprotonated detectably unless the surrounding *pH* exceeds 6 [13]. Thus, ion-exchange interactions with

Si–OH are practically impossible at the *pH* of the present impregnating solution (pH=1.12). The *pH* value is comparable to the pH_{zpc} (=1–2) [14] of the support. Under these conditions, the surface of silica is either zero-charged or slightly positively-charged. Accordingly, a minor proportion of the Si–OH groups would then be protonated to Si–OH_2^+. Hence, the dominant adsorptive interactions at the $PdCl_4^{2-}/SiO_2$ aqueous interfaces, if any, would be electrostatic in nature. This type of interaction would lead to the formation of weakly bound $\{SiOH_n^{(n-1)+}PdCl_m^{(m-2)-}\}$ species [8] during the impregnation.

Upon drying at 110°C, $PdCl_2$ deposits (see XRD of Pd/Si(D) in Fig. 4) and subsequently interacts with support surface groups (most probably with Si–OH groups) to form the DRS-anticipated Si–O–Pd^{n+} species (Fig. 5). Leaving chlorides are presumably eliminated as HCl, a likely reaction product with surface-OH groups [5]. Hence, the TG-detected low surface-OH content of Pd/Si(D) (Fig. 2), as compared with SiO_2, is explicable.

The fact that Pd/Si(C) exhibits a largely similar DR spectrum (c, Fig. 5) to that of Pd/Si(D) may indicate that calcination of the latter material at 300°C for 17 h does not detectably alter the nature of the Pd-surface complexes. This might confirm that the close proximity of Pd^{2+} in Pd/Si(D) is indeed dominated by oxygen-containing species.

TG analysis consistently suggests the conversion of Pd in Pd/Si(D) into PdO_x species (Fig. 2) on high-temperature calcination.

Upon reduction in H_2 at 300°C, the materials thus produced, viz. Pd/Si(R) and Pd/Si(CR), gave rise to the same spectrum (d, Fig. 5). It is void of any bands assignable to Si–O–Pd^{n+} species. It displays, instead, a featureless continuous absorption over the wavelength range examined. This must be related to the XRD-detected reduction of the Pd^{n+}-surface species into Pd^o metal particles (Fig. 4), since the material was rendered too dark in colour to reflect much radiation.

Conclusions

The following conclusions can be drawn from the results presented and discussed above:

(1) Palladium precursor species ($PdCl_4^{2-}$) are weakly adsorbed during the impregnation of silica (pH_{zpc}=1–2) with an acidified solution of $PdCl_2$ (pH= 1.12), the incipient wetness technique being adopted.

(2) Upon drying at 110°C for 17 h in air, $PdCl_2$ is deposited and converted partially into Si–O–Pd^{n+} surface complexes. Cl^- ligands are eliminated, most probably through reactions with the support surface-OH groups.

(3) Heating in H_2 at 300°C for 2 h results in reduction of the Si–O–Pd^{n+} species and the $PdCl_2$ crystallites into Pd^0 metal particles. The metal particle dispersion is improved when the reduction step is preceded by calcination of the dried material at 300°C for 17 h.

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Zusammenfassung — Durch Erhitzung von $PdCl_2$-imprägniertem SiO_2 in H_2 bei 300°C für die Dauer von 2 Stunden wurde ein 5 Gew.%-iger Pd/SiO_2-Katalysator synthetisiert. Man fand, daß die Verteilung der Metallpartikel verbessert wird, wenn der Reduktionsschritt über eine Kalzinierung bei 300°C für die Dauer von 2 Stunden durchgeführt wird. Die Thermogravimetrie des imprägnierten Trägers in Luft, Stickstoff- und Wasserstoffatmosphären wurde verwendet, um die bei den verschiedenen präparativen Schritten (z.B. Trocknen, Kalzinierung und Reduktion) vorkommenden Wechselwirkungen zu verfolgen. Das Feststoffprodukt eines jeden präparativen Schrittes wurde mittels Röntgendiffraktometrie und UV/Vis Diffusreflektanzspektroskopie charakterisiert. Die Ergebnisse zeigen, daß das Palladium im Anschluß an den Trocknungsschritt *(bei 110°C in Luft) in zwei detektierbaren Formen vorliegt: $PdCl_2$-Partikel und* $Si–O–Pd^{n+}$ Oberflächenspezies. Die Kalzinierung scheint die $PdCl_2$-Partikel in die letzteren $Si–O–Pd^{n+}$ Oberflächenspezies umzuwandeln. Die Wasserstoffreduktion wandelt die Oberflächenspezies eventuell in fein dispersierte Pd Metallpartikel um (mittlere Größe=8–14 nm). Keine anderen Reduktionsprodukte, wie z.B. Pd_ySi_x konnten beobachtet werden.