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The preparation of silica supported Pd catalysts: the effect of pretreatment variables on particle size

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The effect of pretreatment on the dispersion of Pd catalysts supported on silica has been studied. The catalysts were prepared from $[Pd(NH_3)_4](NO_3)_2$ as the metal precursor at a pH = 9. The resulting catalysts were characterized using both CO and H_2 chemisorption, transmission electron microscopy, and in-situ UV reflectance spectroscopy. Pretreatment in H_2 resulted in poor Pd dispersions while pretreatment in He or Ar resulted in very high dispersions. Pretreatment in O_2 resulted in moderate dispersions. The results are explained by considering the chemical structure of the adsorbed surface complex under different pretreatment conditions. The chemistry of the decomposition process is considered in detail.

Keywords: Silica supported Pd catalyst; catalyst particle size; CO chemisorption; H_2 chemisorption; Pd dispersion; transmission electron microscopy; *in-situ* UV reflectance spectroscopy

1. Introduction

In the study of catalytic reactions it is often useful to study the effect of metal particle size on the reactivity of supported catalysts. In order to do this it is necessary to control metal particle sizes systematically. Such techniques as high temperature sintering in air or variations in metal loading will, of course accomplish this. However, they may also induce undesirable changes in catalytic properties which may, in some cases, be irreversible. Additionally, it is desirable to compare the activities of catalysts which have similar metal loadings but different particle sizes.

The two methods commonly used in the preparation of supported metal catalysts are impregnation and ion exchange. The difference between the two is sometimes not well understood. For an excellent overview of the two methods, reference is made to paper published by Doorling et al. [1]. In general, the preparation of supported metal catalysts by ion exchange involve strong metal-

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support interactions. Weakly adsorbed metal complexes are usually removed by washing the adsorbed phase with deionized water. Because the adsorbed complexes are strongly bound to the support through coulombic interactions, catalysts prepared by this method are usually highly dispersed [2]. The preparation of supported catalysts by impregnation methods, on the other hand, generally result in catalysts which have lower dispersions [3]. In this method of preparation the interaction between the metal precursor and the support is weak. Because of these weak interactions, the morphology of the resulting catalyst is often guided by pore size distributions [1].

The dispersion of metal catalysts on oxide supports is strongly dependent on preparative methods. Important variables to be considered in controlling metal particle size are the effect of pH [3,4], the nature of the metal-support interaction [5,6], the effect of catalyst pretreatment [5], the morphology of the support [1] and the identity of the metal precursor used [5–8]. Careful attention should also be focussed on the effect of contaminating anions such as chlorine [9,10] and the sensitivity of adsorbed metal complexes to the presence of oxygen [5]. Recently Schwarz et al. [11], have observed that trace amounts of sulfur may have a profound effect on metal dispersions.

The surface chemistry which takes place under pretreatment conditions has not received much attention in the literature. Recently we have studied the decomposition of Pt and Ru amine precursors in different atmospheres [5,12]. Of particular interest is the formation of weakly bound surface intermediates which have a high surface mobility [5]. This enhanced surface mobility may lead to the agglomeration of surface complexes which, on decomposition, may result in the formation of poorly dispersed metal particles. The synthesis of supported bimetallic clusters is influenced to a large extent by surface complex mobilities. For example, supported Pt-Ru bimetallic clusters prepared using chloride precursors show a strong surface enrichment in Pt [3]. When amine precursors, which interact strongly with silica are used, the surface enrichment in Pt is quite modest [7]. The use of ruthenocene (bis-cyclopentadienyl) as the Ru precursor results in preferential surface enrichment in Ru [8].

In this study we consider the pretreatment variables which affect the chemistry associated with the preparation of silica supported Pd catalysts using $[Pd(NH_3)_4](NO_3)_2$ as the metal precursor. Our goal will be to understand the chemistry which defines the morphology of the resulting supported Pd catalysts.

2. Experimental

CATALYST PREPARATION

The metal precursor used in this study was $[Pd(NH_3)_4](NO_3)_2$ (Strem Chemicals, Newburyport, MA). The support (Cab-O-Sil, M-5, surface area 200 m^2/g, average pore size 14 nm, Cabot Corp. Champaign, IL) was washed with a dilute solution of 0.1 N HNO_3 to remove traces of alkali metal ions which might have been present on the support. After washing with deionized water, the acid treated Cab-O-Sil was dried in a vacuum desiccator. The silica slurry was prepared by adding the appropriate amount of deionized water to the powder of the acid treated silica under continuous stirring. The pH of the solution which contained the silica was increased to 9.0 through the dropwise addition of NH_4OH. This pH is higher than that corresponding to the isoelectric point of silica [3,7,8] but lower than that which corresponds to the dissolution point of silica (~ 10) [13,14]. Under these conditions the metal support interaction is maximized due to the strong interaction between the cationic ion precursor in solution and the negative charge generated on the support [4]. The total metal loading was maintained constant at 0.3 mmoles of total metal/g of support. The precursors were dissolved in approximately 15 ml of deionized water and then added to the silica slurry. The pH was readjusted to 9.0 and the slurry was covered and stirred for 12 h. The resulting catalyst slurry was filtered and washed with approximately 50 ml of deionized water to remove the weakly adsorbed precursors in addition to chlorides which interfere with the adsorption of CO and H_2 [9,10]. Following drying and washing with deionized water, the actual metal loading was determined by ICP (Tulane University Analytical Laboratories). The samples were dried in a vacuum desiccator and either stored or pretreated for future studies.

PRETREATMENT

Following drying and prior to a chemisorption experiment, the samples were heated to the desired pretreatment/reduction temperature at a heating rate of 10°C/min. The temperature ramp was controlled by a temperature programmer. Tylan electronic flow controllers were used to control the flow rate of all gases at 30 ml/min. Either Ar or He was used to cool the microreactor which contained the sample. The three different pretreatments used in this study are outlined in fig. 1 and are self explanatory. Deviations from the procedure outlined in fig. 1 were followed when the catalysts were treated in O_2 at different temperatures prior to reduction in H_2 at 400°C.

GAS PURIFICATION

Because trace amounts of oxygen in the ppm range may have a marked effect on catalyst morphology at high temperatures, a special effort was made to exclude O_2 from the He, Ar and H_2 gas streams.

The gases used in this study were purchased from the Lincoln Big Three Co. (Baton Rouge, LA.). Argon, helium, oxygen and hydrogen were Ultra High Purity (UHP) grade (99.999% purity). The carbon monoxide was CP grade with

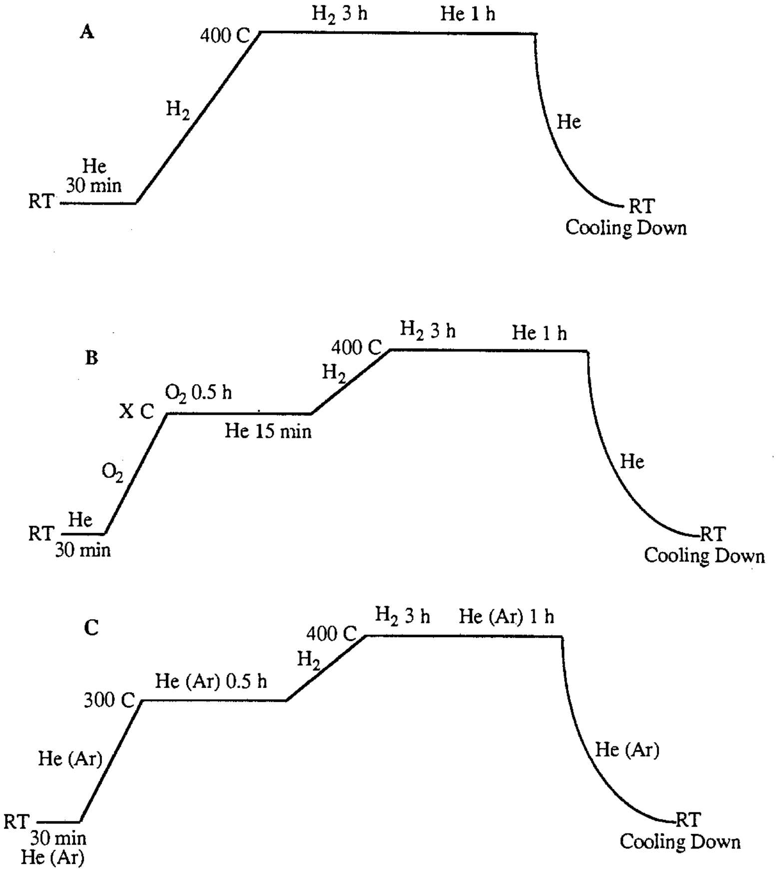


Fig. 1. Diagram of the three different pretreatments: (A) decomposition in H_2; (B) decomposition in O_2 and; (C) decomposition in He or Ar.

a specified purity of 99.0%.

All gases were passed through traps filled with molecular sieves (1/16″ pellets, Linde 13X) to remove moisture. These traps were kept at a temperature of 200 K by means of a dry ice/acetone bath. The helium and argon carrier gases were passed through a High Gas Purifier manufactured by Supelco, Inc. Downstream from the purifier, an additional indicating purifier (OMI-1, Supelco, Inc.) containing a resin and a water reactive solid lithium compound, was installed in order to decrease the oxygen and water content of the carrier gas to less than 10 ppb.

CHEMISORPTION MEASUREMENTS

A 150 to 250 mg sample was placed in a pyrex microreactor and subjected to the standard pretreatment as specified in figure 1. Chemisorption experiments were performed by the dynamic pulse method as described by Sarkany and Gonzalez [15]. Chemisorption experiments using CO were performed at room temperature. In order to reduce β hydride formation, chemisorption experiments using H_2 were performed at 60°C. Under these conditions both weakly chemisorbed and absorbed hydrogen are rapidly eluted from the surface [16,17]. Dispersions obtained using both CO and H_2 chemisorption were cross checked by transmission electron microscopy.

ELECTRON MICROSCOPY

A small portion of a 5 mg sample was suspended in ethanol. The beaker containing the ethanol suspension was placed in an ultra-sonic cleaner and sonicated for a period of one minute. A drop of this well mixed suspension was placed on a carbon coated 300 mesh copper grid. The specimen was placed in the sample holder of the microscope following drying under ambient conditions.

A Phillips EM 410 transmission electron microscope equipped with a LaB_6 crystal was used for this study. It had a maximum magnification of 500 K and a maximum accelerating voltage 100 keV. Two specimens were prepared for each sample and as many as 10 spots from different locations on the grid were imaged in the bright field mode.

IN-SITU DIFFUSE UV REFLECTANCE STUDIES

A UV-VIS spectrophotometer (Perkin Elmer, Lambda 5) was used for this study. The UV reactor system including an *in-situ* cell reactor designed by the Byron Lambert Co. (Franklin Park, IL) has been described in a previous report [3]. The reactor was made of stainless steel and had a gas inlet and outlet in addition to a throughput for inserting a thermocouple. A specially designed stand equipped with a copper block and a heating element could be used for *in-situ* heating up to 500°C. The integrating sphere was externally interfaced with the UV spectrophotometer through the use of fiber optic cables. The reactor was designed so that the integrating sphere could be directly attached to the quartz window of the reactor. A Perkin Elmer 3600 Data station was used to collect and process the data. For solution spectra, the instrument was used without the integrating sphere attachment.

3. Results

CHEMISORPTION MEASUREMENTS

Catalyst dispersions obtained by chemisorption using both CO and H_2 are shown in table 1. Also included in table 1 are dispersion results obtained by

Table 1
Dispersion measurements obtained using different pretreatments

Catalyst precursor	Pretreatment	D_{CO}(%)	D_{H_2}(%)	TEM[100/d(nm)]
$[Pd(NH_3)_4]^{2+}/SiO_2$	H_2 400°C	11	26	20
$[Pd(NH_3)_4]^{2+}/SiO_2$	O_2 100°C, H_2 400°C	40	44	37
$[Pd(NH_3)_4]^{2+}/SiO_2$	O_2 200°C, H_2 400°C	42	37	31
$[Pd(NH_3)_4]^{2+}/SiO_2$	O_2 300°C, H_2 400°C	37	38	24
$[Pd(NH_3)_4]^{2+}/SiO_2$	He (Ar) 300°C, H_2 400°C	67	71	70–80

TEM. The dispersion measurements obtained using CO and H_2 are in reasonable agreement with one another. The adsorption stoichiometries used in CO chemisorption measurements were similar to those used by Joyal and Butt [16,17]. For large Pd particles a stoichiometry corresponding to a CO/Pd(s) ratio of 0.5 was used. For highly dispersed particles a CO/Pd(s) of 0.79 was used, while for intermediate size particles a CO/Pd(s) ratio of 0.65 was found to be satisfactory. Because of the uncertainty in the CO/Pd(s) ratio, dispersion measurements were also cross checked using H_2 chemisorption and TEM.

From the results shown in table 1 it is clear that reduction in H_2 without pretreatment in O_2 leads to rather poor metal dispersions. In this respect the similarity to Pt/SiO_2 catalysts prepared using $[Pt(NH_3)_4](NO_3)_2$ as a precursor is quite striking [5]. Pretreatment in O_2 leads to a substantial improvement in dispersion. The temperature at which pretreatment in O_2 is performed does not appear to have a significant effect on the Pd dispersion. When the decomposition of the surface complex was carried out in the absence of O_2, a very highly dispersed Pd catalyst was obtained. There was no difference in dispersion when the decomposition was carried out in He rather than Ar.

The stability of the supported Pd catalysts prepared using different pretreatment conditions was checked by subsequently oxidizing the catalysts in a flow of O_2 at 300°C followed by re-reduction in H_2 at 400°C. This data, presented in table 2, shows that the catalysts are stable after the initial pretreatment followed by reduction in H_2.

The analysis of the resulting supported Pd catalysts by ICP show a substantial loss of Pd when the decomposition of the surface complex was performed in O_2 (0.94% Pd). Decomposition in H_2 resulted in Pd catalysts with a metal loading corresponding to 1.45% Pd while decomposition in He gave a metal loading of 1.27%. Because subsequent cycling of the reduced catalysts in O_2 at 300°C

Table 2
The stability of supported Pd catalysts following O_2-H_2 cycling

Catalyst	Pretreatment	D_{CO}(%)	Pretreatment	D_{CO}(%)
$[Pd(NH_3)_4]^{2+}/SiO_2$	H_2 400°C	16	O_2 300°C, H_2 400°C	17
$[Pd(NH_3)_4]^{2+}/SiO_2$	He (Ar) 300°C, H_2 400°C	67	O_2 300°C, H_2 400°C	68

followed by re-reduction in H_2 at 400°C resulted in no further loss of Pd, we conclude that the substantial loss in Pd observed when the decomposition was performed in oxygen arose during the decomposition of the surface complex. The Pd loss was not apparent when the decomposition of the surface complex was performed in either H_2 or Ar and must, therefore, be due to an interaction between gas phase oxygen and the surface complex.

TRANSMISSION ELECTRON MICROSCOPY

In order to verify the chemisorption results and to obtain particle size distributions, transmission electron micrographs were obtained for the different pretreatments used. The corresponding electron micrographs are shown in fig. 2(a–d). They confirm the results obtained by chemisorption. Reduction in H_2 without prior oxidation leads to poorly dispersed Pd particles (fig. 2a). Oxygen pretreatment above 100°C following reduction in H_2 improved the Pd dispersions (fig. 2b). Very high dispersions were obtained when the surface complex was decomposed in a rare gas environment and O_2 was excluded (fig. 2(c, d)). The corresponding particle size distributions are shown in fig. 3(a, b). For each pretreatment approximately one thousand particles were analyzed.

DIFFUSE UV REFLECTANCE STUDIES

In order to understand the results obtained using chemisorption and TEM, the chemical anchoring process was studied using diffuse UV reflectance spectroscopy. Particular attention was paid to the chemistry of the decomposition process under different pretreatment conditions. The UV spectrum of silica in an aqueous suspension at 25°C is shown in fig. 4A. The intense sharp band centered at 208 nm is in all probability due to excitons which are not able to migrate through the solid. An exciton bound to a defect is simply an alternative way of describing an excited electronic state of the defect [18]. The intensity of the 208 nm band was considerably smaller for the UV reflectance spectrum of the solid silica. It is rather unfortunate that this silica band centered at 208 nm coincides with the charge transfer band assigned to $NH_3 \rightarrow Pd^{2+}$ for the species $[Pd(NH_3)_4]^{2+}$.

The UV spectrum of $[Pd(NH_3)_4](NO_3)_2$ in aqueous solution at 25°C is shown in fig. 4B. The band centered at 220 nm is a charge transfer band and it is due to the $NH_3 \rightarrow Pd^{2+}$ transition. The band centered at 295 nm is a $d \rightarrow d$ transition characteristic of square planar complexes. The position of these bands is in good agreement with the assignments proposed by Mason and Gray [19].

The diffuse UV reflectance spectrum of $[Pd(NH_3)_4]^{2+}$ adsorbed on silica at a pH of 9 is shown in fig. 5(a–c). The spectrum of the freshly prepared sample shows that the position of the $d \rightarrow d$ transition is observed at 320 nm. The position of the CT band, which was observed for the complex in solution, is such

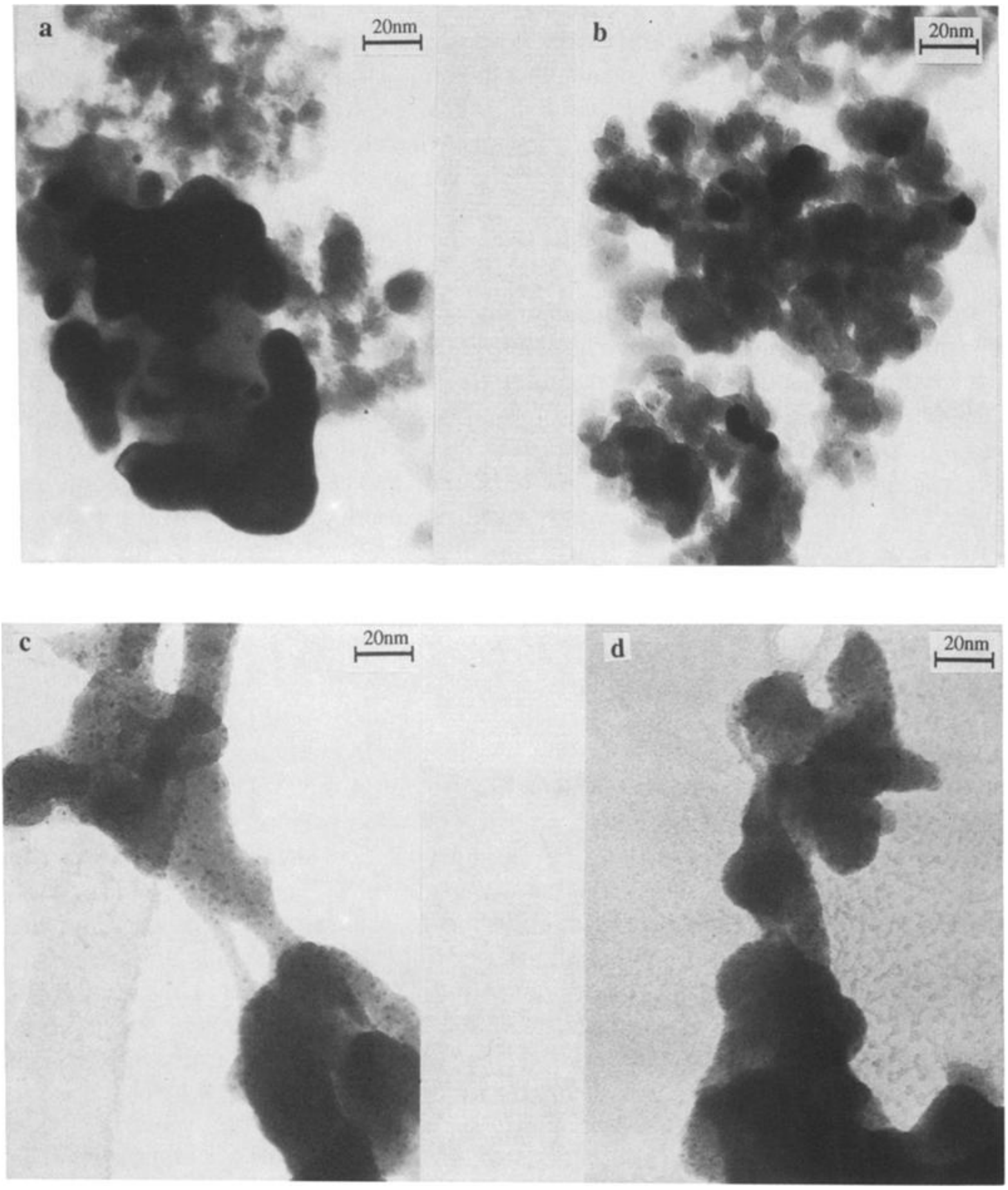


Fig. 2. Transmission electron micrographs of $[Pd(NH_3)_4]^{2+}/SiO_2$ using different pretreatments: (a) H_2 400°C; (b) O_2 100°C, H_2 400°C; (c) He (Ar) 300°C, H_2 40°C; (d) sample c oxidized in O_2 at 300°C following reduction in H_2 at 400°C.

that it is obscured by the strong silica absorption centered at 208 nm. The freshly prepared sample is colorless. However, on exposure to flowing O_2 at 60°C the color was observed to change to yellow (fig. 5a). When the temperature

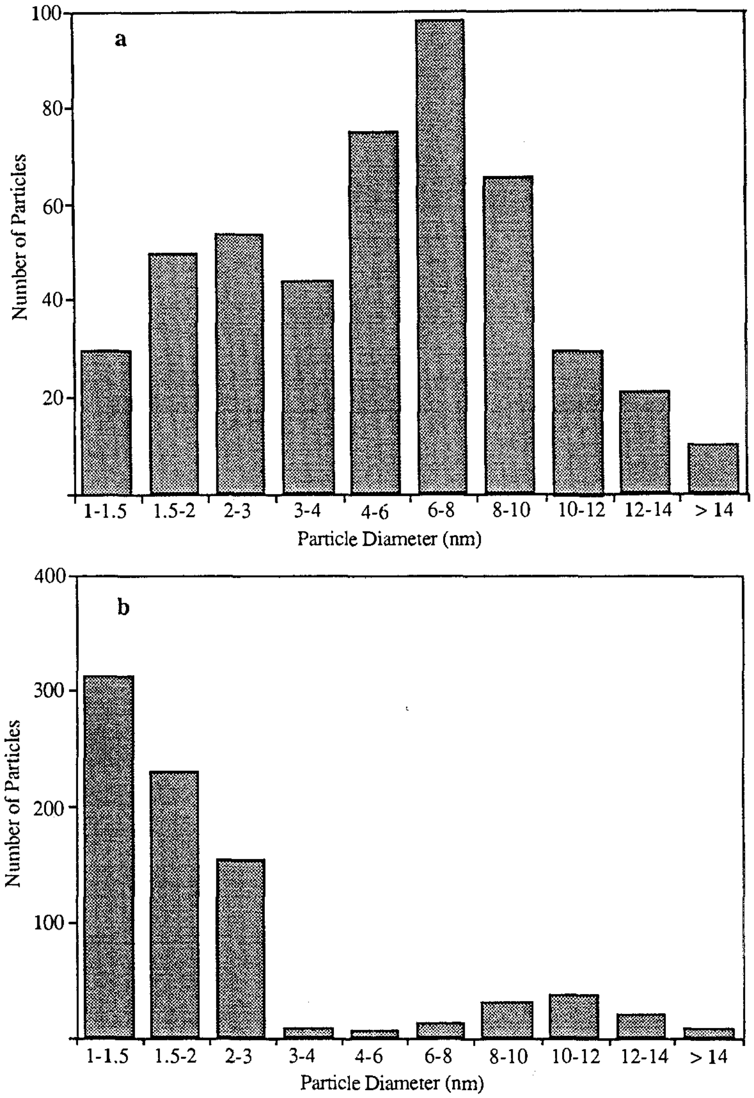


Fig. 3. Particle size distribution of $[Pd(NH_3)_4]^{2+}/SiO_2$ following pretreatments: (a) H_2 400°C; (b) O_2 100°C, H_2 400°C.

was increased in flowing O_2, the intensity of the band corresponding to the d → d transition decreased and its position was observed to shift to higher wavelength. The same effect was observed by Jørgensen [20] who studied the effect of the substitution of NH_3 ligands by H_2O. The position of the d → d transition reported by Jørgensen for $[Pd(NH_3)_4]^{2+}$ was 295 nm. For $[Pd(NH_3)_2(H_2O)_2]^{2+}$ it was 341 nm and for $[Pd(H_2O)_4]^{2+}$ it was 379 nm. For this reason we suggest that heating in O_2 results in the gradual loss of NH_s

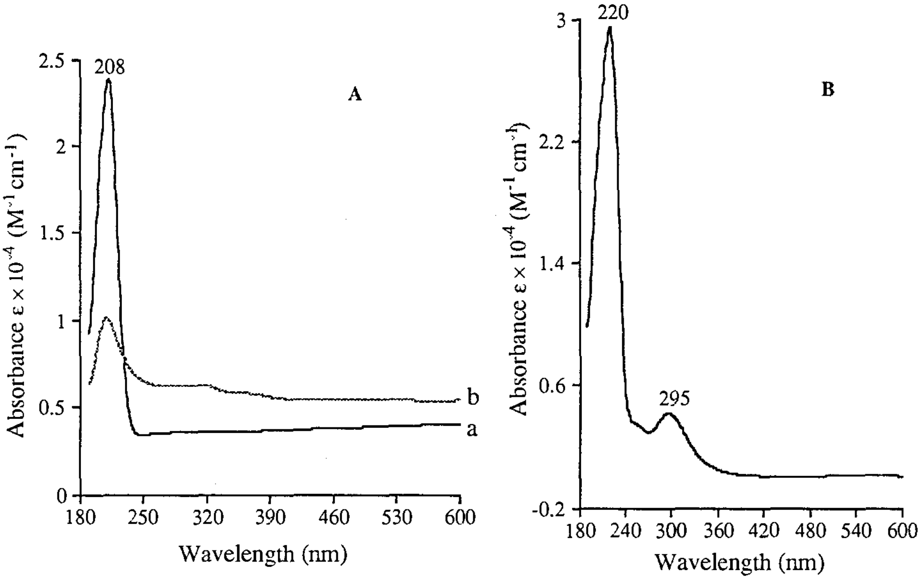


Fig. 4. (A) The UV spectrum of high-surface area silica: (a) in aqueous solution at 25°C; (b) solid in air at 25°C; (B) The UV spectrum of $[Pd(NH_3)_4](NO_3)_2$ in aqueous solution at 25°C.

ligands with a concomitant loss in the square planar symmetry of the adsorbed surface complex. Similar shifts in the position of the d → d transition are observed when the surface complex is heated in either He or Ar (fig. 5b). The appearance of a UV band centered at 245 nm is observed when the surface complex is heated in either O_2 or a noble gas environment. In fact, a comparison of the decomposition spectra shown in fig. 5(a, b) suggests the chemistry involved in the decomposition is the same regardless of the gas phase environment. We tentatively assign the UV band centered at 245 nm to a charge transfer transition between the oxygen on the support and Pd.

The UV spectrum obtained when the decomposition of the adsorbed $[Pd(NH_3)_4]^{2+}$ complex is performed in H_2 is shown in fig. 5c. For decomposition in H_2 the position of the d → d band centered at 320 nm was not observed to shift and the UV band centered at 245 nm was not observed. Reduction to metallic Pd appeared to be complete at a temperature of about 70°C. The UV band assignments of $[Pd(NH_3)_4]^{2+}$ are summarized in table 3.

4. Discussion

The appearance of an absorption band in the UV reflectance spectra upon treatment of the surface complex with oxygen suggests the formation of an intermediate surface complex which may involve oxygen. Because this band is centered at 245 nm it is, in all probability, due to a charge transfer transition.

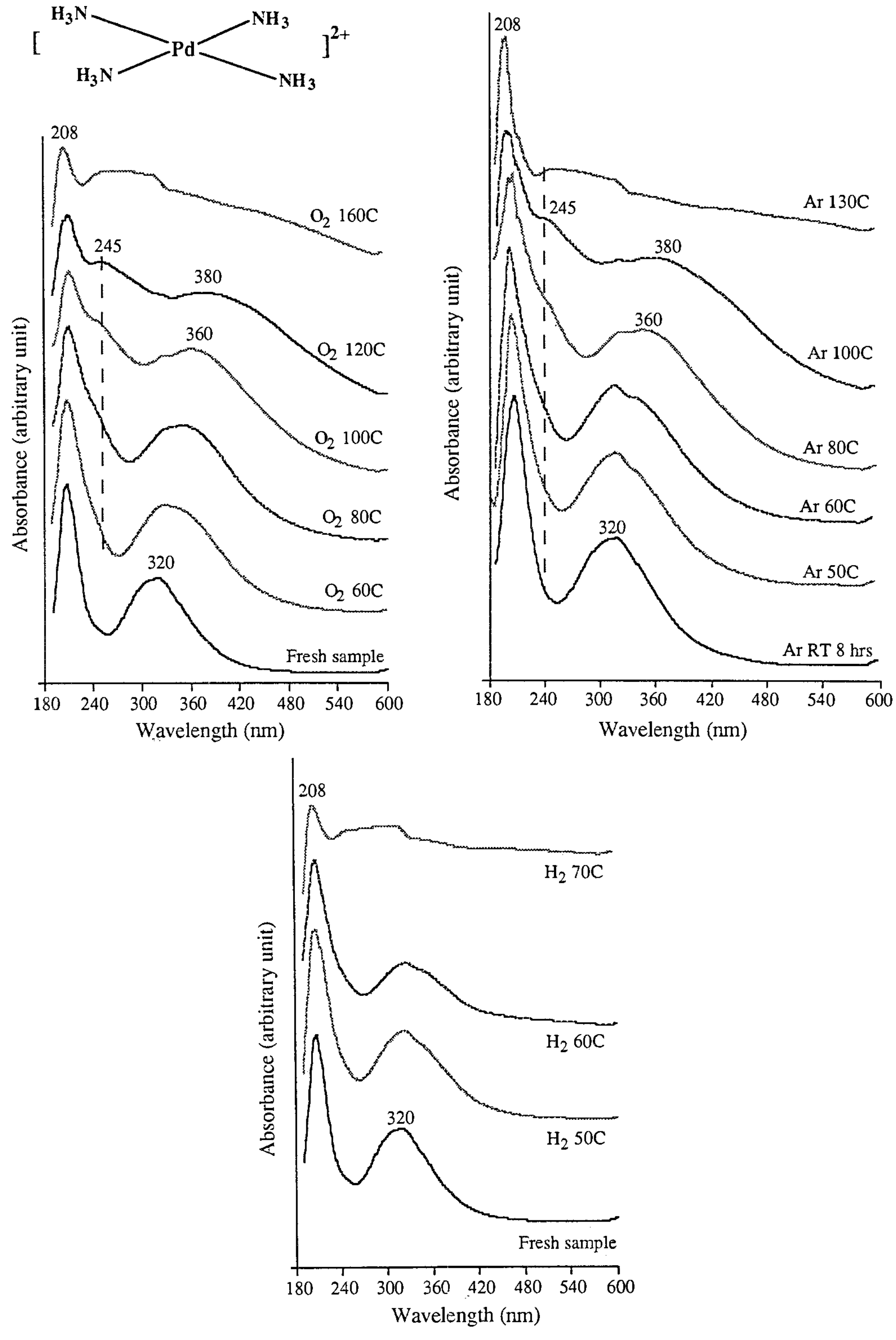


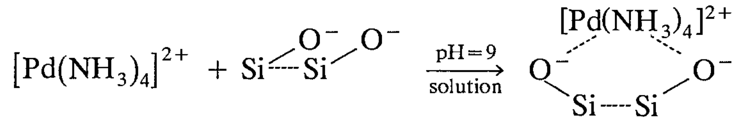
Fig. 5. The UV spectra of $[Pd(NH_3)_4]^{2+}/SiO_2$ treated at different temperatures: (a) in following oxygen; (b) in following helium or argon; (c) in following hydrogen.

Table 3
UV band assignments of $[Pd(NH_3)_4]^{2+}$

Absorption (nm)	Transition	Proposed species	Ref.
295 [a], 297	d → d [b]	$[Pd(NH_3)_4]^{2+}$	[13]
320	d → d [c]	$[Pd(NH_3)_4]^{2+}$	This study
245	$O^- \rightarrow Pd^{2+}$ CT	$Pd^{2+}(O^-_{(s)})_2$	This study
208	Exciton	Silica	This study
220 [a], 185	$NH_3 \rightarrow Pd^{2+}$ CT	$[Pd(NH_3)_4]^{2+}$	[13]

[a] This study; [b] complex in solution; [c] complex adsorbed on silica.

This band was not observed when the surface complex was decomposed in hydrogen. However, the UV reflectance spectrum obtained when the surface complex was decomposed in either He or Ar was identical to that obtained when the decomposition was carried out in oxygen. This immediately rules out the possibility that the charge transfer band observed is due to the formation of PdO_2. Because the Pd dispersion obtained when the decomposition is carried out in a noble gas atmosphere is so much higher than that obtained when the decomposition is performed in oxygen, it is likely that the nature of the metal support interaction is a function of the gas environment present during the decomposition. In order to explain the dispersions obtained using different pretreatment conditions, we suggest that the surface complex is formed according to the following mechanism:



(1)

A similar surface complex has been proposed for the adsorption of $[Pt(NH_3)_4]^{2+}$ and $[Ru(NH_3)_6]^{3+}$ on Cab-O-Sil [5]. Decomposition is accompanied by the evolution of ammonia. The Pd retains its positive charge and is strongly bound to the support. In the presence of gas phase oxygen, oxygen atoms are chemisorbed onto the surface of Pd. Because of the competitive nature of the interaction between support oxygen and chemisorbed oxygen, there is a partial weakening of the surface metal bond. This partial weakening of the surface oxygen-metal bond results in an increase in the surface mobility of the surface complex intermediate which leads, in turn, to agglomeration and a lowering in the metal dispersion. When this gas phase oxygen is not present the surface complex remains strongly bound to the support. This results in a much higher metal dispersion.

The very low Pd dispersion obtained when the reduction is carried out directly in hydrogen can be explained by invoking a surface complex which has a very high surface mobility. In this respect, the similarity between silica supported Pd and Pt catalysts prepared using amine precursors is striking [5]. For the case of $[Pt(NH_3)_4]^{2+}/SiO_2$ catalysts, an intermediate surface complex having the structure $[Pt(NH_3)_2(H)_2]^0$ was identified by diffuse UV reflectance spectroscopy [5] and also by infrared spectroscopy [21]. The signature corresponding to this surface species was a charge transfer band centered at 213 nm [5]. This UV band was not observed for the Pd surface complex treated in H_2. However, it is possible that the same surface complex observed for Pt is also present for Pd. It is not observed spectroscopically due to the strong overlapping silica absorption band centered at 208 nm. Because this surface intermediate bears no surface charge it interacts weakly with the support and diffuses rapidly across the surface. This leads to rapid particle growth and poor metal dispersions.

From the above considerations we feel comfortable in assigning the UV absorption band centered at 245 nm to a charge transfer transition between oxygen from the support to the "d" orbitals of Pd.

5. Conclusion

The important conclusion which emerges from this study is the importance of pretreatment in the control of metal particle size. Pretreatment in hydrogen results in poorly dispersed Pd particles due to weak interactions between the adsorbed surface complex and the support. Decomposition of the surface complex in either Ar or He leads to very highly dispersed Pd particles. Decomposition of the surface complex in oxygen results in intermediate values of the dispersion.

Dispersion measurements obtained using either H_2 or CO chemisorption were in good agreement with dispersion measurements obtained by transmission electron microscopy.

Acknowledgments

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