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Preparation of Pd/SiO$_2$ Catalysts for Methanol Synthesis

I. Ion Exchange of [Pd(NH$_3$)$_4$](AcO)$_2$

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An in-depth analysis of the adsorption via ion exchange (IE) of aminepalladium complexes prepared from palladium acetate on well-characterized commercial gels of silica (Davison, G-59 and G-03) in aqueous alkaline solutions is carried out. The nature of the exchanged species after different IE and washing treatments is scrutinized with diffuse reflectance spectroscopy. It is shown that (i) there is a maximum of IE at pH 10.3; (ii) IE occurs without any exchange of ligands; (iii) adsorption equilibrium is reached in about 1 h and (iv) IE follows a common Frumkin isotherm on both supports.

INTRODUCTION

The activity and selectivity of supported palladium catalysts depend upon the physicochemical nature of their active components in a complex fashion (*1*). Even for a given choice of support and metal precursor the catalytic performance is most often a strong function of the preparation method and/or the sequence of pretreatments prior to having an on-line process (*2, 3*) and, frequently enough, variations in the size of the metal crystallites are sufficient to cause significant changes in the catalytic response for a given reaction (*4*).

These aspects are particularly relevant with regard to the widespread use of Pd/SiO$_2$ catalysts for the synthesis of methanol: Ichikawa *et al.* (*5*) suggested that the selectivity among the reactions of CO and H$_2$ can be displaced toward the production of methane instead of methanol by simply decreasing the Pd crystallite size. They were able to detect methanol formation for particle sizes larger than 25 Å (H$_2$/CO = 6, 673 K and 535 kPa). Also, Hicks and Bell (*6*) reported that palladium dispersions within 10–20% gave nearly constant turnover frequencies in the conversion of synthesis gas to methane and methanol (H$_2$/CO = 2.5, 523 K and 1 MPa). Likewise, the effect of the metal dispersion of the catalytic properties of Pd/SiO$_2$ has been studied in other reacting systems, e.g., vinylacetylene (*7*) or styrene (*8*) hydrogenations.

In most cases, however, different types of silicas (with various chemical origins), Pd precursors, and preparation methods have been used simultaneously, rendering it utterly impossible to extract clear, definitive conclusions about the individual role each of these variables plays in the final performance of the catalysts (*9–13*).

To help clarify matters, we have set up an experimental program aimed at the systematic analysis of obtaining Pd/SiO$_2$ on a few, well-purified commercial supports of the same chemical origin, using a single preparation method. Ion exchange (IE) in aqueous media was chosen, since by this means very high metal dispersions on silica are attainable [e.g., Cu/SiO$_2$ (*14, 15*), Pt/SiO$_2$ (*16, 17*), Pd/SiO$_2$ (*5, 18–21*)], and these initial

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dispersions can be decreased with further thermal treatments (*18, 19*).

Among the parameters that influence the adsorption process of aqueous metal complexes via IE on different metal oxide supports, Brunelle (*22*) has pointed out the zero charge point (ZCP) of the oxide, the pH of the solution, and the nature of the metal complex as the most important.

Smith and Reyerson were the first to note the strong adsorption of metal amine complexes on gels of silica (*23*). The amount of Pd^{2+} that may be exchanged by a gel of silica in aqueous ammonium hydroxide, $NH_4OH(aq.)$ increases with pH until an apparently constant maximum value is reached (*24*). With other metal cations, though, the high alkalinity of the aqueous solutions causes a decrease in the exchanged amounts [e.g., Zn^{2+} (*25, 26*), Ni^{2+} (*27*), Co^{2+} (*28*)].

Numerous palladium salts have been used as precursors for the IE of $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ ($n \leq 4$) thereon, where the accompanying anions have been chloride (*5, 10, 18–20, 29, 30*), nitrate (*11, 18, 20*), acetate (*18*), or hydroxide (*31*). Accompanying anions are modifiers of the final activity and/or selectivity of these catalysts: Kikuzono *et al.* (*29*) noted that chloride ions were able to preserve the surface structure of their Pd/SiO_2 and the production of methanol on them, even after using relatively high reduction temperatures on their pretreatments. Likewise, Kelly *et al.* (*13*) reported a positive role of the said anions both as dispersion preservers of the palladium crystallite sizes on silica and as activity promoters toward the methanol synthesis, indicating that the said promotional effect was similar to that of Group IA ions.

We have chosen to exclude any possible promotional effects of chlorine or any other residual anion in the catalyst performance, focusing our attention on the support texture and the conditions of the ion exchange themselves. Palladium (2+) acetate was therefore used as the single metal precursor.

As regards the type of palladium species adsorbed on the silica surfaces after IE, there is no agreement yet. Tetra (*32*)-, tri (*24*)-, or di-aminepalladium (*31*) complexes have been postulated as the exchanged species, without further analysis. Little has been reported about the time scale of the IE process or the influence of the washing conditions (*24, 33*).

This paper, then, reports an in-depth analysis of the adsorption via ion exchange of aminepalladium complexes prepared from $Pd(AcO)_2$, on well-characterized commercial gels of silica in aqueous, alkaline solutions. The nature of the exchanged species after different IE and washing treatments is scrutinized with DRS. Further work on each one of the following preparation steps (i.e., drying, calcining, reduction) and on their influence on the catalytic performance for methanol synthesis is currently in progress (*34*) in our laboratory.

EXPERIMENTAL

Support preparation and characterization. Commercial Davison silicas (Grade 59 and Grade 03) were crushed and sieved through an 80-mesh Tyler screen. These materials were labeled G-59/1 and G-03/1, respectively.

Organic impurities were eliminated by first washing them in an ultrasound bath, at room temperature (RT), with a series of nonchlorinated solvents (hexane, acetone, methanol, distilled deionized water (DDW)), then drying for 2 h at 393 K with forced air circulation (FAC).

Residual metal cations and sulfates were eliminated by washing each of them for 3.5 h at 393 K in a Teflon vessel with 3 *N* nitric acid (*5, 18*), then rinsing with DDW until pH 5.5, and finally drying for 6 h on a stove at 413 K with FAC. These materials were labeled G-59/2 and G-03/2, respectively.

The supports were thermally stabilized during 14 h at 773 K (*21*) and these materials labeled G-59/3 and G-03/3.

The efficiency of these washes was verified by atomic absorption (AA), with previous digestion of the samples in 1.5% aqueous HF, using a Perkin–Elmer Model 5000 unit.

Since these commercial gels of silica are normally synthesized by reacting sodium silicate with sulfuric acid, it is desirable to eliminate residual sulfates as much as possible (*13, 29*). Then IR spectroscopy was used to monitor whether the acid washes were able to eliminate this anion sufficiently and to check the contents of residual organic material. The supports were pulverized, mixed with KBr, and pelletized (10 mg/cm^2). A Perkin–Elmer Model 580B, with a resolution of 2.3 cm^{-1} and ISM = 4, was used.

Specific surfaces (BET-N_2) and pore size distributions were measured with a Micromeritics 2000 apparatus, after outgassing each sample overnight at 623 K. X-ray diffraction was employed to verify the amorphousness of the calcined materials (Rich Seifert JSO-Debyeflex Model 2002, Cu source, Ni filters).

Henceforth, the denominations G-59 and G-03 will indicate the purified, calcined silica supports.

Ion exchanges. A stock solution of 10,000 ppm of tetraaminepalladium acetate, TPAcO, was prepared by dissolving palladium (2+) acetate (Engelhard, 99.5% w/w) in NH_4OH(aq.) and stabilizing the solution for at least 3 days at RT before further use. The formation of the $[Pd(NH_3)_4]^{2+}$ was verified using a Varian UV–VIS–NIR CARY 17D double-beam spectrometer.

Aliquots of the purified and calcined gels of silica, G-59, and G-03, were suspended in NH_4OH(aq.), and the pH was adjusted at each of different selected working values corresponding to the series of experiments described below. The resulting slurries were then stabilized for 6 h prior to the addition of given amounts of the TPAcO stock solution. Unless otherwise indicated, a ratio (*R*) of liquid volume to solid mass equal to 30 ± 0.5 ml/g was used in every case throughout this work.

The pH during IE was controlled by adding concentrated NH_4OH. Every IE experiment was made while the slurries were stirred at 297 K. The palladium-exchanged supports were filtered under vacuum, using 0.45-μm cellulose acetate membranes.

The amount of ion-exchanged TPAcO (expressed as mass units of Pd moles) on the silicas was obtained as the difference between the mass added to each slurry from the stock solution and that remaining in the aqueous solution after a given elapsed time. Atomic absorption was used to measure the concentration of Pd in the solutions.

The uptakes of TPAcO as a function of the alkalinity of the IE solution were investigated at pH values ranging from 9.25 to 11.45, using portions of 2 g of each of the silicas and adding aliquots of the TPAcO stock solution to the suspensions at a rate of 0.05 ml/s at RT, while stirring, so as to have 2.00% w/w nominal loadings of Pd. The suspensions were filtered after 24 h of contact time, and the amount of Pd remaining in the filtrates was analyzed by AA. The solids were washed four consecutive times with diluted NH_4OH(aq.), at the same pH used in the corresponding ion exchange, under agitation, at RT and for 1 h each time (*R* = 30 ± 0.5 ml/g).

The amount of the TPAcO exchanged on the supports as a function of the elapsed time was closely followed at pH 11, and the required amount of TPAcO was added all at once. Thus, aliquots (5 ml) of the suspensions were taken from the system at selected time intervals and quickly filtered; then the Pd concentration of the filtrates was measured. Nominal or expected Pd loadings of 2.62% w/w and 2.03% w/w on G-59 resp. G-03 were chosen to perform the experiments, using 9 g of each support.

To study the influence of (i) the pH of the washing solution and (ii) the number of washes on the ion-exchanged palladium complex, each of the former G-59 and G-03 filter cakes was subdivided into two fractions. The first fraction of each of the cakes was washed for 1 h, under agitation (R = 30 ± 0.5 ml/g), with four consecutive portions of diluted NH_4OH(aq.) (pH 11), and the suspensions were filtered between washes. The remaining fraction was in turn washed with four consecutive portions of DDW (pH 6.5), under the same operating conditions.

Finally, adsorption isotherms of the ion exchange of TPAcO on G-59 and G-03 were measured at 297 K and pH 11. Thus, suspensions containing 2 g each of the pH preconditioned silicas received aliquots of the TPAcO stock solution at a rate of 0.05 ml/s. Nominal loadings of Pd equal to 0.5, 1.0, 2.0, 4.0, and 12.0% w/w were used with G-59, and nominal Pd loadings equal to 1.0, 2.0, 4.0, 8.0, and 16.0% w/w were used with G-03. The suspensions were filtered after 24 h of contact time, and the amount of Pd remaining in the filtrates was analyzed by AA. The solids were washed four consecutive times with diluted NH_4OH(aq.) at pH 11, under agitation, at RT and for 1 h each time (R = 30 ± 0.5 ml/g).

Diffuse reflectance spectroscopy (DRS) was employed for the identification of the aminepalladium complexes adsorbed on the gels of silica after the IE. Pellets of 2.5-cm diameter and 0.3-cm thickness were obtained by pressing the wet cakes at 20 kg/cm^2, then placing them on the UV–VIS–NIR spectrometer, which was furnished with an integrating sphere covered with barium sulfate. Blank spectra from wet G-59 and G-03 were also taken to properly normalize data.

RESULTS

Support characterization. Table 1 details the results of the chemical analysis of the G-59 and G-03 supports. The content of cationic impurities, notably Ca, Mg, and Na, was significantly lowered after the HNO_3 acid wash. Both surface and bulk cations seem to be leached out whenever an acid treatment of the silicas is involved (*35, 36*).

The asymmetric stretching of the O=S=O group (1412 cm^{-1}) and the Si–O–S vibration (925 cm^{-1}) bands were used to follow the contents of residual sulfates on the silicas (*37*). Figure 1 shows well-resolved sulfate bands, centered at 1405 cm^{-1}, which correspond to spectra taken from each of the support samples. The intensity of these bands was normalized by comparing them with the Si–O–Si bending mode signal (800 cm^{-1}) (*38*).

From Fig. 1 it can be visualized that, although the initial content of sulfate of G-03 is higher than that of G-59, the purified and

TABLE 1

Residual Contents of Metal Impurities on G-59 and G-03 Silica Gels after Chemical Purification

Element tested[b]	Sample[a]					
	G-59(*) (ppm)	G-59/1 (ppm)	G-59/2 (ppm)	G-03(*) (ppm)	G-03/1 (ppm)	G-03/2 (ppm)
Al	265	<125	<125	133	<125	<125
Ba	—	<250	<250	—	<250	<250
Ca	500	725	179	715	<50	<50
Sr	—	<125	<125	—	<125	<125
Fe	35	57	<50	105	<50	<50
Mg	—	134	43	—	8	<5
Ni	—	90	94	—	138	103
K	—	26	<20	—	<20	<20
Na	223	199	<20	371	259	<20

[a] (*) Manufacturer's catalog values; /1, as received; /2, after organic and acid washes.

[b] By atomic absorption.

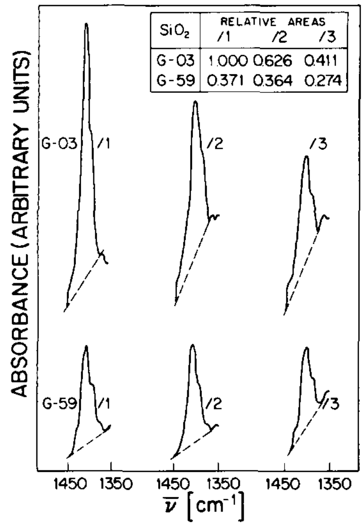


FIG. 1. Infrared spectra corresponding to the ν(O=S=O) (1450 cm^{-1}) band, normalized with respect to the δ(Si–O–Si) (800 cm^{-1}) signal. Sample codes are the following: /1, as received; /2, after organic and acid washes; /3 same as /2, then calcined 14 h at 773 K.

TABLE 2

BET (N_2) Specific Surfaces (S_g) and Pore Volumes (V_g) of the Gels of Silica

Sample	S_g(m^2/g)		V_g(cm^3/g)
	Manufacturer's catalog values	This work	This work
G-59/1[a]	340	300	—
G-59/1[b]	—	270	—
G-59/3[c]	—	254	1.17
G-03/1[a]	700	621	—
G-03/1[b]	—	616	—
G-03/3[c]	—	558	0.26

[a] As received.

[b] As received, then calcined 14 h at 773 K.

[c] Washed (organic and acid washes), then calcined 14 h at 773 K.

calcined supports, G-03/3 and G-59/3, have smaller, similar total amounts of this anion. Morrow *et al.* (*37*) have also reported that calcination treatments lower the content of sulfates. The IR spectra showed a complete absence of nitrate or organic residue.

Table 2 shows the surface areas of each support: (/1) as received, (/2) after the chemical purification, and (/3) after the thermal stabilization treatments, as well as their final pore volumes. The chemical and thermal pretreatments lead to smaller surface areas on both supports, that of G—59 being somewhat larger, probably because of the different contents of metal impurities of these silicas (*35*, *36*). Figures 2 and 3 show the N_2 adsorption–desorption isotherms and the pore size distributions of the G-59/3 and G-03/3 stabilized supports.

It follows that the morphology of these supports differs significantly: G-59 is a moderate surface area silica (S_g = 254 m^2/g) with a macropore structure, whereas G-03 is a large surface area support (S_g = 558 m^2/g) with a micropore structure. The unimodal pore size distributions were calculated with a cylindrical pore model. their characteristic modal radii were found to be 83 and 16 Å for G-59/3 resp. G-03/3.

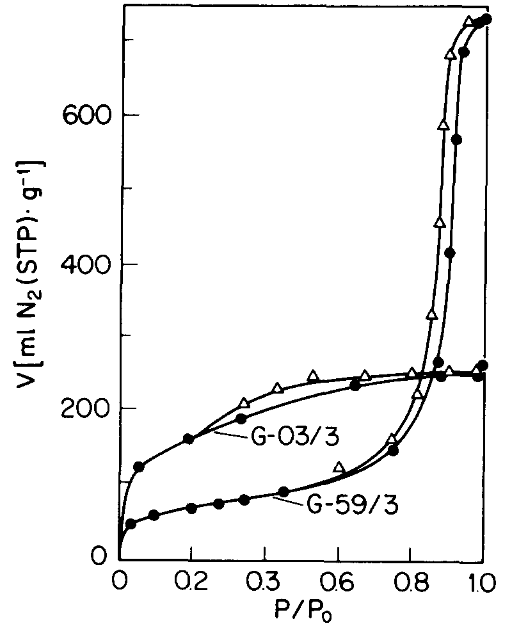


FIG. 2. Nitrogen adsorption isotherms (T = 78 K) on purified and calcined G-59 and G-30 silicas. Sample codes are as indicated in Fig. 1.

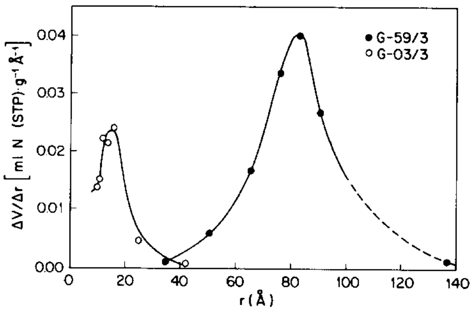


FIG. 3. Pore size distribution of purified and calcined G-59 and G-03. Sample codes are as indicated in Fig. 1.

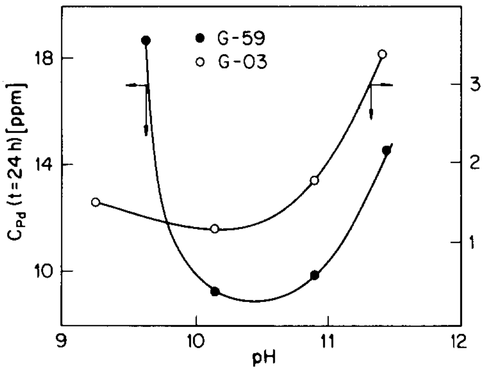


FIG. 4. Equilibrium concentrations of dissolved TPAcO (expressed as ppm Pd) vs pH of the aqueous solutions, after 24-h contact times with suspensions of G-59 and G-03 silicas. [T = 297 K; $C_{Pd}(t$ = 0 h) = 660 ppm; R = 30 ± 0.5 ml solution/g support].

IE of TPAcO vs pH of the exchange solution. Table 3 summarizes the results of these experiments. The last column in the table contains the balance from the initial amount of Pd added and the subtracted values of the residual Pd contents in the exchange solution after 24 h of IE, C_{Pd} (t = 24 h), and the collected residual Pd contents of the four washing filtrates (see the previous two columns of the table); it is labeled "effective Pd loading."

Figure 4 shows that the C_{Pd} (t = 24 h) values become minimized at pH levels between 10 and 11, with shallow minima at pH ≅ 10.3 for both silicas, indicating that maximum ion exchange is achieved whenever medium levels of alkalinity in the exchange solution are used.

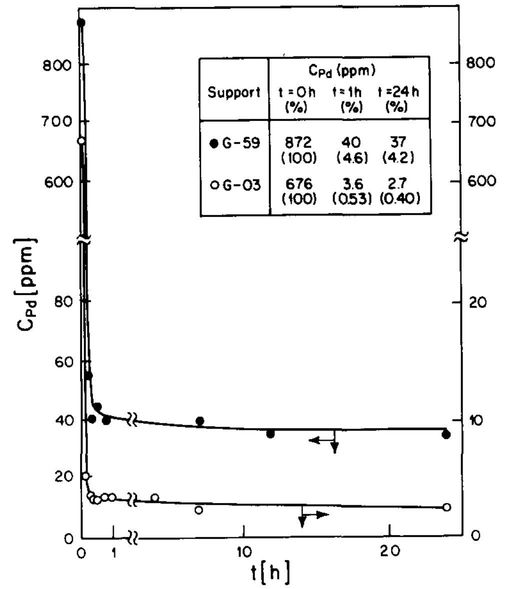
Residual contents of Pd on the solutions were always higher when G-59 was used than when ion exchanging occurred on G-

TABLE 3

Pd Effective Loadings (% Pd, w/w) after Ion Exchange (IE) of TPAcO on G-59 and G-03 Silica Gels vs pH of the Suspensions (R = 30 ± 0.5 ml solution/g support; T = 297 K)

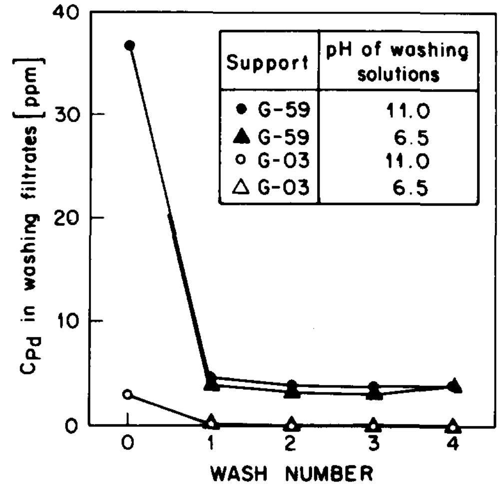
Sample codes[a]	Working pH	Concentration of TPAcO in solution		Pd effective loading (% Pd, w/w)
		$C_{Pd}(t$ = 24 h)[b] (ppm Pd)	C_{Pd} in washing filtrates[c] (ppm Pd)	
PH1-59	9.65	18.7	2.3	1.90
PH2-59	10.15	9.3	1.8	1.93
PH3-59	10.90	9.8	1.3	1.93
PH4-59	11.45	14.5	1.2	1.92
PH1-03	9.25	1.5	0.0	1.98
PH2-03	10.15	1.2	0.0	1.98
PH3-03	10.90	1.8	0.0	1.97
PH4-03	11.45	3.4	0.4	1.96

[a] PHi-59 or -03 corresponds to the ith working pH used in the IE process of TPAcO on G-59 resp. G-03.
[b] $C_{Pd}(t$ = 0 h) was 660 ppm Pd. It corresponds to a 2% Pd, w/w, nominal loading.
[c] Average of four washes (washing time: 1 h/each; R = 30 ± 0.5 ml/g; T = 297 K).



Support	C_{Pd} (ppm) t = 0 h (%)	 t = 1 h (%)	 t = 24 h (%)
● G-59	872 (100)	40 (4.6)	37 (4.2)
○ G-03	676 (100)	3.6 (0.53)	2.7 (0.40)

FIG. 5. Concentration of TPAcO in aqueous solution (pH 11) vs adsorption contact time, on G-59 and G-03, expressed as ppm Pd (graph) and as a percentage of the initial concentration used (box). [T = 297 K; R = 30 ± 0.5 ml solution/g support].



Support	pH of washing solutions
● G-59	11.0
▲ G-59	6.5
○ G-03	11.0
△ G-03	6.5

FIG. 6. Concentration of Pd in the washing filtrates as a function of the number of washes, for two different washing pH values. [T = 297 K; R = 30 ± 0.5 ml solution/g support; 1 h contact time per wash].

03, since the liquid-to-solid ratio, R, was the same for both supports and S_g for G-59 was about half the surface area of G-03. Under Discussion it will be shown that, despite the microporous nature of G-03, no effects due to geometrical limitations of the IE were present for these Pd loadings.

IE of TPAcO vs exchange time. Figure 5 shows the measured values of the concentration of TPAcO in the exchange solution (expressed as C_{Pd} in ppm) at increasing contact times with each of the silicas. A pH of 11 was used to perform these experiments. The initial concentration of Pd C_{Pd} (t = 0) is that corresponding to the addition of the TPAcO stock to the NH_4OH(aq.) without previous suspension of the support. Initial time (t = 0) stands for that immediately after the addition of the TPAcO stock to the slurries.

The concentration of TPAcO decayed sharply during the first minutes following its addition to the slurries, and then it slowly diminished for the rest of the IE. Immediately after the addition of the TPAcO stock, the pH of the slurries decayed about 0.3 units. Concentrated NH_4OH(aq.) was immediately added in a controlled fashion to keep the pH at 11 throughout each of the experiments.

The amount of aminepalladium complexes ion-exchanged after the first hour of contact time was 99.6% w/w and 99.9% w/w complete for G-59 resp. G-03 of the total TPAcO exchanged after 24 h, for nominal (expected) loadings of 2.62 and 2.03% Pd w/w, respectively. Thus, it can be inferred that for all practical purposes the IE is complete after 1 h of contact time on these slurries.

After 24 h contact time the final content of ion-exchanged Pd complexes on the wet supports was 2.50 and 2.02% Pd w/w on G-59 resp. G-03, prior to any further washing.

Influence of the pH of the washing solution and the number of washes on the IE of TPAcO. As indicated under Experimental, each of the former G-59 and G-03 filter cakes was subdivided into two fractions. The first fraction of each was washed with four consecutive portions of diluted NH_4OH(aq.) (pH 11), and the suspensions were filtered

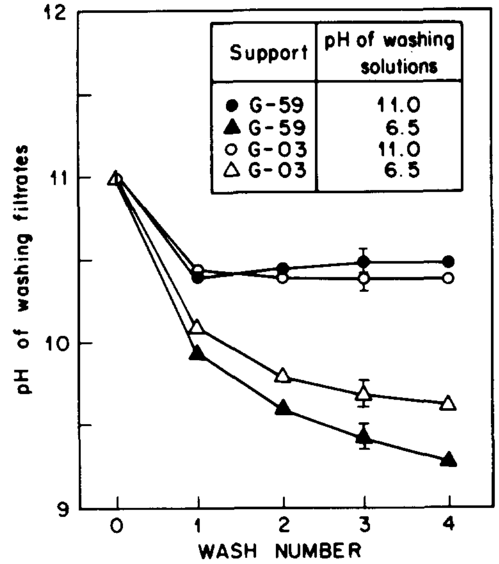


FIG. 7. pH of the washing filtrates as a function of the number of washes, for two different washing pHs. [T = 297 K; R = 30 ± 0.5 ml solution/g support; 1 h contact time per wash].

TABLE 4

Adsorption Equilibrium Loadings (Γ_i) of TPAcO on G-59 and G-03 vs Pd^{2+} Activities (a_i) in Aqueous Solution

Sample	$\Gamma_i \times 10^4$ (mmol Pd/m^2)	a_i (mol/liter)
A1-59	1.7	7.26×10^{-6}
A2-59	3.4	2.10×10^{-5}
A3-59	6.7	8.57×10^{-5}
A4-59	13.2	3.77×10^{-4}
A5-59	18.6	$\sim 7.44 \times 10^{-3a}$
A1-03	1.7	1.06×10^{-5}
A2-03	3.4	1.59×10^{-5}
A3-03	6.7	9.57×10^{-5}
A4-03	12.6	$\sim 1.11 \times 10^{-3a}$
A5-03	17.3	$\sim 7.37 \times 10^{-3a}$

Note. (T = 297 K; pH 11.0; R = 30 ± 0.5 ml solution/g support).

[a] Approximate values. The activity coefficients were calculated with Eq. (1), valid for $I \le 0.01$ (39).

between washes. The remaining fraction was in turn washed with four consecutive portions of DDW (pH 6.5), under the same operating conditions.

Figure 6 shows the concentration of Pd of each of the filtrates, as a function of the number of washes. It is seen that C_{Pd} in the filtrates was the same regardless of the pH of the washing solution for both of the supports used, becoming very low for G-59 and almost negligible for G-03, given the differences in their surface areas, as mentioned above.

Significant variations in the pH of the filtrates in the sequence could be observed when DDW was used as the washing solution (Fig. 7), this feature being most pronounced when G-59 was the support under scrutiny. On the other hand, when the samples were washed with NH_4OH(aq.), the filtrates kept an approximately constant pH, the averaged value of which was 10.4 for both supports.

As a result of the sequence of four washings at pH 11, the final loadings were 2.46 and 2.02% Pd w/w for G-59 resp. G-03. As the nominal expected Pd loadings were 2.62 and 2.03% Pd w/w, respectively, it is apparent that by means of an IE at pH 11, followed by four consecutive washes at the same pH value, 94 resp. 99.45% w/w of the TPAcO was retained as exchanged aminepalladium complexes on the silica surfaces.

Adsorption isotherms of the IE of TPAcO on the silicas. Adsorption isotherms of the ion exchange of TPAcO on G-59 and G-03 were measured for a wide range of nominal Pd loadings on each of these supports, following the same IE procedure and the sequence of four washes with diluted NH_4 OH(aq.), at 297 K and pH 11, as already described. The actual Pd loadings on the surfaces (Γ_i, mmol Pd/m^2 of support surface area) were calculated from the (measured) concentrations on the clarified solutions at contact times of t = 0 h and t = 24 h, as well as the equilibrium activities of TPAcO (a_i) as indicated in Table 4.

The activity coefficients of dissolved TPAcO (γ_i) were estimated using the expression

$$\log \gamma_i = -\frac{Az_i^2\sqrt{I}}{1+\sqrt{I}}, \qquad (1)$$

TABLE 5

Calculated Parameter Values for the Adsorption Isotherms of TPAcO on G-59 and G-03 when Using Langmuir, Temkin, and Frumkin Models

Support	Isotherm[a]						
	Langmuir		Temkin		Frumkin		
	$\beta_i a_i = \frac{\Gamma_i}{\Gamma_s - \Gamma_i}$		$\beta_i a_i = \exp\left(\frac{2g\Gamma_i}{RT}\right)$		$\beta_i a_i = \frac{\Gamma_i}{\Gamma_s - \Gamma_i}\exp\left(\frac{2g\Gamma_i}{RT}\right)$		
	$\beta_i \times 10^{-4}$ (1/mol)	$\Gamma_s \times 10^4$ (mmol/m^2)	$\beta_i \times 10^{-4}$ (1/mol)	$g \times 10^{-13}$ (J/cm^2)	$\beta_i \times 10^{-4}$ (1/mol)	$\Gamma_s \times 10^4$ (mmol/m^2)	$g \times 10^{-13}$ (J/cm^2)
G-59	1.77	12.4	11.4	3.67	1.39	22.0	1.26
G-03	1.43	13.3	23.0	5.52	1.26	18.0	1.35

Note. β_i, adsorption constant of TPAcO in silica at pH 11 and T = 297 K; Γ_s, adsorption saturation value of TPAcO on the adsorbent surface; g, Frumkin interaction parameter among the adsorbed species (*40–43*).

[a] Equilibrium adsorption data taken from Table 4.

where $A_{(T=297\text{ K})} = 0.5110$, z_i is the charge of the TPAcO ion (2+), and I is the ionic strength of the aqueous solution.

Three adsorption isotherms were used to quantitatively characterize the adsorption of the aminepalladium complexes on the silicas: Langmuir, Temkin, and Frumkin (*40–43*). Table 5 contains the model parameters calculated from the experimental data, and Figs. 8 and 9 show the experimental values as well as the goodness of fit of each of these isotherms.

It is apparent that (i) Langmuir's isotherm is able to predict the extent of the adsorption only for low Pd loadings on the silicas; (ii) Temkin's model achieves a good predictive capability only for moderate levels of Pd loadings on G-59; and (iii) Frumkin's isotherm satisfactorily describes the IE and adsorption of TPAcO on the silicas for the full range of Pd loadings tested.

Thus, Pd surface coverages (θ_i) on each of the supports were calculated by ratioing Γ_i and the saturation loading, Γ_s, using the values obtained from the regressions done with the Frumkin's model for the last one of these. Figure 10 shows the fair predictive fit that can be obtained by averaging the set of Frumkin parameters for both silicas. Some of the data points of the figure correspond to a set of scaling-up experiments, where a ten-fold size sample of each support was used to prepare IE G-59 and G-03.

Diffuse reflectance spectroscopy. Aminepalladium complexes show characteristic electronic transitions when excited with UV–VIS radiation, which depend upon the number of amino ligands on the coordination sphere of the Pd^{2+} cation. These characteristic maxima are located between 300 and 370 nm in aqueous solution (Table 6), and the lowest absorption wavelengths correspond to the highest number of coordinated amino ligands.

Figure 11 shows selected DRS spectra corresponding to wet pellets prepared (a) immediately after IE for 24 h at pH 11 and then washed four consecutive times with either (b) diluted NH_4OH(aq.) at pH 11 or (c) distilled deionized water at pH 6.5. All samples ion-exchanged at pH 11 and/or washed at this pH show absorption maxima located at 300 nm with a shoulder at 370 nm, indicating that $[Pd(NH_3)_4]^{2+}$ is the species adsorbed on the surfaces in both cases.

The DRS spectra taken from the supports washed with DDW do not have (for G-59) or faintly show (for G-03) the band shoulder at 370 nm, while a band broadening in the 300 to 370-nm region is apparent.

It is timely to recall here that the pH values of the filtrates for the G-59 and G-03

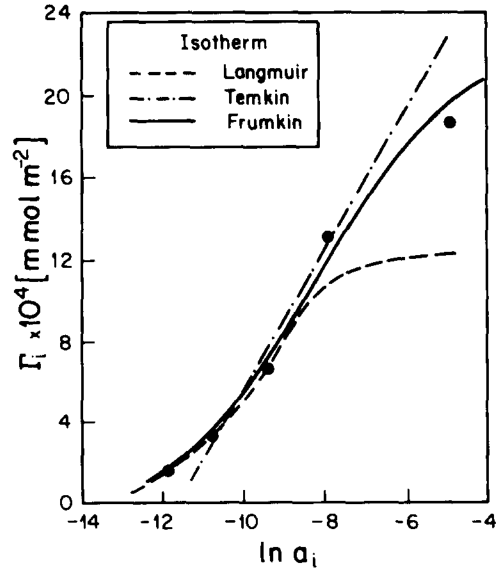


FIG. 8. Adsorption isotherm of TPAcO on G-59 silica. Lines indicate model predictions; symbols (●) indicate experimental results. [$T = 297$ K; pH 11; $R = 30 \pm 0.5$ ml solution/g support].

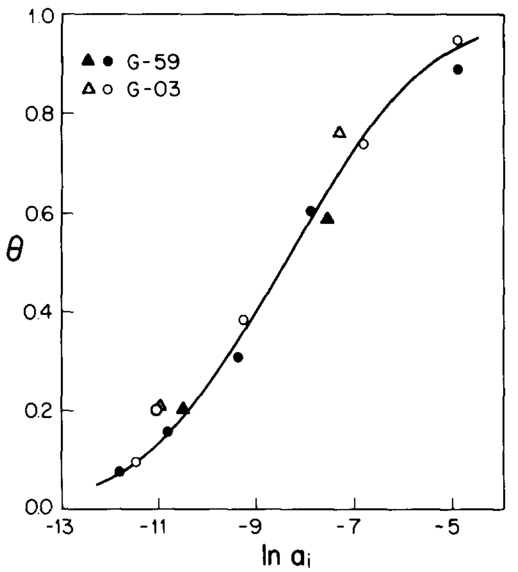


FIG. 10. Adsorption isotherm of TPAcO on G-59 and G-03 silicas in terms of surface coverage (θ) vs activity of TPAcO (ln a_i). The full line corresponds to a fitting using the Frumkin model with the following regression parameters: $\beta_i = 1.32 \times 10^4$ l/mol; $\Gamma_s = 20 \times 10^{-4}$ mmol/m^2; $g = 1.30 \times 10^{13}$ J/cm^2 (see also Table 5). Triangles correspond to tenfold scaling-up of the preparations. [$T = 297$ K; pH 11; $R = 30 \pm 0.5$ ml solution/g support].

supports were 9.30 and 9.65, respectively. The equilibrium diagram of the system of aminepalladium complexes in aqueous solution is shown in Fig. 12. At pH < 10 it is possible to have dissolved species such as $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$, with $n < 4$, and thus

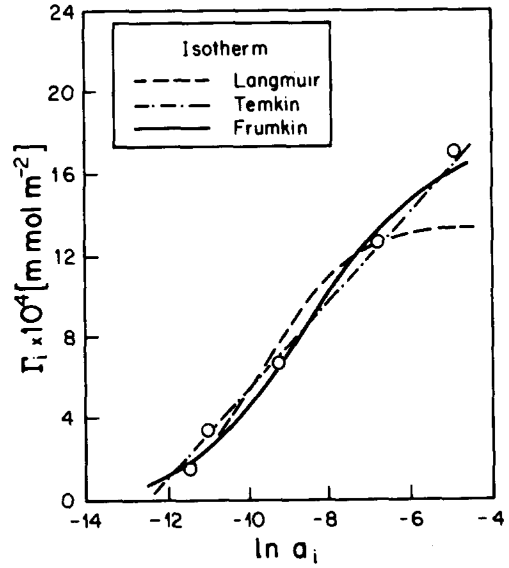


FIG. 9. Adsorption isotherm of TPAcO on G-30 silica. Lines indicate model predictions; symbols (○) indicate experimental results. [$T = 297$ K; pH 11; $R = 30 \pm 0.5$ ml solution/g support].

TABLE 6

Maxima of the Characteristic UV-VIS Absorption Bands of Aquoaminepalladium Complexes in Aqueous Solution[a]

Number of amine ligands n	Wavelengths (nm)	
	Ref. (*44*)	Ref. (*45*)
$n = 0$	379	—
$n = 1$	360	366
$n = 2$	341	342
$n = 3$	~317	304 (shoulder 360 nm)
$n = 4$	296 (shoulder 373 nm)[b]	295 (shoulder 370 nm)

[a] Complexes: $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$.
[b] Ref. (*46*).

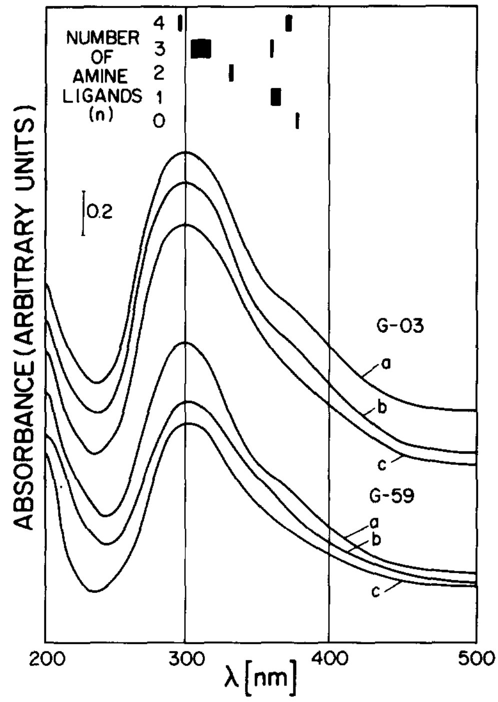


FIG. 11. DRS spectra of TPAcO ion exchanged at pH 11 on G-59 and G-03 (a) after adsorption, then (b) washed at pH 11 or (c) washed at pH 6.5. The upper part of the figure shows the location of the absorption bands of aquoaminepalladium complexes (see also Table 6).

it is possible to infer that part of the tetraaminepalladium complexes initially exchanged on the supports becomes transformed into these latter amineaquo complexes, as discussed below.

The DRS spectra of samples where the IE was done at different values of pH of the TPAcO exchange solution, then washed at this same pH, are shown in Fig. 13. It can be observed from this figure that the aminepalladium complex exchanged on the surfaces was $[Pd(NH_3)_4]^{2+}$ whenever the pH of the exchange TPAcO solution was higher than 10.9 and that when the pH of this exchange solution was lower than 10.5 other complexes of the type $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ were exchanged, which is evidenced by the disappearance of the shoulder at 370 nm and the broadening of the 300- to 370-nm absorption band, as indirectly indicated by the Δλ.

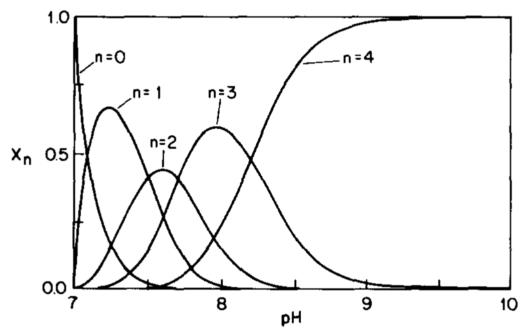


FIG. 12. Equilibrium diagram of the Pd^{2+}–NH_3 system in aqueous solution at T = 298 K (*45*). X_n stands for the molar fraction of the different $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ complexes in solution.

DISCUSSION

These experiments for the adsorption of Pd^{2+} on G-59 and G-03 at pH values ranging from 9.25 to 11.45 by means of the IE of TPAcO indicate that exchange yields averaging 96.5% can consistently be achieved, with an adsorption maximum for pH ≅ 10.3. This maximum occurs as a consequence of at least two phenomena:

(i) First, the IE equilibrium on the oxide surfaces in itself is concerned. Silicas are among the hydrolizable solid oxides; their surfaces, in contact with an aqueous solution, are subjected to the generalized equilibria

$$M\text{-OH}_2^+ \underset{H^+}{\overset{-H^+}{\rightleftarrows}} M\text{-OH} \underset{H^+}{\overset{-H^+}{\rightleftarrows}} M\text{-O}^-, \qquad (2)$$

where M represents one of the metal cations at the oxide surface (M = Si, Al, Ti, etc.) attached to oxygen in an acid, then an alkaline environment, from left to right (*47*).

The amount of charged surface groups (CSG) on these oxides, M–OH^+ and M–O^-, depends upon the pH of the solution and the chemical nature of the oxide, through its ZCP (*22*). It is generally accepted that the CSG resulting from the protonation/deprotonation equilibrium of the M–OH groups are the adsorption sites of an IE active ion and that their concentration determines the total amount of negative and positive species that can become adsorbed on the solid surface, i.e., the IE process is normally interpreted with an electrostatic model (*22, 48–52*).

The ZCP of silicas at 297 K is about 2.9 (*52*). Therefore, at $pH > 2.9$ these solid surfaces can adsorb positively charged species. Moreover, the surface concentration of the $Si–O^-$ groups increases notably above pH $\cong 5$ (*52*), which translates into the greater amounts of $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ that are ion exchanged and adsorbed on the gels at higher levels of alkalinity (Fig. 4). Similar behavior of aminepalladium complexes adsorbed on silica was observed by Sulcek *et al.* (*24*) ($7 < pH < 10.3$) and on alumina by Contescu and Vass (*53*). Other authors (*16*) have reported that the amount of adsorbed amino complexes of platinum on silica ($7 < pH < 9$) and aluminas ($9 < pH < 10$) is a strong function of pH. A quantitative picture of the dependence on pH of the IE and adsorption process is duly discussed in the following paragraphs.

(ii) Second, concomitant solubility phenomena are involved. The solubility of the oxide support and the possible participation of its dissolved moieties are routinely disregarded while the IE and adsorption processes are studied or modeled.

Silicas dissolve at least partialy at pH values beyond 5.5 (*22*), and a depolymerization of gels of silica with further dissolution of the monomer occurs even in neutral aqueous medium. The rate of this depolymerization process increases with pH, but it is inversely proportional to the content of dissolved metal ions (*54*).

In this regard, Dushina *et al.* (*27, 54, 55*) analyzed the content of dissolved silicic acid after Cu^{2+} (at neutral pH) and Ni^{2+} (basic pH) were adsorbed on a gel of silica. They observed a partial conversion of the polysilicic acid to the hydrosilicates of the adsorbing metal in both cases, although after prolonged contact times with the IE solution (longer than 60 days). A parallel decrease in the concentration of these metal ions in the solution, which these authors ascribed to the precipitation of the corresponding insoluble silicates, was also observed. However, when the product of the concentrations of Ni^{2+} and SiO_3^{2-} in equilibrium with the NH_4OH(aq.) solution was smaller than the solubility product of the nickel silicate, the adsorbed amount of Ni^{2+} decreased at higher concentrations of NH_4OH(aq.) whereas that of dissolved silicic acid increased (*27*).

In our case the gels of silica were previously stabilized for 6 h at the working pH, then kept in contact with the TPAcO solution for 24 h. At these moderate contact times, just a slight dissolution of the silicas, although higher at increasing experimental values of the pH set to perform the IE (*27, 54, 55*), is to be expected. The dissolved silicic acid also undergoes a deprotonation and then it is able to associate $[Pd(NH_3)_n(H_2O)_{4-n})]^{2+}$ species.

In summary, the appearance of adsorption maxima of the aminepalladium complexes on these silicas at pH $\cong 10.3$ is plausibly the result of at least the two abovementioned concomitant processes: an increase in the concentration of surface $Si–O^-$ groups and the partial dissolution of the gels of the support at higher pH values.

Instead, competitive adsorption between NH_4^+ and Cu^{2+} amine complexes was assumed by Martini and Burlamacchi (*56*) to justify the smaller uptakes of these metal complexes on SiO_2 that they found at high pH values. However, these authors did not take into account the solubility of silica, even though the basicity of their IE solutions was high ($pH > 11.8$).

It is to be expected that chemically equivalent silicas, after equal chemical purification and thermal stabilization treatments, may be able to show the same behavior toward the adsorption of a given cation or complex under the same experimental conditions if and when no diffusional phenomena interfere. Indeed, as was shown under Experimental, the adsorption of tetraaminepalladium complexes on G-59 and G-

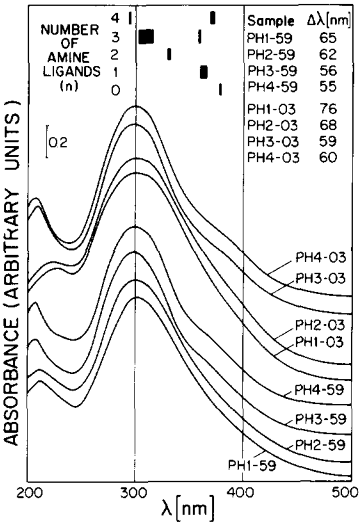


FIG. 13. DRS spectra of TPAcO ion exchanged on G-59 and G-03, after adsorption and prior to washing. Samples and sample codes correspond to those of Table 3. Experimental conditions are the same as those in Fig. 11.

03 follow Frumkin isotherms without significant differences in the model parameters corresponding to both supports (Table 5 and Figs. 8 and 9).

The Frumkin isotherm can be considered a generalization from the Langmuir isotherm whenever there is a linear dependence of the standard adsorption enthalpy with respect to coverage and the adsorbed species are able to interact with each other. The interaction parameter, g, is positive whenever these adsorbed species attract (*41, 42*).

Our experimentally obtained g values (Table 5) seem to indicate that the adsorption of positively charged tetraaminepalladium complexes becomes facilitated immediately after an initial coverage is achieved. The origin of this attractive force ($g > 0$) is not obvious to us at the moment, although a similar attractive adsorption pattern has been reported for the adsorption of copper complexes on silica in acid pH (*57*).

The mean distance between two nuclei of Pd in the adsorbed aminepalladium complexes after IE at pH 11 and 297 K, assuming monolayer coverages, is approximately 9 Å (*17, 56*).

Average values of the Frumkin parameters were used for the simultaneous fitting of combined experimental data with a single Frumkin isotherm, for the adsorption of aminepalladium complexes on both supports (Fig. 10). The individual values of the saturation coverages on G-59 and G-03, Γ_s, differ and, as shown in Figs. 8 and 9, the uptakes on G-03 are systematically smaller than those on G-59. The smaller regressed Γ_s value for G-03 may well be an artifact. G-03 is microporous (modal pore radius = 16 Å) while G-59 is a macroporous silica (modal pore radius = 83 Å) and then the accessibility to the Si–O$^-$ sites on the former support is limited.

We believe that the observed differences in Γ_s are not due to a different density of silanol groups, or to a different level of surface impurities of both silicas, for the following reasons:

—Under usual/normal ambient conditions the surfaces of silica gels are fully hydroxilated, having an —OH group per surface Si atom ($\cong$5 OH/nm^2) (*36, 58, 59*). Although after extensive heating under vacuum the surface density of silanol groups decreases, as observed by IR (*60–62*) or H^1-NMR (*62*), this is not the case with our supports because after their calcination they were largely exposed to atmospheric water vapor (*60*). Moreover, their preconditioning in alkaline solution for 6 h guaranteed a full regeneration of the surfaces, since rehydration is catalyzed by alkalies in aqueous media (*35*).

—Our experimental data reveal that the chemical purification of the silicas was quite satisfactory (Table 1). The final content of impurities was significantly reduced, and the nature of these was the same for both G-59 and G-03.

The nature of the Pd^{2+} complexes adsorbed on the silicas during the IE and/or washing processes depends upon the pH of the exchange and/or washing solutions.

Thus, DRS spectra evidenced the single presence of adsorbed $[Pd(NH_3)_4]^{2+}$ whenever pH > 10.5, whereas for pH < 10.1, $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ with $n < 4$ were also observable.

These findings are in direct agreement with the postulate that these IE and washing processes have reached thermodynamic equilibrium with the corresponding IE and washing solutions, because (i) the DRS-observed species correspond vis-à-vis those expected to be predominant at each pH (see the equilibrium diagram of the aminepalladium complexes in aqueous alkaline medium, Fig. 12), and (ii), as indicated in Fig. 5, the time scale for the establishment of equilibria between the silica surfaces and the IE or washing solutions is shorter than the contact time of the experiments.

Work by other groups is coincident in this regard (*32, 33*). Garbowski and Mathieu, after placing a Y zeolite in contact with a solution of $[Pd(NH_3)_4]^{2+}$ in concentrated ammonium hydroxide (23% w/w) showed by DRS that the species adsorbed by IE was of the same type as that of the solution (*32*). Bozon-Verduraz *et al.* (33) also observed that the nature of aminepalladium complexes on silica or alumina depends upon the washing and drying conditions to which the supports are subjected. From the DRS spectra they suggested that there is an exchange between NH_3 and H_2O ligands on adsorbed surface $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ complexes during washing and drying.

From a more general standpoint, our results for the IE of the aminepalladium complexes at pH > 10.5 are typical of adsorption mechanisms without exchange of ligands, after Summers and Ausen (*63*). These authors studied the reaction of complexes of noble metals (Pt, Pd, Rh, Ir, Au, Ru) with alumina in aqueous solution and have suggested that there are two different types of pathways to establish the adsorption/exchange. One of these pathways involves the reaction of the noble metal complex with the surface site(s) and a concomitant displacement of ligands from its coordination sphere (that was the case when using complexes containing Cl^- ligands). The other pathway does not involve such ligand displacements, as was the case when using $[M(NH_3)_4]^{2+}$ and $[M(NH_3)_5Cl]^{2+}$ amino complexes (M = noble metal).

Other authors have studied the IE of Cu^{2+} (*56, 64, 65*) or Ni^{2+} (*66*) amine complexes on silica, using ESR or DRS. These ions present an octahedral coordination and are able to form complexes of the types $[M(NH_3)_n(H_2O)_{6-n}]^{2+}$, with $n \leq 5$ for $M = Cu$ and $n \leq 6$ for $M = Ni$ in aqueous ammonium hydroxide. From ESR data, Martini and Basetti (*64*) proposed that the copper-adsorbed species upon IE at pH 12.4 on silica was $[Cu(NH_3)_5]^{2+}$, with the sixth ligand (H_2O) having been substituted for by a surface $Si–O^-$ group. From DRS spectra taken after IE of Cu^{2+} (*65*) and Ni^{2+} (*66*) amino complexes, it was concluded that the surface species that resulted upon adsorption at pH 11 were of the $M(NH_3)_4(SiO)_2$ type, with $M = Cu$, Ni. The substitution of two H_2O ligands by surface $Si–O^-$ was deduced from shifts of the DRS absorption maxima (a batochromic displacement of about 15 nm per each coordinated H_2O molecule was characteristic).

Aminepalladium complexes are square planar, and they have at most four ligands. Square planar complexes of transition ions with d^8 configuration, such as Pd^{2+}, Pt^{2+}, Ni^{2+}, Au^{3+}, Rh^{1+}, and Ir^{1+}, generally undergo bimolecular nucleophilic substitutions, in contraposition with the predominantly dissociative pathway of octahedral complexes (*67*). In all of our experiments, whenever $[Pd(NH_3)_4]^{2+}$ was adsorbed onto the silicas by IE there was no displacement of the DRS absorption maxima, and we believe the process occurs without liberation or substitution of ligands on the coordination sphere of Pd^{2+}.

Although it seems reasonable to assume that square planar complexes are able to display properties associable to those with distorted octahedral symmetry when dissolved in polar solvents, it is also known that Ni^{2+} is able to increase its coordination number somewhat faster than Pd^{2+} and much faster than Pt^{2+} (*68*). This would explain the observed differences in the IE processes of their amine complexes.

Work by Watt *et al.* (*69–71*), related to electrodeposition mechanisms of octahedral and square planar complexes in aqueous solution, has also shown the dissimilarities between these two types of complexes: the electrodeposition of a metal from octahedral complexes of Ni^{2+}, Co^{2+}, and Cu^{2+} is dissociative (*69, 70*), whereas that from square planar complexes of Pd^{2+}, Pt^{2+}, and Au^{2+} did not involve any dissociation of (halide, cyanide, or amine) ligands (*71*). The results of this work for the IE and adsorption of Pd^{2+} amine complexes and those for Ni^{2+} or Cu^{2+} (*56, 64, 65*) certainly agree with those of Watt *et al.* (*69–71*), originating in a complementary technique, thus allowing us to advance a well-founded model for the deposition of amine complexes of transition metals dissolved in aqueous solutions onto the surfaces of hydroxilated oxides (see Eq. (3) below).

A few authors have tried in the past to infer the nature of the metal complexes adsorbed on silica by indirect methods, e.g., by means of a quantitative follow-up of the number of liberated H^+ (*24–26*). Thus, Sulcek *et al.* (*24*) postulated the existence of $(SiO)_3[Pd(NH_3)_3]^-$ on the surface, after IE at pH $\cong$ 10, instead of the adsorbed $[Pd(NH_3)_4]^{2+}$ species that is observed by DRS as the predominant one. These authors used the empirical equation deduced by Vydra and Stara (*28*) to describe the IE on silica of amine complexes of Ag^{1+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, and Co^{+3}, under thermodynamic equilibrium. We think that the direct DRS evidence hereby presented is forceful enough and that it supercedes previous experimental efforts.

It was reported under Experimental that (i) a decrease in the pH followed the addition of TPAcO to the suspensions of both silica gels and that (ii) the higher the loading of TPAcO at constant *R* the more notable was this lowering in pH.

These phenomena are of course consistent with an IE mechanism and, because the Si–OH groups of the surface may interact in NH_4OH(aq.) solution via an acid/base reaction between the (acid) silanol groups and the NH_3 base, the lowering in pH during the adsorption of the $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ complexes must be due to the relaxation in the aqueous medium of NH_4^+ species held to the surface $Si{-}O^-$. Thus, bearing in mind that the surface electroneutrality must be preserved, we can advance the IE equation

$$2\,Si{-}O^-\,NH_4^+ + [Pd(NH_3)_n(H_2O)_{4-n}]^{2+} \rightleftarrows [(Si{-}O)_2]^{2-}[Pd(NH_3)_n(H_2O)_{4-n}]^{2+} + 2\,NH_4^+. \quad (3)$$

Other authors (*1, 18*) have proposed the same stoichiometric coefficients for adsorption processes via IE on silicas (Eq. (3)). Still, Contescu and Vass (*53*) have suggested instead the convenience of using a variable stoichiometry to model the IE on aluminas, this coefficient being equal to 2 for pH > 10.4, which is entirely empirical but probably useful for large-scale manufacturing of supported Pd via ion exchange.

Equation (3) is valid for the relatively broad range of pH values we have studied. It accounts for the nature of the adsorbed species and the decrease in pH observed after the addition of TPAcO to G-59 and G-03.

CONCLUSIONS

Yields averaging 96.5% can be consistently achieved, after ion exchange of TPAcO at room temperature on G-59 and G-03 silicas, at pH values ranging from 9.25 to 11.45. The interplay of both the ZCP and the solubility of the supports provokes the appearance of adsorption maxima for the IE at pH 10.3, with an increase in the concentration of surface $Si{-}O^-$ groups counterbalanced by the partial dissolution of the silica gels when higher pH is used for the exchange.

It is shown that these chemically equivalent silicas show the same behavior toward the adsorption of the aminepalladium complexes: a common Frumkin isotherm is able to describe the IE equilibrium process on these supports. This IE equilibrium is reached in about 1 h.

Our DRS data indicate that the process of adsorption by ion exchange occurs without liberation or substitution of ligands on the coordination sphere of the Pd^{2+} complexes.

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