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Effect of Calcination Temperature of Alumina on the Adsorption/Impregnation of Pd(II) Compounds

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A series of alumina supports derived from a common source material was subjected to a range of calcination temperatures and the results of this treatment on the adsorption of Pd(II) compounds were studied. Increasing calcination temperature lead to a decrease in BET surface area and produced a series of alumina samples carrying different inventories of hydroxyl groups. The surface chemistry of these hydroxyl groups was studied using mass and potentiometric titration techniques and from these data the protonation/deprotonation equilibrium constants for the surface hydroxyl groups were obtained. This allowed us to construct the pH-dependent surface charge distribution for each alumina sample. Cationic and anionic Pd(II) complexes were used to titrate the negative and positive surface charge sites. We find that the adsorption mechanism is primarily controlled by electrostatic effects in that saturation capacities of adsorbed complex showed a correlation with the surface charge density evaluated at the pH used for the adsorption/impregnation experiments.

INTRODUCTION

There are a minimum of three intrinsically connected phenomena that occur during aqueous adsorption/impregnation of catalytic metals onto oxide supports. They are: pH-dependent surface charge development of the oxide, pH-dependent aqueous speciation of the catalytic precursor, and surface adsorption by complexation or coordination.

Active aluminas are extensively used as catalysts, co-catalysts, catalyst supports, and adsorbents. The starting reagents, preparative techniques for these precursors, and their thermal history have a great influence on the physicochemical properties of aluminas (*1–4*). When the first two of these variables is held constant, many of the properties of alumina are controlled by their extent of hydration. If they are heated, some of the adsorbed water is desorbed while some reacts to form hydroxyl groups. At high temperature, these as well as pre-existing hydroxyl groups, gradually condense to eliminate water. Important catalytic properties are associated with sites created on the surface during removal of hydroxyl groups. The active sites have been proposed to involve abnormal exposure of lattice metal (M) ions (*5*) or creation of strained M–O–M linkages on the surface when hydroxyl groups are removed (*6*). Some degree of strain is known to characterize crystal surfaces (*7*). Dehydration thus exposes a strained oxide surface which is abnormally reactive. The strain need not be uniformly distributed over the surface but could be concentrated at relatively few sites (*8*).

The hydroxyl inventory on oxide surfaces is, indeed, complex, and very little is known about the pH-dependent surface charge development of aluminas carrying different inventories of hydroxyl groups. Our laboratory has begun to study these classes of materials with the ultimate goal of modeling

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the adsorption/impregnation process. To characterize the exchange properties of such a series, a simplifying assumption is made: adsorption of ionic solutes is controlled by surface charge. This is not true unless the ionic solute neither hydrolyzes to form hydroxo complexes in solution nor interacts with the surface through any nonelectrostatic bond. These possibilities appear to depend upon the metal ion/oxide system studied and the experimental conditions (*8*, *9*). In this study each has been carefully considered, and Pd(II) ions and alumina, which appear to conform to an electrostatically dominated (adsorption) interaction (*10*), have been chosen.

To date, there have been several studies of catalytic metal ion adsorption on different oxide supports. Coordination reactions between ionic complexes and surface hydroxyl groups have been shown to occur with some mono- and di-valent cations (*9*, *11*, *12*). Brunelle (*13*) has proposed an adsorption model which emphasizes the electrostatic aspects of the adsorption process. Wang and Hall (*14*) have shown that such an electrostatic mechanism can be used to interpret the adsorption of several metal ions on different supports (i.e., TiO_2, Al_2O_3, SiO_2, and MgO). However, since these supports differ greatly in their surface characteristics, they are not amenable to a *systematic* investigation of the adsorption of metal ions from solution. The objective of the present study is to alter systematically the surface characteristics of a single support (Al_2O_3) so that the effect of different hydroxyl inventories can be related to the adsorption properties of Pd(II) ions.

pH-Dependent Surface Charge Development of Alumina

The surface chemistry of an oxide surface in contact with an aqueous solution is determined to a large extent by the protonation/deprotonation of their hydroxyl groups. The equilibria may conveniently be expressed as (*15*):

$$[MOH_2^+] \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [MOH] \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [MOH^-] \quad (1)$$

$$\leftarrow \text{PZC} \rightarrow$$

Decreasing pH Increasing pH.

By appropriate adjustment of pH, the surface may carry a net positive or negative charge. At a specific pH, the surface has zero charge. This point of zero charge (PZC) more correctly defines the situation where there is net zero charge on the surface; it is readily determined by either mass titration or potentiometric titration methods (*16*, *17*). The pH at the PZC has a specific value for each oxide, which depends on the electronic character of the metal–oxygen bond and the stoichiometry of the surface.

The point of zero charge, where $[MOH_2^+]$ equals $[MO^-]$, is related to the two intrinsic acidity constants by the following equation (*18*):

$$\text{PZC} = \frac{(\text{p}K1 + \text{p}K2)}{2}. \quad (2)$$

The fraction of charged sites at the PZC is related to the difference in the two p*K* values (i.e., p*K*2 − p*K*1) (*15*, *19*). The value of p*K*2 − p*K*1 is denoted as DPK (*16*). It has been demonstrated in the literature that the DPK is also an important parameter for determining the pH-dependent distribution of ionizable surface groups (*15*, *20*).

Numerous models have been proposed for describing the surface charge development of metal oxide surfaces. These include the constant capacitance model (*18*), the diffuse layer model (*21*), the Stern model (*22*), and the triple layer model (*9*). Each representation is distinguished by the manner in which it depicts the electric double layer (edl).

We have found that a simple diffuse layer model accurately predicts the adsorbed amounts of ionic solutes (*23*). The diffuse layer model possesses simplicity in that all adsorption is assumed to occur in one surface layer, thus eliminating multiple planes for adsorption at the surface and the associated fitting parameters.

In this study, DPK values are determined by graphical extrapolation combined with a numerical technique according to the procedures described by Noh and Schwarz (*23*). In this method, it is not assumed that the presence of positive or negative sites can be ignored for the pH range where negative or positive sites, respectively, become dominant. Thus, data near the PZC can also be utilized in the extrapolation technique. To avoid any ambiguity in extrapolation of the data to the PZC, a least-squares error regression is applied for a given set of data. Another advantage of the DPK determination by this method is that the value of N_s, the total number of ionizable sites, can also be estimated. The three parameters, PZC, DPK, and N_s, are the requisite data base for evaluating the pH-dependent surface charge development of an alumina surface.

pH-Dependent Aqueous Speciation of Pd(II) Precursors

The chemical state of palladium (II) ions in aqueous media containing chloride and/or ammonium ions depends on the pH and on other solution variables (*24*). The palladium (II) ions form various complex species with chloride and/or ammonium ligands, with electric charges between -2 to $+2$. We studied the adsorption of palladium (II) species on alumina at pH values of 1.4 and 10.8 where palladium (II) species are stable as $PdCl_4^{2-}$ (pH < 2) and $Pd(NH_3)_4^{2+}$ (pH $>$ 8.0), respectively (*24*).

EXPERIMENTAL

A series of alumina supports was prepared by calcining aluminum hydroxide which was prepared by precipitation of aluminum nitrate by ammonia solution. The aluminum nitrate (Aldrich Chemical, ACS Reagent Grade) contained <0.005 wt% insolubles, <0.001 wt% Cl^-, <0.002 wt% Fe, and <0.005 wt% SO_4^{2-}. Traces of these components may have been present in the aluminum hydroxide even after the 10 washings of the gel; no elemental analysis was attempted. The calcination temperatures were varied from 675 to 1175 K. The BET surface areas were determined by nitrogen adsorption using a Quantasorb Apparatus (Quanta Chrome Corp.). The PZC values were determined by mass titration (*16, 17*), which involves finding the asymptotic value of the pH of an oxide/aqueous slurry as the oxide mass content is increased. A Corning pH meter (Model No. 145) was used to measure the pH of the solutions equilibrated for 48 h. The values obtained are summarized in Table 1. Acid–base titrations were carried out to determine the surface charge on the alumina supports. Although PZC values of each alumina could be determined from potentiometric titrations, we favored the PZC results from the mass titration method. The reasons for this are discussed elsewhere by Noh and Schwarz (*16, 23*). For potentiometric titrations, HNO_3, NaOH, and $NaNO_3$ were the acid, base, and electrolyte used. In a typical experiment, 11 vials of 25-ml capacity were filled with 20 ml of $NaNO_3$ electrolyte solution; 200 mg of alumina support was weighed and placed into each bottle. Different amounts of acid or base (HNO_3 or NaOH) were added to each bottle; five bottles for acid, five bottles for base, and one without acid or base. A 10-μl micropipette was used to add the acid or base, and the amounts were recorded. The bottles were then placed on a mechanical shaker and equilibrated for 48 h. They were filtered after equilibration, and pH values for each solution were measured. The pH meter was calibrated at pH 4.0 and 10.0 by standard buffers. These experiments were repeated for different ionic strengths of the $NaNO_3$ electrolyte solution (0.001, 0.01, and 0.1*M*).

For palladium adsorption experiments, a 40–80 mesh fraction of the alumina supports was used. The anionic $PdCl_4^{2-}$ was prepared by dissolving palladium chloride (AR Grade, Johnson Matthey) in excess hydrochloric acid; the final pH of the stock solution was 1.4. The cationic palladium tetramine complex $[Pd(NH_3)_4^{2+}]$ was prepared

TABLE 1

Effect of Calcination Temperature on the PZC, BET Surface Area, Total Number of Ionizable Sites, and DPK Values of Alumina Supports

S. No	Calcination temperature (K)	PZC	Total number of sites/g.cat ($\times 10^{-20}$)	DPK	BET area (m^2/g)
1	675	7.6	17.70	3.10	281.2
2	775	7.8	3.98	3.94	234.9
3	875	8.0	2.60	4.36	185.6
4	975	8.66	3.64	6.63	151.6
5	1075	8.68	3.90	7.84	134.4
6	1175	8.69	2.74	7.00	91.3

by adding required amounts of ammonia solution to a palladium chloride solution; the final pH of the solution was 10.8.

The cation/anionic palladium complex adsorption experiments were carried out by varying the initial palladium concentration at constant initial pH (i.e., isotherm measurements). The starting pH was adjusted by adding the appropriate amounts of 2*N*-hydrochloric acid (for $PdCl_4^{2-}$ adsorption) and ammonia (for $Pd(NH_3)_4^{2+}$ adsorption) solutions to 20 ml of the diluted stock solution before addition of 1g of the alumina support. The amount of HCl added never exceeded 0.2 ml (approximately 5 drops). After stirring for 3 h at room temperature, the contents were filtered and washed with 10 ml of deionized water six times in order to recover the external solution. This extensive washing procedure could remove weakly adsorbed Pd(II) precursors, and such a possibility will be discussed later. The amount absorbed on alumina at equilibrium was calculated from the decrease in the palladium concentration, which was determined by atomic absorption spectroscopy (Perkin Elmer AA Spectrometer Model 2380). The materials were dried under mild conditions (20 h at 350 K).

RESULTS AND DISCUSSION

The BET surface areas, PZCs, total number of ionizable sites, N_s, and DPK values of the alumina supports are summarized in Table 1. Figure 1 shows the effect of calcination temperature on the BET surface areas of the alumina supports. The BET surface areas decreased with an increase in calcination temperature. This can be attributed to the destruction of some of the small pores. Figure 1 also shows the effect of calcination temperature on the PZC of each support. The PZC values increased gradually with calcination temperature. The dependence of PZC on calcination temperature appears to be related to the presence of chemically bound water on the surface of the support material which affects the protonation/deprotonation properties of the hydroxyl groups, thus influencing the behavior of the whole phase. A similar observation was reported for hydrated RuO_2 by Ardizzone *et*

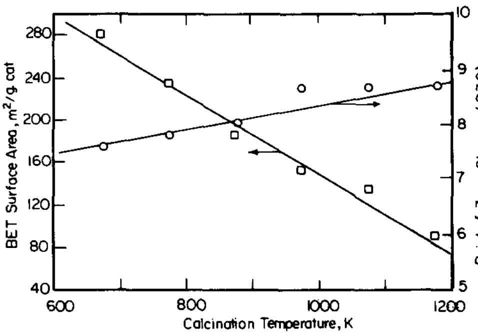

FIG. 1. Effect of calcination temperature on the BET surface area and PZC of the alumina supports: □ = BET surface area, ○ = PZC.

al. (*25*). They reported a gradual increase in PZC with calcination temperature irrespective of the starting material from which the RuO_2 was derived. The PZC values of our alumina samples are in agreement with literature reported values (*25*).

The total number of ionizable sites and DPK values of the alumina supports were calculated according to the method described by Noh and Schwarz (*23*). This is a modified method similar to that proposed by Huang and Stumm (*27*) to determine the DPK values of amphoteric oxide supports. The validity and advantages of this method were described by Noh and Schwarz (*23*). The results are summarized in Table 1. The total number of ionizable sites decreased initially up to a calcination temperature of 875 K and a further increase in calcination temperature led to a gradual increase in total number of sites. The initial decrease in total number of ionizable sites can be attributed to the dehydration/dehydroxylation during calcination. As the calcination temperature increases, there is a possibility for the formation of anionic vacancies. This may be also one of the reasons for the increase in PZC as a function of calcination temperature. The increase of anionic vacancies with calcination temperature was discussed by Knözinger and Ratnasamy (*28*). They reported a gradual decrease of ^{-}OH groups with calcination temperature. Their study also demonstrated a gradual increase of surface coordinately unsaturated oxygen atoms with calcination temperature. Finally, Table 1 shows that the DPK values systematically increase with an increase in calcination temperature.

What is of importance to this study is the number and "strength" of the adsorption sites during impregnation because this factor will control, among other things, the adsorption capacity. This "strength" is assumed to be electrostatic in origin and is reflected by the protonation/deprotonation equilibrium constants which, in turn, are determined by the PZC and DPK. These quantities do vary significantly with calcination temperature when we keep in mind the logarithmic relationship between these equilibrium constants, the PZC and the DPK. We report our results on the basis of grams of catalyst rather than on an area basis because the values of N_s are relatively insensitive to thermal treatment following heating at 675 K, while the BET area decreases monotonically with increasing calcination temperature. The surface density of hydroxyl groups determined by other procedures, reported by Knözinger and Ratnasamy (*28*) for their alumina calcined at 675 K, is 5.5 per 100 Å^2, while we find a value of 6.3 per 100 Å^2 for our alumina calcined at the same temperature. This agreement suggests that our method for evaluating N_s is consistent with other reports in the literature.

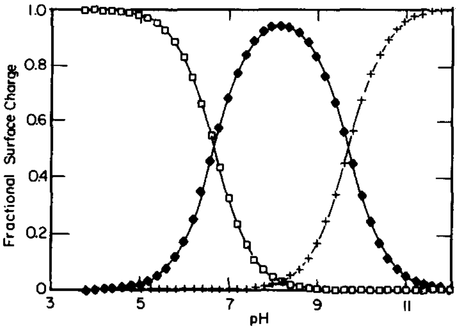

FIG. 2. Surface charge speciation as a function of pH on the alumina support: □, positive species; ◆, neutral; +, negative.

Now, having obtained the PZC, N_s, and DPK values, we calculated the ionization constants, pK1 and pK2, and the surface charge development on each of the alumina supports as a function of pH. The pK1 values ranged from 4.58 to 6.68 and for pK2 from 9.62 to 12.42, depending on calcination temperature. These results are in good agreement with literature reported values for aluminas calcined in the temperature range of this study (*27*).

Figure 2 illustrates the fractional surface charge speciation of a typical alumina support as a function of pH. The intersection points of the surface charge speciation

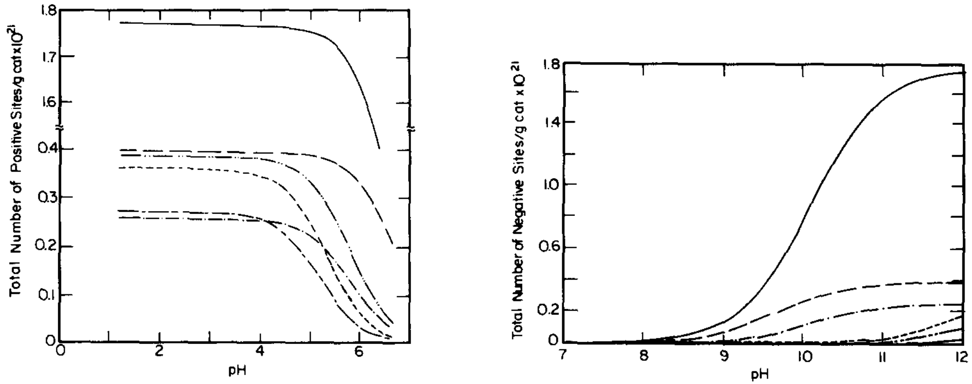

FIG. 3. (a) Total number of positive sites as a function of pH on the alumina supports; (b) total number of negative sites as a function of pH on the alumina supports: ——— = 675 K, — — = 775 K, –·–·– = 875 K, - - - - - = 975 K, –··–··– = 1075 K, –––– = 1175 K.

curves occur at the p$K1$ and p$K2$ values, i.e., surface ionization constants of the support material. From Fig. 2, it is clear that the surface attains a net zero charge at pH (PZC), while at pH < PZC the surface has a net positive charge and at pH > PZC it has a net negative charge. From Fig. 2, it is also noted that at pH values far away from the PZC, i.e., $|(\text{PZC} - \text{pH})| \geq 3$ (*16*), the surface attains either all positive or all negative charge.

Figure 3 was constructed to establish a basis for conducting the Pd(II) adsorption experiments. The fractional surface charge was converted to an absolute number of charge carriers using the N_s values obtained for each support. A portion of the pH-dependent surface charge development for each of the alumina samples is shown in the low-pH (positive charge dominated) and high-pH (negative charge dominated) regions. The vertical cuts at pH 1.4 and 10.8 show that there is a change in the number of positive/negative charge carriers which depends on the sample's calcination temperature. The number of positive sites remains essentially constant after an initial sharp decrease following the 675 K calcination. At pH = 1.4, the number of positive sites is the same as the total number of ionizable sites. On the other hand, the number of negative sites decreases systematically with increasing calcination temperature. At the highest temperatures, we note that there is a substantial number of unionized sites (c.f., Table 1).

If equilibrium adsorption experiments are carried out at these pH values, and if the aqueous speciation of the Pd(II) compound is known, then we would expect that the saturation capacities for Pd(II) adsorption would "track" the number of charge carriers provided adsorption was predominantly controlled by electrostatic interactions. Indeed, we find this to be the case and it is discussed in the next two sections.

PALLADIUM(II) ANIONIC COMPLEX ADSORPTION

Table 2 summarizes the results of $PdCl_4^{2-}$ adsorption and the total number of positive sites for each alumina support as a function of calcination temperature. The total number of positive sites was calculated at a pH of 1.4, since the $PdCl_4^{2-}$ adsorption experiments were carried out at pH = 1.4. The adsorption experiments were performed at this low pH to ensure a simple speciation of the Pd(II) anionic complex. It has been reported (*23*) that at a pH = 2.0 ~40–50% of the $PdCl_4^{2-}$ is converted to $PdCl_3(H_2O)^-$; below this pH, $PdCl_4^{2-}$ is the dominant species. In these experiments, we varied the initial concentration of palladium and care-

TABLE 2

Effect of Calcination Temperature on the Total Number of Positive and Negative Sites and Adsorption Capacities of $PdCl_4^{2-}$ and $Pd(NH_3)_4^{2+}$ on Alumina Supports

S. No	Calcination temperature (K)	Number of positive sites/g.cat ($\times 10^{-20}$)	$PdCl_4^{2-}$ Adsorption capacities, molecules/g ($\times 10^{-20}$)	Langmuir constants lit/mol ($\times 10^{-3}$)	Number of negative sites/g.cat ($\times 10^{-20}$)	$Pd(NH_3)_4^{2+}$ Adsorption capacities, molecules/g ($\times 10^{-20}$)	Langmuir constants lit/mol ($\times 10^{-3}$)
1	675	17.70	1.90	1.30	14.77	0.382	1.60
2	775	3.98	1.23	7.34	3.71	0.369	3.54
3	875	2.60	1.03	5.61	2.12	0.271	3.88
4	975	3.64	1.15	3.37	0.23	0.251	2.56
5	1075	3.90	0.98	9.50	0.06	0.175	3.76
6	1175	2.74	0.79	7.55	0.07	0.158	1.94

fully controlled the initial pH to be constant. In addition, the mass of the support material and volume of palladium were held constant.

Adsorption data at constant pH obey the Langmuir isotherm

$$\frac{q}{s} = \frac{KC}{(1 + KC)}, \qquad (3)$$

where q (molecules/g.cat) is the adsorbed amount at equilibrium, s is the saturation capacity, and C is the equilibrium concentration in solution (mols/lit). This simple equation was chosen because it well represents a broad spectrum of experimental adsorption isotherms. Other isotherms such as Henry, Freundlich, or Tempkin can be described by Eq. (3) over a certain concentration range depending on the values of $KC_{\max}$ (*29*). In addition, the parameters of the Langmuir isotherm, equilibrium constant K (lit/mol) and the adsorption capacity of the supports (molecules/g), have physical meaning in terms of adsorption–desorption equilibria. These parameters were determined from the least-squares analysis of Eq. (3) (correlation coefficients between 0.98–0.99) and are also presented in Table 2. Figure 4 illustrates the anionic adsorption capacities of the alumina supports as a function of calcination temperature. They decrease systematically with increasing thermal treatment, whereas the total number of ionizable sites remains essentially constant with thermal treatment. Such an effect is likely due to the changes in the protonation/deprotonation equilibrium constants resulting in a hydroxyl inventory that is more difficult to protonate for samples treated at higher temperature. The magnitude of the sorption capacities is always less than the total number of positive sites, which at a pH = 1.4 is equal to the total number of sites on the supports which can accommodate $PdCl_4^{2-}$ either by exchange or electrostatic effects. We believe the discrepancies between the total number of positive sites and amount of adsorbed complex are due to the extensive (6 times) washing of the sample after impregnation. Weakly bound Pd(II)

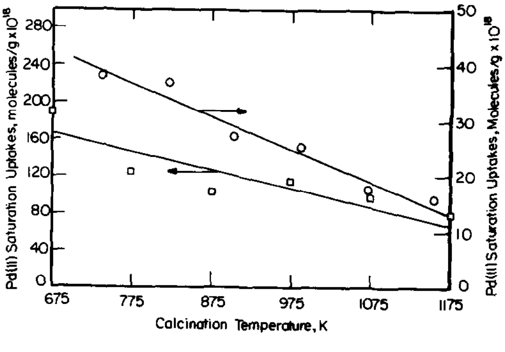

FIG. 4. $PdCl_4^{2-}$ and $Pd(NH_3)_4^{2+}$ saturation capacities on the alumina supports as a function of calcination temperature: □ = $PdCl_4^{2-}$, ○ = $Pd(NH_3)_4^{2+}$.

complexes will be removed in this step. The effects should be greatest at the higher calcination temperatures when the Pd(II)/Al_2O_3 interaction is weaker. Indeed, this is what is found (c.f. Table 2).

The adsorption behavior of hydrous alumina surfaces has been interpreted by the site-binding model (*9, 11, 18, 27, 30*). In this model, the adsorption of metal complexes is assumed to occur through electrostatic attraction. This model has been shown to be reasonable when other oxide–solution reactions such as complex instability and support dissolution are not important (*9*). This model has been used to characterize the adsorption-equilibria of hydrated metal cations and/or metal complex anions on various supports (*9, 11, 18, 27*). Thus, the site-binding model explains the pH dependence of the parameters in the Langmuir adsorption isotherm. The Langmuir constant, K, is an apparent equilibrium constant that includes a term for the electrostatic interaction energy. The intrinsic value of the Langmuir constant can be obtained by extrapolation to the pH (PZC). This results in an expression

$$\log K_{\mathrm{INT}} = \log K + \frac{Ze\phi}{2.3kT} \qquad (4)$$

where Z is a stoichiometric coefficient and ϕ is the surface potential evaluated at the pH of the adsorption measurement. It can be shown that ϕ is linearly related to the difference $|\mathrm{pH} - \mathrm{pH(PZC)}|$ (*9*). In our experiments, the pH was maintained constant, however, the PZCs of each support changed with calcination temperature. The results in Table 1 strongly suggest that these changes were small such that $|\mathrm{pH} - \mathrm{pH(PZC)}|$ should remain essentially constant. Indeed, the results show that K is reasonably constant over the entire range of samples. The exact value of the constant of proportionality between ϕ and $|\mathrm{pH} - \mathrm{pH(PZC)}|$ and the fact that Z depends on pH(*24*) precludes our evaluating K_{INT}. In any case, the results of $PdCl_4^{2-}$ adsorption on our alumina supports are in good agreement with the site-binding model.

PALLADIUM(II) CATION COMPLEX ADSORPTION

Table 2 summarizes the results of $Pd(NH_3)_4^{2+}$ adsorption and the total number of negative sites for each alumina support as a function of calcination temperature. The total number of negative sites was calculated at pH of 10.8. These isotherms were constructed similar to those of $PdCl_4^{2-}$ isotherms, and the Langmuir parameters were calculated accordingly. These values are also given in Table 2. Figure 4 illustrates the cation adsorption capacities of the alumina supports as a function of calcination temperature. The behavior is similar to that for Pd(II) anion adsorption. Here, however, we note that the saturation capacities for the samples calcined at the highest temperatures exceed the total number of negative sites on these supports. Recall, adsorption was carried out at pH = 10.8 and comparing the results given in Table 1 and shown in Fig. 3, we find that there are a considerable number of un-ionized sites on the surface of these aluminas. If transfer to these sites by exchange were to occur, then the apparent "enhanced" adsorption can be explained. Such a situation would, of course, be in violation of the site-binding model. The magnitude of the effects we see appears to be small; we conclude that the site-binding model can adequately represent both Pd(II) anion and cation adsorption.

An analysis similar to that for the anion adsorption results can be applied here. We see that the apparent values of K are approximately constant for all the samples. Finally, the values of K are consistently lower in this case compared to those for anion adsorption. When adsorption is strong, K is larger, and we see from the results in Table 2 that the sorption capacity is higher by ~ a factor of 5–6 for the Pd(II) anions. These findings are consistent with those reported by Contescu and Vass (*24*).

$Pd(NH_3)_4^{2+}$ adsorption experiments were also carried out as a function of pH on a single alumina support (calcined at 975 K) in order to further demonstrate that the adsorption process is principally controlled by electrostatic effects. These adsorption experiments were carried out at pH values ranging from 8.5 to 10.8, and the mass of the support, palladium concentration, and total volume of solution were maintained constant. The palladium concentration used was slightly less than that used to achieve saturation at pH = 10.8. The adsorption amounts and total number of negative sites are summarized in Table 3 as a function of pH. It is found that the number of negative sites as well as the palladium adsorbed amounts increased with increasing pH. Figure 5 illustrates this effect of pH on $Pd(NH_3)_4^{2+}$ adsorption. These results show that the $Pd(NH_3)_4^{2+}$ adsorption is proportional to the number of negative sites. As the pH is lowered, the number of negative sites decrease and there is a corresponding increase in the number of un-ionized sites. The apparent "enhanced" adsorption, which increases with decreasing pH, is ascribed to deviations from the site-binding model due to direct exchange with hydroxyl groups. The PZC of this alumina is 8.66 (Table 1). If adsorption is electrostatically controlled, at the PZC the surface attains a net zero charge. From Table 3 and Fig. 5, it is clear that at pH = 8.66, the palladium adsorption is zero.

TABLE 3

Effect of pH on the Surface Charge Development and $Pd(NH_3)_4^{2+}$ Adsorption on Alumina (Calcined at 975 K)

S. No	pH	Total number of negative sites/g.cat ($\times 10^{-18}$)	$Pd(NH_3)_4^{2+}$ Adsorption molecules/g.cat ($\times 10^{-18}$)
1	8.5	0.038	*
2	9.5	1.228	3.44
3	10.0	3.857	9.26
4	10.8	23.03	24.50

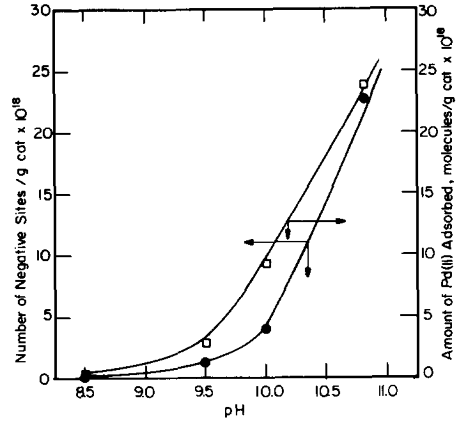

FIG. 5. Effect of pH on the adsorption of $Pd(NH_3)_4^{2+}$ and surface charge speciation on alumina support calcined at 975 K: □ = Pd(II) adsorption amounts, ● = positive sites.

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