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Anion Adsorption on Alumina

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A series of inert metal complex anions with net charges of −1 to −3 have been used to examine the anion adsorption process on alumina. We have found that this process involves the simultaneous coadsorption of both hydrogen ion (from added acid) and complex anion. Adsorption is fast and depends only slightly upon changes in solution ionic strength and complex anion concentration. The adsorption process is also reversible with the addition of base. These findings are interpreted on a molecular level in the following way. A surface-bound hydroxyl group is protonated, thereby creating a positively charged surface group which can bind a complex anion by electrostatic attraction. The addition of base removes the positively charged surface group by reaction with the bound proton and releases the complex anion. This work implies that one may vary a catalyst metal loading simply by controlling the amount of acid present in a preparation where an inert metal complex anion is employed.

INTRODUCTION

Catalyst preparation is one of the least understood areas of heterogeneous catalysis, although it is recognized that preparative effects can have a major impact on finished catalyst properties. Consequently, as improvements in catalytic performance are sought, more emphasis is being placed on the study of catalyst preparation and how preparative variables affect catalyst properties. The initial interaction of metal complexes in solution with alumina has received some attention (*1–10*), but the details of solution adsorption processes involved in a typical catalyst preparation remain unclear.

A general consideration of the chemical properties of alumina and metal complexes suggest that two basic processes can occur. Adsorption may result either by an ion exchange or by a direct reaction mechanism. The former process should depend primarily upon the charge of the metal complex, the latter upon its chemical reactivity. Both process will show considerable dependence upon the state of the alumina surface, which may be varied by pretreatment, and upon solution parameters such as pH.

This study attempts to focus on the ion exchange process which occurs in the absence of any direct chemical reaction between complex and alumina. The properties of the alumina are held constant by a uniform, mild pretreatment step, and the choice of complexes is dictated by the need for extreme chemical inertness. Typically, noble metal catalysts are prepared from solutions of anionic complexes at low pH, conditions under which anion exchange is likely to occur. Thus several anionic complexes were selected for studies of their adsorption by alumina. The adsorption behavior of alumina in an acidic aqueous suspension has been examined (*11–13*) and the pH-dependent features of the alumina surface in contact with acid have been carefully studied by Ahmed (*14*). It was pointed out in Ahmed's work that anion adsorption on alumina can occur by a coupled process involving the adsorption of both protons and anions. This idea is clearly borne out by this work and its implications for catalyst preparation will be developed in the following sections.

METHODS

A Cary 14 uv/visible spectrophotometer was used for all spectroscopic measure-

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ments. An Orion Model 801 pH meter, equipped with a standard pH electrode, was used for all pH measurements. The meter was calibrated with standard buffers of pH values 7.00 and 4.01 before each experiment.

The complexes $K_3Co(CN)_6$ (*15*), $KCo(EDTA) \cdot 2H_2O$ (*16*) (EDTA = ethylenediaminetetraacetate, $C_{10}H_{12}N_2O_8^{-4}$), $K_3CoOx_3 \cdot 3H_2O$ (*17*) (Ox = oxalate, $C_2O_4^{-2}$), $K_3CrOx_3 \cdot 3H_2O$ (*13*), and $K_3RhOx_3 \cdot H_2O$ (*18*) were prepared and purified by literature procedures. The complex $K_2Pt(CN)_4$ was purchased from Alfa.

The alumina used in this study was prepared by grinding Grace LBD low-density 3.2-mm alumina spheres and collecting the −48 + 65 mesh (200–300-μm) fraction. This material was washed and hydrated by suspension in boiling deionized water for 24 h. The washing procedure was repeated twice more with fresh deionized water which eliminated most of the very fine material on the larger particles and assured a neutral reaction to water. The washed material was dried for several days in flowing room-temperature air. The BET surface area was found to be 122 m^2/g.

Solutions of acid were prepared by dilution of the reagent-grade concentrated acids and standardized by titration against potassium carbonate. Solutions of the complexes at various concentrations were prepared gravimetrically, and their extinction coefficients were determined. All complexes were found to obey Beer's Law in the concentration range used in the adsorption experiments. Standard quantitative procedures were followed for all manipulations and spectroscopic work.

The adsorption experiments were performed according to the following general procedure. A solution of the complex was prepared (0.04–0.005 *M*) in neutral deionized water and an aliquot (25–50 ml) added to a 2.000-g sample of alumina. The quantity of complex added was usually 25–50% more than that adsorbed. The mixture was stirred for 10 min and allowed to settle for 2 min. A sample (0.5–1.5 ml) of solution was withdrawn, filtered with a 0.2-μm filter, and its visible spectrum was recorded. An aliquot of acid (0.5 ml) was then added to the original slurry, and the stirring–settling–sampling sequence was repeated. This procedure was followed with each subsequent addition of acid.

Ionic strength adjustments in the series of experiments with $Co(CN)_6^{-3}$ were made by the addition of reagent-grade sodium perchlorate to the solution of the complex. No changes in extinction coefficient or band positions were noted over the ionic strength range of ~0.05–0.5 *M*.

Transmission visible spectra of the complexes adsorbed on alumina were obtained in the following way. After the last addition of acid in the adsorption experiment, the alumina was allowed to settle and most of the solution was decanted. The solid was washed three times each with deionized water, acetone, and 1,2-dichloroethane. The sample was shaken for 10 min with each wash. A 1,2-dichloroethane slurry of the solid was loaded into a 1-mm-rectangular quartz cell and allowed to settle. The spectrum of the sample was run against a matched reference cell containing blank alumina which had been washed in a similar fashion. This method gave a useful wavelength range of 650–350 nm. Immersion of the sample in 1,2-dichloroethane, which has a refractive index close to that of alumina, minimized scattering of the light beam to an effective blank absorbance of ~0.2.

RESULTS

General Features of Adsorption

The adsorption of inert metal complex anions depends in a relatively simple fashion on the amount of acid present in the adsorption system. Figure 1 illustrates the adsorption of $Co(CN)_6^{-3}$ on alumina as a function of the amount of $HClO_4$ added. Each point on the curve represents a measurement taken after 12 min of contact between the solution and alumina. Qualita-

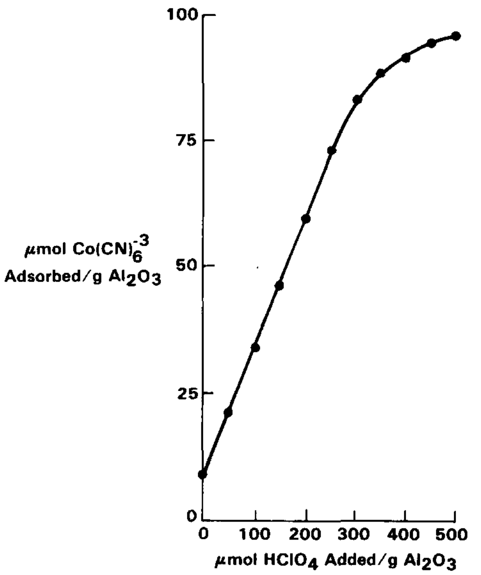

FIG. 1. The adsorption of $Co(CN)_6^{-3}$ vs added $HClO_4$. Initial $Co(CN)_6^{-3}$ concentration = 10^{-2} *M*.

tive rate measurements indicate that effective adsorption equilibrium is reached in less than 10 min and remains stable for several hours. This was found to be true even at very low concentrations (<0.001 *M*) and suggests that the curve in Fig. 1 is free of any features attributable to either adsorption or diffusion kinetic parameters.

The adsorption curve has both a linear and a curved region. The linear region, occurring with small amounts of added $HClO_4$ and both $Co(CN)_6^{-3}$ and alumina surface in excess, indicates a stoichiometric adsorption of $Co(CN)_6^{-3}$ as a function of acid added, the slope giving a molar ratio of 0.28 mmol $Co(CN)_6^{-3}$ adsorbed per millimole of $HClO_4$ added. The nonlinear region of the adsorption curve, occurring with larger amounts of added acid, seems to be due to a limiting of surface area for adsorption since $Co(CN)_6^{-3}$ is still in excess. Adsorption drops nearly to zero on further small additions of acid, although some further increase in adsorption (5–10%) can be obtained on addition of a large amount of acid. Interpretation of the nonlinear region is difficult because the kinetics of rearrangement of the adsorbed anion may control maximum surface packing and also because the alumina surface will be attacked at these higher acid concentrations. One might conclude that the decrease in adsorption is due to surface saturation, and that the amount of $Co(CN)_6^{-3}$ adsorbed in this region gives only a qualitative measure of the amount required for surface saturation.

The behavior of the solution pH in the presence and absence of the adsorption of $Co(CN)_6^{-3}$ is shown in Fig. 2. This figure illustrates the pH changes that occur in the acid/alumina and acid/alumina/anion systems as small amounts of acid are added. The corresponding changes that occur when acid is added to pure water are included for comparison. It is clear from these curves that the presence of alumina buffers the solution pH change due to some adsorption of the acid. The addition of an adsorbable anion such as $Co(CN)_6^{-3}$ increases this buffering action and suggests that the presence of such an anion increases the capacity of alumina to adsorb acid. This is consistent with Fig. 1 and indicates the coupling of the anion adsorption process with acid adsorption by alumina. Addi-

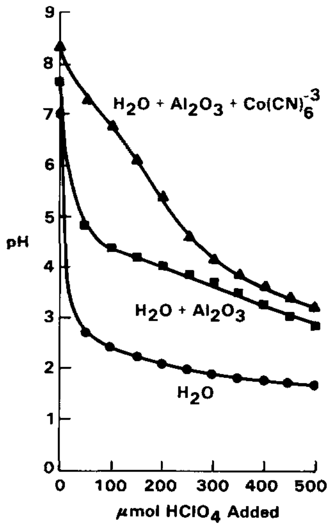

FIG. 2. pH changes in the H_2O–Al_2O_3–$Co(CN)_6^{-3}$ system vs added $HClO_4$. Total volume 25.00 ml, 1.00 g Al_2O_3, 10^{-2} *M* $Co(CN)_6^{-3}$.

tional qualitative indications of the coadsorption of acid and anion are that acid adsorption by alumina is reversible when the acidified alumina is washed with enough water. In the combined acid/anion system, neither acid nor anion can be removed by a similar water wash. It appears that a larger ion with greater negative charge dramatically stabilizes the adsorbed state, vide infra.

The adsorption of $Co(CN)_6^{-3}$ is, however, reversible if a base such as KOH is added in an amount equivalent to that of acid used in the adsorption experiment. Figure 3 illustrates the reversibility on addition of base. This experiment was conducted by first adsorbing $Co(CN)_6^{-3}$ by adding acid in a fashion similar to that in Fig. 1. After 250 μmol $HClO_4$ had been added, the adsorption was reversed by adding small aliquots of KOH. It is clear from Fig. 3 that $Co(CN)_6^{-3}$ readily desorbs from alumina as acid is removed from the system. The slopes of the two lines are equal within experimental error and are of opposite sign. This, coupled with the above observations, indicates that adsorption is a reversible, linear function of the total acid present in the system.

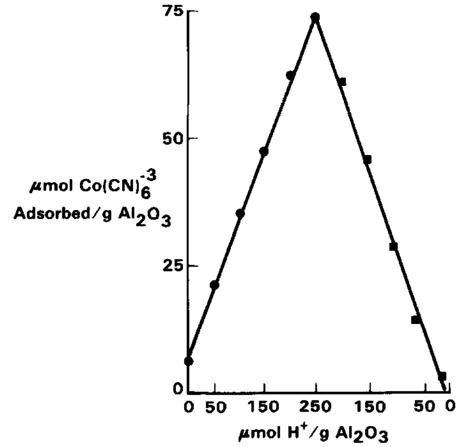

FIG. 3. The reversibility of $Co(CN)_6^{-3}$ adsorption on the addition of base.

Adsorption Dependence on Solution Parameters

The method used to conduct the adsorption experiment shown in Fig. 1 necessarily results in changes in both complex anion concentration and solution ionic strength. A series of experiments were performed to evaluate the effect of complex concentration on the adsorption of $Co(CN)_6^{-3}$ by varying the initial concentration of $Co(CN)_6^{-3}$ while holding the amount of alumina and $HClO_4$ constant. This results in varying equilibrium concentrations of $Co(CN)_6^{-3}$ after adsorption occurs; the results are presented in Fig. 4 as a plot of the amount of $Co(CN)_6^{-3}$ adsorbed versus the equilibrium concentration of $Co(CN)_6^{-3}$. The plot suggests a slight positive dependence of the amount adsorbed on the concentration of $Co(CN)_6^{-3}$ since the least-squares slope is 0.184 mmol adsorbed/M. The dependence of the amount adsorbed is quite small over the concentration range covered in obtaining data for Fig. 1 (0.01–0.002 M), suggesting that Fig. 1 has no features attributable to changing $Co(CN)_6^{-3}$ concentration.

The decreasing anion concentration that occurs during the adsorption experiment results in decreasing ionic strength. For the experiment illustrated in Fig. 1, the ionic strength decreases smoothly from 0.06 to 0.045 M. Since changing ionic strength (μ) may exert subtle effects on the adsorption process, a series of experiments were performed to determine what these effects might be. The changes in the adsorption of $Co(CN)_6^{-3}$ in the presence of varying amounts of added $NaClO_4$ are illustrated in Fig. 5. The slope of the linear region of the system with $\mu = 0.25M$ is ~10% less than that for the natural system with $\mu = 0.06M$; thus this region of the adsorption curve is only mildly affected by increasing μ. The nonlinear region is much more sensitive to changing ionic strength, giving substantially lower estimates of the amount of $Co(CN)_6^{-3}$ required for surface saturation.

These effects are not interpretable in any quantitative fashion; one can rationalize

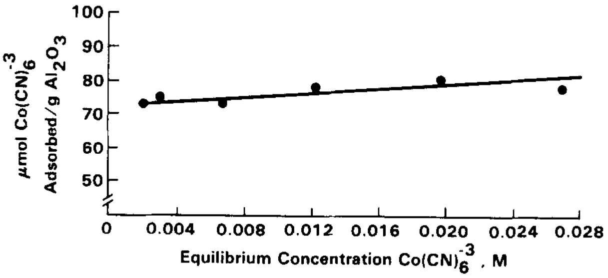

FIG. 4. Adsorption dependence on the equilibrium concentration of $Co(CN)_6^{-3}$.

that variations in the adsorption curve reflect either changes in the solution structure of $Co(CN)_6^{-3}$ or competition between ClO_4^-, present in high concentration, and $Co(CN)_6^{-3}$ for adsorption sites. Either process will result in changes in both adsorption stoichiometry and surface saturation. These effects are evident only at relatively high ionic strength or ClO_4^- concentration. Changing the competing anion to Cl^- by running the adsorption experiment with HCl (at the natural ionic strength) gives results identical with those when $HClO_4$ is used. This is to be expected since a −1 ion is not likely to effectively compete with a −3 ion (at equal concentrations) for adsorption sites.

Adsorption Dependence on Anion Charge

The adsorption behavior of several inert anions of varying charge is illustrated in Fig. 6, and the slope of the linear portion of each curve is given in Table 1. It appears that a characteristic range of slope values can be specified based on charge. Thus for −3 ions, the slopes fall in the range of 0.21–0.30 mmol adsorbed per millimole of $HClO_4$ added. Similar ranges for −2 and −1 ions may occur around 0.38 and 0.56, respectively. However, it is clear from the range of values observed for the isostructural series of MOx_3^{-3} [M = Cr(III), Co(III), Rh(III)] ions that factors other than charge have some effect on adsorption. Ionic charge density and its effect on the size of

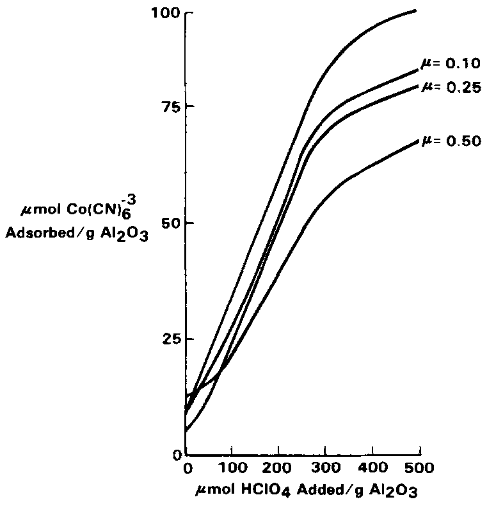

FIG. 5. The dependence of $Co(CN)_6^{-3}$ adsorption on ionic strength (μ, M). $NaClO_4$ added to adjust ionic strength.

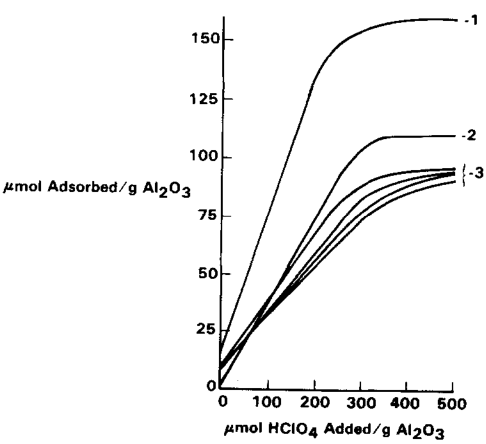

FIG. 6. Adsorption vs charge for several ions (charge:ion). −1: $Co(EDTA)^-$; −2: $Pt(CN)_4^2$; −3 (in order of decreasing slope): $RhOx_3^{-3}$, $Co(CN)_6^{-3}$, $CoOx_3^{-3}$, $CrOx_3^{-3}$. Initial complex concentrations = $10^{-2}\,M$.

the hydration sphere about an ion in solution should have an important effect on the adsorption process. Consequently, experiments with other anions of different sizes in each charge group may eliminate any distinct differences in the adsorption behavior between charge groups.

The question of competition for adsorption sites between the acid anion and complex anion becomes more important when the charge of the acid anion is equal to or larger than that of the complex anion. Thus the adsorption of singly charged Co $(EDTA)^-$ may be dependent on the anion of the acid used in the adsorption experiment. To test for such a dependence, the adsorption of $Co(EDTA)^-$ was measured using HCl and H_2SO_4 as the added acids. The results of these experiments are compared with those obtained with $HClO_4$ in Fig. 7. Except for some minor deviations, the adsorption behavior of $Co(EDTA)^-$ in the presence of Cl^- or ClO_4^- is equivalent. This suggests that any competition, if present, is relatively independent of changes in the acid anion provided that the charge is not changed. The adsorption behavior in the presence of SO_4^{-2}, however, is dramatically different from that observed in the presence of either Cl^- or ClO_4^-. The adsorption of $Co(EDTA)^-$ is suppressed at low SO_4^{-2} concentrations and becomes negative ($Co(EDTA)^-$ desorbs) at higher SO_4^{-2} concentrations. This negative adsorption is most likely due to a direct displacement of adsorbed $Co(EDTA)^-$ by SO_4^{-2} as the SO_4^{-2} concentration is increased.

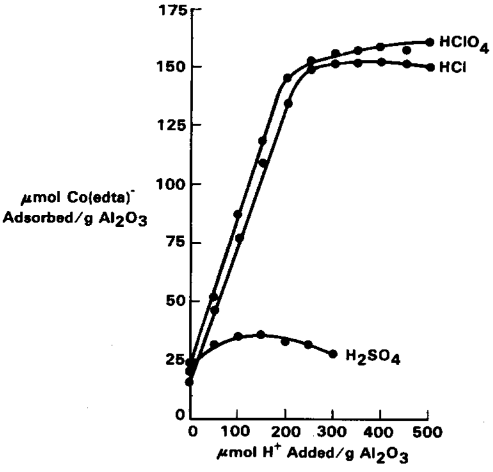

FIG. 7. The dependence of $Co(EDTA)^-$ adsorption on the type of acid added.

Adsorption of cationic or neutral inert cobalt complexes such as $Co(NH_3)_6^{+3}$, $Co(NH)_3)_5Br^{+2}$, or $Co(NH_3)_3(NO_2)_3$ does not occur under the conditions of these experiments. This is consistent with the generally known behavior of alumina in that significant cation exchange occurs only at high pH (>9). For the specific case of $Co(NH_3)_6^{+3}$, no detectable adsorption occurred over a period of 2 weeks at pH 9–12.

Characterization of the Adsorbed State

The visible spectra of some of the anions from Fig. 6 in both the solution and adsorbed state are compared in Fig. 8. The similarity between the adsorbed and solid-state spectra shows that these ions are adsorbed without specific chemical reaction since the primary coordination sphere about each remains intact. Peak positions and peak intensity ratios for those anions with two peaks remain essentially unchanged. Peak widths do change on adsorption since vibrational freedom is increased by the close association of anion and surface, resulting in a broadening of the adsorption band. In general, there is a remarkable similarity between the spectra of solution and adsorbed ions; thus the assumption that these ions undergo adsorption without reaction, implicit throughout the discussion of the results, is clearly justified. This point is illustrated further when the behavior of these inert anions is compared with a more reactive anion like $PtOx_2^{-2}$, whose spectrum displays peak shifts of 80 nm on adsorption. This latter system is mentioned here only to emphasize a crucial point; a subsequent paper will deal with the question of complex ion reactivity.

DISCUSSION

The experimental results are readily interpreted on a molecular level by reactions 1 and 2, where the hydroxyl groups are attached to the alumina surface.

$$\overset{|}{\underset{|}{\mathrm{Al}}} - \mathrm{OH} + \mathrm{H}^+ \leftrightarrow \overset{|}{\underset{|}{\mathrm{Al}}} - \mathrm{OH_2}^+, \tag{1}$$

$$y\ \overset{|}{\underset{|}{\mathrm{Al}}} - \mathrm{OH_2}^+ + \mathrm{M}^{-n} \leftrightarrow (\overset{|}{\underset{|}{\mathrm{Al}}} - \mathrm{OH_2}^+)_y\mathrm{M}^{-n}. \tag{2}$$

The formation of a positively charged surface group occurs when a surface hydroxyl group is protonated on addition of acid (reaction 1). This gives rise to the buffering action observed on addition of acid to an aqueous slurry of alumina. The presence of an anionic species in solution results in the formation of an electrostatically bound state which can be disrupted by the loss of the positive surface group. This can occur with the addition of base. The stability of the surface-anion pairing seems to be enhanced by increasing size and charge of the adsorbed anion, since simple anions like Cl^- or $\mathrm{ClO_4}^-$ do not lead to strong adsorption of the corresponding acids. The acid–base properties of the alumina surface have been well documented in previous work on the adsorption of cations by alumina (*6, 7, 11–14*), although its anion adsorption properties have generally been ignored.

The stoichiometry of the overall process is given by the slope of the linear region of the adsorption curve. Ideally, y should be equal to n in reaction 2. However, the partitioning of added acid between surface and solution effectively lowers the amount of anion adsorbed for each addition of acid. Thus the observed stoichiometry will depend upon how well the electrostatic properties of a particular ion affect the partitioning of the acid. Put another way, the equilibrium constant for reaction 2 will dominate the observed adsorption stoichiometry. As indicated by the results for the series of ions $\mathrm{MOx_3}^{-3}$ [M = Co(III), Cr(III), Rh(III)], this effect can have a significant impact on the stoichiometry within a group of anions of fixed charge.

At higher surface coverages the stoichiometric adsorption process breaks down and adsorption begins to decrease as further increments of acid are added. Packing of the adsorbed anion on the surface is probably controlling here since a significant fraction of the surface is covered by adsorbed anions. If one takes the amount of $\mathrm{Co(CN)_6}^{-3}$ adsorbed from the last point in Fig. 1, assuming that the anion is a hard sphere with a circular projection on a solid surface of 50 Å^2, then 23% of the available surface is covered by this anion. It is certain that an anion of −3 charge will carry a secondary hydration sphere of at least one layer of water molecules, thus increasing its effective size considerably. In the case of $\mathrm{Co(CN)_6}^{-3}$, consideration of a single layer of water molecules will lead to a calculated surface coverage of at least 50%. Electrostatic repulsion will further decrease packing densities of adsorbed anions such that near "monolayer" coverage for a given anion may be realized.

This work suggests a number of different ways that anion adsorption could affect catalyst preparation:

1. Since anion adsorption appears to be a nearly stoichiometric process, catalyst loadings can be readily controlled by the addition of a stoichiometric amount of acid. This would be an easier, more accurate method than the more conventional ap-

TABLE 1

Slopes of the Linear Regions for Anions in Fig. 6

Anion	Slope[a]
$Co(CN)_6^{-3}$	0.28
$CoOx_3^{-3}$	0.23
$CrOx_3^{-3}$	0.22
$RhOx_3^{-3}$	0.30
$Pt(CN)_4^{-2}$	0.38
$Co(EDTA)^-$	0.56

[a] Units: mmol adsorbed/mmol $HClO_4$ added.

proach of trying to control the pH of an aqueous alumina slurry.

2. The preparation of catalysts from acid salts, i.e., Pt/Al_2O_3 from H_2PtCl_6, must be carried out with some care. Since H_2PtCl_6 serves as a source of H^+, any significant excess of H_2PtCl_6 in the preparation will lead to a catalyst saturated with $PtCl_6^{-2}$. The loading of such a catalyst would be independent of the solution concentration of H_2PtCl_6, as was observed by Maatman *et al.* (*10*).

3. The mixing of two or more metal components in the preparation of a multimetallic catalyst will be very sensitive to the charges of the individual ions in the impregnating solution. Segragation of ions of differing charges may occur during adsorption or, if particularly high loadings are desired, the more highly charged ion may be preferentially adsorbed. Ideally, all metal complexes in such a system should bear the same charge and be of the same complex type. For example, a bimetallic Co/Rh catalyst could be prepared from mixtures of the oxalato complexes, $CoOx_3^{-3}$ and $RhOx_3^{-3}$. We have observed the equal adsorption of both $CrOx_3^{-3}$ and $CoOx_3^{-3}$ from solutions containing both these ions, as well as the displacement of adsorbed $Co(EDTA)^-$ by $CoOx_3^{-3}$.

4. Maximum catalyst loadings are determined by the physical size and charge of the adsorbing metal complex. Attempts to

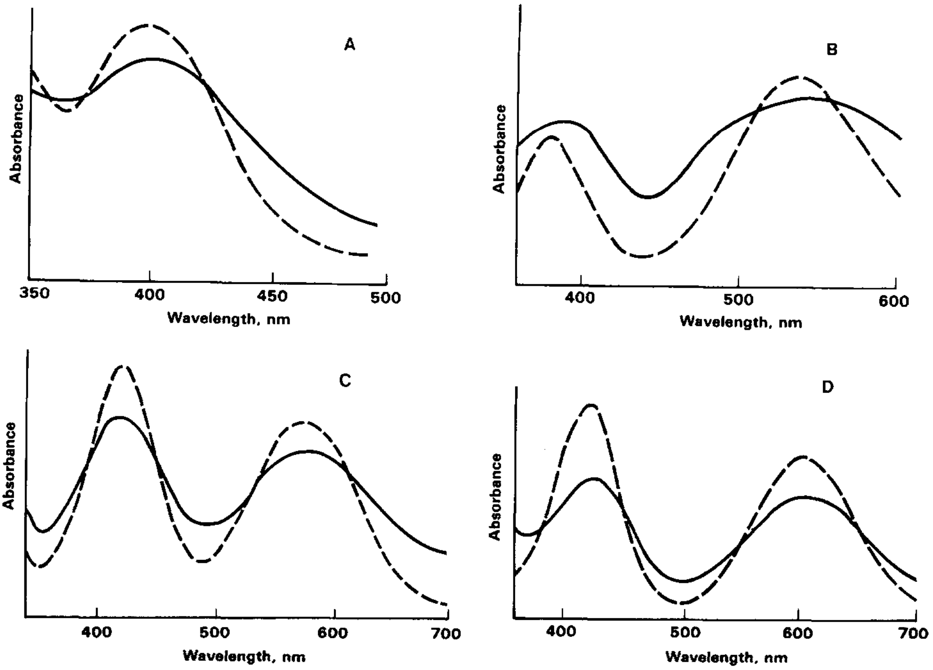

FIG. 8. The adsorbed (——) and solution (- - -) state visible spectra of (A) $RhOx_3^{-3}$, (B) $Co(EDTA)^-$, (C) $CrOx_3^{-3}$, and (D) $CoOx_3^{-3}$.

achieve higher loadings may result in two types of adsorbed metal complexes, one strongly adsorbed at near monolayer coverage and another in more weakly held overlayers. The latter would more likely lead to lower dispersions in the finished catalyst.

CONCLUSION

The anion adsorption process occurring on alumina appears to be relatively simple when examined in the absence of complicating chemical reactions and variations in the surface state of alumina. The parameters which exert the most impact on adsorption are anion charge and the amount of acid present, both of which are easily controlled. The use of the nonreactive anion adsorption process in catalyst preparations offers a high degree of control over finished catalyst loadings simply by the addition of the correct amount of acid corresponding to the desired level of anion adsorption. After adsorption, the catalyst can be washed to remove undesirable ions before a calcination step which may lead to their incorporation into the support.

On a more basic level, the specific knowledge of the anion adsorption process and the factors which affect it recommend its use as a solution technique for the study of the effects of pretreatment on the adsorption properties of alumina.

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