JOURNAL OF CATALYSIS 78, 88–95 (1982)

Differential Cation Exchange Capacity (DCEC) of Nickel Supported on Silica–Aluminas

W. TSAI,* J. A. SCHWARZ,*[,1] AND C. T. DRISCOLL†

*Department of Chemical Engineering and Materials Science and †Department of Civil Engineering, Syracuse University, Syracuse, New York 13210

Received February 8, 1982; revised June 17, 1982

Differential cation exchange capacity (DCEC) is the difference between the cation exchange capacity of a metal-supported catalyst and the support alone. DCEC values of two nickel catalysts (0.88 and 10% by weight) on a series of silica–alumina supports have been measured. For alumina-rich samples, DCEC values for both weight loadings of nickel are comparable. The silica-rich samples were different, with the lower weight loaded catalysts exhibiting higher DCEC values than the 10% nickel catalysts. The similarities and differences shown by this metal–support system can be traced to the chemical environment of the catalyst preparation. Adsorption and reaction studies are in accord with the reported DCEC values. This technique appears to be a potentially useful method for disclosing metal–support interactions.

INTRODUCTION

Historically, cation exchange capacity (CEC) measurements have been used to study catalyst acidity (*1*) and its application to silica–alumina cracking catalysts is well-documented (*2*). We have used the displacement of a surface saturated with sodium by potassium in a buffered solution (pH 7) to obtain the CEC of a homologous series of silica–alumina supports and nickel catalysts derived from these supports. We refer to the difference between these values as the differential cation exchange capacity (DCEC).

Cation exchange capacity arises from the existance of surface charge. For dispersed metal catalysts, one must consider the origins of surface charge for both the support and the metal-supported catalyst. In the former case, there are two mechanisms by which charge might originate on a surface. The first is due to pH-dependent charge (*3*). Here, surface functional sites associated with oxides may protonate (Brønsted acidic site) or deprotonate (Brønsted basic site) with decreases or increases in solution pH, respectively. Dehydration may cause these functional groups to be converted to Lewis sites. The magnitude of pH dependent charge is a function of surface characteristics as well as solution composition. To evaluate the nature of pH-dependent surface charge it is useful to define the terms zero point of charge (ZPC) and isoelectric point of the solid (IEP(s)) (*3*). ZPC designates the pH of a system, however complex, at which there is no net charge on solid particles. If surface charge is regulated only by the protonation/deprotonation of a simple oxide system, then ZPC may be termed (IEP(s)). When the pH of the solution is below the ZPC the surface will exhibit a positive charge, conversely when the solution pH is greater than the ZPC of the oxide of interest, the surface will be negatively charged.

Surface charge may be constant, which results from isomorphic substitution of a foreign cation into the lattice of an oxide. An example of this would be the incorporation of aluminum into the silica tetrahedron structure during the preparation of a silica–alumina catalyst.

Surface charge may develop during formation of metal-supported catalysts due to

---

[1] To whom correspondence should be addressed.

0021-9517/82/110088-08$02.00/0

isomorphic substitution. For example, the elevated temperatures, that accompany the catalyst reduction phase, might facilitate isomorphic substitution. Alternatively, the solution through which the metal is applied may be acidic, resulting in a partial dissolution of the support. Upon increases in temperature (due to reduction) the support could reform, and the initial disruption (dissolution) of the support may enhance incorporation of the metal into the support lattice.

If incorporation occurs in the *primary layer* defined by the support surface and the "underside" of the metal crystallite, the accessibility from the gas phase of these support–metal interaction sites is unlikely. However, to preserve overall electroneutrality, a layer of counterions, which is termed the ion-exchange capacity, will associate with the charged surfaces. Because surface charge is generally negative, cation-exchange capacity is generally of particular interest. Exchange capacity may either increase or decrease for a metal-supported catalyst when compared with the support alone. It is not possible to directly relate the measured DCEC to an extent of interaction. That is, a quantitative measure of the *amount* of metal substituted into the support lattice cannot be determined because the area of the interaction zone is unknown. Typical gas phase adsorption cannot be used because of the unaccessibility of the sites. In considering the metal-supported catalyst, therefore, either oxide protonation/deprotonation (support function) or isomorphic substitutions (metal and/or support function) may result in surface charge. Thus the DCEC technique provides a method of disclosing potential support–metal interactions, however, it is not possible to assess the origin of charge (pH-dependent charge or constant charge due to isomorphic substitution).

In the sections to follow we will first describe the procedures used for catalyst preparation in this study. The wide range of support compositions resulted in systematic changes in DCEC measurements. These changes may be due in part to the environment of the support during generation of the catalyst. Environmental variations during preparation of conventional catalysts are usually unavoidable and more than likely go unnoticed. DCEC results for two weight loadings of nickel catalysts will be presented. The effect of support composition and metal loading will be discussed. To our knowledge, no catalytic information is available from catalysts which cover as wide a range of support compositions and extent of metal loading as we report here. However, limited correlations can be made with adsorption and reaction studies and these will be made.

EXPERIMENTAL

Seven silica–alumina catalysts ranging in composition from 0 to 100% silica were obtained from Dr. D. A. Hickson of the Chevron Research Company. The physico chemical properties of the received catalysts are reported in Table 1. The procedure for their preparation has been presented previously (*4*). Samples were calcined at Chevron at 1000°F.

The CEC values of both the support and the metal supported catalysts were measured after a standard heat pretreatment. The heat treatment was done in a controlled gas oven under an inert nitrogen atmosphere at a gas flow rate of 60 cm^3/min. The same procedures were followed consistently for each sample since it was observed that CEC values of the catalysts vary with the temperature and the duration of the heating period. This was probably due to the varying degrees of hydration of the support. Provided the standard heat pretreatment was followed the reproduceability was extremely good for a given sample (see later discussion) and thus DCEC values for the metal-supported catalysts could be compared as a function of support composition and metal loading.

The catalysts were prepared utilizing the incipient wetness technique with $Ni(NO_3)_2$

TABLE 1

Physicochemical Properties of Silica–Alumina Supports

Nominal Al_2O_3 (wt%)	Analyzed Al_2O_3 (wt%)	Analyzed sodium (wt%)	Analyzed chloride (wt%)	Surface area (m^2/g)	Pore volume (ml/g)	Skeletal density (g/cm^3)
100	99.38	0.003–0.010	0.37	341–346	0.311	3.191–3.2
90	88.45	0.005–0.020	0.13	437–446	0.460	2.894
75	76.80	0.009–0.020	0.03	402–431	0.268	2.776
66	68.63	0.017–0.02	<0.01	315–373	0.227	2.673–2.678
25	26.09	0.019–0.03	<0.01	405–425	0.569	2.407–2.413
10	11.19	0.031–0.04	<0.01	524–548	0.754	2.292–2.316
0	0.436	0.008–0.02	<0.01	378–385	0.891	2.217

solution. Prior to impregnation, the supports were calcined at 550°C for 3 hr. Two weight loadings, 10 and 0.88% by weight of nickel were prepared. The latter loading corresponded to 150 μmol of metal/g of support. The minimum amount of exchangeable sodium (CEC) was found to correspond to ~ 150 μmol/g of support. Thus, if metal cations interacted specifically with exchange sites, it was likely that these effects would be observed at this lower loading. Merrill *et al.* (*5*) reported that a quasi-equilibrium was reached within 2–3 hr for the adsorption of Ni^{2+} on alumina, therefore a 5-hr impregnation was chosen for this study. The solutions were equilibrated at 20°C during impregnation and continuously agitated by a mechanical stirrer. The pHs of the impregnating solutions were found to be 1.93 for the 10% weight loading and 3.84 for the 0.88% weight loading. The impregnated catalysts were dried and then stored in a desiccator before further treatment. We have described the wet chemical treatment in detail because the final properties of the catalysts are influenced by these early stages of preparation. The chemistry of the preparation of nickel based catalysts has already received considerable attention by Bartholomew and co-workers (*6, 7*). In particular, their work has focused on the effect of reduction conditions on metal dispersion and surface properties.

The reduction and surface areas of the impregnated catalysts were determined in a Quantasorb adsorption apparatus. After impregnation and drying, the catalysts were ground to size between 100 and 150 mesh, which helped to eliminate any by-passing and mass transfer effects during reduction. The specific reduction program recommended by Bartholomew and Farrauto (*6*) was followed. During this processing the hydrogen pressure was 15 psi and the flow rate was 100 cm^3/min. The hydrogen was prepurified by passage through a liquid nitrogen trap. The pressure of nitrogen (ultrahigh purity) was 30 psi and the flow rate was maintained at 100 cm^2/min for all pretreatment steps. During chemisorption the nitrogen flow rate was 30 cm^3/min. Hydrogen was injected into the calibrated gas line in 0.1 cm^3 doses. The amount adsorbed was determined by a thermal conductivity detector. The volume of hydrogen adsorbed at room temperature was converted to an absolute metal area by assuming a size for hydrogen of $6.8 \times 10^{-2}(nm)^2$/atom (*7*). The metal areas for the 10% nickel catalysts on 0 and 100% silica were in good agreement with those reported previously using a similar reduction program (*6*). The metal areas for the 0.88% catalysts scale with weight loading as reported before (*6*). It should be noted that the metal area varies with support composition and BET surface area, a point to be discussed later.

The procedures for determining the CEC of the supports and metal-supported catalysts subsequent to the standard heat pretreatment of 550°C for 14 hr are outlined below:

(1) Catalysts were preweighed and equilibrated[2] with three portions of 30 ml 1 *M* sodium acetate solution. The exchange solution was removed by filtration in a Buchner funnel.

(2) Samples and the vessel were carefully washed with 30 ml of distilled water.

(3) Samples were then washed by three aliquots at 30 ml isopropanol. Isopropanol was used rather than methanol or ethanol to minimize hydrolysis during the leaching process (*8*).

(4) Three aliquots of 30 ml 1 *M* potassium acetate were used to displace the sodium.[3]

(5) The sodium content of the solution was determined potentiometrically with a sodium ion selective electrode in conjunction with an Orion 701A Ionanalyzer.

CEC values are a function of solution pH. The exchange solutions were maintained at pH 7 by an acetate buffer and no change of pH was observed during measurements. DCEC results subtract out the effect of the support, therefore removing any influence of the buffering ions.

The CEC values in meq/g of sample are shown for each of the supports and metal supported catalysts in Table 2. Also shown in Table 2 are the metal areas determined by hydrogen chemisorption and the average BET surface areas of the support (Table 1).

For most supports four separate CEC determinations were made on samples ranging in weight from 0.5 to 1 g, the mean and standard deviation of these results are reported (Table 2). For the metal-supported catalysts, usually two determinations were made. The reproduceability of the CEC values are most likely a reflection of the standard heat pretreatment and uniform method of handling all samples.

RESULTS

The results of metal loading and CEC values as a function of support composition have been presented in Table 2 on a mass basis. One of us (JAS) (*4*) and others (*1*) have found it more meaningful to compare catalyst properties on a support surface area basis. To demonstrate the validity of this approach the metal surface area per gram of catalyst and per unit area of catalyst are shown in Figure 1 as a function of support composition.[4] Metal area varied erratically with different support compositions on a mass basis, however, the metal area per unit area of catalyst was found to be independent of support composition. Furthermore, it was found that the metal area was linearly proportional to the support area. We will proceed to represent the data presented in Table 2 on an area basis.

DCEC values for the 10 and 0.88% nickel-supported catalysts are shown in Fig. 2 as a function of support composition. The DCEC values are based on unit area of the support and were obtained from Table 2 as the difference between the metal-supported and support CEC values. There were differences for the two weight loadings particularly for the silica-rich compositions. The DCEC values of the 10% nickel catalyst decreased as the alumina content decreased. Below 75% alumina (by weight) the DCEC values decreased to nearly zero. In the silica-rich region our results are in accord with results presented more than 20 years ago by Uchida and Imai (*9*) for acidity measurements made by quinoline chemi-

---

[2] Exchange reactions are typically fast. No detailed studies of the kinetics of this exchange process were conducted and a standard 3 hr equilibration period under constant agitation was used for all samples.

[3] KCl and lithium acetate were also employed in controlled tests to determine the effect of electrolytes composition on the displacement reaction. No effects on the CEC values were observed.

[4] The support areas for the metal loaded catalysts were assumed to be the same as those reported in Table 1. Previous results have shown there is virtually no difference between the two support areas determined by BET measurements (*9*).

TABLE 2

Summary of CEC Values for Supports and Metal-Supported Catalysts

Support nominal wt% Al_2O_3	Average BET area (m^2/g)	Ni metal area (10%)	Ni metal area (0.88%)	CEC (support) (meq/g)	CEC (Ni, 10%) (meq/g)	CEC (Ni, 0.88%) (meq/g)
100	343.5	5.4	—	0.148 ± 0.001	0.32, 0.33	0.35, 0.357
90	441.5	7.	—	0.159 ± 0.002	0.293, 0.301	0.388, 0.389
75	416.5	6.5	—	0.22 ± 0.012	0.31, 0.315	0.393, 0.397
66	344	5.24	0.2	0.295 ± 0.005	0.287	0.406, 0.414
25	415	6.5	—	0.453 ± 0.009	0.486	0.698, 0.703
10	536	8.2	0.34	0.408 ± 0.006	0.399, 0.41	0.673, 0.703
0	381.5	6.1	—	0.356 ± 0.002	0.369, 0.372	0.646, 0.65

sorption on a series of silica–alumina coprecipitated nickel catalysts where the nickel loading was maintained at ~ 3% by weight.

Nickel catalysts prepared on silica and alumina supports with weight loadings less than 1% appeared to exhibit catalytic and adsorption behavior different from nickel catalysts prepared with higher (>1%) weight loading (*10*). These earlier results are compatable with ours and will be discussed in more detail shortly.

The DCEC values for the 0.88% nickel catalysts show again high values for the alumina-rich support compositions. A slight minimum in the DCEC is shown in Fig. 2 near the middle range of silica–alumina content, which again rises and remains essentially constant as the silica content increases to 100%.

DISCUSSION

Our primary aim is to interpret the basis for the differences in the DCEC values for the two weight loadings of nickel as a function of support composition. To understand the DCEC values as both the metal loading and support composition is varied, one

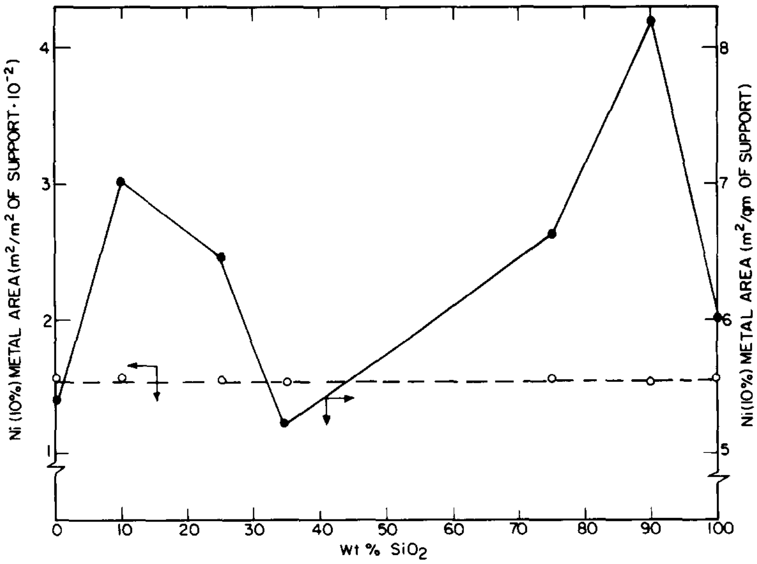

FIG. 1. Metal surface area (from H_2 chemisorption) per gram (—), and per unit support area (----) as a function of support composition. Note the data are best represented on an area basis. Estimated accuracy of data is ± 10%.

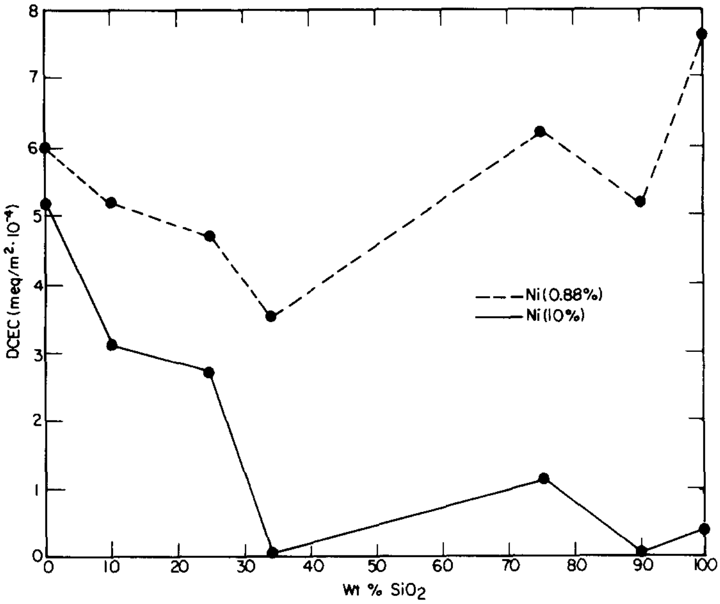

FIG. 2. DCEC/area of the 0.88% (----) and 10% (—) nickel catalysts as a function of support composition. Note the differences that exist for the silica-rich compositions.

needs to examine more closely the aqueous phase chemical system that exists during catalyst preparation.

The ZPC of Al_2O_3 is such that in solutions with pH values less than 9.2 the surface charge of an alumina particle will be positive. Likewise NiO has an estimated ZPC of 11–14 (*11*). Therefore, the observed increase in CEC due to the presence of Ni on Al_2O_3 (Fig. 2) would most reasonably be attributed to isomorphic substitution of nickel into an alumina lattice. The nickel to oxygen radius ratio (0.52 (*12*)) is within the range of an octahedral structure. Assuming that Al_2O_3 exhibits a conventional octahedral structure, it is reasonable that nickel might substitute in the alumina lattice, resulting in a charge deficit and an increase in CEC. The radius ratio of aluminum and oxygen is close to the value bordering stable, tetrahedral and octahedral configurations; therefore aluminum may exhibit either configuration. However, the octahedral structure of Al_2O_3 is generally observed (*13*).

Nickel is a hydrolyzing metal, impregnating solutions are characteristically acidic. In our study, the pH values of impregnating solutions for 0.88 and 10% nickel catalysts were 3.84 and 1.93, respectively. Alumina is quite soluble in low pH solutions (*13*). Dissolution of the support would facilitate the incorporation of nickel into the alumina lattice.

DCEC values were slightly lower for the high metal loading under Al_2O_3-rich conditions. This might be attributed to the tendency to form NiO in the higher nickel system. The elevated ZPC of NiO would tend to increase the surface charge and decrease the DCEC value.

Results of the silica-rich system are more difficult to interpret than the alumina-rich system, although observed differences in DCEC values under different metal loadings were apparent. The CEC of the high nickel system was essentially no different from that of the support alone, while the low nickel system exhibited an increase in CEC when compared to the support alone, in the silica-rich region. Due to the low ZPC, of SiO_2, the support should exhibit a negative charge at pH 7 (the exchange solution pH) and an elevated CEC. The addition of NiO (ZPC $\approx$ 11–14) should effectively decrease the CEC; however this conflicts with the observed results. This leads us to suggest isomorphic substitution as a possible mechanism by which charge originates at the catalyst surface. The nickel–oxygen radius ratio (0.52) is more conducive to substitution into an octahedral structure (Al_2O_3) than a tetrahedral structure (SiO_2). While isomorphic substitution is the only plausible explanation for the observed DCEC values, steric considerations appear to contradict this.

The differences in DCEC values between high and low nickel-loaded catalysts, in the silica-rich region, may have been due to the pH of the impregnating solution. The pH of the low nickel system was above the ZPC of SiO_2, while the pH of the high nickel impregnating solution was near or below the ZPC of SiO_2. It is likely that even though the nickel concentration was lower in the 0.88% Ni system, a metal–SiO_2 association may be enhanced due to the favorable surface charge of the SiO_2. Such an association might facilitate the incorporation of nickel into SiO_2 under high temperature reduction conditions. It is interesting to note that the mass of nickel incorporated into SiO_2 ($\approx$98%) represents almost all of the applied nickel for the low weight loading condition. This analysis assumes conservation of charge, therefore 2 × DCEC is equivalent to the moles of nickel incorporated into SiO_2 by isomorphic substitution. It is possible that under high nickel loading conditions some nickel was incorporated into the SiO_2 structure. However if this occurred, positively charged NiO would have to be present on the catalyst surface, to effectively counter the CEC increase due to isomorphic substitution and maintain no net change in CEC.

While these mechanisms are tentative, they do suggest the significance of the environmental conditions under which the catalyst was prepared. These conditions may strongly influence subsequent catalytic behavior.

We have described the interactions that occur between a supporting electrolyte ($Ni(NO_3)_2$) and oxide support as the support composition and the electrolyte concentration vary systematically. The question then arises as to what effect these preparation variables have on the final catalytic behavior of the resulting supported metal catalysts. The existing literature, to our knowledge, has not considered as wide a range of support compositions and metal weight loadings as we have. However, the adsorptive and catalytic behavior over a limited subset of the catalysts we have studied has been presented and will be summarized here. At the outset of this summary, we state that the observed "catalytic" effects are in agreement with the conclusions we have presented based on the DCEC results. Furthermore our results have been interpreted on the basis of the genesis of the metal supported catalyst, i.e., the DCEC results originate from the chemical system existing during the solution phase preparation of the metal-supported catalyst. The effect of nickel loading on the adsorption of NH_3 has been studied on silica and alumina supports (*10*). For alumina a pronounced increase in ammonia adsorption with metal concentration was observed in the region below 1% by weight of nickel. Above the 1% loading, the increase in adsorption with metal concentration was negligible. The information presented indicated that the surface acidity of both alumina and silica (i.e., ammonia adsorption) was increased by the addition of nickel. These results were interpreted in terms of a model in which the nickel was considered to be in two distinct phases, a dispersed phase associated with the catalyst lattice and a nondispersed or bulk phase similar to the bulk oxide. In further support of our findings, it was reported in their work that magnetic susceptibility measurements on the Ni/Al_2O_3 system suggested that the nickel existed as octahedrally coordinated Ni^{2+} ions even at high concentrations of nickel ($\sim$9% by weight).

Uchida and Imai (*9*) reported on the activity and selectivity for ethylene polymerization of a series of nickel-supported silica–alumina catalysts. Here the weight loading of nickel was relatively high at 3% and only the silica-rich range of support compositions were studied ($0 \leq \frac{\mathrm{Al}}{(\mathrm{Si} + \mathrm{Al})} \leq 0.5$). Their results showed that both the activity and the selectivity change in a particular manner that was greatly dependent on the alumina content. They concluded that a small amount of nickel oxide produced a large number of acidic sites, besides those of silica–alumina alone, and the number of acidic sites produced were greatly dependent on the alumina content. Furthermore, they concluded only the acidic sites produced with nickel oxide act effectively for the ethylene polymerization and that the acid sites thus produced promote the polymerization to an equal extent, regardless of the aluminum content. Nickel incorporation into the support lattice was suggested.

The general picture that emerges from these catalytic studies is that nickel addition to silica, alumina, and silica–aluminas increases the CEC of the catalyst as compared to the CEC of the support alone and that this change in CEC is responsible for the "unique" chemistry of these systems. We have presented evidence that through an understanding of the chemistry of the system during the preparation of a metal-supported catalyst, one can perhaps control the catalytic properties of the final catalyst. For example, low weight loadings of nickel on silica (<1% by weight) might behave catalytically similar to higher weight loadings of nickel on alumina. When precious metals are involved the economics of catalyst production might be substantially influenced. These final ideas are, of course, speculative. Work in our laboratory will continue to examine these premises.

ACKNOWLEDGMENT

The authors appreciate the helpful discussions with Professor E. G. Derouane and partial support of this effort by NATO Grant 1898.

REFERENCES

1. Fripiat, J. J., 12th National Conference on Clays and Clay Materials.
2. Flockhart, B. D., and Pink, R. C., *J. Catal.* **4,** 90 (1965).
3. Parks, G. A., *In* "Equilibrium Concepts in Natural Water Systems" (W. Strumm, Ed.). Adv. in Chem. Series 67, ACS, Washington, D.C.
4. Schwarz, J. A., *J. Vac. Sci. Technol.* **12,** 321 1975.
5. Merrill, R. P., Komiyama, M., and Harnsberger, H. F., *J. Catal.* **63,** 35 (1980).
6. Bartholomew, C. H., and Farrauto, R. J., *J. Catal.* **45,** 41 (1976).
7. Bartholomew, C. H., and Pannell, R. B., *J. Catal.* **65,** 390 (1980).
8. Peech, M., "Methods of Soil Analysis," Section 59. Amer. Soc. of Agronomy, Madison, Wisconsin, 1968.
9. Uchida, H., and Imai, H., *Bull. Chem. Soc. Japan* **35,** 995 (1965).
10. Barth, R. T., and Pinchok, R. N., *J. Phys. Chem.* **68,** 655 (1964).
11. Parks, G. A., *Chem. Rev.* **65,** 177 (1965).
12. "Handbook of Chemistry and Physics," 41st ed. Chemical Rubber Publishing Co., Cleveland, Ohio.
13. Bohn, H., McNeal, B., and O'Connor, G., "Soil Chemistry." John Wiley, New York, 1979.