The Effect of Chloride on the Point of Zero Charge of γ-Al$_2$O$_3$

In aqueous suspension, the surface of γ-alumina can be treated as a diprotic acid (1) that undergoes the dissociation reactions

$$AlOH_2^+ \xrightleftharpoons{K_1^{int}} AlOH + H_s^+ \qquad (1)$$

$$AlOH \xrightleftharpoons{K_2^{int}} AlO^- + H_s^+ \qquad (2)$$

$$H_s^+ \rightleftharpoons H_b^+ \qquad (3)$$
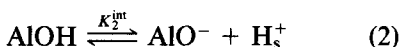
where H_s^+ denotes surface hydrogen ions and H_b^+ solution hydrogen ions. $AlOH_2^+$, $AlOH$, and AlO^- are the surface groups on alumina and K_1^{int} and K_2^{int} are the intrinsic acid dissociation constants. From the above equilibria, it is seen that the surface charge development, i.e., the relative concentration of positive, neutral, and negative charge surface groups, is a function of the pH of the electrolyte. A convenient and simplistic index to determine the capacity for adsorption of negative or positive species onto oxides conforming to this model is the point of zero charge (pzc). It corresponds to that pH value at which there exists no net charge on the oxide surface. The pzc is the average of the pKs of the two intrinsic acidity constants (2) and, therefore, its value depends on the sample used.

As a measure of the adsorption capacity, the pzc value provides a measure of the range of pH values that can be used to prepare metal-supported catalyst precursors by adsorption. Recently (3–7), it was shown that by either changing the temperature of the supporting electrolyte or adding dopants, the pzc of γ-alumina could be shifted so as to expand the range of pH values that can be used to prepare metal-supported catalytic precursors. The dopants considered to date have been electropositive elements: lithium (5, 6), sodium (4, 6),

magnesium (8), and electronegative fluorine (5, 6). Less work has been done to learn the effects of chloride as a dopant, but such information is valuable since the chloride concentration on typical reforming catalysts is an important consideration in the performance of these catalysts.

The objective of this report is to present our findings on the effect of varying low levels of chloride additions on the pzc of a commercial alumina typically used as a support for preparing reforming catalysts. The highest level of Cl$^-$ studied corresponds to that value found on a 0.3% by weight Pt/Al$_2$O$_3$ catalyst.

The support material used in this work is a $\frac{1}{16}$-in. extrudate γ-alumina (American Cyanamid, Lot 85-NA-1402) ground to 40–80 mesh. Before use it was calcined in a 5 cm^3/min flow of air at 773 K for 3 h. Its BET surface area is 194 m^2/g.

Five groups of chloride-doped alumina samples were prepared by contacting 3 g of γ-Al$_2$O$_3$ with 3 ml of solution containing varying amounts of hydrochloric acid. The HCl/Al$_2$O$_3$ suspensions were constantly agitated and dried at room temperature. The samples were placed in an oven for 3 h at 473 K to remove any residual water. After removal from the oven, the samples were calcined in 5 cm^3/min of air flow for 3 h at 773 K. The chlorinated aluminas were stored in a desiccator prior to use.

Mass titration (9) was used to measure the pzc of the pure and chlorided supports. At each chloride loading, five solutions were prepared by adding chlorinated alumina to air-saturated distilled water in various proportions. The amount of chloride-doped alumina present in solution ranged from 10^{-2} to 20% by mass. The solutions,

202

TABLE 1

Weight Loadings of Chloride
on γ-Al$_2$O$_3$

Sample	Weight loading (wt%)[a]
A	0.35
B	0.17
C	0.076
D	0.045
E	0.026
F	0.0

[a] Determined by XRF.

along with a sample of distilled water containing no alumina, were covered tightly and constantly agitated for 24 h. In addition, solutions of undoped alumina were prepared at the same weight loadings given above and contacted for 24 h.

A Corning pH meter (Model 145) was calibrated with standard buffers at pH 4 (Fisher SO-B-98) and pH 10 (Fisher SO-B-116). The pH values of the solutions were measured in increasing mass%, starting with the distilled water sample. The calibration of the pH meter was then checked with the above buffers and the pH values of the undoped alumina samples were measured in the same manner. The solutions were filtered and stored, while the doped-alumina solids were placed on a shaker and allowed to dry at room temperature. These procedures were repeated for each of the five groups of chloride-doped aluminas.

To check if any of the chloride had been leached from the alumina during the 24-h contact with water, the 20 mass% solutions of the high weight loading Cl$^-$/Al$_2$O$_3$ samples (A and B) were analyzed for chloride content. This was accomplished by using a Dionex Model 2020i chloride ion chromatograph sensitive to 1 part per billion. In both cases, no chloride was detected in the solution and thus it is assumed that no chloride was present in any of the solutions containing the lower levels of chlorinated alumina. X-ray fluorescence (XRF) was used to determine the actual chloride loadings of the

alumina samples which had been used in the mass titration experiment and had been subsequently dried in the air; results are given in Table 1. The intended and actual weight loadings of chloride were found to be the same within experimental error. This was expected because, at the low levels used, chloride is strongly bound to the Al$_2$O$_3$ surface.

The mass titration curves for representative samples are presented in Fig. 1. In each case, an asymptote of the pH vs mass fraction of support added to the water is found. This limiting value is an estimate of the pzc of the modified support (9). The pzc of the pure Al$_2$O$_3$ sample is in good agreement with that determined by acid/base titration in our laboratory (9) as well as with values retrieved from the literature (10–14). However, pzc values different from that determined here have also been reported for γ-alumina (15). Figure 2 shows the pH corresponding to the pzc as a function of the measured chloride concentration on the γ-alumina carrier. The change in the pzc is ~3 pH units, decreasing sharply at low chloride levels and reaching approximately a constant value at the highest chloride levels. This saturation value occurs for chloride concentrations of ~100 μmol/g of Al$_2$O$_3$.

The regulation of the pzc of γ-Al$_2$O$_3$ by addition of dopants has been studied by Lycourghiotis and co-workers (3–7) and recently by Mulcahy and co-workers (8). The fluorided aluminas had pzc values that decreased with increasing concentration of the dopant. A saturation value of the pzc was found where an increase in the dopant concentration resulted in no further change in the pzc. The pH change ranged from 2–3 pH units from the undoped sample to the highest dopant level studied. Our results for the chlorided samples follow a similar trend which might be expected for electronegative dopants.

We propose a model for the effect of Cl$^-$ doping on the pzc of γ-alumina. Upon contact with chloride ions, N_T, the number of
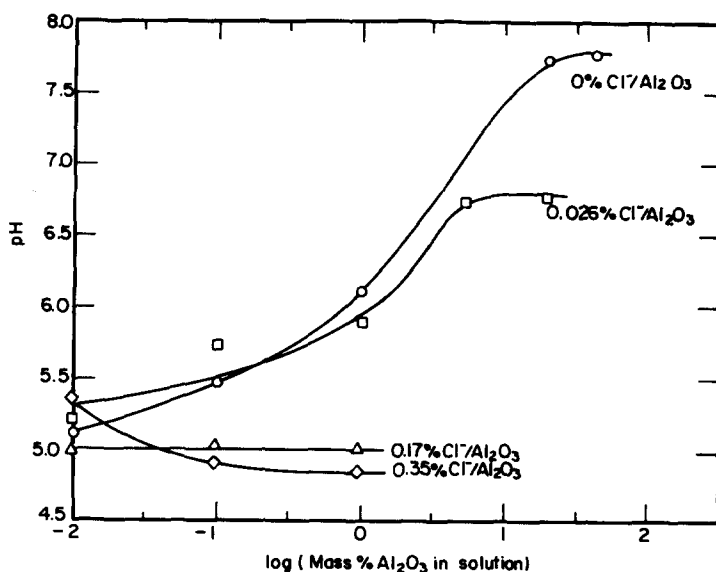
FIG. 1. Mass titration curves for various chloride-doped aluminas. The estimated error in the pH is approximately the size of the data points. The chloride levels indicated are the weight loadings.

amphoteric sites, decreases because of chloride exchange. We note that the results presented in Fig. 1 qualitatively support this assertion. As the Cl^- concentration increases the mass fraction of added solid required to achieve an asymptotic pH value decreases. Chloride has a higher electronegativity (χ) than that of OH. We estimate the value $\chi_{OH} = \sqrt{\chi_O\chi_H} = 2.7$ (*16*) whereas $\chi_{Cl} = 3.0$ based on Pauling's electronegativity scale. In this scheme, each chloride ion would affect a hydroxyl group adjacent to its exchange site, weakening the O–H bond of its acid proton. This is reflected as an increase in both K_2^{int} and K_1^{int}, which results in a decrease in the measured pzc.

FIG. 2. The pzc of the doped aluminas as a function of the chloride concentration on the support.

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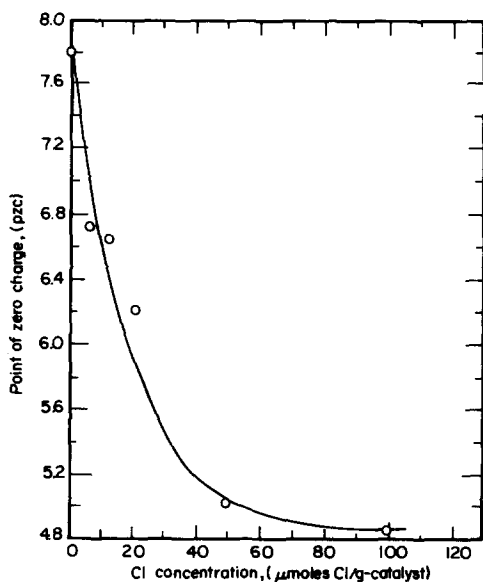
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J. A. MIETH
J. A. SCHWARZ[1]

Department of Chemical Engineering and Materials Science
Syracuse University
Syracuse, New York 13244

Y.-J. HUANG
S. C. FUNG

Exxon Research and Engineering Company
Corporate Research Laboratories
Clinton Township
Route 22 East
Annandale, New Jersey 08822

[1] To whom correspondence should be addressed.