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Development of Carriers with Controlled Concentration of Charged Surface Groups in Aqueous Solutions

I. Modification of γ-Al_2O_3 with Various Amounts of Sodium Ions

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The point of zero charge (ZPC), the surface acidity constants of γ-Al_2O_3, and the concentrations of charged surface groups $\overline{\text{Al}}\text{OH}_2^+$ and $\overline{\text{Al}}\text{O}^-$ over a wide pH range were determined potentiometrically for a series of carriers prepared by modification of γ-Al_2O_3 with various amounts of sodium ions. It was shown that 0.083 mmol Na^+/g of γ-Al_2O_3 is sufficient to increase drastically the ZPC value (from 5.3 to 9.7) and the concentration of $\overline{\text{Al}}\text{OH}_2^+$ over the pH range 1–9. Moreover, this amount is sufficient to decrease the surface acidity constants and minimize the concentration of $\overline{\text{Al}}\text{O}^-$ in the pH range mentioned. Thus the pH range in which γ-Al_2O_3 can adsorb negatively charged active species is extended, due to doping, from 1–5 to 1–9. The above effect was attributed to the tendency of sodium ions to replace the H^+ of the $\overline{\text{Al}}\text{OH}$, forming

$$\overline{\text{Al}}\text{–}\overset{\delta(-)}{\text{O}}\text{–}\overset{\delta(+)}{\text{Na}}$$

which serve as adsorption sites for H_s^+, thus facilitating protonation of the adjacent surface hydroxyls. An additional increase in the sodium content changes the concentrations of the positive and negative surface groups markedly, but it does not affect the surface acidity constants and ZPC values: It was found that the concentration of $\overline{\text{Al}}\text{OH}_2^+$ increases linearly with Na^+ content at pH values lower than the ZPC. This was explained assuming that the small amount of Na^+ dissolved during equilibration is adsorbed specifically on the shear plane of the double layer, forming "ion pairs" with $\overline{\text{Al}}\text{OH}$ and releasing hydrogen ions on the surface. On the contrary, there was no correlation between sodium content and concentration of $\overline{\text{Al}}\text{O}^-$ at pH values higher than the ZPC. The practical consequences of the sodium effects from the preparative point of view are discussed with respect to the adsorption on γ-Al_2O_3 of Mo, V, W, and Cr species.

INTRODUCTION

Many supported catalysts used in industry are prepared by *adsorption* of a suitable species of an active ion on the surface of a carrier. This process takes place during the wet impregnation of carrier with an aqueous solution containing the species to be adsorbed. The *dispersity* of active ions achieved using this method is much higher than that obtained using classical impregnation where the deposition of the supported phase occurs by precipitation during the step of drying. This justifies the use of the former method when a quite expensive active ion has to be deposited on the surface of a carrier. Nevertheless, deposition via adsorption does not lead to the preparation of supported catalysts with large *active surface*. This is due to the fact that the amount of active ion that can be deposited through adsorption is relatively small as compared to that deposited by precipitation. Increase of the extent of adsorption would be achieved by increasing the surface concentration of the sorptive sites located on the carrier surface. According to a model developed by Brunelle (*1*) these sites are either positively or negatively charged surface groups which *exclusively* adsorb

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negative or positive active ion species, respectively.

γ-Alumina is the most important carrier used in catalysis. This oxide exhibits three types of surface groups. In fact, it is well established that γ-Al_2O_3 in aqueous suspensions can be treated as a diprotic acid (*2*):

$$\underset{\textbf{(I)}}{\overline{\text{Al}}\text{OH}_2^+} \overset{K_1^{\text{int}}}{\rightleftharpoons} \underset{\textbf{(II)}}{\overline{\text{Al}}\text{OH}} + \text{H}^+_{(s)}$$

$$\overline{\text{Al}}\text{OH} \overset{K_2^{\text{int}}}{\rightleftharpoons} \underset{\textbf{(III)}}{\overline{\text{Al}}\text{O}^-} + \text{H}^+_{(s)}$$

$$\text{H}^+_{(s)} \rightleftharpoons \text{H}^+$$

$\overline{\text{Al}}\text{OH}_2^+$, $\overline{\text{Al}}\text{OH}$, and $\overline{\text{Al}}\text{O}^-$ represent positive, neutral, and negative surface groups, respectively. The $\text{H}^+_{(s)}$ and H^+ denote the hydrogen ions on the surface of the support and in the aqueous solution, respectively.

From the above equilibria it can be conceived that the relative concentrations of **I**, **II**, and **III** depend on the pH of the impregnating solution. Thus, an increase in the concentration of $\overline{\text{Al}}\text{OH}_2^+$ ($\overline{\text{Al}}\text{O}^-$) and consequently in the extent of adsorption of one negative (positive) species could be achieved by decreasing (increasing) pH (*3, 4*). Although this method seems to be very simple it creates serious problems in many instances: Thus, at a given pH where the resulting concentration of $\overline{\text{Al}}\text{OH}_2^+$ ($\overline{\text{Al}}\text{O}^-$) enhances the adsorption of a negative (positive) species this species may not be stable. Moreover, γ-Al_2O_3 may be partially dissolved and the deposition via precipitation may not be negligible. We need, therefore, an alternative method for regulating the concentration of the charged surface groups of γ-Al_2O_3 throughout the pH range. In a previous preliminary communication we showed that the surface acidity constants of γ-Al_2O_3, K_1^{int} and K_2^{int}, the point of zero charge (ZPC), and thus the relative concentrations of **I**, **II**, and **III** could be changed by doping this carrier with a given amount of Na^+ and F^- ions (*5*). It was observed that modification with 0.166 mmol Na^+/g of γ-Al_2O_3 caused a considerable decrease in K_1^{int} and K_2^{int}. Moreover, this modification brought about an increase in the ZPC from 5.3 to 9.7. These results strongly suggest that the surface modification by Na^+ ions results in an increase in the relative concentration of $\overline{\text{Al}}\text{OH}_2^+$ at pH values lower than the ZPC. The opposite effects were observed after modification with 0.125 mmol F^-/g of γ-Al_2O_3. Aiming at establishing a simple method for tailor-made regulation of the relative concentrations of **I**, **II**, and **III**, throughout the pH range, in the present work we studied the variation of pK_1^{int}, pK_2^{int}, ZPC, and relative concentrations of **I**, **II**, and **III** at each pH with sodium ion content. Specifically, we have attempted to answer the following questions: (i) What is the maximum amount of sodium ions needed to maximize the ZPC of γ-Al_2O_3? (ii) How is Na^+ content related to the relative population of surface groups mentioned at each pH? (iii) What is the mechanism of sodium action?

Although electrophoretic mobility measurements of surface charge and ZPC have recently been used in the field of catalysis (*6–10*), the method of potentiometric titration, developed during the last two decades (*11–22*), was used in the present study, because by this technique one can determine the charge *on the surface* of the solid rather than on the shear plane of the double layer around the γ-Al_2O_3 particles. Determinations performed by both methods give the same result only in those cases in which specific adsorption does not occur (*22, 23*).

EXPERIMENTAL

Preparation of the samples. The specimens studied are denoted by Na–X–γ-Al_2O_3 where X represents the nominal composition as millimoles of Na^+ per gram of γ-Al_2O_3 (commercial Houdry Ho 415). These specimens are compiled in Table 1. Specimens with serial numbers 2–7 were prepared by dry impregnation of the carrier with aqueous solutions of $NaNO_3$ [Merck p.a.]. Sample 1 was "prepared" by dry impregnation of the carrier with pure solvent

TABLE 1

Nominal Compositions and Specific Surface Areas (SSA) of the Samples Prepared

Serial No.	Notation	SSA ($m^2\ g^{-1}$)
1	Na–0.226–γ-Al_2O_3	123.0
2	Na–0.309–γ-Al_2O_3	125.3
3	Na–0.392–γ-Al_2O_3	127.6
4	Na–0.621–γ-Al_2O_3	118.0
5	Na–0.984–γ-Al_2O_3	100.4
6	Na–1.560–γ-Al_2O_3	87.7
7	Na–2.470–γ-Al_2O_3	62.2

(distilled water). After impregnation, the samples were dried at 110°C for 2.5 h and then calcined in air at 600°C for 12 h. The sodium contained in the undoped sample originates from the carrier. The specific surface areas of the samples studied were determined by the BET method using a Perkin–Elmer (Model 212-D) sorptometer. Pure nitrogen and helium (both 99.99% of purity) were used as adsorption gas and carrier gas, respectively.

Potentiometric titrations. Potentiometric titrations were performed at 25.0 ± 0.1°C, in a thermostated double-walled Pyrex vessel with a Perspex lid equipped with holes for electrodes and nitrogen gas. Titrant solutions were delivered by a microburette (Gilmont ± 1 μl) and pH was recorded with a recording pH-meter (Beckmann, Model Electroscan TM 30) employing the cell:

SCE|$KNO_{3(c)}$, suspension under study|GE.

A combination pH electrode (Pye Unicam) was used for pH measurements and it was standardized before and after each experiment with NBS standard buffer solutions prepared as follows (*24*): 0.025 *M* KH_2PO_4 + 0.025 *M* Na_2HPO_4, pH 6.860, and 0.008695 *M* KH_2PO_4 + 0.03043 *M* Na_2HPO_4, pH 7.410 at 25°C. Potassium nitrate stock solutions were made by using reagent grade solid (BDH AnalaR) without any further purification. Potassium hydroxide solutions (Merck Titrisol) were standardized against potassium hydrogen phthalate using phenolophthalein indicator. Nitric acid standard solutions were prepared by diluting concentrated reagent grade nitric acid (Malinckdrot AnalaR) and were standardized with standard potassium hydroxide by potentiometric titration.

Titration of the alumina suspensions was done at 0.1, 0.01, and 0.001 *N* potassium nitrate background electrolyte. In all cases a time period of 18–20 h was found to be necessary to reach a constant value of the suspension pH. Following equilibration, a small quantity of 0.1 *N* KOH solution (0.1–0.5 ml) was added to render the alumina surface negative. After 15–20 min, the new equilibrium value at pH, noted as the initial pH, was recorded. The suspension was then titrated by the addition of small aliquots of nitric acid titrant (15–20 μl). pH was recorded as a function of the volume of titrant added to the suspension. Titrant additions and corresponding pH values of the suspensions were recorded every 2 min.

Determination of the point of zero charge. According to Breeuwsma (*25*) and Block (*26*) one can determine from the titration data the quantity $[(\Gamma_{H^+} - \Gamma_{OH^-}) - (\Gamma_{H^+} - \Gamma_{OH^-})_{in}]$ as a function of pH, following the equation

$$(\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-}) \equiv [(\Gamma_{H^+} - \Gamma_{OH^-}) - (\Gamma_{H^+} - \Gamma_{OH^-})_{in}] = \left(C \cdot \Delta V - \left[(V + \Delta V) \cdot \left(\frac{10^{-(pH)} - 10^{-(14-pH)}}{\gamma_1}\right) - V \cdot \left(\frac{10^{-(pH)_{in}} - 10^{-(14-pH)_{in}}}{\gamma_1}\right)\right]\right) / W \cdot S. \quad (1)$$

Γ_{H^+} and Γ_{OH^-} represent the number of microequivalents of adsorbed H^+ and OH^- per square meter of the surface of the solid, respectively. The subscript "in" stands for the initial state. *C*, ΔV, *V*, $(pH)_{in}$, γ_1, *W*, and *S* denote, respectively, the concentration of titrant (*N*), the titrant volume increment (liters), the volume of suspension before titration (liters), the initial pH, the activity coefficient for univalent ions, the weight (g), and the specific surface area

(m^2/g) of the solid dispersed. The values of the activity coefficient for the Z-valent ions used can be calculated from Davies' equation (*27*):

$$\log \gamma_z = -A \cdot Z^2 \cdot (\sqrt{I}/(1 + \sqrt{I}) - 0.3I) \tag{2}$$

where I is the ionic strength and $A = 0.5115$ at 25°C. Typical plots of the quantity determined using Eq. (1) against pH at three different ionic strengths are illustrated in Fig. 1. The pH value corresponding to the intersection point is identified as the zero point of charge because only at this pH value is the left-hand side of Eq. (1) independent of the ionic strength (*22, 23, 25, 26*). The y axis could be rearranged so that the intersection point corresponds to a net surface charge equal to zero. This is obtained by subtracting the quantity $(\Gamma_{H^+} - \Gamma_{OH^-})_{in}$ corresponding to the distance AB from each value on the y axis. The curves thus obtained can be transformed to illustrate the variation of the surface charge, $\sigma_0 = F \cdot (\Gamma_{H^+} - \Gamma_{OH^-})$, with pH of the suspension (Fig. 2a).

The increase in the absolute value of the net surface charge with concentration of the indifferent electrolyte observed at each pH for the undoped specimen is in agreement with the literature (*25*). The opposite effect was observed for all doped specimens studied (compare the Figs. 2a and b).

Determination of the surface acidity constants. The methods used for the determination of surface acidity constants are based on the various models developed so far to describe the oxide/solution interface. The "constant capacitance model" of Stumm and co-workers (*28–30*), the "diffuse layer model" of Stumm, Huang, and Jenkins (*2, 31*), the "Stern model" modified by Westall and Hohl (*32*), the "site-binding model" of Yates *et al.* (*33*) and finally the "triple layer model" developed by Davis *et al.* (*34, 35*) must be mentioned. This last approach has been principally adopted in the present work.

The intrinsic acid dissociation constants, K_1^{int} and K_2^{int}, are defined by

$$K_1^{int} = \frac{(H_s^+)\overline{AlOH}}{(\overline{AlOH_2^+})} \tag{3}$$

$$K_2^{int} = \frac{(H_s^+)\overline{AlO^-}}{(\overline{AlOH})} \tag{4}$$

The surface concentration of the protons adsorbed on the solid particles is related to the bulk solution concentration by

$$(H_s^+) = (H^+) \cdot \exp\left(-\frac{F \cdot y_0}{RT}\right) \tag{5}$$

where F and y_0 denote the Faraday constant and the potential on the surface of

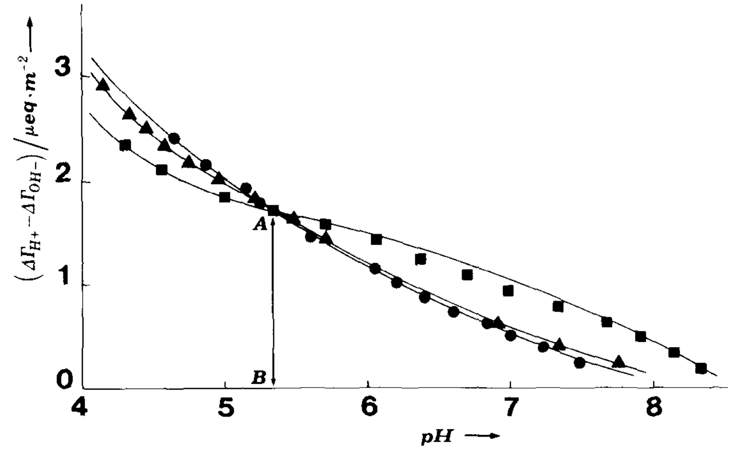

FIG. 1. Relative adsorption density $(\Delta\Gamma_{H^+} - \Delta\Gamma_{OH^-})$ versus pH for Serial No. 1 (●, 0.1; ▲, 0.01; ■, 0.001 M KNO_3).

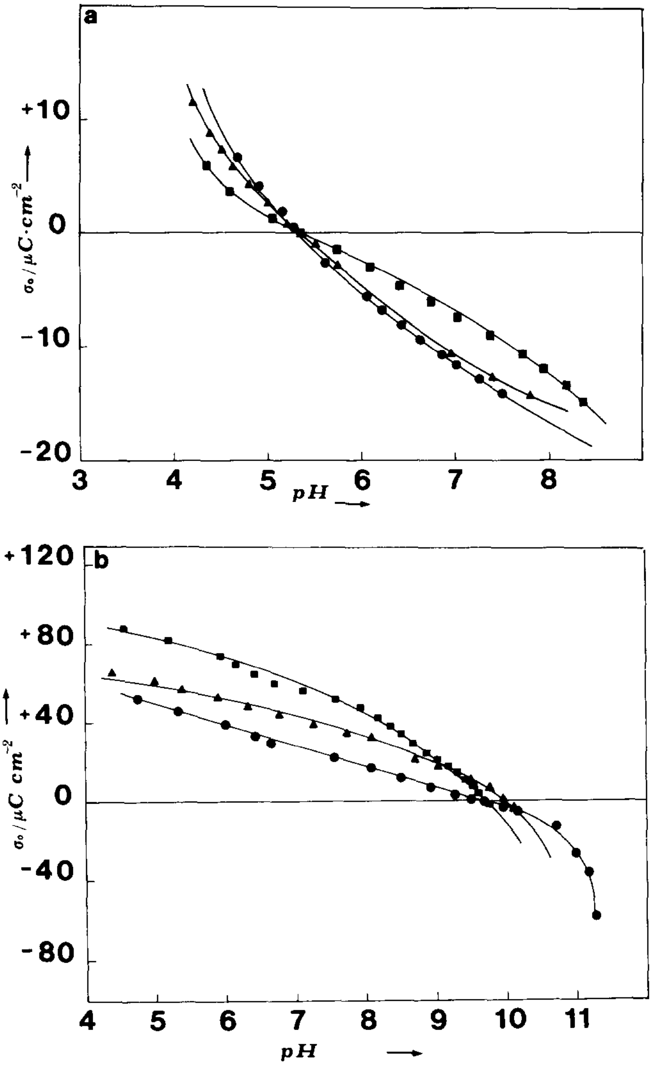

FIG. 2. (a) Surface charge (σ_0) versus pH for Serial No. 1 (●, 0.1; ▲, 0.01; ■, 0.001 *M* KNO_3). (b) Surface charge (σ_0) versus pH for Serial No. 2 (●, 0.1; ▲, 0.01; ■, 0.001 *M* KNO_3).

solid particles, respectively. The fraction of positively and negatively charged sites is related to the surface charge and the total concentration of **I**, **II**, and **III**, denoted by N_s, by, respectively,

$$a_+ = \frac{+\sigma_0}{N_s} \simeq \frac{(\overline{Al}OH_2^+)}{(\overline{Al}OH_2^+) + (\overline{Al}OH)} \quad (6)$$

$$a_- = \frac{-\sigma_0}{N_s} \simeq \frac{(\overline{Al}O^-)}{(\overline{Al}O^-) + (\overline{Al}OH)} \quad (7)$$

The value of N_s, determined by tritium exchange, has been found to be equal to 8 × 10^{18} sites/m^2 or 128 μC/cm^2 (*36, 37*). The $+\sigma_0$ and $-\sigma_0$ are determined at pH values lower and higher than the ZPC, respectively, where the concentrations of $\overline{Al}O^-$ and $\overline{Al}OH_2^+$ are considered to be negligible, respectively.

By combining relations (3), (5), and (6) as well as relations (4), (5), and (7), the following equations are derived:

$$pK_1^{\text{int}} = \text{pH} + \log\left(\frac{a_+}{1 - a_+}\right) + \frac{F \cdot y_0}{2{\cdot}3RT} \tag{8}$$

$$pK_2^{\text{int}} = \text{pH} - \log\left(\frac{a_-}{1 - a_-}\right) + \frac{F \cdot y_0}{2{\cdot}3RT} \tag{9}$$

Since the value of the potential on the surface of the particles is unknown throughout the pH range, with the exception of the ZPC, the pK_1^{int} and pK_2^{int} cannot be obtained directly from Eqs. (8) and (9). However, one can determine these parameters by extrapolating the curves pH + $\log(a_+/(1 - a_+))$ vs a_+ and pH − $\log(a_-/(1 - a_-))$ vs a_- at $a_+ \rightarrow 0$ and $a_- \rightarrow 0$, respectively. In fact at this point, namely, at the ZPC, y_0 is equal to zero; thus the intercepts of the above curves become equal to pK_1^{int} and pK_2^{int}, respectively. The graphical determination of pK_2^{int} for the sample with serial number 1 is illustrated as an example, in Fig. 3. Analogous plots reported by Davis *et al.* (*34*) show a linear variation of the pH ± $\log(a_\pm/(1 - a_\pm))$ vs $a_\pm$. This is presumably due to the fact that most of their plots are limited within the region $0 < a_\pm < 0.05$. In fact, the curves reported in a region wider than the above are similar to our curves (*38*). A slight variation of the so determined pK_1^{int} and pK_2^{int} values with ionic strength has been observed in all specimens studied. This variation could reflect the formation of "ion pairs," $\overline{\text{AlO}}^-\text{-K}^+$ and $\overline{\text{AlOH}}_2^+\text{-NO}_3^-$, namely, the function of an additional mechanism for charging the surface of the specimens (*34, 35*). In that case, however, plots of pH + $\log(a_+/(1 - a_+))$ − $\log[\text{NO}_3^-]$ vs a_+ and pH − $\log(a_-/(1 - a_-))$ + $\log[\text{K}^+]$ vs a_- should provide pK_1^{int} and pK_2^{int} values with variance lower than that obtained from the corresponding plots mentioned before (*34, 35*). In our case the plots containing the logarithms of $[\text{NO}_3^-]$ and $[\text{K}^+]$ gave $pK_{1,2}^{\text{int}}$ values with relatively high variance (see, for instance, Fig. 3) suggesting that there is no formation of the "ion pairs" mentioned. This is in excellent agreement with the literature (*20, 25*). Therefore, the determination of $pK_{1,2}^{\text{int}}$ values in the present work was based on plots of pH ± $\log(a_\pm/(1 - a_\pm))$ vs $a_\pm$.

The value of N_s and the determined values of pK_1^{int} and pK_2^{int} were inserted in a computer program [MINEQL (*39–41*)] and the surface charge as well as the concentration of species **I**, **II**, and **III** was calculated

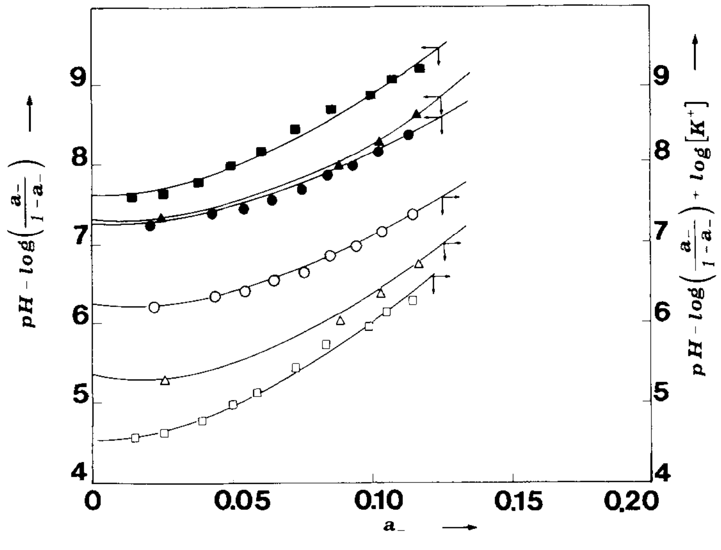

FIG. 3. Variation of pH-log($a_-/1 - a_-$) and pH-log($a_-/1 - a_-$) + log[K$^+$] versus the fraction of negatively charged sites a_- for Serial No. 1 (● and ○, 0.1; ▲ and △, 0.01; ■ and □, 0.001 *M* KNO$_3$).

throughout the pH range. In this program the only adjustable parameter used to fit the experimental data, namely, the surface charge measured, with model calculations is the inner layer capacitance. Calculations were done with a BBC microcomputer. It must be noted that the ZPC of a solid is related to pK_1^{int} and pK_2^{int} by the relationship

$$\mathrm{ZPC} = \frac{pK_1^{int} + pK_2^{int}}{2}. \qquad (10)$$

Determination of the solubility of the supported ions. It is possible that a portion of the supported sodium was transferred in the aqueous suspension by dissolution during equilibration. This was determined for all samples titrated at three different values of ionic strength. The determination was done in the supernatant after filtration of the corresponding suspension. A flame photometer (Dr. B. Lange) equipped with a sodium filter was used.

RESULTS

Table 2 compiles the ZPC values and surface acidity constants determined for the specimens examined. Inspection of this table shows excellent agreement between experimental and calculated ZPC values. An abrupt increase in the ZPC of the unmodified γ-Al_2O_3 from 5.30 to 9.70 is observed after modification with a very small amount (that is, 0.083 mmol/g γ-Al_2O_3) of sodium cations. An additional increase in the sodium content to 1.560 mmol Na^+/g of γ-Al_2O_3 has practically no effect on the ZPC. A further slight increase from 9.70 to 10.10 is observed when the sodium content increases from 1.560 to 2.470 mmol Na^+/g of γ-Al_2O_3. Similar variation is observed in the values of the surface acidity constants with sodium content.

TABLE 2

Experimental and Calculated Values of the Point of Zero Charge (ZPC) from $(pK_1^{int} + pK_2^{int})/2$ and Surface Acidity Constants (pK_1^{int}, pK_2^{int}) for the Samples Titrated

Serial No.	Experimental ZPC	pK_1^{int}	pK_2^{int}	Calculated ZPC
1	5.30 ± 0.10[a]	3.10 ± 0.10	7.40 ± 0.10	5.30 ± 0.07
2	9.70 ± 0.20	7.60 ± 0.30	11.76 ± 0.05	9.60 ± 0.20
3	9.70 ± 0.20	7.90 ± 0.30	11.40 ± 0.30	9.70 ± 0.20
4	9.70 ± 0.20	7.60 ± 0.05	11.90 ± 0.20	9.80 ± 0.10
5	9.40 ± 0.10	7.40 ± 0.20	11.30 ± 0.10	9.30 ± 0.10
6	9.70 ± 0.20	7.92 ± 0.02	11.80 ± 0.20	9.80 ± 0.10
7	10.10 ± 0.10	8.31 ± 0.06	11.90 ± 0.10	10.10 ± 0.07

[a] Errors given are the standard deviations.

Variation of the concentration of charged surface groups ($\overline{\mathrm{Al}}\mathrm{OH}_2^+$ and $\overline{\mathrm{Al}}\mathrm{O}^-$), calculated by using the MINEQL program, with pH of the suspension is illustrated in Fig. 4 for all specimens prepared. The curves in this figure refer to an ionic strength of 10^{-1} *M* KNO_3. Similar curves have been obtained for two other ionic strengths examined. One can observe that doping of γ-Al_2O_3 with very small amounts of sodium ions, namely, 0.083 mmol/g γ-Al_2O_3, causes a drastic increase in the concentration of $\overline{\mathrm{Al}}\mathrm{OH}_2^+$ in the pH region 5–8. In this region, Na doping results in the disappearance of the negative surface groups. These effects account for the considerable increase in the ZPC mentioned before. An additional increase in the sodium content changes the concentrations of the positive and negative surface groups markedly, yet it practically has no effect on pK_1^{int}, pK_2^{int}, and ZPC values. There is a very good correlation between the concentration of $\overline{\mathrm{Al}}\mathrm{OH}_2^+$ and the concentration of sodium on the γ-Al_2O_3 surface as well as in the solution, at pH values lower than the ZPC, where the population of these groups is considerable. Such a correlation at pH 8.5 is illustrated in Fig. 5. On the contrary, no correlation was found between sodium content and concentration of $\overline{\mathrm{Al}}\mathrm{O}^-$ at pH values higher than ZPC. The pH values at which a full transformation of the $\overline{\mathrm{Al}}\mathrm{OH}$ into $\overline{\mathrm{Al}}\mathrm{OH}_2^+$ could be achieved were estimated by extrapolating the lines of Fig. 4 to lower pH values. These values are compiled in Table 3. Table 4 summarizes the amount of supported sodium cations which enters into solution during equilibration, as well as the amount of sodium left on the surface following equilibration. The sodium

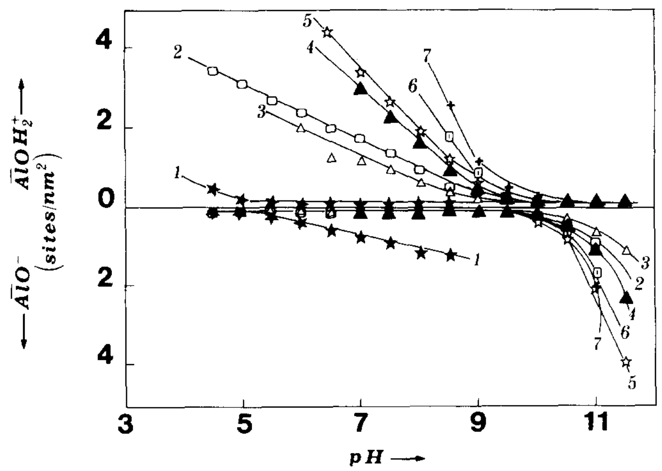

FIG. 4. Variation of charged sites ($\overline{Al}OH_2^+$ and $\overline{Al}O^-$) versus pH for the samples titrated. Numbers correspond to the serial numbers of the samples.

solubility increases with the nominal dopant concentration and decreases with the ionic strength of the solution. However, the amount of sodium dissolved, being of the order of 10^{-5} *M*, cannot practically affect the ionic strength of the suspensions.

DISCUSSION

Our results allow us to answer the questions stated in the Introduction:

(i) It is shown that a very small amount of sodium changes the "acid–base" properties of γ-Al_2O_3 drastically. In fact, 0.083 mmol Na^+/g of support is sufficient to increase considerably the pK_1^{int}, pK_2^{int}, ZPC, and concentrations of the positively charged surface groups. Moreover, this amount of modifier is sufficient to minimize the negatively charged surface groups in a wide pH range. These facts are in excellent

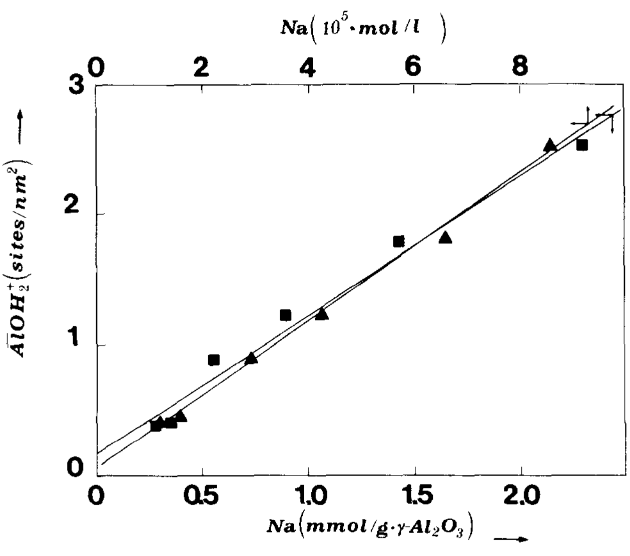

FIG. 5. Variation of positively charged groups ($\overline{Al}OH_2^+$) for 0.1 *M* KNO_3 at pH 8.5 versus (■) the real concentration of sodium on the γ-Al_2O_3 surface and (▲) the concentration of dissolved sodium.

TABLE 3

pH Values at Which Transformation of the surface Groups into $\overline{\text{Al}}\text{OH}_2^+$ Could Be Achieved

Serial No.	pH
1	[a]
2	[a]
3	[a]
4	3.50
5	4.79
6	5.50
7	6.56

[a] A complete transformation into $\overline{\text{Al}}\text{OH}_2^+$ cannot be obtained.

agreement with the well-known property of Na^+ ions to promote creation of basic sites and suppress the formation of acidic sites on the surface of this support (*42–45*).

The sharp increase in the ZPC, pK_1^{int}, and pK_2^{int} values and the different effect of ionic strength on the σ_0-vs-pH curves, observed after doping with the minimum amount of sodium ions, show that the Na originally present in the carrier behaves quite differently from the Na added by impregnation. This different behavior presumably reflects the different repartition of the two kinds of sodium along the radius of an alumina grain. In fact, the microdistribution of the deposited Na is expected to favor surface deposition as compared to the more uniform microdistribution of the Na originally present in the carrier. Since the surface parameters studied here are affected by the sodium ions located on the surface, the above-mentioned behavior of the deposited sodium is quite expectable.

From a preparative point of view the practical consequences of the sodium effects mentioned are obvious. The pH range in which $\gamma\text{-Al}_2\text{O}_3$ can adsorb negatively charged species is extended from 1–5 to 1–9. This extension facilitates the selective adsorption of desired negative species (*46*). To take a typical example, $\gamma\text{-Al}_2\text{O}_3$-supported molybdena catalysts are usually prepared by impregnation of the support with an aqueous solution of heptamolybdate (*47*). The kind of Mo species present in the impregnating solution depends on its pH, specifically, the $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{28}^{4-}$ are dominant at $\text{pH} < 5$, whereas in the pH range 8–10 the MoO_4^{2-} is practically the only species present in solution (*48, 49*). Thus, for a selective deposition of the MoO_4^{2-} to be achieved, the adsorption must take place in the above-mentioned pH range. Our results show that in this range the extent of MoO_4^{2-} adsorption on the un-

TABLE 4

Distribution of Na^+ Ions between the $\gamma\text{-Al}_2\text{O}_3$ Surface and Indifferent Electrolyte Solutions for the Samples Titrated

Serial No.		Surface Na^+ (mmol/g of $\gamma\text{-Al}_2\text{O}_3$)			Dissolved Na^+ ($10^5 \times$ mol/liter)		
	KNO_3 (*M*):	10^{-1}	10^{-2}	10^{-3}	10^{-1}	10^{-2}	10^{-3}
1		0.210	0.209	0.210	0.803	0.843	0.790
2		0.285	0.277	0.274	1.211	1.617	1.722
3		0.361	0.353	0.339	1.600	1.936	2.666
4		0.562	0.558	0.552	2.923	3.142	3.457
5		0.898	0.890	0.882	4.309	4.686	5.117
6		1.428	1.407	1.400	6.596	7.612	8.015
7		2.298	2.272	2.246	8.601	9.982	11.200

modified support must be small because the concentration of $\overline{Al}OH_2^+$ is close to zero (see Fig. 4). This prediction is in line with the work of Hall and Wang (*3*) who found that the amount of the $Mo^{(VI)}$ adsorbed on γ-Al_2O_3 at pH 9 is about 14 times smaller than that adsorbed at pH 0.85. It is suggested that the increase in the concentration of $\overline{Al}OH_2^+$ achieved by the doping mentioned will promote the selective adsorption of MoO_4^{2-}. This is expected to enhance the selective adsorption of WO_4^{2-}, VO_4^{3-}, and presumably CrO_4^{2-} on the γ-Al_2O_3 surface (*3, 50*). Experiments are now in progress to confirm this assumption. It is very important that the shift in the ZPC mentioned has been obtained by adding very small amounts of sodium, because in some cases modification with relatively large amounts of this modifier causes catalytic deactivation (*51–53*).

(ii) Figure 4 suggests that a considerable increase in the extent of adsorption can be achieved in the pH range 1–10 by increasing the sodium content. At pH 8.5, for instance, one can expect that the concentration of adsorbed MoO_4^{2-} will be three times greater in the sample with the maximum sodium content as compared with that in the unmodified support (see Fig. 5). However, this prediction requires experimental testing because it does not take into account several side effects produced on the support by modification with relatively large amounts of sodium, namely, decrease in the specific surface area and change in the pore volume.

Since the slope of the curve $[\overline{Al}OH_2^+]$ vs pH generally increases with Na^+ content on the extent of adsorption of negative species is expected to increase as pH decreases. Inspection of Table 3 shows that an amount of sodium in excess of 0.621 mmol/g γ-Al_2O_3 is necessary in order to achieve a full transformation of the surface groups into $\overline{Al}OH_2^+$. Moreover, Table 3 shows that this critical pH increases with sodium content. The values compiled in Table 3 are extremely useful for the estimation of the *minimum* amount of sodium required to maximize the extent of adsorption of negative species at a given pH.

The absence of any correlation between sodium content and $\overline{Al}O^-$ concentration at pH values higher than 9.70 could be partly attributed to the low reliability of the potentiometric measurements at this high pH. However, our results show that modification by sodium ions cannot be used to systematically vary the concentrations of negative groups at pH values higher than 9.70.

(iii) A mechanism of the sodium action must offer reasonable answers to the following questions:

(a) In what manner does a very small amount of sodium ions increase considerably the pK_1^{int}, pK_2^{int}, and thus the ZPC values?

(b) How does an increase in the sodium ions in excess of 0.309 mmol/g of γ-Al_2O_3 cause an increase in $\overline{Al}OH_2^+$ concentration but does not influence the pK_1^{int} values?

(c) Why, in sodium-doped specimens, does the concentration of the charged groups at a given pH increase with decreasing ionic strength of the solution (Fig. 2b)?

To answer the above questions we must recall the modes whereby sodium is deposited on the surface of γ-Al_2O_3 (*54–56*). In the first place sodium ions neutralize the surface $\overline{Al}OH$ groups, forming

$$\overline{Al}\text{–}\overset{\delta(-)}{O}\text{–}\overset{\delta(+)}{Na}.$$

Second they form islands of Na^+ species ($NaNO_3$, $NaNO_2$, Na_2O, . . .) supported on the carrier surface. The first and second mechanisms predominate in specimens with low and high sodium content, respectively.

Therefore, it seems reasonable to us to suggest that the

$$\overline{Al}\text{–}\overset{\delta(-)}{O}\text{–}\overset{\delta(+)}{Na}$$

groups, prevailing in the least modified

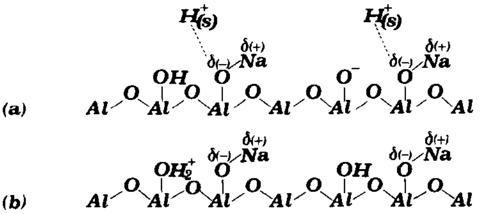

FIG. 6. Schematic representation of the effect of the $\overline{\text{Al}}$–O–Na groups on the pK_1^{int}, pK_2^{int}, and ZPC values for the specimen containing 0.309 mmol Na^+/g of γ-Al_2O_3.

specimen, are mainly responsible for the increase in pK_1^{int}, pK_2^{int} and ZPC values. The effect of these groups on the parameters mentioned could be explained assuming that they promote adsorption of hydrogen ions, on sites adjacent to $\overline{\text{Al}}$–OH and $\overline{\text{Al}}$–O^- groups, facilitating the surface reactions mentioned in the Introduction (Fig. 6). The lack of an additional increase in the parameters mentioned with increasing sodium content could be attributed to the fact that the sodium ions in excess of 0.309 mmol Na^+/g γ-Al_2O_3 are deposited mainly via the second mechanism. The increase in the concentration of $\overline{\text{Al}}OH_2^+$ groups with Na^+ content at a given pH , pK_1^{int} remaining the same, could be explained as follows: The sodium ions originating from the islands are dissolved and subsequently adsorbed specifically in the shear plane of the double layer, forming "ion pairs" with the surface $\overline{\text{Al}}$OH groups and releasing on the surface hydrogen ions [$\overline{\text{Al}}OH + Na^+_{(s)} \rightleftarrows \overline{\text{Al}}O^- \ldots Na^+ + H^+_{(s)}$]. This assumption is in excellent agreement with the literature (*34, 35*). The $H^+_{(s)}$ released promote the formation of additional $\overline{\text{Al}}OH_2^+$ groups reacting with the adjacent $\overline{\text{Al}}$OH groups through the charging mechanism described in the Introduction. In such a case an increase in the concentration of the $\overline{\text{Al}}OH_2^+$ groups with the amount of dissolved Na^+ ions is to be expected (Fig. 5).

Since the amount of dissolved Na^+ ions increases with decreasing ionic strength, the mechanism proposed can, moreover, explain why, in sodium-doped specimens, the concentration of $\overline{\text{Al}}OH_2^+$ increases as the ionic strength decreases. The same mechanism explains the increase in the negative groups because to $\overline{\text{Al}}O^-$ groups formed through the charging mechanism mentioned in the Introduction, must be added the negative parts of the $\overline{\text{Al}}O^- \ldots Na^+$ also measured by potentiometric titration.

In view of the above considerations, the slight increase in ZPC, pK_1^{int}, and pK_2^{int}, values upon an increase in sodium from 1.560 to 2.470 mmol Na^+/g of γ-Al_2O_3 seems rather unexpected. However, taking into account the considerable decrease in the specific surface area from 87.7 to 62.2 m^2 g^{-1} one could attribute the above-mentioned increase to the drastic change in the texture of the support brought about after modification with the maximum amount of sodium.

REFERENCES

1. Brunelle, J. P., *Pure Appl. Chem.* **50,** 1211 (1978).
2. Huang, C. P., and Stumm, W., *J. Colloid Interface Sci.* **43,** 409 (1973).
3. Hall, W. K., and Wang, L., *J. Catal.* **77,** 232 (1982).
4. Houalla, M., Kibby, C. L., Petrakis, L., and Hercules, D. M., *J. Catal.* **83,** 50 (1983).
5. Vordonis, L., Koutsoukos, P. G., and Lycourghiotis, A., *J. Chem. Soc. Chem. Commun.*, 1309 (1984).
6. Kittaka, S., and Morimoto, T., *J. Colloid Interface Sci.* **75,** 398 (1980).
7. Gil-Lambias, F. J., and Escudey-Castro, A. M., *J. Chem. Soc. Chem. Commun.*, 478 (1982).
8. Gil-Lambias, F. J., Santos-Blanco, J., and Escudey-Castro, A. M., *J. Catal.* **83,** 225 (1983).
9. Gil-Lambias, F. J., Escudey-Castro, A. M., Lopez-Agudo, A., and Garcia-Fierro, J. L., *Ibid. J. Catal.* **90,** 323 (1984).
10. Göbölös, S., Wu, Q., and Delmon, B., *Appl. Catal.* **13,** 89 (1984).
11. Parks, G. A., and De Bruyn, P., *J. Phys. Chem.* **66,** 967 (1962).
12. Parks, G. A., *Chem. Rev.* **65,** 177 (1965).
13. Lyklema, J., *Croat. Chim. Acta* **43,** 249 (1971).
14. Tadros, Th., and Lyklema, J., *J. Electroanal. Chem.* **17,** 267 (1968).
15. Tadros, Th., and Lyklema, J., *J. Electroanal. Chem.* **22,** 1 (1969)

16. Healy, T. W., and Fuerstenau, D. W., *J. Colloid Interface Sci.* **20,** 376 (1965).
17. Healy, T. W., Herring, A., and Fuerstenau, D. W., *J. Colloid Interface Sci.* **21,** 435 (1966).
18. James, R. O., and Healy, T. W., *J. Colloid Interface Sci.* **40,** 65 (1972).
19. James, R. O., Stiglich, P. J., and Healy, T. W., *Faraday Discuss. Chem. Soc.* **59,** 142 (1975).
20. Yates, D., and Healy, T. W., *J. Chem. Soc. Faraday Trans. 1* **76,** 9 (1980).
21. Yates, D., and Healy, T. W., *J. Colloid Interface Sci.* **55,** 9 (1976).
22. Yopps, J. A, and Fuerstenau, D. W., *J. Colloid Interface Sci.* **19,** 61 (1964).
23. Hunter, R. J., "Zeta Potential in Colloid Science—Principles and Application," Academic Press, London/New York, 1981.
24. Bates, R. G., "pH-Determination." Wiley, New York, 1973.
25. Breeuwsma, A., "Adsorption of Ions on Hematite (α-Fe_2O_3)," Ph.D. thesis Agricultural University, Wageningen, 1973.
26. Block, L., "The Ionic Double Layer of Zinc Oxide in Aqueous Electrolyte Solutions," Ph.D. thesis, State University, Utrecht, 1968.
27. Davies, C. W. "Ion Association." Butterworths, London, 1962.
28. Stumm, W., Hohl, H., and Dalang, F., *Croat. Chim. Acta* **48,** 491 (1976).
29. Hohl, H., and Stumm, W., *J. Colloid Interface Sci.* **55,** 281 (1976).
30. Stumm, W., Kummert, R., and Sigg, L., *Croat. Chim. Acta* **53,** 291 (1980).
31. Stumm, W., Huamg, C. P., and Jenkins, S. R., *Croat. Chim. Acta* **42,** 223 (1970).
32. Westall, J., and Hohl, H., *Adv. Colloid Interface Sci.* **12,** 265(1980).
33. Yates, D., Levine, S., and Healy, T. W., *J. Chem. Soc. Faraday Trans. 1* **70,** 1807 (1974).
34. Davis, J. A., James, R. O., and Leckie, J. O., *J. Colloid Interface Sci.* **63,** 480 (1978).
35. James, R. O., Davis, J. A., and Leckie, J. O., *J. Colloid Interface Sci.* **65,** 331 (1978).
36. Sprycha, R., *J. Colloid Interface Sci.* **96,** 551 (1983).
37. Huang, C. P., "The Chemistry of the Aluminum Oxide–Electrolyte Interface," Ph.D. thesis, Harvard University, 1971.
38. Marinsky, J. A., Lin, Fu. G., and Chang, K. S., *J. Phys. Chem.* **87,** 3139 (1983).
39. Westall, J. C., Zachary, L. J., and Morel, F. M. M., "MINEQL, a Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems," Tech. Note No. 18, Water Qual. Lab., Dept. of Civil Eng., MIT, 1976.
40. Westall, J. C., "MICROQL: I. A Chemical Equilibrium Program in BASIC," EAWAG. Swiss Fed. Inst. Technol., Duebendorf, 1979.
41. Westall, J. C. "MICROQL: II. Computation of Adsorption Equilibria in BASIC," EAWAG. Swiss Fed. Inst. Technol., Duebendorf, 1979.
42. Figoli, N. S., Hillar, S. A., and Parera, M. J., *J. Catal.* **20,** 230 (1971).
43. Scharme, L. D., *J. Phys. Chem.* **20,** 2070 (1974).
44. Deo, A. V., Chuang, T. T., and Dalla Lana, I. G., *J. Phys. Chem.* **75,** 234 (1971).
45. Fledorow, R., and Dalla Lana, I. G., *J. Phys. Chem.* **84,** 2779 (1980).
46. D'Aniello, M. J., Jr., *J. Catal.* **69,** 9 (1981).
47. Tsigdinos, G. A., Chem, H. Y., and Streusand, B. J., *Ind. Eng. Chem. Prod. Res. Dev.* **20,** 619 (1981).
48. Aveston, J., Anacker, E. W., and Johnson, J. S., *Inorg. Chem.* **3,** 735 (1964).
49. Honig, D. S., and Kustin, K., *Inorg. Chem.* **11,** 65 (1972).
50. Baes, D. F., and Mesmer, R. E., "The Hydrolysis of Cations." Wiley Interscience, New York, 1976.
51. Lycourghiotis, A., Defossé, C., and Delmon, B., *Bull. Soc. Chim. Belg.* **91,** 613 (1982).
52. Lycourghiotis, A., and Vattis, D., *React. Kinet. Catal. Lett.* **21,** 23 (1982).
53. Kordulis, Ch., Lycourghiotis, A., Voliotis, S., and Pomonis, P., *Appl. Catal.* **15,** 301 (1985).
54. Lycourghiotis, A., Defossé, C., Delannay, F., Lemaitre, J., and Delmon, B., *J. Chem. Soc. Faraday Trans. 1* **76,** 1677 (1980).
55. Lycourghiotis, A., Defossé, C., Delannay, F., and Delmon, B., *J. Chem. Soc. Faraday Trans. 1* **76,** 2052 (1980).
56. Lycourghiotis, A., Vattis, D., and Aroni, Ph., *Z. Phys. Chem. (N.F.)* **121,** 257 (1980).