

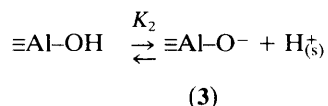
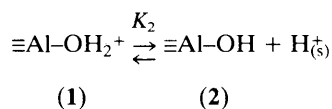
Regulation of the Point of Zero Charge and Surface Acidity Constants of $\gamma\text{-Al}_2\text{O}_3$, using Sodium and Fluoride Ions as Modifiers

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A novel method to control the values of the point of zero charge, acidity constants, and surface charge of $\gamma\text{-Al}_2\text{O}_3$, used as a catalyst support, is reported; the method, based on the selective doping of the carrier by ions, has been tested with sodium and fluoride modification.

The deposition of an active phase on the surface of $\gamma\text{-Al}_2\text{O}_3$ is the critical step in the synthesis of catalysts supported on $\gamma\text{-Al}_2\text{O}_3$. Use of wet impregnation followed by filtration or centrifugation results in deposition *via* adsorption. Increase of the extent of adsorption, which assists preparation, may be achieved by controlling the surface charge of $\gamma\text{-Al}_2\text{O}_3$.¹ The mechanism by which the surface becomes charged in aqueous solution can be described by the equilibria shown in Scheme 1,² where $\text{H}^+_{(s)}$ and $\text{H}^+_{(aq)}$ represent the hydrogen ions at the surface and in the aqueous solution, respectively. The relative concentrations of (1), (2), and (3) and hence the net surface charge depend on the values of the surface acidity constants



Scheme 1. Surface reactions at the $\gamma\text{-Al}_2\text{O}_3$ -water interface.

pK_1 and pK_2 , the point of zero charge, as well as the pH of the impregnating solution. Although control of the surface charge and consequently the extent of adsorption by regulating pH seems to be an attractive method,³ it creates serious problems in many instances. Thus, at a given pH where the resulting surface charge enhances adsorption, the form of the active ion which is deposited may not be stable. Furthermore, $\gamma\text{-Al}_2\text{O}_3$ may be partially dissolved and deposition through precipitation may not be negligible. The development therefore, of an alternative method for regulating the surface charge of $\gamma\text{-Al}_2\text{O}_3$ particles could prove to be useful in the preparation of supported catalysts.

This communication reports the first results obtained from experiments in which the surface charge of $\gamma\text{-Al}_2\text{O}_3$ is controlled by doping with ions such as Na^+ and F^- throughout the pH range. Work with different cations and anions in varying amounts is in progress. The samples were prepared by dry impregnation. The $\gamma\text{-Al}_2\text{O}_3$ used was Houdry Ho 415 (100–150 mesh). Sodium and fluoride ions were deposited using sodium nitrate and ammonium fluoride.^{4,5} All samples were dried for 2.5 h at 110 °C and subsequently calcined at 600 °C for 12 h. The samples were then suspended in KNO_3 background electrolyte (0.5 g l⁻¹). The point of zero charge and the H^+ and OH^- adsorption isotherms were determined by potentiometric titration of the suspensions, at different inert electrolyte concentrations.⁶ The intersection of the

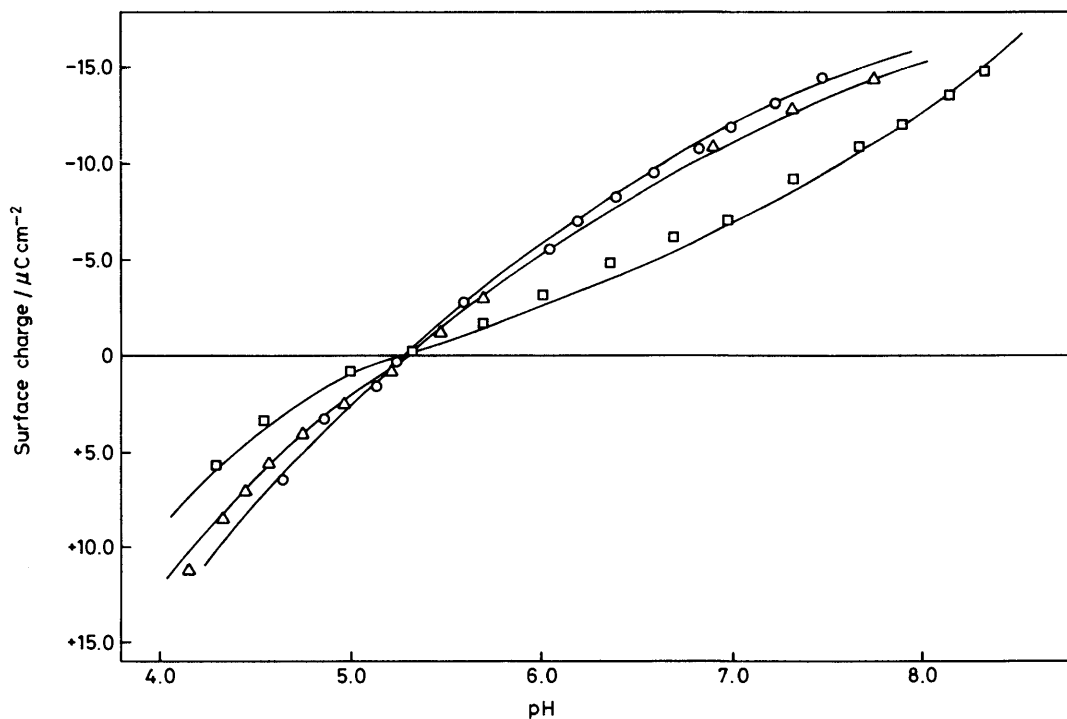


Figure 1. Surface charge of pure $\gamma\text{-Al}_2\text{O}_3$ as a function of pH, at different ionic strengths: (○) 0.1 M, (Δ) 0.01 M, (□) 0.001 M KNO_3 .

Table 1. Experimental and calculated values of the point of zero charge $[(pK_2 + pK_1)/2]$ and the surface acidity constants (pK_1, pK_2) for γ - Al_2O_3 samples.

Sample	Experimental point of zero charge	pK_1	pK_2	Calculated point of zero charge
γ - Al_2O_3	5.30 ± 0.10^a	3.10 ± 0.10	7.40 ± 0.10	5.30 ± 0.07
Na- γ - $Al_2O_3^b$	9.70 ± 0.20	7.90 ± 0.30	11.40 ± 0.30	9.70 ± 0.20
F- γ - $Al_2O_3^c$	3.40 ± 0.10	1.30 ± 0.10	5.30 ± 0.10	3.30 ± 0.07

^a Errors given are the standard deviations. ^b 0.392 mmol Na^+ per g of γ - Al_2O_3 . ^c 0.125 mmol F^- per g of γ - Al_2O_3 .

titration curves for the KNO_3 concentrations employed (0.1, 0.01, and 0.001 M), pointed to the absence of specific adsorption. Prior to titration, the samples were equilibrated in a nitrogen atmosphere with continuous stirring for 18 h. Nitric acid (0.1 M) delivered by a microburette was used to titrate the suspensions for pH values 3–11. In Figure 1, typical surface charge–pH curves are given. The surface acidity constants pK_1 and pK_2 were calculated from the titration curves using the triple layer model proposed by Davis, James, and Leckie.^{7,8} The characteristics of the samples titrated, the calculated values for pK_1 and pK_2 , and the experimental and calculated² point of zero charge, are summarized in Table 1. It can be seen that the point of zero charge and pK_1 and pK_2 are significantly affected by the presence of doping agents. Thus, we have demonstrated that the surface charge at each pH and subsequently the supporting properties of γ - Al_2O_3 can be controlled in order to achieve the maximum adsorption of the required species.

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