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

III. Regulation of the Point of Zero Charge, Surface Dissociation Constants, and Concentration of Charged Surface Groups of SiO2 by Variation of the Solution Temperature or by Modification with Sodium Ions

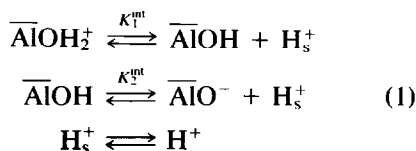K. Ch. Akratopulu, L. Vordonis, and A. Lycourghiotis[1]

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The point of zero charge (ZPC), the surface dissociation constants, and the concentration of the charged surface groups, $\overline{SiOH_2^+}$ and $\overline{SiO^-}$, of silica over a wide pH range were determined by potentiometric titrations for pure silica at various temperatures between 25 and 5°C and for a series of very low-Na$^+$-doped silicas at 25°C. A precise regulation of the ZPC can be achieved in the range 2.80–5.80 by varying the suspension temperature between 25 and 5°C. Decrease of the temperature in this range causes an increase in the ZPC, allowing an extension of the pH range in which this carrier can adsorb negative species. Increase in the concentration of the $\overline{SiOH_2^+}$ ($\overline{SiO^-}$) groups, which are the sites for the adsorption of negative (positive) species, is achieved in this range by decreasing (increasing) the suspension temperature. The values of enthalpy of deprotonation of the $\overline{SiOH_2^+}$ and $\overline{SiOH}$ groups, determined for the first time by Van't Hoff plots, suggest that the surface equilibria are endothermic, thus explaining the effect of temperature on the surface acidity constants. A considerable increase in the ZPC at 25°C was observed in silica doped with 0.083 mmol Na$^+$ per gram of SiO$_2$. Further increase in the sodium content had no appreciable effect on the ZPC value. Moreover, it was found that the sodium ions promote the protonation of the $\overline{SiO^-}$ rather than of the $\overline{SiOH}$ groups. In fact, an almost complete disappearance of the negative groups was observed after modification with the very low amount of Na$^+$ mentioned above. These results suggest that the modification by sodium of spherical or cylindrical silica grains might prove to be a method quite useful in cases where a central macrodistribution of positive species is desirable. The agreement between the values of the surface charge measured experimentally at each pH with those obtained from the difference $(\overline{SiOH_2^+}) - (\overline{SiO^-})$ suggests that the behavior of silica suspensions, both in the absence and in the presence of dopants, may be explained by the triple-layer model. © 1988 Academic Press, Inc.

INTRODUCTION

Two methods have been recently developed for regulating the point of zero charge (ZPC) and the concentration of the charged surface groups (CSG) of γ-Al$_2$O$_3$ in aqueous suspensions *(1–6)*. These groups ($\overline{AlOH_2^+}$, $\overline{AlO^-}$), resulting from the protonation–deprotonation equilibria (Eq. (1)),[2]

$$\overline{AlOH_2^+} \overset{K_1^{int}}{\rightleftharpoons} \overline{AlOH} + H_s^+$$

$$\overline{AlOH} \overset{K_2^{int}}{\rightleftharpoons} \overline{AlO^-} + H_s^+ \qquad (1)$$

$$H_s^+ \rightleftharpoons H^+$$

are considered to be the adsorption sites, the concentration of which determines the amount of an active ion that may be deposited on the surface of this carrier by adsorption of a negative or positive species. Thus, the regulation of ZPC and CSG throughout the pH range achieved by these methods is expected to help the preparation

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[2] H_s^+, H^+: hydrogen ions on the surface of the γ-Al$_2$O$_3$ and in the bulk solution, respectively.

of highly active surface-supported catalysts based on this carrier.

The first method involved doping of γ-Al_2O_3 with various amounts of a basic (Na^+, Li^+) or acidic (F^-) modifier (1–3, 5). It was found that the basic modifiers cause an increase in the ZPC and of the concentration of the $\overline{AlOH_2^+}$ groups over a wide pH range. Therefore, these modifiers can be used to increase the extent of adsorption of negative species. The F^- ions, however, cause a shift in the ZPC to lower values as well as an increase in the concentration of the $\overline{AlO^-}$ groups. Therefore, they may be used to enhance the adsorption of positive species. Although this method proved to be very effective for regulating the parameters mentioned above, it is not convenient when a precise regulation of the ZPC is necessary because even a very small amount of a dopant causes a sharp shift in the value of this parameter. Moreover, although the dopants used may promote the activity of several supported catalysts (7–11), they may cause catalytic deactivation in other cases (12–15).

The second method consists of varying the temperature of the impregnating solution (4–6). In the pH range 4.50–9.00, this method proved very effective at regulating of the value of ZPC precisely. Increase (decrease) in the temperature of the impregnating solution resulted in considerable extension of the pH range in which γ-Al_2O_3 can adsorb negative (positive) species. Moreover, an increase (decrease) in the concentration of the $\overline{AlOH_2^+}$ ($\overline{AlO^-}$) at a given pH and ionic strength was achieved by increasing the temperature of the impregnating solution. The effect of temperature was interpreted on the assumption that the surface equilibria (Eq. (1)) are exothermic. The values of ΔH obtained from linear plots of ln $K_{1 \text{ or } 2}^{int}$ vs $1/T$ were consistent with the assumption. These methods were developed to overcome problems inherent in the simple method (16–21) for regulating the concentration of the CSG by changing the pH of the impreg-

nating solution in the cases where this change promotes the surface dissolution of the carrier, the deposition of the active phase by spontaneous precipitation, and the transformation of the species to be deposited.

In the present work we extend our study, aiming for the development of industrial carriers with controlled concentration of CSG and ZPC and applying the methods previously described for silica, an important carrier used for the preparation of many supported catalysts. Although this carrier presents a very high specific surface area, it has two disadvantages, quite important from the viewpoint of the preparation of supported catalysts by adsorption (see Fig. 1):

(i) Although the pH range in which SiO_2 is soluble depends on the preparation/ pretreatment conditions, in most cases it is partially dissolved at pH higher than ≈ 5.50 (22), making it difficult to deposit an active ion by adsorption of a suitably charged species beyond this pH.

(ii) Since the ZPC of this carrier is equal to 2.80, only a very narrow pH range is suitable for the deposition of negative species (22). The deposition of positive species, on the other hand, does not present serious problems, because it can be done over a wide pH range (pH > 2.80), though with certain difficulties at pH higher than ≈ 5.50. Thus it is clear that an increase of the ZPC of silica from 2.80 to 5.50 as well as an increase of the concentration of the $\overline{SiOH_2^+}$ groups in the pH range 1.00–5.00 would increase the amount of negative species deposited on this carrier by adsorption in this pH range and thus the active surface of the resulting supported catalysts.
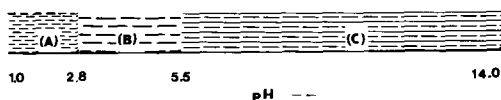

FIG. 1. pH regions in which the silica surface is positive, negative, or partially soluble. (A) Positive surface; (B) negative surface; (C) partial dissolution.

Another problem related to the preparation of supported catalysts using spherical or cylindrical silica grains is the achievement of a desired radial concentration profile. Three extreme cases should be mentioned: the eggshell profile, the uniform profile, and the macrodistribution where the active phase is concentrated in the center of a spherical grain or in the central axis of a cylindrical grain. The achievement of the first and second deposition profile does not usually create serious problems. It may be obtained by changing the impregnation time, pH, ionic strength, or by adding several antagonistic ions (23, 24). It is more difficult to obtain the third type of spatial profile, because this requires an almost complete disappearance of the $\overline{\text{Si}}\text{O}^-$ groups located on the periphery of the grain when the deposition takes place by adsorption of positive species. This could be achieved by predepositing ions (e.g., Na$^+$) on the outer parts of the silica grain, provided that doping with these ions causes the negative groups to disappear.

The increase in the ZPC and the concentration of the $\overline{\text{Si}}\text{OH}_2^+$ groups and the elimination of the $\overline{\text{Si}}\text{O}^-$ groups are attempted in the present study by doping silica with *very small amounts* of Na$^+$ ions and by changing the temperature of the impregnating solution.

EXPERIMENTAL

Preparation of the doped samples. The samples prepared are denoted by Na-X-SiO$_2$ where X represents the nominal composition in millimoles of Na$^+$ per gram of SiO$_2$ (Ketjen F-6, 100–150 mesh). The samples with $X = 0.083$, 0.166, and 0.332 were prepared by dry impregnation of the support with aqueous solutions of NaNO$_3$ (Merck, p.a.). The sample with $X = 0.000$ was "prepared" by dry impregnation of the carrier with distilled water. The impregnation was followed by drying at 110°C for 2.5 h and air-calcination at 500°C for 6 h. The specific surface areas of the samples

were determined by the BET method using a Perkin–Elmer (Model 212-D) sorptometer. Nitrogen and helium (both 99.99% pure) were used as adsorption gas and carrier gas, respectively.

Determination of ZPC, pK_1^{int}, pK_2^{int}, and the concentration of the CSG. Potentiometric titrations of aqueous suspensions of the samples Na-X-SiO$_2$ ($X = 0.000$–0.332) were carried out at 25°C. In addition, suspensions of untreated silica were titrated at 5, 10, 15, 20 and 25°C. The aqueous suspensions were equilibrated for 18–20 h before titration. This period was found to be necessary for a constant value of the suspension pH to be reached. In all cases the titrations were performed at 0.1, 0.01, and 0.001 M KCl (Merck, Suprapur) used as background electrolyte. The pH was recorded every 2 min as a function of the volume of titrant added to the suspension. Full details of the setup and procedure used as well as the method followed for the determination of the title parameters have been described elsewhere (2, 4, 25). However, two points concerning the dependence of the activity coefficient and the negative logarithm of the dissociation constant of water, pK_w, on the suspension temperature should be reported.

We have used the well-known Davies equation for monovalent ions (26) to calculate the values of the activity coefficient:

$$\log \gamma_1 = -A[\sqrt{I}/(1 + \sqrt{I}) - 0.3I] \quad (2)$$

The value of the parameter A depends on the suspension temperature (27) [0.4952 (5°C), 0.4989 (10°C), 0.5028 (15°C), 0.5070 (20°C), and 0.5115 (25°C)]. The pK_w values used at each temperature were determined from Eq. (3) (27):

$$pK_w = \frac{4471.33}{T} - 6.0846 + 0.017053T \quad (3)$$

The only assumptions involved are the following: (i) The only charging mechanism for the silica surface in aqueous solutions is that described from the following equilibria:
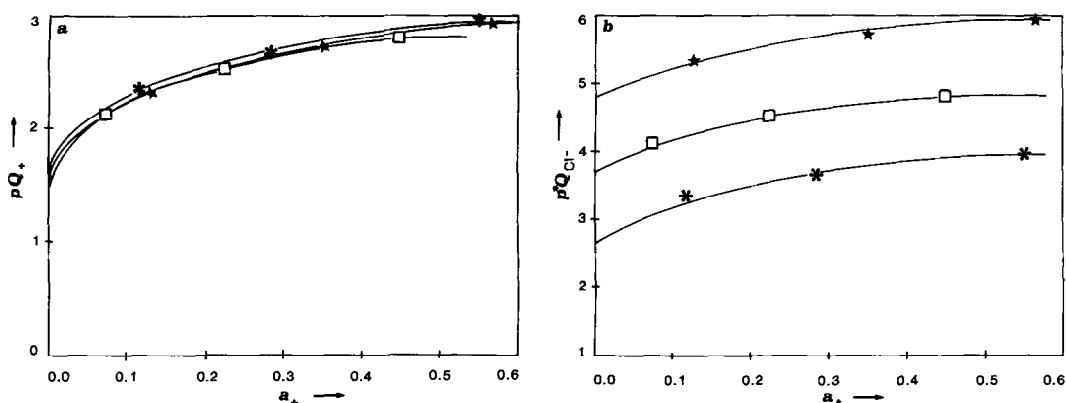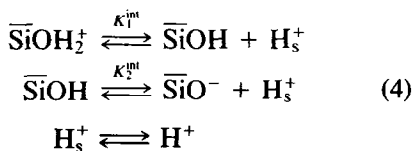
FIG. 2. Dependence of $pQ_+ \equiv pH + \log a_+/(1 - a_+)$ (a) and $p^*Q_{Cl^-} \equiv pH + \log[a_+/(1 - a_+)] - \log[Cl^-]$ (b) on the fraction of the positively charged sites, a_+, at three different values of ionic strength corresponding to 0.1 (*), 0.01 (□), and 0.001 (★) M KCl. $T = 20°C$.

$$\overline{SiOH_2^+} \underset{K_1^{int}}{\rightleftarrows} \overline{SiOH} + H_s^+$$

$$\overline{SiOH} \underset{K_2^{int}}{\rightleftarrows} \overline{SiO^-} + H_s^+ \qquad (4)$$

$$H_s^+ \rightleftarrows H^+$$

(ii) The total number of surface hydroxyl groups (N_s) is equal to 5 sites/nm^2 (80.1 μC/cm^2) in all specimens studied (28). The absence of specific adsorption of the background electrolyte, which would result in the formation of the ion pairs $\overline{SiO^-} \cdots K^+$ and $\overline{SiOH_2^+} \cdots Cl^-$ (29), should be tested experimentally. This can be done for the Cl^- ions by comparing the variance of the $pQ_+ \equiv pH + \log[a_+/(1 - a_+)]$ with that of the $p^*Q_{Cl^-} \equiv pH + \log[a_+/(1 - a_+)] - \log[Cl^-]$ values obtained for three different values of ionic strength at $a_+ \to 0$ ($a_+ = +\sigma_o/N_s$, $+\sigma_o$: positive surface charge determined experimentally). In all cases the variance of the $p^*Q_{Cl^-}$ values was found to be much higher than that of the pQ_+ values, suggesting the absence of an additional charging mechanism due to the formation of the $\overline{SiOH_2^+} \cdots Cl^-$ ion pairs (2). A typical example is illustrated in Fig. 2. Comparison of the variances mentioned above for the $pQ_- \equiv pH - \log[a_-/(1 - a_-)]$ and $p^*Q_{K^+} \equiv pH - \log[a_-/(1 - a_-)] + \log[K^+]$ for all specimens studied showed that $\overline{SiO^-} \cdots K^+$ ion pairs are not formed

under our experimental conditions (see, for example, Fig. 3).

The second assumption implies that the modification of the carrier with sodium does not change the concentration of the surface hydroxyls substantially. A calculation which takes into account the specific surface area of the doped specimens shows that this is the case. In fact, even in the case where each Na$^+$ ion deposited replaces the proton of one surface hydroxyl group, the concentration of the remaining hydroxyls will be equal to 4.9, 4.8, and 4.7 sites/nm^2 for the samples with 0.083, 0.166, and 0.332 mmol Na$^+$/g of SiO$_2$, respectively. This small change in N_s value is not expected to affect the values of the parameters determined. This was confirmed in all cases by calculating these parameters on the assumption that N_s is equal to 5.0, 4.9, 4.8, or 4.7 sites/nm^2. A typical example is illustrated in Fig. 4.

Finally, it should be noted that the various parameters used in this work were determined on the basis of the triple-layer model developed by Davis, James, and Leckie (30, 31). The applicability of this model to our system was tested by comparing the surface charge measured experimentally at each pH with the one calculated from the difference $(\overline{SiOH_2^+}) - (\overline{SiO^-})$. A
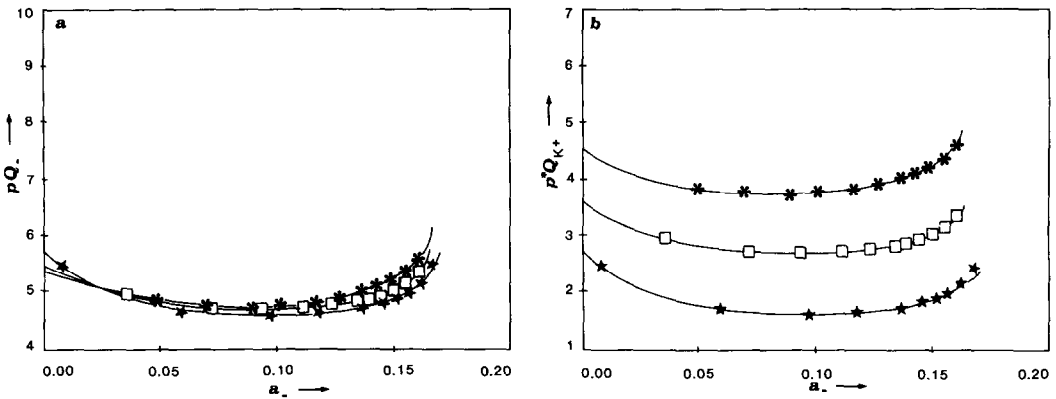
FIG. 3. Dependence of pQ_- $\equiv$ pH $-$ $\log[a_-/(1 - a_-)]$ (a) and $p^*Q_{K^+}$ $\equiv$ pH $-$ $\log[a_-/(1 - a_-)]$ + $\log[K^+]$ (b) on the fraction of the negatively charged sites, a_-, at three different values of ionic strength corresponding to 0.1 (∗), 0.01 (□), and 0.001 (★) M KCl. T = 20°C.

satisfactory agreement was found in all cases. Two typical examples are illustrated in Fig. 5.

RESULTS AND DISCUSSION

Regulation of the ZPC, pK_1^{int}, pK_2^{int}, and Concentration of the CSG by Changing the Temperature of the Impregnating Suspension

Regulation of the ZPC. Figure 6 illustrates the variation of the ZPC with the temperature of the silica suspension. It can be observed that *a precise regulation of the*

ZPC value from 2.80 to 5.78 can be achieved by a simple decrease of the suspension temperature from 25 to 5°C. The practical consequences of this effect are obvious: A decrease in the temperature of the impregnating suspension from 25 to 5°C allows for an extension of the pH range in which silica can adsorb negatively charged species by almost 3 pH units. The decrease in temperature of the impregnating suspension may have another favorable effect: It will possibly decrease the surface solubility of silica.
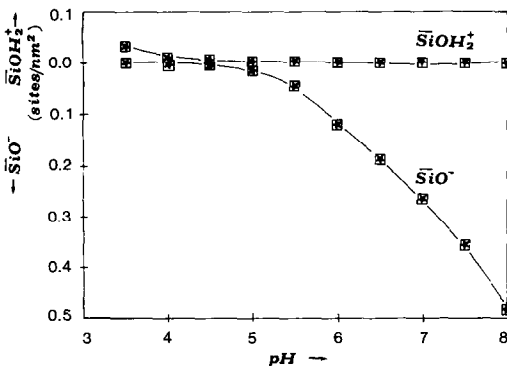
The satisfactory agreement obtained

FIG. 4. Variation of the concentration of the charged surface groups with pH of the sample Na–0.166–SiO₂ for N_s equal to 5.00 (★) and 4.80 (□) sites/nm². The ionic strength corresponds to 0.1 M KCl.
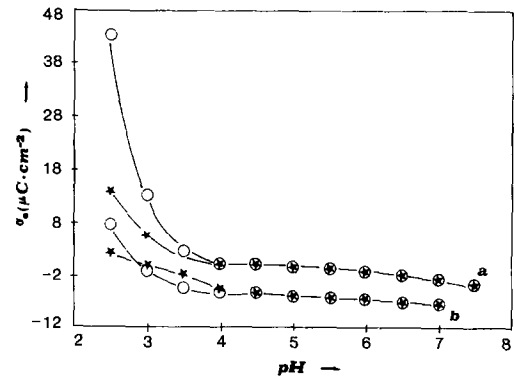

FIG. 5. Variation of the experimental (○) and calculated (★) values of σ_0 with pH for the samples Na–0.083–SiO₂ (a) and untreated SiO₂ at 25°C (b). The ionic strength corresponds to 0.1 M KCl.
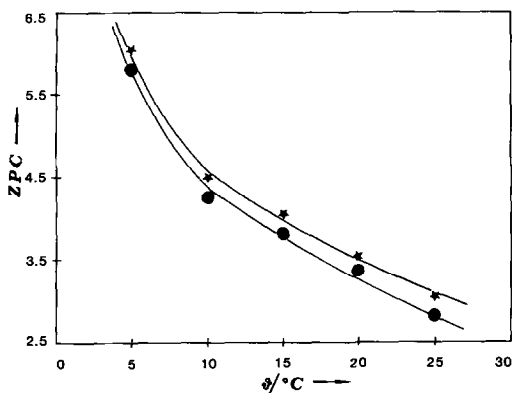
FIG. 6. Variation of experimental (●) and calculated from $(pK_1^{int} + pK_2^{int})/2$ (★) values of ZPC with the suspension temperature of the untreated SiO_2.

between the experimental and calculated values of ZPC using corresponding values of K_1^{int} and $K_2^{int}[(pK_1^{int} + pK_2^{int})/2 = ZPC]$ corroborates the validity of the method followed for the determination of the surface acidity constants (2, 3).

Regulation of the concentration of the CSG. Figure 7 illustrates the variation of the concentration of the $\overline{Si}OH_2^+$ groups with the temperature of the silica suspension at five typical pH values lower than the maximum value of the ZPC obtained (5.78). One can observe that decrease in the temperature of the impregnating suspension gen-
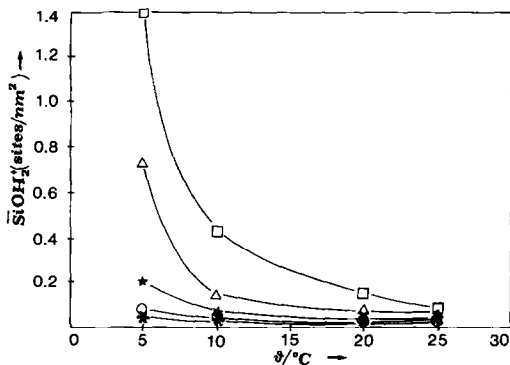
erally causes an increase in the concentration of the $\overline{Si}OH_2^+$ groups. This effect becomes more pronounced as pH decreases. Thus, at pH = 3.00, a change in the temperature from 25 to 5°C is sufficient to increase the surface concentration of the $\overline{Si}OH_2^+$ groups, on which the negative species are adsorbed, from 0.06 to 1.40.

The dependence of the concentration of the negative groups calculated at pH = 3.00, 3.50, 4.00, 4.50, and 5.00 with the suspension temperature is illustrated in Fig. 8. It can be seen that decrease in the suspension temperature resulted in reduction of the concentration of the $\overline{Si}O^-$ groups. It is noticeable that a complete disappearance of these groups, which are the adsorption sites for positive species, is observed at 5°C for all pH values examined.

Variation of the Surface Acidity Constants with Temperature of the Impregnating Suspension

The results presented in the previous paragraphs can be summarized as follows: Decrease in the suspension temperature causes an increase in the ZPC and the concentration of the $\overline{Si}OH_2^+$ groups as well as a decrease in the concentration of the $\overline{Si}O^-$ groups. The equilibria (Eq. (4)) show that these results may be explained if the

FIG. 7. Variation of the concentration of the positive groups with the suspension temperature of the untreated SiO_2 at different pH values: 3.00 (□), 3.50 (△), 4.00 (★), 4.50 (○), and 5.00 (∗). The ionic strength corresponds to 0.1 M KCl.
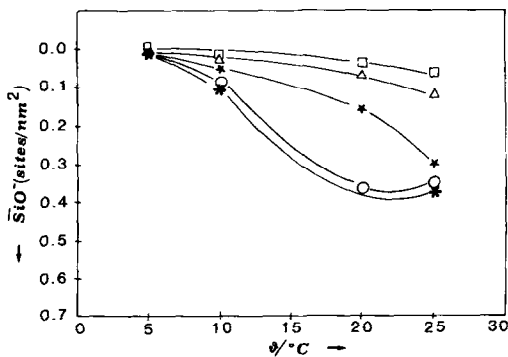

FIG. 8. Variation of the concentration of the negative groups with the suspension temperature of the untreated SiO_2 at different pH values: 3.00 (□), 3.50 (△), 4.00 (★), 4.50 (○), and 5.00 (∗). The ionic strength corresponds to 0.1 M KCl.
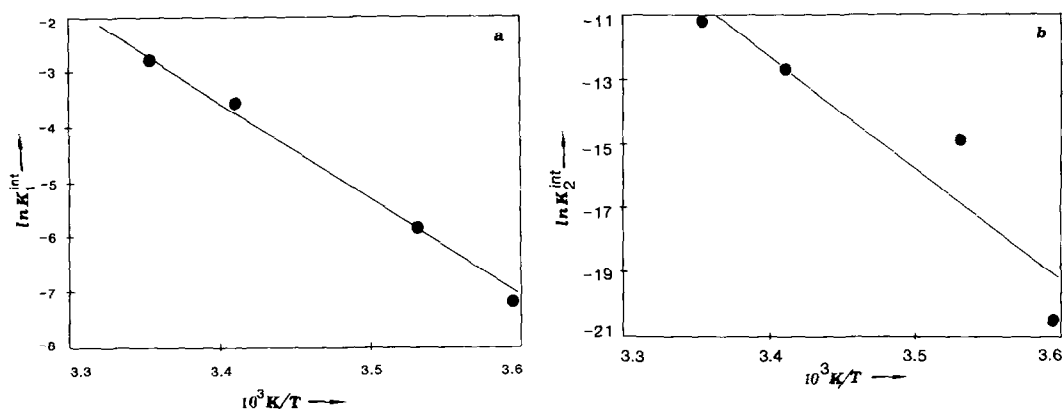
FIG. 9. Plots of the ln K_1^{int} (a) and ln K_2^{int} (b) versus $1/T$ for the surface dissociation of the $\overline{SiOH_2^+}$ and $\overline{SiOH}$ groups, respectively.

deprotonation processes of the $\overline{SiOH_2^+}$ and $\overline{SiOH}$ are assumed to be endothermic. The curves ln $K_{1 \, or \, 2}^{int}$ vs $1/T$ illustrated in Fig. 9 are consistent with this assumption.

Assuming that the surface of the silica particles can be simulated with a two-dimensional ideal solution, the chemical potential for each species involved in Eq. (4) is given by Eq. (5) (32).

$$\mu_i = \mu_i^o - RT \ln c_i$$
$$i \equiv \overline{SiOH_2^+}, \overline{SiO^-}, \overline{SiOH}, \text{ or } H_s^+ \quad (5)$$

In this equation c_i represents the surface concentration in mol dm^{-2} of the ith species and μ_i^o its standard-state chemical potential taken for $c_i = 1$ mol dm^{-2}. By a well-established procedure (33), Eq. (6) and (7) can be easily derived from Eq. (5).

$$\ln K_1^{int} = -\frac{\Delta H_1^o}{R} \cdot \frac{1}{T} + \frac{\Delta S_1^o}{R} \quad (6)$$

$$\ln K_2^{int} = -\frac{\Delta H_2^o}{R} \cdot \frac{1}{T} + \frac{\Delta S_2^o}{R} \quad (7)$$

These equations allow the determination of the standard-state enthalpies and entropies of the surface deprotonations of the $\overline{SiOH_2^+}$ and $\overline{SiOH}$ groups from the slopes and intercepts, respectively, of the lines shown in Fig. 9. The values obtained are summarized in Table 1. The positive ΔH_i^o

values explain the increase in the concentration of the $\overline{SiOH_2^+}$ groups and ZPC as well as the decrease of the $\overline{SiO^-}$ groups with the decrease in the suspension temperature. Moreover, comparison of the ΔH_1^o with ΔH_2^o value shows that K_2^{int} is more temperature-sensitive than K_1^{int}, revealing that the main reason for the increase of the ZPC following a decrease in the suspension temperature is the disappearance of the negative groups rather than the formation of additional positive groups.

Comparison of the present results with those obtained for γ-Al_2O_3 (4) shows that the direction of the enthalpy changes which accompany the deprotonation of the protonated and neutral hydroxyls depends on the nature of the carrier. For the moment we cannot explain why these reactions are exothermic for γ-Al_2O_3 and endothermic for SiO_2.

TABLE 1

Enthalpies and Entropies of the Surface Processes Illustrated in Eq. (4)[a]

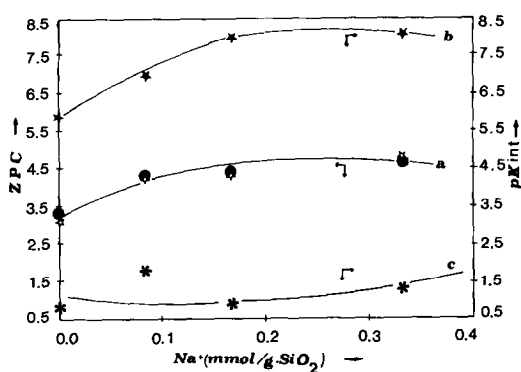| i	ΔH_i^o/K J mol^{-1}	ΔS_i^o/J K^{-1} mol^{-1}
1	150 ± 10	490 ± 30
2	290 ± 80	900 ± 300

[a] Errors given are standard deviations.

FIG. 10. Variation of experimental and calculated values of ZPC and surface acidity constants (pK_1^{int}, pK_2^{int}) with sodium content. (☆) Experimental ZPC; (●) calculated ZPC ((pK_1^{int} + pK_2^{int})/2); (*) pK_1^{int}; (★) pK_2^{int}.

Regulation of the ZPC, pK_1^{int}, pK_2^{int}, and Concentration of the CSG by Doping Silica with Sodium Ions

Figure 10 illustrates the variation of the ZPC, pK_1^{int}, and pK_2^{int} values with sodium content. It shows that a considerable increase in the ZPC from 3.25 to 4.20 may be achieved by doping silica with an amount of sodium as low as 0.083 mmol Na^+ per gram of SiO_2. Further increase in the sodium content causes a slight increase in the ZPC from 4.20 to 4.80. The good agreement between the experimental and calculated ZPC values suggests that the change of the ZPC is due to the change of the values of the surface dissociation constants brought about by doping. However, comparison of curve 10a with the curves 10b and 10c shows that sodium doping does not markedly affect the surface dissociation constant of the positive group, pK_1^{int}, the value of which oscillates randomly about a mean value with the sodium content. Therefore, the change in the (pK_1^{int} + pK_2^{int})/ 2 ≡ ZPC should be attributed to the change of the pK_2^{int}. This indicates that sodium doping should promote the protonation of the $\overline{Si}O^-$ but not of the $\overline{Si}OH$ groups. The above was confirmed by inspection of the dependence of the concentration of the

$\overline{Si}OH_2^+$ and $\overline{Si}O^-$ groups, determined at various pH values, with the sodium content. In fact, an almost complete disappearance of the $\overline{Si}O^-$ groups was observed after modification with the minimum Na^+ concentration (Fig. 11) even at pH 4.50, in contrast to the insignificant change due to modification observed in the concentration of the $\overline{Si}OH_2^+$ groups.

The experimental evidence presented herein shows that the method of modification with a basic modifier could be extremely useful in the cases where a central microdistribution of positive species on spherical or cylindrical silica grains has to be achieved. On the other hand, this method is not effective in promoting the adsorption of negative species.

On the Applicability of Our Findings to Catalyst Preparation

We must discuss the limitations of our findings, mainly concerning the achievement of a desired macrodistribution, to actual methods used in catalyst preparation. First, it should be mentioned that the prediction of a central macrodistribution of an active element achieved by doping the periphery of SiO_2 grains by sodium ions is
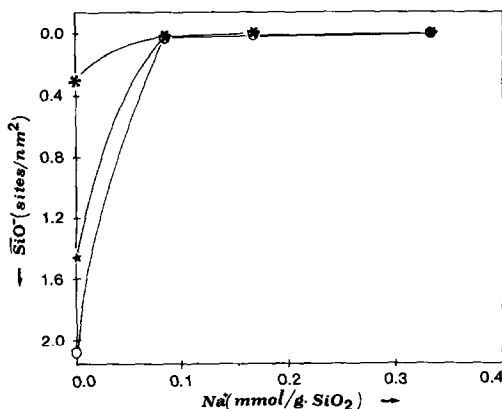

FIG. 11. Variation of the concentration of the negative groups with sodium content at pH 3.50 (*), 4.00 (★), and 4.50 (○). The ionic strength corresponds to 0.1 M KCl.

based on the assumption, which seems to be quite reasonable, that the sodium ions deposited by adsorption and stabilized by heating on the outer part of the SiO_2 grains will cause a disappearance of the $\overline{SiO^-}$ groups inside the Na-doped region. The fact that Na^+ is a non-potential-determining ion and thus does not strongly adsorb on oxide supports is not expected to create serious problems because the $\overline{SiO^-}$ groups disappear completely after modification with very low amount of Na^+ ions. Second, it should be stressed that the ZPC and the concentration of CSG are not the only, though very important, factors that affect the extent of adsorption and thus the achievement of a desired macrodistribution. One should take into account the ionic strength, the concentration of the solution, and the impregnation time. Third, the change in the suspension temperature and the sodium doping may change other factors involved in the catalyst preparation besides the ZPC and the concentration of CSG. Therefore, our predictions need experimental verification. However, preliminary experimental results obtained by our group with respect to the adsorption of Mo^{6+}, Ni^{2+}, and Co^{2+} on Na-doped γ-Al_2O_3 (*34*) confirm our predictions. Needless to say, the regulation of the ZPC and the concentration of CSG contribute only to the fabrication of catalysts prepared by adsorption.

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