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

II. Modification of γ-$\mathrm{Al_2O_3}$ with Various Amounts of Lithium and Fluoride Ions

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Two series of carriers were prepared by doping γ-$\mathrm{Al_2O_3}$ with various amounts of $\mathrm{Li^+}$ and $\mathrm{F^-}$ ions and the point of zero charge (ZPC), the surface acidity constants as well as the concentration of the charged surface groups, $\overline{\mathrm{Al}}\mathrm{OH}_2^+$ and $\overline{\mathrm{Al}}\mathrm{O}^-$ were determined potentiometrically over a wide pH range. It was found that 0.621 mmol $\mathrm{Li^+}$ per g of γ-$\mathrm{Al_2O_3}$ were sufficient to cause a shift of the ZPC from 5.30 to 9.80. Accordingly, the concentration of adsorption sites for negative species ($\overline{\mathrm{Al}}\mathrm{OH}_2^+$) was increased, while the surface acidity constants decreased and the formation of $\overline{\mathrm{Al}}\mathrm{O}^-$ sites was inhibited. Further increase in the lithium content causes a marked increase in the concentration of the $\overline{\mathrm{Al}}\mathrm{OH}_2^+$ groups at pH lower than 8.0. Comparison of the effects caused due to the lithium doping with those observed after sodium modification studied previously, showed that lithium can be used instead of sodium in the cases where the latter causes catalytic deactivation. However, larger amounts of lithium, as compared with that of sodium, are necessary in order for the same increase in the concentration of the $\overline{\mathrm{Al}}\mathrm{OH}_2^+$ groups at a given pH to be achieved. A mechanism similar to that adopted for the sodium-doped alumina has been used to explain the $\mathrm{Li^+}$ effects observed in the present study. Concerning the doping by $\mathrm{F^-}$ ions it was observed that modification of γ-$\mathrm{Al_2O_3}$ with 0.125 mmol $\mathrm{F^-}$ per g of γ-$\mathrm{Al_2O_3}$ decreases the ZPC from 5.30 to 3.40. $\mathrm{F^-}$ doping thus can be used to extend the pH range, where positive species could be deposited on γ-$\mathrm{Al_2O_3}$ by adsorption, at lower pH values. Moreover, this modification brings about an increase in the concentration of the adsorption sites for positive species, $\overline{\mathrm{Al}}\mathrm{O}^-$, as well as in the values of the surface acidity constants. Additional increase in the concentration of the $\mathrm{F^-}$ ions provokes a considerable increase in the concentration of the $\overline{\mathrm{Al}}\mathrm{O}^-$ groups at pH higher than 3.40 though it does not further affect the values of ZPC and surface acidity constants.

INTRODUCTION

It is well established that γ-$\mathrm{Al_2O_3}$, the most important carrier used in catalysis, presents ampholytic properties (*1*). In fact, it exhibits three kinds of surface groups namely, $\overline{\mathrm{Al}}\mathrm{OH}_2^+$, $\overline{\mathrm{Al}}\mathrm{OH}$, and $\overline{\mathrm{Al}}\mathrm{O}^-$, in aqueous suspensions. The relative concentration of these groups depends on the pH, ionic strength of the aqueous suspension, and the values of the surface acidity constants K_1^{int} and K_2^{int} (*2, 3*).

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

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

$$\mathrm{H}_s^+ \rightleftharpoons \mathrm{H}^+$$

There is a pH value, defined as point of zero charge (ZPC), at which the concentration of (I) is equal to that of (III) and negligible as compared with the concentration of (II). pH values equal, higher, and lower than ZPC, render the surface of γ-$\mathrm{Al_2O_3}$ neutral, negative, and positive, respectively. The ZPC for γ-$\mathrm{Al_2O_3}$ is found at pH 5.30 ± 0.10 (*2, 3*). The dependence of the relative concentrations of (I), (II), and (III), and hence of the ZPC value, on the values of pH, K_1^{int}, and K_2^{int} is easily understand-

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able from the above equilibria. The dependence on the ionic strength is due to the fact that this parameter influences the potential, y_0, developed on the surface of the γ-Al_2O_3 particles and thus the concentration of the adsorbed hydrogen ions (H_s^+), at a given pH $\{(H_s^+) = (H^+) \exp(-F \cdot y_0/2.3\,RT)\}$ (*4*).

The deposition of an active ion on the γ-Al_2O_3 surface is the most critical step in the preparation of supported catalysts based on this carrier. In many cases this occurs via adsorption of suitable species. Increase of the amount of an active ion deposited through adsorption results to the augmentation of the *active surface,* which is extremely desirable from the preparative point of view. According to the current ideas the $\overline{Al}OH_2^+$ and $\overline{Al}O^-$ surface groups are the sorptive sites for the negative and positive species and they are used for the deposition of active ions (*2, 3, 5*). Increase in the surface concentration of the $\overline{Al}OH_2^+$ ($\overline{Al}O^-$) is, therefore, necessary when an enhancement in the adsorption of a negative (positive) species is sought. The method followed in practice includes a proper regulation in the pH of the impregnating solution (*6–8*). This method, seemingly very simple, may become problematic in some cases. More specifically at the pH value where the adsorption is promoted, the species to be adsorbed may not be stable and the carrier may be partially dissolved (*5*). Moreover, deposition by precipitation may occur in considerable extent, resulting to low dispersity of the supported phase. Analogous problems may be caused by changes in the ionic strength of the impregnating solution.

A research program recently undertaken by our group aims at developing an alternative method for regulating the ZPC of γ-Al_2O_3 and the surface concentration of (I), (II), and (III) at a given pH and ionic strength (*2, 3*). This task is pursued by doping γ-Al_2O_3 with the appropriate ions. In the first paper of this series (*3*) the influence of the content of the Na^+ ions on the concentration of (I), (II), and (III) at various pH as well as on the ZPC, pK_1^{int}, and pK_2^{int} values has been examined. It was found that doping with very small amount of sodium ions, namely, 0.083 mmol Na per g of γ-Al_2O_3, is sufficient to bring about an increase in the pK_1^{int}, pK_2^{int}, and ZPC values from 3.10 to 7.60, from 7.40 to 11.76, and from 5.30 to 9.70, respectively. Consequently by this doping a very considerable expansion of the pH range where a *negatively charged* species could be deposited through adsorption was achieved. Within this range the modification mentioned increased the concentration of the $\overline{Al}OH_2^+$ groups at each pH. Increment in the sodium content from 0.309 to 2.470 mmol Na^+ per g of γ-Al_2O_3 had no further effect on the pK_1^{int}, pK_2^{int}, and ZPC values, although an increase in the concentration of (I) and (III) at pH lower and higher than ZPC has been observed, respectively.

The purpose of the present work is twofold: first we aim at enlarging pH range in which a *positively charged* species can be adsorbed on the γ-Al_2O_3 surface. This is attempted by doping the γ-Al_2O_3 with various amounts of F^- ions. More precisely we study the influence of the concentration of F^- ions on ZPC, pK_1^{int}, and pK_2^{int} values as well as on the surface concentration of (I), (II), and (III). Second, we aim at finding out a different type of cations whose action is similar to that of Na^+ cations. This is done because in some cases sodium cations result in deactivation of the supported catalysts (*9*). For this reason, the effect of Li^+ ions has been studied.

The determination of the required parameters was achieved using the method of the potentiometric titrations (*3*).

EXPERIMENTAL

Preparation of the samples. The specimens containing Li^+ and F^- ions are denoted by Li-*x*-γ-Al_2O_3 and F-*x*-γ-Al_2O_3, respectively, where *x* represents the nominal composition expressed as millimoles of the dopant ion per g of γ-Al_2O_3. The specimens prepared are illustrated in Table 1.

TABLE 1

Nominal Compositions and Specific Surface Areas of the Samples Prepared

Serial No.	Notation	SSA ($m^2\ g^{-1}$)
1	γ-Al_2O_3	123.0
2	Li-0.392-γ-Al_2O_3	138.9
3	Li-0.621-γ-Al_2O_3	121.6
4	Li-0.984-γ-Al_2O_3	118.8
5	Li-1.560-γ-Al_2O_3	115.4
6	Li-2.470-γ-Al_2O_3	98.0
7	F-0.125-γ-Al_2O_3	135.2
8	F-0.468-γ-Al_2O_3	131.7
9	F-1.978-γ-Al_2O_3	99.5
10	F-3.818-γ-Al_2O_3	77.4

The Li^+- and F^--doped specimens were prepared by dry impregnation of γ-Al_2O_3 (Ho 415, Houdry) with aqueous solutions of $LiNO_3$ (Ferrak, reinst) and NH_4F (Carlo Erba R.P.), respectively. Sample 1 was "prepared" by dry impregnation of the carrier with pure solvent (distilled water). After impregnation the specimens were dried at 110°C for 2.5 h and then air-calcined at 600°C for 12 h.

The specific surface areas of the specimens studied were determined by a multiple-point BET method, using a Perkin–Elmer (Model 212-D) sorptometer. Pure nitrogen and helium (both 99.99% of purity) were used as adsorption and carrier gas, respectively.

Determination of ZPC, pK_1^{int}, pK_2^{int}, and the surface concentration of the surface groups. The setup and procedure used as well as the method followed for the determination of the title parameters were described in detail in the first paper of this series (*3*). The assumptions involved in the determination of $\overline{Al}OH_2^+$ and $\overline{Al}O^-$ groups concentration is the validity of the protonation–deprotonation equilibria shown in the introduction and that the total number of surface hydroxyl groups (N_s) is 8 sites/nm^2. A concominant correction for the N_s due to modification would have no effect in the determined K_1^{int} and K_2^{int} values. A simple calculation based on the assumption that the number of sites is reduced by 50% would lead to a difference in the values of the determined $pK_{1,2}^{int}$ within the experimental error (*3*).

Determination of the solubility of the Li^+ and F^- ions. In order to investigate whether a portion of Li^+ and F^- ions is dissolved in the aqueous solution during equilibration (*3*), the solubility of these ions was determined for all samples titrated, in the supernatant after filtration of the corresponding suspension. A flame photometer (Dr. B. Lange) equipped with a lithium filter and a fluoride-ion selective electrode (Orion Type 94-09) were used for the determination of the Li^+ and F^- ions, respectively. The F^--ion selective electrode was calibrated in solutions equilibrated with γ-Al_2O_3 in order to offset Al^{3+} interference due to solubility.

RESULTS

The variation of the experimental and calculated ZPC values as well as of the constants pK_1^{int}, pK_2^{int} with the lithium content for the samples 1–6 is illustrated in Fig. 1. An inspection of this figure shows that modification with 0.392 mmol Li^+ per g of γ-Al_2O_3 does not affect the ZPC value signifi-

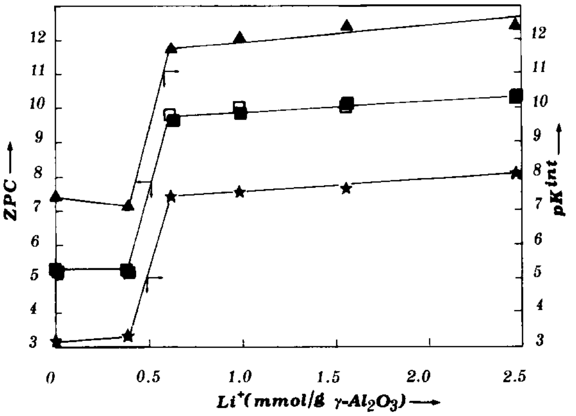

FIG. 1. Variation of the experimental and calculated values of ZPC as well as of the surface acidity constants (pK_1^{int}, pK_2^{int}) with lithium content for samples 1–6. (□) Experimental ZPC, (■) calculated ZPC (ZPC = (pK_1^{int} + pK_2^{int}/2)), (★) pK_1^{int}, (▲) pK_2^{int}.

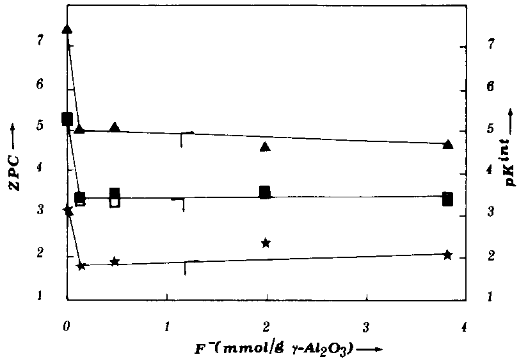

FIG. 2. Variation of the experimental and calculated values of ZPC as well as of the surface acidity constants (pK_1^{int}, pK_2^{int}) with the fluoride content for samples 1, 7–10. (□) Experimental ZPC, (■) calculated ZPC (ZPC = (pK_1^{int} + pK_2^{int}/2)), (★) pK_1^{int}, (▲) pK_2^{int}.

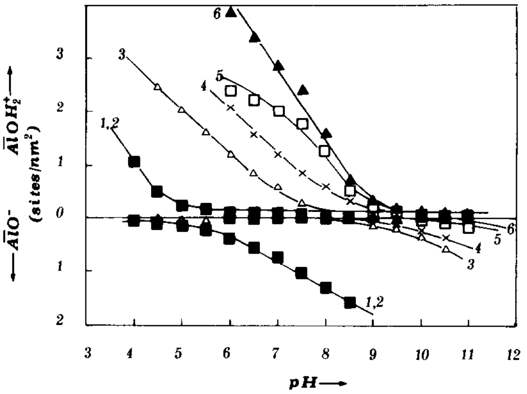

FIG. 3. Dependence of the concentration of the charged groups, ($\overline{\text{Al}}\text{OH}_2^+$) and ($\overline{\text{Al}}\text{O}^-$), on the pH of suspension for samples 1–6.

cantly. A sharp increase of the ZPC from 5.30 to 9.80 is observed after modification with 0.621 mmol Li^+ per g of γ-Al_2O_3. Further slight increase of the pH of the ZPC from 9.80 to 10.28 is observed when the x value increased from 0.621 to 2.470. In this region one can observe a linear dependence of the ZPC on the x value. Similar variation is observed in the values of pK_1^{int} and pK_2^{int} with the lithium content.

Figure 2 illustrates the variation of the parameters mentioned before with the fluoride content for samples 1 and 7–10. It can be seen that modification of γ-Al_2O_3 with 0.125 mmol F^- per g of γ-Al_2O_3 is sufficient to decrease the ZPC value from 5.30 to 3.40. Additional increase in the F^- content up to x = 3.818 does not practically affect the ZPC value. Similar variations can be observed in the values of pK_1^{int} and pK_2^{int} with the fluorine content.

Figures 1 and 2 show that there is an excellent agreement between the experimental and calculated values of ZPC for all samples titrated.

The dependence of the concentration of charged surface groups on the pH of the suspension of Li^+ and F^- dopes samples are illustrated in Figs. 3 and 4, respectively. The curves of these figures refer to ionic strength 0.1 M KNO_3. Similar curves have been obtained in 0.01 and 0.001 M KNO_3. Figure 3 shows that modification with 0.392 mmol Li^+ per g of γ-Al_2O_3 has no influence on the concentration of the charged surface groups over the entire pH range examined. Modification with larger amount of lithium causes a marked increase in the concentration of $\overline{\text{Al}}\text{OH}_2^+$ groups at pH lower than 8.0. In the same region the Li-doping results in an almost complete disappearance of the $\overline{\text{Al}}\text{O}^-$ groups. On the contrary, modification by F^- ions provokes a drastic increase in the concentration of $\overline{\text{Al}}\text{O}^-$ groups in pH values lower than 5.30, whereas it does not

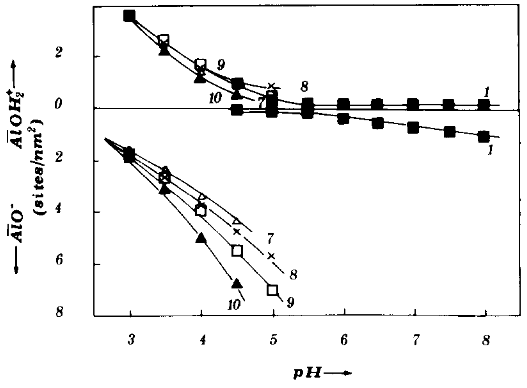

FIG. 4. Dependence of the concentration of the charged groups, ($\overline{\text{Al}}\text{OH}_2^+$) and ($\overline{\text{Al}}\text{O}^-$) on the pH of suspension for samples 1 and 7–10.

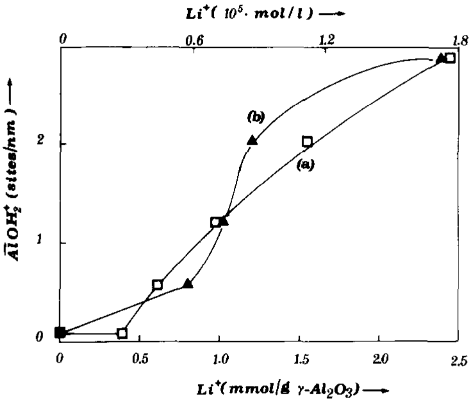

FIG. 5. Variation of the positively charged groups ($\overline{\text{Al}}\text{OH}_2^+$) with the true concentration of lithium on the γ-Al_2O_3 surface (□) and the concentration of dissolved lithium (▲) at pH = 7 and ionic strength corresponding to 0.1 M KNO_3.

affect the concentration of the $\overline{\text{Al}}\text{OH}_2^+$ groups. Moreover, Figs. 3 and 4 show that there is a correlation of the concentration of $\overline{\text{Al}}\text{OH}_2^+$ and $\overline{\text{Al}}\text{O}^-$ groups with Li^+ and F^- content in the pH range 5.0–8.0 and 3.0–5.0, respectively. Examples of this correlation for the Li^+ and F^- doped specimens at pH = 7 and pH = 4.50 are illustrated in Figs. 5 and 6, respectively. The concentration plots of $\overline{\text{Al}}\text{OH}_2^+$ vs dissolved Li^+ and of the concentration of $\overline{\text{Al}}\text{O}^-$ vs dissolved F^- are shown as well.

The pH values at which a full transformation of the $\overline{\text{Al}}\text{OH}$ into $\overline{\text{Al}}\text{OH}_2^+$ ($\overline{\text{Al}}\text{O}^-$) could be achieved, were estimated (for lithium (fluoride) samples) by extrapolating the lines of Fig. 3 (4) to lower (higher) pH values. These values are shown in Table 2.

Table 3 summarizes the amount of the supported lithium and fluoride ions which goes into solution during equilibration as well as the amount of supported ions remaining on the surface after equilibration. The solubility of the ions used as modifiers increases with the nominal dopant concentration and decreases with the ionic strength of the solution. Moreover, the solution concentration of the ions dissolved being of the order of 10^{-5} M cannot practically affect the ionic strength of the suspensions.

TABLE 2

pH Values at Which Complete Transformation of the Surface Groups into $\overline{\text{Al}}\text{OH}_2^+$ and $\overline{\text{Al}}\text{O}^-$, for Li-Doped and F-Doped Samples, Respectively, Could Be Achieved

Serial No.	pH
1	—[a,b]
2	—[a]
3	—[a]
4	0.45
5	1.17
6	1.79
7	8.24
8	7.67
9	5.31
10	4.86

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

[b] A complete transformation into $\overline{\text{Al}}\text{O}^-$ cannot be obtained irrespective of the value of pH.

DISCUSSION

The lithium action. Our results clearly demonstrate that the modification with Li^+

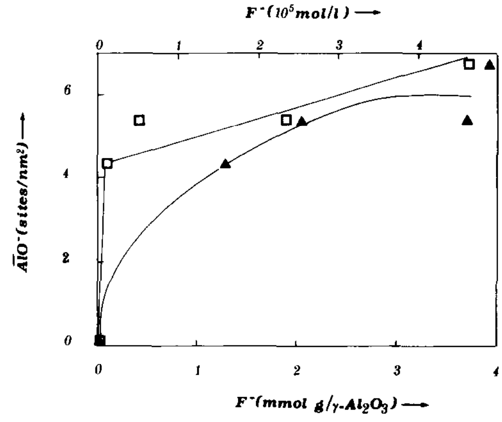

FIG. 6. Variation of negatively charged groups ($\overline{\text{Al}}\text{O}^-$) with the concentration of the surface and surface ion-paired fluoride (□) and with the concentration of dissolved fluoride (▲) at pH = 4.5 and ionic strength corresponding to 0.1 M KNO_3.

TABLE 3

Distribution of Li^+ and F^- Ions between γ-Al_2O_3 Surface and Indifferent Electrolyte Solutions for the Samples Titrated

Serial No.	KNO$_3$ (M)		
	10^{-1}	10^{-2}	10^{-3}
	Surface Li^+ (F^-) (mmol per g of γ-Al_2O_3)		
1	—	—	—
2	0.392	0.392	0.392
3	0.609	0.608	0.607
4	0.969	0.968	0.967
5	1.543	1.540	1.539
6	2.435	2.429	2.425
7	0.093	0.091	0.064
8	0.417	0.407	0.326
9	1.886	1.845	1.827
10	3.720	3.690	3.661

ions causes similar effects to those observed after the Na^+ doping (*2*). Thus, these ions could be used in order to enlarge the pH range in which a *negative species* can be deposited via adsorption from 1.00–5.30 to 1.00–10.20. Moreover, they show that in the pH range 1.0–8.00 a considerable increase in the concentration of the sites responsible for the adsorption of negative species could be achieved by increasing the concentration of the modifier. Finally, the disappearance of the $\overline{\text{AlO}}^-$ groups at pH lower than 8 could be exploited to inhibit the adsorption of *positive species* in this pH range. This might be proved extremely useful in the cases where a desired macrodistribution of an active ion on an alumina pellet has to be achieved (*10*).

However, the action of Li^+ and Na^+ ions is not identical. Some salient differences must be mentioned: (i) The modification by Li^+ ions does not cause considerable decrease in the specific surface area of the γ-Al_2O_3. Thus, the maximum amount of this modifier is necessary to decrease the SSA from 123.0 to 98.0 m^2 g^{-1} (*3*). (ii) Relatively large amount of Li^+ ions is necessary in order for a considerable increase in the ZPC, pK_1^{int}, and pK_2^{int} values to be achieved. Thus, modification by 0.621 mmol Li^+ per g γ-Al_2O_3 is required to increase the ZPC from 5.30 to 9.80 whereas 0.083 mmol Na^+ per g γ-Al_2O_3 are sufficient to achieve the same increase in the ZPC. (iii) The ZPC, pK_1^{int}, and pK_2^{int} values of the Na^+ containing specimens are kept practically constant upon increase of x from 0.392 to 1.560. On the contrary, concerning the Li^+-doped samples a constant, though small, increment in the values of these parameters is observed as x increases from 0.621 to 2.470. (iv) The concentrations of the $\overline{\text{AlOH}}_2^+$ groups at pH lower than 8 as well as the slopes of cruves, 1, 2, 3, 4, 5, and 6 are smaller compared with those of the Na^+-doped specimens (*3*). Moreover the pH value required for a full transformation of $\overline{\text{AlOH}}$ into $\overline{\text{AlOH}}_2^+$ groups due to the lithium modification (Table 2) is smaller than that obtained by the sodium doping (*3*). This comparison clearly shows that *lithium is a "basic modifier" though weaker than sodium.*

To explain the differences in the behaviour between Li^+ and Na^+ ions we must recall the model adopted for the state of the deposited Na^+ ions (*3*). A slightly different model is adopted here for the state of the supported Li^+ ions (*11*): (a) Li^+ ions diffuse into γ-Al_2O_3 lattice during calcination. (b) They neutralize the surface $\overline{\text{AlOH}}$ groups forming $\overline{\text{Al}}\text{—}\overset{\delta(-)}{\text{O}}\text{—}\overset{\delta(+)}{\text{Li}}$ groups. (c) They form islands of Li^+ compounds supported on the γ-Al_2O_3 surface. These islands are aggregates of lithium, for instance $LiNO_3$, or tridimensional compounds between Li and Al, e.g., $LiAl_2O_8$ and/or $Li_2Al_2O_4$. In most cases these compounds were ill-defined by X-ray analysis, presumably because of their low concentration and/or their poor crystallinity.

It seems to us reasonable to assume that the Li^+ ions located in the interior of the carrier do not affect their surface properties. Moreover, in agreement with our results for the γ-Al_2O_3–Na system (*3*), we may assume that the $\overline{\text{Al}}\text{—}\overset{\delta(-)}{\text{O}}\text{—}\overset{\delta(+)}{\text{Li}}$ groups are mainly responsible for the increase in the ZPC, pK_1^{int}, and pK_2^{int}, whereas the islands of Li compounds mentioned are mainly responsible for the increase in the concentration of the $\overline{\text{AlOH}}{}_2^+$ groups at pH lower than 8.0. Finally, in agreement with the literature (*11*), we assume that the extent of processes (a) and (b) is greater in the case of Li-doped carriers, whereas process (c) is favored in the case of the sodium-based system. In both systems the relative extent of process (c) increases at the expense of the relative extents of processes (a) and (b) upon increasing the dopant concentration (*11*).

The relatively large extent of process (a) in the Li-based system explains the differences (i) and (ii) mentioned before. Thus, for instance, the amount of the Li^+ ions remaining on the surface in the sample Li-0.392-γ-Al_2O_3 is too small to change the values of the pK_1^{int}, pK_2^{int}, and ZPC as well as the concentration of (I), (II), and (III) (Fig. 5, curve a). The difference (iii) reflects the fact that the concentration of the $\overline{\text{Al}}\text{—}\overset{\delta(-)}{\text{O}}\text{—}\overset{\delta(+)}{\text{Li}}$ increases in the range $0.621 < x < 2.470$, whereas the concentration of $\overline{\text{Al}}\text{—}\overset{\delta(-)}{\text{O}}\text{—}\overset{\delta(+)}{\text{Na}}$ remains constant. Moreover, we attribute the higher value of the ZPC obtained in the Li-2.470-γ-Al_2O_3 specimen (ZPC = 10.28) as compared to that obtained for the Na-2.470-γ-Al_2O_3 specimen (ZPC = 10.10) to the relatively high extent of the process (b) for the Li^+-doped specimen mentioned before. The relatively small extent of the process (c) for the Li-based specimens could be taken into account for the difference (iv) (*3*).

As in the case of the sodium-based system, the increase in the concentration of the $\overline{\text{AlOH}}{}_2^+$ groups for the specimens with $0.621 \leq x \leq 2.470$ could be attributed to following mechanism: The Li^+ ions dissolved from the islands are adsorbed specifically in the shear plane of the double layer forming "ion pairs" (*12, 13*) with the $\overline{\text{AlOH}}$ groups, thus releasing hydrogen ions ($\overline{\text{AlOH}} + \text{Li}^+_{(s)} \rightarrow \overline{\text{AlO}}^- \ldots \text{Li}^+ + \text{H}^+_{(s)}$) on the surface. The released $\text{H}^+_{(s)}$ enhance the formation of additional $\overline{\text{AlOH}}{}_2^+$ groups through the charging mechanism mentioned in the Introduction. The increase of the concentration of the $\overline{\text{AlOH}}{}_2^+$ with the amount of the dissolved Li ions (Fig. 5) corroborates the function of the mechanism postulated. However, the nonlinearity of curve (b) in Fig. 5 suggests that the mechanism mentioned is not the only one responsible for the increase of the concentration of the $\overline{\text{AlOH}}{}_2^+$ groups for the specimens with $0.621 < x < 2.470$. The contribution of the surface $\overline{\text{Al}}\text{—}\overset{\delta(-)}{\text{O}}\text{—}\overset{\delta(+)}{\text{Li}}$ species seems to be significant.

The fluorine action. Our observations show that modification with very small amounts of F^- ions can be used to exploit the pH range 3.40–5.30 for the adsorption of positive species on γ-Al_2O_3 surface (Fig. 2). Moreover, they suggest a considerable increase in the extent of adsorption of such species at pH higher than 3.40 by increasing the dopant concentration (Figs. 4 and 6).

It is essential to note that the doping by F^- ions does not usually create serious problems concerning the catalytic activity of the supported catalysts. There are, on the contrary, many supported catalytic systems where the incorporation of F^- ions into the support has been proved to promote the catalytic activity. Typical examples are the H.D.S. catalysts based on Co, Mo or Ni, Mo sulfide supported on γ-Al_2O_3 (*14–17*). Moreover, one can notice that a complete transformation of $\overline{\text{AlOH}}$ into $\overline{\text{AlO}}^-$ (Table 2) can be obtained even at pH equal to 5.3 after fluorination with an amount of F^- ions ($x = 1.978$) which can be considered to be necessary to promote the carbonium ion reactions taking place on the supports in the dual function supported catalysts (*18*).

Our results are generally in agreement with the literature (*18–25*). In fact, it is accepted that it is possible to increase, by fluorination, the total number of acid sites and

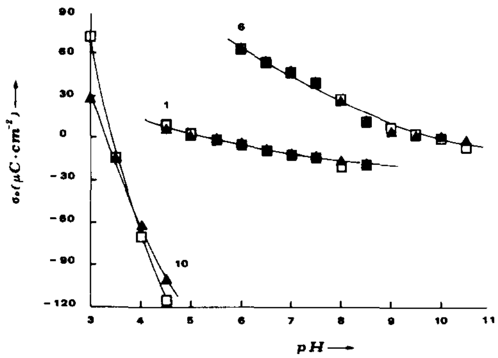

FIG. 7. Experimental (☐) and calculated surface charge (▲) for the samples 1, 6, and 10 as a function of pH. The ionic strength corresponds to 0.1 *M* KNO_3.

acid strength of γ-Al_2O_3. In particular, it is established that the total number of Brønsted sites, directly related with our experimental data, increases with fluorine content. This is presumably due to the fact that, after fluorination, the less acidic hydroxyl groups are removed while strongly acidic hydroxyls are created.

The sharp increase in the concentration of the $\overline{\text{AlO}}^-$ groups observed after modification with 0.125 mmol F^- per g of γ-Al_2O_3 can be attributed to the abrupt increase in the values of K_1^{int} and K_2^{int} brought about by this amount of F^- ions (compare Figs. 2 and 6).

Moreover, in order to explain the additional increase in the concentrtion of the $\overline{\text{AlO}}^-$ groups with the F^- content in the range $0.125 < x \leq 3.818$, where the values of K_1^{int} and K_2^{int} remain practically constant, we assume the following mechanism:

$$\overline{\text{AlOH}} + F^-_{(\text{aq})} \rightarrow \overline{\text{Al}}^+ \ldots F^- + \text{OH}^-_{(\text{s})}$$

$$\overline{\text{AlOH}} + \text{OH}^-_{(\text{s})} \rightarrow \overline{\text{AlO}}^- + \text{H}_2\text{O}$$

To be specific: the dissolved F^- ions (Table 3), $F^-_{(\text{aq})}$, are specifically adsorbed in the shear plane of the double layer forming "ion pairs" with the $\overline{\text{Al}}^+$ and releasing on the surface hydroxyl ions, $\text{OH}^-_{(\text{s})}$. This assumption is in excellent agreement with the literature (*12*, *13*). The $\text{OH}^-_{(\text{s})}$ released promote the formation of additional $\overline{\text{AlO}}^-$ reacting with the adjacent $\overline{\text{AlOH}}$. In such a case an increase in the concentration of the $\overline{\text{AlO}}^-$ groups with the amount of the dissolved F^- ions is to be expected (Fig. 6).

The calculation of the concentration of the $\overline{\text{AlOH}}_2^+$ and $\overline{\text{AlO}}^-$ used in the present work was based on the triple layer model developed by Davis *et al.* (*12*, *13*). The agreement between the values of the surface charge measured experimentally at each pH, with the corresponding ones calculated from the difference $((\overline{\text{AlOH}}_2^+)-(\overline{\text{AlO}}^-))$ demonstrates the applicability of the above-mentioned model to our system (Fig. 7).

CONCLUSION

Modification of γ-Al_2O_3 with various amounts of Li^+ and F^- ions allowed us to reach the following conclusions:

(i) Doping of γ-Al_2O_3 with 0.621 mmol Li^+ per g of γ-Al_2O_3 is sufficient to extend the pH range that can be used for the adsorption of *negative* species from 1.00–5.30 to 1.00–9.80 as well as to drastically suppress the formation of adsorption sites for positive species. At pH lower than 8.0 increase in the Li^+ content increases considerably the concentration of the former sites. Therefore, lithium can be used instead of sodium in the cases where the latter causes catalytic deactivation.

(ii) Doping of γ-Al_2O_3 with 0.125 mmol F^- per g of γ-Al_2O_3 promotes on this support the formation of adsorption sites for *positive species* in the pH range 5.30–3.40. At pH higher than 3.40 the concentration of the sites mentioned increases markedly with the F^- content.

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