JOURNAL OF CATALYSIS **124**, 315–323 (1990)

Molybdenum-oxo Species Deposited on Alumina by Adsorption

II. Regulation of the Surface Mo^{VI} Concentration by Control of the Protonated Surface Hydroxyls

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Received June 13, 1989; revised February 14, 1990

The adsorption of $Mo_xO_y^{z-}$ species from aqueous solutions on the surface of pure and Na^+ or Li^+-doped γ-aluminas was studied over a pH range between 3.0 and 8.5 and temperatures ranging from 10 to 55°C. The variations in pH with the concentrations of the impregnating solutions observed and analysis of the isotherms demonstrated that the following findings reported for adsorption on pure γ-alumina at $T = 25°C$ and pH 5 are also valid for adsorption on pure and sodium-doped aluminas performed at various pH values and temperatures: (i) The contribution of precipitation to the deposition is negligible. (ii) The adsorption constant for the MoO_4^{2-} ions is larger than those for the isopolyanions. (iii) The adsorbed $Mo_xO_y^{z-}$ ions are located on energetically equivalent but distinct sites of the inner Helmholtz plane, created mainly by the protonated surface hydroxyls. (iv) Lateral interactions are exerted between the adsorbed $Mo_xO_y^{z-}$ ions resulting in the formation of $Mo_xO_y^{z-}$ . . . $Mo_xO_y^{z-}$ oligomers. Moreover, it was demonstrated that the regulation of the concentration of the protonated surface hydroxyls makes it possible to deposit by adsorption very large amounts of Mo^{VI} on the γ-alumina surface. Although the sodium doping was found to be the most attractive from the view point of maximization of the extent of adsorption, it may be suggested that it promotes the formation of the catalytically inert sodium molybdate. Therefore the second best method of regulation, namely the change in the impregnating temperature, may prove to be the most convenient in practice. © 1990 Academic Press, Inc.

INTRODUCTION

The catalytic activity of a supported catalyst is usually determined by the amount and dispersion of the active phase. An increase in the surface of the supported phase, being the precursor of the active one, may be achieved by depositing substantial amounts of a supported phase by use of dry or wet impregnations followed by drying. In these cases the deposition of the supported phase takes place principally by uncontrolled precipitation in the step of drying. Evidently, such methods, resulting in low dispersion, should not be applied in the cases of the expensive active ions or when it is desired to maintain a very good control over the local concentration of the adsorbed ions. In these cases the increase in the active surface should be attempted by increasing dispersion. This end may be achieved using adsorption equilibrium for depositing the supported phase followed by filtration to remove the supernatant. Although equilibrium adsorption results in high dispersions, satisfactorily high values of active surface cannot be attained because the amount of the phase deposited by adsorption is limited by the relatively low concentration of sorption sites.

In the case of γ-Al_2O_3, which is an important carrier, a survey of the recent literature dealing with the dependence of the amount deposited by adsorption (*1–8*) demonstrates that a number of experimental results concerning the pH of the impregnat-

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0021-9517/90 $3.00
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ing solution may be explained assuming that protonated [$\overline{\text{Al}}\text{OH}_2^+$] and deprotonated [$\overline{\text{Al}}\text{O}^-$] surface hydroxyls are responsible for the adsorption of negatively and positively charged species. These results may be explained, at least qualitatively, taking into account the protonation–deprotonation equilibria:

$$\begin{aligned} &\overline{\text{Al}}\text{OH}_2^+ \overset{K_1^{\text{int}}}{\rightleftharpoons} \overline{\text{Al}}\text{OH} + \text{H}_s^+ \\ &\overline{\text{Al}}\text{OH} \overset{K_2^{\text{int}}}{\rightleftharpoons} \overline{\text{Al}}\text{O}^- + \text{H}_s^+ \qquad (1) \\ &\text{H}_s^+ \rightleftharpoons \text{H}_{\text{aq}}^+ \end{aligned}$$

However, studies directly relating adsorption data and concentration of charged surface groups are scarce in the literature (*7*). On the other hand, although pH control is a very simple method for regulating the concentration of charged surface groups, it has several disadvantages: it may cause surface dissolution of the support, it may transform the species to be adsorbed, unwanted species may precipitate, etc. These deficiencies have motivated the development of alternative methods for regulating the concentration of the surface species (*9–12*). Employing such methods changes the surface acidity constants, making it possible for the regulation to be done at constant pH. This is achieved either by changing the temperature of the impregnating solution or by doping the carrier. Specifically, it is found that increasing the temperature of the impregnating solution increases the concentration of the protonated hydroxyl groups. The same effect is caused by doping the carrier with Na^+ and Li^+ cations whereas modification by F^- anions increased the concentration of the deprotonated hydroxyl groups.

This paper is the second part of a work aimed at the investigation of molybdena/γ-alumina catalysts prepared by adsorption equilibrium using γ-alumina-based carriers with controlled concentration of charged surface groups. The first part dealt with the elucidation of the mechanism of adsorption of molybdates on the γ-alumina surface through theoretical analysis of the isotherm and electrochemical measurements. The main goal of the present paper is to examine whether the regulation of the concentration of the $\overline{\text{Al}}\text{OH}_2^+$ achieved by changing pH, changing temperature, or doping the carrier can be employed for increasing the amount of Mo^{VI} species deposited by adsorption. Specifically, we attempted to correlate adsorption data obtained from the analysis of the isotherms with the concentration of the $\overline{\text{Al}}\text{OH}_2^+$ groups. Our second goal was to compare the two methods developed in our laboratory, namely, change of impregnation temperature and doping of the carrier, with the traditional change of pH from the view point of maximizing the extent of adsorption of Mo^{VI} species on γ-Al_2O_3 substrates. Work to be reported later involves an exhaustive characterization (including determinations of the active surface) and determination of the catalytic properties of the samples investigated. We hope that the whole work will demonstrate the effectiveness of the methods established by us (*9–12*) for maximizing the active surface and consequently the catalytic activity of catalysts prepared by supporting molybdena on γ-alumina.

EXPERIMENTAL

The adsorption experiments performed in this work may be classified as follows: First, adsorption of molybdates at constant temperature, 25°C, and pH in the range 3.0–8.5 on pure γ-Al_2O_3 (100–150 mesh powder produced by crushing Houdry Ho 415 γ-alumina extrudates, $S_{\text{BET}} = 123\ \text{m}^2/\text{g}$, water pore volume $= 0.45\ \text{cm}^3/\text{g}$). Second, adsorption of molybdates on pure γ-Al_2O_3 at pH 5 and various temperatures in the range 10–55°C. Third, adsorption of molybdates on doped carriers prepared by modifying γ-Al_2O_3 with various amounts of Li^+ and Na^+ ions. The doped carriers have been prepared and characterized as detailed elsewhere (*10, 11*). Details concerning the adsorption experiments have been reported in the first paper of this series.

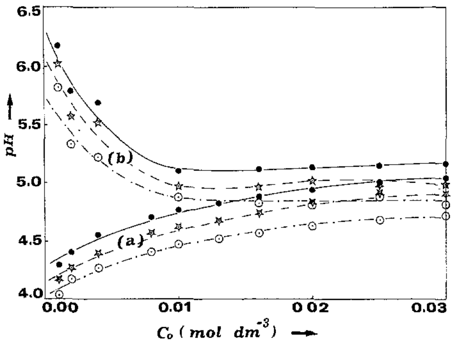

FIG. 1. Variations in the pH measured before (curves a) and after (curves b) adsorption with the initial concentration of the Mo^{VI}, (●) 10°C, (☆) 25°C, (⊙) 45°C, $I = 0.1$ M NH_4NO_3.

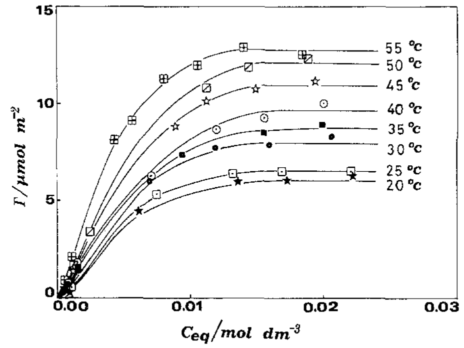

FIG. 3. Surface concentration of Mo^{VI} as a function of the equilibrium Mo^{VI} concentration at various temperatures of the impregnating suspension of the undoped carrier. pH 5, $I = 0.1$ M NH_4NO_3. Temperature values are indicated.

The carriers studied are denoted by Na-x-γ-Al_2O_3 and Li-x-γ-Al_2O_3, where x represents the amount of the dopant ion expressed in millimoles per gram of γ-Al_2O_3. The undoped carrier is denoted by Na-0.226-γ-Al_2O_3 to take into account the amount of sodium initially contained in the untreated γ-alumina.

RESULTS

Figures 1a and 1b show typical curves illustrating the variation in the pH measured before, pH_{in}, and after, pH_f, adsorption with the Mo^{VI} concentration, C_0, measured before adsorption (*13*). It may be seen that pH_{in} increased with the concentration of the Mo^{VI}, whereas pH_f and therefore the difference pH_f–pH_{in}, being always positive, decreased.

Figures 2 and 3 illustrate the adsorption isotherms obtained for the undoped carrier at various pHs and temperatures. Figures 4 and 5 illustrate the adsorption isotherms obtained for the doped carriers containing various amounts of sodium and lithium concentrations. It may be seen that in all cases the experimental points showed an excellent fit to an S-type isotherm.

As discussed below, the isotherms presented herein may be analyzed using Eq.

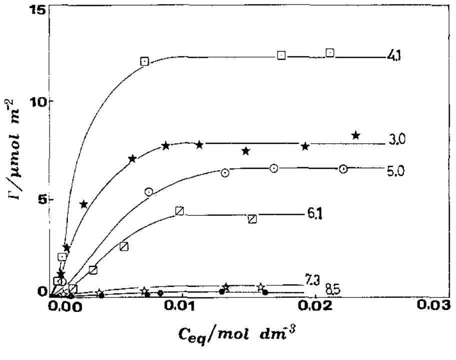

FIG. 2. Surface concentration of Mo^{VI} as a function of the equilibrium Mo^{VI} concentration at various pH values of the impregnating suspension of the undoped carrier. $T = 25°C$, $I = 0.1$ M NH_4NO_3. pH values are indicated.

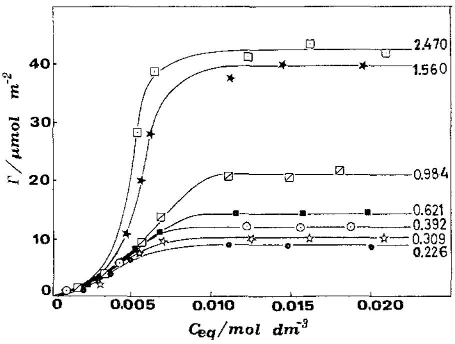

FIG. 4. Surface concentration of Mo^{VI} as a function of the equilibrium Mo^{VI} concentration for the sodium-doped carriers [Na-x-γ-Al_2O_3]. pH 5, $T = 25°C$, $I = 0.1$ M NH_4NO_3. The values of x are indicated.

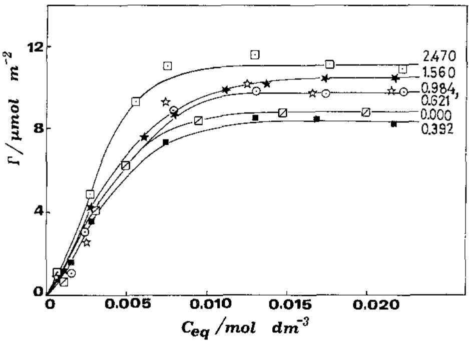

FIG. 5. Surface concentration of Mo^{VI} as a function of the equilibrium Mo^{VI} concentration for the lithium-doped carriers [Li-x-γ-Al_2O_3]. pH 5, $T = 25°C$, $I = 0.1$ M NH_4NO_3. The values of x are indicated.

(2) derived in the first paper of this series. This analysis allowed the determination of the saturation surface Mo^{VI} concentration, Γ_m, corresponding to the plateau of the isotherms, as well as of the lateral interaction energy, E, and the adsorption constant, $\tilde{K}$. In Tables 1, 2, and 3 the values of these parameters are presented at various pHs, temperatures, and sodium and lithium concentrations. From Table 1 it may be seen that the value of Γ_m increased as the pH decreased from 8.5 to 4.1, dropping upon further decrease in the solution pH to 3.0. Moreover, Table 2 shows that Γ_m remained practically constant in the range 10–25°C, whereas it increased considerably when the temperature increased from 25 to 55°C. Finally, Table 3 shows that Γ_m generally increased with the dopant concentration. Similar but not identical trends were found for the value of E whereas no trends were observed for the adsorption constant.

As was suggested in the first paper of this series (*13*), the moieties responsible for the creation of the adsorption sites in the IHP are mainly $\overline{Al}OH_2^+$. Therefore, it is now reasonable to examine in detail the dependence of the saturation surface concentration of the Mo^{VI} compiled in Tables 1, 2, and 3 on the concentration of the $\overline{Al}OH_2^+$ groups regulated by varying pH (*10*), temperature (*12*), and dopant concentration (*10, 11*). The variation in the $\overline{Al}OH_2^+$ concentration with these parameters is illustrated in Figs. 6, 7a, and 8, respectively.

In the first paper of this series, and on the basis of a few results selected from the present work, we suggested that the neutral surface hydroxyls should play a minor role, if any, in the adsorption of the molybdates. In fact, in all cases we observed negative correlations between the saturation surface concentration of the Mo^{VI} and the concentration of the $\overline{Al}OH$ groups, irrespective of the method followed for the regulation of the latter. Figure 7b illustrates an example of these negative correlations.

DISCUSSION

In all cases studied, the variations in the pH with the Mo concentration, (see the typ-

TABLE 1

Values of the Saturation Surface Concentration of Mo^{VI}, the Lateral Interaction Energy, and the Adsorption Constant Determined for the Undoped Carrier, Na-0.226-γ-Al_2O_3, at $T = 25°C$ and Various pH Values

	pH	Γ_m (atom Mo^{VI} nm^{-2})	E (kJ mol^{-1})	$\tilde{K}$ (mol^{-1} dm^3)
1	3.0 ± 0.1	4.50 ± 0.10	4.1 ± 0.1	717.8 ± 33.1
2	4.1 ± 0.1	7.47 ± 0.06	17.0 ± 0.1	60.0 ± 0.5
3	5.0 ± 0.1	3.79 ± 0.06	10.5 ± 0.3	115.7 ± 2.3
4	6.1 ± 0.1	2.29 ± 0.18	7.6 ± 0.6	52.0 ± 4.0
5	7.3 ± 0.1	0.31 ± 0.02	1.6 ± 0.1	121.0 ± 8.0
6	8.5 ± 0.1	0.09 ± 0.01	0.7 ± 0.1	58.0 ± 9.0

Note. $I = 0.1$ M NH_4NO_3.

TABLE 2

Values of the Saturation Surface Concentration of Mo^{VI}, the Lateral Interaction Energy, and the Adsorption Constant Determined for the Undoped Carrier, Na-0.226-γ-Al_2O_3, at pH 5 and Various Temperatures

	T (°C)	Γ_m (atom Mo^{VI} nm^{-2})	E (kJ mol^{-1})	$\tilde{K}$ (mol^{-1} dm^3)
1	10	4.1 ± 0.1	10.0 ± 0.3	106.2 ± 3.8
2	15	4.1 ± 0.1	10.0 ± 0.3	109.4 ± 4.2
3	20	3.5 ± 0.1	7.2 ± 0.2	154.1 ± 6.1
4	25	3.8 ± 0.1	10.5 ± 0.3	115.7 ± 2.3
5	30	4.5 ± 0.1	12.4 ± 0.3	90.9 ± 2.7
6	35	4.9 ± 0.1	16.6 ± 0.2	59.9 ± 0.8
7	40	5.1 ± 0.2	12.6 ± 0.6	93.9 ± 4.8
8	45	6.1 ± 0.1	17.3 ± 0.3	58.3 ± 1.2
9	50	7.0 ± 0.1	19.0 ± 0.2	21.1 ± 0.3
10	55	8.5 ± 0.2	6.5 ± 0.1	67.8 ± 1.7

Note. $I = 0.1$ M NH_4NO_3.

ical curves 1a and 1b) were identical with those obtained for the undoped support at $T = 25$°C and pH 5 (*13*). This indicates that the assumption we have made, that the contribution of the precipitation of various Mo^{VI} species to the overall deposition is negligible, is valid at all temperatures, pHs, and dopant concentrations studied (*13, 14*). Moreover, this strongly suggests that in all cases the adsorption constant of the MoO_4^{2-} ions is larger than those of the isopolyanions (*13*).

As already mentioned, the *S*-type isotherms obtained are described well by Eq. (2), derived in the first paper of this series:

$$1/\Gamma = 1/\Gamma_m + 1/\Gamma_m \tilde{K} C_{eq} \exp[\lambda\Gamma/RT]. \quad (2)$$

In Eq. (2) Γ, Γ_m, $\tilde{K}$, C_{eq}, and $\lambda = E/\Gamma_m$ represent the surface Mo^{VI} concentration determined experimentally, the saturation

TABLE 3

Values of the Saturation Surface Concentration of Mo^{VI}, the Lateral Interaction Energy, and the Adsorption Constant Determined for the Sodium- and Lithium-Doped Carriers at pH 5 and $T = 25$°C

	Carrier	Γ_m (atom Mo^{VI} nm^{-2})	E (kJ mol^{-1})	$\tilde{K}$ (mol^{-1} dm^3)
1	Na-0.226-γ-Al_2O_3	3.8 ± 0.1	10.5 ± 0.3	115.7 ± 2.3
2	Na-0.309-γ-Al_2O_3	7.0 ± 0.1	19.8 ± 0.1	14.9 ± 0.2
3	Na-0.392-γ-Al_2O_3	5.9 ± 0.1	16.3 ± 0.3	20.3 ± 0.4
4	Na-0.621-γ-Al_2O_3	9.4 ± 0.3	24.8 ± 0.8	12.0 ± 0.4
5	Na-0.984-γ-Al_2O_3	12.3 ± 0.2	34.3 ± 0.7	10.9 ± 0.2
6	Na-1.560-γ-Al_2O_3	24.1 ± 1.2	63.0 ± 3.0	4.1 ± 0.2
7	Na-2.470-γ-Al_2O_3	25.9 ± 0.6	74.0 ± 2.0	9.0 ± 0.2
8	Li-0.392-γ-Al_2O_3	5.5 ± 0.3	14.1 ± 0.8	96.0 ± 5.6
9	Li-0.621-γ-Al_2O_3	6.0 ± 0.6	15.0 ± 1.0	96.4 ± 10.5
10	Li-0.984-γ-Al_2O_3	6.1 ± 0.3	16.1 ± 0.8	46.2 ± 2.9
11	Li-1.560-γ-Al_2O_3	6.5 ± 0.1	16.6 ± 0.3	151.1 ± 9.0
12	Li-2.470-γ-Al_2O_3	6.7 ± 0.1	18.4 ± 0.2	9.0 ± 0.1

Note. $I = 0.1$ M NH_4NO_3.

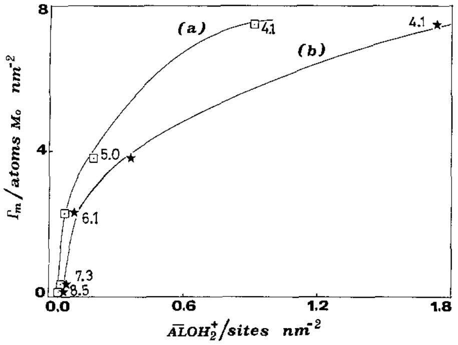

FIG. 6. Saturation surface Mo^{VI} concentration achieved at various pH values as a function of the concentration of the protonated surface hydroxyls regulated by varying the pH of the impregnating suspension of the undoped carrier. The concentrations of the $\overline{AlOH_2^+}$ groups were determined in the absence, curve a (Refs. (*10–12*)), and presence, curve b, of molybdates. pH values are indicated.

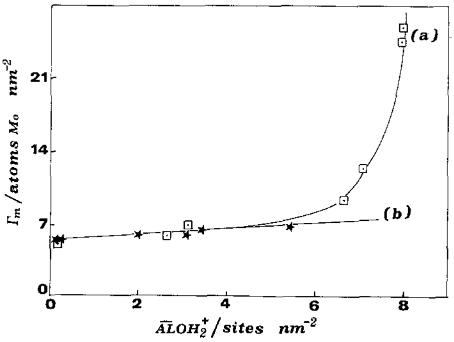

FIG. 8. Saturation surface Mo^{VI} concentration obtained for the doped carriers (Na-x-γ-Al_2O_3 (a), Li-x-γ-Al_2O_3 (b)) as a function of the concentration of the protonated surface hydroxyls regulated by varying the Li^+ (*11*) or Na^+ (*10*) content.

surface Mo^{VI} concentration, the adsorption constant, the Mo^{VI} concentration determined in the solution after adsorption (*13*), and the lateral interaction energy divided by Γ_m. Typical examples are illustrated in Fig. 9. They confirm that in all cases studied here the $Mo_xO_y^{z-}$ ions are located on energetically equivalent but distinct sites of the inner Helmholtz plane of the double layer, presumably forming ion pairs with the surface $\overline{AlOH_2^+}$ groups, and that considerable lateral interactions exist between the adsorbed $Mo_xO_y^{z-}$ ions (*13*).

The smooth curves obtained in the plots of Γ_m vs [$\overline{AlOH_2^+}$] (Figs. 6, 7a, and 8) suggest that the variation in Γ_m with pH, temperature, and dopant concentration, presented in Tables 1, 2, and 3, may be attributed to the corresponding variations in the surface concentration of the $\overline{AlOH_2^+}$ groups. In fact, it may be observed that in

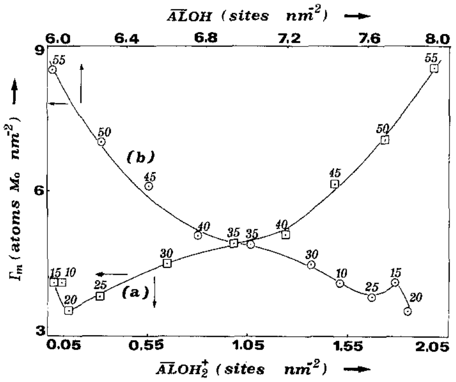

FIG. 7. Saturation surface Mo^{VI} concentration achieved at various temperatures as a function of the concentration of the protonated (curve a) and neutral (curve b) surface hydroxyls regulated by varying the temperature of the impregnating suspension of the undoped carrier (Ref. (*12*)). Temperature values are indicated in degrees centigrade.

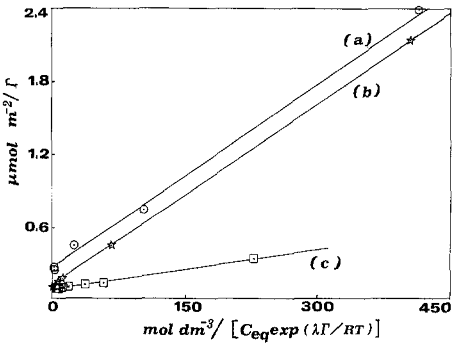

FIG. 9. Reciprocal surface concentration of Mo^{VI} as a function of $(1/C_{eq})\exp(\lambda\Gamma/RT)$. The solid lines represent the values calculated using Eq. 2: (a, c) undoped carrier (Na-0.226-γ-Al_2O_3), T = 25°C, pH 6, and T = 55°C, pH 5, respectively; (b) doped carrier (Na-0.392-γ-Al_2O_3), T = 25°C, pH 5.

almost all cases, an increase in the concentration of the protonated surface hydroxyls resulted in an increase in the value of Γ_m. However, several features of the plots mentioned above should be discussed. The fact that the plots illustrated in Figs. 6, 7a, and 8 are not identical suggests that the important parameters for the adsorption process, other than $\overline{AlOH_2^+}$ concentration, change with pH, temperature, and dopant concentration. This fact is also indicated by the deviation from the linearity of the plots 6a, 6b, 7a, and 8a. It is reasonable to attribute this deviation to the change in the composition of the impregnating solution with pH and temperature. On the other hand, the increase in the slope of the curve in Fig. 8a could be attributed to the increasing formation of supported sodium molybdate with the Na^+ concentration (*15–17*). Comparison of plot 6a with plot 6b confirmed earlier results suggesting that the adsorbed $Mo_xO_y^{z-}$ ions in the inner Helmholtz plane increased the concentration of the $\overline{AlOH_2^+}$ groups and thus of the positive surface charge (*13*). Comparison of plots 8a and 8b suggested that up to a critical sodium concentration—where formation of the sodium molybdate presumably does not occur in considerable extent—the value of Γ_m is independent of the kind of dopant.

The fact that values of Γ_m illustrated in Figs. 6, 7a, and 8 are higher than those obtained for $[\overline{AlOH_2^+}]$ was attributed to the following (*13*):

(i) Participation of the neutral hydroxyls to the adsorption cannot be precluded.

(ii) With the exception of curve 6b, the concentration of the $\overline{AlOH_2^+}$ groups had been determined in the absence of molybdates.

(iii) The adsorption of the $Mo_xO_y^{z-}$ with $x > 1$ is possible.

Next we compare the methods used for regulating the concentration of the $\overline{AlOH_2^+}$ groups, aimed at maximizing the extent of adsorption. The maximum Γ_m values achieved (and the corresponding composition of the resulting catalysts) are compiled in Table 4. Inspection of this table clearly shows that the most attractive method for maximizing Γ_m is doping with sodium. However, in view of the formation of the catalytically inert sodium molybdate (*15–17*) it is possible that the second best method, namely, the change in the impregnating temperature, may prove to be the most convenient in this case. This method has, moreover, the advantage over the traditional method of changing the pH that it is not expected to introduce complications due to considerable changes in the stability of the species to be adsorbed. However, it is obvious that a final selection among the

TABLE 4

Compilation of the Maximum Γ_m Values Achieved and the Corresponding Percentage Composition in wt% MoO_3 of the Resulting Catalysts Using the Various Methods Employed for Regulating the Concentration of the $\overline{AlOH_2^+}$ Groups

Method	Γ_m (atom Mo^{VI} nm^{-2})	wt% MoO_3
Change of pH (Na-0.226-γ-Al_2O_3 pH 4.1, T = 25°C)	7.47 ± 0.06	18.0%
Change of temperature (Na-0.226-γ-Al_2O_3 pH 5, T = 55°C)	8.50 ± 0.20	20.0%
Doping by Li^+ (Li-2.470-γ-Al_2O_3 pH 5, T = 25°C)	6.70 ± 0.10	16.5%
Doping by Na^+ (Na-2.470-γ-Al_2O_3 pH 5, T = 25°C)	25.90 ± 0.60	43.2%

method developed should be attempted after completing the detailed characterization and determination of the catalytic activity of the specimens, which is currently being carried out. The last column of Table 4 shows that the regulation of the $\overline{\text{Al}}OH_2^+$ group concentration makes it possible to deposit by adsorption very large amounts of Mo^{VI} on the γ-Al_2O_3 surface.

The values of the adsorption constant and the lateral interaction energy obtained as illustrated in Tables 1, 2, and 3 show interesting features. Concerning $\tilde{K}$ we must explain the variation in the $\tilde{K}$ values obtained at the same temperature (Tables 1 and 3) and the fact that the $\tilde{K}$ values obtained at the same pH but at various temperatures (Table 2) do not obey a Van't Hoff equation. The nomenclature here is the same as that in Ref. (*13*), i.e.,

$$\tilde{K} = \Sigma_i[(a_i/55.5)\exp(-Z_iF\Psi_{\mathrm{IHP}}/RT - \Delta G^0_{\mathrm{cs},i}/RT)],$$

where a_i is a coefficient relating the total equilibrium concentration with that for the ion i of valency Z_i, Ψ_{IHP} is the potential in the inner Helmholtz plane, and $\Delta G^0_{\mathrm{cs},i}$ is the contribution of the chemical interactions between $Mo_xO_y^{z-}$ ions and support to the whole change of the chemical free energy. Taking into account that Ψ_{IHP} and a_i depend on pH (*13*), it may easily be explained why $\tilde{K}$ does not remain constant as pH is changed. Moreover, Ψ_{IHP} and $\Gamma G^0_{\mathrm{cs},i}$ are expected to be sensitive to the changes of the support surface caused by varying the dopant concentration. Therefore, a change in $\tilde{K}$ with the concentration of the dopant ion is to be expected. Moreover, the fact that the various a_i's are temperature dependent, presumably with different temperature coefficients, is sufficient to explain why the $\tilde{K}$ values compiled in Table 2 cannot be described by the Van't Hoff equation.

CONCLUSIONS

The following conclusions may be drawn from this work. (i) The mechanism of the Mo^{VI} deposition established for undoped γ-Al_2O_3 at pH 5 and $T = 25$°C (*13*) is generally valid for this support in the range of pH 4.0–8.5 and temperature 20–55°C as well as for the Li^+- and Na^+-doped aluminas. (ii) It was demonstrated that the regulation of the concentration of the protonated surface hydroxyls makes it possible to deposit by adsorption very large amounts of Mo^{VI} on the γ-Al_2O_3 surface. (iii) Among the methods used for maximizing adsorption the most attractive was found to be sodium doping. However, in view of the formation of the catalytically inert sodium molybdate, it is possible that change in the impregnating temperature, the second best method, may prove to be the most convenient.

ACKNOWLEDGMENTS

Partial financial support for this project from the Greek Award Granting Authority (IKY) is gratefully acknowledged. We also express our thanks to Mrs. A. Didachou for the preparation of the manuscript.

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