Journal of Catalysis **183,** 400–404 (1999)
Article ID jcat.1999.2407, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Simultaneous Deposition of W(VI) and Co(II) Species on the γ-Alumina Surface

Nikos Spanos

Foundation of Research and Technology Hellas, Institute of Chemical Engineering and Chemical Processes at High Temperatures, P.O. Box 1414, GR-26500 Patras, Greece

Received October 20, 1998; revised January 4, 1999; accepted January 5, 1999

The simultaneous deposition of W(VI) and Co(II) species on the γ-alumina surface from aqueous solutions has been studied. Mutual promotion in the deposition of W(VI) and Co(II) species was observed due to the strong lateral attractions exerted between the codeposited W(VI) and Co(II) species. A model was developed according to which the deposition of cobalt takes place through the adsorption of one Co^{2+} ion at a site created by one deprotonated surface hydroxyl, whereas the deposition of tungsten takes place mainly via adsorption of the WO_4^{2-} and $HW_6O_{20}(OH)_2^{5-}$ ions at sites created by the protonated surface hydroxyls. The adsorbed WO_4^{2-} [$HW_6O_{20}(OH)_2^{5-}$] ions increased [decreased] with increasing pH. The total tungsten (cobalt) deposited decreased (increased) with increasing pH. © 1999 Academic Press

INTRODUCTION

The classic method of preparation of supported catalysts, that is, dry (incipient wetness) or wet impregnation followed by drying, calcination, and/or activation, usually results in low dispersity of the supported phase. Low dispersity of the supported phase is generally undesirable, especially when a relatively expensive ion is deposited. This disadvantage may be overcome by using the method of equilibrium deposition followed by filtration (EDF) which results in relatively high dispersity of the supported phase. An increasing number of studies dealing with the preparation of supported catalysts using EDF have appeared in the literature (1–13). Although EDF results in high dispersity, the total amount of the supported phase and thus the active surface achieved is not always sufficient because the concentration of deposition sites, depending on the impregnation parameters, is often low. A number of studies have been devoted to the regulation of the concentration of the deposition sites, which in the case of oxidic supports are the various types of surface hydroxyls (undissociated, protonated and deprotonated) (14–17). Unfortunately, in some cases the amount of active species deposited by EDF is not sufficient even though the concentration of deposition sites has been maximized. This is, for instance, the case for the deposition of Co^{2+} and Ni^{2+} on the surface of γ-Al_2O_3 (18).

Recent studies have provided strong evidence that the amount of an active species deposited by EDF may be increased by simultaneously depositing a species of the opposite electric charge (19, 20). Investigation of the simultaneous deposition (codeposition) by EDF of Mo(VI) and Co(II) or Ni(II) species on the γ-alumina surface has shown that the amounts deposited are larger in the case of Mo and much larger in the case of Co(II) or Ni(II) in comparison with the amounts obtained by depositing each species separately. The mutual promotion in deposition was ascribed to the observed increase in the energy of lateral attractions between the codeposited species.

The primary question arising from the above studies is whether the aforementioned mutual promotion in the deposition of Mo(VI) and Co(II) or Ni(II) species on γ-alumina is a special case of a general phenomenon. It is obvious that an answer to this question necessitates a thorough examination of several catalytically interesting binary systems. The results of the investigation of W(VI) and Co(II) species codeposition on γ-alumina using EDF are reported in this Research Note.

Despite the limited work on the mechanism of deposition of W(VI) species on γ-Al_2O_3 and of Co(II) species on the same substrate (18, 21–25), reports on W(VI) and Co(II) codeposition on γ-Al_2O_3 are very rare. The most important tasks of this work were (i) to investigate where a mutual promotion in the deposition of W(VI) and Co(II) species takes place; (ii) to clarify the mode of deposition of these species, that is, by adsorption or by chemical reaction with the undissociated surface hydroxyls or by both; and (iii) to find the type of W(VI) species (monomeric or polymeric) deposited at different pH values of the impregnating solution. This feature is significant in the preparation of W–Co/γ-alumina catalysts, because the catalytic activity

0021-9517/99 $30.00

depends on the kind of W(VI) species (monomeric or polymeric) (26).

The widely accepted triple-layer model for the electrical double layer (edl) and the two-pK/one-site model for charging the surface mechanism were applied in the present study. In view of the recent development of multisite models for γ-alumina [e.g., (27)], the one-site model is of course an approximation, but a very useful one for modeling complicated depositions on electrolyte solution/γ-alumina interfaces.

EXPERIMENTAL

Equilibrium deposition filtration. Equilibrium deposition experiments were done at $25.0 \pm 0.1^\circ$C over the pH range 4.2 to 6.7. In each experiment a 0.014 dm^3 of W(VI)- and Co(II)-containing solutions with concentrations for both species gradually increased from 1×10^{-3} to 2×10^{-2} mol dm^{-3} was used. The surface concentrations (mol m^{-2}) of W(VI), Γ_W, and Co(II), Γ_C, were determined from the difference in the concentrations (mol dm^{-3}) in the impregnating solutions of W(VI) and Co(II), before ($C_{o,W}$, $C_{o,C}$) and after ($C_{eq,W}$, $C_{eq,C}$) deposition. Full details concerning the equilibrium deposition experiments as well as the materials used in this study have been reported elsewhere (19, 21).

Microelectrophoresis. Electrophoretic mobilities of the γ-alumina particles were measured in 0.01 mol dm^{-3} ammonium nitrate solutions at $25.0 \pm 0.5^\circ$C as a function of pH with a laser-Doppler velocimetric device (Zetasizer 5000, Malvern Instruments Ltd., Worcestershire, Great Britain) with an applied field strength of ca. 80 V cm^{-1}. Prior to the mobility measurement the suspension was completely dispersed in an ultrasonic bath for 10 min. This length of time was determined to be needed for the complete disagreggation of the suspended particles by testing sonication times from 5 min to 1 h. Particle size was also measured with the same instrument, resulting in a mean of 871 ± 135 nm. The velocity of the particles was measured at a certain depth of the cell where solvent is at rest (stationary level). The concentration of the suspensions was adjusted within the operational limits of the instrument and the suspension pH was adjusted by the addition of standard solutions of hydrochloric acid or potassium hydroxide (Merck, titrisol). The suspension pH was measured before and after the mobility measurements. The reported electrophoretic mobilities are the averages of at least ten sets of measurements (spread of values ±10% of the reported mean values).

Potentiometric titrations. The experimental procedure concerning the potentiometric titrations of electrolyte solutions or suspensions has been described in detail elsewhere (17). According to this technique, the electrolyte solution or suspension is titrated using an acid and the pH is recorded every 3 min as a function of the volume of titrant added. The above technique (fast titration) allows for determination of the amount of hydrogen ions consumed (H_c^+) for the protonation of the deprotonated and undissociated surface hydroxyls of the oxidic support. Details on this determination have been reported elsewhere (18).

RESULTS AND DISCUSSION

Qualitative Approach

Qualitative analysis of the results obtained from equilibrium deposition experiments and from electrophoretic mobility measurements is first undertaken. Figure 1 illustrates a typical example of the isotherm for the uptake of W(VI) (curve a) and Co(II) (curve c) obtained during their codeposition at pH 4.2. These isotherms are compared with those obtained for the uptake of W(VI) (curve b) (21) and Co(II) (curve d) (18) species when they are deposited separately, i.e., during deposition of one species in the absence of the other. Two important features may be observed: One is the type of isotherm obtained. In the case of the simultaneous deposition, the isotherms are S type, while in the case of separate deposition of W(VI) and Co(II) species, the isotherms are L type. The other feature is that the saturation surface concentration, Γ_m, corresponding to the plateau of the respective isotherms, obtained for W(VI) [Co(II)] species in the presence of Co(II) [W(VI)] species, is slightly higher [significantly higher] than that obtained for W(VI) (21) [Co(II) (18)] species in the absence of Co(II) [W(VI)] species. It should be noted here that similar features have been observed at all pH values studied (pH range 4.2 to 6.7). It may thus be inferred that a mutual promotion in the

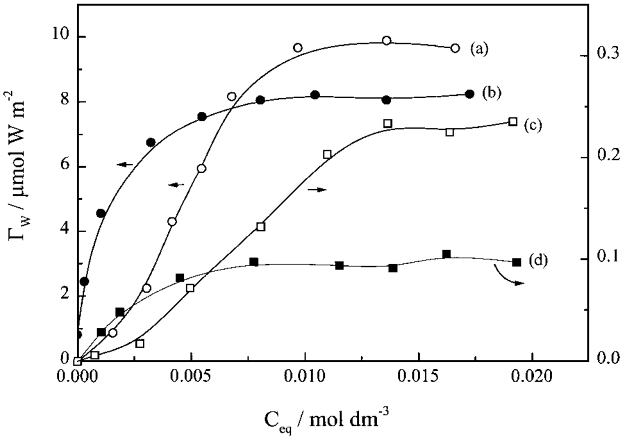

FIG. 1. W(VI) (a, b) and Co(II) (c, d) uptake obtained in the presence (a, c) and absence (b, d) of Co(II) and W(VI) species, respectively, as a function of the equilibrium W(VI) and Co(II) concentrations, respectively. $T = 25^\circ$C, $I = 0.15$ mol dm^{-3} NH_4NO_3, pH 4.2. Curves b and d were obtained from Refs. (21) and (18), respectively.

deposition of W(VI) and Co(II) species takes place during their codeposition using the EDF technique.

The two types of isotherms, S and L, imply that the lateral interactions between the deposited W(VI) and Co(II) species are stronger in the case of their codeposition than in the case of their separate deposition (28). Moreover, the S-type isotherm implies that the codeposited W(VI) and Co(II) species are located at energetically equivalent sites at the inner Helmholtz plane (IHP) of the edl (28). Solution speciation including W(VI) and Co(II) species was done using the speciation software SURFEQL (29). The calculations showed that under the experimental conditions of this study (pH in the range 4.2–6.7, total tungsten and cobalt concentration between 1×10^{-3} and 2×10^{-2} mol dm^{-3}), the total tungsten is present in the form of negatively charged tungstate ions $[H_xW_yO_z(OH)_m^{n-}]$, cobalt is present as hydrated Co^{2+} ions, while the concentration of cobalt hydroxo or ammonia complexes is negligible (30). Thus, the stronger lateral interactions are electrostatic attractions between the deposited anionic species of W(VI) and cations of Co(II), resulting in the already mentioned mutual promotion of the deposition for the $W_xO_y^{z-}$ and Co^{2+} ions caused by the Co^{2+} and $W_xO_y^{z-}$ ions, respectively.

The mutual promotion in deposition of $W_xO_y^{z-}$ and Co^{2+} ions during their codeposition may also be inferred from the characterization of the prepared samples by X-ray fluorescence (XRF, GTN Spectrace). It was found that the intensity of the peaks corresponding to both cobalt and tungsten for the sample WO_3–CoO/γ-Al_2O_3 is higher than the intensity of the respective peaks of cobalt in the case of the sample CoO/γ-Al_2O_3 and of tungsten in the case of the sample WO_3/γ-Al_2O_3.

Additional information concerning the plane of the double layer where the deposited $W_xO_y^{z-}$ and Co^{2+} ions are located could be obtained from the values of ζ potential (the potential at the shear plane of the edl), which in the presence of these ions was found to be negative in the pH range 2–10. It should be noted that the iep of γ-alumina impregnated in 0.01 mol dm^{-3} NH_4NO_3 solution, i.e., in the absence of W(VI) and Co(II) species, has been found to be at about pH 8.0 (18). The shift of the positive ζ-potential values obtained at pH < 8.0 in the absence of $W_xO_y^{z-}$ and Co^{2+} ions to negative values obtained in the presence of these ions is characteristic of superequivalent adsorption of anions taking place at the IHP (31). This suggestion is substantiated by the fact that the amount of $W_xO_y^{z-}$ deposited ions is significantly larger than the amount of the Co^{2+} ions deposited (cf. Figs. 1a and 1c) and thus the location of these ions at the IHP should overcompensate for the positive surface charge and thus shift the positive ζ potential, obtained in the absence of these ions at pH < 8.0, to negative values.

Finally, the location of the deposited Co(II) ions at the IHP may also be investigated by analyzing mathematically the corresponding isotherms obtained for the uptake of Co(II) ions. The analysis was possible because, as already mentioned under our experimental conditions all of the cobalt is present as hydrated Co^{2+} ions, whereas similar analysis of the deposition isotherms for W(VI) species was not possible, because more than one W(VI) species is present in the solution. The analysis was done following a procedure described in detail elsewhere (18) for the derivation and testing of two equations corresponding to deposited ions, located first in the diffuse part of the double layer and second on the surface of the solid. It was found that none of these equations fitted the experimental data. Assuming the triple-layer model and since both the surface and the diffuse part of the electrical double layer are excluded as possible sites for the location of the deposited Co(II) ions, they should be located at the IHP.

From the above considerations it may be concluded that the preparation of WO_3–CoO/γ-Al_2O_3 catalysts with codeposition of W(VI) and Co(II) species using the EDF method results in larger amounts of supported phase WO_3–CoO in comparison with the quantities obtained when W(VI) and Ni(II) species are separately deposited using the EDF method. As already mentioned in the Introduction, a feature that affects the activity of the prepared WO_3–CoO/γ-Al_2O_3 catalysts is the type of W(VI) species deposited, i.e., monomeric or polymeric. Unfortunately the qualitative approach of the phenomenon does not allow for the detailed investigation of this feature. The speciation of the deposited species is possible only by means of a detailed model, which may describe the particular role of each species.

Speciation of the Deposited Species: Codeposition Model

Employing the same methodology used for the development of the models describing the simultaneous deposition of Mo(VI) and Co(II) species (19) as well as of Mo(VI) and Ni(II) species (20) on the γ-alumina surface, a model describing the codeposition of W(VI) and Co(II) species on the γ-alumina surface may be established. According to this model the deposition of W(VI) species takes place through adsorption of one WO_4^{2-} or one $HW_6O_{20}(OH)_2^{5-}$ ion at a site created by one protonated surface hydroxyl ($AlOH_2^+$), whereas the deposition of Co(II) species takes place via adsorption of one Co^{2+} ion at a site created by one deprotonated surface hydroxyl (AlO^-), resulting in the formation of the adsorbed species shown in the following equilibria:

$$AlOH_2^+ + WO_4^{2-} \leftrightarrow AlOH_2^+ \cdots WO_4^{2-}, \qquad [1a]$$

$$AlOH_2^+ + HW_6O_{20}(OH)_2^{5-} \leftrightarrow AlOH_2^+ \cdots HW_6O_{20}(OH)_2^{5-}, \qquad [1b]$$

$$AlO^- + Co^{2+} \leftrightarrow AlO^- \cdots Co^{2+}. \qquad [2]$$

TABLE 1

Saturation Surface Concentration, Energy of the Lateral Interactions Corresponding to W(VI) [Co(II)] Deposition in the Absence (Columns a) and Presence (Columns b) of Co(II) [W(VI)] Species, and the Deposition Constant Corresponding to Co(II) Deposition in the Absence (Column a) and Presence (Column b) of W(VI), at Different pH Values

			E (kJ mol^{-1})					
	Γ_m (μmol m^{-2})		W(VI)		Co(II)		K_C	
pH	W(VI)	Co(II)	a ($E_{w,a}$)	b (E_w)	a ($E_{C,a}$) ($\times 10^2$)	b (E_C)	a	b
4.2	9.47	0.23	−0.72[a]	6.23	0.0[b]	13.61	268.0[b]	19.92
5.1	8.02	1.38	6.83[a]	7.45	1.7	15.04	227.0	31.36
6.2	7.38	2.41	4.15[a]	5.12	4.4[b]	11.37	180.0[b]	19.67
6.7	7.13	2.86	2.34[a]	6.17	5.3[b]	8.53	203.0[b]	68.86

[a] Reference (21).

[b] Reference (18).

The right-hand side of the aforementioned adsorbed species is located at the IHP, whereas the left-hand side of these species is located on the surface of γ-alumina. Concerning the deposition of W(VI) through chemical reaction of WO_4^{2-} ions with the undissociated surface hydroxyls (AlOH), it was found to be negligible, contrary to the deposition of W(VI) in the absence of Co(II) species, where the contribution of the undissociated surface hydroxyls to the total W(VI) deposition was found to be significant (25).

On the basis of equilibria [1a], [1b], and [2] the following equations describing the deposition of $W_xO_y^{z-}$ and Co^{2+} ions were derived:

$$\frac{1}{\Gamma_W} = \frac{1}{\Gamma_{W,m}} + \frac{1}{\Gamma_{W,m}\tilde{K}C_{eq,W}\exp(E_W\Gamma_W/\Gamma_{W,m}RT)}, \quad [3]$$

$$\frac{1}{\Gamma_C} = \frac{1}{\Gamma_{C,m}} + \frac{1}{\Gamma_{C,m}K_C C_{eq,C}\exp(E_C\Gamma_C/\Gamma_{C,m}RT)}. \quad [4]$$

Here E_W and E_C are the energy of lateral interactions between the adsorbed $W_xO_y^{z-}$ and Co^{2+} ions, respectively. $\tilde{K}$ and K_C are constants corresponding to the deposition of W(VI) and Co(II) species, respectively. The plots of $1/\Gamma_W$ versus $1/C_{eq,W}\exp(\lambda_W\Gamma_W/RT)$ and $1/\Gamma_C$ versus $1/C_{eq,C}$ $\exp(\lambda_C\Gamma_C/RT)$, where the parameters λ_W and λ_C are equal to $E_W/\Gamma_{W,m}$ and $E_C/\Gamma_{C,m}$, respectively, are expected to be linear for the appropriate λ_W and λ_C values. It is therefore possible to determine the values of $\Gamma_{W,m}$, $\tilde{K}$, E_W and $\Gamma_{C,m}$, K_C, E_C. Table 1 lists the values of the saturation surface concentration, $\Gamma_{W,m}$ and $\Gamma_{C,m}$, energy of lateral interactions, E_W and E_C, and deposition constant, K_C, determined from Eqs. [3] and [4] at different pH values. Columns a and b correspond to the separate deposition of W(VI) and Co(II) species and to their codeposition. A considerable increase in the energy of the lateral interactions between the deposited W(VI) and Co(II) species due to the presence of Co^{2+} and $W_xO_y^{z-}$ ions, respectively, may be observed at almost all pH values investigated, thus corroborating the qualitative conclusion that stronger attractions are exerted between the simultaneously deposited $W_xO_y^{z-}$ and Co^{2+} ions than in the case in which the $W_xO_y^{z-}$ and Co^{2+} ions are deposited separately.

Provided that the deposition constant K_C is a function of the interactions (chemical and electrical) between the deposited species and the substrate (32), the lower values of K_C (Table 1) imply that the strength of interactions of the adsorbed Co^{2+} ions with γ-alumina is lower in the presence than in the absence of W(VI) species. Therefore, the increased attractive lateral interactions in combination with the lower strength of the $Co \cdots Al_2O_3$ interactions are expected to inhibit the formation of the catalytically inactive $CoAl_2O_4$, when a WO_3–CoO/γ-Al_2O_3 catalyst is prepared by depositing simultaneously both W(VI) species and Co(II) ions using the EDF method.

Figure 2 shows the maximum amounts of W(VI) species deposited according to equilibria [1a] (curve a) and [1b]

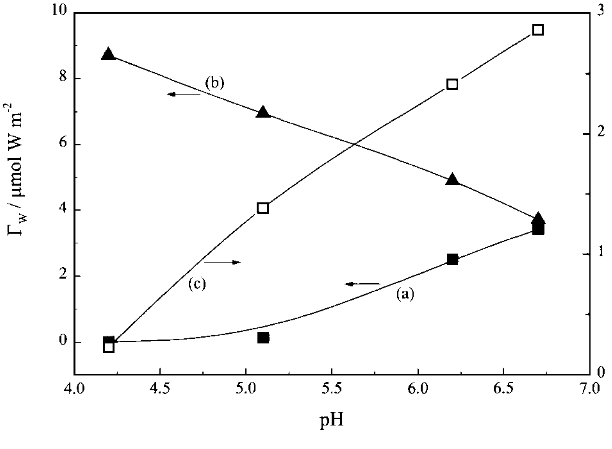

FIG. 2. Variation with pH of the maximum amounts of W and Co deposited through adsorption of the WO_4^{2-} (a) and $HW_6O_{20}(OH)_2^{5-}$ (b) ions on sites created by $AlOH_2^+$ groups and through adsorption of the Co^{2+} ions (c) on sites created by AlO^- groups.

(curve b) and Co(II) species deposited according to equilibrium [2] (curve c). The observed decrease with pH in the maximum amount of W deposited through adsorption of the $HW_6O_{20}(OH)_2^{5-}$ ions (curve b) should predominate on the observed increase with pH of the maximum amount of W deposited through adsorption of the WO_4^{2-} ions (curve a), thus resulting in the decrease in $\Gamma_{W,m}$ with pH as shown in Table 1. This variation in the amount of $HW_6O_{20}(OH)_2^{5-}$ and WO_4^{2-} ions deposited with pH is expected to lead to CoW/γ-Al_2O_3 catalysts, prepared by codepositing W(VI) and Co(II) species using the EDF method, where the amount of polymeric species increases at the expense of monomeric species with decreasing pH. This is indeed the case for W/γ-Al_2O_3 catalysts prepared either by EDF (26) or by incipient wetness impregnation [e.g., (23, 33)]. In the latter case, instead of pH, the parameter affecting the structure of the formed WO_3 is the W loading, which in the samples prepared with codeposition of W(VI) and Co(II) species using the EDF method increases as pH decreases (Table 1).

Finally, concerning the total amount of Co deposited, it was found to increase with pH (Table 1, curve c of Fig. 2). The above-mentioned trends show that it is possible to maximize the catalytic activity of WO_3–CoO/γ-Al_2O_3 catalysts, prepared by codeposition of W(VI) and Co(II) species using the EDF method, by selecting the appropriate pH value of the impregnating solution so as to obtain supported phase WO_3–CoO with the optimum values for the ratios W/Co and monomeric/polymeric W(VI) species.

The above-mentioned considerations in combination with the conclusions of related previous studies (19, 20) show that mutual promotion in the deposition of two active species with opposite charges on the surface of γ-alumina seems to be a more general effect taking place during their codeposition using EDF.

ACKNOWLEDGMENTS

Experimental facilities made available by Professor P. G. Koutsoukos and useful discussions throughout this study are gratefully acknowledged.

REFERENCES

1. Wang, L., and Hall, W. K., *J. Catal.* **77**, 232 (1982).
2. Wang, L., and Hall, W. K., *J. Catal.* **66**, 251 (1980).
3. Kasztelan, S., Grimblot, J., Bonnelle, J. P., Payen, E., Toulhoat, H., and Jacquin, Y., *Appl. Catal.* **7**, 91 (1983).
4. Caceres, C. V., Fierro, J. L. G., Agudo, A. L., Blanco, M. N., and Thomas, H. J., *J. Catal.* **95**, 501 (1985).
5. van Veen, J. A. R., De Wit, H., Emeis, C. A., and Hendriks, P. A. J. M., *J. Catal.* **107**, 579 (1987).
6. Mulcahy, F. M., Fay, M. G., Proctor, A., Houalla, M., and Hercules, D. M., *J. Catal.* **124**, 231 (1990).
7. Sonnemans, J., and Mars, P., *J. Catal.* **31**, 209 (1973).
8. Williams, C. C., Ekerdt, J. G., Jehng, J. M., Hardcastle, F. D., and Wachs, I. E., *J. Phys. Chem.* **95**, 8791 (1991).
9. Brunelle, J. P., *Pure Appl. Chem.* **50**, 1211 (1978).
10. Ng, K. Y. S., and Gulari, E., *J. Catal.* **92**, 340 (1985).
11. Kim, D. S., Kurusu, Y., Wachs, I. E., Hardaste, F. D., and Segawa, K., *J. Catal.* **120**, 325 (1989).
12. Vermaire, D. C., and van Berge, P. C., *J. Catal.* **116**, 309 (1989).
13. Tewari, P. H., and Lee, W., *J. Colloid Interface Sci.* **52**, 77 (1975).
14. Hohl, H., and Stumm, W., *J. Colloid Interface Sci.* **55**, 281 (1976).
15. Davis, J. A., and Leckie, J. O., *J. Colloid Interface Sci.* **67**, 90 (1978).
16. Vordonis, L., Koutsoukos, P. G., and Lycourghiotis, A., *J. Chem. Soc. Chem. Commun.*, 1309 (1984).
17. Vordonis, L., Koutsoukos, P. G., and Lycourghiotis, A., *J. Catal.* **98**, 296 (1986).
18. Vordonis, L., Spanos, N., Koutsoukos, P. G., and Lycourghiotis, A., *Langmuir* **8**, 1736 (1992).
19. Spanos, N., and Lycourphiotis, A., *Langmuir* **10**, 2351 (1994).
20. Spanos, N., and Lycourghiotis, A., *J. Colloid Interface Sci.* **171**, 306 (1995).
21. Karakonstantis, L., Kordulis, Ch., and Lycourghiotis, A., *Langmuir* **8**, 1318 (1992).
22. Spanos, N., and Lycourghiotis, A., *J. Chem. Soc. Faraday Trans.* **89**, 4101 (1993).
23. Salvati, L., Jr., Makovsky, L. E., Stencel, J. M., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **85**, 3700 (1981).
24. Brady, R. L., Southmayd, D. W, Contescu, Cr., Zhang, R., and Schwarz, J. A., *J. Catal.* **129**, 195 (1991).
25. Karakonstantis, L., Bourikas, K., and Lycourghiotis, A., *J. Catal.* **162**, 295 (1996).
26. Karakonstantis, L., Matralis, H. K., Kordulis, Ch., and Lycourghiotis, A., *J. Catal.* **162**, 306 (1996).
27. Contescu, C., Hu, J., and Schwarz, A. J., *J. Chem. Soc. Faraday Trans.* **89**, 4091 (1993).
28. Giles, C. H., Smith, D., and Huitson, A., *J. Colloid Interface Sci.* **47**, 755 (1974).
29. Faughnan, J., "SURFEQL: An Interactive Code for the Calculation of Chemical Equilibria in Aqueous Systems," W. M. Keck Laboratories 138-78, California Institute of Technology, Pasadena.
30. Smith, R. M., and Martell, A. E., "Critical Stability Constants," Vol. 4. Plenum, New York, 1981.
31. Bockris, J. O'M., and Reddy, A. K. N., "Modern Electrochemistry," Vol. 2, Chap. 7. Plenum, New York, 1976.
32. Hough, D. B., and Rendall, H. M., *in* "Adsorption from Solution at the Solid/Liquid Interface" (G. D. Parfitt and C. H. Rochester, Eds.), Chap. 6. Academic Press, London, 1983.
33. Vuurman, M., and Wachs, I. E., *J. Phys. Chem.* **96**, 5008 (1992).