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The Effect of the Isoelectric Point on the Adsorption of Molybdates on Fluoride-Modified Aluminas

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The isoelectric point (IEP) of γ-alumina was modified by the addition of various amounts of fluoride. The modified aluminas were used as supports for molybdenum catalysts prepared by equilibrium adsorption at pH = 6.5. Also, the adsorption of molybdate on supports containing various amounts of fluoride was studied as a function of pH. The amount of molybdenum adsorbed on the fluoride-modified aluminas was found to decrease as the IEP of the carrier decreased. An electrostatic model is used to interpret the results. © 1987 Academic Press, Inc.

INTRODUCTION

Supported catalysts are often prepared by an impregnation method which consists of contacting a high surface area metal oxide with a solution containing the active phase precursor salt. Impregnation is a complicated process involving the interaction of two systems: an electrolyte solution which may contain multiple adsorbing species, and a solid which is often irregularly shaped, having heterogenous surface sites. Various types of reactions, such as ion exchange, condensation, or coordination, can occur at the solid/solution interface. Also, the strength and number of adsorbate-surface interactions are influenced by a multitude of factors including the pH of the solution, concentration and hydrolyzability of metal ions, impurities, and ion charge (*1*). Because adsorption properties can affect the dispersion, repartition, and speciation of supported metal catalysts, it is important for the process to be understood. Yet to date, few studies have dealt systematically with the mechanism of adsorption of catalytically important metal ions on oxide surfaces.

One mechanism used to explain the adsorption of metal ions on metal oxides involves coordination of hydrated ionic complexes with surface hydroxyl groups. According to this mechanism, a water ligand in a hydrated complex is replaced by a surface metal oxide (M–O–) group. Coordination reactions have been shown to operate in the adsorption of some mono- and divalent cations on metal oxides (*2*).

According to another mechanism which has been described by Brunelle (*3*), the adsorption of many cationic and anionic metal complexes on metal oxides can be explained primarily by consideration of the isoelectric point (IEP) of the oxide, the pH of the impregnating solution, and the charge on the metal complex. At a pH below the isoelectric point, an oxide will have a positive surface charge because of hydrogen ion adsorption, or reaction of hydrogen ions with surface hydroxyl groups. In such a case, anions will be attracted to the interfacial layer and bound electrostatically to the surface. Likewise, if the pH of a solution containing metal oxide particles is higher than the isoelectric point of the oxide, the surface will be charged negatively and cations will be drawn from the solution to the interfacial layer.

Wang and Hall (*4*) have shown that the mechanism described by Brunelle can readily explain the adsorption characteristics of various metal ions on titania, silica,

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alumina, and magnesia. However, the use of supports with vastly differing adsorption characteristics makes direct correlation between subtle IEP changes and the adsorption of metal ions difficult. Therefore, it is of interest to examine systematically the influence of the IEP on the adsorption of metal ions, using a single support for which the IEP can be varied. Alteration of the IEP of the support can be accomplished by using additives. The present study is intended to examine the influence of the isoelectric point of the support on the adsorption of molybdate species on fluoride-modified alumina.

EXPERIMENTAL

ESCA spectra were recorded using an AEI ES200A electron spectrometer equipped with an aluminum anode (AlKα = 1486.6 eV) operated at 12 kV and 22 mA. The base pressure in the analysis chamber was typically below 5×10^{-8} Torr. Data acquisition was controlled by an APPLE IIc microcomputer. Samples were dusted onto double-sided tape and mounted on a water-cooled probe for ESCA analysis.

IEP's were determined by a drift method (*5*). The pH of distilled water (25 ml) was adjusted to values near the expected IEP of the alumina with HNO_3 and/or NH_4OH. A sample of modified alumina (0.3 g) was poured into this solution and the change in pH (ΔpH) was measured 30 sec afterward. Several runs were made for each modified alumina. A plot of ΔpH vs initial pH was made and the IEP was determined as the point at which the change in pH was zero. IEP values obtained in this manner were reproducible to ±0.1 pH unit.

X-ray diffraction (XRD) data were obtained using a Diano 700 diffractometer equipped with a graphite monochromator and a copper X-ray tube, the latter operated at 50 kV and 25 mA.

SAMPLE PREPARATION

A Harshaw γ-alumina support (BET surface area 170 m^2/g) was modified by pore volume impregnation with appropriate amounts of aqueous NH_4F (Aldrich Chemical Co.) solutions to yield modified alumina supports containing 0, 0.5, 1, 2, 3, 4, and 5% fluoride by weight. The fluoride-modified aluminas were dried overnight at 120°C and calcined at 600°C for 16 h. The fluoride-modified aluminas were impregnated with 0.0079 *M* ammonium heptamolybdate (Fisher Scientific Co.) by equilibrium adsorption in the following manner. One gram of alumina and 50 ml of 0.0092 *M* ammonium heptamolybdate solution were placed in a 125-ml Erlenmeyer flask along with a glass-coated magnetic stir bar. The pH of the solution was adjusted to 6.5 with dilute NH_4OH, HNO_3, and distilled water. The final volume of solution in the flask was 58 ml. The alumina and solution were stirred for 24 h before filtration. The filtered solid was dried overnight at 120°C. A pH of 6.5 was chosen for the impregnation because it was expected that the influence of the alumina IEP on molybdenum uptake would be greatest at this point. The molybdenum contents of the impregnated aluminas were determined by X-ray fluorescence using molybdenum–alumina samples prepared by incipient wetness for calibration. The fluorine content of samples was determined by fusion of alumina samples with sodium hydroxide, dissolution of the fusion products in water, and analysis of the solution for fluoride with a fluoride ion selective electrode (*6*).

RESULTS

The pH of impregnation (6.5) varied slightly over the 24-h impregnation period. Table 1 lists the initial and final pH's of the impregnating solutions. The final pH values ranged from 6.5 for 5% F/Al_2O_3 to 7.3 for 0.5% F/Al_2O_3.

Examination of the XRD patterns obtained from fluoride-modified aluminas revealed only the diffraction lines characteristic of γ-alumina. The surface areas of the aluminas decreased from 170 for the

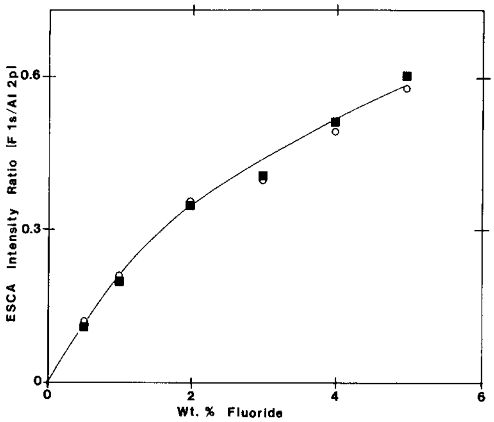

FIG. 1. Variation of ESCA F 1*s*/Al 2*p* intensity ratio as a function of nominal fluoride content. Before molybdate adsorption, ■; after molybdate adsorption, ○. pH of adsorption = 6.5.

TABLE 1

Initial and Final pH of Impregnation for Each Support

Support	Initial pH	Final pH	Surface area (m^2/g)
0%F/Al_2O_3	6.49	7.01	172
0.5%F/Al_2O_3	6.50	7.25	161
1%F/Al_2O_3	6.48	7.02	154
2%F/Al_2O_3	6.50	6.90	150
3%F/Al_2O_3	6.52	6.81	145
4%F/Al_2O_3	6.48	6.52	143
5%F/Al_2O_3	6.49	6.53	145

unmodified support to 145 m^2/g for the support containing 5% fluoride.

No loss of bulk fluorine resulted from molybdenum impregnation as determined by bulk sample analysis. Figure 1 shows a plot of ESCA F 1*s*/Al 2*p* intensity ratios before and after molybdenum impregnation as a function of fluorine loading. One observes that there is no significant change in the ESCA F 1*s*/Al 2*p* intensity ratio after adsorption of molybdate, indicating that no significant loss of surface fluoride occurred as a result of molybdenum impregnation.

Figure 2, curve A, shows the variation in molybdenum loading as a function of the fluoride content. An addition of only 1% fluoride to the alumina support brings about a 34% decrease in molybdenum content. Larger amounts of fluoride decrease the molybdenum content even further, so that for alumina containing 5% fluoride, the amount of molybdenum present is only 40% that of the sample containing no fluoride.

Figure 2, curve B, illustrates the variation of the IEP of the fluoride-modified

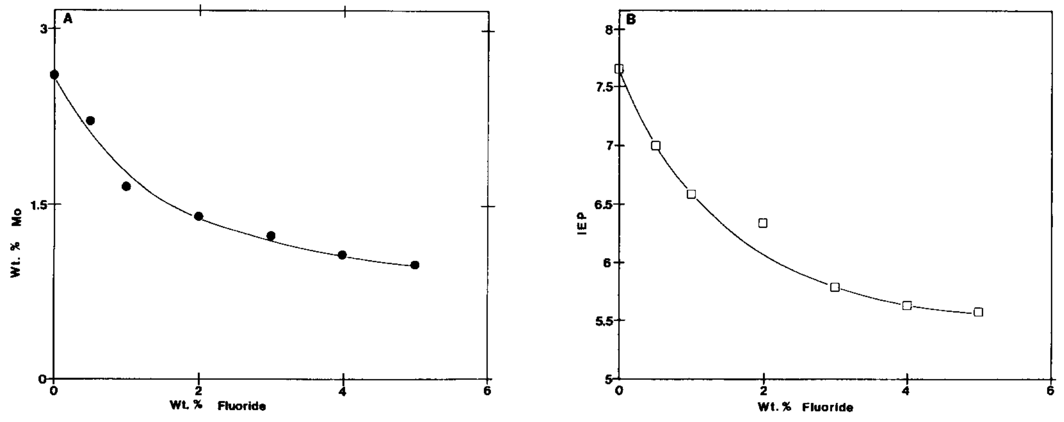

FIG. 2. Effect of fluorine addition on molybdenum uptake and IEP of support. (A) Variation of molybdenum uptake as a function of nominal fluoride content, ●. (B) Variation of isoelectric point as a function of nominal fluoride content, □. pH of impregnation = 6.5.

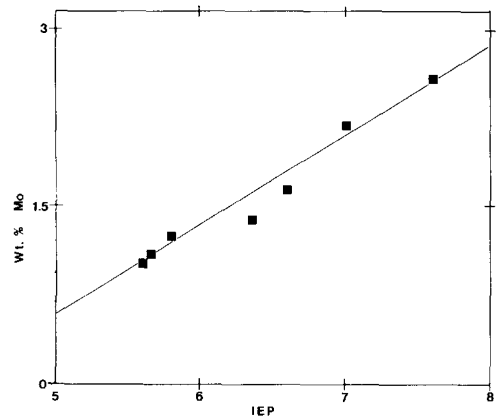

FIG. 3. Variation of molybdenum uptake as a function of the isoelectric point of the support. pH of impregnation = 6.5.

aluminas as a function of the nominal fluoride content. A decrease in the IEP with increasing fluoride content is observed. Figure 2, curve B, also indicates that the initial additions of fluoride have the greatest effect on the IEP of the alumina. A relationship between molybdenum uptake and the IEP of the support is suggested by the shapes of Figs. 2A and 2B. This relationship is illustrated in Fig. 3, which shows the variation of molybdenum loading with the IEP of the support. As the IEP of the support decreases, the molybdenum loading decreases. Assuming a linear relationship between the variables, the correlation coefficient was determined to be 0.97, corresponding to a level of significance below 0.001.

DISCUSSION

The decrease in molybdenum content with increasing fluoride cannot be attributed to a decrease in the surface area of the support on addition of fluoride. There was at most a 15% decrease in alumina surface area when fluoride was added while a decrease of up to 60% in molybdenum content was observed. The linear correlation shown in Fig. 3 is maintained when molybdenum surface concentration (atoms/nm^2) is plotted as the ordinate (correlation coefficient = 0.97).

The results can be understood best in terms of the effect of the IEP on adsorption. According to Brunelle (*3*), when the pH of the impregnating solution is below the IEP of the oxide, the surface of the oxide becomes positively charged and negative ions should be adsorbed. If the pH increases toward the IEP of the support, the number of negative species adsorbed from solution should decrease. Likewise, if the IEP of the support is decreased toward the pH of the solution, the number of anions adsorbed should decrease. In the present case, molybdate anions exist as negatively charged solution species. Molybdate ions exist as both MoO_4^{-2} and $Mo_7O_{24}^{-6}$ (approximately 1 : 1) in solution at pH = 6.5 (*4*). At pH = 6.5, the surface of alumina (IEP = 7.6) should be positively charged due to reactions with hydrogen ions and should therefore attract and adsorb MoO_4^{-2} and $Mo_7O_{24}^{-6}$ ions from solution. Since the IEP of alumina decreases upon addition of fluoride (Fig. 2B), the surface of the fluoride-modified aluminas should be less positively charged in solution at pH = 6.5 than the surface of the unmodified alumina and should adsorb less molybdate. From Fig. 3, it is clear that this occurs.

To corroborate the evidence of Fig. 3 that the IEP of the support plays an important role in the adsorption of molybdates, molybdates were adsorbed from solutions having various pH's onto aluminas containing 0, 1, and 3% fluoride. The impregnation procedure was the same as for the adsorption carried out at pH = 6.5. Figure 4 shows the amount of molybdenum adsorbed as a function of pH for the three supports. Wang and Hall have shown that the adsorption of molybdates on alumina above pH = 2 is determined primarily by the degree of surface charging, rather than being due to the changes of molybdenum species with pH; surface charging is controlled by the IEP of the

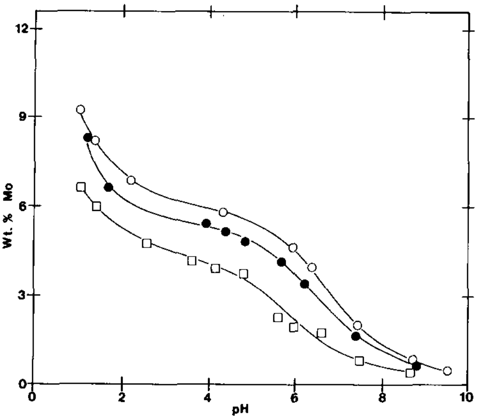

FIG. 4. Molybdenum uptake on modified and unmodified alumina as a function of pH of impregnation. 0% F/Al_2O_3, ○; 1% F/Al_2O_3, ●; 3% F/Al_2O_3, □.

alumina and the pH of the impregnating solution. Below pH = 2, it was suggested that the increase in molybdenum uptake might be due to different exposed crystal planes of the support or the formation of higher polymeric molybdate species on the surface. It is interesting to note that a distinct increase in molybdenum uptake on both alumina and titania below pH = 2 was observed by Wang and Hall (*4*). In the present study there is also an increase in molybdenum uptake at pH < 2 for the fluoride-modified aluminas. Since these increases in molybdenum uptake on titania, alumina, and fluoride-modified alumina all occur at the same pH, it appears that the nature of the species in solution must be responsible. The causes of this increase may include the formation of $Mo_8O_{26}^{-4}$ below pH = 2 (*4, 7*) or precipitation of molybdenum oxide hydroxide at pH = 1.2 (*8*). In the case of alumina, which exhibits a much larger increase in molybdenum uptake than titania, an additional factor may be the formation of larger $AlMo_{12}O_{40}^{-5}$ ions, since alumina dissolves below pH = 2.

The similarity in the shapes of the three adsorption curves in Fig. 4 indicates that the modified aluminas have retained many of their adsorption characteristics. Figure 4 also shows that for any given pH, the molybdenum content decreases with increasing fluoride content, i.e., decreasing IEP.

Finally, it must be noted that while the data can be easily understood in terms of an electrostatic model, other factors may also have an effect. For instance, since molybdate ions interact with surface hydroxyl groups, replacement of surface hydroxyls with fluoride might lead to blockage of adsorption sites, thus decreasing molybdenum uptake. Furthermore, although an electrostatic model can be used to predict the adsorption of metal ions on metal oxides, the situation is more complex than it appears, since for adsorption to occur, a reaction must take place (*9*). However, from the evidence presented here and elsewhere (*3, 4*), the IEP of the support appears to be a very important factor in determining molybdenum uptake on alumina.

CONCLUSION

The amount of molybdate adsorbed on fluoride-modified alumina at pH = 6.5 decreases with increasing fluoride content. This trend can be readily understood by consideration of the IEP's of the various modified aluminas studied. The adsorption of molybdates on alumina as a function of pH can be interpreted in terms of the IEP of the support and the molybdenum species present in solution.

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