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Effect of F and Mg on the Dispersion of Mo/Al_2O_3 and W/Al_2O_3

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Samples containing 8% Mo and 15% W supported on magnesium- and fluoride-modified aluminas were prepared by incipient wetness impregnation and examined in the dried and calcined states using X-ray photoelectron spectroscopy (XPS, ESCA). The presence of fluoride as an additive decreased the dispersion of the Mo and W phases for dried samples. The opposite effect was observed for dried Mg-modified samples. The effects of F and Mg addition largely disappeared when the samples were calcined. The results are interpreted in terms of the interactions between Mo and W species and the basic hydroxyl groups of the alumina. © 1993 Academic Press, Inc.

INTRODUCTION

The first stage of supported catalyst preparation usually involves wetting the support with a solution containing the active phase precursor; these precursors are often metal oxyanions ($Mo_7O_{24}^{6}$, $W_{12}O_{39}^{-6}$, etc.). During impregnation and the drying step which follows, a variety of interactions can occur between the active phase precursor and the support surface (*1, 2*). These interactions often determine the dispersion and repartition of the active phase, and ultimately the catalyst performance. The adsorption of metal oxyanions on metal oxides has been extensively studied for this reason. Adsorption of perrhenate (*3, 4*), chromate (*4, 5*), vanadate (*5, 6*), permanganate (*4*), tungstate (*4, 5, 7*), and molybdate (*4, 5, 8–13*) on alumina (*3–6, 8–14*), titania (*5, 7, 11*), magnesia (*5*), and silica (*5*) has been well documented. The effects of fluoride (*10, 14–20*), magnesium (*15, 16, 21*), sodium (*17*), and lithium (*17*) additives on the adsorption characteristics and surface chemistry of alumina have also been examined. The use of fluoride as an additive is of particular interest since fluoride is used as a modifier in hydrodesulfurization (HDS) catalysts containing tungsten or molybdenum (*9*).

Fluoride modification of alumina leads to a decrease in the number of hydroxyl groups on the surface (*14, 18*). Basic hydroxyl groups are especially susceptible to replacement by fluoride (*14, 21, 22*). These same hydroxyl groups are thought to be responsible for the strong interactions between molybdates and alumina surfaces (*4, 14, 9, 10, 20, 23*). This has been illustrated by a number of studies and is reflected by the decrease in molybdate adsorption which is observed for alumina modified with fluoride (*15, 16*).

Modification of alumina with magnesium also leads to changes in the alumina hydroxyl groups. There is an increase in the basicity of the support and in the number of hydroxyl groups upon magnesium addition (*15, 16, 21*). The increase in adsorption of molybdate and tungstate which occurs with increasing magnesium content indicates increased interaction between molybdate (and tungstate) and basic surface hydroxyl groups produced by magnesium modification (*16*).

The equilibrium adsorption studies cited above (*3–20*) provide a basis for understanding the adsorption of metal ions on metal oxides and also show the effect of

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modifiers on adsorption. However, catalysts prepared by equilibrium adsorption are ideal systems in that samples are prepared under well controlled conditions of pH, temperature, active phase precursor concentration, etc., making the samples homogeneous and relatively free of precipitated phases. Therefore, catalysts prepared by equilibrium adsorption may be quite different from industrial catalysts which are prepared by incipient wetness, since incipient wetness preparations provide opportunity for more complex interactions of active phase and support, and are often heterogeneous.

The purpose of the present study is to illustrate that the interactions between active phase and support in catalysts prepared by incipient wetness may be understood from studies of "ideal" systems prepared by equilibrium adsorption. To this end, the effect of F and Mg additives on the dispersion of Mo and W active phases of Mo/Al_2O_3 and W/Al_2O_3 samples prepared by incipient wetness is examined. Furthermore, the dispersion of Mo and W is monitored for dried and calcined samples in order to trace the origins of additive effects.

EXPERIMENTAL

Sample Preparation

Preparation of the fluoride and magnesium modified aluminas is described in detail elsewhere (*16*). Briefly, the method consists of impregnating alumina with NH_4F or $Mg(NO_3)_2$ by incipient wetness, followed by drying in air at 120°C for 8 h and calcination in air at 600°C for 16 h. Adsorption of molybdate and tungstate on the modified aluminas is also described elsewhere (*16*). Adsorption was carried out from dilute solutions at pH = 6.5 for fluoride modified aluminas and pH = 9.3 for magnesium modified aluminas. These pH's were chosen because they are optimum for showing the effect of F and Mg addition on the adsorption of molybdate and tungstate on alumina (*16*).

Preparation of 8% Mo and 15% W (by weight) samples supported on the modified aluminas was carried out by incipient wetness impregnation of the modified aluminas (ground to <200 mesh) with 0.26 *M* ammonium heptamolybdate (Sigma) (pH = 5.4) or 0.16 *M* ammonium metatungstate (Cerac) (pH = 4.4), followed by drying in air for 8 h at 120°C and calcination in air for 16 h at 500°C. The molybdenum loading chosen is the *nominal* value for monolayer coverage on alumina having an N_2 BET surface area of 170 m^2/g (ca. 8% Mo) (*14*). The loading of W was chosen so that the W/Al and Mo/Al atomic ratios were the same.

Instrumentation

ESCA spectra were recorded using a Leybold–Heraeus LHS-10 electron spectrometer equipped with an aluminum anode (Al$K\alpha$ = 1486.6 eV) operated at 12 kV and 20 mA. The pressure in the chamber during analysis was below 5×10^{-8} Torr. Data acquisition was controlled by an HP-1000 computer. Samples were ground to <200 mesh, dusted onto double-sided tape, and mounted on a probe for ESCA analysis. ESCA binding energies are reported relative to the Al 2*p* line at 74.5 eV (*23*).

Fluorine analysis of the calcined samples was conducted as described elsewhere (*15*, *24*), using an ion-selective electrode; dried support samples were used as calibration standards. Determination of isoelectric points (IEP) was made by a drift method, and metal loadings were determined by X-ray fluorescence (XRF). Both methods have been described previously (*15*, *16*).

RESULTS

F and Mg ESCA Intensities

The ESCA F 1*s*/Al 2*p* and Mg *KLL*/Al 2*p* intensity ratios were measured for dried and calcined 8% Mo and 15% W samples prepared by incipient wetness, and for the modified aluminas before Mo or W impregnation. These ratios are plotted as function of initial additive loading in Fig. 1 and 2. The F 1*s*/Al 2*p* intensity ratios for the support and for the dried samples increase linearly to a F/Al atomic ratio of 0.09 (3 wt% F) and deviate from linearity for higher F loadings. For cal-

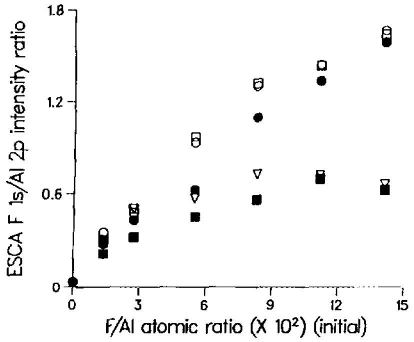

FIG. 1. Variation of ESCA F 1*s*/Al 2*p* intensity ratio as a function of fluoride loading for fluoride-modified alumina before impregnation (●), dried after impregnation with Mo (□) and W (○), and calcined after impregnation with Mo (■) and W (▽).

TABLE 1

Fluoride Content of Mo and W Catalysts Before and After Calcination

F/Al atomic ratio before calcination (× 10²)	F/Al atomic ratio after calcination (× 10²)	
	Mo catalysts	W catalysts
1.4	1.3	1.4
2.7	1.8	2.4
5.5	3.5	3.5
8.3	4.6	5.0
11.2	5.7	6.3
14.1	6.0	—

cined F containing samples, the F 1*s*/Al 2*p* intensity ratios increase up to an F/Al atomic ratio of 0.03 (1 wt% F) and level off at higher loadings.

The most important feature of Fig. 1 is that there is no change in the ESCA F 1*s*/Al 2*p* intensity ratio when the fluoride-modified supports are impregnated with Mo or W and then dried. However, on calcination, there is a significant decrease in the ESCA F 1*s*/Al 2*p* intensity ratio relative to the dried samples. This decrease is accompanied by loss of fluoride, as shown by the results of chemical analyses given in Table 1.

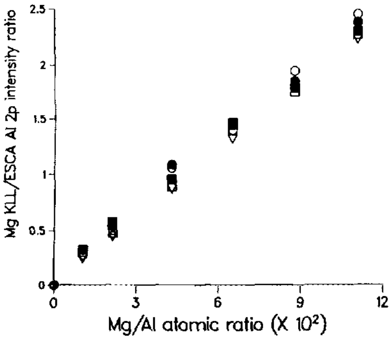

FIG. 2. Variation of Auger Mg KLL/ESCA Al 2*p* intensity ratio as a function of magnesium loading for magnesium-modified alumina before impregnation (●), dried after impregnation with Mo (□) and W (○), and calcined after impregnation with Mo (■) and W (▽).

Different behavior is observed for Mo and W supported on magnesium modified alumina. Figure 2 shows that the Mg *KLL*/Al 2*p* intensity ratio increases linearly with magnesium loading and is not different for either dried or calcined samples, with or without added Mo or W.

Mo and W ESCA Intensities

The effects of fluoride and magnesium addition on the ESCA Mo 3*d*/Al 2*p* and W 4*f*/Al 2*p* intensity ratios of the dried samples are shown in Fig. 3. The ESCA Mo 3*d*/Al 2*p* and W 4*f*/Al 2*p* intensity ratios (□) both decrease with increasing fluoride content. Conversely, for samples prepared using magnesium-modified aluminas, the ESCA Mo 3*d*/Al 2*p* and W 4*f*/Al 2*p* intensity ratios (●) increase with increasing magnesium content.

The influence of fluoride and magnesium on the Mo 3*d*/Al 2*p* and W 4*f*/Al 2*p* intensity ratios largely disappears when the samples are calcined. This is illustrated in Fig. 4, which shows that after calcination of the 8% Mo and 15% W samples, fluoride and magnesium have only a slight effect on the ESCA Mo 3*d*/Al 2*p* and W 4*f*/Al 2*p* intensity ratios. The ESCA Mo 3*d*/Al 2*p* and W 4*f*/Al 2*p* ratios remain relatively constant, regardless of

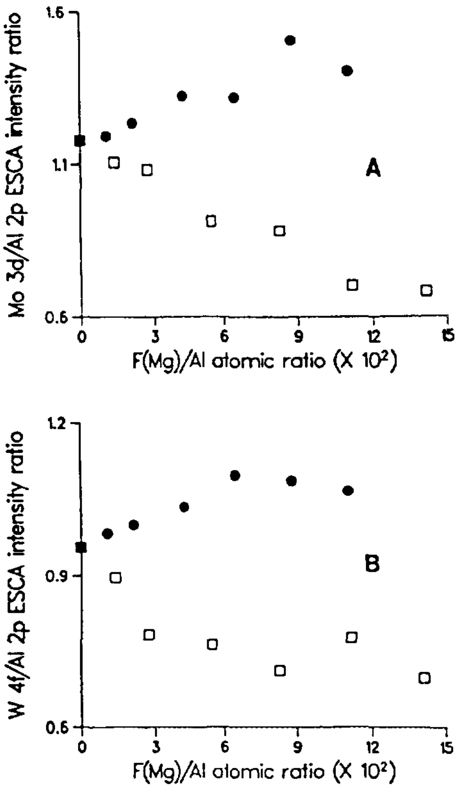

FIG. 3. Variation of (A) ESCA Mo 3d/Al 2p and (B) W 4f/Al 2p intensity ratios as a function of fluoride (□) and magnesium (●) loading. Samples are (A) 8% Mo/Al$_2$O$_3$ and (B) 15% W/Al$_2$O$_3$, prepared by incipient wetness and dried for 8 h at 120°C.

modifier loading. The mean value of the Mo 3d/Al 2p ratio for calcined Mo/F/Al$_2$O$_3$ samples is 1.30 ± 0.06; for Mo/Mg/Al$_2$O$_3$, the mean value is 1.36 ± 0.06. For calcined W/F/Al$_2$O$_3$ and W/Mg/Al$_2$O$_3$ the mean W 4f/Al 2p values are 1.02 ± 0.06 and 1.09 ± 0.04, respectively.

Binding energies of all species remained constant (±0.2 eV) for all samples and are shown in Table 2.

DISCUSSION

Adsorption of Molybdate and Tungstate on Modified Aluminas

The results obtained for samples prepared by *incipient wetness* are best understood in terms of the adsorption of molybdate and tungstate on modified aluminas. The effects of fluoride and magnesium modification of alumina on its characteristics and adsorption properties have been described elsewhere (*15*, *16*), but are summarized here for the purpose of comparing samples prepared

TABLE 2

Binding Energies of Photoelectrons from Samples Prepared by Incipient Wetness

Peak	Binding energy (eV)
Mo 3$d_{5/2}$	233.0
W 4$f_{7/2}$	36.7
F 1s	685.2
Mg *KLL*	306.8

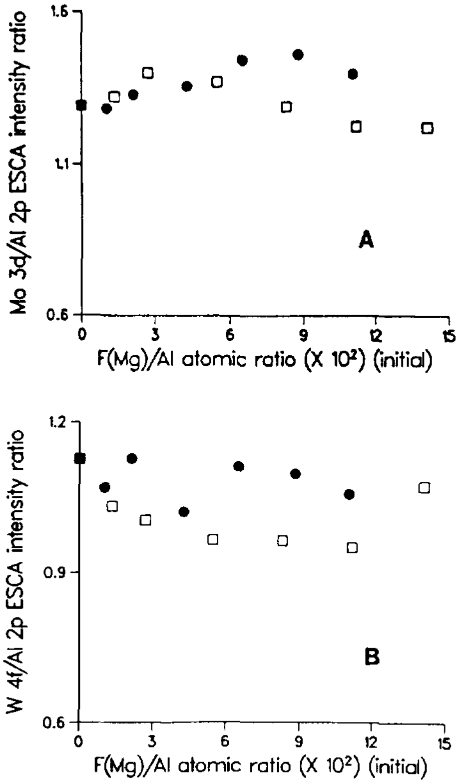

FIG. 4. Variation of (A) ESCA Mo 3d/Al 2p and (B) W 4f/Al 2p intensity ratios as a function of fluoride (□) and magnesium (●) loading. Samples are (A) 8% Mo/Al$_2$O$_3$ and (B) 15% W/Al$_2$O$_3$ prepared by incipient wetness and calcined for 16 h at 500°C.

TABLE 3

Surface Area of Fluoride- and Magnesium-Modified Aluminas

Sample F/Al atomic (× 10^2)	Surface area (m^2/g)	Sample Mg/Al atomic (× 10^2)	Surface area (m^2/g)
0	170	0	170
1.4	161	1.1	189
2.7	154	2.1	181
5.5	150	4.3	169
8.3	145	6.5	162
11.2	143	8.8	157
14.1	145	11.1	151

by *equilibrium adsorption* with those prepared by *incipient wetness*.

The addition of fluoride and magnesium to alumina leads to a decrease in the alumina surface area with increasing modifier content. This effect is shown in Table 3. An important characteristic of alumina which is affected by additives is the isoelectric point (IEP). The dependence of the alumina IEP on fluoride and magnesium loadings is shown in Fig. 5. The IEP decreases with increasing fluoride loading and increases with increasing magnesium loading. This change in alumina IEP affects it adsorption characteristics. The uptake of molybdate and tungstate on fluoride modified alumina at pH = 6.5 is shown as a function of fluoride loading in Fig. 6. Figure 7 illustrates the uptake of molybdate and tungstate on Mg-modified alumina at pH = 9.3 as a function of magnesium loading. The variations of molybdate and tungstate uptake as a function of modifier loading parallel the effect of the modifiers on IEP, as shown in Fig. 5. Molybdate and tungstate uptake decreases with increasing fluoride content and increases with increasing magnesium loading.

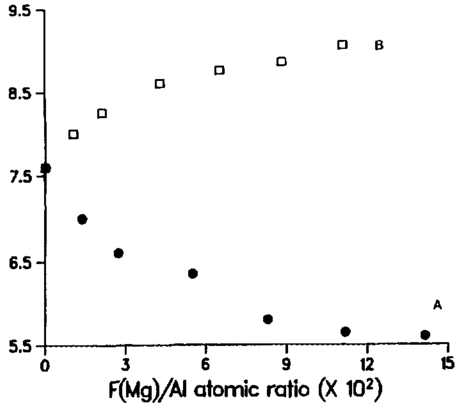

FIG. 5. Variation of IEP of fluoride and magnesium modified aluminas as a function of fluoride (●) and magnesium (☐) loading.

Changes of the alumina surface resulting from addition of fluoride and magnesium are important because they play a role in determining the adsorption behavior of molybdate and tungstate. The decrease in the IEP of alumina caused by addition of fluoride results from replacement of basic hydroxyl groups by fluoride (*14, 22*). Since these basic hydroxyl groups are believed to be adsorption sites for molybdate and tungstate (*14, 16, 22*), the ability of alumina to adsorb molybdate and tungstate is reduced by the presence of fluoride.

Addition of magnesium to alumina causes an increase in the number of basic hydroxyl groups on the support (*16, 21*), reflected by an increase in IEP with increasing magnesium content. The increase in the number of basic hydroxyl groups leads to increased adsorption of molybdate and tungstate.

Mo(W)/Al_2O_3 Samples Prepared by Incipient Wetness

Effect of F and Mg on dried samples. The dispersion of the Mo and W phases in dried Mo/Al_2O_3 and W/Al_2O_3 samples prepared by incipient wetness impregnation is determined largely by interactions of molybdate and tungstate ions with the hydroxyl groups of alumina during impregnation and drying (*4, 9, 10, 14, 22*). By replacing hydroxyls with fluoride, sites for adsorption and interaction of molybdate and tungstate with the support are decreased in number. Therefore, if catalysts having the same metal loading are prepared by incipient wetness on

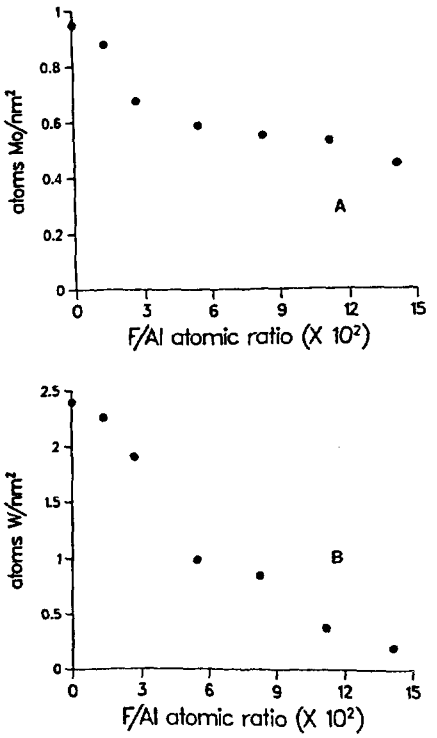

FIG. 6. Uptake of molybdate (A) and tungstate (B) on fluoride modified alumina at pH = 6.5 by equilibrium adsorption as a function of fluoride loading.

modified aluminas, the dispersion of Mo and W should be lower on supports containing fluoride. The decrease in ESCA Mo $3d$/Al $2p$ and W $4f$/Al $2p$ intensity ratios with increasing fluoride loading (Fig. 3) for dried samples is consistent with decreased dispersion of Mo and W brought about by replacement of alumina hydroxyl groups by fluoride. Okamoto *et al.* (*20*) have observed a similar decrease in the ESCA Mo/Al intensity ratio for catalysts supported on fluoride modified alumina, which was also attributed to the replacement of basic alumina hydroxyl groups by fluoride.

The increase of molybdate and tungstate uptake by magnesium modified aluminas observed in equilibrium adsorption studies should translate into an increase in dispersion of Mo and W for Mo/Al_2O_3 and W/Al_2O_3 samples prepared by incipient wetness on magnesium-modified supports. This is consistent with Fig. 3, which shows that the ESCA Mo $3d$/Al $2p$ and W $4f$/Al $2p$ intensity ratios for the samples prepared by incipient wetness increase with magnesium loading. However, it cannot be ruled out that the observed increases in intensity ratio may be due to changes of repartition of the Mo and W phases as a function of Mg loading.

Effect of F and Mg on calcined samples. Figure 8 shows the variation of Mo $3d$/Al $2p$ and W $4f$/Al $2p$ ratios of the dried and calcined samples as a function of Mg loading for Mg-modified alumina. Figure 8A shows that the ESCA Mo $3d$/Al $2p$ intensity ratio of the calcined samples is only slightly higher than for dried Mo/Al_2O_3 samples; Fig. 8B shows the same effect for ESCA W $4f$/Al $2p$

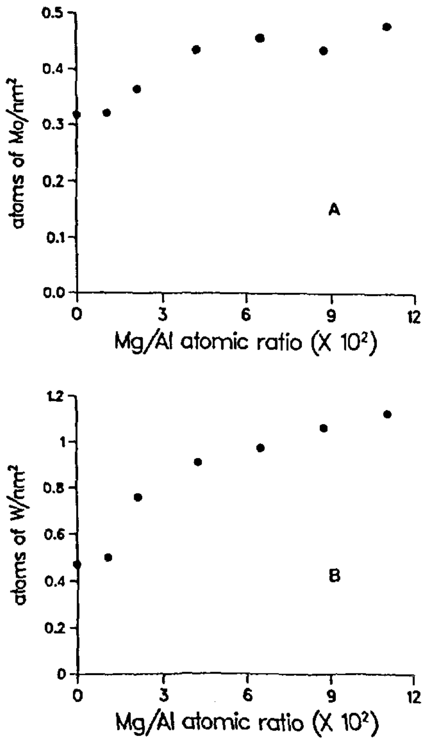

FIG. 7. Uptake of molybdate (A) and tungstate (B) on magnesium modified alumina at pH = 9.3 and pH = 10, respectively, by equilibrium adsorption as a function of magnesium loading.

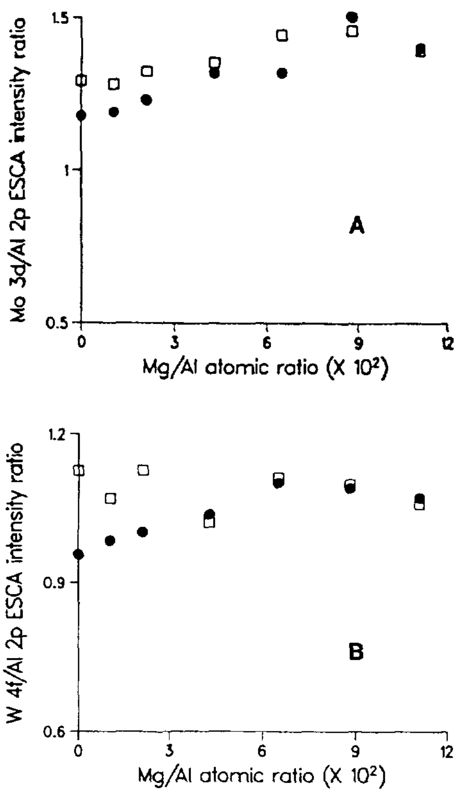

FIG. 8. Variation of (A) ESCA Mo 3*d*/Al 2*p* and (B) W 4*f*/Al 2*p* intensity ratios with magnesium loading for dried (●) and calcined (☐) 8% Mo/Al_2O_3 and 15% W/Al_2O_3 catalysts prepared by incipient wetness impregnation.

ratios. The small increases in intensity ratio seen are probably due to an increase in dispersion caused by calcination. Knoezinger (*25*) and others have shown that well-dispersed molybdenum phases can be produced on alumina by treating physical mixtures of molybdenum trioxide and alumina at temperatures lower than that used for calcination in the present study. Thus, Mo and W species on the dried samples may become mobile during calcination.

While calcination of Mo and W samples containing magnesium results in only small increases of intensity ratio, calcination of samples prepared on fluoride modified aluminas show, significant increases in the Mo 3*d*/Al 2*p* and W 4*f*/Al 2*p* ESCA intensity ratios. This effect is shown in Fig. 9, where the intensity ratios of the dried (●) and calcined (☐) samples are plotted as a function of fluoride loading. The increases in intensity ratio which occur on calcination can be attributed to an increase in molybdenum and tungsten dispersion. As is the case for Mo and W samples supported on Mg modified alumina, this increase may be caused by the mobility of molybdenum and tungsten phases at elevated temperatures (*25*). Also, since Mo and W phases are less well dispersed on dried F-modified alumina than on dried Mg-modified alumina, the relative magnitude of change in Mo and W dispersion which is possible for F-modified alumina is much greater than for Mg-containing samples.

The increase in molybdenum and tungsten dispersion on calcination can also be related to the loss of fluoride which occurs on calcination of fluoride-modified alumina which has been impregnated with molybdate or tungstate (see Fig. 1 and Table 1). This loss cannot be an effect of calcination alone, since the original modified aluminas were calcined at 600°C without loss of fluoride (*15*). Also, the fluoride cannot be lost by formation of volatile fluorides of Mo or W, since XRF analysis of dried and calcined samples indicates that Mo and W are not lost from the samples on calcination. It has been stated that molybdate has a greater affinity for alumina than fluoride (*10*); it is most likely that during calcination, fluoride is replaced by molybdate and tungstate species. One possibility is that a reaction such as the following occurs during calcination:

$$(NH_4)_6Mo_7O_{24} + 6 \rangle Al{-}F \rightarrow \rangle Al_6Mo_7O_{24} + 6\,HF + 6\,NH_3.$$

Such a reaction would lead to loss of fluoride with no loss of Mo or W. Regardless of the reaction mechanism, at elevated temperatures, molybdate and tungstate are capable of interacting with alumina surface sites occupied by fluoride, resulting in loss of the fluoride. This phenomenon, coupled with

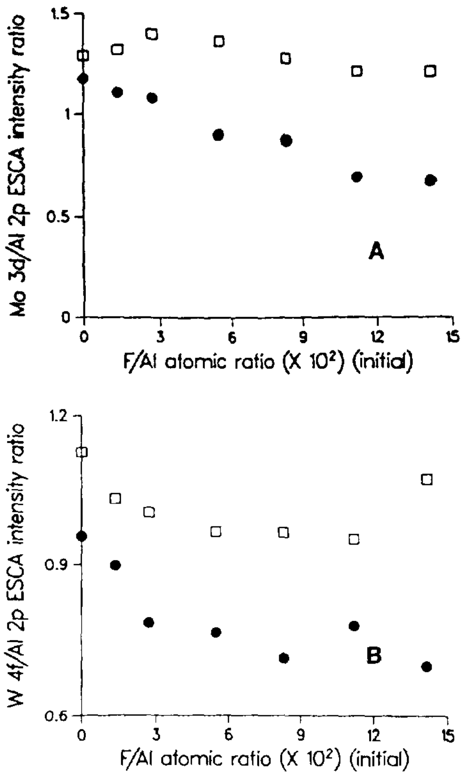

FIG. 9. Variation of (A) ESCA Mo 3*d*/Al 2*p* and (B) W 4*f*/Al 2*p* intensity ratios as a function of fluoride loading for dried (●) and calcined (□) 8% Mo/Al_2O_3 and 15% W/Al_2O_3 catalysts prepared by incipient wetness impregnation.

the mobility of Mo and W species, can lead to increased dispersion of Mo and W over the modified alumina on calcination. This is in agreement with Miciukiewicz *et al.* (*19*), who reported that the presence of fluoride does not affect the Mo dispersion on calcined catalysts. The high Mo dispersion on calcined $Mo/F\text{–}Al_2O_3$ catalysts observed by these authors was suggested to be due to the interaction of molybdenum species with "non-OH sites" on the alumina surface. In view of the loss of fluoride from calcined samples observed in the present study, it is likely that the "non-OH sites" referred to (*19*) are in fact fluoride sites which were formed by exchange of fluoride with basic hydroxyls.

CONCLUSION

The use of fluoride as a support additive in Mo/Al_2O_3 and W/Al_2O_3 catalysts prepared by incipient wetness leads to a decrease in the dispersion of the active phase for dried catalysts. This effect is due to replacement of basic hydroxyl groups by fluoride, which causes loss of adsorption sites for molybdate and tungstate. On calcination, the dispersion of Mo and W supported on fluoride modified alumina increases, reverting to a dispersion similar to that observed for samples prepared on unmodified alumina. The increase in dispersion of Mo and W supported on fluoride modified alumina which occurs on calcination is attributed to mobility of Mo and W species and to reaction of molybdate or tungstate with alumina surface sites occupied by fluoride. This reaction leads to a loss of fluoride from the alumina.

The use of magnesium-modified aluminas as supports for Mo or W causes an increase in the dispersion of the active phase on the dried catalyst, relative to the same catalyst prepared on unmodified alumina. The dispersion of Mo and W phases on Mg-modified alumina increases on calcination, but are not significantly affected by the presence of Mg.

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