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Adsorption of Perrhenate on Modified Aluminas

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Series of rhenium catalysts were prepared by equilibrium adsorption on unmodified alumina and alumina containing F and Mg additives. The uptake of perrhenate on alumina was dependent on the pH and the concentration of nitrate in the impregnation solution. Uptake of perrhenate at pH 6.5 on F modified alumina decreased with increasing F loading; for Mg-modified aluminas, perrhenate uptake at pH 9.3 increased with increasing Mg content. A correlation was observed between perrhenate uptake and the isoelectric point (IEP) of the modified supports. These data are interpreted on the basis of electrostatic attractions which occur between perrhenate ions in solution and alumina surfaces. Competition between nitrate and perrhenate for adsorption sites satisfactorily accounts for the effect of nitrate on perrhenate adsorption. © 1994 Academic Press, Inc.

INTRODUCTION

Supported catalysts are often prepared by contacting a high surface area metal oxide support with a solution containing an active phase precursor ion. These precursors often are metal oxyanions such as molybdate, tungstate, vanadate, chromate, and perrhenate. During the impregnation step and the drying step which follows, a variety of interactions can occur between the active phase and the support. These interactions often determine the dispersion and repartition of the active phase, and ultimately catalyst performance. The adsorption of metal oxyanions on metal oxides has been studied extensively for this reason (1–12). Most of these studies have focused on the adsorption of molybdates and tungstates on alumina or modified aluminas. Early work dealing with molybdate and tungstate adsorption ascribed the adsorption of these ions to electrostatic attractions defined by the isoelectric point (IEP) of the support, the pH of the adsorption solution, and the charge of the adsorbing ion (1, 9, 12, 13). Later studies have shown that adsorption of molybdate and tungstate on alumina is due to interaction with two types of alumina surface sites (4, 7, 14). Further, it is believed that surface reactions between the oxyanions and the alumina surface anchor the oxyanions to the surface (4, 7, 14). In addition, studies of molybdate and tungstate adsorption on fluoride- and magnesium-modified aluminas have shown that the IEP of the modified support has a marked effect on the uptake of these oxyanions from solution (14). This effect is believed to stem from changes in the number of basic hydroxyl sites on the alumina surface brought about by modifier addition.

Other metal oxyanions, such as vanadate, chromate, and perrhenate, are often assumed to adsorb on alumina in a manner analogous to that of molybdate and tungstate. However, comparatively few studies of the adsorption of vanadate, chromate, and perrhenate have actually been conducted (1, 2, 10, 14). It has recently been shown that the adsorption of perrhenate on alumina occurs in a manner different from that in which molybdate and tungstate adsorb (14). This study indicated that while molybdate and tungstate adsorbed on alumina by some type of surface reaction, adsorption of perrhenate could be explained solely by electrostatic attractions. Another difference between the adsorption of perrhenate and that of the other metal oxyanions is that the other ions may polymerize, while perrhenate does not (15). Thus, while the adsorption of molybdates and tungstates may be greatly complicated by covalent interactions with alumina or polymerization in solution, the adsorption of perrhenate should be relatively free of these interferences.

The purpose of the present work is to study the relatively interference-free adsorption of perrhenate on alumina as a function of pH. Also, the influence of the IEP of the support on the adsorption of perrhenate will be examined. The IEP of an alumina support can be altered by modifying alumina with varying amounts of F and Mg for this purpose.

EXPERIMENTAL

Sample Preparation

Harshaw γ-alumina (surface area = 170 m^2/g) was modified by incipient wetness impregnation with enough aqueous NH_4F or $Mg(NO_3)_2$ to produce supports nominally containing 0–5% F or Mg. The modified aluminas were

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then dried in air at 120°C overnight and calcined in air at 600°C for 16 h.

The modified aluminas were impregnated with rhenium by equilibrium adsorption using 0.064 *M* ammonium perrhenate (Aesar). To 50 ml of perrhenate solution were added 1 g of alumina and enough HNO_3, NH_4OH, and water to bring the volume of the solution to 58 ml and the initial pH to a specified value. The initial pH of solutions containing unmodified alumina was varied from 2 to 10 in order to examine the effect of pH on perrhenate uptake. Ammonium nitrate was added to several of these preparations to investigate the effects of nitrate. The initial pH for solutions used to impregnate F-modified aluminas was 6.5, while for Mg-modified aluminas, the initial pH was brought to 9.3. The final pH for these preparations ranged from 6.71 to 7.26 for F-modified samples; final pH for Mg-modified samples ranged from 9.15 to 9.35. The error in pH measurements is estimated to be ±0.05 pH units. The mixtures were stirred for 24 h, filtered, and the residue dried overnight in air at 120°C. The pH's of impregnation were chosen for comparison with an earlier study on the adsorption of molybdate (12).

Analysis

Rhenium content of the catalysts prepared by equilibrium adsorption was determined by X-ray fluorescence (XRF) using samples prepared by incipient wetness for calibration. Analyses were reproducible to ±5%. The fluoride content of samples was determined by fusion of alumina samples with sodium hydroxide, dissolution of the fusion products in water, and analysis of the solutions using a fluoride-ion-selective electrode (16). The magnesium content of samples was determined by analysis of the impregnation solutions using atomic absorption spectroscopy (AA). Nitrate concentrations were calculated from the amounts of HNO_3 and NH_4NO_3 added to impregnation solutions.

IEPs were determined by a drift method (17). Approximately 0.2 g of modified alumina was added to 25 ml of distilled water, the pH of which had been adjusted with HNO_3 and/or NH_4OH. The pH of the alumina slurry was then measured. This procedure was then repeated several times, and a plot of the change of pH (ΔpH) vs initial pH was constructed. The IEP was taken to be that pH at which $\Delta pH = 0$. IEP values obtained in this way were reproducible to ±0.1 pH unit.

RESULTS

Adsorption on Unmodified Aluminas

Figure 1 shows the adsorption isotherm for perrhenate on unmodified alumina as a function of the pH of impregnation (□). As the pH of adsorption increases, uptake of perrhenate decreases. At high pH, the isotherm approaches a metal loading determined by the amount of impregnation solution remaining in the pores of the alumina after impregnation ("occluded" Re loading = 0.5%). For pH > 6, these data are in agreement with those of Wang and Hall (2). For pH < 6, the observed uptake of perrhenate appears to be erratic.

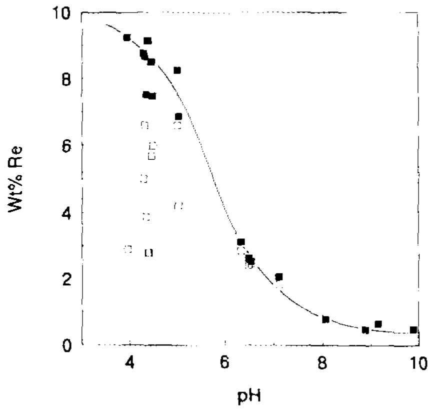

FIG. 1. Variation of observed (□) and theoretical (■) uptake of perrhenate on unmodified alumina as a function of final pH of the impregnation solution.

From previous studies, it is known that perrhenate uptake on alumina is sensitive to the presence of nitrate (14). Assuming that nitrate and perrhenate compete for adsorption sites and have the same affinity for the alumina surface, it is possible to calculate a theoretical adsorption isotherm for perrhenate on alumina in the absence of competing anions, which is also shown in Fig. 1 (■). The theoretical uptakes were calculated using the data of Table 1 and the formula

$$T = (O)\{([ReO_4^-] + [NO_3^-])/[ReO_4^-]\},$$

where T is the theoretical uptake, O is the observed uptake, and $[ReO_4^-]$ and $[NO_3^-]$ are the concentrations of perrhenate and nitrate, respectively, in the impregnation solution. Note that the plot of theoretical perrhenate uptake as a function of pH is a smooth curve which greatly diminishes the erratic variation of the observed perrhenate uptake. Also, it should be noted that the theoretical curve is similar in shape to plots of observed molybdate and tungstate uptake as a function of pH reported in the literature (1, 9).

Adsorption of Perrhenate on Modified Aluminas

The F- and Mg-modified aluminas have been characterized elsewhere (9). Briefly, the surface areas of the aluminas decreased with modifier content from 170 to 145 m^2/g over the range of modifier loadings studied (see Table 2). X-ray diffraction (XRD) of the aluminas showed only

TABLE 1

Observed and Theoretical Uptake of Perrhenate on Alumina as a Function of pH

Initial pH	Final pH	Observed Re uptake (atoms/nm^2)	Theoretical Re uptake (atoms/nm^2)	Conc. NO_3^- (mol/L)
2.04	3.95	0.568	1.181	0.121
3.06	4.29	1.00	1.75	0.041
2.59	4.32	1.34	1.76	0.017
1.79	4.34	0.768	1.49	0.052
2.27	4.38	0.548	1.79	0.125
2.80	4.40	0.548	1.79	0.125
3.88	4.46	1.14	1.71	0.028
3.60	4.48	1.21	1.51	0.014
2.84	5.02	1.34	1.68	0.014
2.18	5.03	0.838	1.36	0.034
6.72	6.33	0.560	0.613	0.0052
5.11	6.49	0.470	0.510	0.0052
5.90	6.54	0.480	0.705	0.026
6.50	7.11	0.354	0.398	0.0069
8.13	8.06	0.150	0.150	0
9.03	8.89	0.092	0.092	0
9.30	9.15	0.126	0.126	0
10.00	9.90	0.092	0.092	0

Note. Concentration of ReO_4^- = 0.055 *M*.

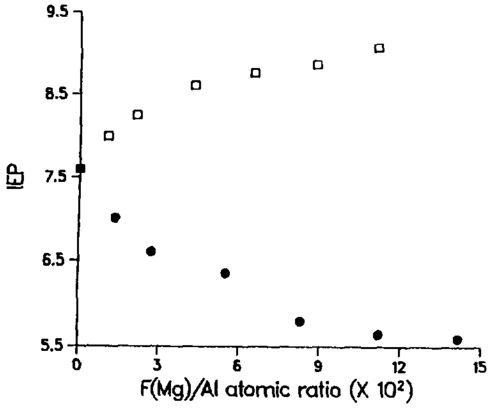

FIG. 2. Variation of support IEP with F (●) and Mg (□) loading.

the diffraction pattern for γ-alumina. X-ray photoelectron spectroscopy (XPS) revealed that F and Mg were well dispersed over the alumina surface. Most important for the purpose of this study, the IEP of the aluminas varied with modifier loading. As shown in Fig. 2, addition of 5 wt% F (F/Al atomic ratio = 0.141) to the alumina decreased the IEP from 7.6 to 5.6, while modification with 4.5% Mg (Mg/Al atomic ratio = 0.111) increased the IEP from 7.6 to 9.1.

Figure 3 shows the relationship between the amount of perrhenate adsorbed and the fluoride content of the support. The amount of perrhenate adsorbed is expressed as the number of metal atoms adsorbed per unit area of the fluoride-modified alumina. The trends observed in Fig. 3 do not change if metal content is expressed more simply as weight percent. From Fig. 3, it can be seen that perrhenate uptake per unit surface area decreases with increasing fluoride loading, much like the decrease in IEP observed in Fig. 2. This similarity suggests a correlation between perrhenate uptake and the IEP of the support. This correlation is shown in Fig. 4, which illustrates the number of Re atoms adsorbed per unit surface area as a function of IEP.

The relationship between perrhenate uptake and the magnesium content of Mg modified aluminas is shown in Fig. 5. The increase in perrhenate uptake with increasing Mg content shown in Fig. 5 can also be related to the IEP of the support. As shown in Fig. 6, perrhenate uptake increases with increasing IEP.

DISCUSSION

Adsorption on Unmodified Aluminas

Early models used to explain the adsorption of metal oxyanions on metal oxide supports emphasized the importance of impregnation solution pH, IEP of the support,

TABLE 2

Surface Area of F and Mg 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

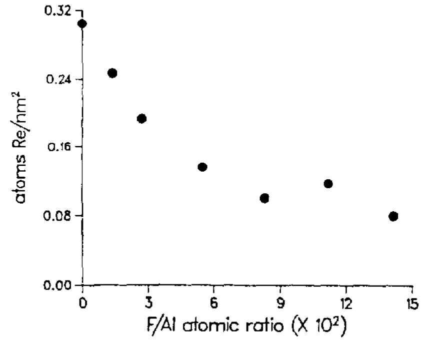

FIG. 3. Variation of perrhenate uptake at pH 6.5 as a function of F loading on F-modified alumina.

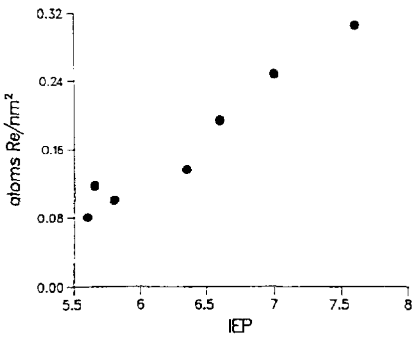

FIG. 4. Variation of perrhenate uptake at pH 6.5 as a function of IEP for F-modified alumina.

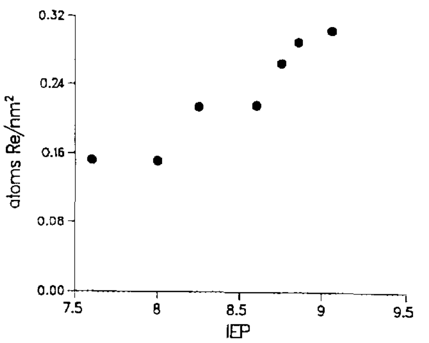

FIG. 6. Variation of perrhenate uptake at pH 9.3 as a function of IEP for Mg-modified alumina.

and charge of the adsorbing ion (13). For pH's less than the IEP of the support, surface hydroxyl groups are protonated; the positively charged surface then attracts and adsorbs anions from solution. For pH > IEP, the support surface becomes negatively charged because of deprotonation, and adsorption of cations occurs. This simple electrostatic model of the adsorption process was used originally to explain adsorption of molybdate, tungstate, and perrhenate on alumina (1, 9). It has since been learned that while the adsorption isotherms of molybdate and tungstate on alumina as a function of pH are consistent with this model, the actual processes by which molybdate and tungstate adsorb are not accurately described by the model (4, 7, 14). It has been shown that the adsorption of molybdate and tungstate on alumina is fundamentally different from the adsorption of perrhenate. Perrhenate uptake is known to be sensitive to the presence of nitrate and is easily rinsed from the alumina surface with biphthalate buffer. However, it has also been shown that adsorption of perrhenate on alumina is satisfactorily described using a simple electrostatic model (14).

From data plotted in Fig. 1, which were not corrected for nitrate concentration (□), it is not readily apparent that the adsorption of perrhenate is consistent with the above electrostatic model, much less that this model describes the actual adsorption process. However, the model simply assumes that at pH < IEP, negative species are attracted to the positively charged surface. Therefore, both nitrate (when present) and perrhenate should adsorb on the alumina at pH < IEP, and competition between the two ions for adsorption sites should be expected.

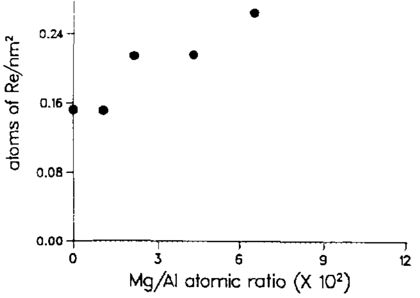

FIG. 5. Variation of perrhenate uptake at pH 9.3 as a function of Mg loading on Mg-modified alumina.

The theoretical curve shown in Fig. 1 (■) illustrates that competition between nitrate and perrhenate does occur. The erratic nature of the perrhenate adsorption data for pH < 6 largely disappears when the data are corrected for the presence of nitrate in solution. Theoretical perrhenate adsorption, that is, calculated adsorption of perrhenate in the absence of nitrate, appears to increase smoothly with decreasing pH, due to the buildup of positive charge on the alumina surface which occurs with decreasing pH.

The description of perrhenate adsorption given above does not consider complicating effects such as dissolution of the support (18) or ionic strength (19). The alumina used in this study is known to dissolve at pH < 3. The effect of this phenomenon is unknown, but it may ultimately limit the loading of ReO_4^- which can be achieved by equilibrium adsorption. Variations in ionic strength can change the thickness of the electric double layer and affect the activity of ReO_4^-. In the present study, activity coefficients for ReO_4^- ranging from 0.81 to 0.72 have been calculated (assuming a size of 400 pm for ReO_4^-). Thus, activity effects may contribute to the observed adsorption of perrhenate, but are not sufficient to account completely for the observed effect of nitrate on perrhenate adsorption.

Adsorption of Perrhenate on F- and Mg-Modified Aluminas

The adsorption of perrhenate on F- and Mg-modified aluminas, as shown in Figs. 3–6, closely mirrors the adsorption of molybdate and tungstate on the same supports (9). The key to understanding the results shown in Figs. 3–6 lies in comprehending the changes of the alumina surface which occur on addition of F and Mg. Addition of F to alumina results in replacement of basic alumina hydroxyl groups by F (20, 21). This loss of basic hydroxyl groups from the alumina surface has two related effects which are reflected by the changes in alumina IEP shown in Fig. 2. First, the support becomes acidic. Second, easily protonated hydroxyl groups which can act as adsorption sites for anions are lost. Thus, adsorption of perrhenate on two supports which contain different levels of F should be greater for the support with the lesser amount of F (if the adsorptions are carried out at the same pH). This is illustrated in Fig. 3.

The increase in perrhenate uptake which occurs with increasing Mg content can be understood in similar terms. Magnesium is a basic additive, as reflected by the variation of IEP with Mg loading (Fig. 2). It has been shown that Mg addition to alumina causes an incrase in the number of basic hydroxyl groups on the support surface (22), which, on protonation, provide positive sites for adsorption of perrhenate. Thus, adsorption of perrhenate at pH 9.3 increases with increasing Mg loading (Fig. 5).

With respect to the observed correlation between perrhenate uptake and the IEP (Figs. 4 and 6), it is of interest to examine these results in light of the models describing the IEPs of composite oxides proposed by Schwarz *et al.* (23). According to these authors, the IEP of a composite oxide surface can be either considered as characteristic of the whole surface (common hydroxyl model) or of the individual component oxides (composite hydroxyl model). A close inspection of our results indicates that the first concept cannot satisfactorily account of the adsorption data since it implies that significant adsorption of anionic species occurs on surfaces containing essentially neutral and negative sites (pH of adsorption higher than the IEP; see, for example, Fig. 6).

In contrast, the adsorption results can be readily explained by the "composite hydroxyl model." Using this model, the IEP of the support is considered to be a surface area weighted average of the IEPs of the surface phases present; i.e., each surface phase has its own IEP, which contributes to the observed IEP of a given material. Thus, the surface of Mg-modified alumina would be composed of regions of MgO and Al_2O_3, with IEPs of 12 and 7.6, respectively. At pH 9.3, the exposed Al_2O_3 will be negatively charged and should therefore adsorb little or no ReO_4^-. However, regions of the surface covered by MgO should have a positive charge at pH 9.3 and should adsorb ReO_4^-. Perrhenate adsorption should therefore increase with Mg loading, which is observed in Fig. 5. Based on the above-mentioned model, the observed increase in the IEP of the alumina with Mg addition indicates an increase in the fraction of the alumina surface covered by MgO. Consequently, the correlation between the Re uptake and the IEP simply reflects the expected increase in Re adsorption with increasing positive surface charge on the Mg-modified fraction of the alumina surface.

The adsorption results for the F-modified supports are also consistent with the "composite hydroxyl model." The surface of F-modified alumina would consist of an exposed alumina fraction (IEP = 7.6) positively charged at the pH of adsorption ($\approx$6.5) and thus capable of adsorbing Re anions at the indicated pH and a fluorinated fraction which cannot adsorb perrhenate. Thus, the observed decrease in the Re uptake with decreasing IEP (on F addition) can be attributed to a reduction in the positive surface charge resulting from the decrease in the fraction of exposed alumina surface.

CONCLUSIONS

The adsorption of perrhenate on alumina may be understood in terms of a simple electrostatic model in which the pH of the solution, IEP of the support, and charge of the adsorbing ion are important parameters. Addition of other anions (nitrate) to the impregnation solution reduces the uptake of perrhenate for $pH < 6$, but this decrease can be accounted for by assuming that perrhenate and other anions compete for adsorption sites on the alumina surface. Adsorption of perrhenate on F- and Mg-modified aluminas was determined to be similar to the adsorption of molybdate and tungstate on these same supports. Uptake of perrhenate increases with increasing support IEP, and may be understood by consideration of the attraction of perrhenate for a positively charged surface.

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REFERENCES

1. Wang, L., and Hall, W. K., *J. Catal.* **77,** 232 (1982).
2. Wang, L., and Hall, W. K., *J. Catal.* **82,** 177 (1983).
3. Wang, L., and Hall, W. K., *J. Catal.* **66,** 251 (1980).
4. Van Veen, J. A. R., and Hendricks, P. A. J. M., *Polyhedron* **5,** 75 (1986).
5. Kasztelan, S., Grimblot, J., Bonnelle, J. P., Payen, E., Toulhoat, J., and Jacquin, Y., *Appl. Catal.* **7,** 91 (1983).
6. Caceres, C. V., Fierro, J. L. G., Lopez Agudo, A., Blanco, M. N., and Thomas, H. J., *J. Catal.* **95,** 501 (1985).
7. Van Veen, J. A. R., De Wit, H., Emeis, C. A., and Hendriks, P. A. J. M., *J. Catal.* **107,** 579 (1987).
8. Sonnemans, J., and Mars, P., *J. Catal.* **31,** 209 (1973).
9. Mulcahy, F. M., Houalla, M., and Hercules, D. M., *in* "Proceedings, Ninth International Congress on Catalysis" (M. J. Phillips and M. Ternan, Eds.), p. 1968. The Chemical Institute of Canada, Ottawa, 1988.
10. Meunier, G., Mocaer, B., Kasztelan, S., Le Coustumer, L. R., Grimblot, J., and Bonnelle, J. P., *Appl. Catal.* **21,** 329 (1986).
11. Segawa, K., Kim, D. S., Kurusu, Y., and Wachs, I. E., *in* "Proceedings, Ninth International Congress on Catalysis" (M. J. Phillips

and M. Ternan, Eds.), p. 1960. The Chemical Institute of Canada, Ottawa, 1988.
12. Mulcahy, F. M., Houalla, M., and Hercules, D. M., *J. Catal.* **106,** 210 (1987).
13. Brunelle, J. P., *Pure Appl. Chem.* **50,** 1211 (1978).
14. Mulcahy, F. M., Fay, M. J., Proctor, A., Houalla, M., and Hercules, D. M., *J. Catal.* **124,** 231 (1990).
15. Baes, C. F., and Mesmer, R. E., "The Hydrolysis of Cations," pp. 211–225, 253–261. Wiley, New York, 1976.
16. Palmer, T. A., *Talanta* **19** 1141 (1972).
17. Jirotova, K., *Appl. Catal.* **1,** 165 (1981).
18. Santacesaria, E., Carra, S., and Adami, I., *Ind. Eng. Chem. Prod. Res. Dev.* **16,** 41 (1977).
19. Heise, M. S., and Schwarz, J. A., *J. Colloid Interface Sci.* **113,** 55 (1986).
20. Vordonis, L., Koutsoukos, P. G., and Lycourghiotis, A., *J. Catal.* **101,** 186 (1986).
21. Okamoto, Y., and Imanaka, T., *J. Phys. Chem.* **92,** 7102 (1988).
22. Yamagata, N., Owada, Y., Okazuki, S., and Tanabe, K., *J. Catal.* **47,** 358 (1977).
23. Schwarz, J. A., Ugbor, C. T., and Zhang, R., *J. Catal.* **138,** 38 (1992).