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Indirect radiotracer study of the adsorption of chromate ions on γ - Al_2O_3 and direct study of the adsorption of sulfate ions on Cr_2O_3 using ^{35}S -labelled H_2SO_4

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Abstract The specific adsorption of sulfate ions on Cr_2O_3 was studied by a radiotracer technique using ^{35}S -labelled sulfuric acid in low concentrations ($c < 10^{-3}$ mol dm^{-3}) in the presence of a large excess of perchlorate supporting electrolyte. The pH and concentration dependence were determined. It was found that the extent of adsorption is determined by the protonation of the surface sites, similar to other oxides studied previously. A comparison of Cr_2O_3 and Al_2O_3 in this respect shows that the protonation of the former takes place at significantly lower pH values than that of the latter. The indirect radiotracer study of the adsorption of chromate on Al_2O_3 was carried out using labelled sulfate ions as indicator species. The results obtained show that the adsorption strength of chromate species is very low in comparison to sulfate ions and a regular Langmuir-like adsorption behaviour can be observed. It is believed that the observations presented may contribute to a better understanding of the behaviour of surface layers with a mixed oxide content.

Keywords Chromium oxide · Sulfate ions · Aluminum oxide · Chromate ions · Radiotracer technique

Introduction

The idea of a radiotracer study of adsorption phenomena on oxide/electrolyte interfaces was prompted by the

important role played by these systems in many branches of chemistry, especially in colloid and electrochemistry [1, 2, 3, 4, 5, 6, 7]. The practical importance of the knowledge of the behaviour of metal oxides and hydroxides is connected with the fact that they are products of corrosion processes. This problem has been discussed in detail [7].

In previous communications [6, 7] the usefulness of the application of an indirect radiotracer technique for the investigation of the adsorption of anions and corrosion inhibitors on oxide surfaces was demonstrated using ^{35}S -labelled sulfate ions as indicator species (for the definition and principle of the method, see [8, 9]).

The study of the adsorption of phosphate ions on γ - Al_2O_3 and hematite was reported previously [6], while the adsorption of various organic and inorganic corrosion inhibitors on hematite has also been investigated [7]. In the latter case, chromate ions were considered as one of the inorganic inhibitors.

It is well known that a chromate conversion coating is used as a pretreatment for aluminum alloys; for instance, Alclad 2024 is used in aircraft applications [10]. Although the composition and structure of these coatings are very complex, it can be assumed that chromate ad- and absorption into Al_2O_3 formed on the surface and the adsorption processes on reduced chromate species, various Cr(III) oxides and hydroxides, could play an important role in the behaviour of the coating. Thus in the first approximation the study of chromate adsorption on Al_2O_3 and the investigation of anion adsorption on Cr_2O_3 can be suggested as models for adsorption studies.

In the present communication an attempt will be made to obtain an insight into the properties of these two model systems using a single labelled ion, $^{35}\text{SO}_4^{2-}$, for the radiotracer studies. This means that, in the case of chromate adsorption on Al_2O_3 , an indirect method should be used, while the study of the adsorption of labelled sulfate ions on Cr_2O_3 could give direct information on the specific adsorption of anions.

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Experimental

The experimental technique and setup for the radiotracer study of sorption processes are described in previous papers [1, 2, 3, 4, 5, 6, 7]. The principle of the method used in the present study is the measurement of radiation intensity originating from adsorbed species on a powdered oxide layer sprinkled on a thin plastic foil that serves simultaneously as the window for radiation measurement. The measurements were carried out at ambient temperature in an argon atmosphere, bubbling argon in the solution phase and letting it through the gap between the bottom of the measuring cell and the detector. Generally the amount of $\gamma\text{-Al}_2\text{O}_3$ and Cr_2O_3 referred to the geometric surface area of the bottom of the cell was $20\text{--}50\text{ mg cm}^{-2}$. This thickness can be considered as infinite with respect to the soft β -radiation of ^{35}S .

In most of the experiments the concentration of labelled species was at least one order of magnitude lower than that of the supporting electrolyte in order to obtain information concerning the specific adsorption of the former species on the oxide surface.

^{35}S -labelled H_2SO_4 (Amersham, specific activity: 200 MBq mmol^{-1}) was used for the preparation of the solutions, mostly with perchlorate supporting electrolyte.

A commercial Cr_2O_3 powder was used (Reanal), while the $\gamma\text{-Al}_2\text{O}_3$ sample was the same as that used in previous studies [4, 5, 6], where its specification is given.

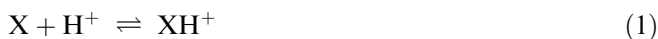
Results and discussion

Sulfate adsorption on Cr_2O_3

pH and concentration dependence of the adsorption of sulfate ions

Similar to the studies carried out with hematite and $\gamma\text{-Al}_2\text{O}_3$, the first experiments were aimed at the determination of the pH dependence of the specific adsorption of sulfate species in order to obtain information on the pH range where measurable adsorption occurs. These studies were carried out in the presence of 1 mol dm^{-3} NaClO_4 supporting electrolyte and at a low sulfate concentration ($c < 10^{-3}\text{ mol dm}^{-3}$), as required for the determination of specific adsorption without the interference of electrostatic effects.

Figure 1 shows the pH dependence in a count rate versus pH plot. The character of this curve is very similar to those obtained in the cases of Fe_2O_3 and Al_2O_3 . This type of behaviour was interpreted in terms of the protonation of the oxide surface characterized by an equilibrium formulated by the equation:



The tendency of attaining a limiting value in the surface protonation is also in accordance with the observations made with other oxides.

In the case of equilibrium:

$$k_a c_{\text{H}^+} (1 - \theta_{\text{H}^+}) - k_d \theta_{\text{H}^+} = 0 \quad (2)$$

and:

$$K c_{\text{H}^+} = \frac{\theta_{\text{H}^+}}{(1 - \theta_{\text{H}^+})} \quad (3)$$

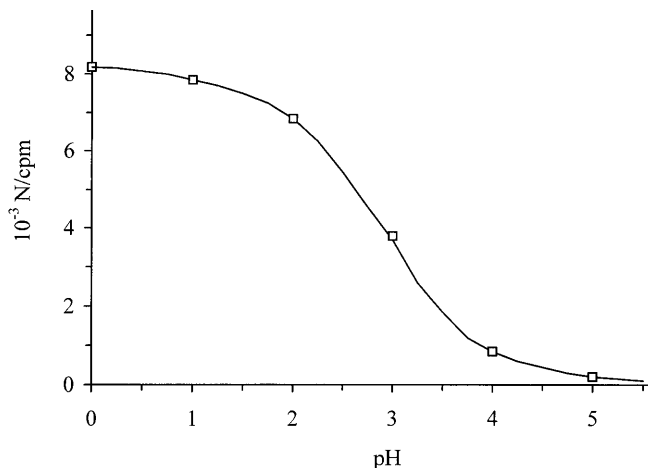


Fig. 1 pH dependence of the count rate proportional to the adsorption of labelled sulfate ions ($c = 2 \times 10^{-4}\text{ mol dm}^{-3}$ H_2SO_4) in the presence of a large excess of ClO_4^- ions (1 mol dm^{-3}). Amount of $\text{Cr}_2\text{O}_3 = 35\text{ mg cm}^{-2}$

where k_a and k_d are the rate constants of the adsorption and desorption processes, respectively, $K = k_a/k_d$, and θ_{H^+} is the coverage with respect to the protonated surface sites. For $\frac{\theta_{\text{H}^+}}{1 - \theta_{\text{H}^+}} = 1$, $\log K = \text{pH}$.

Thus from the count rate versus pH curve we are able to estimate the value of the protonation equilibrium constant. Taking into consideration the data presented in Fig. 1, the estimated $\log K$ value is about 2.5. This value is significantly lower than that found for Al_2O_3 or Fe_2O_3 (see later).

Changing the pH, the ratio of HSO_4^- and SO_4^{2-} ions in the solution phase also changes, owing to the $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$ equilibrium. However, in accordance with fundamental thermodynamic considerations, it is not possible to draw conclusions concerning the state of the adsorbed species on the basis of these measurements.

Using powders it was an important point to obtain reliable information concerning the equilibrium or steady-state adsorption values. After stirring the powder the radiation intensity following the deposition of the powder remained unaltered, as shown in Fig. 2. The value observed was considered as the final one.

The concentration dependence of the adsorption of sulfate species was determined in 1 mol dm^{-3} HClO_4 supporting electrolyte. The results obtained are presented in Fig. 3. A similarity with other oxides is evident in this respect as well (Langmuir-like behaviour with a tendency to a limiting value at not too high concentrations).

Study of the reversibility of the adsorption

The ‘‘mobility’’ of the adsorbed species is an important question if we treat the adsorption phenomena in terms of isotherms. In order to speak unambiguously about

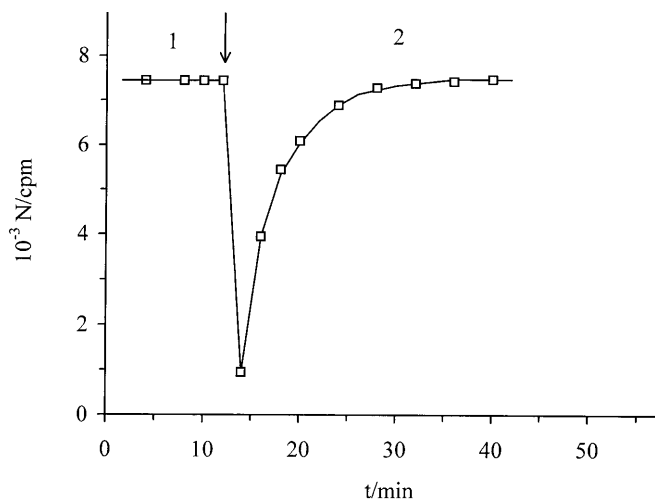


Fig. 2 Study of the reliability of the measurements. (1) 2×10^{-4} mol dm^{-3} labelled H_2SO_4 in 1 mol dm^{-3} HClO_4 using 35 mg cm^{-2} Cr_2O_3 . (2) The transient state following the stirring of the powder for 1 min

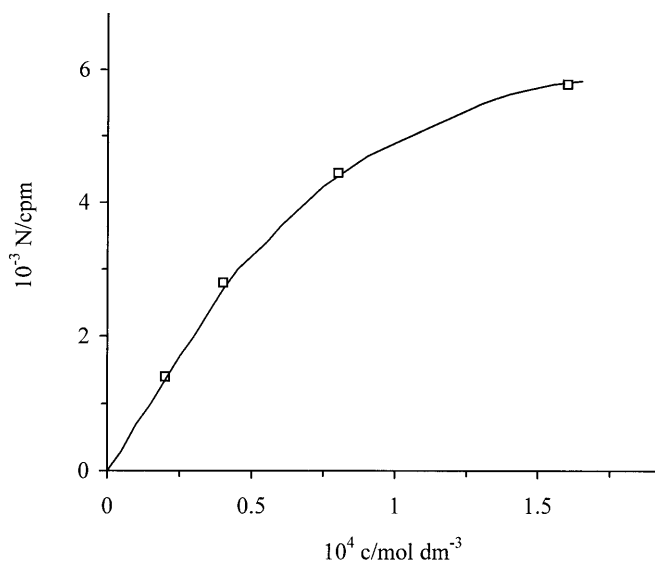


Fig. 3 Concentration dependence of the adsorption of labelled species in 1 mol dm^{-3} HClO_4 . $\text{Cr}_2\text{O}_3 = 40 \text{ mg cm}^{-2}$

adsorption equilibrium or about equilibrium states with respect to the adsorbed species, the investigation of their desorption rate is of great importance. The reversibility with respect to pH changes is well demonstrated by Fig. 4, where the change in the count rate following pH changes are shown.

On the other hand, the study of the exchange of labelled adsorbed species with non-labelled ones added to the solution phase in a great excess reveals that a part of the adsorbed sulfate ions is strongly bound to the surface. This is demonstrated by Fig. 5. Data presented in Fig. 5 demonstrate that Cl^- ions do not exert a significant influence on the adsorption of sulfate ions. Section 2 in Fig. 5 shows that, despite the addition of Cl^- ions in a

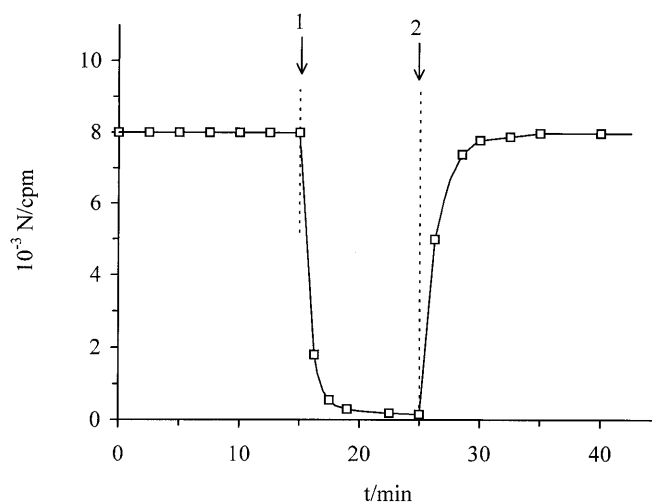


Fig. 4 Reversibility with respect to abrupt pH changes: (1) from pH 2 to 13; (2) from pH 13 to 2; solution: 2×10^{-4} mol dm^{-3} H_2SO_4 in 1 mol dm^{-3} NaClO_4

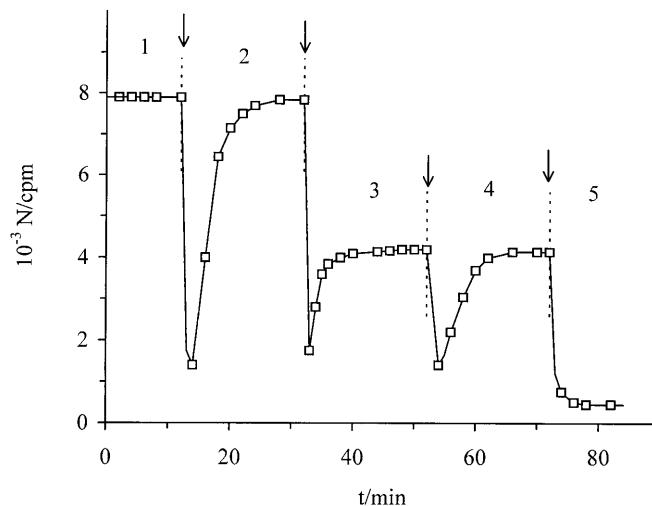


Fig. 5 Study of the behaviour of adsorbed labelled sulfate species. (1) Initial state as in the case of Fig. 2. (2) Addition of 2×10^{-2} mol dm^{-3} NaCl and stirring of the Cr_2O_3 powder. (3) Addition of 2×10^{-2} mol dm^{-3} non-labelled H_2SO_4 . (4) Washing with water. (5) Shift of the pH to 13

concentration of two orders of magnitude higher than that of sulfate species, there is no change in the radiation intensity following the deposition of Cr_2O_3 powder stirred up after the addition of NaCl . In contrast to this, the addition of non-labelled H_2SO_4 (section 4) results in a rapid decrease in the count rate; however, part of the adsorbed species remains on the surface. This part cannot be eliminated by washing the oxide powder (section 4). However, on adding NaOH to the solution phase and shifting the pH to 13, an almost complete elimination of the adsorbed species takes place (section 5). The relative amount of the strongly adsorbed species depends on the condition of how long the Cr_2O_3 powder was in contact

with the solution of the labelled species in acid medium. It can be assumed that the existence of this apparently "irreversible" part could be connected with the strong complexation of sulfate species into the protonated surface Cr(III) species. By shifting the pH to higher values the sulfate ions could be replaced by OH^- ions.

Indirect study of the adsorption of CrO_4^- ions on $\gamma\text{-Al}_2\text{O}_3$

The evaluation technique of the indirect method is discussed in detail in review articles [8, 9] and in previous studies with $\gamma\text{-Al}_2\text{O}_3$ and hematite [6, 7].

The first step in the investigation is the study of the influence of chromate species on the adsorption of labelled sulfate ions. The result of this study is shown in Fig. 6. The data reported in Fig. 7 could be analyzed on the basis of the considerations and equations discussed previously [6, 7]. In accordance with these considerations, the linearity of the plot of reciprocal values of the radiation intensities versus chromate concentration (Fig. 7) proves that the adsorption of chromate species can be described by a Langmuir-like isotherm, as shown by Fig. 8 where the relative coverage values (calculated on an arbitrary scale) are plotted against the chromate concentration.

It follows from the results presented above that the adsorption strength of chromate species is significantly lower than that of sulfate ions, as a measurable displacement of adsorbed sulfate species occurs only at high $\text{CrO}_4^-/\text{SO}_4^{2-}$ ratios. This means that in the presence of sulfate ions, even at their low concentration, no significant adsorption of chromate ions takes place, at least under the conditions studied here, as it is well known that the state of chromate species strongly depends on the pH.

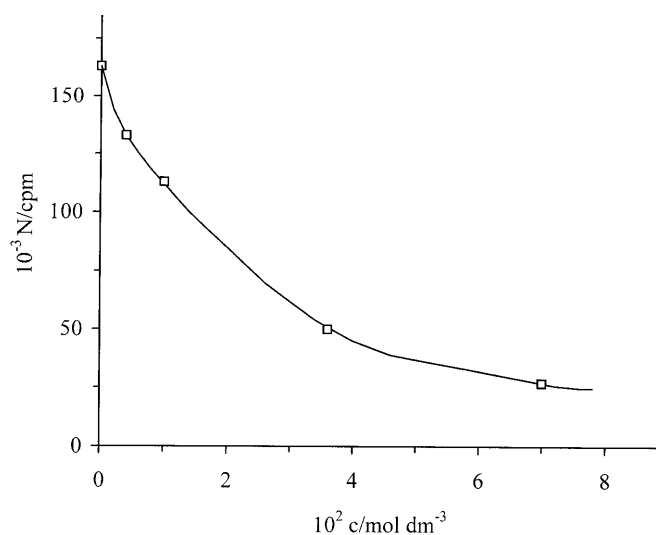


Fig. 6 Effect of addition of CrO_4^{2-} species on the adsorption of labelled sulfate ions present in a concentration of $4 \times 10^{-5} \text{ mol dm}^{-3}$ in $0.25 \text{ mol dm}^{-3} \text{ HClO}_4$ supporting electrolyte; $30 \text{ mg dm}^{-2} \text{ Al}_2\text{O}_3$

Comparison of the protonation equilibrium

It is very important to take into consideration that the protonation equilibrium of Cr_2O_3 and Al_2O_3 differs significantly. In Fig. 9 the pH dependence of sulfate adsorption on the two oxides is compared on a relative scale. These curves reflect the protonation equilibrium of the oxides.

It follows from the comparison of the two curves that the protonation on Cr_2O_3 takes place mainly in the pH range where Al_2O_3 attains its limiting value. Therefore, it could be expected that in the case of the mixed presence of the two oxides the overall sorption behaviour at pH values above 4 would be determined by that of Al_2O_3 .

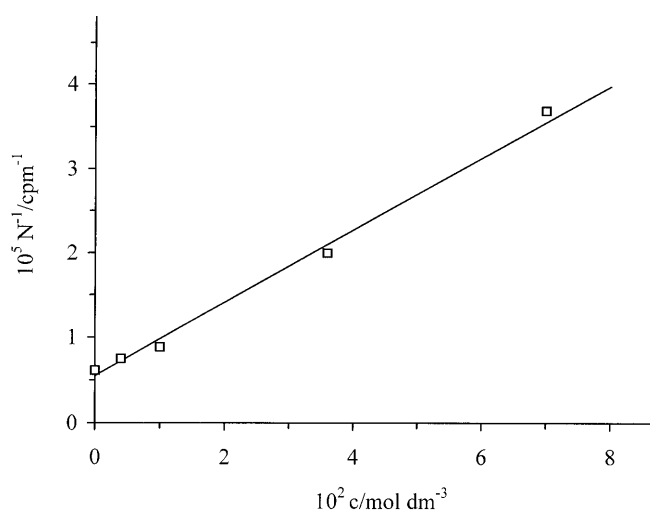


Fig. 7 $1/N$ versus chromate concentration plot on the basis of data reported in Fig. 6

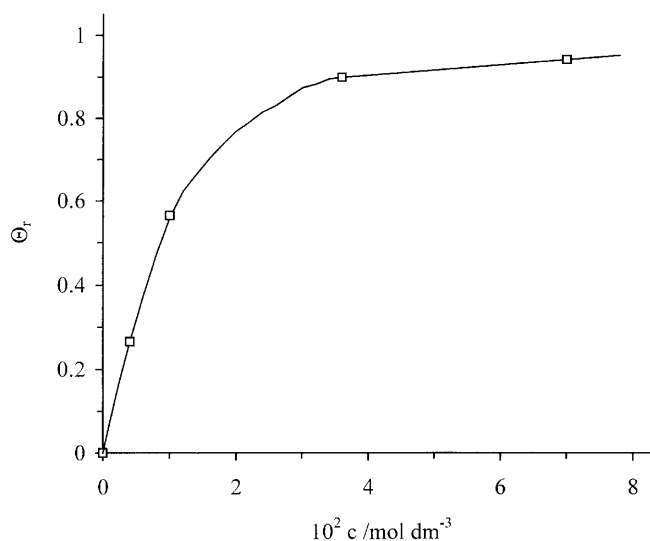


Fig. 8 The calculated adsorption isotherm of CrO_4^{2-} species expressed in coverage on an arbitrary scale

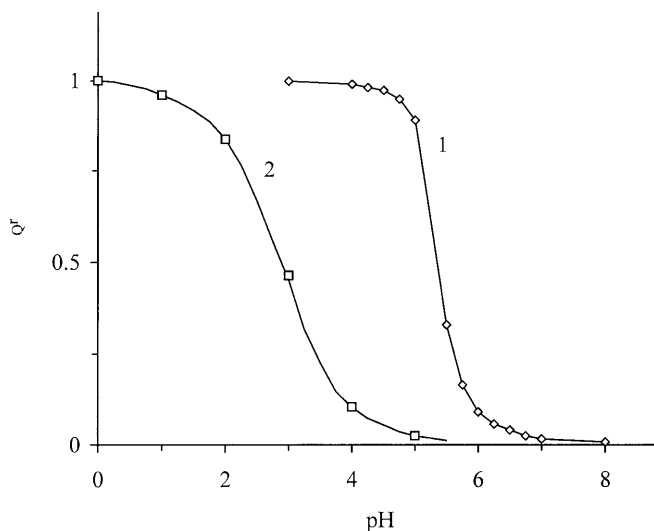


Fig. 9 Comparison of the pH dependence of the adsorption of sulfate ions (on arbitrary relative scale) in the case of γ - Al_2O_3 (1) and Cr_2O_3 (2)

Conclusions

The experimental results presented above can be considered as a first radiotracer approach to the problem of the adsorption behaviour of a mixed oxide layer formed by treatment of an Al surface. It would be very

important to separate, for instance, the role of Cr(III) species [obtained by reduction of Cr(VI) species] from that of the aluminum oxide/hydroxide in the surface layer. It is an important observation that the adsorbability of chromate ions on Al_2O_3 is significantly lower than that of sulfate ions. It follows from this that the results of the treatment of Al_2O_3 covered Al surfaces with chromate could be influenced by the presence of sulfate ions. Further studies are required to clarify the background of the phenomena presented here.

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