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Comparison of the specific adsorption of sulfate (HSO_4^-) ions on Cr and Cr_2O_3

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Abstract The specific adsorption of sulfate ions on powdered Cr was studied by a radiotracer technique using ^{35}S -labeled sulfuric acid in low concentration ($c < 10^{-3} \text{ mol dm}^{-3}$) in the presence of a large excess of perchlorate supporting electrolyte. The pH and concentration dependence were determined. On the basis of a comparison of the results obtained for Cr_2O_3 and Cr, it can be assumed that, similar to other metals, the overall sorption behavior of Cr is determined by the protective oxide film present on the surface.

Keywords Chromium · Chromium oxide · Radiotracer technique · Specific adsorption · Sulfate ions

Introduction

In a previous communication [1], results obtained from a radiotracer study of the specific adsorption of sulfate ions on Cr_2O_3 were reported. Both the pH and concentration dependence were determined. It was found that the extent of adsorption is determined by the protonation of the surface sites of Cr_2O_3 , similar to other oxides studied recently [2, 3, 4, 5, 6, 7, 8]. On the other hand, on the basis of literature data and our own experiments, it was demonstrated in previous communications [9, 11] that the pH dependence of the specific anion adsorption on metals is solely determined by the sorption properties of the (more or less) protective oxide layer formed on these metals. This was shown in the case of Al and Zn [9], Ti [10] and Bi [11]. It was of interest that the potential of the metal did not play a significant

direct role in the overall adsorption behavior (evidently, the potential could exert indirect influence through the formation or reduction of the oxide layer). Considering this situation, the aim of the present communication is to show that the sorption behavior of powdered Cr metal is very similar to that of Cr_2O_3 , indicating that the overall adsorption process is determined by the protective oxide layer formed on Cr metal.

It should be mentioned that despite the wealth of review articles on the behavior of metal oxide/electrolyte interfaces (see, for instance [12, 13, 14, 15]), few data are available for the Cr_2O_3 /electrolyte interface. Chromium(III) oxide hydroxide colloidal films have recently been used to model the passivated surface of stainless steel in in-situ IR studies of anion adsorption [16, 17]. However, the behavior of the thin film studied should differ from that of the Cr_2O_3 figuring in the present comparison.

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, 8, 9, 10, 11]. The principle of the method used in the present study is the measurement of radiation intensity originating from adsorbed species on a powdered metal (or 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 the powder referred to the geometric surface area of the bottom of the cell was 20–50 mg cm^{-2} . This thickness can be considered as infinite with respect to the depth of propagation of the soft β radiation of ^{35}S .

In most of the experiments the concentration of labeled 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 adsorbent surface. ^{35}S -labeled H_2SO_4 (Amersham, specific activity: 200 MBq mmol^{-1}) was used for the preparation of the solutions, mostly with perchlorate supporting electrolyte. Riedel-de-Haën chromium powder (98–99%) was used and the Cr_2O_3 powder was the same material (Reanal) used in the previous study [1].

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As was analyzed in a previous communication [5], the reproducibility of the measurements, the reproducibility of the responses of the system studied to changes in its parameters, is a crucial problem in the case of powdered adsorbents deposited on the bottom of the cell. For the attainment of the adsorption equilibrium, an intensive stirring of the solution with the dispersed adsorbent is required. The stirring is very important in the case of the study of the pH dependence of adsorption (pH changes were carried out by addition of HClO₄ and NaOH). In the case of the attainment of equilibrium, the radiation intensity measured following the deposition of adsorbent particles stirred up previously with the solution remains the same whatever the number and intensity of the stirring procedure.

Results and discussion

pH and concentration dependence of the adsorption of sulfate ions

Similarly to the studies carried out with Cr₂O₃, 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 NaClO₄ supporting electrolyte and at a low sulfate concentration ($c < 10^{-3}$ mol dm⁻³), as required for the determination of specific adsorption without the interference of electrostatic effects (the pH changes were achieved by addition of HClO₄ or NaOH using the same powder).

Curve (1) in Fig. 1 shows the pH dependence of the adsorption (the count-rate values measured directly are transformed into relative coverage values by dividing each count-rate value by the highest count-rate value observed). The character of curve (1) is very similar to that obtained in the case of Cr₂O₃ (see curve 2 in Fig. 1), although there is a significant shift as to the pH range where a measurable adsorption can be observed. This shift can be interpreted in terms of the differences in the protonation constants of bulk Cr₂O₃ and the surface oxide layer formed on the metal. The protonation pro-

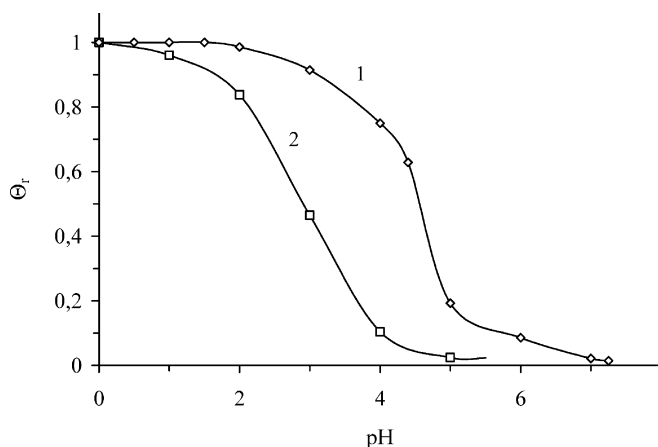


Fig. 1 pH dependence of the adsorption (on a relative scale) of labeled sulfate ions ($c = 2 \times 10^{-4}$ mol dm⁻³ H₂SO₄) in the presence of a large excess of ClO₄⁻ ions (1 mol dm⁻³): Cr (1); Cr₂O₃ (2)

cess can be characterized by an equilibrium formulated by the equation:



where X is a surface site. The tendency of attaining a limiting value in the surface protonation in the case of Cr is also in accordance with the observations made with Cr₂O₃.

In the case of equilibrium:

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

and:

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

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 $\theta_{H^+}/(1 - \theta_{H^+}) = 1$, $\log K = \text{pH}$.

According to the model assumption outlined in [3], the specific adsorption of sulfate species occurs only on the protonated surface sites. Thus from the count rate versus pH curve at constant sulfate concentration 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 for Cr₂O₃ is about 3, while for the surface oxide on Cr it is about 4.5. This difference in the estimated K values can be explained with the assumption that there could be a difference in both the structure and composition of the oxides. It should be borne in mind that changing the pH the ratio of HSO₄⁻ and SO₄²⁻ ions in the solution phase also changes, owing to the HSO₄⁻ \rightleftharpoons SO₄²⁻ + 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.

It is, however, interesting that there is no difference between the concentration dependence of the adsorption

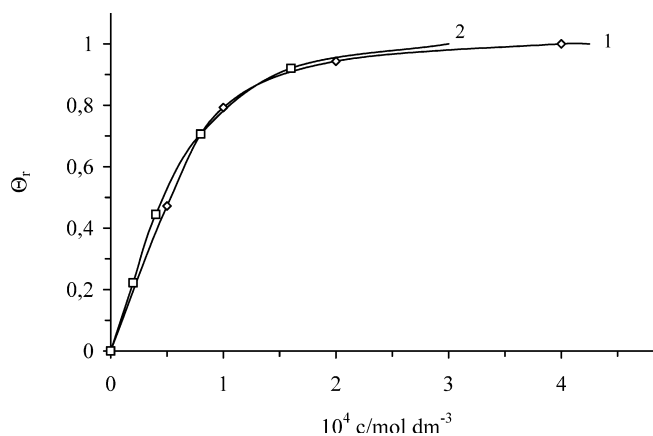


Fig. 2 Concentration dependence of the adsorption of labeled species in 1 mol dm⁻³ HClO₄: Cr (1); Cr₂O₃ (2)

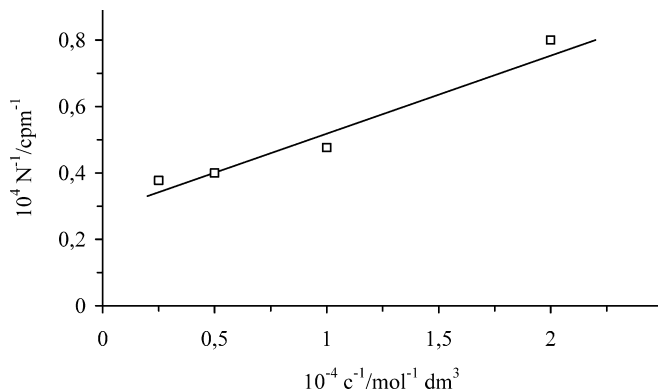


Fig. 3 The plot of the reciprocal values of count-rate versus the reciprocal values of the concentration of labeled sulfate ions

of sulfate species on the two adsorbents in 1 mol dm^{-3} HClO_4 supporting electrolyte (Fig. 2). In both cases a Langmuir-like behavior with a tendency to a limiting value at not too high concentrations was found. This is reflected by the linearity of the $1/N$ versus $1/c$ plot (Fig. 3).

Conclusions

The experimental result presented above constitutes another proof of the important role of the surface oxide layer in the specific adsorption of sulfate ions on a metal.

The characteristic pH dependence of the specific adsorption of sulfate ion on Cr can be explained only in terms of the protonation of the oxide layer formed on the metal.

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