

Monodispersed Chromium(III) Hydroxide Particles – Exchangeability of Sulphate Ions

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Kinetics of ligand exchange between sulphate ions (present in the core of monodispersed chromium hydroxide particles in the form of chromium basic sulphate) and hydroxyl ions has been studied. In addition, the effect of pH on the extent of this exchange has been investigated. Preliminary results showed that the rate of exchange is relatively high and substantially exceeds the rate for water exchange described in the literature for soluble $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ species. This observation contradicts the suggestion by some authors¹ that the rate of $\text{SO}_4^{2-}/\text{OH}^-$ ligand exchange at the solid/liquid interface is very slow.

INTRODUCTION

Monodispersed chromium(III) hydroxide particles can be obtained by forced hydrolysis of diluted chrom alum solutions at elevated temperature.^{2–5} It was shown by many researchers^{3–6} that the product of such hydrolysis contains some sulphate ions incorporated into the bulk of the particles. Sulphate ions play a special role in the particle formation process. No particles can be produced by hydrolysis of simple Cr(III) salt solutions, *e.g.* perchlorates, nitrates *etc.*^{5,7} Recent studies proved that sulphate ions play a

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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very important role during the nucleation stage.⁴ At that stage, the particle core consisting almost exclusively of basic chromium sulphate is formed. Sulphate ions can be removed from the particles by washing with acids or bases. Bases are much more effective than acids because they allow complete removal of sulphate ions.^{3,4,6} Particles washed only with water usually contain about 6% of sulphur.^{4,6}

In a previous paper⁴ we reported that the apparent point of zero charge (p.z.c.) of monodispersed chromium hydroxide particles containing about 19% of sulphate ions was at $\text{pH} < 4$ while the p.z.c. of sulphate free sample was equal to 8.3. In that case, we explained the discrepancy in the p.z.c. values between the samples assuming the interference of $\text{SO}_4^{2-} / \text{OH}^-$ ligand exchange process with surface protonation/deprotonation reactions responsible for the surface charge creation. Our explanation was criticized by Giacomelli *et al.*¹ In their experiments with precipitated chromium hydroxide, these authors found that the sulphate concentration in the dispersion was independent of pH during potentiometric titration experiments. In addition, based on the literature data for water exchange in aqueous $[\text{Cr}(\text{H}_2\text{O})_6]^{3-}$ solutions,⁸⁻¹⁰ they suggested that the $\text{SO}_4^{2-} / \text{OH}^-$ ligand exchange at the solid/liquid interface is also a very slow process and therefore it can not contribute significantly to the pH changes due to acid/base dissociation of surface hydroxyl groups during the potentiometric titration of the dispersion.

The aim of this paper was to evaluate the rate of ligand exchange between sulphate and hydroxyl ions in the monodispersed chromium(III) hydroxide / electrolyte solution system. The effect of solution pH on the extent of $\text{SO}_4^{2-} / \text{OH}^-$ exchange was also investigated.

EXPERIMENTAL

Particle Preparation

Monodispersed chromium hydroxide particles were prepared in the same way as described earlier.²⁻⁵ The particles were washed repeatedly with water only and were subsequently stored in a polyethylene bottle as a concentrated dispersion. The amount of sulphur in the solids was about 6.3%, as determined analytically.

Rate of $\text{SO}_4^{2-} / \text{OH}^-$ exchange

All experiments were performed in the setup used earlier for potentiometric titration of the monodispersed chromium hydroxide particles dispersion.⁴ Sodium hydroxide solution (0.05 dm³) of a given concentration was poured into the vessel. Then, a small amount of concentrated dispersion of monodispersed $\text{Cr}(\text{OH})_3$ particles was added to the electrolyte solution so that the final concentration of the particles in the dispersion was 2 g dm⁻³. The dispersion pH was monitored during the experiment

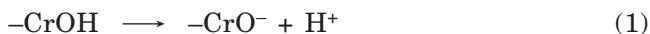
at different time intervals. After stirring for a given time, the sample was collected, the particles were removed from the sample by high-speed centrifugation, and the concentration of sulphate ions in the supernatant was determined analytically.

Effect of pH on SO_4^{2-}/OH^- Exchange

Monodispersed chromium(III) hydroxide particles dispersion (0.05 dm^3) containing 2 g dm^{-3} solids was titrated with sodium hydroxide solution (concentration 1 mol dm^{-3}). After each addition of sodium hydroxide, the dispersion was stirred for one hour. This time of equilibration was selected based on the rate of SO_4^{2-}/OH^- exchange. After that, the sample was collected, particles were removed by centrifugation and the sulphate concentration in the supernatant was determined analytically.

RESULTS AND DISCUSSION

Surface charge at the oxide/electrolyte interface is formed as a result of dissociation of surface hydroxyl groups, ¹¹⁻¹⁴ e.g.:



and possible complexation reactions of the supporting electrolyte ions.^{11,14,15} Reactions (1) and (2) are both pH dependent and the net surface charge can be determined from potentiometric titration data.

The above approach is based on the assumption that no other reactions in which H^+ and OH^- ions could be consumed take place in the system. If the sample contains impurities that can undergo exchange reactions with H^+ (OH^-) ions, some of the potential determining ions will be consumed in this reactions. This possibility has to be taken into account while calculating the surface charge density from potentiometric titration data. Knowledge about the rate of exchange between ions in a given system is a very important issue. If the exchange is extremely slow, then its effect on potentiometric titration data may be neglected.

The amounts of sulphate ions released from the sample of monodispersed chromium hydroxide particles as a function of time (for two different initial pH values; $\text{pH} = 12$ and $\text{pH} = 12.5$) are presented in Figure 1. An example of pH changes of the dispersion as a function of time in the same system is presented in Figure 2 (initial value of $\text{pH} = 12$). As observed from Figures 1 and 2, the process of exchange of sulphate ions for hydroxyl ions and the accompanying changes of pH are relatively fast. Fast »equilibrium«

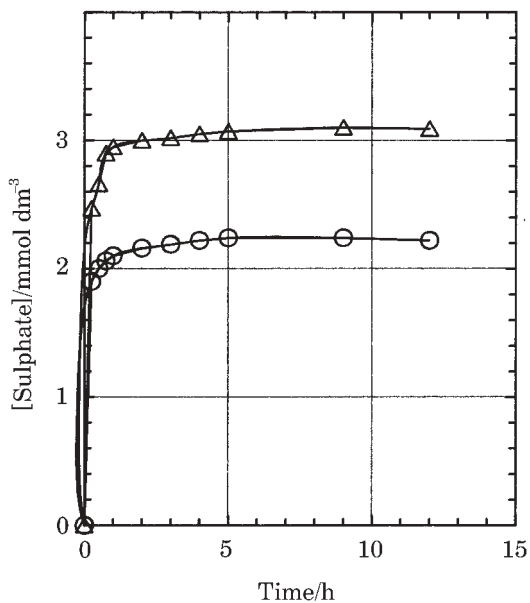


Figure 1. Amount of sulphate ions released from monodispersed chromium hydroxide particles (mmol dm^{-3}) vs. time. Solid concentration: 2 g dm^{-3} ; initial pH: 12 (O), 12.5 (Δ).

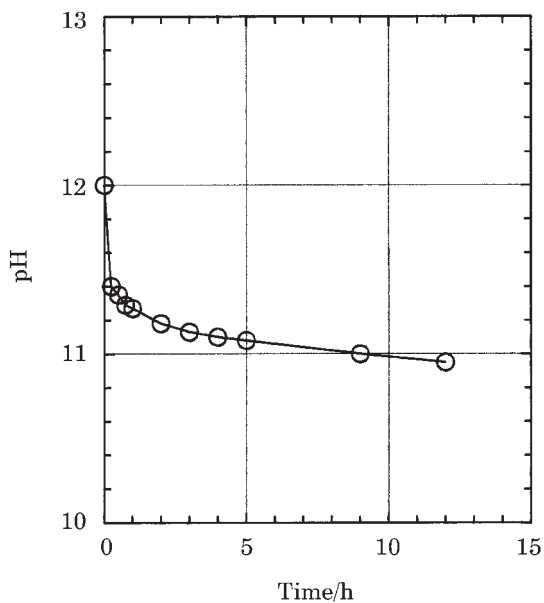


Figure 2. Change of pH of monodispersed $\text{Cr}(\text{OH})_3$ suspension vs. time. Solid concentration: 2 g dm^{-3} . Initial pH: 12 (O).

was achieved after less than one hour. Increase in the concentration of sulphate ions observed in Figure 1 is only due to ion exchange, *e.g.*:



Decrease of pH observed in Figure 2 is due to both $\text{SO}_4^{2-}/\text{OH}^-$ ligand exchange and surface reactions (1) and (2).

The data presented in Figures 1 and 2 support very well our earlier assumption on rapid exchangeability of sulphate ions during the potentiometric titration of monodispersed chromium hydroxide particles.⁴ Though the process of sulphate/hydroxyl exchange observed for monodispersed Cr(OH)_3 particles is diffusion controlled, it is much faster than the process of water exchange described in the literature for $[\text{Cr(H}_2\text{O)}_6]^{3+}$ species in aqueous solutions.

The amount of sulphate ions released from the sample of chromium hydroxide particles, as a function of the amount of base (NaOH) added to the dispersion, is presented in Figure 3. The maximum theoretical concentra-

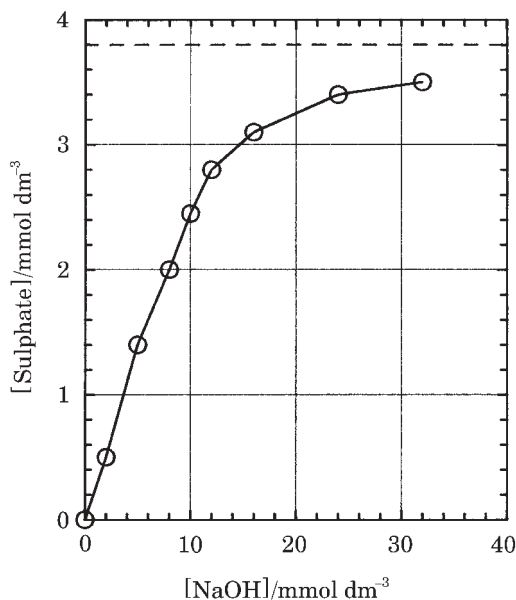


Figure 3. Amount of sulphate ions released from monodispersed chromium hydroxide particles as a function of sodium hydroxide concentration. Solid concentration: 2 g dm^{-3} . Dashed line presents maximum possible theoretical concentration of sulphate ions in the system (6.3% sulphur level in solid particles).

tion of sulphates in the system (corresponding to a sulphur content of 6.3%) is presented as a dashed line. As observed, the amount of sulphate ions released (exchanged for OH^-) increases with increasing the amount of sodium hydroxide added to the system (increasing pH). For higher NaOH concentrations, the curve approached the theoretical value (dashed line), *i.e.* sulphate ions were almost completely removed from the solids.

The data presented in Figures 1–3 shed some light not only on the rate of $\text{SO}_4^{2-}/\text{OH}^-$ ligand exchange at the solid/liquid interface but they can also explain why the removal of sulphates from the particles by washing with alkaline solutions is the most effective. To be removed from the particles, the sulphate ions have to be exchanged for other ions. Washing with water is ineffective because the concentration of OH^- ions in water is extremely low. High efficiency SO_4^{2-} removal by washing with alkaline solutions (high pH) is due to the high concentration of OH^- ions and rapid $\text{SO}_4^{2-}/\text{OH}^-$ exchange, as shown in Figure 1. When acids are used to remove sulphates from the monodispersed $\text{Cr}(\text{OH})_3$ particles, the sulphate/anion exchange can take place. However, the rate of such a reaction may be slower than that for $\text{SO}_4^{2-}/\text{OH}^-$ exchange and therefore acids may be less effective than bases for removing sulphates.

In conclusion, sulphate ions present in the core of monodispersed chromium(III) hydroxide particles in the form of chromium basic sulphate can be easily exchanged by hydroxyl ions. The process of $\text{SO}_4^{2-}/\text{OH}^-$ ligand exchange is, contrary to intuition, much faster than that observed for water exchange in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ species in aqueous solutions.

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SAŽETAK

Monodisperzne čestice kromova(III) hidroksida – zamjena sulfatnih iona

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Proučavana je kinetika zamjene sulfatnih i hidroksidnih iona u površinskom sloju monodisperznih čestica kromova hidroksida gdje su sulfatni ioni prisutni u obliku kromova baznog sulfata. Ispitivan je utjecaj pH na doseg zamjene. Preliminarni su rezultati pokazali da je brzina zamjene relativno visoka i da znatno premašuje brzinu zamjene molekula vode za otopljenu vrstu $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ koja je opisana u literaturi. Ovaj nalaz proturječi sugestijama nekih autora (Ref. 1) prema kojima je brzina zamjene $\text{SO}_4^{2-} / \text{OH}^-$ u međupovršini čvrsto/tekuće vrlo niska.