

Anion Exchange Studies on Hydrous Chromium Oxide

JAVED IQBAL, M. LATIF MIRZA AND SHAISTA MALIK
Chemistry Department, Islamia University, Bahawalpur, Pakistan

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Summary: The oxyanion exchange and adsorption behaviour of chromate, molybdate, phosphate and dichromate have been studied in acidic and basic media over hydrous chromium oxide predried at 37°C. The distribution coefficient (K_d) is pH dependent and the selectivity is in the order $\text{Cr}_2\text{O}_7^{2-} > \text{MoO}_4^{2-} > \text{CrO}_4^{2-} > \text{PO}_4^{3-}$. The polyvalent anions are strongly adsorbed in acidic media and cannot be eluted under the prevailing experimental conditions, whereas sodium hydroxide is found to be an effective eluent.

Introduction

A number of insoluble hydrous oxides, for example Cr (III), Zr(IV), Sn (IV), Th(IV) etc. have been investigated in the past for adsorption and ion exchange studies with inorganic materials [1-5]. Hydrous zirconium oxide, however, follows unusual selectivity pattern for polyvalent anions as compared with monovalent anions [3-4]. Our earlier report indicates cation exchange nature of hydrous chromium oxide (HCrO) [5]. The present investigations are carried out to understand the adsorption and anion exchange studies of chromate, dichromate, phosphate and molybdate on HCrO.

Results and Discussion

Hydrous chromium oxide begins to lose water (Fig. 1) at 80°C and the maximum weight loss (~ 29%) is attained at 300°C. The weight loss between 300°C to 700°C is relatively small with the rate 1-3% after each 100°C, the total reaching 42% of the initial weight. The weight loss between 700°C to 800°C is negligibly small (~ 0.5%). No further weight loss occurs upto 1200°C. The weight loss upto 300°C may be attributed due to elimination of the interstitial or free water and further increasing the temperature (300°-700°C), chemically bonded water is lost.

The infrared spectra of HCrO dried at three different temperatures is shown in Fig. 2. The spectra show four absorption bands, the first between 3100 to 3500 cm^{-1} with maximum at ~3382 cm^{-1} (s), the second between 1500 and 1606 cm^{-1} with maximum at 1580 cm^{-1} (m) respectively. These bands were compared with i.r spectra of water and metal-oxygen bands in the literature [9-13] and

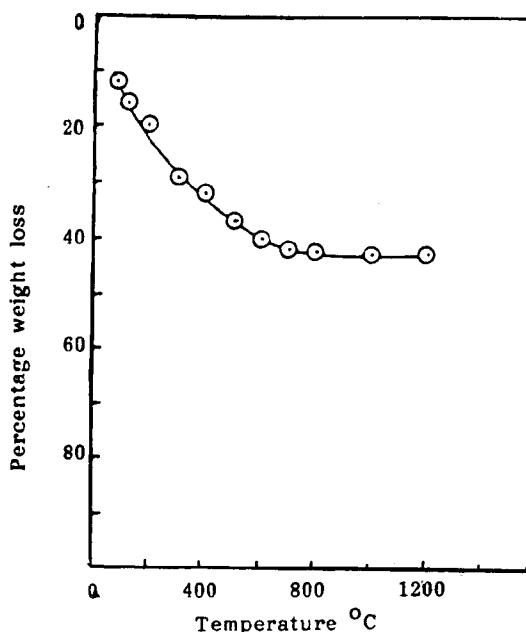


Fig. 1: Percentage weight loss of Hydrous Chromium Oxide.

assigned that the first band is due to the interstitial water and the hydroxyl groups, the second and the third of interstitial water, and the fourth Cr-O group. The decreasing ratio of optical densities of OH and Cr-O with increasing drying temperature (Table-1) indicates loss of water.

The distribution coefficients for the polyvalent anions with respect to their relative equilibrium towards HCrO at varying concentration of HCl and NaOH were determined and plotted as shown in Fig. 3 and 4. In acidic

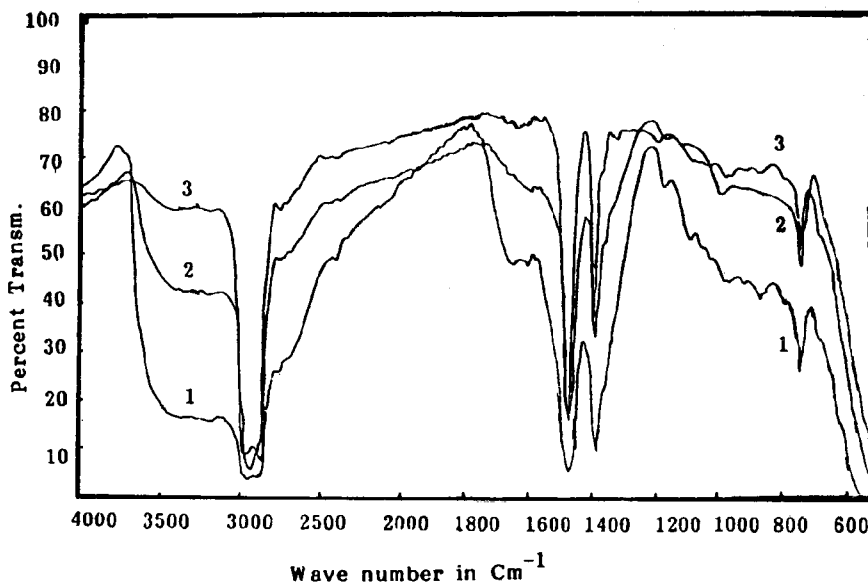


Fig. 2: Infra-red spectra of Hydrus Chromium Oxide (I) dried at 37° (2) dried at 200° (3) dried at 400°

Table-1: Optical densities at the maximum absorption of the OH group and Cr-O bond

Drying temperature of the HCrO	3382 cm ⁻¹ log 1/I _o (OH)	725 cm ⁻¹ log 1/I _o (Cr-O)	Ratio OH/Cr-O
37°C	0.77	0.58	1.33
200°C	0.38	0.30	1.27
400°C	0.23	0.25	0.92

Table-2: log K_d (ml/g) and separation factor (α*) for anions on hydrus chromium oxide

Solution parameter	Anions			
	Phosphate	Chromate	Molybdate	Dichromate
10 ⁻³ M HCl log α (K _d)	2.6	3.0	3.15	3.60
0.1M NaOH log α K _d	1.15	1.05	1.14	1.14
	1.25	1.17	1.07	1.50
0.2M to 0.8 NaOH log α K _d	0.75	1.25	1.50	1.75
	1.57	1.20	1.17	1.17

*Separation factor for neighbouring ions.

media the anions were rapidly and inversely exchanged with HCrO. The distribution coefficient of anions increases continuously with increasing concentration of HCl, whilst it decreases at first with increasing concentration of NaOH then becomes constant. The plot of log K_d against molarities of HCl is linear (Fig. 3), however a non-linear plot is observed in the basic medium (Fig. 4). Since the polyvalent anions in the acidic media were very strongly adsorbed, their removal from the exchanger was not possible. However, the anions phosphate, chromate, molybdate and dichromate were separated from one another using

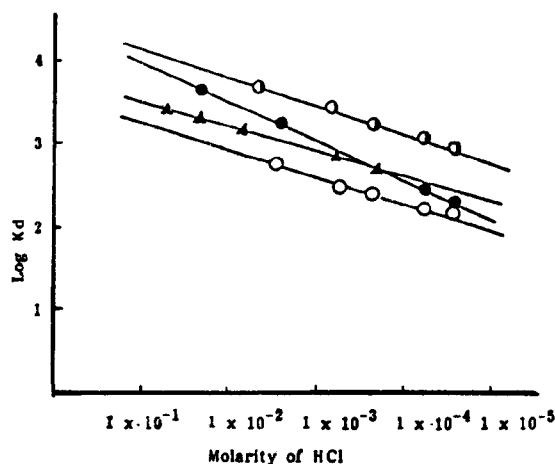


Fig.3: Logarithm of K_d values of polyvalent anions against molarity of HCl. PO₄ (O), CrO₄ (▲), MoO₄ (●), Cr₂O₇ (⊙).

0.1 M, 0.25 M, 0.35 M and 0.4 M sodium hydroxide solutions respectively. The displacement of weakly adsorbed anions, for example, phosphate, can be achieved quantitatively upto 95% elution, whereas strongly held anion, for example, chromate can only be removed by prolonged treatment with sodium hydroxide which gives about 90% recovery. The small irreversible exchange probably results from changes in the structure of exchanger as they are treated with

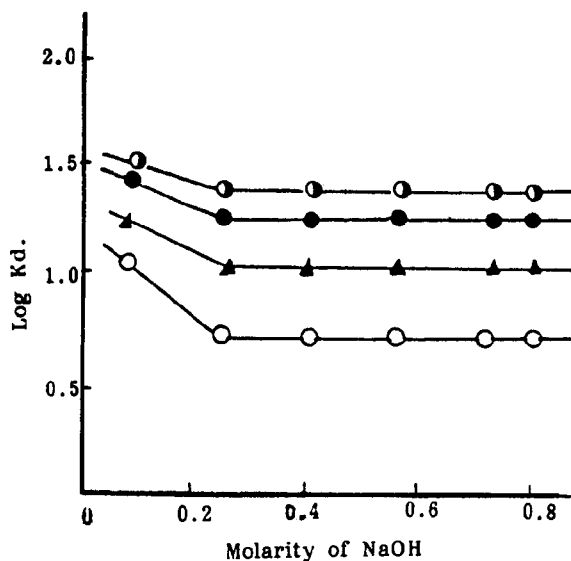


Fig.4: Logarithm of K_d values of polyvalent anions against molarity of NaOH. PO_4^{3-} (O), CrO_4^{2-} (Δ), MoO_4^{2-} (\bullet), $\text{Cr}_2\text{O}_7^{2-}$ (\circ).

sodium hydroxide and presumably increases covering of exchange sites by the products of slow reversible hydrolysis reactions.

Experimental

Hydrous chromium oxide was prepared as described earlier [5]. The resin HCrO was dried at 37°C, ground and sieved by screening. For batch equilibrium and column operation, material of mesh size 150 were selected. When the material was dried at 600°C, the water contents were 39.71% and the molar ratio of dichromate and water was 1:5.52. The infrared spectra of the ion-exchanger was measured on Hitachi Infrared Spectrophotometer Model 260-50. The mull was prepared by grinding about 1 mg of the resin with a drop of Nujol and pressed between plates of AgCl. The spectra was recorded over the region 4000-600 cm^{-1} . Percentage weight loss was done on Gallenkamp Hot Box oven (37°-200°C) and Carbolite Furnace (200°-1200°C). The sample was heated for one and a half hour at each temperature.

The resin HCrO (0.25 g) was tumbled with 5 ml (500 ppm) solution of the desired anion. Most of the individual coloured anions were adsorbed in a few minutes time, but to attain equilibrium the solutions were tumbled for 24 hours under thermostatic conditions ($25 \pm 2^\circ\text{C}$). The

distribution coefficients (K_d) were calculated for HCrO dried at 37°C. The quantitative analysis of the polyvalent anions were done by using usual spectrophotometric methods [6,7].

Any adhering fine particles, if present, in the exchanger which could block a column were removed by shaking with distilled water and decanting the cloudy solution after the bulk of the material had settled. This was repeated until the water above the bulk solid was clear. A column (8.0 cm x 0.8 cm) was then set and loaded with HCrO resin. 0.5 M HCl was allowed to percolate through the resin to form an anion exchanger. The resin was then washed with deionized water. The bubbles were removed by inverting the column several times.

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