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# Anionic clay-like behaviour of $\alpha$ -nickel hydroxide: chromate sorption studies

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## Abstract

While the sorption capacity of  $\alpha$ -nickel hydroxide for the chromate ion is comparable with that of hydrotalcite-like anionic clays, the control samples of  $\beta$ - and  $\beta_{bc}$  (bc: badly crystalline)-nickel hydroxide show negligible sorption. This provides direct evidence for the clay-like nature of  $\alpha$ -nickel hydroxide.

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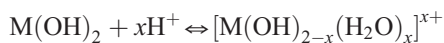
*Keywords:* Anionic;  $\alpha$ -Nickel hydroxide; Chromate

## 1. Introduction

Two polymorphic modifications of the hydroxide of Ni(II) have been reported in the literature [1]. Both crystallize in a layered hexagonal structure derived from that of the mineral brucite,  $Mg(OH)_2$  [2]. Of these, the thermodynamically more stable form,  $\beta$ -nickel hydroxide, is isostructural with brucite (P-3m1,  $a = 3.12 \text{ \AA}$ ,  $c = 4.6 \text{ \AA}$ ). The other form called the  $\alpha$  modification was for long thought to be a hydrated form having the composition  $3Ni(OH)_2 \cdot 2H_2O$  [3]. However, later work involving detailed investigation of the composition [4,5] revealed that the  $\alpha$  modification is a hydroxyl deficient phase, having the composition  $Ni(OH)_{2-x}(A^{n-})_{x/n} \cdot yH_2O$  where  $A^{n-} =$  nitrate, carbonate or carboxylate [6]. The anions are

intercalated between the layers. The resultant structure, with an enhanced basal spacing ( $7.6\text{--}8 \text{ \AA}$ ), is evocative of the structure of hydrotalcite-like anionic clays [7]. A similar  $\alpha$  modification of cobalt hydroxide is also known [8]. In earlier papers [4] we compared the PXRD patterns of the  $\alpha$ -hydroxides of Ni and Co with those of the corresponding Al-containing hydrotalcites and showed that the two classes of compounds are isostructural.

The origin of the anionic clay-like structure of the  $\alpha$ -hydroxides has been attributed to a protonation mechanism



whereby the brucite-like metal hydroxide layers acquire a positive charge [4]. Anions are then intercalated in the interlayer region to restore charge-neutrality.

Clay-like materials are characterized by (1) their ability to exchange the intercalated ions and (2) a

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large sorption capacity for the exchangeable ion. We report here the high sorption capacity of  $\alpha$ -nickel hydroxide for the chromate ion.

## 2. Experimental

$\beta$ -Nickel hydroxide was obtained from Aldrich Chemical (USA). All other reagents used in this study were GR grade obtained from E. Merck (India) and used as such.  $\alpha$ -Nickel hydroxide was prepared by cathodic deposition on a nickel plate from a nickel nitrate solution [9].  $\beta_{bc}$  (bc: badly crystalline)-nickel hydroxide was prepared by ageing the  $\alpha$ -hydroxide in 1 M KOH for 1 month.

In a typical sorption experiment, approximately 150 mg of the hydroxide sample was stirred in 50 ml of distilled water for 24 h. To this slurry, 50 ml of a standard  $K_2Cr_2O_7$  solution (pH=6.5) was added. The mixture was stirred for 1 h and then centrifuged. The amount of  $CrO_4^{2-}/Cr_2O_7^{2-}$  ions in the centrifugate was determined by potentiometric titrations using a standard ammonium ferrous sulphate solution. The solid residue was washed repeatedly with water until the washings were free from ions, filtered and dried at 65 °C to constant weight.

The samples were characterized by X-ray powder diffraction (JEOL JDX8P Powder Diffractometer, Co  $K\alpha$ ,  $\lambda=1.79$  Å) and infrared spectroscopy (Nicolet Model Impact 400D FTIR spectrometer, KBr pellets, 4-cm<sup>-1</sup> resolution).

Chromate sorption by the  $\alpha$ -hydroxide was carried out at room temperature (27 °C) with  $K_2Cr_2O_7$  solutions of various concentrations and an isotherm plotted. A similar isotherm was also obtained at 4 °C.

Kinetics of sorption was followed by taking 10-ml aliquots of the reaction mixture at various intervals of time and estimating the Cr(VI) content in these aliquots by colorimetry.

## 3. Results and discussion

Fig. 1a shows the X-ray powder diffraction pattern of the  $\alpha$ -nickel hydroxide. The material is poorly crystalline and is characterized by the appearance of a low angle reflection at 7.6 Å corresponding to the basal spacing. This spacing is adequate to include nitrate ions in  $C_{2v}$  symmetry [10]. The IR spectrum of the same sample is shown in Fig. 2a. Apart from the vibrations due to the hydroxyl ions in high (3400 cm<sup>-1</sup>) wavenumber region and the Ni–O–H bending vibrations in the low (640 cm<sup>-1</sup>) wavenumber region, strong absorptions are seen in the range 1500–1000 cm<sup>-1</sup>. These vibrations are attributed to  $NO_3^-$  ions intercalated in the  $C_{2v}$  symmetry and are discussed in detail elsewhere [5].

The PXRD pattern and the IR spectrum of the material obtained after the sorption reaction are shown in Figs. 1b and 2b, respectively. The diffraction pattern does not show any change except for a slight broadening of the reflections after the sorption reaction. This shows that, except for a slight loss in crystallinity, the structure of  $\alpha$ -nickel hydroxide has remained unchanged. The basal spacing has also not changed and this is in keeping with the observations made on other  $CrO_4^{2-}$ -containing layered double hydroxides [11]. The infrared spectrum after the sorption reaction shows a significant decline in the intensity of vibrations due to the intercalated  $NO_3^-$ .

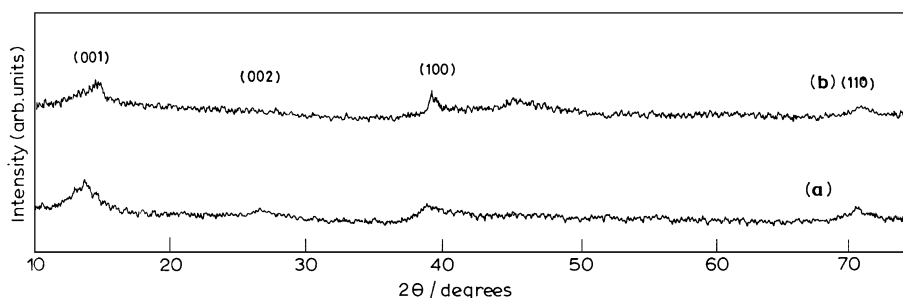


Fig. 1. Powder X-ray diffraction patterns of  $\alpha$ -nickel hydroxide recorded before (a) and after (b) chromate sorption.

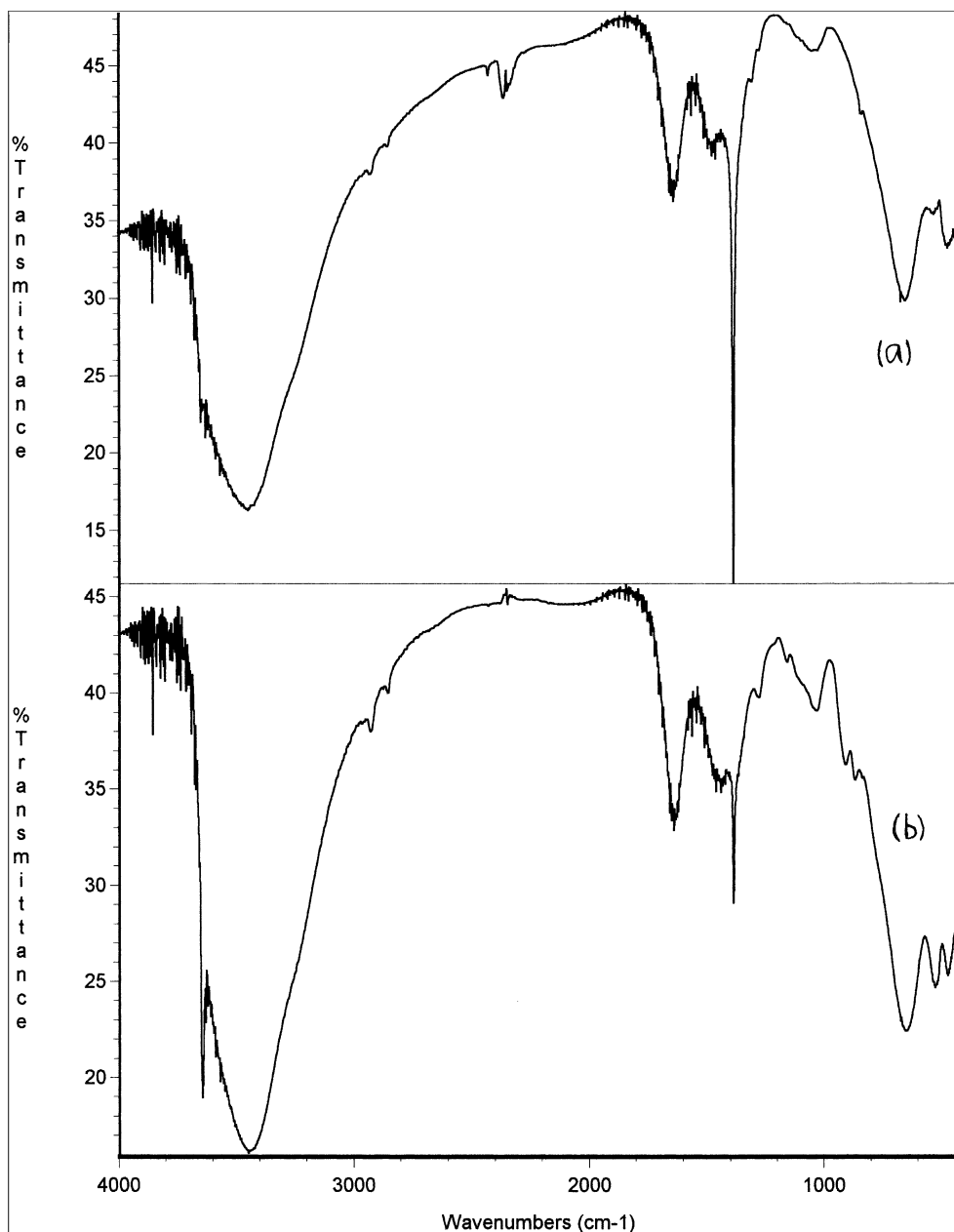


Fig. 2. Infrared spectra of  $\alpha$ -nickel hydroxide recorded before (a) and after (b) chromate sorption.

Additional peaks are seen at 840, 865 and 900  $\text{cm}^{-1}$  testifying to the inclusion of chromate ions into the structure [11].

The sorption capacity of  $\alpha$ -nickel hydroxide at a chromate concentration of 33 mM is found to be

comparable to the capacity of the Ni-Fe LDH and 550% the capacity of  $\beta$ -nickel hydroxide (see Table 1). This difference in the sorption capacities of  $\alpha$  and  $\beta$ -nickel hydroxides can arise for two reasons: (1) the difference in the particle size and particle morphology

Table 1  
Chromate sorption capacities of various polymorphs of nickel hydroxide compared with that of Ni–Fe LDH

Sample	Amount of $\text{CrO}_4^{2-}$ sorbed	
	mg/g sample	mol/mol sample
$\alpha$ -Nickel hydroxide	96	0.091
$\beta$ -Nickel hydroxide	17	0.013
$\beta_{bc}$ -Nickel hydroxide	28	0.023
Ni–Fe LDH [12]	120	0.122

or (2) the difference in their structures. To eliminate the first possibility, the sorption capacity of  $\beta_{bc}$ -nickel hydroxide was determined. This material has a structure and basal spacing same as that of the  $\beta$ -hydroxide and a particle morphology same as that of the  $\alpha$ -nickel hydroxide [13]. It was found to have a sorption capacity comparable to that of the  $\beta$ -hydroxide but much lower than that of the  $\alpha$  hydroxide. This indicates that the high sorption capacity of  $\alpha$ -nickel hydroxide is due to the structural differences between the two polymorphic modifications.  $\alpha$ -Nickel hydroxide comprises of positively charged layers and, like the anionic clays, incorporates the chromate ions in the interlayer region. This results in a capacity comparable to that of the LDHs [12]. On the other hand, the  $\beta$ -hydroxides have a compact structure comprising the charge-neutral layers

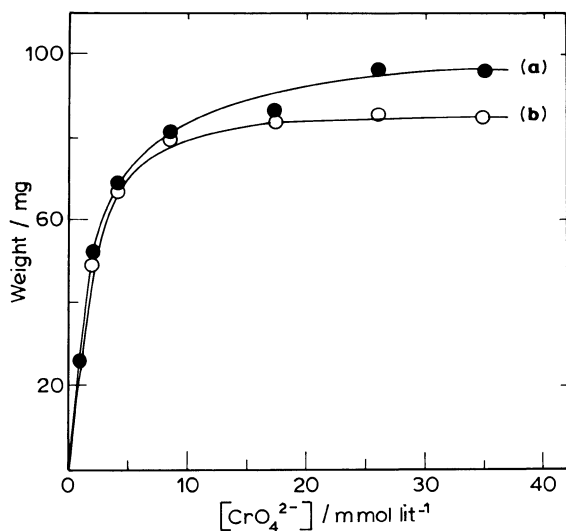


Fig. 3. Sorption isotherms measured at 27 °C (a) and 4 °C (b), respectively.

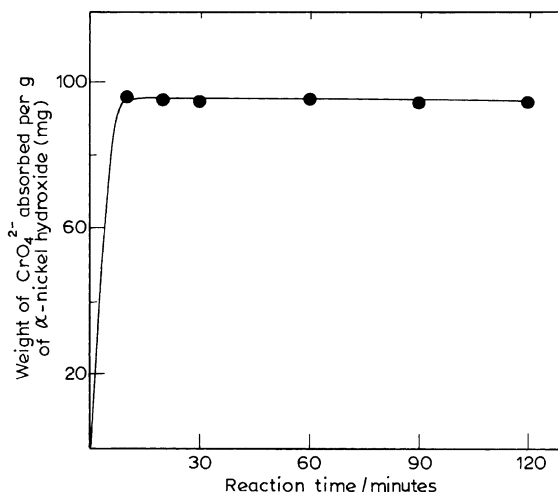


Fig. 4. Sorption capacity estimated as a function of time at a chromate concentration of 33  $\text{mM l}^{-1}$ .

of the composition  $[\text{Ni}(\text{OH})_2]$  and a low basal spacing, 4.6 Å. The sorption capacity of  $\beta$ -hydroxides arises mainly due to adsorption on the surface of the particles. The small difference in the sorption capacities of the  $\beta$ - and  $\beta_{bc}$ -hydroxides is attributable to the difference in particle size and morphology.

Fig. 3 shows the sorption isotherms obtained at two different temperatures. The sorption capacity saturates at a low chromate concentration of 8.25 mM. The sorption capacity is also found to decrease with temperature, contrary to what is expected of a simple Langmuir-type adsorption. This indicates that the sorption occurs through a process with an activation barrier involving chemical exchange of the nitrate ions for the incoming chromate ion. This further confirms that the sorption is due to the intercalation of chromate ions in the interlayer region.

Fig. 4 shows the variation of the sorption capacities with reaction time when the chromate concentration is 33 mM. It can be seen that the reaction is complete in 10 min. This is in line with what is observed in the case of anion exchange reactions of hydrotalcites [14].

#### 4. Conclusions

In conclusion, we have shown here that the  $\alpha$ -hydroxide of nickel exhibits anionic clay-like behav-

our. This is in accordance with the structural model that we have proposed for this compound.

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