INVESTIGATION OF THE EFFECTS OF HEAT TREATMENT ON THE β-Ni(OH)$_2$–β-NiOOH SYSTEM USING IR SPECTROSCOPY

T.S. HORÁNYI

Research Institute for Technical Physics of the Hungarian Academy of Sciences, Budapest H-1325 P.O.B. 76 (Hungary)

(Received 2 June 1988)

ABSTRACT

The thermal characteristics of the β-Ni(OH)$_2$–β-NiOOH system, in comparison with the thermal behaviour of pure β-Ni(OH)$_2$, have been studied by IR spectroscopy in the 400–4000 cm^{-1} region. The IR spectra of samples treated at various temperatures between 20 and 300°C, are presented together with some results obtained by thermogravimetric measurements. In addition to conventional IR analysis at ambient temperatures, an in-situ spectroscopic technique has also been used in the course of heat treatment in order to obtain information on the nature of the water adsorption observed on partly dehydrated hydroxides. Direct experimental verification of a previous assumption that the decomposition of the partly charged nickel hydroxide takes place in two almost independent steps is furnished by this IR method.

INTRODUCTION

In a previous paper [1], the thermal stability of the β-Ni(OH)$_2$–β-NiOOH system was examined. The need for these investigations was motivated by a number of reasons. For instance, the thermal behaviour of the β- and α-type (including turbostratic) nickel hydroxides has been extensively studied [2–8], while there are relatively few works dealing with the β- or γ-nickel oxyhydroxides [9–11]. As well as conventional thermal analysis which was applied in our recent study [1], numerous experimental techniques are known and used for the examination of the characteristic structural changes occurring during the thermal treatment of nickel hydroxides and their oxidation products [2–11]. Of these techniques, in the case of nickel hydroxides and their related compounds, infrared spectroscopy has an enormous advantage compared to other methods, namely the extreme sensitivity of this method to small changes in the chemical bonds of hydroxyl groups and

water molecules. The thermal decomposition of these compounds (accompanied by the evolution of H_2O and O_2) can be readily followed using this technique. Because of the above mentioned sensitivity of infrared spectroscopy, this method has frequently been used in the analysis of nickel hydroxides and oxyhydroxides [2,3,6,8,12–21]. Consequently, the IR spectra of these compounds are known in detail. Therefore, the following study concentrates solely on the changes connected with the decomposition process.

The aim of this paper is to give direct experimental evidence, using IR spectroscopy, that the decomposition of partly charged (electrochemically oxidized) β-nickel hydroxide occurs in two almost independent steps. According to the conclusion drawn in ref. 1, the loss of active oxygen (decomposition of NiOOH) starts at a notably lower temperature than the decomposition of $Ni(OH)_2$.

Some aspects of water adsorption on the partly dehydrated β-$Ni(OH)_2$–β-NiOOH system have been studied in order to demonstrate the ability of NiO (formed during the thermal treatment of partly charged nickel hydroxides) to adsorb a relatively large amount of water at ambient temperatures. The knowledge of the main features of the water adsorption is necessary for the accurate interpretation of the dehydration process of the partly charged nickel hydroxide.

Some thermogravimetric measurements have also been carried out in order to confirm the conclusions drawn from the results of the IR analysis.

EXPERIMENTAL

The preparation of β-$Ni(OH)_2$ and the electrochemical oxidation procedures yielding the β-$Ni(OH)_2$–β-NiOOH system are given in detail elsewhere [1].

A double-beam Specord 75 IR spectrophotometer was used for recording IR spectra in the 400–4000 cm^{-1} region. Using an infrared temperature control unit, it was possible to measure the IR spectra of samples during a heat treatment from 20 to 250°C. For these IR measurements, nickel hydroxide or oxyhydroxide powder was pressed on a KBr disk at 5 MPa. In the other cases, following a heat treatment of 2 h, samples were mixed and pelleted with KBr, and the spectra were recorded at room temperature. In spite of the graphite content of the partly charged nickel hydroxide (20 wt.%, which was necessary to ensure electrical conductivity of the nickel hydroxide electrode subjected to charge–discharge cycles) satisfactory IR spectra could be obtained independent of which sampling technique was chosen.

The weight loss curves of nickel hydroxide and oxyhydroxide were measured at various temperatures with a Mettler thermoanalyser, and the oxidation states of samples were determined by iodometric titration.

RESULTS

Although the IR spectra of β-NiOOH and, especially, of β-Ni(OH)$_2$ have been presented by several authors [12–20], it is worth specifying those absorption bands whose changes are characteristic for the dehydration process. (See Figs. 1(A) and 1(B)). The absorption band located near 3640 cm^{-1} arises from the stretching vibration of non-hydrogen-bonded hydroxyl groups. The broad band having a centre at approximately 3440 cm^{-1} can be attributed to the stretching mode of adsorbed water molecules. However, as can be seen in Fig. 1(B), the band related to the formation of hydrogen bonded hydroxyl groups (charged state) appears at the same frequency. Bands at 520 cm^{-1} and 570 cm^{-1} are attributed to the in-plane deformation vibration of non-hydrogen-bonded and hydrogen-bonded hydroxyl groups, respectively. The absorption observed at 460 cm^{-1} is due to the Ni–O stretching vibration.

IR spectra obtained in the 1000–3000 cm^{-1} region are not presented because the characteristic bands of adsorbed impurities (CO_3^{-2}, SO_4^{-2}) are not of importance to the dehydration process, and because the weak absorption at around 1640 cm^{-1}, due to the bending vibration of adsorbed water, cannot be considered here because of its relatively low intensity.

The IR spectra of samples pelleted with KBr following a thermal treatment for 2 h at various temperatures are given in Figs. 1(A) and 1(B). The
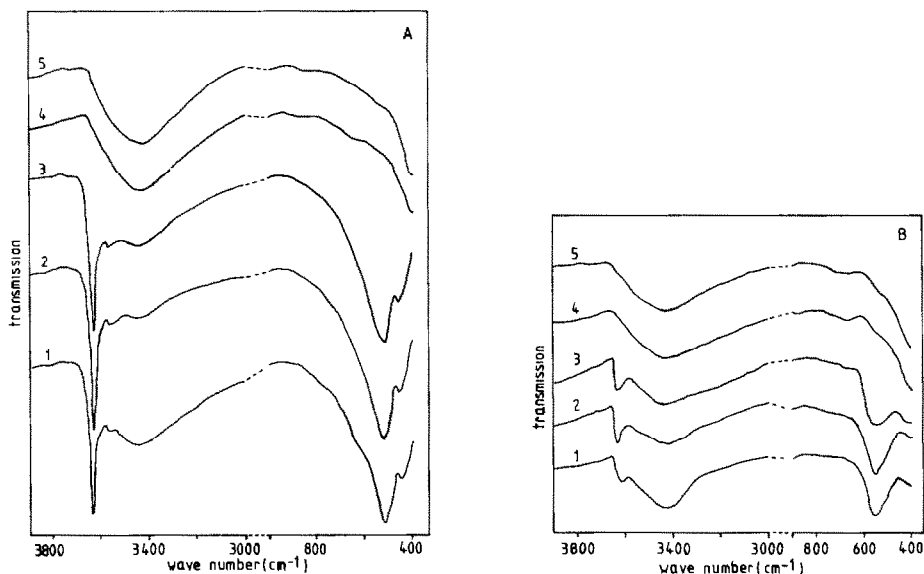

Fig. 1. Infrared spectra of (A) β-Ni(OH)$_2$ and (B) the β-Ni(OH)$_2$–β-NiOOH system (oxidation state of 2.66), recorded at room temperature after 2 h of heat treatment. 1, 20 °C; 2, 150 °C; 3, 200 °C; 4, 250 °C; 5, 300 °C.
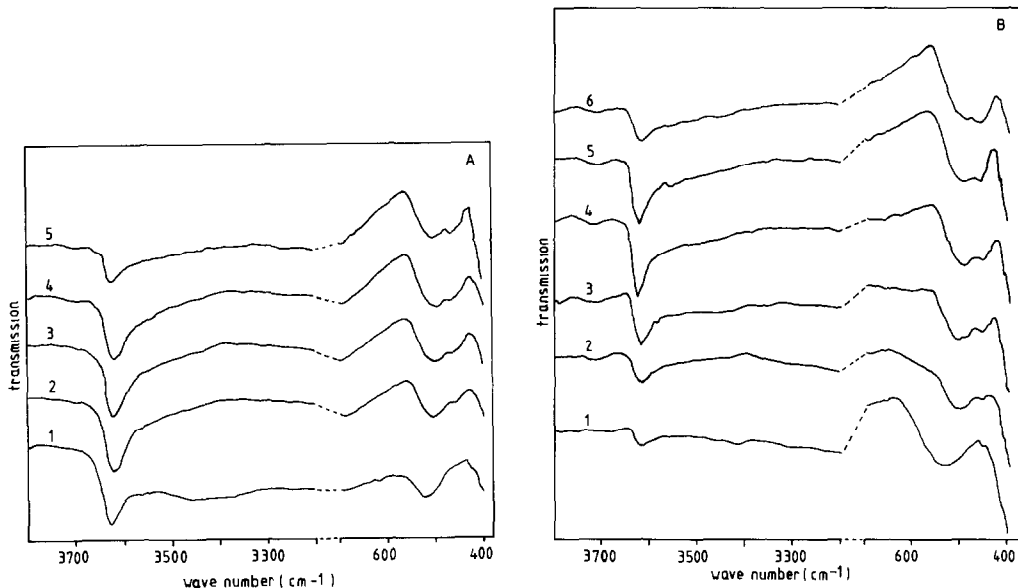
Fig. 2. Infrared spectra of (A) β-Ni(OH)$_2$ and (B) the β-Ni(OH)$_2$–β-NiOOH system (oxidation state of 2.66), recorded at varying temperatures after 20 minutes of heat treatment at that temperature, A: 1, 20 °C; 2, 150 °C; 3, 200 °C; 4, 250 °C; B: 1, 20 °C; 2, 100 °C; 3, 150 °C; 4, 200 °C; 5, 250 °C, and following two hours of heat treatment, A: 5, 250 °C and B: 6, 250 °C.

3640 cm^{-1} band of partly charged nickel hydroxide has an increased intensity when the sample is treated above room temperature, whereas no change in the intensity of the absorption at this wavenumber can be observed in the IR spectra of β-Ni(OH)$_2$ between 20 and 200 °C. In both cases, however, this band practically disappears when the temperature of the heat treatment attains 250 °C. With respect to the absorption band at 570 cm^{-1} related to the NiOOH content of partly charged nickel hydroxide, it can be seen that this band is still present after a heat treatment at 200 °C. However, the presence of NiOOH cannot be observed above 200 °C because of unwanted water adsorption.

When KBr pellets were prepared and spectra recorded at room temperature, it was not possible to obtain spectra free from the absorption originating from water adsorption. Thus, bands at 3440 cm^{-1} and 1640 cm^{-1} were always present in the spectra, and, in the case of samples treated above 200 °C, the lack of distinct bands in the 400 –750 cm^{-1} region is also a consequence of water adsorption.

It was possible to obtain IR spectra of β-Ni(OH)$_2$ and of the β-Ni(OH)$_2$–β-NiOOH system at various constant and defined temperatures between 20 and 250 °C after 20 min of heat treatment (see Figs. 2(A) and 2(B)). Thus, the dehydration reaction of the hydroxides could be continuously followed and IR spectra free from unwanted bands of adsorbed water
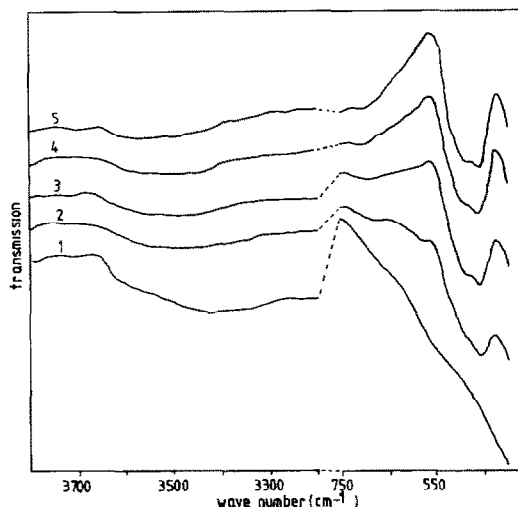
Fig. 3. Variation of the infrared spectra of the partly dehydrated β-Ni(OH)$_2$-β-NiOOH system (dehydrated at 300 °C) with the temperature of recording. 1, 20 °C; 2, 100 °C; 3, 150 °C; 4, 200 °C; 5, 250 °C.

(adsorbed during mixing and pelleting with KBr) could be recorded. In the spectra of pure β-Ni(OH)$_2$, the decrease in the intensity of bands at 3640 cm^{-1} above 200 °C is the most conspicuous effect although an increase in the relative intensity of the Ni–O stretching band at 460 cm^{-1} can also be observed (see Fig. 2(A)). The decomposition of the NiOOH content of the partly charged material is indicated by the increasing and decreasing intensity of the absorption bands at 3640 cm^{-1} and at 570 cm^{-1}, respectively (Fig. 2(B)). However, by 250 °C, the intensity of the "free" hydroxyl band (3640 cm^{-1}) is decreasing slowly, indicating that the dehydration of the Ni(OH)$_2$ content is the dominant process at this higher temperature. In the

TABLE 1

Extent of dehydration reaction at various temperatures

Material	Temperature (°C)	Oxidation state after heat treatment	Relative amount of material transformed in 120 minutes (wt.%)
β-Ni(OH)$_2$	200	< 2.005	3.5 ± 2
	250	2.035 ± 0.005	81 ± 2
	300	2.025 ± 0.005	90 ± 2
β-Ni(OH)$_2$ – β-NiOOH oxidation state of 2.66	150	2.51 ± 0.02	8.5 ± 2
	200	2.24 ± 0.02	49 ± 2
	250	2.060 ± 0.005	73 ± 2
	300	2.040 ± 0.005	77 ± 2

IR spectra of the β-Ni(OH)$_2$–β-NiOOH system dehydrated at 300°C for 2 h and pressed on a KBr disk (Fig. 3), the two absorption bands due to the Ni–O stretching and to the OH in-plane deformation vibration are still present, indicating that the dehydration reaction is not complete. On the basis of spectra given in Figs. 2 and 3, it may be clear that the elimination of adsorbed water (indicated both by the decrease of the intensity of the 3440 cm^{-1} band and by the appearance of distinct bands in the 400–750 cm^{-1} region) takes place up to 150°C.

Supposing that the weight loss observed below 150°C mainly originates from the loss of adsorbed water, the relative amounts of β-Ni(OH)$_2$ and of the β-Ni(OH)$_2$–β-NiOOH system transformed at a given temperature value can be determined. These data are listed in Table 1 in order to facilitate the discussion of results obtained by IR spectroscopy.

DISCUSSION

The partly charged nickel hydroxide is known to be a heterogeneous mixture of two solid solutions [22]; thus there is nothing unusual in the existence of two types of almost independent dehydration reactions, the decomposition of both the Ni(OH)$_2$ and of the NiOOH [1]. The conventional thermal analysis used in ref. 1, however, was not suitable to obtain direct experimental evidence for the occurrence of these processes. The results of the present paper enable us to provide the required direct evidence. Thus, as has been mentioned, the continuous decrease in intensity of the 570 cm^{-1} band (due to the hydrogen bonded hydroxyl groups) with increasing temperature indicates the decomposition of the NiOOH content (see Fig. 2(B)). This loss of active oxygen content leads to the decomposition of the hydrogen bonded structure of the partly charged state, and may result in the increase of the intensity of the band related to the "free" hydroxyl groups. In fact, an increase in the intensity of the 3640 cm^{-1} band at temperatures not higher than about 200°C was observed. From this, it can also be concluded that the dehydration of the Ni(OH)$_2$ content of the partly charged material does not take place at a noticeable rate, otherwise a slow decrease in the intensity of this band would be observed. In fact, the IR spectra recorded at higher temperatures (above 200°C) already show that the decomposition of nickel hydroxide occurs at a considerable rate (Fig. 2(B)).

It seems clear from the presence of the band corresponding to the in-plane deformation vibration of the OH groups at higher temperatures that the dehydration reaction is still not complete. However, numerical evaluation of the extent of the dehydration reaction could only be carried out using the results of the thermal analysis. The data summarized in Table 1 demonstrate that in contrast to the behaviour of pure β-Ni(OH)$_2$, the

decomposition of the β-Ni(OH)$_2$-β-NiOOH system takes place in a fairly wide temperature range and is far from being complete even at 300°C. Here we must mention that following a 2 h heat treatment, the rate of the decrease of weight (corresponding to the rate of the decomposition reaction) tends to a low value, and in the case of treatments carried out above about 250°C, it is practically reduced to zero. Consequently, if β-Ni(OH)$_2$ or the β-Ni(OH)$_2$-β-NiOOH system is maintained at a constant temperature for a sufficient period, it will attain a stable and defined state similar to an equilibrium system. This behaviour, perhaps, is not so surprising if we accept that, according to the reaction

$$NiO + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \rightarrow NiOOH$$
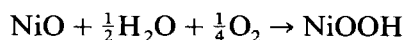
an oxidation process is operative during the heat treatment. The formation of Ni^{3+} ions in the decomposition of nickel hydroxide is proved by the fact that the oxidation state of partly dehydrated nickel hydroxide is always higher than 2 (see Table 1), which is in good agreement with the results reported in the literature [3,23,24].

Unfortunately, no IR evidence could be obtained to demonstrate the formation of NiOOH. The reason for this may be that the NiOOH formed in the oxidation reaction is probably not hydrogen bonded because of its low concentration.

Although the water molecules bound by NiO may play a prominent role in the decomposition and oxidation processes [3], it can only be concluded that the NiO had an increased ability to bind water below 150°C, and that the appearance of absorption bands at 3440 cm^{-1} and 1640 cm^{-1} cannot be avoided whenever IR analysis is determined at room temperature. This latter fact deserves particular attention because in some works [2,3], the appearance of bands related to adsorbed water in the IR spectra of dehydrated nickel hydroxides has been incorrectly interpreted as suitable proof of the presence of water molecules at higher temperatures.

REFERENCES

1 T.S. Horányi, Thermochim. Acta, 1989, in press.
2 S. Le Bihan and M. Figlarz, Thermochim. Acta, 6 (1973) 319.
3 F. Fievet and M. Figlarz, J. Catal., 39 (1975) 350.
4 B. Mani and J.P. de Neufville, Mat. Res. Bull., 19 (1984) 377.
5 W. Dennstedt and W. Löser, Electrochim. Acta, 16 (1971) 429.
6 M. Sakashita and N. Sato, Bull. Chem. Soc. Jpn., 46 (1973) 1983.
7 E. Kádár, L. Sors, S. Kulcsár and E. Kánya, Thermochim. Acta, 107 (1986) 27.
8 J.R. Sohn and D.J. Ri, Hwahak Konghak, 21 (1983) 305.
9 O. Rademacher, K. Wiesener and E. Prikryl, Z. Phys. Chem. Leipzig, 257 (1976) 354; 258 (1977) 113.
10 A.N. Kuznecov, B.G. Vilenskaya, I.N. Zakharov and E.P. Artyukhova, Zh. Fiz. Khim., 42 (1968) 472.

150

11 M.A. Aia, J. Electrochem. Soc., 114 (1967) 418.
12 F.P. Kober, J. Electrochem. Soc., 112 (1965) 1064; 114 (1967) 215.
13 C. Cabannes-Ott, Ann. Chim., 13 (1960) 944.
14 I.S. Shamina, O.G. Malandin, S.M. Rakhovskaya and L.A. Vereshchagina, Elektro-
   khimiya, 10 (1974) 1571; 10 (1974) 1745; 12 (1976) 573.
15 O.G. Malandin, I.K. Kuchkaeva, A.V. Vasev, P.N. Bityuckiy, L.A. Vereshchagina and
   G.V. Suchkova, Elektrokhimiya, 14 (1978) 1380.
16 O.G. Malandin, S.M. Rakhovskaya, A.B. Vasev, L.A. Vereshchagina and G.B. Suchkova,
   Elektrokhimiya, 16 (1980) 1041.
17 S. Le Bihan and M. Figlarz, Compt. Rend. (Paris), C 272 (1971) 580; J. Cryst. Growth,
   13–14 (1972) 458.
18 P. Oliva, J. Leonardi, J.F. Laurent, C. Delmas, J.J. Braconnier, M. Figlarz, F. Fievet and
   A. de Guibert, J. Power Sources, 8 (1982) 229.
19 N. Minkova, M. Krusteva and G. Nikolov, J. Mol. Struct., 115 (1984) 23.
20 D.C. Trivedi, Trans. SAEST, 21 (1986) 45.
21 F. Hahn, D. Floner, B. Beden and C. Lamy, Electrochim. Acta, 32 (1987) 1631.
22 R. Barnard, C.F. Randell and F.L. Tye, J. Appl. Electrochem., 10 (1980) 109; J.
   Electroanal. Chem., 119 (1981) 17.
23 J. Deren and J. Stoch, J. Catal., 18 (1970) 249.
24 F. Fievet, P. Germi, F. de Bergevin and M. Figlarz, J. Appl. Cryst., 12 (1979) 387.