

A Sol-Gel Process for the Preparation of Micro-Spheroids of Nickel (II) Hydroxide*

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The sol-gel procedure for the preparation of nickel(II) hydroxide micro-spheroids of definite size and shape is described.

The process is a two-stage operation. In the first stage the concentrated sol of $\text{Ni}(\text{OH})_2$ is produced by a sequence of precipitation, centrifugation, resuspension and electro dialysis. In the second stage the sol is transformed into a gel in a column in the counter-current flow of a dehydrating alcohol. Flow rate control of the sol and of the dehydrating agent allow preparation of spherical particles of different diameters in the range of 0.1 to 0.3 mm.

INTRODUCTION

The interest in nickel(II) oxide and nickel has been revived in recent years due to their characteristic semiconducting properties and general technological importance, *e. g.* plating, catalysis, and batteries. Therefore further investigation was encouraged towards the study of their electrochemical properties, as well as to the precise surface and adsorption studies.

Nickel(II) hydroxide is used as the starting substance to obtain samples of nickel(II) oxide and nickel, through a rather simple heating procedure^{1,2} of transformation of nickel(II) hydroxide to nickel(II) oxide at temperatures between 250 and 1300 °C³. At higher temperatures (about 1300 °C) nickel is obtained by reduction.

Usually, two types of samples were used in nickel-nickel(II) oxide studies, either a) single crystals or b) powdered samples. The preparation of single crystals usually involves difficult procedures and complicated apparatus⁴⁻⁷.

The powdered samples of NiO are easily prepared either by mechanical procedures such as crushing⁸ or by different preparation procedures such as evaporation⁹ or reduction of nickel(II) compounds¹⁰. The dimensions of the particles obtained and used were from 2.5 μm to 0.1 μm . Nickel(II) hydroxide powders are easily prepared by precipitation of nickel(II) compounds, under the conditions described earlier¹¹. However, the disadvantage of the powdered samples is related to the undefined shape and size of particles.

Therefore efforts are encouraged to prepare samples of pure nickel(II) hydroxide of definite size and shape. The slow precipitation method for preparation of nickel(II) hydroxide¹¹ combined with the modified sol-gel procedure for uranium(V) hydroxide proposed earlier¹² were employed.

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EXPERIMENTAL

Preparation of nickel(II) hydroxide

Nickel(II) hydroxide was prepared by precipitation from aqueous solutions of analytical grade nickel(II) chloride (Hopkin and Williams Ltd., England) and sodium hydroxide (Merck Co., Darmstadt), under the conditions described earlier¹¹. The preparation was based on very slow drop by drop addition (approximately 30 min) of 1 M sodium hydroxide, to a vigorously stirred 0.2 M nickel(II) chloride.

The freshly prepared nickel(II) hydroxide suspension was washed four or five times combined with centrifugation with doubly distilled water to remove any excess of chloride ions.

Deionisation of suspension

The deionisation of nickel(II) hydroxide suspension was carried out by electro-dialysis in a specially designed three compartment cell described earlier¹¹⁻¹³, with only small modifications. Two plexiglass cells suitable for laboratory preparations were used. The volume of the central compartment was 75 ml and the other 1100 ml. The central compartment was divided from the cation and anion compartments and its platinum electrodes by cation and anion exchange membranes (Zeolit »Permaplex« C-20 and A-20, Water Softeners Ltd., England). The active exchange area per membrane was 32 and 144 cm² for the small and the large cell, respectively. The central compartment contained a nickel(II) hydroxide suspension which was continuously stirred while the side compartments contained only slightly alkaline water.

The electro-dialysis was carried out by employing a constant current source at the maximum current density at the membrane of 0.2 mA cm⁻². The electro-dialysis usually lasted up to 72 hours after which the specific conductivity of the supernatant liquid was less than $2 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$.

Preparation of stable sol

Attention was paid to find out suitable conditions at which nickel(II) hydroxide is a stable sol. It was desirable to achieve the stability of the purified sol without any additions of the stabilizing agents recommended in literature¹⁴⁻¹⁸. Therefore the deionised suspension of nickel(II) hydroxide was heated up to 70 °C and vigorously stirred for at least two hours, always taking care not to allow peptization to occur. The sol was then concentrated up to 1.8 M on a rotating vacuum evaporator thermostated at 30 °C. The concentrated sol showed thixotropic characteristics, and accordingly the evaporation was carried out intermittently, the intervals being used for vigorous shaking of the sol to achieve fluidity. Fig. 1. is an electron micrograph of a stable sol.

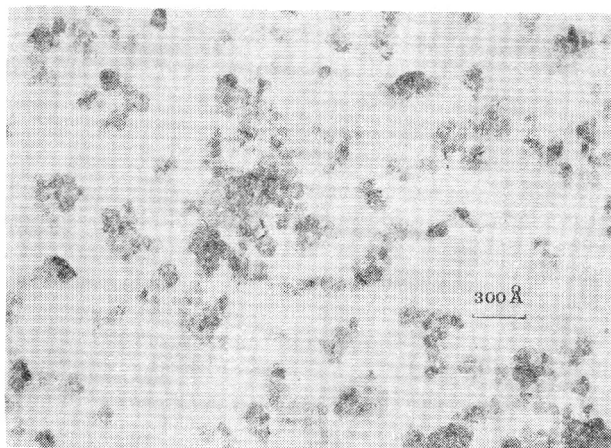


Fig. 1. Electron micrograph of the stable sol of nickel(II) hydroxide produced at room temperature. The average particle size is 100 Å and more.

Transformation from sol to gel

The transformation of nickel(II) hydroxide to nickel(II) hydroxide gel micro-spheroids of definite size and shape distribution occurred when a thin jet of concentrated sol was introduced at the top of a column with the counter current flow of an organic dehydrating solvent. The sol was dispersed to fine particles and gel micro-spheroids were formed during the fall through the column.

The apparatus consists of a glass column and a dispersion system both supplied by peristaltic pumps as shown in Figs. 2 and 3. The dispersion system employed consists of a set of capillaries through which the sol is driven into the column. The dimensions of the micro-spheroids were determined by the flow rate of the hydroxide sol through the capillaries and also by controlling the rate of drop detachment.

Two dimensions of glass columns were used. The smaller one, height 110 cm and diameter 9.5 cm, for laboratory experiments and the semi-industrial type of a column, height 476 cm and diameter 20 cm.

Mixtures of long-chain alcohols a) »Alphanol« 79 (Shell, Germany) — mixed normal primary and α -methyl substituted primary aliphatic alcohols, with some

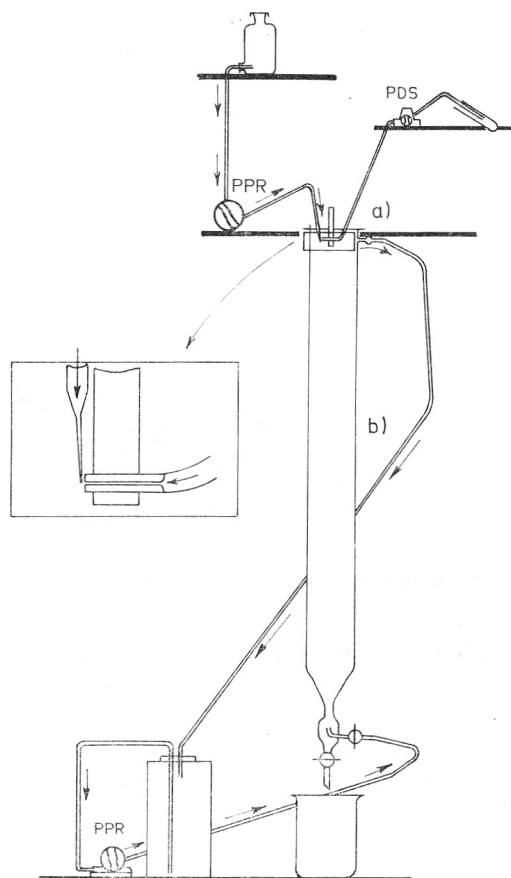
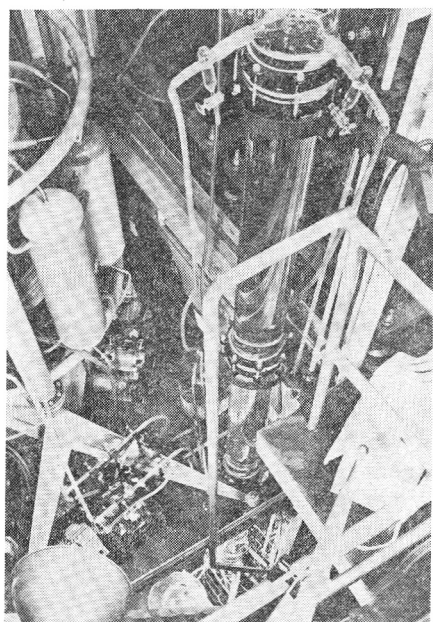


Fig. 2. Photograph of the apparatus used for preparation of nickel(II) hydroxide micro-spheroids.

Fig. 3. Schematic diagram of the apparatus used for preparation of nickel(II) hydroxide micro-spheroids: a) the dispersion system, b) the column and the flow chart; PPR-peristaltic circulation pumps, DPS-sol dosage pump. Insert shows capillaries for drop production.

saturated cyclic alcohols and b) »Nonanol« (Shell, Germany) — essentially 3,5,5-trimethylhexanol-1, were used as dehydrating solvents.

The particles should float in the organic solvent for at least three hours. The floating of the particles through the column is determined by the rate of the counter current flow of the organic solvent which could be easily adjusted.

When the drag of the counter current flow is less than the gravitational force acting on the particles, the dehydration is considered to be slow, and the particles form clusters instead of micro-spheroids. Therefore the recirculation should be adjusted to keep the particles floating.

Also the choice of dehydrating solvent plays an important role. Better results were achieved when »Nonanol« was used, as its total water absorption is 2 times larger than that of »Alphanol« 79.

Gel micro-spheroids thus obtained were washed in petroleum ether and then dried at approx. 10^{-3} Torr (1 Torr = 101.325/760 kPa) for few hours.

CHARACTERIZATION OF THE MICRO-SPHEROIDS

The nickel(II) hydroxide micro-spheroids obtained by the procedure described are spherical particles of a light green colour and are stable in air. The micrograph of the sample is given in Fig. 4.

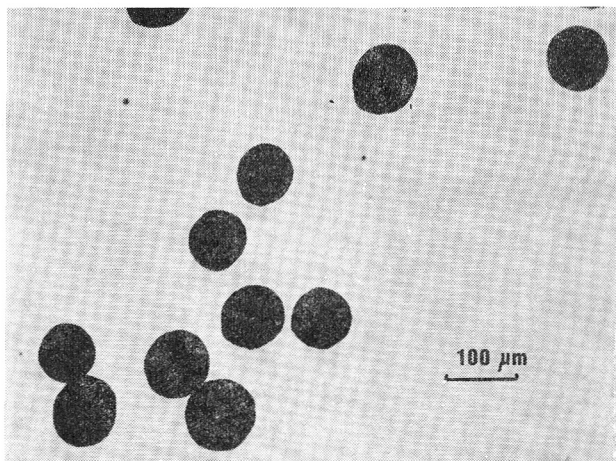


Fig. 4. Micrograph of nickel(II) hydroxide micro-spheroids dried at 10^{-3} Torr in air. The average particle diameter is 120 μm .

Chemical analysis of the micro-spheroids

An elemental carbon and hydrogen analysis was performed to determine the quantity of the organic dehydrating agent left on the surface of the micro-spheroids. The analysis gave 2.7% w/w carbon and 2.5% w/w hydrogen. These impurities were removed in further transformation procedure of nickel(II) hydroxide to nickel(II) oxide by heating to 700 °C in air, as the further analysis showed 0.26% carbon and 0.12% hydrogen.

Preparation of nickel(II) oxide micro-spheroids

The preparation was carried out by employing the heating procedure proposed earlier^{1,2}. The process runs continuously and can easily be followed through the change of colour of the sample, as the light green colour, charac-

teristic for nickel(II) hydroxide is changed to the grey one of nickel(II) oxide. The temperature at which the transformation begins was observed to be 230 °C while the transformation is complete at 715 °C.

Granulometric analysis of the samples

The size distribution of the particles was determined by granulometric analysis using a standardized sieve set (Soiltest Inc., Chicago). Different sizes of the micro-spheroids obtained are shown in Fig. 5.

Infrared analysis and X-ray spectrum

Infrared spectra of nickel(II) hydroxide micro-spheroids and nickel(II) oxide micro-spheroids incorporated in KBr pellets were run on a Perkin Elmer 137 spectrometer.

The characteristic spectrum of nickel(II) hydroxide is observed although the minor CH-impurities are observed as a band at $\sim 3000 \text{ cm}^{-1}$. On the contrary, the spectrum of nickel(II) oxide obtained from nickel(II) hydroxide micro-spheroids shows that all of impurities are eliminated.

The X-ray analysis was carried out on a Philips Diffractometer PW 1010/30 with $\text{CuK}\alpha$ beam.

The powder method was employed to indicate the degree of crystallinity of the samples prepared. The x-ray analysis of nickel(II) micro-spheroids was compared with the analysis of the crystalline sample of nickel(II) hydroxide¹⁹.

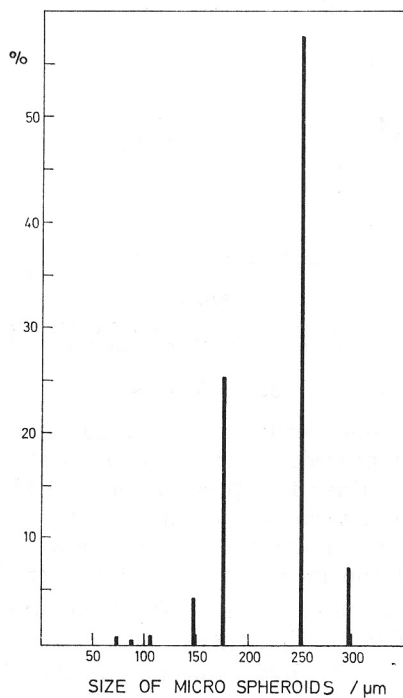


Fig. 5. Diagram showing the particle size distribution after the granulometric classification of nickel(II) hydroxide micro-spheroids.

The characteristic reflexes for crystallinity of nickel(II) hydroxide are only poorly evident in the case of our sample, which indicates our sample as amorphous.

Determination of specific surface area of micro-spheroids

The specific surface area of micro-spheroids was determined by argon gas adsorption using the BET method²⁰. The typical value found was $75 \text{ m}^2\text{g}^{-1}$ for particles of 150 to 250 μm in diameter. The complete adsorption isotherm (Fig. 6) for argon shows essentially an absence of hysteresis and consequently the samples have no micropores. Further adsorption studies are in progress.

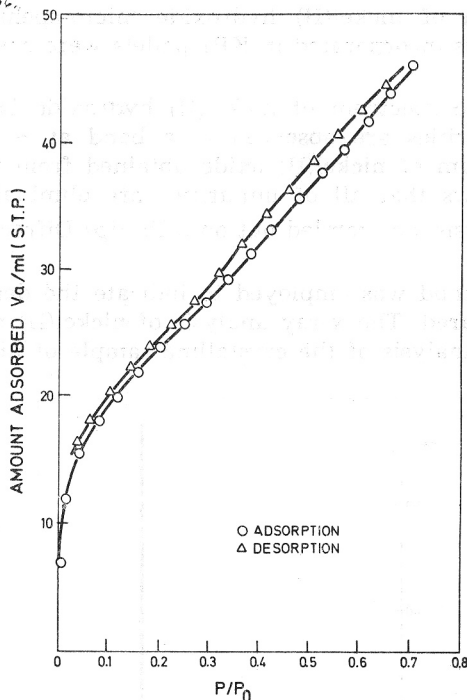


Fig. 6. The adsorption isotherm for argon on nickel(II) hydroxide micro-spheroids of 115 to 250 μm in diameter and of a specific surface area of $75 \text{ m}^2/\text{g}$.

CONCLUSIONS

Nickel(II) hydroxide micro-spheroids were obtained by employing a rather simple, modified sol-gel procedure. The controlled slow precipitation method was preferred over the rather fast preparation procedures proposed earlier¹¹.

Comparatively pure material was obtained in the sol form as no stabilizing agents were added. Electrodialysis has been shown to proceed successfully at a current density at the membrane of 0.2 mA cm^{-2} .

Transformation of a stable sol was shown to proceed best in a column filled with nonanol as dehydrating agent.

An advantage of nickel(II) hydroxide micro-spheroids is that the particles are of definite size and have defined specific surface area what enables further use in adsorption and surface investigations. The particles are compact and

micropores are absent which could be an advantage when the pellets of microspheroids, or pressed electrodes are prepared.

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IZVOD

Sol-gel-postupak za pripremu mikrosferoida niklova(II) hidroksida

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Opisan je postupak za pripremu mikrosferoida niklova(II) hidroksida određene veličine i oblika. Postupak se sastoji od dvije faze: u prvoj se priprema sol $Ni(OH)_2$ nizom operacija (taloženje, centrifugiranje, ponovno suspendiranje i elektrodijaliza), a u drugoj se sol pretvara u gel, u koloni kroz koju se u protustruji pušta dehidrirajućí dugolančani alkohol. Prikladnim izborom brzina protoka sola i dehidrirajućeg sredstva mogu se pripremiti sferne čestice raznih promjera, od 0,1—0,3 mm.

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