Preparation and characterization of nanosized nickel oxide

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Nanosized nickel oxide was synthesized by a simple liquid-phase process to obtain the hydroxide precursor and then calcined to form the oxide. The precursor and the nickel oxide were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), thermal analysis (TG) and temperature-programmed reduction (TPR). The results indicated that the particle size of nickel oxide was controlled by the calcined temperature \( T \). Mixed phases of nickel oxide and nickel hydroxide were present as the \( T \) was lower than 300 °C. Non-stoichiometric nickel oxide \( (\text{NiO}_x, x = 1.2) \) was formed between 250 °C and 400 °C and a pure nickel oxide was formed as the \( T \) arrived 500 °C. The particle size of nickel oxide changed as the calcined temperature was controlled under 250 °C, 300 °C, 400 °C and 500 °C, the order was 5.6 nm, 6.5 nm, 11 nm and 17 nm, respectively.

KEY WORDS: nickel oxide; nickel hydroxide; particle size.

1. Introduction

Nanosized materials, such as metal oxides have attracted much attention recently because of their unusual chemical and physical properties which are different from those of bulk materials [1–3]. In particular, nanosized nickel oxides, NiO, are widely used in many technological applications because they exhibit particular catalytic [4,5], anomalous electronic [6,7] and magnetic [8, 9] properties. Another important application of NiO is in a battery system [10,11]. Non-stoichiometric nickel oxide is a good P-type semiconductor owing to its defect structure [12] and it is also a potential gas sensor for \( \text{H}_2 \) [13]. These applications can be enhanced by decreasing the particle size, preferably to less than 10 nm, and are highly dependent on particle size; the precise control of the size and distribution in a nanometer regime is required.

Techniques for the nano-scale particle preparation have been developed in the last years [14–16]: The chemical routes are widely used to produce a powder product owing to its relative simplicity and its low energy consumption. The present investigation is an attempt towards better controlling the preparation of non-stoichiometric nickel oxide \( (\text{NiO}_x) \). For this purpose we choose a simple liquid-phase process to obtain the hydroxide precursor and then have it calcined to form the oxide.

In this paper, we report the thermal behavior of \( \text{Ni(OH)}_2 \) and \( \text{NiO}_x \) particles and the characterization of nanosized \( \text{NiO}_x \) particles (a controlled size in the 5–20 nm region). To accomplish this work object TG, XRD, IR and TPR are performed to characterize the obtained nickel hydroxide and nickel oxide.

2. Experimental

2.1. Catalyst preparation

Nanosized nickel oxide was synthesized by a simple liquid-phase process as follows: Using \( \text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) as precursor, the 0.6 M solution was heated and kept at 80 °C, then with a magnetic stirring, \( \text{NH}_4\text{OH} \) was added slowly into the solution until pH = 7 was attained. Here a green colloid solution was obtained which was filtered and washed several times with distilled water, then dried at 100 °C for 10 h to obtain the as-prepared precursor, \( \text{Ni(OH)}_2 \) powder. The powder was calcined separately at 250, 300, 400 and 500 °C respectively for 3 h to obtain the nickel oxide.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with Cu \( \text{K}_{\alpha 1} \) radiation \( (\lambda = 1.5405\text{Å}) \) at 40 kV and 30 mA with a scanning speed in 2θ of 4° min\(^{-1}\). The crystallite sizes of nickel hydroxide and nickel oxide were estimated using the Scherrer equation.

The infrared spectra were obtained by a Perkin Elmer spectrum GX spectrometer in the range of 1500–4000 cm\(^{-1}\). One milligram of each powder sample was diluted with 200 mg of vacuum-dried IR-grade KBr and subjected to a pressure of 8 tons.

Thermal gravimetric analysis (TG/DTG) was carried out using a Seiko SSC5000 TG system. The rate of heating was maintained at 10 °C min\(^{-1}\) and the mass of

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the sample was \( \sim 10 \) mg. The measurement was carried from RT to 800 \( ^\circ \)C under air flowing with a rate of 100 ml min\(^{-1}\).

Reduction behavior of nickel hydroxide and nickel oxide was studied by temperature-programmed reduction (TPR). About 50 mg of the sample was heated in a flow of 10\% \( \text{H}_2/\text{N}_2 \) gas mixture at a flow rate of 10 ml min\(^{-1}\). During TPR, the temperature was increased by 7 \( ^\circ \)C min\(^{-1}\) increments from room temperature to 700 \( ^\circ \)C.

3. Results and discussion

3.1. Characterization of the prepared nickel hydroxide

Figure 1 shows the XRD pattern of the as-prepared precursor, \( \text{Ni(OH)}_2 \). It indicates that all the major peak positions and relative intensities match the JCPDS 14-0117 file identifying \( \beta\)-\( \text{Ni(OH)}_2 \), with a hexagonal structure. The infrared spectrum of the as-prepared precursor is shown in figure 2. The spectrum displays a sharp peak at 3640 cm\(^{-1}\) and this confirms that the as-prepared precursor is \( \beta\)-\( \text{Ni(OH)}_2 \) [17]. This sharp peak in the OH stretching vibration is shown by \( \beta\)-\( \text{Ni(OH)}_2 \) because of the absence of hydrogen bonding between hydroxyl groups [18]. In addition to the stretching vibration of the OH bond, other extremely broad, diffuse bands centered around 3450 and 1630 cm\(^{-1}\) are assigned to the existence of water.

Figure 3 shows the TG/DTG curves for the decomposition of \( \text{Ni(OH)}_2 \) under a dynamic air (100 ml min\(^{-1}\)) environment. The TG curve shows three weight loss steps (assigned as D1, D2 and D3) and the DTG curve shows the maximum loss rate of a D2 step at 280 \( ^\circ \)C, while both the D1 and D3 steps are not obvious. Prior to 250 \( ^\circ \)C, the tardy weight loss should be came from desorption of water on \( \text{Ni(OH)}_2 \) surface in heating process. The weight loss of 16\% in step D2 is mainly caused by the dehydroxylation of \( \text{Ni(OH)}_2 \) to \( \text{NiO} \) (theoretical weight loss is 19.4\%) and accompanies the oxidation of \( \text{Ni}^{2+} \) to a higher oxidation state, \( \text{NiO}_x \) (where \( x \) is stoichiometry to be evaluated), according to equations 1 and 2.

\[
\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O} \tag{1}
\]
\[
\text{NiO} + (x - 1)/2\text{O}_2 \rightarrow \text{NiO}_x \tag{2}
\]
\[
\text{NiO}_x \rightarrow \text{NiO} + (x - 1)/2\text{O}_2 \tag{3}
\]

The deviation between an experimental and theoretical value may be the further oxidation of \( \text{Ni}^{2+} \) to a higher occurrence of an oxidation state. Obviously, only a little amount of the higher oxidation state exists. The weight loss of 4\% in step D3 should be caused due to the decomposition of an unstable \( \text{NiO}_x \) that changed into \( \text{NiO} \), as the temperature was above 290 \( ^\circ \)C according to equation 3. On combining this \( x \) value with the weight loss of D2 and D3 in Figure 3, a \( \sim 1.2 \) is therefore estimated.

Figure 4 shows the TPR profile of the as-prepared precursor, \( \text{Ni(OH)}_2 \). The reductive signal of \( \text{Ni(OH)}_2 \) in TPR proceeded by one step at 370 \( ^\circ \)C according to equation 4.

\[
\text{Ni(OH)}_2 + \text{H}_2 \rightarrow \text{Ni} + 2\text{H}_2\text{O} \tag{4}
\]

The ratio of nickel hydroxide species is quantitatively determined from the consumption of hydrogen in TPR traces. The \( N_{\text{H}_2}/N_{\text{Ni}} \) is 1.02.

![Figure 1. XRD pattern of the as-prepared precursor, \( \text{Ni(OH)}_2 \).](image-url)