A Simple Way to Prepare Nanosize NiO Powder by Mixing Acidic Ni Compound with Basic Ni Compound

Deock-Soo Cheong*, Dong Hun Yun**, Sang Hwan Park**, and Chang-Sam Kim***†

*Department of MATSE, Dankook University, Cheonan 330-714, Korea

**Division of MATSE, Korea Institute of Science and Technology, Seoul 136-791, Korea

***Battery Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

(Received October 5, 2009; Accepted October 26, 2009)

ABSTRACT

Nanosize NiO powder was prepared by mixing acidic nickel nitrate with basic nickel carbonate. The particle size and morphology of NiO were mainly governed by the mole ratio of the nitrate to the carbonate. The effects were studied by DSC, XRD, FTIR, and SEM. Heat treatment conditions influence the particle size distribution of produced NiO powder extensively for the case of 3N7C (3 moles of the nitrate and 7 moles of the carbonate) and 4N6C, but only slightly for 1N9C and 2N8C. Uniform pseudo-spherical NiO particles were obtained in 50~70 nm for 1N9C and 30~60 nm for 2N8C by calcination at 750°C for 2 h.

Key words : Nanosize NiO, Nickel nitrate, Basic nickel carbonate, Calcination effects, DSC

1. Introduction

NiO is an important inorganic material. It is extensively used in catalysis, electrochromic films, magnetic materials, gas sensors, cathodes of alkaline batteries, and anodes of solid oxide fuel cells (SOFC).¹⁻⁶⁾ There are many chemical methods reported for the synthesis of NiO particles, including the precipitation of acidic nickel salt such as NiCl_2 , $\text{Ni}(\text{NO}_3)_2$ or NiSO_4 with base such as NaOH, NH_4HCO_3 , $\text{CO}(\text{NH}_2)_2$, or ammonia,⁷⁻⁹⁾ forming nickel complex with ligands, such as oxalic acid, citric acid, malic acid, etc.,¹⁰⁻¹⁷⁾ using molten salt,^{18,19)} etc. All these methods are accomplished by the introduction of other chemicals, so the by-products have to be removed by filtration and washing.

If a basic metal compound can be used as a base instead of a common base, such as an ammonia solution or NaOH, then there will be no need to remove formed salts, which makes the process simple and economic.

In this paper we would like to introduce a simple way to prepare NiO powder by inducing reactions between acidic Ni precursor and basic Ni precursor by mixing, followed by calcination. We found it interesting that the ratio of the acid to the base governs the particle size and morphology of the produced NiO powder.

2. Experimental Procedure

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity 98.0% Aldrich Chem., U.S.A.) and

$2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2$ (purity 99.0% Aldrich Chem., U.S.A.) were used as received. The two nickel compounds were mixed at a mole ratio of the acid to the base of 1:9 (1N9C), 2:8 (2N8C), 3:7 (3N7C) and 4:6 (4N6C). The mixtures were prepared as aqueous slurries by ball milling for 8 h. The slurries were dried using a rotary evaporator and then subjected to calcination. Heat treatment conditions were varied and the effects were studied. The dried mixtures (~30 mg) were heated to 700°C in an alumina crucible at a heating rate of 10°C/min under flowing air using TG/DSC (Model STA 409C, Netzsch Co., Germany). The DSC of the 2N8C showed an endothermic peak at 308°C. The mixture was heated to its set-on and set-off temperatures and cooled rapidly to room temperature. The powders were subjected to XRD (Model DMAX IIa, Rigaku Co., Japan) and FTIR (Model 100 with ATR, Perkin-Elmer Inc., U.S.A) analysis. The powder morphology was observed by SEM (Model 3000M, Hitachi Co., Japan).

3. Results and Discussion

The strategy to prepare uniform NiO powder is derived from the following; i) NiO powder can be obtained by the calcination of almost any nickel compound in air.^{20,21)} ii) NiO powder obtained from the calcination of $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$ at 650°C for 2 h shows 50~100 nm cube crystals and that from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ consists of two kinds of cubic particles ranging from about 100 nm to 800 nm in size, which indicates that there are two kinds of growing modes,²²⁾ and iii) acidic nickel nitrate can react with basic nickel carbonate via the Lewis acid-base interaction. If the proper amount of the nickel nitrate is introduced to the nickel carbonate to control the growing mode of *in-situ* formed NiO particles, uni-

†Corresponding author : Chang-Sam Kim

E-mail : cskim@kist.re.kr

Tel : 82-2-958-5483 Fax : +82-2-958-5548

Fig. 1. DSC curves of NiO precursors of: (a) 1N9C, (b) 2N8C, (c) 3N7C, and (d) 4N6C heated in an alumina crucible at a heating rate of 10°C/min under flowing air.

Fig. 2. DSC curves of: (a) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (b) $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2$ heated in an alumina crucible at a heating rate of 10°C/min under flowing air.

form spherical nanosize NiO powder may be obtained.

Thus, the nickel compounds were mixed at various mole ratios and their DSC curves are shown in Fig. 1. Comparing their curves with those of the carbonate and the nitrate shown in Fig. 2, considerable differences were observed. The nickel carbonate shows two endothermic peaks at ~100 and 305°C and the nitrates four endothermic peaks at 68, 187, 253, and 325°C. However, the mixtures show new peaks. 1N9C and 2N8C show a single new strong endothermic peak at 302°C and 308°C, respectively, but 3N7C shows two endothermic peaks around 222 and 305°C and 4N6C at 211

Fig. 3. XRD patterns of the 2N8C precursor heated to various temperatures of its DSC curve and then cooled rapidly to ambient temperature: (a) 280°C, (b) 370°C, and (c) 430°C.

and 310°C. Both of them show a shoulder peak around 326°C, which indicates that some of the nitrate remained. The single peak for 1N9C and 2N8C indicates that almost no nitrate or the carbonate remains. The 2N8C mixture was heated to the set-on and set-off temperatures of its DSC curve without holding at a heating rate of 10°C/min and were cooled rapidly, and their XRD patterns are shown in Fig. 3. NiO was not formed by 280°C but by 370°C, and further heating to 430°C increased the intensity slightly, which is assigned as a cubic phase (JCPDS card file 73-1523). However, their FT-IR shown in Fig. 4 indicates that there is $\text{Ni}(\text{OH})_2$ due to the presence of peaks around 3500 and 1630 cm^{-1} assigned to O-H stretching and bending, respectively. Therefore the endothermic peaks around 310°C are attributed to the formation of crystalline NiO and amorphous $\text{Ni}(\text{OH})_2$, and this is also supported by the dark grey color.

The mixtures were heated to 750°C at a heating rate of 5°C/min and then held at that temperature for 2 h. Their SEM pictures shown in Fig. 5 indicate that calcined 1N9C and 2N8C show homogeneous pseudo spherical particles with an average particle size of ~50 nm and ~70 nm, respectively, but 3N7C and 4N6C consists of two kinds of particles: small spherical particles and large cubic crystals, which was attributed to the free nickel nitrate that was not fully dissipated the heat due to the rapid heating rate. Thus, the mixtures were heated to 200°C at a heating rate

Fig. 4. FTIR spectra of the 2N8C samples heated to various temperatures as in Fig. 3 (a) 280°C, (b) 370°C, and (c) 430°C.

Fig. 5. SEM pictures of the various NiO precursors of: (a) 1N9C, (b) 2N8C, (c) 3N7C, and (d) 4N6C heated to 750°C at a heating rate of 10°C/min and held at that temperature for 2 h.

of 5°C/min and then at 1°C/min to 450°C and held at that temperature for 2 h. Their SEM pictures in Fig. 6 show that 1N9C and 2N8C are homogeneous and ~20 nm, but 3N7C consists of mainly ~50 nm and a few ~150 nm cubes, 4N6C shows 200~300 nm cubic crystals with some ~20 nm particles. It is assumed that nanosize NiO particles grow into large crystals assisted by the Ni nitrate somehow. It is interesting that 4N6C shows more cubic particles for the calcined mixture at 450°C than that at 750°C but the cube sizes are almost same. It is believed that the cubic particles

Fig. 6. SEM pictures of the various NiO precursors of: (a) 1N9C, (b) 2N8C, (c) 3N7C, and (d) 4N6C heated to 450°C at various heating rates and held at that temperature for 2 h.

Fig. 7. SEM pictures of the various NiO precursors as heated in Fig. 6 and then further heated to 750°C at a heating rate of 2°C/min and held at that temperature for 2 h.

are grown at 450°C and are hardly influenced by higher calcination temperature. In the hope of obtaining uniform particles, the mixtures were held at 450°C for 2 h and then heated to 750°C at a heating rate of 2°C/min and held at the temperature for 2 h. The SEM pictures shown in Fig. 7 are well-grown crystals and more uniform for all the combina-

tions. The 1N9C and 2N8C provide pseudo spherical particles with sizes of 50~70 nm and 30~60 nm, respectively, which are not greatly influenced by either heating rate or by calcination temperature. However, 3N7C shows particles of ~80 nm with a few ~150 nm particles and the 4N6C show well grown cubic particles of ~150 nm with some larger cubes and some aggregates. The crystals had smoother surface than those calcined at 450°C but the size remained almost same. This proves that the growth is limited by their combination, and the slow heating contributes to suppress the fast coalescence of small particles to result in more uniform growth.

The above observations reveal that a proper combination like 1N9C and 2N8C can produce uniform nanosize NiO particles. This simple approach can be applied to the preparation of other metal oxides.

4. Conclusions

Nano size NiO powder was prepared by simply mixing acidic nickel nitrate with basic nickel carbonate and followed by calcination. The mole ratio of the acid to the base governs the morphology and size distribution of the formed NiO powder. The proper mole ratio, 2N8C, provided pseudo spherical NiO powder in 30~60 nm by heat treatment at 750°C for 2 h.

Acknowledgment

We are grateful for the financial support by the Korea Energy Management Corporation under grant 2008-N-FC12-J-03-3-040.

REFERENCES

1. C. L. Camer and K. J. Klabunde, "The Catalytic Methanol Synthesis Over Nanoparticle Metal Oxide Catalysts," *J. Mol. Catal. A. Chem.*, **194** 227-36 (2003).
2. J. R. Sohn and J. S. Han, "Physicochemical and Catalytic Properties of NiO-TiO₂ Modified with WO₃ for Ethylene Dimerization," *Appl. Catal. A Gen.*, **298** 168-276 (2006).
3. E. L. Miller and R. E. Rocheleau, "Electrochemical Behavior of Reactively Sputtered Iron-Doped Nickel Oxide," *J. Electrochem. Soc.*, **144** [9] 3072-77 (1997).
4. M. Yoshio, Y. Todorov, K. Yamato, H. Noguchi, J. Itoh, M. Okada, and T. Mouri, "Preparation of Li_xMn_xNi_{1-x}O₂ as a Cathode for Lithium-ion Batteries," *J. Power Sources*, **74** 46-53 (1998).
5. V. Biju and M. A. Khadar, "Analysis of AC Electrical Properties of Nanocrystalline Nickel Oxide," *Mater. Sci. Eng., A*, **304** 814-17 (2001).
6. F. Tietz, F. J. Dias, D. Simwonis, and D. Stover, "Evaluation of Commercial Nickel Oxide Powders for Components in Solid Oxide Fuel Cells," *J. Euro. Ceram. Soc.*, **20** 1023-34 (2000).
7. X. Deng and Z. Chen, "Preparation of Nano-NiO by Ammonia Precipitation and Reaction in Solution and Competitive Balance," *Mater. Lett.*, **58** 276-80 (2004).
8. F. Porta, S. Recchia, C. Bianchi, F. Confalonieri, and G. Scari, "Synthesis and Full Characterisation of Nickel(II) Colloidal Particles and Their Transformation Into NiO," *Colloids Surf (A): Physicochem. Eng. Aspects*, **155** 395-404 (1999).
9. X. Xin, Z. Lu, B. Zhou, X. Huang, R. Zhu, X. Sha, Y. Zhang, and W. Su, "Effect of Synthesis Conditions on the Performance of Weakly Agglomerated Nanocrystalline NiO," *J. Alloys and Compd.*, **427** 251-55 (2007).
10. L. Xiang, X. Y. Deng, and Y. Jin, "Experimental Study on Synthesis of NiO Nano-particles," *Scripta Mater.*, **47** 219-24 (2002).
11. X. M. Liu, X. G. Zhang, and S. Y. Fu, "Preparation of Urchinlike NiO Nanostructures and Their Electrochemical Capacitive Behaviors," *Mater. Res. Bull.*, **41** 620-27 (2006).
12. C.-J. Li, X.-X. Huang, Y. Shi, and J.-K. Guo, "Preparation and Characteristics of Nanocrystalline NiO by Organic Solvent Method," *Mater. Lett.*, **51** 325-30 (2001).
13. B. Malecka, A. Malecki, E. Drozd-Ciesla, L. Tortet, P. Llewellyn, and F. Rouquerol, "Some Aspects of Thermal Decomposition of NiC₂O₄·2H₂O," *Thermochim. Acta*, **466** 57-62 (2007).
14. Y. Wu, Y. He, T. Wu, T. Chen, W. Weng, and H. Wan, "Influence of Some Parameters on the Synthesis of Nanosized NiO Material by Modified Sol-gel Method," *Mater. Lett.*, **61** 3174-78 (2007).
15. Q. Li, L.-S. Wang, B.-Y. Hu, C. Yang, L. Zhou, and L. Zhang, "Preparation and Characterization of NiO Nanoparticles Through Calcination of Malate Gel," *Mater. Lett.*, **61** 1615-18 (2007).
16. Y. Wang, C. Ma, and X. Sun, "Preparation of Nanocrystalline Metal Oxide Powders with the Surfactant-mediated Method," *Inorg. Chem. Commun.*, **5** 751-55 (2002).
17. T. Sreethawong, S. Chavadej, S. Ngamsinlapasathian, and S. Yoshikawa, "A Modified Sol-gel Process-derived Highly Nanocrystalline Mesoporous NiO with Narrow Pore Size Distribution," *Colloids Surf (A): Physicochem. Eng. Aspects*, **296** 222-29 (2007).
18. E. I. Eweka and D. H. Kerridge, "Molten Sodium Nitrite-sodium Nitrate-potassium Nitrate Eutectic: The Reactions and Spectra of Iron(III), Cobalt(II), Nickel(II) and Copper(II) compounds," *Thermochim. Acta*, **290** 133-38 (1996).
19. Y. Wang, J. Zhu, X. Yang, L. Lu, and X. Wang, "Preparation of NiO Nanoparticles and Their Catalytic Activity in the Thermal Decomposition of Ammonium Perchlorate," *Thermochim. Acta*, **437** 106-9 (2005).
20. C. Popescu, I. Ursu, M. Popescu, R. Alexandrescu, I. Morjan, I. N. Mihailescu, and V. Jianu, "Specific Features of Nickel Oxides Obtained by Thermal and Laser Induced Decomposition of Nickel Salts. A Comparative Study," *Thermochim. Acta*, **164** 79-90 (1990).
21. W. Brockner, C. Ehrhardt, and M. Gjika, "Thermal Decomposition of Nickel Nitrate Hexahydrate, Ni(NO₃)₂·6H₂O, in Comparison to Co(NO₃)₂·6H₂O and Ca(NO₃)₂·4H₂O," *Thermochim. Acta*, **456** 64-68 (2007).
22. Y. Li, Z.-y. Luo, C. Yu, D. Luo, Z. Xu, and K. Cen, "The Impact of NiO on Microstructure and Electrical Property of Solid Oxide Fuel Cell Anode," *J. Zhejiang Univ. SCI.*, **6B** 1124-29 (2005).