Preparation and thermal decomposition of basic nickel carbonates

Olga Aleksandrova

Abstract. Among the known nano-sized materials, ultrafine metal oxides, in particular nickel oxide, which is currently used as semiconductors, are of particular interest; sensor elements of gas sensors; ferrite components; as anode materials in electrochemical devices and solid oxide fuel cells; and also as a catalytically active component of catalysts in a number of chemical syntheses. Currently, various methods are known for producing powder nanosized oxides, one of them is the method of thermal decomposition of oxygen-containing inorganic compounds. The use of basic metal carbonates as a starting reagent is preferable, from an environmental point of view, compared to other salts. The production of ultrafine nickel oxide powders by thermolysis of basic salts does not require the use of complex equipment, and the return of carbon dioxide and water vapor back into the cycle makes it possible to make the technological scheme low-waste.

Purpose of the work. Production of basic nickel carbonate (BNC) of constant stoichiometric composition using ammonia-carbonate technology and its subsequent thermal decomposition.

Research objectives:

– determination of the conditions for the maximum degree of dissolution of nickel hydroxide in ammonium carbonate aqueous solutions, depending on the initial concentrations and molar ratios of ammonium bicarbonate and an aqueous solution of ammonia in the reaction mixture and the time of dissolution, the temperature of the process;

– synthesis of basic nickel carbonate of constant stoichiometric composition by hydrothermal method and investigation of the process of its thermal decomposition with the formation of ultrafine nickel oxide by thermogravimetry, X-ray phase analysis and transmission electron microscopy;

– obtaining empirical dependences of the standard Gibbs energies of the formation of basic metal carbonates (OCM) $\Delta fG°(298)$ on the sum of the standard Gibbs energies of formation $\Sigma\Delta fG°(298)$ of their structural parts by comparative calculation;

– development of a method for impregnating an inert carrier with a nickel-containing solution of nickel ammonia complexes to obtain a catalytically active nickel oxide layer of a given thickness;

– development of a technological scheme for the stages of synthesis and thermal decomposition of basic nickel carbonate to obtain ultrafine nickel oxide powders as a finished product.

Scientific novelty of the work.

1. For the first time, the solubility of coarse nickel hydroxide in an ammonia-carbonate aqueous solution was studied depending on the initial concentrations and molar ratios of NH_4HCO_3 and $NH_3 \cdot H_2O$ in the reaction mixture, as well as time (10-60 min) and temperature (20, 30 and 40 °C).

2. Thermodynamic calculations of quantitatively significant equilibrium forms were performed: HCO_3^-, $NH_3 \cdot H_2O$, H_2CO_3, NH_4^+, OH^- in the reaction mixture and a stoichiometric equation of the reaction of dissolution of $Ni(OH)_2$ in a solution of NH_4HCO_3 and $NH_3 \cdot H_2O$ was proposed.

3. A mechanism is proposed and constants of the rate and activation energy of the $Ni(OH)_2$ dissolution process in ammonium carbonate aqueous solutions at temperatures of 20, 30 and 40 °C. are calculated.

4. The empirical dependence of the standard Gibbs energies of the formation of basic metal carbonates $\Delta fG°(298)$ was obtained and the standard Gibbs energies of the formation of basic nickel carbonates of various stoichiometric composition, which are absent in thermodynamic databases, were calculated.

5. The scientific foundations of $Ni_2(OH)_2CO_3$ synthesis have been developed of stoichiometric composition from solutions of aqua-ammonia nickel complexes, providing the production of ultrafine NiO powder with a narrow size distribution of spherical particles (d = 10-11 nm).

Theoretical and practical significance of the work. The conditions of synthesis using the ammonia-carbonate technology of the OCN stoichiometric composition $Ni_2(OH)_2CO_3$ have been determined. The temperature range of the thermolysis process of WINDOWS has been established, providing the formation of NiO with an average particle size of 10-11 nm. A technological scheme for the production of ultrafine nickel oxide, operating in a closed cycle, has been developed.

The results obtained can be used in the production of nickel oxide catalysts at the following enterprises: Ekat LLC, NIAP-CATALYZER LLC, Angarsk Plant of Catalysts and Organic Synthesis OJSC, TsTK-EVRO CJSC, HaldorTopsoe, as well as in battery systems: LLC "InEnergy", LLC "World of Batteries", LLC

"Kursk Battery Plant" and in the production of anodes for solid oxide fuel cells at JSC "NEVZ-CERAMICS", JSC "Chepetsk Mechanical Plant", LLC "International Energy Saving Corporation", LLC "IntechGmbH".

The practical significance of the work is confirmed by the issuance of the Russian Federation patent for invention No. 2630956, date of receipt: 09/06/2016, release date: 09/15/2017.

The following provisions are submitted for protection:

1. The results of physico-chemical methods for studying the processes of dissolution of nickel hydroxide in ammonium carbonate aqueous solutions, depending on the initial concentrations and molar ratios of ammonium bicarbonate and aqueous ammonia solution in the reaction mixture, as well as on the time of dissolution and the temperature of the process.

2. The results of the synthesis of a precipitate of basic nickel carbonate of constant stoichiometric composition by hydrothermal method and the study of the process of its thermal decomposition with the formation of ultrafine nickel oxide by thermogravimetry, X-ray phase analysis and transmission electron microscopy.

3. A method for impregnating an inert carrier with a nickel-containing solution of nickel ammonia complexes to obtain a catalytically active layer of a given thickness and a catalytically active nickel oxide formed on the surface of the inert carrier.

4. Technological scheme of the stages of synthesis and thermal decomposition of basic nickel carbonate to obtain ultrafine nickel oxide powders as a finished product.