Combustion modes during the synthesis of ZnO from aqueous solutions of zinc nitrate with various fuels

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Recently, much attention has been paid to the study of a simple, energy-saving method for producing nanopowders of oxides, promising for industrial use, based on the synthesis during combustion of reagent solutions of highly exothermic redox reactions (Solution Combustion Synthesis – SCS) [1, 2]. In the case of the synthesis of zinc oxide nanopowder ZnO, the most common use is as an oxidizer of zinc nitrate $Zn(NO_3)_2$, and as a fuel of urea $CO(NH_2)_2$, glycine $C_2H_5NO_2$ or citric acid $C_6H_8O_7$, which are soluble in water, have low decomposition temperatures, are available and inexpensive [3, 4]. The equations of ZnO synthesis reactions using these fuels have the following form:

$$Zn(NO_3)_2+\frac{5}{3}\varphi CO(NH_2)_2+\frac{5}{2}(\varphi-1)O_2=ZnO+\frac{10}{3}\varphi H_2O+\frac{5}{3}\varphi CO_2+(\frac{5}{3}\varphi+1)N_2, \quad (1)$$

$$Zn(NO_3)_2+\frac{10}{9}\varphi C_2H_5NO_2+\frac{5}{2}(\varphi-1)O_2=ZnO+\frac{25}{9}\varphi H_2O+\frac{20}{9}\varphi CO_2+(\frac{5}{9}\varphi+1)N_2, \quad (2)$$

$$Zn(NO_3)_2+\frac{5}{9}\varphi C_6H_8O_7+\frac{5}{2}(\varphi-1)O_2=ZnO+\frac{20}{9}\varphi H_2O+\frac{10}{3}\varphi CO_2+N_2. \quad (3)$$

In these equations, the dimensionless criterion φ, characterizing the ratio of fuel and oxidizer, shows whether excess oxygen is released or, conversely, the oxygen missing for complete oxidation of the elements is consumed from the surrounding gas environment during synthesis in combustion of reagents aqueous solution. This paper presents the results of an experimental study of the types and characteristics of combustion during the solution synthesis of ZnO nanopowder according to equations (1)-(3) when heating a vessel with the solution on a hot plate. First, there is a relatively slow process of heating the solution from the initial temperature to the boiling point and subsequent boiling off of the main amount of solvent, as a result of which a viscous mixture of reagents (gel) is formed. Then the temperature of the gel increases rapidly due to the beginning of a chemical reaction with intense heat and gas release, which leads to various types of combustion: 1) flameless combustion without the formation of luminous zones, 2) smoldering with the formation of focus and frontal luminous zones, 3) spontaneous ignition and slow volumetric combustion with the formation of flame, 4) spontaneous ignition and very rapid explosive combustion with the formation of flame. In the first three cases, combustion leaves behind a loose or dense cake of solid combustion products in the vessel, and in the fourth case, explosive combustion leads to the ejection of the reacting mixture and combustion products from the vessel, so that practically nothing remains in the vessel. For the used fuels, along with combustion type determination, such combustion characteristics were found as: 1) delay time of the combustion start, 2) duration of combustion, 3) the coefficient of conservation of the mass of the product as the ratio of the mass of the combustion product remaining in the reaction vessel after the experiment to the theoretical mass of the product calculated by the reaction equation. Combustion types and characteristics dependences on the value of the criterion φ, the volume (layer thickness) of the solution and the heating rate of the solution on the hot plate were determined.

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