Technological theory of nanometer-ZnO production in industry

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Abstract

In terms of chemical engineering theory, the operating domain of nanometer ZnO production has been analyzed in detail by means of uniform precipitated method. The reacting system of ZnO production is a complicated system with series, parallel, reversible, and multiphase reactions. The author finds that the independent reaction number is 6. The free degree of the reactions is 7. The proportional ratio of reactants is $C_{(CO(NH_2)_2)}$:$C_{(Zn(NO_3)_2)} \geq 3.5 : 1$. The operating domain is illustrated by the proportional concentrations $CO(NH_2)_2$: $Zn^{2+} = 1 : 2.5$; Zn^{2+}:H_2O=1:11; $CO(NH_2)_2$:H_2O=1:3. The value of pH is key factor of the reaction system and a better pH value is 6.5. Other key factors are temperature and time of the reactions.

Keywords: nanometer ZnO, industrial production of nano-ZnO, uniform precipitated method, operating domain, chemical equilibrium, phase equilibrium, reaction production of ZnO, and technical skill of ZnO production.

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1 Introduction

Nanometer ZnO is one of the most important chemicals and functional materials. It has better properties of sound, light, electricity, magnetism, mechanics as well as chemical

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catalysis[1,2]. Nowadays research is mainly focusing on the study of micro ZnO structures[3,4,5]; preparation of ZnO in laboratory[6,7,8,9]; properties of ZnO measurement[7,10,11]; capabilities of ZnO applications[12,13,14] among others. How to realize industrial production of nanometer ZnO on a large scale remains an area less investigated up to now. This paper reports on a study on the industrial production of ZnO by uniform precipitated method in liquid. In terms of analysis of reacting system of ZnO production, the author illustrates the process of ZnO production and the industrial operating domain of ZnO production. The study enhances the technical method for the production of nanometer ZnO on an industrial scale.

1.1 Uniform precipitated method in liquid

Uniform precipitated method is a good procedure for preparing nanometer ZnO in a liquid state, in which crystal ion of reactant can be lured to release slowly and uniformly from the liquid and to form nanometer particles. It was first and respectively reported in the year 1937, by two chemists, a Chinese Tang Yongkang and American Willard[15]. The method has a number of advantages: First, the precipitator, such as $CO(NH_2)_2$ or $C_6H_{12}N_4$, does not directly react with precipitated component of reactants. Second, the reacting conditions of this method are mild and easily controlled. Third, the size of product particles distributes uniformly[7]. In uniform precipitated method, the first step of precipitation is the key of controlling morphology of particles; the second step of ZnO precursor decomposed is the key approach of controlling particle size[16,17]. None but the two steps combine together in harmony, the proper ZnO particles in morphology and size could be obtained. In this paper, $CO(NH_2)_2$ is used as precipitator in the chemical reactions. The following are the reacting stoichiometric equations[7,15,18]:

$$CO(NH_2)_2 + 3H_2O = CO_2 + 2NH_3 \cdot H_2O \tag{1}$$

$$CO_2 + H_2O = H_2CO_3 = CO_3^{2-} + 2H^+ \tag{2}$$

$$NH_3 \cdot H_2O = NH_4^+ + OH^- \tag{3}$$

$$Zn^{2+} + 4NH_3 = [Zn(NH_3)_4]^{2+} \qquad K_{\text{steady}} = 2.88 \times 10^9 \tag{4}$$

$$Zn^{2+} + OH^- = Zn(OH)_2 \qquad K_{sp} = 7.71 \times 10^{-17} \tag{5}$$

$$Zn^{2+} + CO_3^{2-} = ZnCO_3 \qquad K_{sp} = 1.19 \times 10^{-10} \tag{6}$$

$$Zn(OH)_2 = ZnO + H_2O \tag{7}$$

$$ZnCO_3 = ZnO + CO_2 \tag{8}$$

where K_{steady} is called stability constant of reaction, and K_{sp} is called solubility product constant of reaction. For ①,②,③ reactions, the stoichiometric equations can be regarded as parallel hydrolyzed reactions of $CO(NH_2)_2$. Equations ④,⑤,⑥ are parallel reactions for compound of ions forming products. When the reactions mentioned above occur within the same time, serial reactions appear between equation ① and ④, ② and ⑥, ③ and ⑤. Equations ⑦ and ⑧ are parallel decomposed reactions in state of solid phase under higher temperature, which is 350°C[16]. In reality the formula of reaction ⑦ and ⑧ should be $Zn_5(CO_3)_2(OH)_6 \cdot H_2O$ for $Zn(OH)_2$ and $ZnCO_3$ respectively, so $Zn_5(CO_3)_2(OH)_6 \cdot H_2O$ is unsteady[19]. Reactions from ① to ⑥ are liquid reactions system, while ⑦ to ⑧ belongs to solid reactions system in parallel. We know that the chemical reaction process is a very complicated system. Here in this paper, we just discuss reactions from ① to ⑥ in state of liquid. In the view of the production, the more precipitated products of $Zn(OH)_2$ and $ZnCO_3$ (as called precursor) are produced, the more final products of nanometer ZnO will be gained. From the view of phase equilibrium and precipitated equilibrium, a higher productivity of ZnO production can be obtained if product of ZnO precursor precipitated could be removed from the reacted system continuously. For this fact, analyzing the conditions of chemical reacted system in the state of liquid production will be very important for large industrial production.

2 Nano-ZnO production in industry

2.1 Independent reaction number and free degree

Chemical stoichiometric equation represents the proportional relationship between every component of reactants and that of products in chemical reaction process. For a simple reaction system, its general stoichiometric equation can be written as $\sum_{i=1}^{n} v_i A_i = 0$, where v_i is called stoichiometric coefficient of component i. For reactants, v_i adopts negative, whereas for products it is positive. A_i refers to any of materials of component i in the reaction. If it is a complicated reacting system, chemical stoichiometric equations can be described as $\sum_{i=1}^{n} v_{ij} A_i = 0, j = 1,2,3 \cdots m,\ i = 1,2,3 \cdots n$, where v_{ji} is the stoichiometric coefficient of j chemical reacted equation. For reactants v_{ji} adopts negative sign, positive belongs to products, A_i represents any of the materials of i component in the reactions. In matrix form, complicated chemical stoichiometric equations are written as follows:

$$\begin{bmatrix} v_{11} & v_{12} & \dots & v_{1n} \\ v_{21} & v_{22} & \dots & v_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ v_{m1} & v_{m2} & \dots & v_{mn} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ \vdots \\ A_n \end{bmatrix} = 0$$

Assume a system of coinstantaneous m reactions, the independent reaction number is just the order of matrix. As for the chemical equations of ZnO production, the reacted system matrix of reactions' coefficient can be illustrated, according to the equations from ① to ⑧, as follows:

$$\begin{bmatrix} -1 & -3 & 1 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 & 1 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -4 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} CO(NH_2)_2 \\ H_2O \\ CO_2 \\ NH_3H_2O \\ CO_3^{2-} \\ H^+ \\ NH_4^+ \\ OH^- \\ Zn^{2+} \\ [Zn(NH_3)_4]^{2+} \\ Zn(OH)_2 \\ ZnCO_3 \end{bmatrix} = 0$$

The matrix order of the equation above after calculation is 6, that is to say, there are 6 independent reactions in the system. The free degree of the reacted system is:

$$F = N + 2 - \phi - R = 14 + 2 - 3 - 6 = 7$$

where N is the number of components, φ is number of phases, and R is number of independent reactions. When temperature and pressure have been fixed, there are only five variables, which are concentrations of the components occurred in the reaction system. There are three original reactants, which are $CO(NH_2)_2$, H_2O, Zn^{2+}, and two products which are $ZnCO_3$ and $Zn(OH)_2$ in the reaction system. It is a two stage method of ZnO-production, first stage is liquid reaction process, and second stage is degradation of solid. Here only first stage is discussed, as for the second stage will be discussed in another paper. Just because of this reason, there are only three original reactants should be concerned about in the industrial production of nano-ZnO.

2.2 Operating domain analysis of reactants

Reactions illustrated above from ① to ⑥, among them, equation ①, ②, and ③ are hydrolyzed reaction and form a cascade reaction of urea. Equation ② and ③ constitute a parallel and reverse reaction. Equation ④, ⑤ and ⑥ are complex reactions in multiphase. They are also parallel precipitated reactions. Equation ①, ② and ③ form cascade reactions with ④, ⑤ and ⑥ respectively, meanwhile ④, ⑤ and ⑥ are also reversible parallel reactions. These complex reactions make industrial production change into complicated situation, on the other hand, urge the scientific researchers to find out and explore the relationship between these reactions.

Table 1: $L_9(3^4)$ cross-experimental table.

Experiment No.	A $Zn(NO_3)_2$ quantity (250ml) measure	B $CO(NH_2)_2$ quantity (250ml) measure	C Temperature °C	D Reaction time *h*
1	0.2M (0.05mol)	0.6M (0.15mol)	81	3
2	0.2M	1.0M (0.25mol)	87	3.5
3	0.2M	1.5M (0.375mol)	97	4
4	0.3M (0.075mol)	0.6M	87	4
5	0.3M	1.0M	97	3
6	0.3M	1.5M	81	3.5
7	0.4M (0.1mol)	0.6M	97	3.5
8	0.4M	1.0M	81	4
9	0.4M	1.5M	87	3

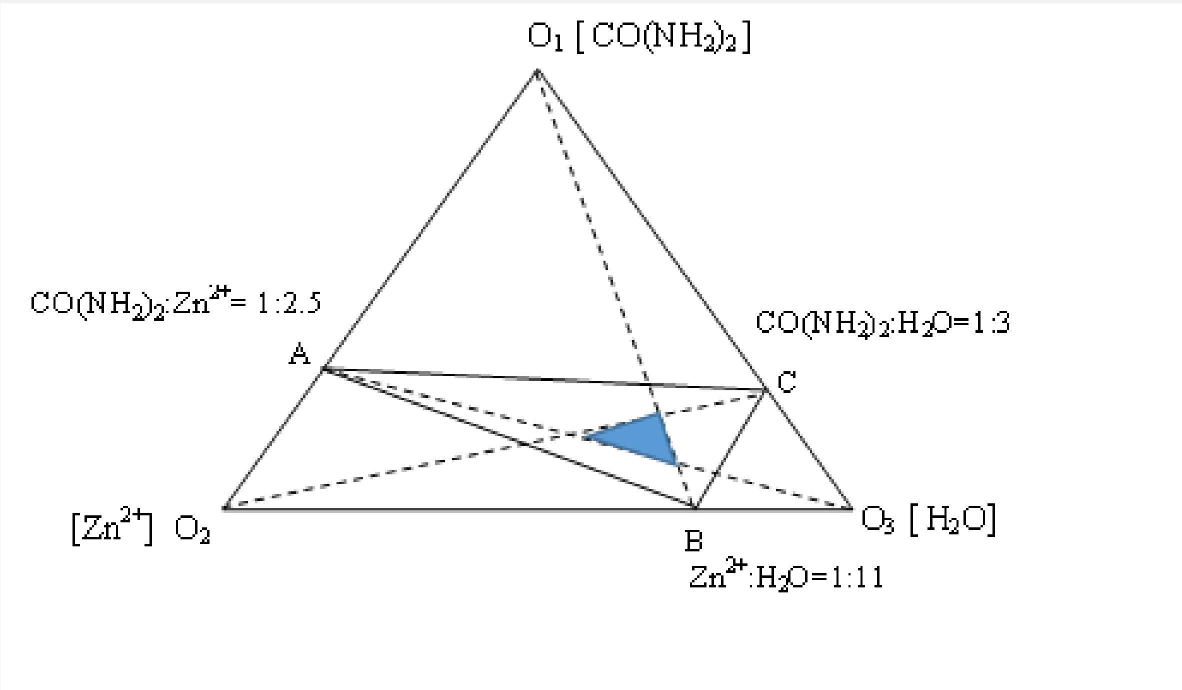

Figure 1: Component plot of reactants for operating domain

It is clear that there are only three original reactants, $CO(NH_2)_2$, Zn^{2+}, H_2O, and then the author can draw a plot of three components and instruct the production of ZnO using the plot. It is called operating domain of concentration in industrial production. For the 7 free degrees calculated above, when temperature and pressure are defined, there are only 5 free degrees - reactant concentrations. Because of $Zn(OH)_2$ and $ZnCO_3$ are solid, the concentration of them are not changed and equal to 1. The free degree becomes 3, that means the final results are determined by the concentration of $CO(NH_2)_2$, Zn^{2+}, respectively, except of H_2O. When $CO(NH_2)_2$ concentration is fixed, Zn^{2+} concentration does ascertain too if the reaction is reacted thoroughly. Our aim is to make Zn^{2+} change into solid through the reaction ⑤ and ⑥ as soon as possible. Table 1 shows cross-experimental values for the production of nano-ZnO.

The operating domain is shown in Figure 1. Point O_1 refers to $CO(NH_2)_2$ mole concentration, while O_2 is Zn^{2+} mole concentration, whereas O_3 is H_2O mole quantity, and the line connects two points of O_1, O_2 ,O_3 respectively, to form an equilateral triangle plot. By means of stoichiometric equation, triangle line O_1O_2 denotes the quantity of Zn^{2+} concentration proportional to $CO(NH_2)_2$ concentration. Then O_2O_3 is the concentration of Zn^{2+} and O_1O_3 is the concentration of $CO(NH_2)_2$. Any point inside of the triangle, expresses the proportional quantity among three components $CO(NH_2)_2$, Zn^{2+} and H_2O. Point A on the triangle line O_1O_2 shows the reacted proportion between $CO(NH_2)_2$ and Zn^{2+} when they react thoroughly, in which $CO(NH_2)_2$: Zn^{2+} =1:2.5 according to stoichiometric equations. Point B is the concentration of Zn^{2+} totally reacted in solution, in which Zn^{2+}:H_2O=1:11. Similarly point C is the concentration of $CO(NH_2)_2$ wholly reacted, giving $CO(NH_2)_2$:H_2O=1:3.

With the line connecting point A', B', C', another domain of triangle can be obtained, which constitutes operating domain of reactants. Inside of triangle ABC, any point represents the proper proportional relations on Zn^{2+}, $CO(NH_2)_2$ and H_2O when reactions take place between them completely. The triangle district O_2AB denotes excessive Zn^{2+} quantity reacted in the reaction system. So does O_1AC indicate excessive $CO(NH_2)_2$ quantity reacted. The triangle O_3BC expresses dilution of H_2O. These three districts do not have economic reactions and may extremely waste materials if reactions occur in one of them.

Line O_1B denotes the constant proportional value of Zn^{2+}:H_2O and from B to O_1, $CO(NH_2)_2$ quantity increased continuously.

Line O_2C denotes the constant proportional value of $CO(NH_2)_2$:H_2O and from C to O_2, Zn^{2+} quantity increased continually.

Line O_3A denotes the dilution process of $CO(NH_2)_2$ and Zn^{2+} in the same proportion from A to O_3.

The point of intersection between line O_1B, O_2C, and O_3A (intersect point A', B', C' unwritten in the figure) form a new region (the dark field), that is the optimum operating domain. According to the author research[7,18], under the condition of normal pressure, the optimum technological conditions to obtaining the highest nano-ZnO productivity is: reaction temperature bigger than 97°C, reaction time longer than 3.5 hours, and a proportional value of $C_{(CO(NH_2)_2)}$:$C_{(Zn(NO_3)_2)}$ $\geq$3.5:1. That means the concentration of $CO(NH_2)_2$ should be much more than that of $Zn(NO_3)_2$. The results told us that the theory is different from practice. Point A should move up a little to point O_1, and the operation domain of production would be near the line AC and further above AC a little. Why would the operation be like these? Next are the reasons.

2.3 Equilibrium analysis

For nanometer ZnO production, there are three final substances obtained in the reaction process, they are $[Zn(NH_2)_2]^{2+}$, $Zn(OH)_2$, $ZnCO_3$, which $Zn(OH)_2$, $ZnCO_3$ are in the form of $Zn_5(CO_3)_2(OH)_6 \cdot H_2O$ occurred in solid state. $Zn(OH)_2$, $ZnCO_3$ are the objective precipitate, which ordinarily exist in crystal mixture called nanometer ZnO precursor. Obviously, if the precursor is removed continuously out of the reaction solution, the complex reaction system would move to the positive direction according to the equilibrium theory. $[Zn(NH_3)_4]^{2+}$ is dissoluble byproduct which will consume a lot of ammonia. That is why concentration of $CO(NH_2)_2$ is much bigger than that of theoretical calculation. How to obtain more products $Zn(OH)_2$, $ZnCO_3$ is the crux of the matter and is also the core to improve economic benefits in industrial production.

Mole concentration of $[Zn(NH_3)_4]^{2+}$ and Zn^{2+} can be obtained by analyzing equilibrium of equations ④, ⑤ and ⑥ above respectively:

Equilibrium constant of equation[20] ④ is: $k_c = \frac{C_{[Zn(NH_3)_4]^{2+}}}{C_{Zn^{2+}} \cdot C^4_{NH_3}} = 2.88 \times 10^9$

Equilibrium constant of equation[20] ⑤ is: $k_{sp} = C_{Zn^{2+}} \cdot C^2_{OH^-} = 7.71 \times 10^{-17}$

Equilibrium constant of equation[20] ⑥ is: $k'_{sp} = C_{Zn^{2+}} \cdot C_{CO_3^{2-}} = 1.19 \times 10^{-10}$

When the precipitates appear in the reaction system and equilibrium of reactions comes out, the Zn^{2+} mole concentration in liquid is same. To rearrange the three constant equilibrium equations above, new relative equations come forth as follows:

$$C_{[Zn(NH_3)_4]^{2+}} = \frac{k_{sp} \cdot k_c}{C^2_{OH^-}} \cdot C^4_{NH_3} = \frac{k'_{sp} \cdot k_c}{C_{CO_3^{2-}}} \cdot C^4_{NH_3} \quad (9)$$

From equation ⑨, the mole concentration of $C^2_{OH^-}$ or $C_{CO_3^{2-}}$ must be increased in order to reduce byproduct $[Zn(NH_3)_4]^{2+}$. The techniques are:

1. To control the pH value in the reaction process,
2. Adding substances including OH^- and CO_3^{2-},
3. At the same time decreasing concentration C_{NH_3}

Reducing C_{NH_3} is difficult in the reacting system using uniform precipitated method. The only way is adjust the pH value and regulate the temperature. The experiment makes clear[7,18] that the pH value usually maintains a range of 5.5-8.0 and nanometer ZnO precursor can be gained during the production under normal temperature and ordinary pressure. The production operation keeps pH=6.5. Beyond the range of 5.5-8.0, there is no ZnO precursor occurred because Zn^{2+} salt is amphoteric compound and for other reasons as discussed above, for example, the equilibrium reason. The range of temperature of reaction is 87-100°C, and the best temperature range is bigger than 97°C. Under 60°C the reaction is difficult to proceed. From equations ④, ⑤ and ⑥, the best step is to continually remove the nanometer ZnO precursor precipitate away from reactor in industrial production, if the objective products can be gained effectively.

In the reaction process, the blend of reactants must be sufficient. Other problems, for example, the concentration distribution and temperature distribution in reactants solution, engineering problems affected by micro mixing and macro blending in reactor, will be discussed in other paper.

3 Conclusions

The preparation of nanometer ZnO used uniform precipitated method in large scale industrial production has been investigated, the conclusions are as follows:

1. The reacted system preparing ZnO particles precursor is a complex multiphase system with series, parallel, reverse reaction process. The independent reacted number is 6 and the reacted free degree is 7.
2. The final result is reaction temperature bigger than 97°C, reaction time longer than 3.5 hours, proportional value of $C_{(CO(NH_2)_2)}$:$C_{(Zn(NO_3)_2)} \geq 3.5 : 1$.
3. The ideal operating domain of reactant is triangle district surrounded by line O_1B, O_2C, O_3A, the proportional concentrations are $CO(NH_2)_2$: $Zn^{2+} = 1 : 2.5$; Zn^{2+}: H_2O=1:11; $CO(NH_2)_2$: H_2O=1:3. See Figure 1.

4. The pH value is a key factor and its range is 5.5-8.0, the optimum pH=6.5.

Besides, it is necessary that the precursor particles should be continually removed out of reactor in order to enhance the productivity of ZnO products.

Author Bio

Wang Jiuliang (born 1964) graduated from Science and Technology University of East China in 1986, majoring in chemical engineering. In 2003, graduated from Yan Shan University and gained master degree. Now the author engages in teaching and research of chemistry and chemical engineering. Main research areas are chemical reaction engineering and inorganic materials.

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