

Preparation of Micron Co_3O_4 by Liquid-Phase Precipitation

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Abstract

Co_3O_4 powder has a wide range of applications in the fields of catalysts, magnetic materials and electrochemistry. Especially after the 1990s, the demand for lithium ion battery industry has grown tremendously. The traditional wet preparation of Co_3O_4 powder cannot meet the requirements of the battery industry. Exploring suitable methods and theories for controlling particle size and morphology is of great significance for the preparation of battery-grade Co_3O_4 powder. CoCl_2 was used as the cobalt source, NH_4HCO_3 was used as the precipitant, and the precursor was prepared and further calcined to obtain Co_3O_4 powder. The results show that the molar ratio is the main factor affecting the precursor phase in the preparation of Co_3O_4 in CoCl_2 - NH_4HCO_3 system. The suitable process conditions for the system are a molar ratio of NH_4HCO_3 to CoCl_2 of 4.5:1, a concentration of CoCl_2 of 13 g/L, a reaction temperature of 60°C , and a reaction time of 10 hours. The median diameter of Co_3O_4 prepared by the reaction conditions is about $9\text{ }\mu\text{m}$.

Keywords

Micron, Co_3O_4 , Particle Size Control, Liquid Phase Precipitation

1. Introduction

In recent years, LiCoO_2 has been the main material of the positive electrode of lithium ion battery [1]. It is a structure formed by Co_3O_4 as a support and Li^+ distributed inside the support. Since Co_3O_4 is so important in the structure of LiCoO_2 , in order to prepare high-performance LiCoO_2 , it is necessary to strictly control the performance indexes of the raw material Co_3O_4 . Experiments have shown that when the particle size is small, the distribution is uniform, the specific surface area is large and the shape is spheroidal, Co_3O_4 has a better electrochemical performance [2].

At present, the main technical criterion of the battery-grade Co_3O_4 products are: the median diameter is 2 - 25 μm , the phase is cubic Co_3O_4 , the appearance is black powder, and the crystal morphology is spherical or spheroidal. In this context, the precipitation method is used to investigate the influence of different parameters on the particle size distribution of Co_3O_4 . It is of certain significance to prepare Co_3O_4 powder suitable for lithium ion batteries [3].

2. Experimental Procedure

A certain amount of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water to prepare a certain concentration of CoCl_2 aqueous solution (according to Co^{2+} : 90 g/L, 10 mL of CoCl_2 aqueous solution required $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 3.65 g). NH_4HCO_3 was dissolved in 26.8 mL of deionized water to prepare an aqueous solution of NH_4HCO_3 , and the molar ratio of NH_4HCO_3 to CoCl_2 was a certain number (1.8 - 5). The two solutions were then mixed in a beaker. Before starting the feeding, pre-add deionized water (5, 30, 55, 80, 105 mL) in the three-necked bottle, heat the water in the water bath to the temperature required for the reaction (40°C, 50°C, 55°C, 60°C, 70°C), and pour the mixed solution into it, a certain stirring strength and temperature are maintained throughout the process. In the reaction, the pH value is continuously measured with a pH meter. After a certain period of time (6, 8, 9, 10, 12 h), the product is taken out, and then solid-liquid separation is performed by suction filtration. 1 L of normal temperature deionized water was used to wash the solid precipitate. The solid sample was dried for 2 h at 105°C. The precursor powder product was grinded, and then calcined at 850°C - 900°C for 8 h to obtain the Co_3O_4 powder.

3. Reaction Principle

CoCO_3 is a poorly soluble compound with a small solubility product K_{sp} value, so it is easy to achieve supersaturation. According to the principle of crystallography, the CoCO_3 precipitates through two stages, namely the formation of crystal nuclei and the growth of crystals, which determine the size of the CoCO_3 particles [4]. The crystallization process of insoluble compounds in aqueous solution is characterized by easy nucleation and difficult to grow particles [5]. In this paper, an ammonia complexing agent is added to the reaction system (Co^{2+} first reacts with NH_4^+ forming cobalt ammine complex ions, and then it reacts with CO_3^{2-} to form CoCO_3), the other reaction conditions are regulated to control the supersaturation of CoCO_3 in the solution, so that the nucleation and growth rate of CoCO_3 crystals reach a suitable ratio.

4. Results

When the reaction temperature was set at 55°C, the reaction time was 8 hours, and the pre-filled water amount was 5 mL, the molar ratio of ammonium hydrogencarbonate to cobalt chloride was changed, and the effect on the particle size of the precursor was as shown in **Figure 1**. As the molar ratio increases, the

precursor particle size first increases and then decreases. When the molar ratio of NH_4HCO_3 to CoCl_2 was 1.8 - 3, the precursor prepared was purple and the pH was changed from 6.7 to 7. When the molar ratio of NH_4HCO_3 to CoCl_2 is 4, 4.5 and 5, the precursor obtained is pink, and the pH is changed from about 7.1 to 7.6.

The particle size distribution results obtained at a molar ratio of 4.5:1 are shown in **Figure 2**. The D50 of precursor was $6.13\ \mu\text{m}$ and the particle size distribution was narrow.

The precursors obtained at different molar ratios were subjected to XRD test, and the results obtained are shown in **Figure 3**. The molar ratio has an important

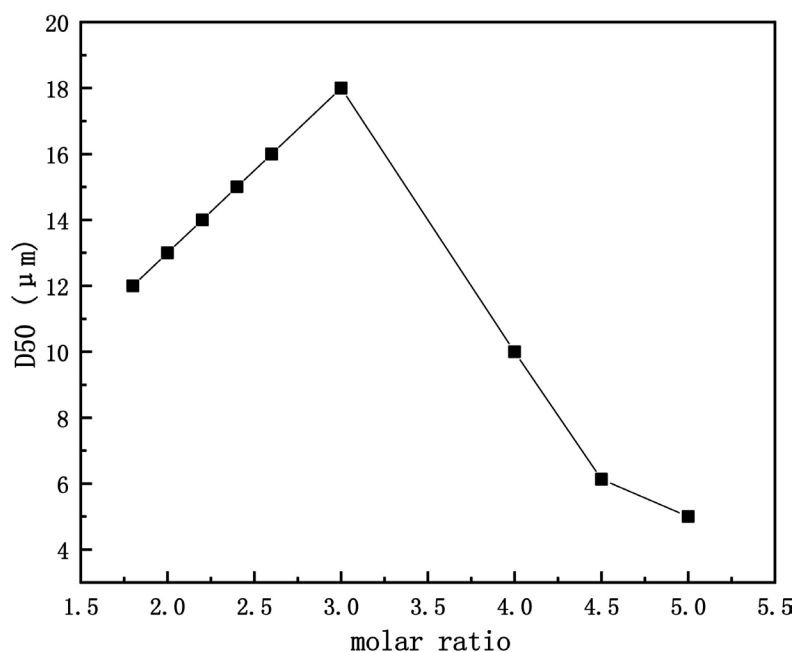


Figure 1. Effect of molar ratio of NH_4HCO_3 to CoCl_2 on the median diameter of the precursor.

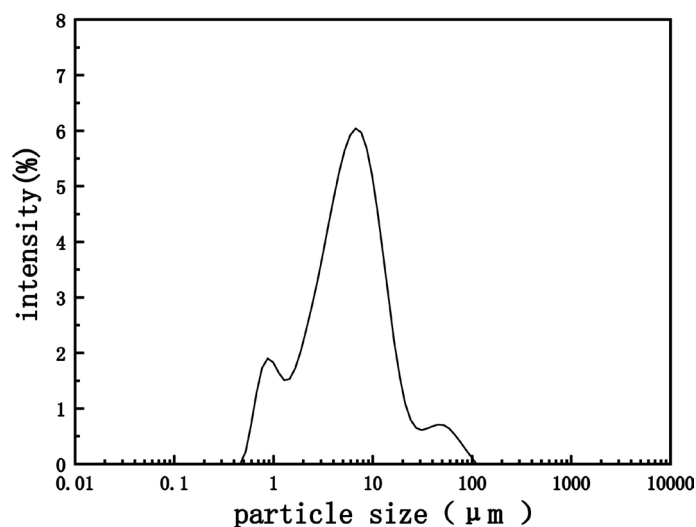


Figure 2. Precursor particle size distribution at a molar ratio of 4.5:1.

influence on the precursor phase. When the molar ratio ≤ 3 , the precursor obtained is basic cobalt carbonate ($\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11(\text{H}_2\text{O})$); when the molar ratio is equal to 4.5, the precursor is a mixture of cobalt carbonate (CoCO_3) and basic ammonia cobalt carbonate ($(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 4\text{H}_2\text{O}$). When the molar ratio of NH_4HCO_3 to CoCl_2 is 4.5:1, it is closer to the requirement of battery grade Co_3O_4 . Therefore, 4.5:1 was chosen as the appropriate molar ratio.

The above other experimental conditions are unchanged. When the molar ratio of NH_4HCO_3 to CoCl_2 is 4.5:1, the pre-filled water amount (concentration) is changed, and each group of variables is added with 30, 55, 80, 105 mL of pure water, respectively. The effect of pre-filled water on the particle size of the precursor is shown in **Figure 4**. With the increase of water volume, the particle size of the precursor gradually decreased. It was found that the D50 of the precursor was 5.08 and 3.36 μm when the water was added at 30 and 55 mL, respectively. The pH changes were 6.7 - 7.8 and 6.8 - 7.6, respectively. The particle size distribution when adding 30 mL of water is shown in **Figure 5**. However, in order

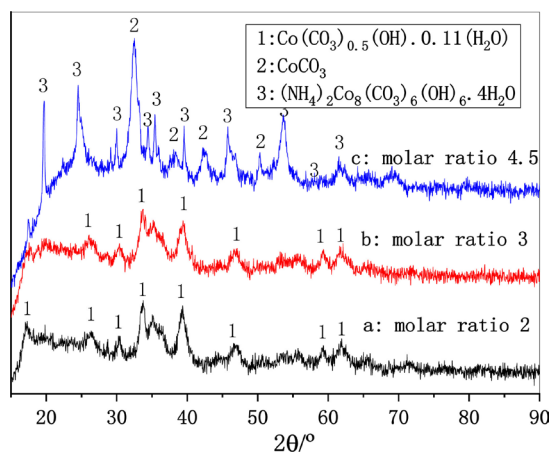


Figure 3. XRD pattern of the precursor obtained at different molar ratios.

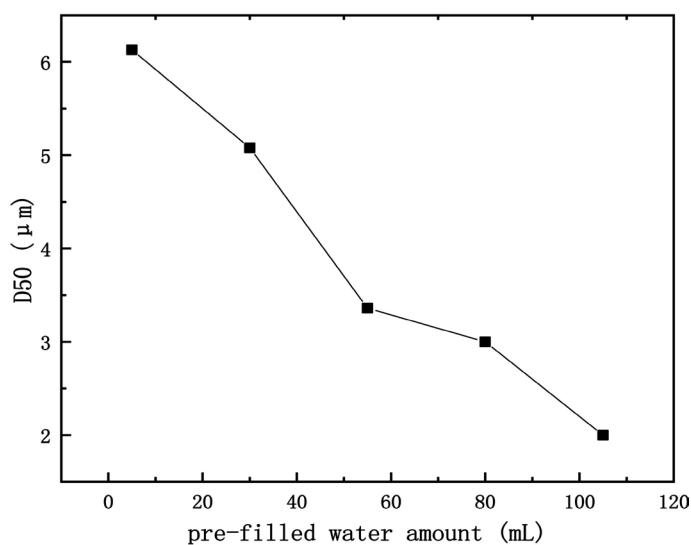


Figure 4. Effect of pre-filled water on the median diameter of the precursor.

to ensure that the final product of Co_3O_4 has a particle size between 2 and 25 μm , a water supply of 30 mL is selected.

The above other experimental conditions are unchanged. When the pre-filled water volume is 30 mL, the temperature is changed. The temperature of each group is 40°C, 50°C, 60°C, 70°C, and the previous temperature is 55°C. The effect of temperature on the particle size of the precursor is shown in **Figure 6**. As the temperature increases, the particle size of the precursor increases gradually. It is found that the particle size distribution of the precursor is best at 60°C as shown in **Figure 7**. And the D50 was 7.30 μm , the pH varies from 7.1 to 8.1.

The above other experimental conditions are unchanged. When the reaction temperature is 60°C, the variables of each group are 6, 9, 10, 12 h, and the previous reaction time is 8 h. The effect of time on the particle size of the precursor

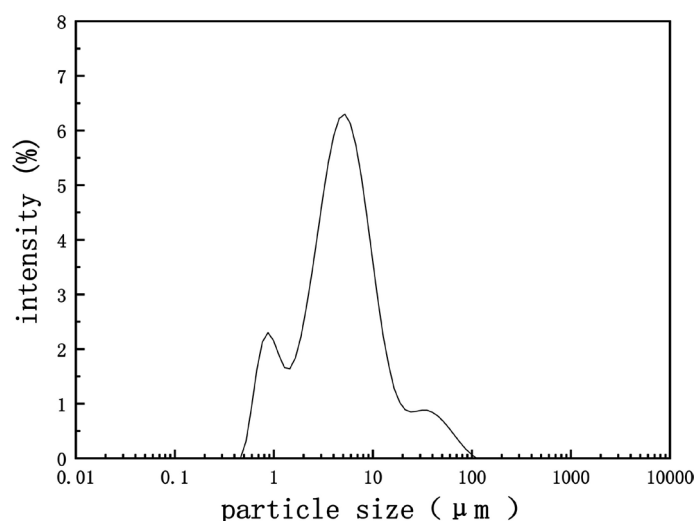


Figure 5. Precursor particle size distribution when the pre-filled water volume is 30 mL.

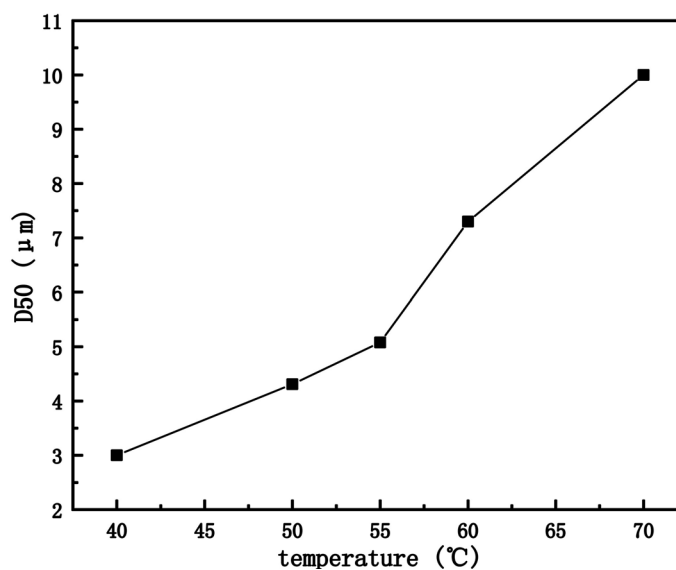


Figure 6. Effect of temperature on the median diameter of the precursor.

is shown in **Figure 8**. With the increase of time, the particle size of the precursor increased. Finally, the particle size distribution with a reaction time of 10 hours is best as shown in **Figure 9**, the pH was changed within 7.4 - 8.2, and the D50 was 8 μm . 10 hours was chosen as the reaction time.

The final precursor was prepared under these conditions and calcined at 850°C. The XRD patterns of the precursor and calcined product are shown in **Figure 10** and **Figure 11**, respectively; the morphology obtained by scanning electron microscope is shown in **Figure 12** and **Figure 13**, respectively. The particle size distribution calcined product is shown in **Figure 14**. The obtained precursor and Co_3O_4 phase are relatively single, with few heterophases, and their morphology is a mixture of spherical and fibrous. The calcined product has a median diameter of 9.08 μm and a narrow particle size distribution range.

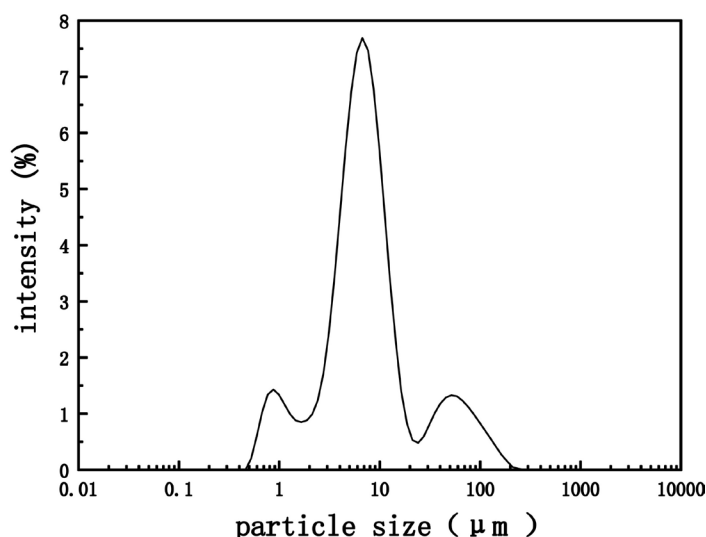


Figure 7. Precursor particle size distribution at a reaction temperature of 60°C.

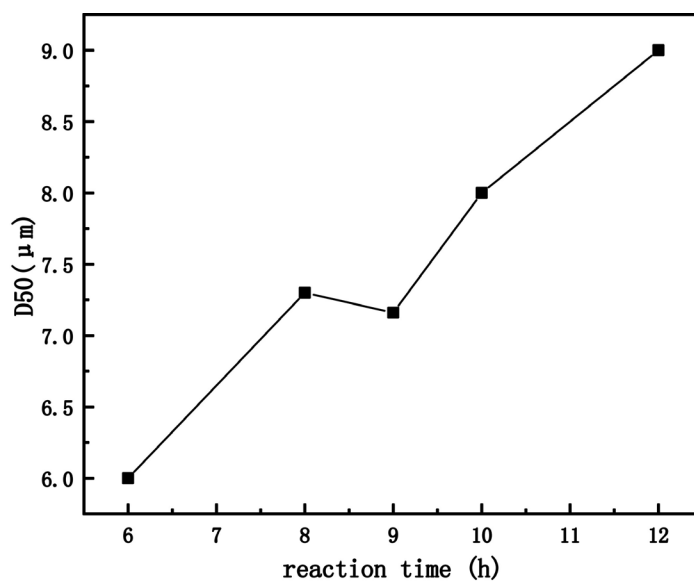


Figure 8. Effect of reaction time on the median diameter of the precursor.

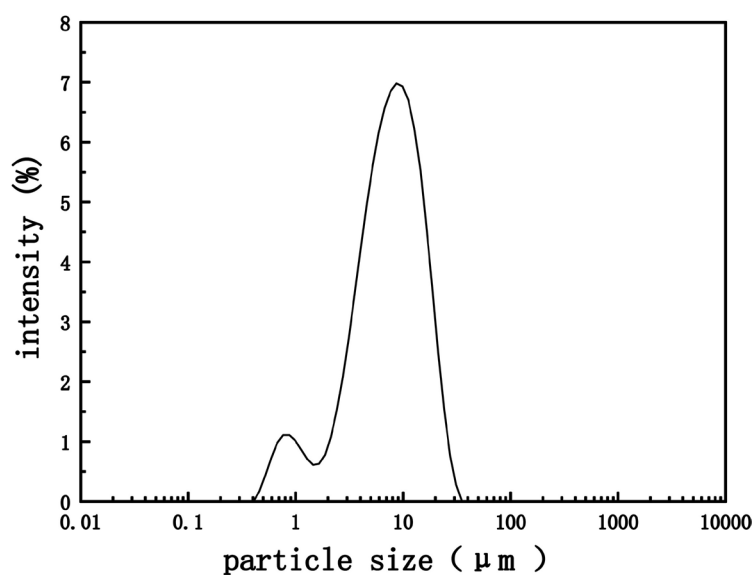


Figure 9. Particle size distribution of the precursor at a reaction time of 10 h.

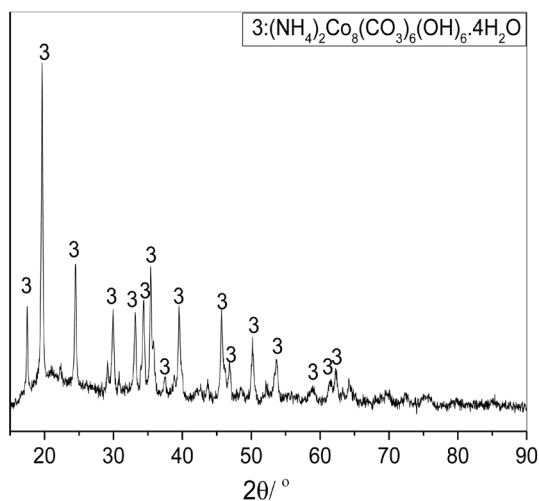


Figure 10. Precursor phase.

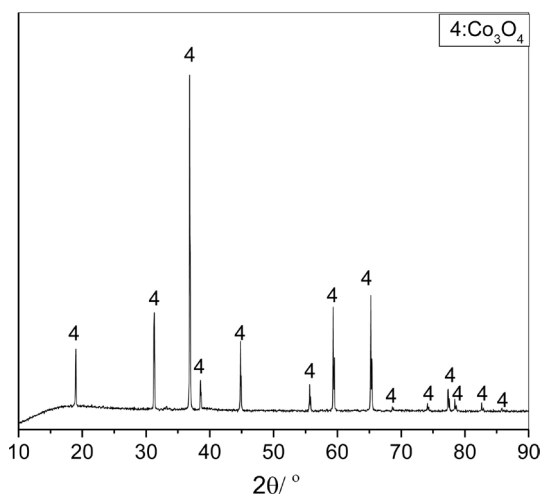


Figure 11. Calcined product phase.

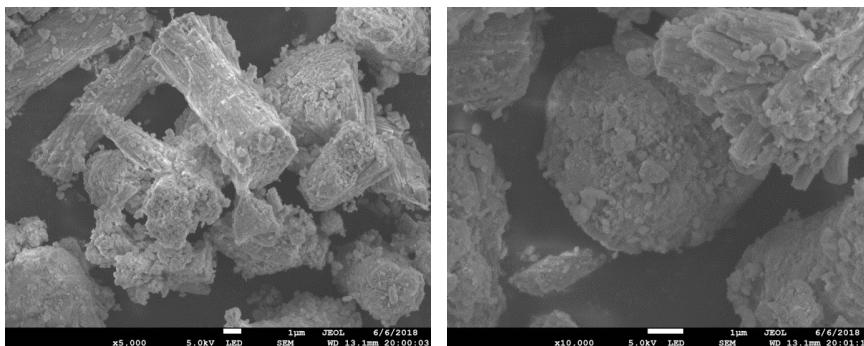


Figure 12. Morphology of the precursor.

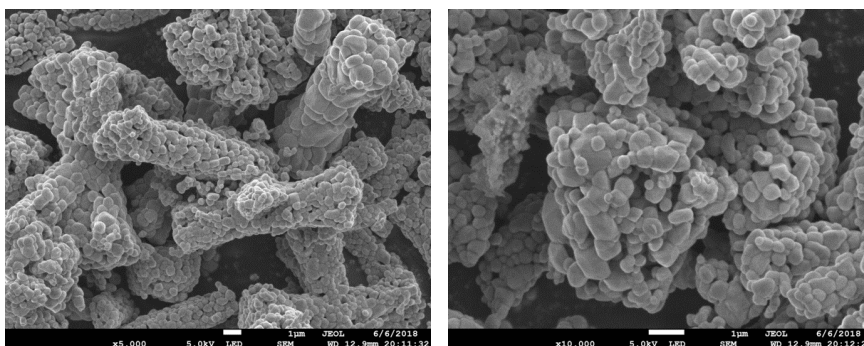


Figure 13. Morphology of calcined product.

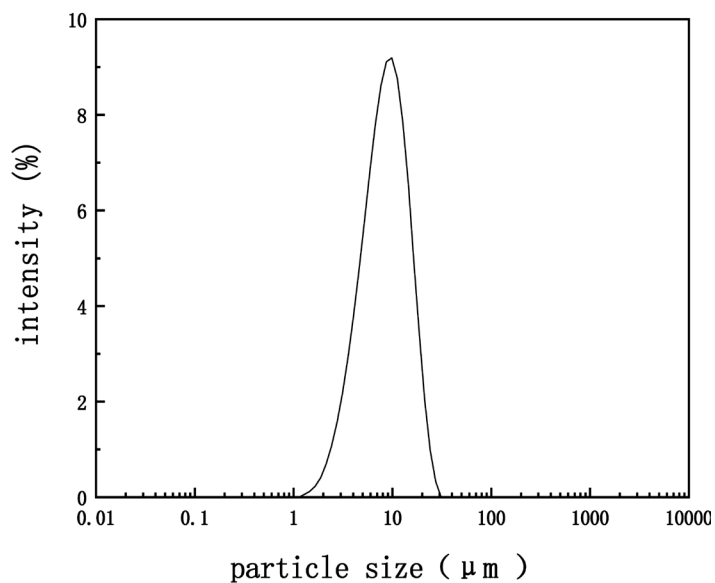


Figure 14. Size distribution of calcined product.

5. Discussion

The relative magnitude of the rate of nucleation and the growth directly determines the type of precipitated material and the size of the precipitated particles [6].

Increasing the reaction temperature generally reduces the supersaturation of the solution. Since the nucleation rate of CoCO_3 is relatively sensitive to the

change of supersaturation, although the increase of reaction temperature may increase the speed of various processes, the increase of nucleation rate is correspondingly weakened by the decrease of supersaturation. Therefore, increasing the temperature is more conducive to the increase of the growth rate of the nucleus. On the other hand, if the temperature is too high, the kinetic energy of the reactant molecules is increased too fast and it is not conducive to the formation of a stable crystal nucleus. Increasing the temperature promotes the dissolution of the small particle crystals and redeposition on the surface of the large particles [7]. Therefore, low temperature precipitation is favorable for the formation of fine crystals, and high temperature precipitation is favorable for the formation of larger crystals, as the temperature increases, the particle size of the precursor increases (**Figure 6**).

Analysis of the formation process of CoCO_3 crystals shows that the formation and growth of crystal nuclei takes a certain time, and the crystallization conditions are different, and the time required is also different [8]. In this project, the longer the time, the larger the precursor grain growth and the larger the particle size (**Figure 8**).

6. Conclusions

- The reactant molar ratio in the NH_4HCO_3 to CoCl_2 system is one of the most direct factors affecting the precursor phase. When the molar ratio of NH_4HCO_3 to CoCl_2 is ≤ 3 , the precursor obtained is basic cobalt carbonate; When the molar ratio of NH_4HCO_3 to CoCl_2 is equal to 4.5, the precursor is a mixture of cobalt carbonate and basic cobalt carbonate.
- The suitable process conditions for preparing cobalt oxide by NH_4HCO_3 to CoCl_2 system are as follows: the molar ratio is NH_4HCO_3 to CoCl_2 is 4.5:1, the CoCl_2 concentration is 13 g/L, and the reaction temperature is 60°C , the reaction time is 10 hours. The medium diameter of precursor and Co_3O_4 prepared under the conditions is $8\text{ }\mu\text{m}$ and $9\text{ }\mu\text{m}$, respectively.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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