Synthesis and structural characterization of calcium hypophosphite

Ai Qingxue[1, a], Wang Fusheng[2,b] and Guo Aihong[3,c]

[1,2] School of Mining Engineering, North China University of Science and Technology, Tangshan Hebei , China

[3] School of Chemistry Engineering, North China University of Science and Technology, Tangshan Hebei , China

[a]1150960701@qq.com, [b]fswang3418@163.com, [c]83497300@qq.com

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Abstract. Calcium hypophosphate is got from sodium hypophosphite and sodium chloride. The internal morphology and composition of calcium hypophosphate particles are obtained by nanometer particle sizer, scanning electron microscope (SEM) and X-ray diffraction (XRD) and also on. The experimental results show that 2.0 mol/L, 40°C, 100 min under the conditions can get large yield and particle size is minimal about 0.563μm. Calcium hypophosphate is high purity, structure likes rod, and the content of Phosphorus element is high. The method is feasible and subsequent treatment is simple.

Introduction

Calcium hypophosphate is common hypophosphate and utilized corrosion inhibitor, flame retardant, filler, nickel plating additive of chemistry, antioxidant, chemical analysis agent and food additives and so on. Calcium hypophosphite can be prepared by neutralization process or synthetic method of lime and yellow phosphorus [1]. Neutralization process means that neutralization of hypophosphite and slaked lime get calcium hypophosphite. Synthetic method of lime and yellow phosphorus means that yellow phosphorus and slaked lime water synthesize directly and gets calcium phosphate.

In this experiment, the calcium hypophosphate is prepared by the reaction of sodium hypophosphate and anhydrous calcium chloride. This method is feasible, and treatment is simple at the end of experiment. It has some shortcomings that solubility of sodium chloride is not very large and cannot completely separate sodium chloride. To a certain extent, it will affect the purity of calcium hypophosphate [2]. Using nanometer particle sizer, scanning electron microscope (SEM) and X-ray diffraction (XRD) can characterize and analyze calcium phosphate. Compared with ordinary optical microscope, scanning electron microscope (SEM) has the characteristics of high magnification and high resolution. Ion sputtering is the most commonly used coating method [3]. X-ray diffraction is an important means that study the composition of material, the internal atomic or molecular structure [4].

Synthesis of Calcium Hypophosphate. Sodium hypophosphate is one of the important products of phosphorus chemical industry, which is formed by a water compound from its aqueous solution. The crystal is a single with a clear and bright luster of pearl and colorless, without odor [5]. The reaction to sodium hypophosphite and calcium chloride anhydrous stir heated in water bath under the condition of generating calcium hypophosphate. This method is feasible, and treatment is simple at the end of experiment. Chemical reaction equation is

$$2NaH_2PO_2 \cdot H_2O+CaCl_2=2NaCl+ Ca(H_2PO_2)_2+2H_2O$$

When the calcium chloride concentration was set from 1.7mol/L to 2.3mol/L, the content of calcium chloride was fixed to 200ml, according to the concentration of calcium chloride and chemical reaction equation, the quality that complete reaction of sodium hypophosphate and calcium chloride and theoretical quality of the calcium hypophosphate under the different calcium chloride concentration, it was calculated. Data is shown in Table 1.

Table1 Reaction products and quality of products

Number	$CaCl_2$(mol/L)	NaH_2PO_2(g)	$CaCl_2$(g)	$Ca(H_2PO_2)_2$ Theoretical yield (g)	$Ca(H_2PO_2)_2$ Active output (g)	productivity （%）
1	1.7	72.08	37.74	57.80	48.76	84.36
2	1.8	76.33	39.96	61.20	56.11	91.68
3	1.9	80.57	42.18	64.60	61.39	95.03
4	2.0	84.81	44.40	68.00	67.31	98.98
5	2.1	89.04	46.62	71.40	68.90	96.50
6	2.2	93.28	48.84	74.80	72.88	97.43
7	2.3	97.52	51.06	78.20	76.40	97.70

Effect of reactant concentration on the yield and purity of calcium phosphate. According to Table 1, the quality of sodium hypophosphate and calcium chloride were weighed, put in a conical flask, added 200ml water, put in the thermostatic magnetic mixer. The temperature was set at 70 degrees C, the time was 90min. After completely mixing, precipitating, 3 hours after filtering and drying, the drying temperature was 50 and 12 hours, the actual quality of calcium hypophosphate is shown in Table 1. Productivity was calculated by comparing with actual quality and theoretical quality, when the concentration of calcium chloride is 2.0mol/L, the yield of calcium hypophosphate is the largest.

Effects of synthesis temperature and reaction time on the productivity of calcium phosphate. The calcium chloride concentration is 2.0mol/L, the temperature is 40 °C to 70 °C, and the reaction time is 80min to 100min, and yield of calcium phosphate can be calculated. The experimental data is shown in Table 2 when the temperature is 40 °C, reaction time 100min (sample 1), the resulting $Ca(H_2PO_2)_2$ yield the most.

Table2 Orthogonal experiment table of different temperature concentration time

Number	Time (min)	Temperature (°C)	Concentration mol/L	Theoretical yield (g)	Active output (g)	Productivity （%）	Size μm
1	100	40	2.0	68.00	65.38	96.15%	0.563
2	90	40	2.0	68.00	63.39	93.22%	0.894
3	80	40	2.0	68.00	61.20	90.00%	1.561
4	100	60	2.0	68.00	62.90	91.30%	1.430
5	90	60	2.0	68.00	61.49	90.42%	1.195
6	80	60	2.0	68.00	58.86	86.56%	2.789
7	100	70	2.0	68.00	60.43	88.85%	1.083
8	90	70	2.0	68.00	57.79	84.98%	1.299
9	80	70	2.0	68.00	59.76	87.88%	1.082

Grain size analysis

The 9 sample of orthogonal test were analyzed by Z590 nanometer particle sizer and shown in Table 2. The measured reaction conditions was 100min, 40 C, 2.0mol/L. And the average particle size is 0.563μm, is better than other groups of average particle diameter. It belongs to submicron particle. The average particle size of 1 sample 1 is shown Figure 1.

Results

			Size (d.nm...	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	563.3	Peak 1:	577.3	100.0	84.40
PdI:	0.234	Peak 2:	0.000	0.0	0.000
Intercept:	0.723	Peak 3:	0.000	0.0	0.000
Result quality	Refer to quality report				

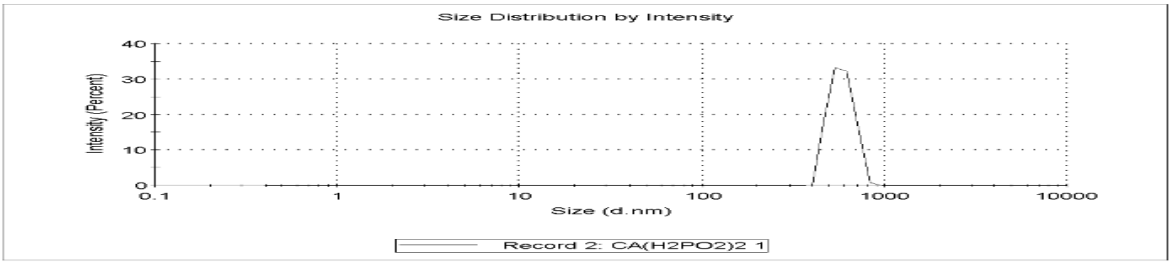


Figure.1 Average particle size of sample 1

Ion sputtering and scanning electron microscopy (SEM)

The 1 sample was sprayed metal in the current 15mA and time was 90s, and then was put into the S-4800N scanning electron microscope observation room. The calcium hypophosphate presents a rod like structure (rectangular), and the two ends of the particle are oval shaped. Particles are smaller and approximately circular, the particle surface is smooth, and no holes, no cracks, and a lot of the particles are regular shape. It is shown Figure 2 and Figure 3.

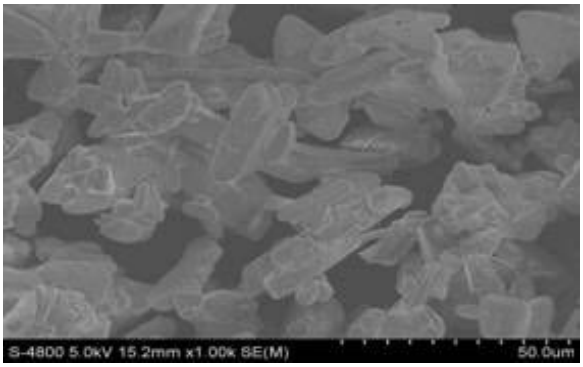


Figure 2. Times of calcium hypophosphite imaged under the magnified1000 times

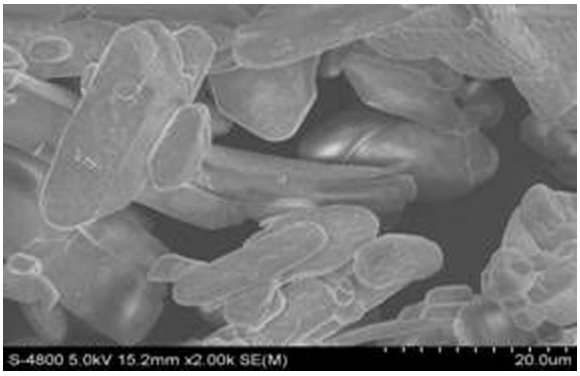
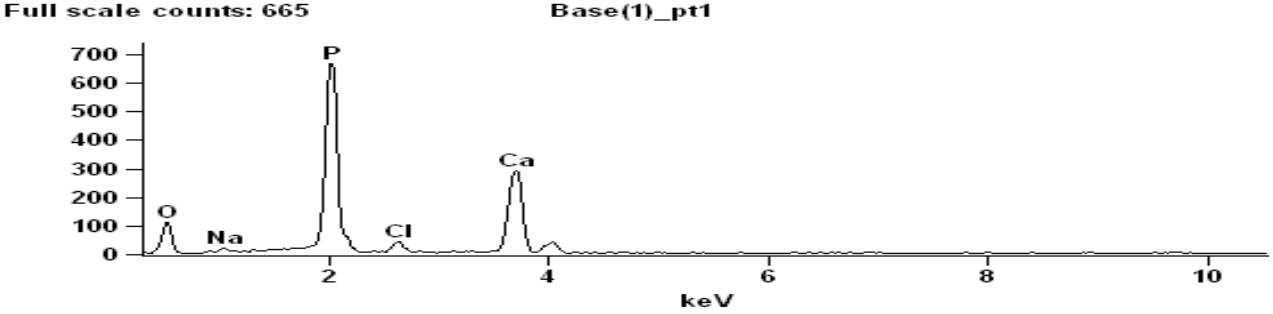


Figure 3. Times of calcium hypophosphitee imaged under the magnified 2000 times

The local area of the sample was scanned and the energy spectrum was obtained (see Figure 4).Phosphorus is the main element in calcium hypophosphate. Energy spectrum selected different area



so that area has different elements. But in general the content of phosphorus is the most about 29.34%.

	Weight·%·				
	O	Na	P	Cl	Ca
Base(1)_pt1	43.23	1.12	29.34	2.31	24.00

Figure. 4 Kinds of elements and their ratio in calcium hypophosphate

XRD ray diffraction (X).

The change of diffraction peak intensity of the main elements in calcium phosphate was analyzed by X-ray diffraction analyzer of DMAX2500PC. XRD selected Cu target, tube voltage was 40kV, and tube current was 100mA. λKa_1=0.15405nm, λKa_2=0.154433nm.XRD can automatically remove λKa_2 by using Jade software to analyze.

The absorption or reflection of various minerals that it is related to the mineral content, mineral matter itself, and other minerals in the mixture, but the same mineral that has variation of the diffraction intensity can approximately reflected change of the content [6]. Figure 5 is shown in Complete XRD map of calcium phosphate.

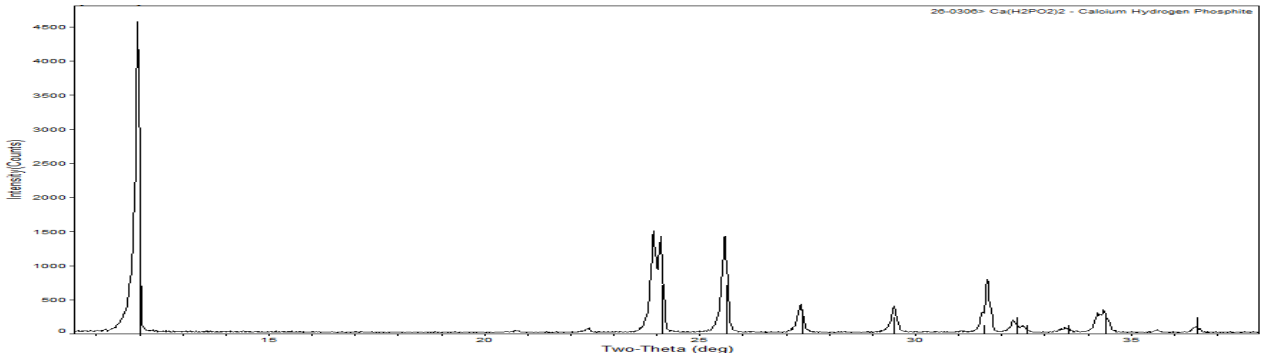


Figure. 5 Complete XRD map of calcium phosphate

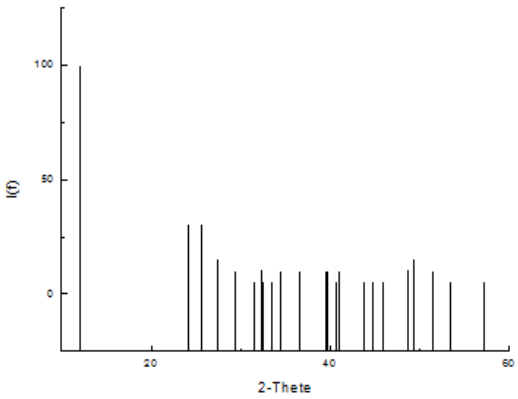


Figure 6 Origin makes calcium hypophosphate standard card map

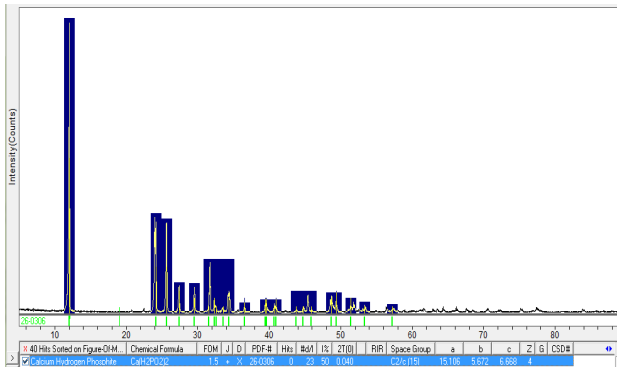


Figure 7 Jade's software makes the calcium hypophosphate map

Jade exports data and Origin makes Figure 6.The XRD map of the calcium hypophosphate is in agreement with standard map through Figure 7 and Figure 6, which proves that the hypophosphate does not contain other substances, and the purity is relatively high.

Conclusions

Sodium hypophosphate and calcium chloride synthesize calcium phosphate. The reaction conditions such as the concentration of raw materials, the synthesis temperature, and reaction time and so on were studied. Finally, the calcium chloride concentration is 2.0mol/L, temperature is 40 °C, reaction time is 100min conditions, the highest yield of calcium phosphate is 96.15%, and the particle size is about 0.563 μm. The structure of Calcium hypophosphate was rod and size is uniform, the content of phosphorus is the highest, and the purity of calcium phosphate is high. Compared with other methods, this method is simple and easy to implement, which greatly reduces the problem that deal impurities.

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