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Analysis on the properties of calcined waste mussel shell

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ABSTRACT

Mussel shell has been calcined on high temperature. Its main components calcium carbonate decomposed into CO_2 andCalcium oxide. Calcium oxide is superbase catalyst for the transesterification reaction. By means of differential thermal balance, the decomposition characteristics of mussel shell have been studied. And of electron microscope, TEM shows grain morphology characteristics of calcination at different calcining temperature. Organic has decomposed during 287^{0}C-458^{0}C. Decomposition of calcium carbonate starts from 600^{0}C to 800^{0}C, when it was balance. By use of orthogonal analysis, the main influence factors of specific surface area have been optimized. The optimal process parameters are 950^{0}C calcination temperature, 120μm initial diameter and 1 hour holding time.

KEYWORDS

Mussel shell;
Differential thermal analysis;
Specific surface area;
Orthogonal design.

INTRODUCTION

In recent years, the market scale of pearl jewelry promoted the rapid development of mussel farming. Annual production of mussel shell over one million tons, mostly of them were discarded as wastes in mussel farming area to cause serious pollution of the local water environment. So it is urgent to solve the environmental problems. The main component of mussel included more than 95% CaCO3, a small number of shells hormone (organic matter and trace elements) and a small amount of K, Na, Zn, Sr, Fe, Mg etc. Furthermore, the Mussel shell contains no Sulfur[1]. By firing mussel shell, higher degree of alkali reactive solid super base calcium oxide has been obtained, which can be used directly to the catalytic bio-diesel production. The decomposition product of the mussel shell contains a small amount of zinc oxide and strontium oxide which can improve the activity of calcium oxide alkali[2]. This method not only made the abandoned mussel shell into treasure but also played the role of the Environmental Protection. So the preparation of highly active calcium oxide has broad application prospects from mussel shell[3].

The decisive factor of the catalytic activity of solid calcium oxide as super base catalyst is specific surface area. The size of mussel shell specific surface area is closely related to the production process, including the particle size of the raw materials, the calcined temperature and the keeping time[4-6] (up to a certain temperature after the thermostat time). Currently, the research of shell is focused on the desulfurization performance, the microstructure and thermodynamic properties[7], etc.

In this paper, by means of electron microscopy, the

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change of CALCINATED surface area can be scanned under the different temperatures. The quality and thermal stability of river mussel shells can be learned by differential thermal balance. The optimal production conditions of catalyst can be received by orthogonal experiment method.

MATERIALS AND METHODS

Five age living mussels in Nanyang Ap River Reservoir were selected as the object of study. Firstly, impurities meat on the mussel shell surface must be stripped away and be washed with tap water, then sediment and other impurities attached to the surface were removed through steel brush. Secondly, the mussel shell soaked for two hours with 0.01% sodium hypochlorite solution then washed it with tap water and steel brush[8], then soaked for 0.5 hours with 0.5% Hydrochloric acid. At last, the shell has been washed four times with distilled water to remove a variety of organic and inorganic impurities on the surface. In a constant temperature oven for 105°C drying for one hour, crushed sieved 60 mesh, 80 mesh, 100 mesh and 120 mesh were obtained by particle diameter of about 250μm, 180μm, 150μm, 120μm the alternate sample[9].

Thermal decomposition principle of mussel shell is following,

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \quad (1)$$

The transient analysis curves of DTA and TG when mussel shell decomposed based on differential thermal balance LCT-2B. 20mg different size shell powder was taken as thermal analysis samples. Parameters have been set sampling interval as 1000ms, uniform temperature as 5°C per minute, and the final temperature is set to 1100°C. Because calcium oxide can be poisoned easily by carbon dioxide and water vapor in the air, the reactor should be carried out under the protection of nitrogen. Mechanism of calcium oxide being poisoned is following:

$$CaO + CO_2 \rightarrow CaCO_3$$
$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

Shell powder treated with alumina crucible in a muffle furnace as 10°C per minute uniform temperature to 800°C, 950°C, 1000°C or 1100°C(constant calcined temperature). Hitachi S-3400N-a°C type scanning electron microscopy was used to observe the morphology of the calcined product of different temperature. Specific surface area of product was measured by low temperature nitrogen adsorption method (BET)[9]. Absorbed-bate used nitrogen, relative pressure is set to 0.15MPa temperature was set at 180°C (nitrogen liquefaction point is -195°C), thus chemical adsorption can be avoided under low temperature.

Determination of the specific surface area generated by BET (It was discovered by three scientists Brunauer, Emmett and Teller.).

Specific surface area refers to the total surface area per gram of powder, particulate lattice outer surface area and crystal lattice empty cavity surface area superimposed, namely Low-temperature adsorption. The theoretical basis was rules that gas was absorbed in the surface porosity of particles. Under conditions of constant temperature and equilibrium state, the solid surface has a certain amount of adsorption of a certain pressure gas. The gas pressure determines the amount of adsorbed.

This method is currently recognized as the standard method for the measurement of solid surface area. The measurement principle is that physical adsorption would occur in the surface of the material (grain interior and the surface of the external through hole) at low temperatures. The physical adsorption is based on multilayer approach, the first layer is not yet saturated adsorption to produce a second layer on which the adsorption. They may produce a second layer on the third layer adsorption, the adsorption equilibrium stability layers adsorption reached equilibrium at the same time. The measurement of gas adsorption pressure and the adsorption volume can be calculated, and so the specific surface area. Isotherm equation is formula (3):

$$\frac{P/P_0}{V(1-P/P_0)} = \frac{C-1}{V_m C} \times P/P_0 + \frac{1}{V_m C} \quad (3)$$

Where V is Volume of gas adsorption (unit is milliliter), V_m is Monolayer saturation adsorption capacity, P is the adsorption pressure/Pa P_0 is the adsorption saturated vapor pressure/ Pa and C is the coefficient.

Here let

$$Y = \frac{P/P_0}{V(1-P/P_0)} \qquad X = P/P_0$$

$$A = \frac{C-1}{V_m C} \qquad B = \frac{1}{V_m C}$$

According to the experimental measurements, drawing the curve of $Y = AX + B$.

So the value of V_m was obtained. The surface area can be obtained by formula (4)

$$S_g = \frac{4.36 \times V_m}{W} \quad (4)$$

RESULTS AND ANALYSIS

Decomposition characteristics and morphology of the mussel

Figure 1 DAT and TG curves shows the mussel shell decomposition process, in the range of 287°C to 458°C, accompanied by a strong exothermic peak and with weightlessness weight loss rate of 4.1%, which presumably because of the decomposition of organic matter and release heat. There was one slight weaken exothermic peak in the range of 383°C to 458°C of the calcium carbonate crystal phase transition from aragonite calcite phase caused by the endothermic weakening of the role in the exothermic decomposition of organic matter. Calcium carbonate decomposition occurs when the temperature rose during 600°C to 800°C , and at the same time, rapid weight loss and more endothermic phenomenon accounted that mussel shell main ingredients generated Calcium oxide and CO_2.

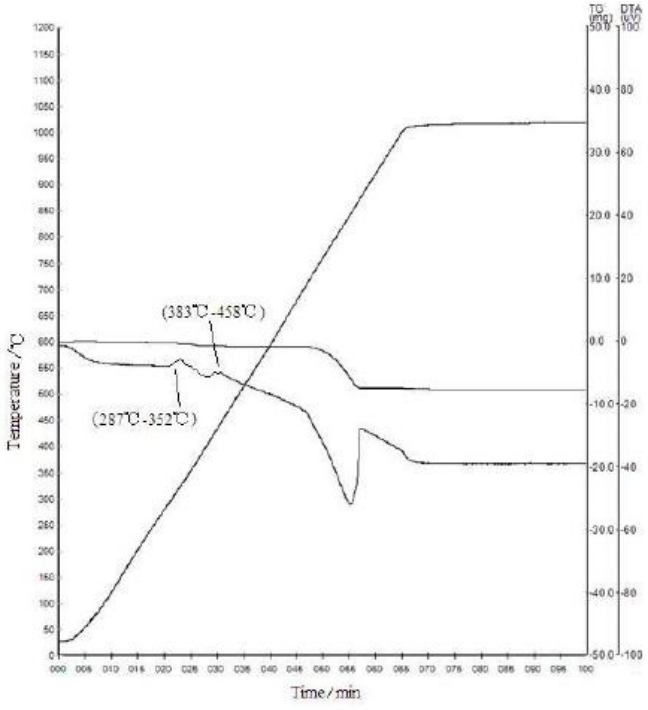

Figure 1 : Thermal analysis spectra of mussel shell

As weight loss rate is known that mussel shell contains about 94.875% of the calcium carbonate. The sample of decomposition was dissolved with 1% hydrochloric acid and was titrated with 5% sodium carbonate solution, then dried in addition. Calculated production was that mussel shell contains about 94.68% of calcium carbonate. When the calcined temperature reached 900°C, TG curve does not change, the decomposition of calcium carbonate reached equilibrium (almost completely decomposition). With continue heating, another period of endothermic generated when lattice defect of calcium oxide gradually reduced. At 1100°C , calcium oxide turned into molten sintering as Figure 2-D as shown. The TEM image shown in Figure 2 for the sample, the product was calcined at different temperatures to 120 mesh particle size mussel product particles gradually refined as the temperature increased.

Powder diffractometer was used to verify the composition of the calcined product. Copper was used

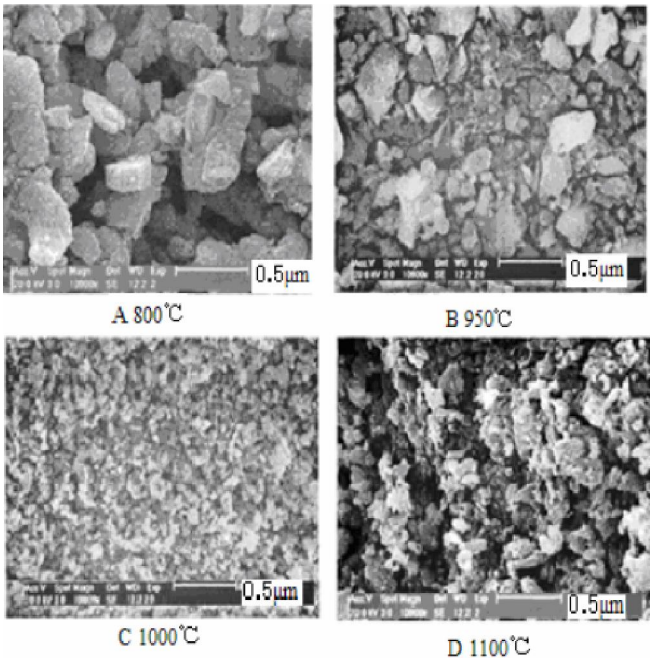

Figure 2 : Scanning electron image of mussel shell calcinations at different temperature

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as the medium. Detecting results were shown in Figure 3. Strong diffraction peak was coincident to that of calcium oxide. It can be seen from the diffraction pattern of the calcined product that calcium carbonate disappeared. Those weak peaks at 100, 102 and 110 represented zinc oxide.

Specific surface area of orthogonal design

The specific surface area of the catalyst particles determines the efficiency of heterogeneous catalytic. Therefore, the orthogonal design method of calcined product was chosen to study the main factors affecting the specific surface area. Pulverized particle diameter R (A), the calcined temperature θ (B) and the holding time t(C), each with four levels of each factor, and average value thereof. Factors and levels shows as TABLE 1.

TABLE 1 : Factors and levels of specific surface are

levels	Diameter /μm	temperature/°C	Holding time/h
	A	B	C
1	120	800	0.5
2	150	950	1
3	180	1000	1.5
4	250	1100	2

TABLE 2 : Orthogonal analysis of calcined product.

No	Factors			Average specific surface area/m^2/g
	A	B	C	
1	1	1	1	31.2
2	1	2	2	42.5
3	1	3	3	51.9
4	1	4	4	36.5
5	2	1	2	27.5
6	2	2	1	38.5
7	2	3	4	36.9
8	2	4	3	29.3
9	3	1	3	30.3
10	3	2	4	43.3
11	3	3	1	37.4
12	3	4	2	40.1
13	4	1	4	31.1
14	4	2	3	33.2
15	4	3	2	34.3
16	4	4	1	27.5
$\overline{K}_{1j}$	40.5	30.0	34.7	
$\overline{K}_{2j}$	37.8	37.8	36.5	
$\overline{K}_{3j}$	33.1	41.7	35.8	
$\overline{K}_{4j}$	31.5	33.4	35.9	
R_j	9.0	11.7	1.7	

Accordance with the requirements of the orthogonal design, strict test arranged in a combination of factors, the experimental program and test results are shown in TABLE 2.

As can be seen from the analysis results, the calcined temperature is the most important factor on the contrast surface area, the initial crushing particle size is more and the holding time is important yet. The calcium carbonate decomposes is a reversible reaction, the higher the temperature, the faster and thorough decomposition, so the particle is refined more rapidly. There was certain lattice distortion among the grains of calcium oxide. As the temperature continues to rise, the lattice atoms reconstruction reduced the gap among each other, thereby reducing the specific surface area of the product. So when the temperature was at 1000 °C,

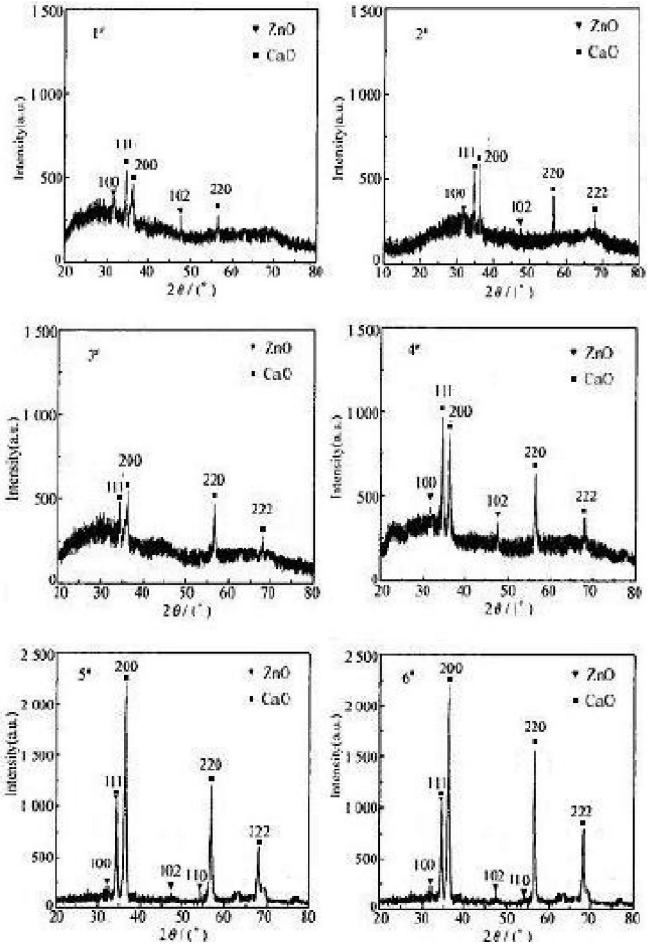

Figure 3 : XRD pattern of calcined product

the product particles reach nanometer level, close to 50nm. Decomposition of the calcium carbonate was from outside to inside, so the smaller the particle the more easily was decomposed and it can easily reach the balance decomposition. Holding time played a certain role on the lattice reconstruction of decomposition products, while their impact is relative minor comparing to the calcined temperature.

Figure 3 is a response curve of a orthogonal analysis. Specific surface area reached maximum only when the original particle size was 120μm, calcining temperature 1000 °C and holding time was one hour. Therefore, from TABLE 2 and Figure 4, the best process of largest specific surface area was B3A1C2. Calcined mussel in accordance with this condition, obtained heterogeneous catalytic 42.53m2 /g, and a higher rate of transesterification obtained when it was applied to the production of bio-diesel. So it fully meets the requirements of catalytic superbase catalysts.

CONCLUSION

(1) The differential thermal analysis of the mussel shell discovered its thermal decomposition rule, which two significant changes have occurred in uniform during the heating process. From the DAT and TG curve of mussel shell, the decomposition of organic and calcium carbonate have generated with the loss of shell weight. Calcium carbonate content can be calculated about 94.68%. DAT curve becomes less steep when the temperature rose to 800°C, while calcium carbonate is almost completely decomposed.

(2) TEM image shows that a small amount of mussel decomposed when the temperature was at 600°C. As the calcined temperature raised, the calcinations become smaller and smaller. The product gradually molten sintering when the temperature is at 1100°C.

(3) By orthogonal experimental design, calcined temperature was the most important factors in the three factors. The initial particles followed by holding time certain. Production conditions of the calcined temperature 950°C, the initial particle size 120μm and the holding time one hour were perfect to obtain the optimum surface area of calcinations.

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