

Synthesis of α -Fe₂O₃ Superfine Powders with Steel Pickling Waste Water and Dust Water in the Production of Bleaching Powder

Li CHEN^{1,a}, Xuemin ZU^{1,b}, Dandan LI^{1,c} and XingYao WANG^{1,d*}

¹Department of Chemistry, School of Science, Tianjin University, Tianjin, China

²Department of Chemistry, School of Science, Tianjin University, Tianjin, China

^a wshrcn@163.com¹, ^b15226185317@163.com,

^clidan748732915@163.com, ^{d*} wxyghw@tju.edu.cn

Abstract. A simple method of resource processing was developed by applying the material preparation technology to hazardous waste utilization. The iron oxide was synthesized by this method with steel pickling waste water and dust water in the production of bleaching powder. The effect of temperature on the synthesis was studied. X-Ray diffraction (XRD), transmission electron microscope (TEM) showed that the iron oxide samples are bright red and spherical α -Fe₂O₃ powders, and the particle size analysis exhibited that the size of samples prepared at 70°C and 80°C were between 250-300nm.

1. Introduction

Bleaching powder is high concentration of calcium hypochlorite. Available chlorine of calcium hypochlorite is as high as 70 percent. Bleaching powder can be used as efficient bleach for cotton, silk products and disinfectant for household, swimming pool and water treatment. Due to the high stability, heat resistance, fit for long distance transportation, bleaching powder has been widely favored. Bleaching powder varies from its raw material. For products made from chlorine, there are two methods of calcium and sodium^[1]. But no matter what kind of technology used, there is dust water in the production of bleaching powder, and this kind of production waste water is called the rinse liquid including sodium hypochlorite. The liquid by-product were commonly known as "rinse liquid"^[2], its main ingredient is Ca(ClO)₂, NaClO, NaCl, CaCl₂ and H₂O. If the rinse liquid direct discharged without any treatment, it will cause very serious environmental pollution, so dealing with rinse liquid effectively will be a benefit both for the bleaching powder industry and environment.

In the steel industry, due to the pickling step^[3] is inevitable, so there are a lot of steel pickling waste water were produced. Steel pickling waste water contain high concentrations of hydrochloric acid and a variety of metal ions^[4], its pH is about 0.2-3.0. The main metal ion of steel pickling waste water is Fe²⁺, also containing a small amount of Fe³⁺, PO₄³⁻, Zn²⁺, and some other impurities^[5]. Therefore, if the steel pickling waste water are directly

* Corresponding author: wshrcn@163.com

discharged without any treatment, it will lead to a series of environmental problems. At present, there was not a good way to solve steel pickling waste water. Some companies spend tens of millions to purchase the large-scale machinery equipment from abroad to treat steel pickling waste water, this method is relatively mature, but the cost is too high, the operation is too difficult. Coupled with the uneven quality of the steel pickling waste water of each enterprise, it is very difficult to use the same set of equipment, with a same program to solve the problem produced by steel pickling waste water. Therefore, how to deal with this problem effectively is not only related to the steel industry's own development, but also closely affect the surrounding environment.

Red iron oxide Fe_2O_3 , also known as iron oxide red, is a traditional and important inorganic pigments. Its chemical formula is $\alpha\text{-Fe}_2\text{O}_3$, and it is red or dark red amorphous powder. Fe_2O_3 has excellent resistance for light, high temperature, alkali and atmospheric effects^[6], its raw materials is simple and easy to obtain. Also it has wide range of uses and minimal toxicity. In the rubber industry and construction engineering industry, Fe_2O_3 can be used as colorant^[7] of artificial marble, terrazzo floor, wall finishing paint. In the electronic telecommunications industry it is an important raw material in the manufacture of the ferrite element^[8]. In the chemical industry, it is a catalyst^[9] and chemical raw materials of the other iron production. In addition, it can be used as a coloring agent and filler for plastic, asbestos, linoleum, leather and so on. Fe_2O_3 commonly used in construction, rubber, plastics and coatings industries, it has an extremely wide range of applications and application prospects. Therefore, researchers continue to research raw materials, synthetic route and optimization scheme of red iron oxide materials. This paper proposes a new method for the synthesis of red iron oxide, with the idea of changing waste into treasure, not only synthesizing high quality nano iron oxide red, but also dealing with the huge environmental polluting problems facing in calcium hypochlorite industry and the steel industry.

The traditional treatment of rinse liquid^[10] and steel pickling waste water^[11] were to make it possible not to pollute the environment. In this work, strong alkaline rinse liquid was mixed with the very acidic steel pickling waste water. Thus rinse liquid not only can be used as a base to neutralize the acidic, but also can act as a strong oxidant because of the strong oxidizing ClO^- to oxidize Fe^{2+} contained in steel pickling waste water. The innovation not only solves the problem of environmental pollution produced by these two waste liquids, but also obtains the high-quality $\alpha\text{-Fe}_2\text{O}_3$ superfine powders. The method for treating wastes not only achieves a clean concept of green chemistry, but also a certain economic benefits, and this achieve a better treatment of rinse liquid and steel pickling waste water.

2. Experimental

Fe_2O_3 nano-particles were synthesized in the liquid phase reaction by mixing rinse liquid with steel pickling waste water. First, the rinse liquid was filtered to get the filtrate A. Second, put the steel pickling waste water under constant conditions of 70°C , then 10%(mass fraction) NaOH solution was added to adjust the pH of steel pickling waste water between 2.5-3, stirring 30min, standing, filtered to get transparent pale green filtrate B. Third, took a certain amount of filtrate A placed in the reactor at a certain temperature, then filtrate B was added slowly, then chlorine with a pungent odor generated, collected the chlorine for other experiments. Fourth, the filtrate B was continued to add until there is no chlorine generating. At this moment substance in the reaction system was acidic orange viscous. Fifth, continued to add the 10% NaOH solution to adjust the pH of reaction system substance to between 7-7.5, then stopped the reaction. At this point the substance in reaction system were a dark red solid-liquid mixture. Sixth, standing, filtrated, the filtrate

was neutral or slightly alkaline solution, it can be used as the reaction aqueous solvent to recycle, the cake solid was red or dark red Fe_2O_3 . At last, the solid was washed several times with distilled water, then filtrated, dried, ground and then heated at 750°C for 2h, red Fe_2O_3 powder were got finally.

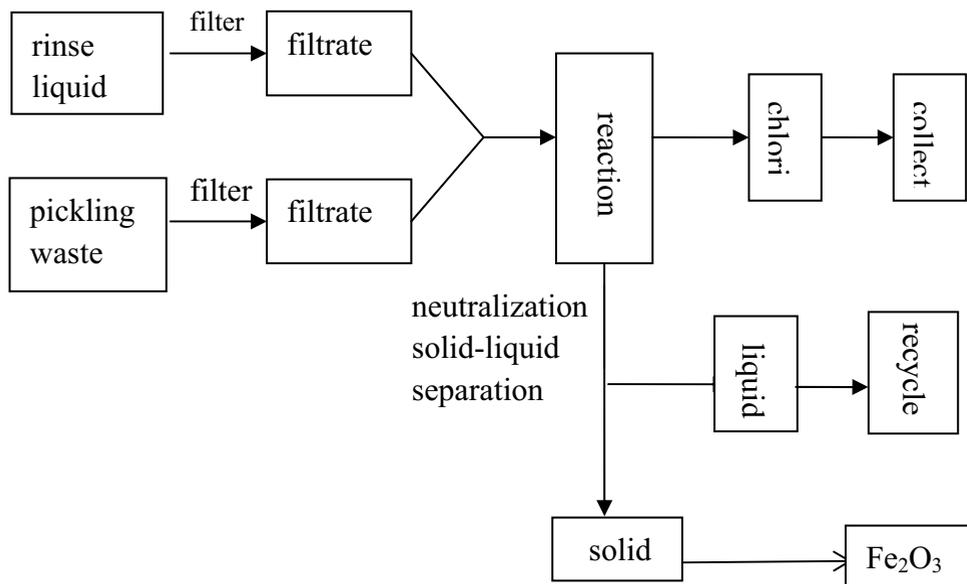


Fig.1. Schematic of the experimental procedure

3. Results and Discussion

When the strong alkaline and oxidation of rinse liquid, which was not only used as a base but also as an oxidant, was mixed with the very acidic steel pickling waste water, the OH^- in rinse liquid neutralizes the H^+ in steel pickling waste water, and the ClO^- in rinse liquid will oxidize Fe^{2+} in steel pickling waste water into Fe_2O_3 . The above principles are as follows:

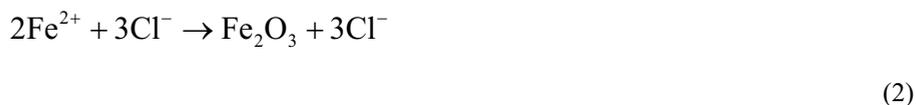


Table 1 presents samples synthesized at different temperatures. According to the contents of table 1, along with the reaction temperature was raised from 20°C to 80°C , the reaction was filtered faster and faster, indicating that the particle size of the product increases, so that the filter easier. The filtrate color was changing from yellowish to colorless at last, indicating that particle size of low temperature product was too small, so they can flow into filtrate through filter paper. So the result was the color of filtrate change

to yellowish. With the reaction temperature increasing gradually, particle size of the product increased more and more, so the amount of particles flowing into filtrate through filter paper were less and less. Until 70°C, almost no product particle flowing through the filter paper, so the filtrate was essentially colorless. Cake color changed from yellow to red and then to dark red, indicating that when the reaction temperature was low the product of the reaction not only contain iron oxide red, but also may contain other impurities like yellow iron oxide. Then the result is a yellow color in product. With the reaction temperature was gradually increasing, the yellow in product color was more and more pale and the red color is more and more obvious. Until 70°C, the color of product was substantially pure red iron oxide color. Following the above analysis, it can be concluded that with the reaction temperature increasing, the particle size of the product increase, the color of the filtrate gradually become colorless, the color of the product gradually turn red and become more and more pure. Therefore, in order to get the best product and achieve zero emission concept of green chemistry, the best choice is to select the reaction temperature at 70-80°C.

TABLE 1 SAMPLES SYNTHESIZED AT DIFFERENT TEMPERATURES

temperature	filtration rate	filtrate color	cake color
20°C	slower	yellowish	yellow-red
30°C	slower	yellowish	yellow-red
40°C	slower	yellowish	yellow-red
50°C	slow	yellowish	yellow-red
60°C	slow	yellowish	yellow-red
70°C	fast	Almost colorless	red
80°C	faster	colorless	dark red

XRD patterns of samples synthesized at different reaction temperatures are presented in Fig.2. When the reaction temperature was 20-50°C, compared with the standard structure of Fe₂O₃(JCPDS card No.39-1346), the XRD peaks of the product has small miscellaneous peaks, indicating that the product contains a certain amount of impurities. When the reaction temperature is increased to 60°C, XRD peaks of the product could be in consistent with the standard structure of Fe₂O₃. The results showed that the products consisted of pure phases. Compared with 60°C and 70°C, the XRD peaks of 80°C XRD is stronger and sharper, indicating the growth of the crystalline of the product is better and more uniform. Therefore, from the analysis of XRD, selecting the reaction temperature 60-80 °C is available.

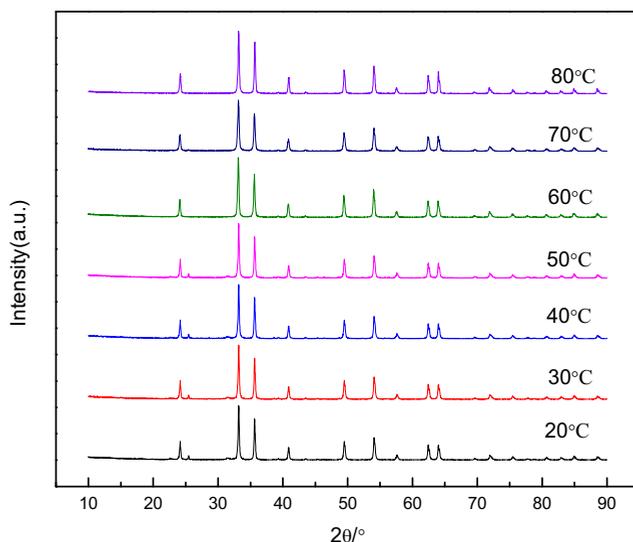
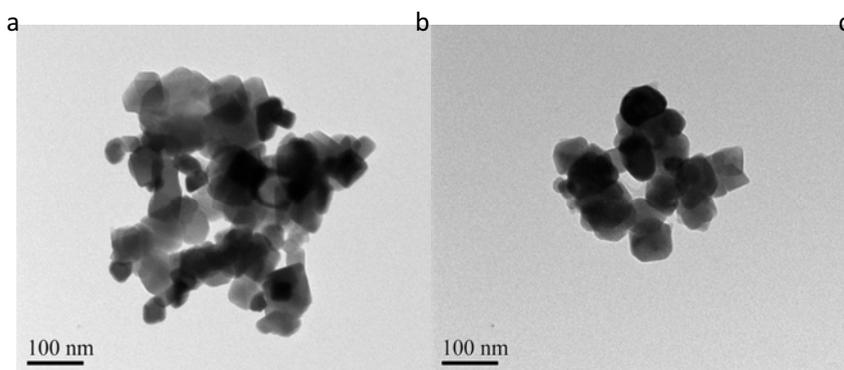


Fig.2. XRD patterns of samples synthesized at different temperature

TEM images of samples synthesized at different reaction temperatures are presented in Fig.2. With the reaction temperature increasing from 60°C to 80°C, the morphology and size of the product particle changed significantly. When the temperature was low, the product was not easily dispersed and easily gathered, the whole particles were similar spherical and granular unevenly distributed. As the reaction temperature was getting higher and higher, the dispersion of the product was getting better and better, the size of the product particle was more uniform and almost all particles are spherical and uniform distributed. Therefore, we can conclude that this reaction requires a higher temperature to obtain good dispersion, uniform particle size and spherical iron oxide red, so choose the optimum reaction temperature is 80°C.



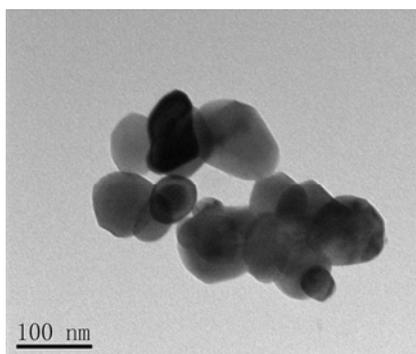


Fig.3. TEM images of synthesized at 60°C(a), 70°C(b) and 80°C(c)

Particle size patterns of samples synthesized at different reaction temperatures are presented in Fig.3. As the reaction temperature was increasing from 20°C to 80°C, the particle size of the product gradually increased from about 50nm to 300nm. It is a good proof to the front judgment on the particle size of the product.

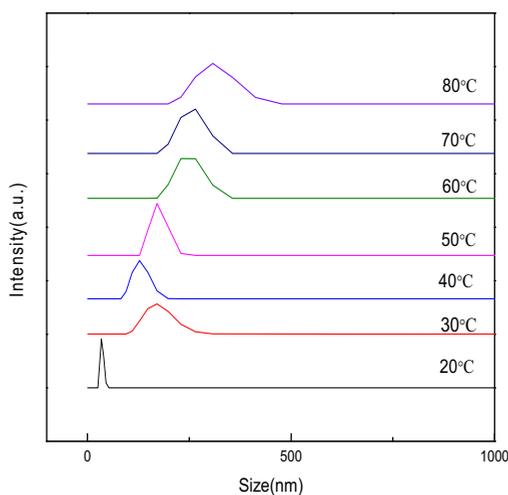


Fig.4. particle size patterns of samples synthesized at different temperature

4. Summary

The spherical α -Fe₂O₃ superfine powders were successfully synthesized with steel pickling waste water and dust water in the production of bleaching powder. The temperature has a very important influence on synthesis, and it is shown on the structure, purity, morphology and particle size of the iron oxide samples. That the pure α -Fe₂O₃ particles synthesized at 80°C have a high-quality with better spherical morphology, bright

red color, small size (300nm) and narrow distribution can be used for red pigment. Our results suggest that this effective, simple, cheaply and fast route based on material preparation technology is a promising method, and will produce tremendous economic and environmental benefits.

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