The Application of Nano-zinc oxide in Petrochemical

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Abstract. In today's world, fossil fuels dominate the energy supply. However, petroleum refining produces many toxic gases, including sulfur oxides, which have caused many serious environmental and health problems. To reduce this negative externality, petroleum firms use desulfurizers to absorb the sulfur. There is a significant drawback, though, as the traditional desulfurizer, like zinc oxide, has quite a low sulfur capacity at room temperature. With the recent developments in nanoparticles, a more efficient desulfurizer has come onto the market. It is called nano-zinc oxide, and due to the larger surface area-to-volume ratio (SA/V ratio), this desulfurizer version can absorb significantly more sulfur in room conditions. Current research shows that nano-zinc oxide has considerable potential in helping firms reduce the emission of sulfur dioxide, and thus lowering the negative externality during fossil fuel production.

Keywords: Nano-zinc oxide, Petroleum refining, Desulfurizer, Nanoparticles.

1. Introduction

The excessive emission of sulfur oxides can cause a lot of harm to the world; for instance, high concentrations of sulfur oxides can damage the soil, thus decreasing the growth of trees and plants. Sulfur dioxide can cause acid rain, which is harmful to human infrastructure. [9] The acute toxicity of inhaling hydrogen sulfide is moderate. Exposure to 800 ppm for 5 minutes can be fatal. Inhalation of 1000 to 2000 ppm may cause unconsciousness, while exposure to lower concentrations may lead to headache, dizziness, and stomach discomfort. [17]

As the former mentions, applying nano-zinc oxide can dramatically increase petroleum firms' desulfurization ability. Thus, to decrease the harm that sulfur oxides bring to human society, several methodologies are used to make nano-zinc oxide, including solutional chemical, spray drying, and micro emulsion methods [10]. However, some firms are still unwilling to use nano-zinc oxide as the main desulfurizer (about 20% in China), contributing to much pollution. [11]

This paper evaluates nano-zinc oxide's synthesis, mechanism, and performance improvement as a petrochemical refining desulfurizer. Nanoparticles are discrete nano-objects with all three Cartesian dimensions less than 100nm, as the International Organization for Standardization (ISO) claimed in 2008. [8]

2. Synthesis of Nano-Zno

2.1 Solution Chemical Method

The solution chemical method involves using a chemical reaction to make nanoparticles.

In manufacturing nano-zinc oxide using the solution chemical method, there are two raw materials: ammonium bicarbonate and ammonium carbonate. [1] The mole ratio of those two should be 1:1 or 6:1. This can make the zinc ion injected into the precipitates slowly and uniformly. The two raw materials should be injected into a breaker simultaneously. After that, the beaker containing the solution mixture is put on an electronic mixer, the temperature should be 20°Cto 50°C, and the PH should be in the range of 5-8. The concentration of the injected zinc sulfate solution should be 0.5-1.55/mol/L. [1] In the reaction, ammonium carbonate (high CO_3^{2-} conc.) hydrolyzes first, increases the PH to 8.5 or above, and causes the carbonate ion to react with zinc（II）to form $ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$'s crystal nucleus. The ammonium bicarbonate is hydrolyzed, then（low CO_3^{2-} conc.）, which HCO_3^- suppresses PH fluctuations, and avoids the particle aggregation due to local oversaturation of Zn^{2+}. After that has been accomplished, the ppt. It is filtered out and rinsed with distilled water. The residual is then dried and baked to form nano-zinc oxide. The order of drying and calining should be carefully done, as first drying (100℃-200℃), second calining （250°C-500°C）. [4] If calcined directly, the sediment will have strain instead, breaking the structure of nano-zinc oxide. In the drying process, the precursor will form a porous structure, providing tunnels for the diffusion of H_2S. In the calcine process, the precursor will change into the cube crystal structure （zinc oxide）, from a layered structure ($ZnCO_3 \cdot 2Zn(OH)_2 \cdot H_2O$), and make the desulfurizer SA/V ratio achieve 60-80 m²/g, which will improve the density of desulfurization at the sites significantly. [3-5]

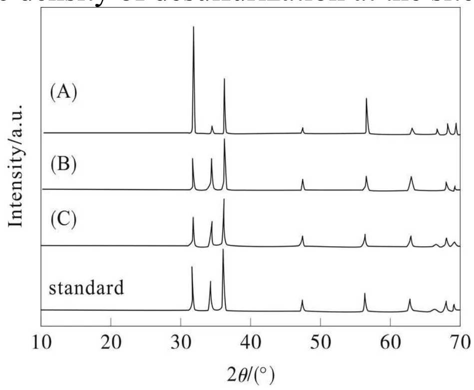

Figure 1: XED of nano-zinc oxide [6]

2.2 Evaluation of Solution Chemical Method

The operating process for the solution chemical method is relatively straightforward. It requires mixing two chemicals and operating at suitable temperatures and pH ranges.

However, the drawbacks of this method are obvious. Firstly, it cannot be used for mass production. That's because the reactants' temperature range and mole ratio are quite controllable when the amount of reactants is in the unit of tons. Secondly, there are still areas for the particles' separation to increase, as shown in the PowerPoint presentation. They might become lamps if no suitable surfactants and string methods are used. To sum up, the chemical solution method is ideal for making nano-zinc oxide in the lab, but it is not a good option for making desulfurizers for industrial use.

2.3 Precipitation-Thermal Decomposition Method

The precipitation-thermal decomposition method first makes the precursor (precipitate) under chemical reaction, then breaks down the ppt. by heat to get the final product. [12]

Industry usually mixes soluble zinc salt, e.g., zinc chloride, and carbonate salt, e.g., sodium carbonate, in a mole ratio of 1:2. The temperature range is 60°C-100°C, [13] the pH range is 8-10, and the reaction time should be between 10 and 120 minutes.

The precursor will then form, which is basic zinc carbonate ($Zn_5(CO_3)_2(OH)_6$). After the precursor forms, filter the PPT. (precursor) and rinse to remove impurities like sodium and chloride ions.

After that has been accomplished, put the PPT into the Ma Fei Furnace, and heat under an inert gas, e.g., Nitrogen atmosphere, to raise the temperature to 300-600°C. Then keep the temperature for 30-300min. The ppt. will decompose to form nano-zinc oxide, releasing carbon dioxide and stream.

After the products are cooled to room temperature, they are ground to obtain nano-zinc oxide with a uniform particle size.

During the manufacturing process, there are several noticeable details. For the precipitation step, the temperature should be at least 60°C, as a colloid will form, which is unsuitable for the following process. The PH range is 8-10, as if it is too high, other kinds of zinc salts might form, which the ratio of Zn^{2+} and CO_3^{2-} is unsuitable for later manufacturing. Moreover, a constant mixing rate is essential for the reaction to succeed. [13]

The temperature of thermal decomposition can determine the diameter of nano-zinc oxide. The research shows that the diameter of nano-zinc oxide is 8-10nm at 300°C and increases to 60nm at 600°C.

2.4 Evaluation of Precipitation-Thermal Decomposition Method

The precipitation-thermal decomposition method has several advantages. First, the production cost is relatively low. Second, this method only needs to heat the PowerPoint once, which uses less energy than the two steps in the chemical solution method (dry and bake). Thus, less energy is required for this method.

Thirdly, the precipitation-thermal decomposing method is less sensitive to the temperature range (60°C-100°C) compared with the temperature range of the solution chemical method (20°C-50°C). Thus, the success rate of the precipitation-thermal decomposition method would be higher than that of the solution chemical method.

However, the negative part of this method is also quite apparent; for example, the reactant ratio should be strictly controlled at 1:2(Zn^{2+}: CO_3^{2-}), which will increase the production cost. The calculation of the chemical equation for the decomposition of basic zinc carbonate shows that 160.3kilograms of carbon dioxide will be released if one ton of basic zinc carbonate is decomposed. To sum up, the precipitation-thermal decomposition method is suitable for the mass production of nano-zinc oxide, if the pollution can be controlled.

3. Desulfurization Mechanism

Once the nano-zinc oxide has been manufactured, the desulfurizer is used.

The nano-zinc oxide will react with hydrogen sulfide and produce stable zinc sulfide. The reaction is irreversible due to the significant thermodynamic equilibrium constant at room temperature, 10^62. [2]

In the reaction process, the hydrogen sulfide molecule will form a covalent bond with the nano-zinc oxide desulfurizer and thus be locked on the surface of the nano-zinc oxide. $ZnO(s)+H2S(g) \rightarrow ZnS(s)+H2O(g)$, $\Delta G=-91607.2+15.2T$ [15].

The reaction can be separated into pore diffusion, surface reaction, and lattice diffusion. At the beginning of the reaction, H2S in the feed gas diffuses through pores and adsorbs onto the surface of the desulfurization agent. Then, H2S undergoes dissociation and other deprotonation processes on the surface of the desulfurization agent to form HS−/S2−, which subsequently reacts with surface zinc ions to produce ZnS. Since the ionic radius of sulfur ions is larger than that of zinc ions, the ZnS formed on the surface encapsulates the unreacted ZnO core. It is generally believed that during the removal of H2S by ZnO, the growth of ZnS follows an intrinsic growth mechanism, and the desulfurization reaction follows a shrinking unreacted core model. As shown in Figure 3, the reaction first forms a ZnS layer on the surface of ZnO. As the reaction proceeds, external S2− ions pass through the ZnS layer to reach the ZnS/ZnO interface and react with Zn2+ ions in the ZnO bulk to form ZnS. The generated ZnS grows from the outside to the inside, while the unreacted ZnO gradually shrinks from the outside inward until the reaction is complete. [15]

Figure 2: reaction between zinc oxide and hydrogen sulfide. [15]

4. Evaluation of Using Nano-Zinc Oxide Desulfurizer

The nano-particles have lots of advantages. Due to a high SA/V ratio, the desulfurization performance at room temperature of a 4 nm ZnO desulfurizer is 16 times that of a 44 nm ZnO desulfurizer. [15] It can lower the total sulfur content to 0.3ppm, satisfying the environmental requirement, e.g., GB 16297. There are no polluted products, and Zinc sulfate can be used in the rubber and coating industries. [14].

However, there are challenges; the most significant ones are low mechanical strength and the inability to return the zinc sulfate produced to nano-zinc oxide. This means the desulfurizer should be constantly changed, which costs a lot.

5. Improvement Strategies

5.1 Recycle the product

Although nano zinc oxide cannot be reused, the waste generated from desulfurization can still create value for enterprises through proper recycling. The principle of recycling nano zinc oxide desulfurization products is relatively simple. First, the waste agent is crushed and roasted at around 500° C, and most of the ZnS is converted into coarse ZnO upon contact with air. Then, impurities are removed through acid decomposition, oxidation slag removal, zinc powder replacement, and precipitation of acid ions, resulting in anhydrous ZnCl2 or ZnSO4 • 7H2O. The generated SO2 can be recovered in two ways: one is producing sulfuric acid, and it can also be absorbed with lime slurry, with the by-product CaSO3 being used for purposes such as dichlorination. [16]

5.2 Morphology Control

The second way to increase the nano-zinc oxide’s desulfurization ability is to change its shape, by using a uniform precipitation method to control the reaction time in 6 hours and 60°C, making the bar-like nano-ZnO with a high length-to-diameter ratio. Its hollow structure can improve sulfur capacity and delay sintering. [7]

6. Conclusion

This paper presents two methods of manufacturing nano-zinc oxide and explains their working principles. It also provides improvements in the desulfurizing ability of nano-zinc oxide.

The solution chemical method is suitable in the lab because it is easy to operate in small quantities and can examine changes in temperature, PH value, and mole concentration, which are important factors for future mass production. The precipitation-thermal decomposition method is suitable for industrial production because it can be easily operated in large quantities and requires less energy than the solution chemical method.

The dieselization process primarily involves exchanging sulfur in sulfur-containing molecules, such as hydrogen sulfide, by utilizing oxygen vacancies in nano-Zinc oxide, and then binding the sulfur to zinc sulfate.

Improvements in the desulfurizing abilities of nano-zinc oxide can be considered in two parts. One uses metal oxides, such as zinc titanate, to enhance the sulfur-containing ability and mechanical strength of nano-zinc oxide. The other is changing the nano-zinc oxide’s particle structure from sphere to bar. However, there are still many areas for improvement, such as developing better manufacturing techniques, utilizing cheaper raw materials, and increasing business popularity.

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