

Review on the Application and Preparation of Ozone Catalysts

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Abstract. This paper reviews the recent advances in the application of ozone catalysts and their preparation. The main categories of ozone catalysts are introduced, and the properties of the more widely used metal oxide catalysts, supported catalysts, carbonaceous material catalysts and novel catalysts are summarized. The supported catalysts and carbonaceous material catalysts have better catalytic effect compared with metal oxide catalysts. The four most commonly used catalyst preparation methods are reviewed, and the prospects for catalyst development based on the current research status are presented.

1. Introduction

In recent years, catalytic ozonation technology has made great progress. The addition of catalysts has moderated the reaction conditions, accelerated the decomposition of ozone, and improved the oxidation capacity. In the reaction process, the catalyst is different, the treatment effect and the treatment cost are very different. Ozone catalyst is the key to realize ozone oxidation technology to reduce treatment cost and improve ozone utilization. Because the homogeneous catalyst exists in the form of transition metal ions, it is easy to lose and waste in practical application. Most metal ions are harmful to the environment, the concentration of transition metal ions is low, and the separation and recovery of transition metal ions is very difficult. Therefore, there are few reports and studies on homogeneous catalysts in domestic and foreign literatures. In order to overcome the above shortcomings, many scholars have carried out a lot of research. Heterogeneous catalyst was prepared from homogeneous catalyst. The catalyst exists in solid form, which is easy to separate solid and liquid, easy to operate, and has high catalytic ozone decomposition efficiency. Compared with homogeneous catalyst, heterogeneous catalyst can be reused many times, no secondary pollution, lower water treatment cost, higher activity and stability [1]. Therefore, non-homogeneous ozone catalysts are more widely used than homogeneous ozone catalysts. With the development of research, many representative catalysts have been prepared which can meet different treatment requirements. The search for an effective and stable catalyst is the key to non-homogeneous catalytic ozone decomposition. Usually catalysts are mainly classified into metal oxide catalysts, supported catalysts, carbonaceous material catalysts as well as novel catalysts.

2. Advances in ozone catalysts

2.1. Metal oxide catalysts

Metal oxide catalyst refers to the catalyst with metal oxide as the main catalytic active component, and its catalytic efficiency depends on the selection of metal ions and its preparation process. Metal oxides can be divided into transition metal oxides and non-transition metal oxides. Transition metal oxide catalysts are widely used in industry because of their low price, simple preparation and better stability and catalytic performance [2]. Metal oxide catalysts are not supported by carriers, which makes their specific surface area low and active components easily lost, and the catalytic degradation effect is not obvious. Transition metals readily gain and lose electrons, a property that facilitates the generation of reactive species and the redox reaction of ozone. Usually catalysts such as Mn_3O_4 , Co_3O_4 , CeO_2 and TiO_2 perform better in catalysis [3].

Normally, the hydroxyl group present on the surface of the metal oxide catalyst is the active site of the reaction, which releases protons and hydroxyl groups into the solution by ion exchange with anions and cations in water, while adsorbing the anions and cations in the solution to the catalyst surface [4]. Due to its low specific surface area, easy leaching of active elements and large microcrystalline structure, the use of non-supported metal oxide catalysts is limited, and the catalytic degradation effect is not obvious, but simply increasing the specific surface area of the catalyst has no significant effect on its activity.

Metal oxide catalysts are often prepared by the precipitation method, which generally involves adding a precipitant to an aqueous solution of metal salts with stirring, and then subjecting the resulting precipitate to a series of steps such as washing, filtering, drying, roasting and activation.

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2.2. Supported catalysts

For heterogeneous catalytic reactions, which occur mainly on the surface of the solid catalyst, and the interior of its body does not play any catalytic role in the catalytic reaction. The pore structure and physicochemical properties of the supported catalyst carrier have a certain influence on the catalyst performance. Compared with metal oxide catalysts, supported catalysts have higher specific surface area and suitable pore structure, and the support usually has a larger specific surface area, which can improve the activity strength and stability of the catalyst. Increasing the contact area between catalyst and pollutant can improve the reaction efficiency, enhance the mechanical strength and improve the utilization rate [5].

The supported catalyst was prepared by using coprecipitation, impregnation, ion exchange and other methods to distribute the metal and metal oxide with catalytic activity on the surface of the carrier. The commonly used catalyst carriers are metal oxides, carbon materials, natural minerals and synthetic inorganic materials. Several commonly used carriers are Al_2O_3 , SiO_2 , molecular sieve and activated carbon [6].

2.3. Carbonaceous material catalysts

Activated carbon has a large specific surface area and abundant pores, which has good adsorption effect and can be used as an excellent catalyst and carrier material. Carbonaceous materials are widely used in various industries due to their unique properties. Carbonaceous materials are mainly represented by activated carbon (AC), modified activated carbon (mGAC) and multi-walled carbon nanotubes (MWCNTs). Carbonaceous materials have abundant active sites, developed pore structure, adsorption capacity and good electron transport properties [7]. Activated carbon has catalytic effect, but its catalytic effect is weak. Some researchers believe that the number of basic groups on the surface of activated carbon affects the catalytic ability [8].

Carbonaceous materials catalyzed ozone oxidation system has the characteristics of strong decontamination performance and high ozone utilization rate, and has been widely used. However, with the increase of the number of cycles, the basic groups on the carbon surface continue to be consumed, the acidic oxygen-containing groups such as phenolic hydroxyl, carboxyl and carbonyl groups continue to accumulate, and the electron density of the graphite layer decreases, thus reducing the catalytic capacity of the system.

2.4. Novel catalysts

The possible causes of catalyst deactivation in ozone catalytic oxidation system are: strong oxidation, strong acid, strong alkali or high temperature, high pressure water can lead to the collapse of catalyst structure; the harsh environment results in the loss of catalyst active components; carbon or some intermediate products cover the surface of the catalyst, preventing the normal catalytic oxidation reaction. Based on the above problems, in order

to promote the advancement of ozone catalytic oxidation technology, it is necessary to develop novel catalysts with high activity and strong stability. Perovskite oxides are favored by many researchers because of their special crystal structure, high thermal and chemical stability.

The problems encountered with the catalyst can be solved by modifying the structure or simply heat treatment. Song J et al. prepared magnetic core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{La}_2\text{O}_3$ nanocatalysts, which exhibit a core-shell structure with Fe_3O_4 as the core, SiO_2 as the middle layer and La_2O_3 as the outer layer, and can greatly promote the production of the hydroxyl radical [9].

3. Preparation method of ozone catalysts

3.1. Impregnation method

The impregnation method is mainly divided into excessive impregnation method, equal volume impregnation method, multiple impregnation method and impregnation precipitation method. The advantage of excessive impregnation method is that the active component is dispersed evenly and the impregnation amount can reach the maximum, but its disadvantage is that the loading of active component can not be controlled well. The advantage of equal-volume impregnation method is that it can easily control the loading of active components, but the disadvantage is that the dispersion is poor. Multiple impregnation method needs to go through multiple impregnation, drying and roasting processes, which is generally suitable for competitive adsorption between compounds when the solubility of impregnation compounds is small or multi-component load, and the process is more complex.

Impregnation method is the main method to prepare the load material. The carrier is impregnated in the liquid containing the active substance, and after the impregnation balance, it is dried, roasted and activated [10]. Bing J et al. prepared $\text{Al}_2\text{O}_3/\text{SBA-15}$ supported catalyst by impregnation method [11]. This method is aimed at the preparation of low content supported precious metal catalysts, but there are also cases of uneven distribution of active substances or unsupported [12].

3.2. Coprecipitation method

Coprecipitation method is an important method for preparing ultrafine powders of composite oxides containing two or more metal elements [13]. The advantage of coprecipitation method is that nano powder materials with uniform chemical composition can be obtained directly through various chemical reactions in the solution, and it is easy to prepare nano powder materials with small particle size and uniform distribution [14, 15]. Wang G et al. prepared bimetallic oxides, and the toluene removal rate reached 85% under optimal conditions [16].

3.3. Ion exchange method

The ion exchange method uses the ion exchanger as a

carrier to introduce the active component in the form of cations. Compared to the impregnation method, this method has a high dispersion of the loaded active components. The catalyst prepared by this method has the characteristics of high catalytic activity and good dispersion of active components. This method is suitable for the preparation of precious metal catalysts with low component content and high utilization rate, as well as acid-base catalysts. The ion exchange method is often used when the molecular sieve is used as the carrier. Jiang C et al. prepared the Fe-Y catalyst by ion exchange method [17].

3.4. Sol-gel method

Sol-gel method is to use compounds containing high chemical active components as precursors, in the liquid phase to evenly mix these raw materials, and hydrolysis, condensation chemical reaction, in the solution to form a stable transparent sol system. The gel was slowly polymerized between aged colloidal particles to form a gel with a three-dimensional network structure. The gel network was filled with solvent that lost fluidity and formed a gel. The gel was dried and sintered to produce molecular and even nanostructured materials.

The sol-gel method is a method in which inorganic substances are solidified by solution, sol, gel, and then heat-treated to form solids of oxides or other compounds. Orge C A et al. prepared La series perovskite catalyst by sol-gel method [18]. Yang Y et al. prepared nano TiO₂ by sol-gel method, and the results showed that the existence of TiO₂ would accelerate the generation of hydroxyl radicals [19].

4. Application of ozone catalyst in catalytic ozonation engineering

In catalytic ozone oxidation system, the volume mass transfer coefficient of ozone is much higher than its decomposition rate constant. If the catalyst wants to achieve the ideal effect, it needs to be combined with the reactor. The traditional reactors mainly include three-phase fluidized bed, fixed bed, bubble reactor, etc., but these reactors have small contact surface and low mass transfer efficiency, which reduces the utilization rate of ozone.

The biggest limitation in ozone-catalyzed oxidation systems is the low utilization rate of ozone, which leads to high treatment costs. Improving the mass transfer efficiency of ozone can effectively improve the utilization rate of ozone, thus reducing the treatment cost. Therefore, the catalyst is combined with the reactor with good mass transfer efficiency to reduce the size of bubbles to increase the gas mass transfer coefficient and further improve the catalytic efficiency of the system.

Khuntia et al. used the catalyst in combination with a microbubble reactor to greatly increase the ozone effective factor. Compared with the general bubbling method, the microbubble method is more beneficial to the oxidation of pollutants and the removal of TOC [20].

Excellent catalysts need to be combined with advanced

reaction technology to achieve efficient wastewater treatment. In order to ensure a large contact surface and increase the solubility of gas and liquid, it is necessary to improve the traditional reactor. The technology of microbubble reactor and microbubble pressurization have become an important direction of application research in this field.

5. Conclusion

In the treatment technology of organic wastewater, heterogeneous catalytic ozone oxidation technology is the reaction of hydroxyl radical generated by ozone under the action of catalyst with organic pollutants, and has been widely used because of its advantages of wide range of action, fast, efficient and pollution-free. The preparation and application of ozone catalyst is the key technology. The development of the technology also highlights some urgent problems.

The supported catalysts have large specific surface area, high activity and good catalytic effect, but the active ingredient is weakly bonded to the carrier and is easily lost during the reaction process and causes secondary pollution. In order to pursue higher catalytic activity, most of the catalysts used in the research are powder or nano form, which are difficult to be widely used in the actual wastewater treatment. It is necessary to develop more stable, efficient and environmentally friendly novel catalysts, improve the preparation method of catalysts, and increase the service life of catalysts. Perovskite catalysts are favored by many researchers because of their high thermal and chemical stability. Perovskite catalysts will be one of the key research directions of ozone catalysts in the future.

The surface properties of catalysts prepared by different preparation methods are different. The reaction mechanism and influencing factors in catalytic ozonation are still unclear. If the factors affecting the surface properties of catalysts are clear, it will have a great guiding effect on the preparation and application of catalysts.

Most reports about catalysts in ozone-catalyzed oxidation systems are still in the laboratory research stage. The wastewater tested by the researchers is not industrial wastewater with complex composition, but mostly organic wastewater with single composition formulated in the laboratory. It can achieve a good catalytic effect in the laboratory, but the composition of the actual industrial wastewater is complex, and the actual industrial organic wastewater should be used as the research object to prepare an efficient catalyst for catalytic ozone oxidation.

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