Study on heterogeneous catalysts for catalytic wet oxidation

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Abstract. Catalytic wet oxidation is a powerful method for the treatment of high concentration refractory organic wastewater. The support and catalyst components constitute heterogeneous catalysts, and the main catalyst, co-catalyst and co-catalyst components. The main catalyst and co-catalyst are the main influencing factors of the catalyst. The preparation methods of catalyst include precipitation method, impregnation method and impregnation precipitation method. The performance evaluation indexes of heterogeneous catalysts include the activity, stability, selectivity and anti-toxic stability, mechanical stability of the catalysts. According to the principle of chemical transfer, the heterogeneous catalytic reaction process consists of seven steps.

1. Introduction
Wet oxidation technology (WO) is an important method for the effective treatment of toxic, harmful and high concentration refractory organic wastewater, which was proposed by the Zimmermann [1] of the United States in the 1950s and has obtained many patents, so it is also called "Zimmerman" method. Wet oxidation (WAO) refers to the process of oxidizing organic pollutants into CO2, H2O and inorganic small molecules under high temperature (150~320 °C) and high pressure (0.5-20 MPa) with oxygen as oxidant (generally air, also called wet air oxidation) [2]. Zimmermann first used WAO to treat paper black liquor in 1958, and the removal rate COD treated reached more than 90% [3]. Because the reaction conditions of WAO high temperature and high pressure require the reactor to be resistant to high temperature and high pressure corrosion resistance, it is inconvenient for industrial amplification, and the reaction process is complex, resulting in various refractory toxic intermediate products (carboxylic acid, benzene, ammonia, etc.), which are difficult to be completely oxidized. To reduce reaction conditions and costs, catalytic wet oxidation (CWAO) was introduced, and in the 1970s, Europeans began WAO powder-like activated carbon was put into the equipment to speed up the reaction [4]. Murakami of Japan [5] and others found that the Cu-based catalyst a good catalytic effect on methanol and was used in related applications, german Bayer company also developed LOPOX catalytic wet oxygen chemical process [6] in the 1980s and applied for a patent, which has been used up to now. CWAO technology is widely used in the treatment of sulfur-containing industrial wastewater [7, 8], pesticide production wastewater [9, 10], papermaking wastewater [11, 12], dye wastewater [13, 14], coke furnace gas desulfurization waste liquid [15, 16], and other industrial wastewater [17, 18].
CWAO technology includes both homogeneous and heterogeneous, heterogeneous catalysis has attracted more and more attention because the catalyst can be recycled, cost saving and avoiding secondary pollution [19, 20].

2. Heterogeneous catalyst

2.1. Composition of heterogeneous catalysts
Solid catalysts can be divided into single component catalysts and multicomponent catalysts according to their constituent components. Single component catalyst means that the catalyst is composed of a single substance, such as a platinum net catalyst for ammonia oxidation to nitric acid. Single component catalysts are less used in industry, because it is difficult for a single substance to meet the multifaceted requirements of industrial production for catalyst performance; and multicomponent catalysts refer to catalysts that are composed of a variety of substances, which can be divided into main catalysts, cocatalysts, cocatalysts and supports according to their role in catalysts [21, 22]. It is shown in Table 1.

| NO. | Classification | Concept | Example |
|-----|---------------|---------|---------|
| 1   | Main catalyst | Main body of multicomponent catalyst, and necessary component | Cu, Fe in Cu-Fe-Pt-Ce/γ-A12O3 catalysis |
| 2   | Co-catalyst   | A substance that acts as a catalyst with the main catalyst | Pt in Cu-Fe-Pt-Ce/γ-A12O3 catalysis |
| 3   | Promotor     | Significantly change the catalyst composition | Ce in Cu-Fe-Pt-Ce/γ-A12O3 catalysis |
| 4   | Carrier      | The dispersant, binder and support of the main catalyst and cocatalyst in the catalyst | γ-A12O3 in Cu-Fe-Pt-Ce/γ-A12O3 catalysis |

2.1.1. Main catalyst. The main catalyst, also known as the active component, is the main body in the multicomponent catalyst and is a necessary component, without which the required catalytic action is lacking. Some of the main catalysts are composed of several substances, but their functions are different, and the catalytic reaction to be carried out can not be completed without one of them. This kind of multi-active component makes the catalyst have a variety of catalytic functions, so it is also called double (multi) functional catalyst. Generally, oxides of transition metals can be used as active components of general oxidation reaction catalysts.

2.1.2. Co-catalyst. Co-catalyst and the main catalyst at the same time play a catalytic role of the material, both indispensable. This is because the activity of the two is very low when they are used alone, but they show high catalytic activity when they form a cocatalyst, so the two are co-catalysts.

2.1.3. Promotor. Promotor is a small amount of material added to the catalyst, which is not active or very active, even negligible, but can significantly change the efficiency of the catalyst. According to the different mechanism of catalytic auxiliaries, they are generally divided into two types: structural auxiliaries and mutating auxiliaries. Structural auxiliaries usually do not affect the nature of active components, which can increase the stability of microcrystals of active components of catalysts and prolong the service life of catalysts. Modulation auxiliaries, also known as electronic auxiliaries, can change the nature of active substances, including the chemical composition of the main catalyst, electronic structure (combination morphology), surface properties or crystal structure, thus improving the activity and selectivity of the catalyst.
2.1.4. Carrier. The support is the dispersant, binder and support of the main catalyst and cocatalyst in the catalyst [23]. It is generally believed that the carrier itself has no or very little activity, and its function is mainly manifested in the following five aspects:

(1) Decentralization. heterogeneous catalysis is an interfacial phenomenon, so the active component of the catalyst is required to have sufficient surface area, which requires increasing the dispersion of the active component to be in the dispersion state of micron or atomic level. The carrier can disperse the active components into very small particles and maintain their stability. Not all catalysts are the larger surface area, the better. The support suitable for surface area and pore structure should be selected according to different reactions.

(2) Stabilization. The support can also act as the stable catalyst active component microcrystals of structural auxiliaries, which can block the microcrystals and prevent the microcrystals from migrating at high temperature.

(3) Support. The support can endow the solid catalyst with a certain shape and size to meet the requirements of the industrial reaction for its hydrodynamic conditions. The support can also make the catalyst have a certain mechanical strength, and do not break the essence or powder in the process of use, which will prevent the catalyst bed resistance to increase, make the fluid distribution uniform, and keep the process operating conditions stable.

(4) For strong exothermic or strong heat absorption reaction, the reaction heat can be removed in time by selecting the carrier with good thermal conductivity to prevent the surface temperature of the catalyst from being too high. For the highly active catalyst components, it can play a dilution role by adding appropriate amount of support to reduce the activity of the catalyst per unit volume to ensure the thermal equilibrium.

(5) Catalytic support. In addition to the above physical action, the carrier has chemical action. in highly dispersed supported catalysts, oxide supports may have strong interactions or induced effects on metal atoms or ionic active components, which will play a catalytic role. The acid-base position of the support can also produce multifunctional catalytic action with metal active components to form multifunctional catalysts.

2.2. Preparation of heterogeneous catalysts

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Table 2. Common preparation methods for heterogeneous catalysts.

| Number | Classification     | Fundamental                                                                 | Common materials                                      |
|--------|--------------------|-----------------------------------------------------------------------------|-------------------------------------------------------|
| 1      | Method of precipitation | The precipitate was added to the aqueous solution containing metal salts, and the resulting precipitate was separated, washed, dried, calcined and formed to obtain the catalyst. | The common precipitant is ammonia or ammonium carbonate |
| 2      | Dip-molding        | Based on the active components impregnated to the porous support in the form of salt solution under the action of surface tension and penetrated to the inner surface. | Commonly used carriers are γ-Al2O3, activated carbon, molecular sieve, ceramics |
| 3      | Impregnation precipitation method | On the basis of impregnation method, supplemented by homogeneous precipitation method | Ammonia or ammonium carbonate, γ-Al2O3, activated carbon, molecular sieves, ceramics |
2.2.1. Method of precipitation. The precipitation method is the most basic method for the preparation of solid catalysts. The basic principle of the precipitation method is to add a precipitator to an aqueous solution containing metal salts in order to form hydrated hydroxides, crystals of carbonates, or gels. The resulting precipitate was separated, washed, dried, calcined, and formed to obtain the catalyst. Precipitation method is widely used to prepare high content of non-noble metals, metal oxides, metal salt catalysts and catalyst supports. During the precipitation process, the types of precipitant, the precipitation temperature, the concentration of solution, the pH value of the solution at the time of precipitation, the feeding sequence and the stirring speed have great influence on the performance of the prepared catalyst.

The most commonly used precipitant in the precipitation method is ammonia or ammonium carbonate, because ammonium salt is easy to remove when washing and heat treatment, and potassium ions or sodium ions are often left in the precipitation when using potassium hydroxide or sodium hydroxide as precipitant, and the pharmaceutical cost of potassium hydroxide is more expensive.

It is not easy or even impossible to obtain uniformly dispersed precipitates when preparing catalysts by ordinary precipitation method. For uniform precipitation method can be used to obtain a uniformly distributed precipitate. It is to add a certain reagent to the solution to be precipitated. This reagent produces ions of the precipitant at a uniform rate in the solution or changes the pH value of the solution obtain a uniform precipitate. Urea is a commonly used reagent. when heated to 50~100℃, urea reacts in solution as follows, seen in Formula (1):

\[ CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2 \]  

(1)

As the above reaction proceeds, the pH value of the solution gradually rises, which can generate uniform metal hydroxide precipitation in the whole solution.

2.2.2. Impregnation method. The impregnation method is based on the impregnation of active components (including cocatalysts) into the porous support under the action of surface tension in the form of salt solution and infiltration into the inner surface. The salts of these metals or metal oxides are uniformly distributed in the fine pores of the support. after heating, a highly dispersed support catalyst is obtained. Because the main components, cocatalysts and supports are mixed in the liquid phase, the distribution is more uniform [25, 26].

The catalyst was prepared by impregnation method. The support was first immersed in a solution containing active components. After reaching the impregnation equilibrium, the remaining solution was removed (or the solution was completely entered into the solid using the appropriate amount of liquid), and then the catalyst was prepared by drying, calcination, activation and other steps. impregnation method is the simplest and economical method to prepare catalysts. It is widely used to prepare supported catalysts, especially noble metal supported catalysts with low content. this method saves the process of filtration, molding and so on, It can also select suitable support to provide the required physical structure (such as specific surface, pore size distribution, mechanical strength, etc.) for the catalyst. In addition, catalysis is prepared by this method the agent can make the metal active components spread on the surface of the support in as fine a form as possible, thus improving the utilization rate of the active components, reducing the usage amount and reducing the preparation cost.

The impregnation method is divided into excess impregnation method and equal volume impregnation method according to the amount of impregnation solution. The amount of impregnation solution used in the excess impregnation method exceeds the adsorption amount of the carrier, while the amount of impregnation solution used in the equal volume impregnation method is exactly equal to the adsorption amount of the carrier, and all the impregnation the carrier after the impregnation was completed.

The main influencing factors of the impregnation method are the impregnation time and the concentration of the impregnation solution. in a certain time range, the longer the impregnation time,
the higher the amount of the active components adsorbed to the carrier, but with the arrival of the impregnation equilibrium point, the adsorption and desorption reached the dynamic equilibrium state, so the appropriate impregnation time should be selected in the actual operation. The higher the concentration of the impregnation solution, the higher the active group component of adsorption.

2.2.3. Impregnation precipitation method. It was developed on the basis of impregnation method, supplemented by homogeneous precipitation method. A precipitant parent (e.g. urea) is pre-added in the impregnation solution. After the impregnation operation is completed, the heating heating temperature causes the precipitator parent to release the precipitated ion (e.g. OH-), thus allowing the precipitate component to deposit on the surface of the carrier. This method combines the advantages of precipitation method with impregnation method to obtain metal oxide supported catalysts with more uniform composition and higher active component content [27].

2.3. Performance evaluation index of heterogeneous catalyst
The reaction performance of the catalyst is the main index to evaluate the quality of the catalyst, which includes the activity, selectivity and stability of the catalyst [28].

2.3.1. Activity of the catalyst. Catalytic activity refers to the degree of acceleration of the catalyst to the reaction, is used to measure the size of the catalyst effect. In other words, the difference between the catalytic reaction rate and the non-catalytic reaction rate. Engineering often describes the activity of the catalyst through such indicators as reaction speed, velocity constant, conversion rate, activation energy, space-time yield (the amount of products obtained per liter of catalyst per hour), and the COD removal rate and decolorization rate of organic matter are often used to characterize the catalytic activity in scientific research experiments.

2.3.2. Selectivity of catalyst. Besides accelerating the chemical reaction, the catalyst can also carry out the reaction in the direction of producing a particular product, which is the selectivity of the catalyst. Seen in Formula (2) for the representation of selectivity (%):

$$ S\% = \left( \frac{\text{The yield of the target product}}{\text{Fractional conversion}} \right) \times 100\% $$.  (2)

The so-called yield of the target product refers to the percentage of the reactant consumed in the production of the target product, and in industry it refers to the amount of the product generated by the consumption of the raw material (reactant) per unit of quantity.

For a catalytic reaction, the activity and selectivity of the catalyst are the two most basic properties. It has been found that the selectivity of the catalyst is often more important than the activity and more difficult to solve in the research and development of the catalyst. Because a catalyst, although very active, if the selectivity is not good, will produce a variety of by-products, which brings a lot of trouble to the separation of products, greatly reduce the catalytic efficiency and economic benefits. Conversely, a catalyst, although not very active, is highly selective and can still be applied in industrial production.

2.3.3. Stability of the catalyst. The stability of the catalyst refers to the time when the catalyst has stable activity under the conditions of use. the longer the stable activity time, the better the stability of the catalyst. The stability of the catalyst includes the following four aspects:

(1) Chemical stability. The catalyst maintains its stable chemical composition and combination state during use, and the active components and cocatalysts do not produce volatilization, loss or other chemical changes.

(2) Thermal stability. under the reaction and regeneration conditions, the catalyst does not destroy its physical and chemical state due to heat in a certain temperature range, and does not produce sintering, microcrystalline growth and crystal phase changes.
(3) Antitoxic stability. The catalyst is not poisoned and deactivated by adsorbing impurities or toxic by-products in the raw materials during the reaction.

(4) Mechanical stability. The solid catalyst should have all kinds of stresses caused by friction resistance, impact, heavy pressure and sudden temperature change during the reaction process, so that the catalyst does not produce comminuted rupture, does not cause the reaction bed resistance to rise or block the pipeline, so that the reaction process runs smoothly.

Comprehensive sewage treatment characteristics, the evaluation of the catalyst in this study mainly considered the activity and stability. high activity, that is high COD removal rate and high decolorization rate; high stability, that is, low dissolution of catalyst metal ions, low concentration in effluent.

In this study, the catalyst with high catalytic activity and good stability is considered as the catalyst with good reaction performance.

2.4. Heterogeneous catalytic reaction process

The heterogeneous catalytic reaction process is accomplished by the following seven steps [29, 30]:

1. The reactants diffuse from the fluid body to the outer surface of the catalyst;
2. The reactants diffuse from the outer surface towards the inner surface;
3. The reactants are adsorbed on the catalyst;
4. Adsorption reacts on the surface of the catalyst;
5. Product desorption from catalyst surface;
6. The product diffuses from the inner surface of the catalyst to the outer surface;
7. The product diffuses from the outside towards the fluid body. Among them, adsorption, reaction and desorption belong to chemical kinetic process, diffusion belongs to physical process; reaction is often controlled by chemical kinetics at low temperature and internal and external diffusion at high temperature.

3. Conclusion

Catalytic wet oxidation is a powerful method for the treatment of high concentration refractory organic wastewater. The composition of heterogeneous catalyst includes two parts: support and catalyst component, and catalyst component includes main catalyst, co-catalyst and co-catalyst 3 parts. The main catalyst and co-catalyst are the main influencing elements of the catalyst. The preparation methods of catalyst include precipitation method, impregnation method and impregnation precipitation method. The performance evaluation indexes of heterogeneous catalysts include the activity, stability, selectivity and anti-toxic stability, mechanical stability of the catalysts. External diffusion, internal diffusion, adsorption, reaction, desorption constitute a heterogeneous catalytic reaction process.

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