Study on Heterogeneous Catalyst Classification Based on CWAO Process of Organic Waste-Water

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Abstract. Catalytic wet air oxidation (CWAO) technology has the characteristics of wide application range, high organic matter removal rate, low secondary pollution and high efficiency, etc., and it has significant effects on the treatment of difficult biodegradable organic waste-water. According to the homogeneity of the phases of the catalytic reaction system, the catalytic reactions can be divided into two categories: homogeneous catalysis and heterogeneous catalysis. The reported catalysts or their active components mainly include four categories: metal salts, metals/supports, oxides/supports, and composite oxides/supports.

1. Introduction
The traditional wet oxidation method is effective for the treatment of high-concentration, toxic, harmful, and difficult biodegradable organic waste-water, but because of its certain shortcomings, it is still limited in practical application [1]. In order to overcome the above deficiencies, catalytic wet oxidation technology has been based on wet oxidation technology since the 1970s, so that the reaction can be completed under milder conditions and in a shorter time [2]. The catalytic wet oxidation method has been applied on an industrial scale in Japan, Europe, America and other countries, and a large number of catalyst patents have appeared every year. In recent years, there has also been a wave of research on catalytic wet oxidation in Europe [3], but there has been less research on this in China. The research and development of new high-efficiency catalysts have high practical value for promoting the application of catalytic wet oxidation in the treatment of various toxic and harmful waste-water.

According to the homogeneity of the phases of the catalytic reaction system, the catalytic reactions can be divided into two categories: homogeneous catalysis and heterogeneous catalysis.

2. CWAO technical characteristics
According to the literature [4-5] research, CWAO technology has the following characteristics, which are summarized in Table 1.
Table 1. Features of CWAO technology.

| No. | classification                          | Technical principle                                                                                                                                 |
|-----|----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| 1   | Wide range of applications             | Under proper operating conditions, CWAO technology can treat sludge, various organic waste-water, and even industrial toxic waste-water such as pesticide waste-water, dye waste-water, papermaking waste-water, petrochemical waste-water and other organic synthetic industrial waste-water. |
| 2   | High organic removal rate and low secondary pollution | Under certain reaction conditions, CWAO technology can oxidize and decompose more than 90% of organic matter in waste-water, and even completely mineralize waste-water. |
| 3   | High efficient                         | Most of the reactions can be completed within 30 to 120 minutes; the residence time of waste-water in the continuous operation process is shorter than that of the biochemical method, and the general CWAO process does not require pretreatment, the process is stable, the device is small and compact, and it takes up less space. |
| 4   | Recyclable energy and useful materials | The reaction heat of the CWAO process can be used to heat materials, and the high temperature and high pressure exhaust gas from the CWAO reaction of high-concentration organic waste-water can be used to generate electricity or generate steam. Among many processes such as activated carbon regeneration, the CWAO process has achieved good results. |
| 5   | High requirements for equipment materials and relatively high one-time investment | CWAO needs to be performed under high temperature and pressure conditions, and the reactor is required to be resistant to high temperature, high pressure and corrosion, so the equipment cost is high. The dirt in the heat exchanger and reactor needs to be cleaned regularly, and the maintenance and management technology requirements of the device are high. |
| 6   | Sometimes incomplete oxidation         | It is not ideal for the degradation of certain organic substances (such as polychlorinated biphenyls, small molecular carboxylic acids, etc.), it is difficult to completely oxidize, and sometimes toxic intermediate products are produced. |

3. Classification of CWAO catalyst

3.1. Classification Overview
Catalytic wet oxidation method is to add a suitable catalyst to the traditional wet oxidation process to reduce the temperature and pressure required for the reaction, improve the oxidative decomposition ability, shorten the reaction time, prevent equipment corrosion and reduce costs. The application of catalyst can speed up the reaction speed, which is mainly explained from two aspects. One is to reduce the activation energy of the reaction; the other is to change the course of the reaction. Due to the selectivity of the catalyst and the different types and structures of organic compounds, the catalyst must be screened and evaluated. Catalysts suitable for oxidation reactions are mostly transition metal oxides because oxygen in the transition metal oxide lattice can be easily introduced and removed [6-9]. Among them, precious metal series [10-13] (such as Pt, Pd as active ingredients) catalysts have high activity, long life, and strong adaptability, but their prices are expensive and their applications are limited. The rare earth catalysts (such as Ce and La as active ingredients) have special physical and chemical properties, show special redox properties, and have been widely used in catalyst research.
[14-17]. Copper-based catalysts show high catalytic activity in the wet oxidation of organic waste-water [18-21], and copper-based catalysts are more economical than precious metal series catalysts [22].

The catalyst used in CWAO technology should have the following characteristics: (1) fast oxidation speed; (2) non-selective, can achieve complete oxidation; (3) stable physical and chemical properties in hot acidic solution; (4) high activity at temperature, long service life, insensitive to toxicants in waste-water; (5) high mechanical strength and wear resistance.

3.2. Category list
According to the state of use of the catalyst, it can be divided into two categories: homogeneous catalysts (dissolved metal salts) and heterogeneous catalysts (metals, oxides, composite oxides). Generally, homogeneous catalysts have higher activity and faster reaction rates than heterogeneous catalysts. However, in the reaction process, because the catalyst is dissolved in the waste-water, in order to avoid economic loss and secondary pollution to the environment due to catalyst loss, and subsequent treatment is required to recover metal ions, thereby increasing the cost of waste-water treatment [23]. Heterogeneous catalysts prevent the loss of catalysts to a large extent. They are easy to separate and have short processing flows, but there is resistance to mass transfer between them. The catalyst may be deactivated by the coating or plugging of waste-water suspensions and reaction intermediates (such as coke and char) [24-25]. The reported catalysts or their active components mainly include metal salts, metals/supports, oxides/supports, and composite oxides/supports [26], as shown in Table 1:

| No. | Category                      | catalysts                                                                 | Cases               |
|-----|-------------------------------|---------------------------------------------------------------------------|---------------------|
| 1   | Metal salt                    | PdCl₂, RuCl₃, RhCl₃, IrCl₄, SnCl₂, CoCl₂, MnCl₂, CuCl₂, FeCl₂, AgNO₃, Cu(NO₃)₂, Fe(NO₃)₃, CuSO₄, NiSO₄, FeSO₄, MnSO₄, ZnSO₄, Fe₃(SO₄)₂, K₂PtO₃, NaAuCl₃, NH₄ReO₄, Na₂Cr₂O₇, Na₂CO₃, Cu(OH)₂, CuSO₄·(NH₄)₂SO₄, Cu(BF₄)₂, Mn(AC)₂ | [27-32]             |
| 2   | Metal / carrier               | Rh/TiO₂, Pt/TiO₂, Ru/TiO₂, Ir/TiO₂, Ni/TiO₂, Ag/TiO₂, Pd/Al₂O₃, Ru/Al₂O₃, Ni/Al₂O₃, Ag/Al₂O₃, Rh/CeO₂, Au/CeO₂, Ir/CeO₂, Pt/CeO₂, Pt/ZrO₂, Pd/ZrO₂ | [33-35]             |
| 3   | Oxide/support                 | WO₃/₅, V₂O₅, MoO₃, ZrO₂, CuO/₅, Cu₂O, Co₃O₄, NiO/₅, Mn₂O₃, CeO₂, Co₃O₄, Fe₂O₃, OsO₂, SnO₂ | [36-40]             |
| 4   | Composite oxide / support     | MnO₂-ZrO₂, Co₃O₄-MnO₂, CuO-Mn₂O₃, CuO-Mn₂O₃, CuO-Mn₂O₃-Bi₂O₃, Mn₂O₃-CeO₂, CuO-ZnO, CuO-NiO, CuO-Mn₂O₃-ZnO, CuO-Mn₂O₃-Fe₂O₃, CuO-ZrO₂, CuO-Mn₂O₃-Co₂O₃, CuO-ZnO-Co₃O₄, CuO-Co₃O₄-TiO₂, Ru₂O₃-ZrO₂, Ru₂O₃-TiO₂, Rh₂O₃-CeO₂, PtO-Co₃O₄, IrO₂-Co₂O₃, PdO-TiO₂, Co₃O₄-BiO, SnO₂-MoO₃, Fe₂O₃-P₂O₅ | [41-45]             |

3.3. Metal salt series catalyst
The most studied and most valued homogeneous catalysts are soluble transition metal salts. Among them, Cu^{2+} with d⁹ electronic structure can form complexes with high catalytic activity. Lei et al. [27] treated Cu (NO₃)₂, Mn(NO₃)₂, FeSO₄ and CuSO₄ respectively to treat printing and dyeing waste-water, and found that the best effect of Cu(NO₃)₂, Mn(NO₃)₂ on the removal rate of CODC₅ was 80 % or more. Imamura et al. [28] studied the catalytic action of various metal nitrates using acetic acid as substrate, and found that Cu (NO₃)₂ had the highest catalytic activity, followed by Fe (NO₃)₃, while the nitrates

Table 2. Familiar catalysts on CWAO.
of other metals had almost no catalytic effect. Aiming at coking waste-water and gas waste-water, Sato Toshio and others [29] used multiple catalysts to simultaneously remove COD and ammonia from waste-water, and found that: Pd, Ru, Rh, Ir, Pt, Ag, Cr, etc. are effective for removing COD. However, only PdCl₂ is effective in decomposing ammonia, and the remaining activities are very low. The order of ammonia decomposing activity is: Pd ≥ Ru, Os > Ir > Rh, Pt. Murakami et al. [30] conducted experiments with various alcohols, amines, carboxylic acids, and surfactants using Cu(NO₃)₂ and CuSO₄, and the results showed that copper salts were effective. Tang Shouyin et al. [31] treated tricyclazole production waste-water and gas waste-water, and found that among single-component metal salts, Cu(NO₃)₂, (NH₄)₆Mo₇O₂₄ had the highest catalytic activity, and the catalytic activity of the three copper salts was: Cu(NO₃)₂ > CuSO₄ > CuCl₂. The catalytic activity of AgNO₃ is the lowest among all reagents.

3.4. Metal / support catalyst

After the soluble salt or hydroxide is impregnated on the support, an oxide/supported catalyst is obtained in a roasting atmosphere of an oxidizing gas, and a metal/support catalyst is obtained in a roasting atmosphere of a reducing gas. In heterogeneous CWAO, noble metals have high activity and stability for oxidation reactions, so they are widely used. In order to make the precious metal have better dispersibility and reduce the amount, it is often used to impregnate it and load it on a carrier with a high specific charge surface, such as alumina (Al₂O₃), silica gel (diatomite, SiO₂), activated carbon (AC), TiO₂, CeO₂, ZrO₂ and so on. Masende et al. [33] developed a Pt/graphite catalyst to treat phenol waste-water, and found that the phenol removal rate reached 99 %. Pt/AC, Pd/AC, Ru/AC catalysts developed by Qin et al. [34] treated chlorophenol waste-water at 435 K and an oxygen partial pressure of 2.6 MPa. It was found that 1 % Pt/AC had the best effect on the removal rate of TOC. It reached 97.9 %, followed by Pd/AC and Ru/AC. The Ir/AC catalyst developed by Gomes et al. [35] treated butyric acid at 160 ℃ and an oxygen partial pressure of 0.69 MPa for 120 minutes. It was found that the catalyst showed good activity during oxidation and the CODCr removal rate reached 60 %.

3.5. Oxide / support series catalyst

Metal oxides as catalysts are classified according to their stability as follows [36]: ① the most stable oxides in high oxidation states (such as the oxides of Ti, V, Cr, Mn, Zn, and Al); ② moderately stable Oxides (such as Fe, Co, Ni and Pb oxides); ③ unstable high oxidation state oxides and precious metals (Pt, Pd, Ru, Au and Ag).

The CuO/γ-Al₂O₃ catalyst developed by Qiu Zumin and others [37], under certain conditions such as H₂O₂ as an oxidant, the CODCr removal rate of dye waste-water reached more than 80%. Fortuny et al. [38] developed a CuO/γ-Al₂O₃ catalyst to treat phenol waste-water and found that the phenol conversion rate reached 95% and the CODCr removal rate reached 90 %.Lin et al. [39] used CeO₂ catalysts obtained by different preparation methods to wet-oxidize and degrade phenol. At 160 ℃ and an oxygen partial pressure of 0.5 to 1.0 MPa, it was found that the removal rate of phenol reached more than 90 % after 120 minutes of reaction. Beziat et al. [40] used RuO₂/TiO₂ to treat organic waste-water. In a sulfurized bed reactor at 150–200 ℃ and a system pressure of 5 MPa, they found that the catalyst has a good mineralization effect on cycloheptanol, succinic acid and acetic acid. And the catalyst was used continuously for 3 months, and its stability was found to be good.
3.6. Composite oxide / support series catalyst

The synergistic effect of certain composite oxides can increase the activity of the catalyst and inhibit the dissolution of active components. The combination of CoO, CuO or NiO with the oxides of Fe (II), Pt or Ru is an effective catalyst. Rare earth elements are widely selected as catalyst active components or carriers due to their special redox properties. The RuO$_2$/γ-Al$_2$O$_3$ catalyst developed by Yang Shaoxia et al. [41] made the removal rate of phenol reach 97.3% under certain conditions, but the catalyst components showed dissolution. RuO$_2$/CeO$_2$/γ-Al$_2$O$_3$ and RuO$_2$/ZrO$_2$/γ-Al$_2$O$_3$ catalysts prepared by doping Ce and Zr have achieved the dual functions of inhibiting the dissolution of components and improving the catalytic activity. Hung et al. [42] used the developed composite oxide catalyst with a molecular ratio (Cu:La:Ce=7:2:1) to treat ammonia-containing waste-water, and the ammonia removal rate reached 91% under certain conditions. Adrian et al. [43] used formaldehyde-containing waste-water as a treatment target and found that the catalyst CuO-ZnO/Al$_2$O$_3$ had a TOC removal rate of 78.7%. Zhang et al. [44] of Canada treated Al$_2$O$_3$ as a carrier and used a composite oxide catalyst prepared by doping CeO$_2$ with Pt and Pd to treat high-concentration papermaking waste-water, and reacted at 150 °C and an oxygen partial pressure of 1.5 MPa for 3 h. It was found that the TOC degradation rate of the catalyst without CeO$_2$ was 40% and the chroma removal rate was 87%, while the TOC degradation rate of the catalyst with CeO$_2$ was 65% and the chroma removal rate was 95%. Wan Jiafeng et al. [45] used γ-Al$_2$O$_3$ as a support to prepare Cu, Cu and Ce, Sn, Cu and Sn catalysts by impregnation method, and found that co-impregnation method is better than the stepwise impregnation method, and 6%Cu-10%Ce/γ-Al$_2$O$_3$ showed the strongest catalytic activity.

4. Conclusion

Wide application range, high organic matter removal rate, low secondary pollution and high efficiency, etc. These are the characteristics of catalytic wet oxidation (CWAO) technology, which has a significant effect on the treatment of difficult biodegradable organic waste-water. According to the homogeneity of the phases of the catalytic reaction system, the catalytic reactions can be divided into two categories: homogeneous catalysis and heterogeneous catalysis. The reported catalysts or their active components mainly include four categories: metal salts, metals / supports, oxides / supports, and composite oxides / supports.

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