Preparation of heterogeneous catalysts based on CWAO technology

Yongli Zhang*

Logistics Department, Guangzhou College of Technology and Business, Guangzhou, China

*Corresponding author e-mail: 2863957925@qq.com

Abstract. Refractory-biodegradable organic wastewater can be effectively treated by catalytic wet oxidation (CWAO). The preparation of non-catalyst is the core of CWAO technology. The preparation methods of heterogeneous catalysts include precipitation method, impregnation method, precipitation impregnation method, sol-gel method and chemical deposition method. According to the different ways of adding metal solution and precipitant, the precipitation method is divided into positive addition method, reverse addition method and combined addition method. According to the impregnation amount, the impregnation method can be divided into equal amount and excessive impregnation method. According to the principle of chemical reaction engineering, heterogeneous CWAO reaction process can be divided into 7 processes, such as internal diffusion and external diffusion. CWAO method is expected to be applied and expanded in pesticide, printing and dyeing, papermaking and other industries.

1. Introduction

With the development of society and the progress of industry, the amount of refractory biodegradable organic wastewater is increasing. Heterogeneous catalytic wet oxidation technology can effectively treat refractory organic wastewater. Heterogeneous catalyst is a key component of CWAO technology. Heterogeneous catalysts include two parts: carrier and active component [1].

The carrier has a great influence on the performance of the impregnated catalyst, which can be used as a support to disperse and bond the main catalyst and auxiliary catalyst, and the acid and base positions in the molecular structure of the carrier can also combine with the active metal components to play a catalytic role, forming a multi-functional catalyst. Studies have shown that common carriers of heterogeneous supported catalysts include alumina (Al₂O₃), silica gel (diatomite, SiO₂), activated carbon (AC), TiO₂, CeO₂, ZrO₂, etc. Al₂O₃ is more widely used due to its large specific surface and high strength [2].

The active component of catalyst is the key to determine the performance of catalyst. There are two indexes to evaluate the catalyst used in wastewater treatment: first, determine the dissolution concentration of the effluent component, and evaluate the stability of the catalyst with this method. The second is to measure COD and absorbance of effluent, calculate COD removal rate and decolorization rate of water sample, and use this to evaluate catalyst activity (high removal rate means high activity). At present, the research focuses on heterogeneous supported catalysts, which have high
activity and stability. Because of the high noble metal catalyst activity, stable performance, but the price is expensive, because of its special physical and chemical properties of rare earth metals to help improve the catalyst activity and stability, and high transition metal catalyst activity but poor stability, so the three components of composite is expected to achieve high activity, strong stability, relatively inexpensive catalyst, the catalyst research and development direction of [3-4].

2. Preparation of heterogeneous catalysts

2.1. Preparation method of catalyst

According to literature statistics, the preparation methods of heterogeneous catalysts are shown in Table 1.

| No. | Category                        | Principle                                                                                                                                   | Cases                |
|-----|---------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| 1   | Precipitation                   | In an aqueous solution of a metallic salt, a precipitating agent is added in order to form a crystal or gel of hydrated oxides, carbonates, or gels. | Wang et al. [5]      |
| 2   | Impregnation method             | The carrier is immersed in a solution containing active components. After reaching equilibrium, the remaining liquid is removed (or the solution is immersed in solid), and the catalyst is obtained after drying, calcining and activation. | Kim et al. [6]       |
| 3   | Precipitation-impregnation      | A new method developed on the basis of the impregnation method and the uniform precipitation method is to prepare the precipitant matrix in the impregnation solution in advance, and after the operation of the impregnation unit is completed, the precipitant component is deposited on the surface of the carrier by heating up. | Yang et al. [7]      |
| 4   | Sol-gel method                  | The metal alcohols or inorganic salts are hydrolyzed to form sol directly or lysed to form sol, and then the solute is aggregated to gel, made into film or directly dried, heat treatment to remove organic components, and finally the solid catalyst of nano particles or block inorganic materials is obtained. | Pinkaewet al. [8]    |
| 5   | Chemical deposition method      | It is a method of using one or more compounds or elemental materials containing film elements to produce films by chemical reactions on the substrate surface. | Kuo et al. [9]       |

The preparation methods of catalysts include precipitation method [5], impregnation method [6], precipitation impregnation method [7], sol-gel method [8], chemical deposition method [9], etc. Sedimentation and impregnation are the commonly used preparation methods. According to the different preparation methods, heterogeneous catalysts can be divided into impregnated catalysts and co-precipitated catalysts.
| No. | Category                        | Implementation of the way                                                                 | Cases               |
|-----|---------------------------------|-----------------------------------------------------------------------------------------|---------------------|
| 1   | Positive addition of precipitation method | The order of addition has a great influence on the properties of the precipitate.         | Zeng et al. [10]    |
| 2   | Backward addition of precipitation method | Adding a salt solution to a precipitant is an inverse addition.                        | Zhang et al. [11]   |
| 3   | Union addition of precipitation method | The addition of the metal salt solution and precipitant to the neutralization tank is proportional to the addition. | Li et al. [12]      |
| 4   | An equivalent impregnation method  | The carrier is mixed with the impregnation solution with just the adsorption capacity, the impregnation solution is just impregnated with the carrier particles without excess. | Zohuri et al. [13] |
| 5   | Excessive impregnation by maceration | The carrier was immersed in the excess impregnation solution (the impregnation liquid exceeded the absorbable volume), and the catalyst was prepared after adsorption and equilibrium. The excess solution was drained, dried and activated. | Quintanilla et al. [14] |

2.2. Precipitation method

In the process of preparing catalyst, precipitation method is widely used. According to the different methods of metal solution and precipitating agent added, precipitation can be divided into positive addition [10], pour addition [11] and [12] and addition, are addition first configuration with a certain concentration of the metal salt solution, followed by precipitating agent configuration into the corresponding concentration of solution, and finally the precipitant solution at a certain speed drops to the metal salt solution, pH to a certain value, is the end point, the formation of precipitation, and then through the suction filter, drying and roasting process, such as the preparation of the corresponding catalyst, this method preparation of catalyst activity is good, but the metal dissolution amount is larger, the catalyst stability is poor, is not conducive to recycling of the catalyst. Addition process and the reverse addition, add with good metal salt solution at a certain rate to the precipitating agent solution, pH to a certain value, is the end point, the formation of precipitation, and then through the suction filter, drying and roasting, proper catalyst preparation, this method than the preparation of the catalyst is stable preparation of catalyst addition, but compared with lower catalytic activity. And addition is to add the metal salt solution and precipitant solution to the preparation vessel at a certain rate at the same time and prepare the corresponding catalyst through the production process. Different precipitation agent has a great influence on the preparation of catalyst, commonly used precipitant have NH3-H2O, Na2CO3, NaHCO3, NaOH and (NH4)2CO3. Strong alkaline, preparation of catalyst particles, and weak alkaline, the formation of catalyst particles is incomplete, according to reports in the literature [13], NH3-H2O, NH3-H2O and other common combination of precipitant precipitant effect is better, is often used as precipitating agent preparation of catalysts. Liu, etc. [14] with ammonia as precipitant was FeTiOx catalyst, selective catalytic reduction of NOx and NH3 gas mixture, the study found that active substances Br nsted acid and Lewis acid exists in the SCR reaction, in which NH3 adsorption mainly in titanium and exist, in the form of NH4+ and NOx is mainly adsorption on the Fe metal active sites in the form of nitric acid dentate.

2.3. Immersion method

The impregnation method is to take the catalyst components in the form of metal salt solution through the surface adhesion and surface tension, load on the carrier with large specific surface area and pore diameter, part of which enters the carrier surface. The salt solution of metal components in the catalyst
was evenly distributed in the fine holes of the carrier, and the corresponding metal oxide catalyst was obtained by drying and roasting. By dipping, impregnation method can be divided into equivalent impregnation method [15-16] and excessive impregnation method, equivalent impregnation method is in a certain quality of carrier, adding just the adsorption of deployment of metal salt solution volume, after the completion of the dipping liquid are all carrier adsorption [17], excessive impregnation method is more than amount of impregnation liquid metal salt solution volume volume, according to certain impregnating solid-liquid ratio [18]. According to the impregnation process, the impregnation method is divided into one-step impregnation method and continuous impregnation method. The one-step impregnation method refers to the one-time adsorption of the metal salt solution with the carrier [19], and the continuous impregnation method refers to the process of preparing catalysts by repeated impregnation, drying and roasting [20]. Hayashi et al. [21] loaded 31 kinds of metal salts onto CeO₂ carrier through the traditional impregnation preparation method, and investigated their use in catalytic synthesis of propylene from ethanol. The study found that the solid solution formed by metal oxide Y₂O₃ and CeO₂ had a high synthesis conversion rate. Rio et al. [22] controlled the formation of catalyst products in the impregnation process by adjusting pH and other factors, avoiding the sintering of Au in the preparation process, and prepared precious metal supported Ce-Zr support catalyst, showing excellent performance in the conversion of CO. Zhao et al. [23] prepared Mn/Al₂O₃, La-Mn/Al₂O₃ and Fe-La-Mn/Al₂O₃ catalysts by impregnation method to catalyze the oxidation of NO and NH3. The study found that the la-modified catalyst significantly improved the performance of the catalyst, resulting in electron transfer between Mn³⁺ and Fe³⁺, and the existence of Mn had the greatest impact on the SCR activity of Fe₀.₀₄La₀.₀₃Mn₀.₀₆/Al₂O₃ catalyst.

The catalyst prepared by impregnation method is more practical because of the advantages of large particle size, easy recovery and reagent saving. Taking Al₂O₃ as the carrier, Sang et al. developed Mn, Fe, Co, Ni and Cu oxides/catalysts respectively [24]. Kim developed CoOx/TiO₂ catalyst using TiO₂ as the carrier [25]. Using CeO₂ as the carrier, Barbier developed Ru, Pd and Pt oxide catalysts [27]. Yang min of dalian institute of chemical compounds of Chinese academy of sciences et al. developed the transition metal cu-zn-al-fe-o catalyst by sol-gel method [27]. Li xiang et al., from tsinghua university, developed a multi-wall carbon nanotube catalyst for the treatment of phenol wastewater, and the removal rate of COD₉ reached 86% [28]. Zhao binxia et al., northwestern university, prepared MnOₓ-CeO₂ series catalysts by co-precipitation method for the treatment of imidacloprid pesticide wastewater. COD removal rate reached 89.3% [29]. Tang wenwei et al. of tongji university developed transition metal CuO/γ-Al₂O₃ catalyst, which was used in emulsion wastewater treatment. COD removal rate reached 68.8% [32]. Under certain conditions, the removal rate of phenol was 97.3% [33] in the RuO₂/γ-Al₂O₃ catalyst developed by Yang shaoxia et al., Harbin Institute of Technology. However, the dissolution of catalyst components was found, and after doping Ce and Zr, RuO₂/CeO₂/γ-Al₂O₃, RuO₂/ZrO₂/γ-Al₂O₃ catalyst and RuO₂/CeO₂/TiO₂ catalyst were prepared. Mariangel et al. studied the treatment of waste water by precious metals Ru/TiO₂ and Pt/TiO₂ [34]. The Cu-O/FSC catalyst developed by zhang yongli et al. [35] (FSC is the carrier of a catalyst factory) can remove 85% COD₉ and 99% decolorization of refractory printing and dyeing wastewater.

### 3. Conclusions

As for the catalytic wet oxidation (CWAO) technology, which has attracted more and more attention from scholars, it can effectively treat organic wastewater which is difficult to biodegrade. The core of CWAO technology is the preparation of non-catalyst, which consists of two parts: carrier and active component. The preparation methods of heterogeneous catalysts include precipitation method, impregnation method, precipitation impregnation method, sol-gel method and chemical deposition method. Precipitation method is divided into positive addition, reverse addition and addition, impregnation method is divided into equal amount and excessive impregnation method. The heterogeneous CWAO reaction process can be divided into 7 processes, such as internal diffusion and external diffusion. The CWAO method is expected to be applied in the treatment of refractory biodegradable organic wastewater.
References

[1] Zhang Y, Hu X, Li H. Study on roasting conditions of copper supported wet oxidation catalyst [J]. Acta intraocular lens, 2010, 39 (1): 272–276.

[2] Chen I P, Lin S S, Wang C H, et al. CWAO of phenol using CeO2/γ-Al2O3 with promoter-Effectiveness of promoter addition and catalyst regeneration [J]. Chemosphere, 2007, 66(26): 172–178.

[3] Mazurek M, Benker N, Roth C. Binary Mixtures of Carbon Supported Pt and Ru Catalysts for PEM Fuel Cells[J]. Fuel Cells, 2006, 6 (3–4): 208–213.

[4] Zhu Hongfa. Preparation and application of catalyst support [M]. Petroleum industry press, 2002.5.

[5] Wang Y, Chen B B, Crocker M, et al. Understanding on the origins of hydroxyapatite stabilized gold nanoparticles as high-efficiency catalysts for formaldehyde and benzene oxidation[J]. Catalysis Communications, 2015, 59: 195-200.

[6] Kim M Y, Lee K, Choi M. Cooperative effects of secondary mesoporosity and acid site location in Pt/SAPo-11 on n-dodecane hydroisomerization selectivity [J]. Journal of Catalysis, 2014, 319: 232-238.

[7] Yang Z B, Zhang Y Y, Ding W Z, et al. Hydrogen production from coke oven gas over LiNi/γ-Al2O3 catalyst modified by rare earth metal oxide in a membrane reactor [J]. Journal of Natural Gas Chemistry, 2009, 18 (4): 407–414.

[8] Pinkaew K, Praserthdam P, Jongsomjit B. Effect of nanocrystallite size of TiO2 in Co/TiO2 and Co/TiO2-Ru catalysts on methanation [J]. Korean Journal of Chemical Engineering, 2013, 30 (01): 50-54.

[9] Kuo C W, Chen B K, Tseng Y H, et al. A comparative study of poly (acrylic acid) and poly(styrenesulfonic acid) doped into polyaniline as platinum catalyst support for methanol electro-oxidation [J]. Journal of the Taiwan Institute of Chemical Engineers, 2012,43:798-805.

[10] Chun-mei Zeng, Li Gou and Junguo Ran. Charging way of coprecipitation preparation of Nd: YAG transparent ceramics [J]. The influence of functional materials, 2014, 17 (45): 17094-17098.

[11] Zhang G, Ren X, Zhang H, et al. MgO/SnO2/WO3 as catalysts for synthesis of ε-caprolactone over oxidation of cyclohexanone with peracetic acid [J]. Catalysis Communications, 2015, 58: 59-63.

[12] Li X, Feng J, Fan H, et al. The dehydrogenation of ethylbenzene with CO2 over Ce1-xZr1-xO2 solid solutions [J]. Catalysis Communications, 2015, 59: 104-107.

[13] Bei Wang, Huanque Zhang, Xinmei Zhang, et al. Effect of different precipitators on magnetic properties of manganese zinc ferrite [J]. Acta intraocular lens, 2015, 44 (03): 604-609+615.

[14] Liu F, He H, Zhang C, et al. Mechanism of the selective catalytic reduction of NOx with NH3 over environmental-friendly iron titanate catalyst [J]. Catalysis Today, 2011, 175: 18-25.

[15] Zhou R H, Damavandi S, Dianat E, et al. Late Transition Metal Catalyst Based on Cobalt for Polymerization of Ethylene [J]. International Journal of Polymeric Materials, 2011, 60(10): 776–786.

[16] Quintanilla A, Casas J A, Rodriguez J J. Catalytic wet air oxidation of phenol with modified activated carbons and Fe/activated carbon catalysts [J]. Applied Catalysis B: Environmental, 2007, 76 (1–2): 135–145.

[17] Pintar A, Batista J, Tišler T. Catalytic wet-air oxidation of aqueous solutions of formic acid, acetic acid and phenol in a continuous-flow trickle-bed reactor over Ru/TiO2 catalysts[J]. Applied Catalysis B: Environmental, 2008, 84: 30-41.

[18] Ma B, Wen F, Jiang H, et al. The synergistic effects of two Co-catalysts on Zn2GeO4 on photocatalytic water splitting [J]. Catalysis Letters, 2009, 134: 78-86.

[19] Wakita H, Takeguchi T, Ueda W. Enhancement of selectivity for preferential CO oxidation over SO2-pretreated Ru/Al2O3 catalyst by the presence of sulfur compounds [J]. Journal of
Molecular Catalysis A: Chemical, 2007, 268: 139-147.

[20] Janjua N K, Firdous N, Bhatti A S, et al. Preparation and catalytic evaluation of Ir and Ru catalysts supported in γ-Al2O3 for hydrazine decomposition in a 1N microthruster[J]. Applied Catalysis A: General, 2014, 479: 9-16.

[21] Hayashi F, Tanaka M, Lin D, et al. Surface structure of yttrium-modified ceria catalysts and reaction pathways from ethanol to propene[J]. Journal of Catalysis, 2014, 316: 112-120.

[22] del Río E, Gaona D, Hernández-Garrido J C, et al. Speciation-controlled incipient wetness impregnation: A rational synthetic approach to prepare sub-nanosized and highly active ceria–zirconia supported gold catalysts [J]. Journal of Catalysis, 2014, 318: 119-127.

[23] Zhao W, Li C, Lu P, et al. Iron, lanthanum and manganese oxides loaded on gamma-Al2O3 for selective catalytic reduction of NO with NH3 at low temperature [J]. Environmental Technology, 2013, 34 (01): 81-90.

[24] Sang-Kyung Kim, Son-Ki Ihm. Nature of carbonaceous deposits on the alumina supported transition metal oxide catalysts in the wet air oxidation of phenol [J]. Topics in Catalysis, 2005, 33 (1–4): 171–179.

[25] Kim M H. Surface Chemical Structures of CoOx/TiO2 Catalysts for Continuous Wet Trichloroethylene Oxidation [J]. Korean Journal of Chemical Engineering, 2005, 22(6): 839–843.

[26] Barbier Jr*J, Oliviero L, Renard B. Role of ceria-supported noble metal catalysts (Ru, Pd, Pt) in wet air oxidation of nitrogen and oxygen containing compounds [J]. Topics in Catalysis, 2005, 33(1–4): 77–86.

[27] Xu A H, He S B, Yang m, et al. Study on copper dissolution of copper-containing spinel catalyst in phenol catalyzed wet oxidation degradation [J]. Environmental science, 2008, 29 (9) : 2518 ~ 2521. (in Chinese with English abstract)

[28] Li X, Yang S X, Zhu W P, et al. Catalytic wet oxidation of phenol and aniline using carbon nanotubes [J]. Environmental science, 2008, 29 (9) : 2522 ~ 2528. (in Chinese)

[29] Zhao bin-xia, Zhang xiao-li,Li hong-ya, et al. Study on the performance of MnOx-CeO2 catalyst for wet oxidized imidacloprid pesticide wastewater [J]. Journal of chemical sciences, 2009, 30 (5) : 965 ~ 970. (in Chinese with English abstract)

[30] Li H Y, Zhang T T, Zhao B X, et al. Catalytic oxidation of H acid wastewater with supported catalyst [J]. Chemical environmental protection, 2011, 31 (5): 459-463. (in Chinese)

[31] Ai X L, Zhao B X, Zhang X Li, et al. Catalytic wet hydrogen peroxide oxidation of coking wastewater by Fe/AC [J]. Journal of environmental engineering, 2011, 5 (8) : 1815- 1819. (in Chinese with English abstract)

[32] Tang W W, Zeng X P, Zhao J F, et al. Stability and application of supported catalysts in wet catalytic oxidation [J]. Environmental pollution control technology and equipment, 2006, 7 (12) : 132 ~ 140. (in Chinese)

[33] Yang X X, Feng Y J, Cai W M, et al. Effect of CeO2 on the wet oxidation degradation of phenol over RuO2/γ-Al2O3 catalyst [J]. Materials engineering, 2003, 11:32 ~ 39. (in Chinese)

[34] Mariángel Martín-Hernández, Julián Carrera, María Eugenia Suárez-Ojeda, et al. Catalytic wet air oxidation of a high strength p-nitrophenol wastewater over Ru and Pt catalysts: Influence of the reaction conditions on biodegradability enhancement[J]. Applied Catalysis B: Environmental, 2012, 123–124: 141–150.

[35] Zhang Y L, Hu X M, Li H. study on roasting conditions of copper supported wet oxidation catalyst [J]. Acta intraocular lens sinica, 2010, 39 (1) : 272 ~ 276. (in Chinese with English abstract)