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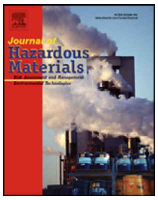

Invited review

Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review

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ABSTRACT

Catalytic wet air oxidation (CWAO) is one of the most economical and environmental-friendly advanced oxidation process. It makes a promising technology for the treatment of refractory organic pollutants in industrial wastewaters. Various heterogeneous catalysts including noble metals and metal oxides have been extensively studied to enhance the efficiency of CWAO. The present review is concerned about the literatures published in this regard. Phenolics, carboxylic acids, and nitrogen-containing compounds were taken as model pollutants in most cases, and noble metals such as Ru, Rh, Pd, Ir, and Pt as well as oxides of Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ce were applied as heterogeneous catalysts. Reports on their characterization and catalytic performances for the CWAO of aqueous pollutants are reviewed. Discussions are also made on the reaction mechanisms and kinetics proposed for heterogeneous CWAO and also on the typical catalyst deactivations in heterogeneous CWAO, i.e. carbonaceous deposits and metal leaching.

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1. Introduction

Wastewaters from industries such as pulp and paper, dyeing, chemical, petrochemical, etc. contain hazardous and refractory organic pollutants which can cause severe problems for the environment. They must be treated to satisfy the stringent water quality regulations and the demand for recycling of water in the process.

Conventional technologies including biological, thermal, and physicochemical treatments have been used to remove the aqueous pollutants. Although biological method is widely applied for the treatment of residual wastewaters, it requires a long residence time for microorganisms to degrade pollutants and is not suitable to treat the toxic contaminants due to biomass poisoning. Incineration is appropriate for the treatment of effluents having more than 100 g/L of chemical oxygen demand (COD). However, it requires an extremely high energy and presents considerable emission of other hazardous compounds such as dioxin and furan [1]. Some other techniques such as flocculation, precipitation, adsorption, air stripping, and reverse osmosis require a post-treatment to dispose of the pollutants from the newly contaminated environment [2]. The aforementioned limitations of conventional methods have encouraged the researchers to develop more efficient and environmental-friendly system for wastewater treatment.

Advanced oxidation processes (AOPs) with the capability of exploiting the high reactivity of hydroxyl radicals in driving oxidation have emerged a promising technology for the treatment of wastewaters containing refractory organic compounds [3]. Several technologies like Fenton, photo-Fenton, wet oxidation, ozonation, photocatalysis, etc. are included in the AOPs and their main difference is the source of radicals. Wet air oxidation (WAO), which was proposed and developed by Zimmermann [4], is one of the most economically and technologically viable AOPs for wastewater treatment. The application range of each AOP is different depending on the flow rate and organic content of effluent to be treated [5]. AOPs based on ozonation and wet peroxide oxidation (WPO) are preferred at low flow rates and low organic loads. Incineration is only suitable for highly concentrated wastewater at low flow rate, while biological treatments appear to be appropriate for high flow rate and low content of organic. Unlike other AOPs, WAO is proper to a high organic loading at high flow rate and can partially cover the application range of incineration and biological methods. Especially, WAO has a great potential for the treatment of effluent containing a high content of organic matter (about 10–100 g/L of COD) and/or toxic contaminants for which direct biological treatment is not feasible. By using WAO, the organic pollutants are either partially oxidized into biodegradable intermediates or mineralized to carbon dioxide, water, and innocuous end products under elevated temperatures (125–320 °C) and pressures (0.5–20 MPa) using a gaseous source of oxygen (either pure oxygen or air) as the oxidant [6]. WAO is not only eco-friendly but also economical as compared to other AOPs using harmful and expensive oxidizing agents like ozone and hydrogen peroxide.

Application of the proper catalysts for WAO process, i.e. catalytic wet air oxidation (CWAO), not only reduces the severity of reaction conditions but also more easily decomposes even refractory pollutants, thereby reducing capital and operational cost [6–18]. Though it varies with type of wastewater, the operating cost of CWAO is about half that of non-catalytic WAO due to milder operating conditions and shorter residence time [19]. Although the homogenous catalysts, e.g. dissolved copper salts, are effective, an additional separation step is required to remove or recover the metal ions from the treated effluent due to their toxicity, and accordingly increases operational costs. Thus, the development of active heterogeneous catalysts has received a great attention because a separation step is not necessary. Various solid catalysts including noble metals, metal oxides, and mixed oxides have been widely studied for the CWAO of aqueous pollutants.

The present article reviews the recently published literature (mainly last ten years) on the heterogeneous CWAO of refractory organic pollutants including phenolics, carboxylic acids, nitrogen-containing compounds, and real wastewaters highlighting the catalytic performances and reaction conditions. Reaction mechanisms and kinetics that have been proposed for the heterogeneous CWAO of organic compounds, mainly phenol, are discussed to help the understanding of heterogeneous catalytic reaction. Finally, discussions are made on the main reason of catalyst deactivation in heterogeneous CWAO, namely carbonaceous deposits and metal leaching.

2. Heterogeneous catalytic wet air oxidation

Various heterogeneous catalysts including noble metals, metal oxides, and mixed oxides have been prepared and tested for the CWAO of model compounds and real wastewaters to find the new catalytic materials with high activity and stability. In this section, the studies on the heterogeneous CWAO of phenolic compounds, carboxylic acids, N-containing compounds, and real wastewaters published in the last decade are discussed, highlighting the catalytic performances and reaction conditions.

2.1. Catalytic wet air oxidation of phenolic compounds

Among the harmful organic compounds, phenolic substances have deserved more attention because of their toxicity and frequency of industrial wastewaters [6,20]. They give off unpleasant odor and taste even at very low concentrations [21]. Moreover, phenol is considered to be an intermediate in the oxidation pathway of higher molecular weight aromatic compounds and thus is mainly taken as a model compound for advanced wastewater treatments [22,23].

2.1.1. Catalytic wet air oxidation of phenol

2.1.1.1. Catalytic wet air oxidation of phenol over noble metal catalysts. Noble metals such as Ru, Rh, Rd, and Pt generally show higher catalytic activity and also higher resistance to metal leaching than base metal oxide catalysts. They are usually supported on γ-Al_2O_3, TiO_2, CeO_2, ZrO_2, and carbon materials with less than 5% of metal loading. Studies on the CWAO of phenol using noble metal catalysts are listed in Table 1.

Among the noble metals used for the CWAO of phenol, Ru is one of the most active catalysts. Pintar et al. [24] reported that the Ru/TiO_2 catalysts enabled complete removal of phenol and total organic carbon (TOC) without the formation of carbonaceous deposits at temperatures above 210 °C and 10 bar of oxygen partial pressure. Castillejos-Lopez et al. [25] studied the CWAO of phenol over 2 wt% Ru catalysts supported on three different supports, i.e. ZrO_2, graphite, and activated carbon (AC). The use of AC as a support enhanced the phenol conversion and mineralization due to the high adsorption capacity of AC. Also, the use of $RuCl_3$ as a ruthenium precursor increased the catalytic activity and selectivity towards CO_2 formation, probably because the residual chorine ions prevent the over-oxidation of ruthenium particle. Barbier et al. [26] demonstrated the activity order of CeO_2 supported noble metals for the CWAO of phenol as follows:

$$Ru/CeO_2 > Pd/CeO_2 > Pt/CeO_2$$

In the presence of Ru/CeO_2 catalyst, almost complete conversion of phenol was achieved after 3 h run under 160 °C and 20 bar of oxygen. Despite the highest initial rates of phenol conversion,