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REVIEW

Progress of catalytic wet air oxidation technology

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KEYWORDS

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Abstract Catalytic wet air oxidation (CWAO) is one of the most economical and environmental-friendly advanced oxidation process for high strength, toxic, hazardous and non-biodegradable contaminants under milder conditions, which is developed on the basic of wet air oxidation. Various heterogeneous catalysts including noble metals and metal oxides have been extensively studied to enhance the efficiency of CWAO. The advances in the research on wastewater treatment by CWAO process are summarized in aspects of reaction mechanism investigation, reaction kinetics study and catalyst development. It is pointed out that the preparation of active and stable catalysts, the investigation on reaction mechanisms and the study on reaction kinetics models are very important for the promotion of CWAO application.

Contents

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1. Introduction

Rapid development of industry promoted rapid growth of economy, but environmental pollution has become a constraining factor of economic development, and high concentrations, toxicity, harmfulness, difficult in biological treatment of wastewater and sludge are still major factors of environmental pollution. Wet air oxidation (WAO) has been proven as one of the efficient technologies to eliminate highly concentrated, toxic and hazardous organic compounds as CO_2, H_2O and other innocuous end products under high temperature and high pressure using oxygen as the oxidant, and without the emissions of NOx, SO_2, HCl, dioxins, furans, and fly ash (Luck, 1999). The WAO is very attractive for treating wastewaters that are too toxic for biological technology to be treated and too dilute for incineration to be eliminated. However, the severe operating conditions and high costs limit its application in wastewater treatment. Catalytic wet air oxidation (CWAO) has gained some attention. The addition of catalysts decreases the operating conditions, enhances the reaction rate, and shortens the reaction time (Luck, 1996; Levec and Pintar, 2007). In recent years, CWAO technology has made many achievements, and the advances in the research on wastewater treatment by CWAO process are summarized in aspects of reaction mechanism investigation, reaction kinetics study and catalyst development. Fig. 1 is schematic diagram of the experimental setup.

2. Reaction mechanisms and reaction kinetics of CWAO

CWAO adds catalyst into the system of traditional WAO, thus it reduces the harsh reaction conditions, increases the oxidation capacity of oxidants and shortens reaction time and thereby it reduces the investment in operating costs. Usually CWAO can be divided into heterogeneous and heterogeneous CWAO according to different forms of catalysts.

Reaction mechanism of CWAO and WAO has no essential difference, and the addition of the catalyst enhances the production of free radicals. Reaction mechanism of WAO is very complicated, and WAO reaction is generally regarded as free radical reactions. The present study is also at a relatively shallow stage, which mainly contains the detection of intermediate and free radicals. Free radical reaction is generally regarded as a chain reaction that is divided into three phases namely chain initiation, chain transfer and chain termination. Li et al. (1991) proposed the mechanism of radical reaction for WAO that has been widely recognized. They believe that there are several free radicals in the reaction system, such as the $O^{\cdot}$, $HO_2^{\cdot}$ and $HO^{\cdot}$, and $HO_2^{\cdot}$, $HO^{\cdot}$ are the primary radicals among them. Robert et al. (2002) applied WAO to treat cellulose and the study showed that $HO^{\cdot}$ and H_2O_2 play the role of intermediates in the initial phase of the oxidation reactions. $HO^{\cdot}$ was detected by the electron spin resonance spectroscopy coupled to the spin trapping technique using the 5,5-dimethyl 1-pyrroline N-oxide (DMPO) as a spin trap agent. The spin adduct (DMPO/$HO^{\cdot}$), resulting from the trapping of $HO^{\cdot}$ with DMPO, showed a characteristic electron spin resonance signal which was inhibited when catalase was added, indicating that $HO^{\cdot}$ was provided from H_2O_2. These transient species were only observed at the beginning of the reaction and were not oxygen dependent. Delgado et al. (2006) studied CWAO of phenol in some detail and high mineralization performances were observed by operating at moderate temperatures and oxygen partial pressures. The mechanism proposed for the

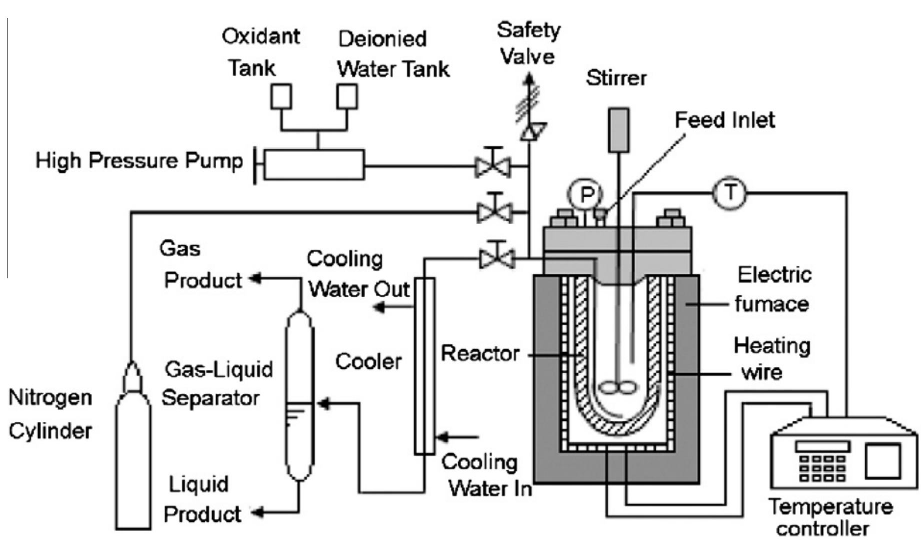

Figure 1 Schematic diagram of the experimental setup.