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Catalytic Wet Air Oxidation of Coke-Plant Wastewater on Ruthenium-Based Eggshell Catalysts in a Bubbling Bed Reactor

M. Yang · Y. Sun · A. H. Xu · X. Y. Lu · H. Z. Du · C. L. Sun · C. Li

Abstract Catalytic wet air of coke-plant wastewater was studied in a bubbling bed reactor. Two types of supported Ru-based catalysts, eggshell and uniform catalysts, were employed. Compared with the results in the wet air oxidation of coke-plant wastewater, supported Ru uniform catalysts showed high activity for chemical oxygen demand (COD) and ammonia/ammonium compounds (NH3-N) removal at temperature of 250 °C and pressure of 4.8 MPa, and it has been demonstrated that the catalytic activity of uniform catalyst depended strongly on the distribution of active sites of Ru on catalyst. Compared to the corresponding uniform catalysts with the same Ru loading (0.25wt.% and 0.1wt.%, respectively), the eggshell catalysts showed higher activities for CODcr removal and much higher activities for NH3-N degradation. The high activity of eggshell catalyst for treatment of coke-plant wastewater can be attributed to the higher density of active Ru sites in the shell layer than that of the corresponding uniform catalyst with the same Ru loading. It has been also evidenced that the active Ru sites in the internal core of uniform catalyst have very little or no contribution to CODcr and NH3-N removal in the total oxidation of coke-plant wastewater.

Keywords Catalytic wet air oxidation · Ru catalysts · Bubbling bed reactor · Eggshell catalyst · Coke-plant wastewater

Coke plant wastewater is generated in the coal coking, coal gas purification, and byproduct recovery processes of coke factories. The composition of the wastewater is complicated and varies from one factory to another, depending on the quality of the raw coal, the carbonation temperature, and the method used for byproduct recovery. As well as the very high ammonia content, there are also harmful anions such as cyanides and thiocyanate, and many toxic organic contaminants, such as phenols, mono- and polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclic compounds and polynuclear aromatic hydrocarbons (PAHs) (Li et al., 2003; Wen et al., 1991). The negative effect of ammonia/ammonium compounds in the environment occurs at three different levels: over-fertilization of surface water; toxicity to waterborne organisms and consumption of oxygen through nitrification. These organic compounds have a long-term environmental impact, while most heterocyclic compounds and polycyclic aromatic hydrocarbons (PAHs) are reported to be mutative and carcinogenic (Melcer et al., 1984; Azhar et al., 1994). Pollution caused by coke plant has been a severe problem for decades all over the world as coal is a main energy resource. It is therefore necessary to remove these substances from coke-plant wastewater to reduce their harm to environments. Because of the presence of not only refractory and biologically inhibitory inorganic anions and organic compounds such as cyanides, thiocyanate, and PAHs, but also nitrogenous heterocyclic compounds in coke-plant wastewater, a conventional activated-sludge system is not efficient in

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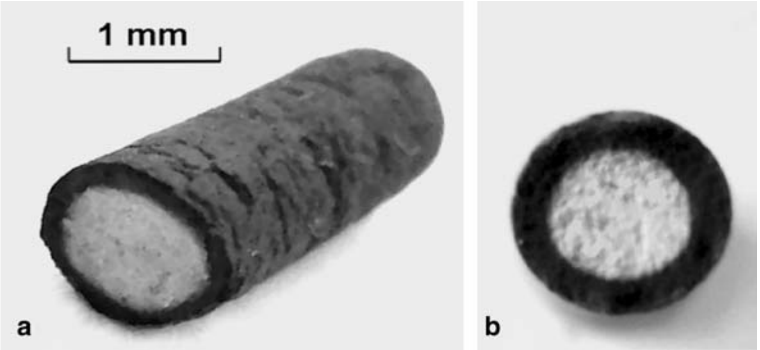

Fig. 1 Photograph of the eggshell catalyst: (a) side view; (b) end view

removing chemical oxygen demand (COD), although it is acceptable for the removal of phenol and biochemical oxygen demand (BOD). It is also difficult to reduce high-strength NH_3 using a conventional biological treatment system (Hockenbury and Grady, 1977). Among the various techniques claimed to be effective and economically competitive for the mineralization of industrial wastewater streams, particular attention has been devoted to the wet air oxidation (WAO) process, which is a liquid-phase oxidation process with air. In this process, toxic or poorly biodegradable organic and inorganic compounds are oxidized totally under extreme conditions of temperature (180–315°C) and pressure (2–15 MPa). Despite the relatively severe reaction conditions, total oxidation of both ammonia/ammonium compounds and ammonium ion transformed from the nitrogen moieties in organic compounds in coke-plant wastewater is quite difficult in the WAO process. Therefore, the more-effective and economically competitive catalytic wet air oxidation (CWAO) process (Cybulski and Trawczynski, 2004; Besson et al., 2003) has become an effective option for the treatment of coke-plant wastewater. As a catalyst, the attractive properties of ruthenium have been highlighted by previous studies due to its very high activity for degradation of NH_3-N and acetic acid, which is a main end product formed during the wet oxidation process. However, this noble metal catalyst is expensive, which restricts its wide application in the treatment of wastewater. Decreasing the noble metal loading is a direct and effective way to reduce the price of this kind of catalyst.

This paper deals with decreasing the ruthenium loading in a Ru/TiO_2 catalyst and the application of a cheaper catalyst for the treatment coke-plant wastewater. To achieve this, the effect of the distribution of active Ru sites on the Ru/TiO_2 catalyst on its catalytic activity for the CWAO of coke-plant wastewater was investigated. Moreover, the different roles of the active Ru sites in the outer layer and the internal core of catalysts in the CWAO processing of organic compounds and ammonia/ammonium compounds in coke-plant wastewater are discussed.

Materials and Methods

Catalysts were prepared using TiO_2 particles (received as columns, HSD Corporation, China). The BET surface area of the TiO_2 was 40 m^2/g, and the void volume was 0.3 mL/g. The particles had an average diameter of 1.5 mm and an average length of 3 mm. The purity of the TiO_2 support is very high with a weight percentage of TiO_2 is 99.665 %. Inorganic impurities in the TiO_2 support are mainly Nb_2O_3, ZrO_2 and SiO_2 (0.072 %, 0.096 % and 0.062 %, respectively). The mechanical crushing strength of the TiO_2 support is high with an axial crushing strength of 1.12×10^3 N/cm^2. The high mechanic strength and purity of the TiO_2 support are crucial to obtain a stable supported catalyst, and the stability of the catalyst is important for its application in the severe hydrothermal reaction conditions of the CWAO process.

Two types of titanium-dioxide-supported Ru catalysts (uniform and eggshell) were prepared and used in this study. Prior to impregnation, the particles were initially washed in distilled water and dried at 120°C for 6 h to remove any dust particles. The uniform catalysts were prepared by incipient wetness impregnation of the supports with ruthenium chloride aqueous solution. The samples were dried at 60°C for 6 h and at 120°C for 6 h, respectively. After the drying procedure, the samples were calcined at 400°C for 6 h.

The two eggshell Ru/TiO_2 catalysts with 0.25 wt% Ru loading and 0.1 wt% Ru loading were prepared by the method of two-step incipient wetness impregnation. In the first impregnation, the TiO_2 supports were impregnated with a 1 mol/L ammonium bicarbonate solution. Following the first impregnation, the samples were dried at room temperature for 1 h. In the second impregnation, the samples were impregnated with a mixed solution of ruthenium chloride and hydrochloric acid. A controlled concentration of hydrochloric acid only neutralizes the ammonium bicarbonate on the outer layer of support, which favors ruthenium trichloride adsorption on the outer layer, which redistributes and aggregates on the outer surface of the eggshell catalyst when dried, resulting in an eggshell dis-

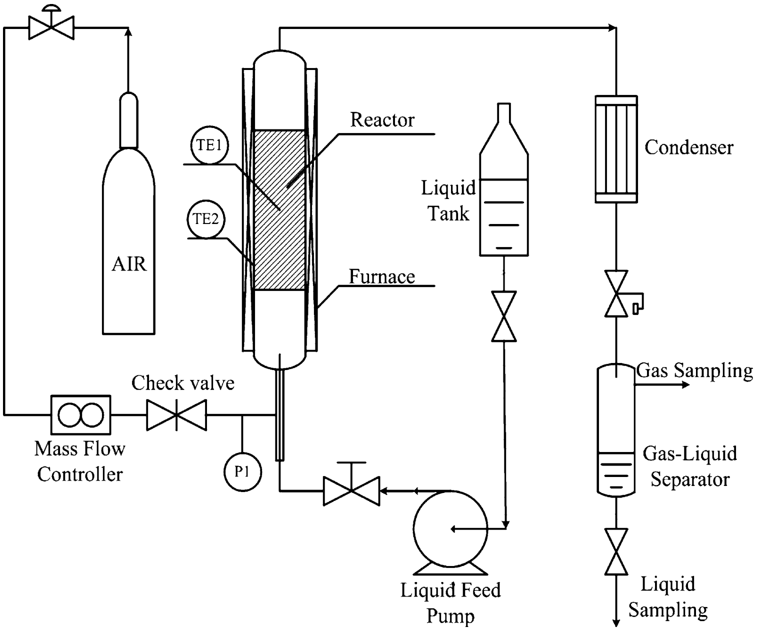

Fig. 2 Schematic diagram of the experiment equipment

Table 1 WAO activities of coke-plant wastewater

CODcr			NH_3-N		
Influent (mg/L)	Effluent (mg/L)	Removal (%)	Influent (mg/L)	Effluent (mg/L)	Removal (%)
5,691	1,117	81	2,726.7	2,830.0	–

Reaction conditions: 250°C and 4.8 MPa. LHSV: 2.0 h^{-1}, air flow rate: 40 cm^3/min (STP)

tribution of the catalytically active component. After the second impregnation, the samples were treated using the same procedures described for the preparation of uniform catalysts.

The two kinds of catalysts were divided into halves and inspected visually to determine the difference in the radial distribution of Ru; a photograph of the eggshell catalyst is shown in Fig. 1. The uniform catalyst showed an evenly black surface, which was clearly different from the white color of the unimpregnated TiO_2 column. The eggshell catalyst had a black shell at the column edge and an interior white circle. The average thickness of the outer shell on the two eggshell catalysts was determined by an optical microscopy to be 0.20–0.25 mm.

The feed wastewater used in this study was effluent from the Dalian Coke Company in China. The CODcr value of the wastewater was 5691 mg/L; the value of NH_3-N (ammonia nitrogen) was 2,727 mg/L and the pH value was 9.3. The wastewater was filtered before being fed into the liquid pump to avoid clogging.

A schematic diagram of the experimental equipment is shown in Fig. 2. Activity testing in the wet air oxidation of phenol was performed at 250°C and 4.8 MPa, LHSV: 2.0 h^{-1}, air flow rate: 40 cm^3/min (STP). The bubbling bed reactor consists of a stainless-steel tube (length 600 mm, ID 20 mm) with a thermocouple well in the center of the reactor. The reactor was packed in three layers: ceramic particles, catalysts and ceramic particles. 15 mL of catalyst was loaded into the constant-temperature zone of the reactor (about 25 cm from the top of the reactor). Air and the coke-plant wastewater flow concurrently up through the reactor. The effluent was condensed in a condenser and separated in a gas–liquid separator.

The amount of chemical oxygen demand (COD) was analyzed by the closed microwave dichromate method using a quick WMX-type CODcr microwave sealed digestion measuring system (Valle et al. 1990). COD proved to be useful in assessing the degree of total oxidation to CO_2 and the small amount of molecular organic acids present. The measurement of the total concentration of both NH_3 and NH_4^+ (NH_3-N) in the coke-plant wastewater was conducted by Nessler's reagent colorimetric method on a Varian Cary-50 spectrometer. The pH values were examined by means of a pH meter (Rano, DFSD).

Results and Discussion

Wet oxidation of coke-plant wastewater was carried out at 250°C and 4.8 MPa; the results are listed in Table 1. The CODcr of wastewater was removed efficiently, with 81% obtained. On the other hand, as shown in Table 1, the concentration of NH_3-N in the WAO of coke-plant wastewater not only does not decrease but actually increases slightly, which can be attributed to the chemical

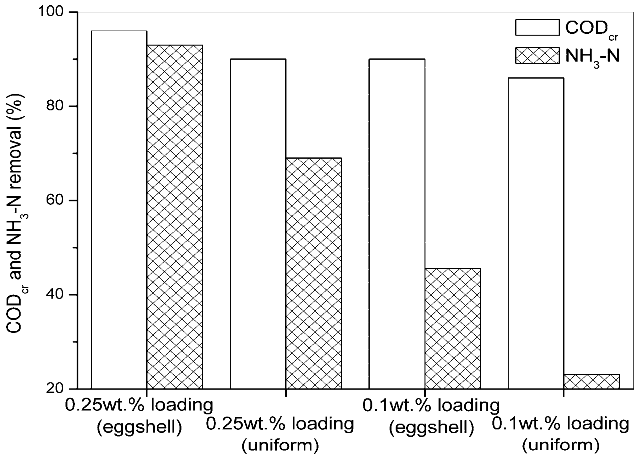

Fig. 3 Activities of eggshell and uniform catalysts with the same Ru loading

inertness of ammonia/ammonium in solution and the formation of ammonium ions converted from nitrogen-containing aromatics in the coke-plant wastewater. This indicates that NH_3-N in coke-plant wastewater is very difficult to oxidize under the reaction conditions studied.

In the CWAO of coke-plant wastewater, the activity of Ru/TiO_2 catalyst was strongly related to the density of the catalytically active component, Ru, on the catalyst. In order to reduce the Ru loading and increase the density of active Ru sites on the catalyst, the activity of the eggshell catalysts with 0.25 wt% and 0.1 wt% Ru loadings were investigated. The activities of the two eggshell catalysts, and for comparison the activities of uniform catalysts with 0.25 wt% and 0.1 wt% Ru loadings are presented in Fig. 3. As indicated, the two COD_{cr} removal values of the eggshell catalysts with 0.25 wt% and 0.1 wt% Ru loadings are 96% and 90%, respectively, which is higher than the values of 90% and 86% for the corresponding uniform catalysts with the same Ru loading under the same reaction conditions. At the same time, the two NH_3-N degradation values of the eggshell catalysts with 0.25 wt% and 0.1 wt% Ru loadings are 93.0% and 45.6%, respectively, which are remarkably higher than the 69.0% and 23.1% values of the corresponding uniform catalysts with the same Ru loading under the same reaction conditions. These results indicate that the activity of the eggshell catalyst is higher than that of the uniform catalyst at the same Ru loading. As presented in Fig. 1, the shell thickness of the eggshell catalyst is about 0.2–0.25 mm. With the support particle diameter of about 1.5 mm, the shell volume can be calculated and is nearly 50% of the volume of the support particle. Therefore, compared to the corresponding uniform catalyst with the same Ru loading, the density of active Ru sites in the shell layer of the eggshell catalyst is approximately twice that of the uniform catalyst. It is reasonably to attribute the higher activity of the eggshell catalyst to its higher density of active Ru sites in the shell layer than that of the uniform catalyst. Moreover, this also suggests that the active Ru sites in the internal core of the uniform catalyst make a very limited or no contribution to the COD_{cr} and NH_3-N degradation in the CWAO of coke-plant wastewater.

As for COD_{cr} removal, it is reasonable to speculate that oxidation of these larger organic compounds mainly takes place on the active Ru sites located in the outer part of the catalyst particles. Coke-plant wastewater is a very complex system that contains many organic compounds, such as phenols, mono- and polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclic compounds and PAHs, which are all large organic molecules with benzene rings. These organic compounds may be oxidized at the outer layer of the catalyst. Meanwhile, catalytic wet air oxidation of organic components in such a complicated mixture is a multistep reaction involving various reactants and intermediates. It is generally accepted that larger organic molecules are oxidized in a CWAO process to smaller intermediates, followed by the further oxidation of the intermediates to end products, usually acetic acid, CO_2 and water (Kojima et al., 2005). Intermediates formed by organic compounds with benzene rings in coke-plant wastewater should reach total oxidation on the outer layer of the catalyst because it is difficult for them to diffuse in the internal pores. Eggshell catalysts with the active metal concentrated in the thin shell area provided more accessible oxidation sites for these larger molecule than uniform catalysts, therefore demonstrated the higher CODcr removal efficiencies of eggshell catalysts than those of uniform catalysts in the oxidation of the coke-plant wastewater.

Due to the relatively large contribution of noncatalytic oxidation to total COD_{cr} removal, these results for COD_{cr}

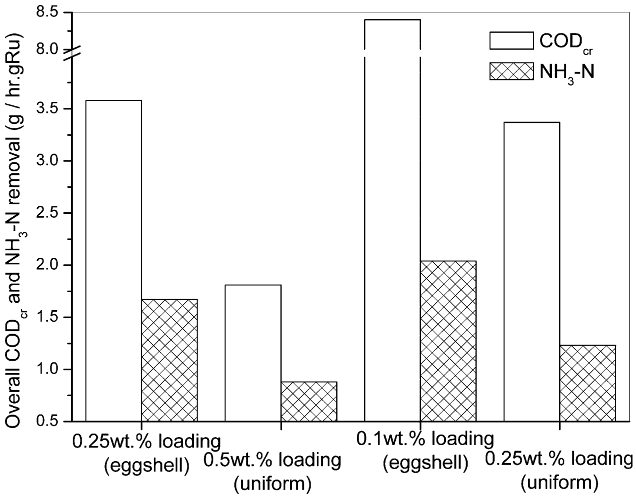

Fig. 4 Overall COD_{cr} and NH3-N removal by eggshell and uniform catalysts

removal by the eggshell catalyst do not satisfactorily indicate that most reactants are degraded in the outer layer of the catalyst in the CWAO process. On the other hand, all NH_3-N is removed by catalysis, which make it more suitable for the investigation of the role of active Ru sites on the outer layer of the catalyst in the treatment of coke-plant wastewater in the CWAO process. It has been found that the activity of supported metal catalyst for NH_3-N conversion is related to its surface oxygen concentration [O] (Qin and Aika, 1998), which suggests that NH_3-N is also degraded in the outer layer of the catalyst.

To further illustrate the effect of the Ru distribution in the outer layer of the catalyst on the oxidation of coke-plant wastewater overall COD_{cr} and NH_3-N removal rates per gram of Ru for a uniform 0.5 wt% Ru loaded and a 0.25 wt% Ru loaded eggshell catalyst are given in Fig. 4. The eggshell catalyst shows a much higher activity than that of the uniform catalyst based on COD_{cr} and NH_3-N removal rates per gram of Ru. At 250°C and 4.8 MPa, the COD_{cr} removal rate for the 0.25 wt% Ru loading eggshell catalyst was about twice that of the 0.5 wt% Ru uniform catalyst. The NH_3-N removal rate for the 0.25 wt% Ru loading eggshell catalyst was also about twice that of the 0.5 wt% Ru uniform catalyst. These results clearly show that the eggshell catalyst is very effective in oxidative destruction of COD_{cr} for large organic compounds and NH_3-N in ammonia/ammonium compounds in coke-plant wastewater. The comparison between the 0.5 wt% Ru loading uniform catalyst and the 0.25 wt% Ru loading eggshell catalyst is useful as the densities of the two catalysts in the outer shell layer were equal because the volume of the outer shell layer was nearly half of the volume of the whole catalyst and there was no active Ru in the internal core of the eggshell catalyst. This indicates that the active Ru sites in the outer layer of the catalyst may play the dominant role in the COD_{cr} and NH_3-N removal and that the active Ru sites in the internal core of catalyst barely contribute to the COD_{cr} and NH_3-N removal in the CWAO processing of coke-plant wastewater. Overall COD_{cr} and NH_3-N removal rates per gram of Ru over a 0.25 wt% Ru loading uniform and a 0.1 wt% Ru loading eggshell Ru catalyst were also shown in Fig. 4. The Ru loading of the 0.1 wt% Ru loading eggshell catalyst was nearly half that of the 0.25 wt% Ru with uniform loading. As indicated in Fig. 4, the CODcr and NH_3-N removal rate with the eggshell catalyst is also about twice that of the 0.25 wt% Ru loading uniform catalyst. This further demonstrates that the active Ru sites in the outer layer of catalyst may be mainly responsible for the CODcr and NH_3-N removal and that the active Ru sites in the internal core of the catalyst make almost no contribution to CODcr and NH_3-N removal in the CWAO processing of coke-plant wastewater.

This study demonstrates that TiO_2-supported ruthenium catalysts are very active for reduction of CODcr and NH_3-N of coke-plant wastewater, and that the activity of the Ru/TiO_2 catalyst was strongly related to the density of ruthenium, the catalytically active component, in the catalyst. The active Ru sites in the outer layer of the Ru/TiO_2 catalyst were responsible for CODcr and NH_3-N removal, while the active sites in the internal core of the catalyst made almost no contribution to CODcr and NH_3-N removal in the CWAO processing of coke-plant wastewater. Eggshell Ru/TiO_2 catalysts showed higher activity for CODcr and NH_3-N removal compared to uniform Ru/TiO_2 catalysts at the same Ru loading. This higher activity could be attributed to the higher density of active Ru sites in the outer shell layer of the eggshell catalysts.

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