Removal of Benzoic Acid by Catalytic Ozonation with CeO_2 Loaded on N, S Co-Doped Activated Carbon Catalyst

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Abstract. N, S co-doped activated carbon (ACNS) was obtained by modification with thiourea and cerium oxide supported on activated carbon (Ce/AC, and Ce/ACNS) were prepared and worked as catalyst for catalytic ozonation of benzoic acid. The catalysts were characterized by elemental analysis, N_2 adsorption-desorption, the pH at the point of zero charge (pH_{pzc}),) and X-ray photoelectron spectroscopy (XPS).In contrast with Ce/AC, Ce/ACNS increased the catalytic activity. The enhanced catalytic performance was attributed to the presence of the N and S atoms may improve the electron density on AC surface and therefore enhance the amount of Ce^{3+} on catalyst surface.

Keywords: Activated carbon, Cerium oxide, Catalytic ozonation, Benzoic acid, Nitrogen and sulfur co-doped.

1. Introduction

CeO_2 is an ozonation catalyst being highly stable and active to remove organic pollutants from wastewater and water [1, 2]. Furthermore, undetectable leaching of Ce was found during the reaction, which was crucial for its industrial application in wastewater treatment. Unfortunately, the effect of AC support was not studied in the preparation of Ce/AC catalyst. The characters of AC surface had a great influence on the catalytic performance of AC supported catalyst. On one hand, AC was not only used as a supporting material, but also an ozonation catalyst due to its excellent properties in porous structures and adsorption capacity [3-5].

Accordingly, the main objective of this work was to study the influence of AC surface on the catalytic performance of Ce/AC catalyst in ozonation process. For this purpose, AC was modified with thiourea so as to introduce nitrogen-containing and sulfur-containing functional groups onto AC surface. Prior to introducing these functional groups, the AC was oxidized by HNO3. The performance of Ce/AC catalysts was evaluated in terms of benzoic acid removal. Moreover, the effect of solution initial pH on the degradation rate of benzoic acid in catalytic ozonation process was investigated.

2. Materials and Methods

2.1 Catalysts Preparation and Characterization

AC was suspended in 300 mL 50% HNO_3 and refluxed at 80 °C for 3 h in a three-necked flask, then filtered and washed with hot distilled water and dried at 110 °C for 12 h. Then, 25 g of the oxidized AC was placed in a round-bottomed flask with 15 g thiourea dissolved in 100 mL of deionized water. The contact was maintained during 30 min under ultrasonic treatment. Then, the carbon residue was filtered, dried in an oven at 110 °C for 24 h and calcined in a tube furnace under a flow of Ar for 3 h at 900 °C, with a heating rate of 10 °C/min. Finally, the samples were cooled to room temperature and stored in a desiccator until their use. The resulting sample was denoted as ACNS.

The Ce/AC and Ce/ACNS catalysts were prepared by incipient wetness impregnation method. Briefly, the AC or ACNS was impregnated with aqueous solution of $Ce(NO_3)_3 \cdot 6H_2O$ to obtain a nominal Ce loading content of 5%. The impregnation was conducted under vacuum and ultrasonic mixing. The resultant samples were dried at 110 °C for 24 h and then heat treated in a tube furnace

under a flow of (N_2 + H_2) for 3 h at 450 °C, with a heating rate of 3 °C/min. The final materials were designated as Ce/AC and Ce/ACNS, relating the support used.

2.2 Ozonation Experiments

The experiments of ozonation were performed in a jacketed glass reactor with the volume of 500 mL and a magnetic stirrer installed. In each experiment, the reactor was filled with 300 mL of benzoic acid solution of initial concentration 50 mg/L. With a laboratory ozone generator, this work adopted the pure oxygen to generate the ozone. Then, ozone was bubbled into the ozone into ozonation reactor through a sintered metal filter at the bottom of the reactor. The stirring rate was maintained at 200 rpm and the reaction temperature was set at 30 °C and maintained constant by circulating water from a thermostatic bath through the jacket. When the desired temperature was reached, catalyst was added in the meantime for launching the reaction. Samples were periodically withdrawn and immediately filtered with 0.45 μm membrane for further analysis.

2.3 Analytical Techniques

The concentration of benzoic acid was determined by High Performance Liquid Chromatograph (HPLC, Shimadzu Prominence LC-20A) equipped with UV detector and C18 reverse phase column (4.6 × 250 mm, 5 μm). The analyses were carried out with a mobile phase of a 5/95 mixture of methanol and ammonium acetate. The detection wavelength was performed at 230 nm. The elution flow rate was 1.0 mL min-1 and the injection volume was 10 μL. The pH of solution was monitored by a PHC-3C pH meter.

3. Results and Discussion

3.1 Characterization of Catalysts

The results of porosity characterization as well as pHpzc are presented in Table 1. The original AC was a highly mesoporous carbon with large specific surface area (SBET, 1318 m^2/g), pore volume (Vt, 1.12 cm^3/g) and high percentage of a mesoporous structure (42.8% for V_{micro} and 57.2% for V_{meso}). An obvious decrease of SBET and Vt was observed after treatment with HNO3. Similarly, it was noted that an obvious decrease in SBET and Vt was observed when the oxidized AC was treated with thiourea, which can be explained by the introduction of sulfur-containing groups. Similar result was reported in other literature [6]. The original AC had a slightly acid property while ACNS showed slightly basic properties, which can be explained by the presence of nitrogen groups having basic properties. Besides, the impregnation of ceria did not substantially change the textural properties of carbon material due to the small loading content.

Table 1. The results of porosity characterization and pH_{pzc} of catalysts

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	pH_{pzc}
AC	1318	1.12	0.39	0.73	6.24
ACNS	1126	0.94	0.31	0.63	7.85
Ce/AC	1256	1.01	0.32	0.69	-
Ce/ACNS	1065	0.88	0.28	0.60	-

XPS studies were carried out to learn about the surface chemical composition of Ce/AC catalysts. The chemical state of N and S in the ACN and ACNS samples was reported elsewhere [7]. Fig. 1 shows the XPS patterns of the Ce 3d region for Ce/AC and Ce/ACNS. The Ce 3d region was fitted with eight peaks, corresponding to four pairs of spin-orbit doublets [8, 9]. Three pairs of peaks (v, u; v_2, u_2; v_3, u_3) are characteristic of the oxidation state Ce^{4+} and the pair (v_1, u_1) corresponds to one of the two pairs of spin–orbit doublets characteristic of the oxidation state Ce^{3+}. According to the XPS results, it was concluded that the Ce^{3+}/Ce^{4+} redox couple existed on the surface of the prepared Ce/AC catalyst. The approach to evaluate the relative percentages of Ce^{3+} on Ce/AC surface took into consideration the relative intensity of the v1 and u1 peaks, as representative of Ce^{3+}, in the total Ce

3d region. The percentages of Ce^{3+} determined by this method were reported as follows. For samples Ce/AC and Ce/ACNS, the relative amount of Ce^{3+} was 24.58% and 28.36%, respectively.

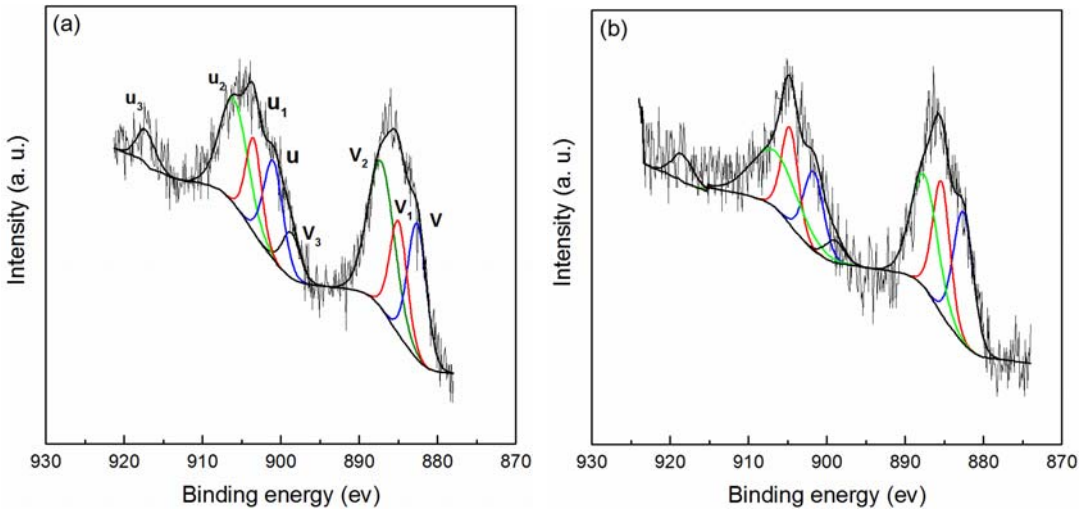

Fig. 1 Experimental and fitted Ce 3d XPS spectra of samples (a) Ce/AC, (b) Ce/ACNS.

3.2 Activity of AC and Ce/AC Catalysts

To investigate the effect of AC supports, AC, ACNS, Ce/AC and Ce/ACNS were used as catalysts for the removal of benzoic acid in solution. The removal rates of benzoic acid in single ozonation and catalytic ozonation are compared in Fig. 2. Moreover, the addition of AC improved the degradation efficiency of benzoic acid compared to single ozonation. The enhanced removal efficiency of benzoic acid must be mainly attributed to an increase in the ozone decomposition into •OH radicals [3-5]. The introduction of N-containing and S-containing groups enhanced the catalytic performance of AC. The similar result was reported in the degradation of naphthalenesulphonic acid by catalytic ozonation with basic activated carbons [6].

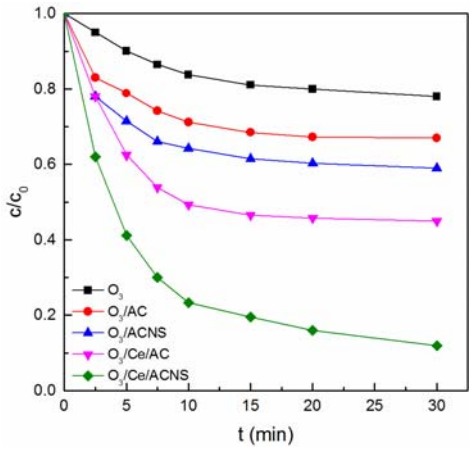

Fig. 2 The removal of benzoic acid in single ozonation and catalytic ozonation.

3.3 Effect of Initial pH

Benzoic acid degradation in single ozonation and catalytic ozonation with Ce/ACNS catalyst at different solution pH was investigated and the results were presented in Fig. 3. It was noted that a similar trend of pH effect was observed in single ozonation and catalytic ozonation with Ce/ACNS. The benzoic acid removal was increased with solution pH due to hydroxyl ions initiating ozone decomposition to generate •OH radicals at an alkaline pH [3, 4]. The results implied that the indirect oxidation via •OH radicals was effective for benzoic acid degradation. Furthermore, the enhancement of benzoic acid removal by the addition of Ce/ACNS, compared with ozonation alone, was greater at acidic pH and became smaller when the pH was increased, which suggested that Ce/ACNS catalyst exerted its catalytic effect mainly at the acidic pH.

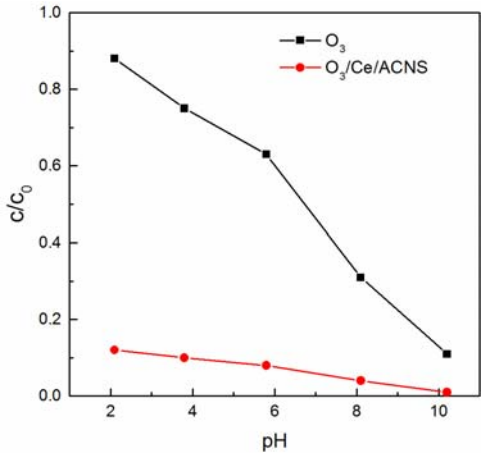

Fig. 3 Effect of pH on benzoic acid degradation in single and catalytic ozonation with Ce/ACNS.

4. Conclusion

N, S co-doped ACNS improved the catalytic activity due to the enhancement of electron density on the surface. The ceria supported catalyst based on ACNS showed the highest catalytic performance, which could be explained that the introduction of N-containing and S-containing surface groups enhanced the electron density on AC surface and more electrons were transferred from the AC basal planes to the metal oxide, and therefore more Ce^{3+} species existed on catalyst surface. Fe/ACNS was an effective and stable catalyst in catalytic ozonation of benzoic acid. It may have a prospective application in the treatment of benzoic acid-containing wastewater.

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