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Chinese Chemical Letters 22 (2011) 209–212

CHINESE CHEMICAL LETTERS

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Simple preparation and catalytic properties of ZnO for ozonation degradation of phenol in water

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Received 28 June 2010

Abstract

ZnO particles about 200 nm were prepared through a facile hydrothermal method. Compared with single ozonation, the degradation efficiency of phenol increased about 23.7% and the degradation efficiency of intermediates improved about four times in the presence of ZnO at 298 K. In addition, the catalyst had good stability in the ozonation process. The influence of temperature was investigated and it was found that the better catalysis efficiency could be obtained at lower temperature.

Keywords: Organic pollutants; Water treatment; Ozone; Catalysis

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Nowadays, pollution from highly toxic organic compounds in the aquatic environment is a serious concern to consider because of its dangers to humans and ecological health. Phenol and phenol derivates have received increased attention as pollutants in the past years due to their high toxicity. Several catalytic oxidation technologies have been developed for the treatment of wastewaters containing phenol and phenol derivates, such as photocatalysis, catalytic wet air/peroxide oxidation and catalytic ozonation [1–4]. Among these methods, catalytic ozonation is a promising process for organic wastewater treatment [2]. First, ozone is an environmentally friendly and practical oxidant since it generates from O_2 and decomposes to O_2, which lacks of secondary pollution. Secondly, the ozonation process can be carried out under normal temperature and pressure. For the treatment of organic pollutants, the search for an active, stable and durable catalyst is an important task.

Nanomaterials, which can exhibit unusual chemical and physical properties, are now gaining attention as heterogeneous ozonation catalysts. The high surface area and good dispersivity of nano-catalyst are favorable to catalysis [5,6]. At the same time, most nano-catalysts are difficult to separate from water. This becomes the main limitation for reuse. It is very significant to develop novel catalysts with good separability as well as remarkable catalysis for water treatment.

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doi:10.1016/j.cclet.2010.10.010

Zinc oxide (ZnO) has wide applications in electronics, catalysis, optoelectronic and sensors. Jung and Choi reported the catalytic decomposition of ozone and *para*-chlorobenzoic acid (*p*-CBA) in the presence of nanosized ZnO, and Huang et al. found a nanometer-ZnO catalyst to enhance the ozonation of 2,4,6-trichlorophenol in water [7,8]. However, both ZnO nano-catalysts were supplied from commercial source. The synthesis of ZnO as ozonation catalyst was rarely reported. The aim of this work is to develop a new route to obtain desirable ZnO ozonation catalyst.

1. Experimental

All chemicals used ($ZnSO_4$, carbamide, NaOH, alcohol and phenol) were of analytical grade, without further purification. All aqueous solutions were prepared with distilled water.

In our experiment, 100 mL of 0.1 mol/L $ZnSO_4$ aqueous solution, 20 mL of 0.5 mol/L carbamide aqueous solution and 20 mL of alcohol were mixed. Then 5 mol/L NaOH aqueous solution was added dropwise to the above solution until the pH of the solution was 11.0. In this process, white suspension formed. Subsequently, the white suspension was placed in sealed Teflon autoclave, heated at 433 K for 12 h and cooled naturally. The resulting white precipitates were washed by water several times and dried at 383 K. The characterization conditions were same as literature [5]. The catalytic degradation of phenol was performed in a semicontinuous flow mode, and the flow rate of ozone was 0.55 mg/min. In a typical catalytic degradation procedure, certain amount of ZnO and 200 mL of simulated wastewater (the initial concentration of phenol was 100 mg/L) were mixed in a flask under thermostatic control. The concentrations of phenol and its oxidized intermediates were determined by a Waters 515 high performance liquid chromatography (HPLC, Waters, USA).

2. Results and discussion

As can be shown in Fig. 1, all the XRD patterns can be readily indexed to pure ZnO (JCPDS 79-0208). No characteristic peaks of impurities were observed. The results indicate the high purity of the products prepared by this approach. TEM images of the as-prepared ZnO are shown in Fig. 2. The products were made up of particles with average size of 200 nm. According to the results of the nitrogen adsorption and desorption isotherms, the BET surface area of ZnO was 36.48 m^2/g and pore structure was not observed.

Fig. 3 shows the degradation of phenol at different ozonation time in single ozonation and catalytic ozonation. It can be seen that the ZnO demonstrated remarkable catalysis efficiency on the ozonation degradation of phenol in water. For example, the residual concentration of phenol was 27.7 mg/L after single ozonation for 60 min, while it was merely 10.5 mg/L in catalytic ozonation. Compared with the single ozonation, the degradation efficiency of phenol increased about 23.7% in presence of catalyst.

Before being degraded to small organic acids, phenol is easily oxidized to more toxic intermediates such as catechol, hydroquinone and *p*-benzoquinone [9–13]. The time dependent concentrations of these intermediates in the single ozonation and the catalytic ozonation were investigated. It can be found that the concentrations of them in catalytic ozonation were lower than those in single ozonation. When the ozonation time reached 60 min, the concentrations of catechol, hydroquinone and *p*-benzoquinone in the catalytic process were 1.1, 2.4 and 0.3 mg/L,

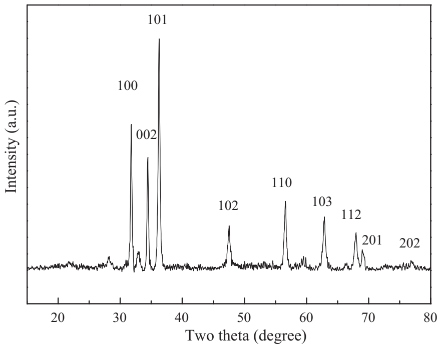

Fig. 1. XRD patterns of as-prepared ZnO.

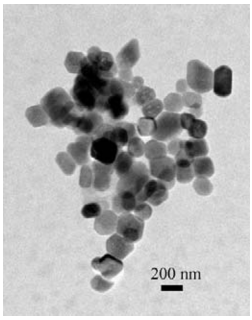

Fig. 2. TEM images of as-prepared ZnO.

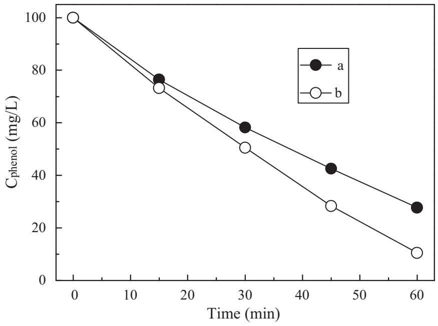

Fig. 3. Time evolution of concentrations of phenol under single ozonation (a) and catalytic ozonation of ZnO (b). Catalyst dose: 0.5 g, reaction temperature: 298 K.

while those in the single ozonation were 7.5, 4.5 and 5.6 mg/L. The total residual concentration of the three intermediates in the catalytic ozonation was only 21.6% of that in the single ozonation. From the above results, we can see that ZnO exhibited high catalytic activity for the ozonation degradation of organic pollutants. According to the decomposition of ozone on surface of ZnO [7,8], the catalysis mechanism may be concluded that ZnO enhanced the transformation of ozone into hydroxyl radicals.

The reusability of the catalyst is important for its practical application. In order to evaluate the activity stability of the catalyst, the reuse experiment was carried out. From Fig. 4, it can be seen that the catalytic activity kept constant and no obvious deactivation was observed when the ZnO was used for six times. That is, the ZnO showed considerable stability in the catalytic process.

As is known, operation temperature influences the ozonation degradation of organic pollutants. Besides 298 K (Fig. 3), we also carried out the catalytic ozonation experiments at 283 and 313 K (Fig. 5). Compared with the results at 298 K, the degradation rate of phenol decreased at lower temperature (283 K), while the degradation rate at 313 K was

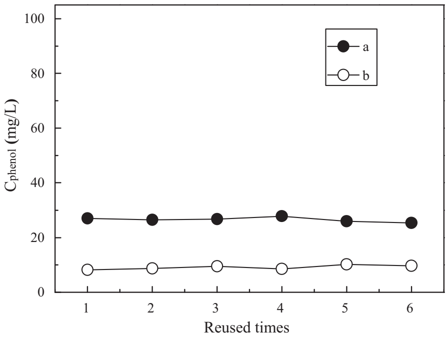

Fig. 4. Degradation of phenol in reuse experiments: (a) single ozonation and (b) catalytic ozonation of ZnO. Catalyst dose: 1.0 g, reaction temperature: 298 K, reaction time: 60 min.

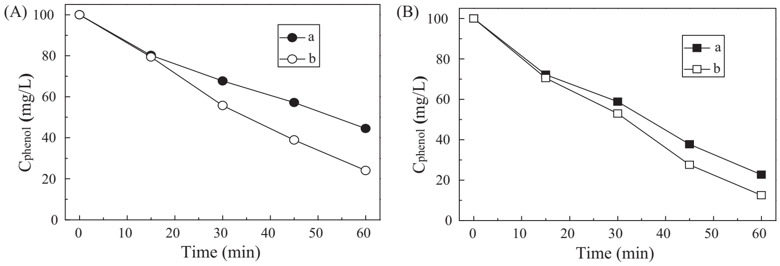

Fig. 5. Time evolution of concentrations of phenol at 283 K (A) and 313 K (B) under single ozonation (a) and catalytic ozonation of ZnO (b). Catalyst dose: 0.50 g.

similar with that of 298 K. The rise of temperature can influence the catalytic ozonation process in three ways: (1) the concentration of ozone in solution is reduced; (2) the transformation from ozone molecules to hydroxyl radicals is accelerated, and the degradation of phenol by hydroxyl radicals is faster than that by ozone molecules [14]; (3) diffusion rate of the reacting substances is enhanced. The efficiency increase in degradation of phenol from 283 to 298 K may be explained that (2) and (3) is predominant. When the temperature increased from 298 to 313 K, (1) was almost equivalent to (2) and (3), then the degradation rate of phenol did not change.

After the single ozonation of 60 min at 283, 298 and 313 K, the removal of phenol were 55.5, 72.3 and 77.3 mg/L, respectively. While after the catalytic ozonation of 60 min at 283, 298 and 313 K, the removal of phenol were 76.0, 89.5 and 87.5 mg/L. That is, the degradation efficiencies of phenol were increased by about 37%, 24% and 13% at 283, 298 and 313 K due to the presence of ZnO. It can be found that the ZnO exhibited certain catalysis activity in the temperatures ranges of 283–313 K. At lower temperature, ZnO exhibited higher catalysis efficiency.

3. Conclusions

In conclusion, using inexpensive raw materials, ZnO particles with good separability were synthesized through a facile hydrothermal method. As-prepared ZnO revealed higher catalysis on ozonation degradation of phenol and its intermediates. In the reuse experiments, the catalytic activity kept constant and no obvious deactivation was observed after six ozonation processes. This result proved the good stability of the catalyst. Through the control experiments carried out at 283, 298 and 313 K, it was found that the better catalysis efficiency could be obtained at lower temperature.

Acknowledgments

The authors gratefully acknowledge the support from the National Natural Science Foundation of China (Nos. 20903048, 20771046 and 21005031), the Fundamental Research Funds for the Central Universities (No. JUSRP30903), the Startup Foundation for Introduced Talents (Nos. 20081789 and 20091207), the Science Foundation for Youth (Nos. 2008LQN002 and 2009LQN11).

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