Catalytic Ozonation of Phenol in Aqueous Solution by Co_3O_4 Nanoparticles

Yuming Dong,^{*} Guangli Wang, Pingping Jiang, Aimin Zhang,^{†,*} Lin Yue,[‡] and Xiaoming Zhang[‡]

School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China

^{*}E-mail: dongym@jiangnan.edu.cn

[†]School of Chemistry and Chemical Engineering, Key Laboratory of Mesoscopic Chemistry, Nanjing University, Nanjing 210093, P. R. China. ^{*}E-mail: zhangam@nju.edu.cn

[‡]School of Food Science and Technology, Jiangnan University, Wuxi 214122, P. R. China

Received June 14, 2010, Accepted August 20, 2010

The degradation efficiencies of phenol in aqueous solution were studied by semi-continuous experiments in the processes of ozone alone, ozone/bulky Co_3O_4 and ozone/ Co_3O_4 nanoparticles. Catalyst samples (bulky Co_3O_4 and Co_3O_4 nanoparticles) were characterized by X-ray diffraction and transmission electron microscopy. The Brunauer-Emmett-Teller surface area, pH_{pzc} and the density of surface hydroxyl groups of the two catalyst samples were also measured. The catalytic activity of Co_3O_4 nanoparticles was investigated for the removal of phenol in aqueous solutions under different reaction temperatures. *Tert*-butyl alcohol had little effect on the catalytic ozonation processes. Based on these results, the possible catalytic ozonation mechanism of phenol by Co_3O_4 nanoparticles was proposed as a reaction process between ozone molecules and pollutants.

Key Words: Cobalt oxide, Catalytic degradation, Nano-catalyst, Catalytic mechanism

Introduction

Aromatic compounds are known pollutants in the effluents of several industries. Among these compounds, phenol is a typical compound produced in the petrochemical, chemical and pharmaceutical industries. Phenol has been classified as a priority pollutant in the USEPA (United States Environmental Protection Agency) list for its highly toxic, carcinogenic, mutagenic, teratogenic properties. Recently, considerable attention has been paid to chemical degradation of phenol.^{1,2}

Ozone, due to its high oxidation ability, has been widely used for the removal of organic pollutants. Single ozonation, in which ozone is used alone for pollutants degradation, organic compounds can not be oxidized quickly and the utilization efficiency of ozone is low. As a result, the single ozonation for water treatment needs a large amount of ozone, which greatly limits its practical application. To overcome the drawback, catalytic ozonation using catalysts to improve degradation efficiency emerged. Catalytic ozonation includes homogeneous catalytic ozonation and heterogeneous catalytic ozonation. Compared with the homogeneous catalytic process, the heterogeneous catalytic ozonation has a notable advantage of no secondary pollutants and is now attracting more and more attention.^{3,4}

Nanomaterials, which can exhibit unusual chemical and physical properties, are novel and promising heterogeneous ozonation catalysts in environment research.⁵⁻¹¹ For instance, Jung and co-workers investigated the catalytic ozonation properties of many nanomaterials (including commercial ZnO , biotic and abiotic prepared iron oxide, biogenic magnetite) and found that nano-catalysts are potentially highly efficient catalysts due to their high surface area and well dispersivity.⁵⁻⁷

As an important functional material, Co_3O_4 has been widely studied as heterogeneous catalysts, anode materials in Li ion rechargeable batteries, solid-state sensors, electrochemical de-

vices *etc.* However, the study on Co_3O_4 used as ozonation catalyst was rare.¹¹ The revelation of catalytic mechanism is very important for understanding the catalysis process and, even more importantly, for designing efficient nano-catalysts. In this paper, the surface chemistry and the catalytic property of Co_3O_4 nanomaterials were investigated in detail to illuminate the mechanism of catalytic ozonation for the degradation of phenol in aqueous solution. Our research may be a motivation for fundamental understanding and a promotion for application of novel catalytic materials.

Experimental

Chemicals. All chemicals used were of analytical grade without further purification. All aqueous solutions were prepared using distilled water. $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 25% ammonia and phenol were supplied by the Sinopharm Chemical Reagent Company.

Preparation of Co_3O_4 samples. The Co_3O_4 nanomaterials were prepared according to a hydrothermal method proposed by our group.¹¹ In a typical procedure, 0.50 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 25.0 mL of water, and 2.5 mL of 25% ammonia was added under vigorous stirring. The mixture was stirred in air for about 10 min to form homogeneous fuscous slurry. Then the suspension was transferred into a 48.0 mL of autoclave, sealed and maintained at 423 K for 3 h. After this, the autoclave was cooled to room temperature naturally. The black solid products were washed with water *via* centrifugation-redispersion, dried at 383 K for 4 h.

Bulky Co_3O_4 was prepared through a pyrogenation route. In our experiment, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was calcined at 1073 K for 4 h under air atmosphere. Then, the product was cooled to room temperature naturally, crushed and sieved into 100 mesh size.

Characterization of Co_3O_4 samples. The compositions and phases of the products were identified by powder X-ray diffraction (XRD) on an X'TRA X-ray diffractometer (ARL, Switzerland) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphologies and sizes of the products were examined by transmission electron microscopy (TEM) with a JEM-200CX (JEOL, Japan) transmission electron microscope at an accelerating voltage of 200 kV.

The nitrogen adsorption and desorption isotherms at 77 K were measured using an ASAP2020 surface area and porosity analyzer (Micromeritics, USA), and the degas conditions was 423 K for 3 h. The Brunauer-Emmett-Teller (BET) specific surface area was calculated using isotherms data. The density of surface hydroxyl groups (expressed in mmol per unit gram), was measured according to a saturated deprotonation method.¹²⁻¹⁴ The pH_{pzc} (pH at which the surface is zero charged) was measured following a powder addition method.^{12,15,16}

Catalytic ozonation procedure. The catalytic degradation of phenol was performed in a semi-continuous flow mode at 298 K. Ozone was generated in a laboratory ozone generator using pure oxygen as gas source. The flow rate of oxygen was 15 mL min^{-1} , and the flow rate of ozone was 0.40 mg min^{-1} . In a typical catalytic degradation procedure, 0.50 g of Co_3O_4 and 200 mL of simulated wastewater (the initial concentration of phenol was 100 mg L^{-1}) were mixed in a flask with stirring under thermostatic control (within $\pm 1 \text{ K}$). Then, ozone was fed into the flask with continuous stirring. At given intervals, 3.0 mL of samples were taken from the reactor and centrifuged for analysis. Single ozonation were carried out using the similar procedure as catalytic ozonation without catalyst.

The concentrations of phenol, and its oxidized intermediates such as catechol, hydroquinone and p-benzoquinone were determined by a Waters 515 high performance liquid chromatography (HPLC, Waters, USA) with a reversed-phase 4.6 mm $\times$ 250 mm C_{18} waters column (Cosmosil, Japan) at room temperature. The elution was carried out by pumping the mixture of methanol and water (6:4, v/v) at a flow rate of 1.0 mL min^{-1} , and an attached Waters 2487 dual λ UV-vis absorbance detector (Waters, USA) was used. The wavelengths were set at 210, 274, 288 and 246 nm for the analysis of phenol, catechol, hydroquinone and p-benzoquinone, respectively.

Results and Discussion

Characterization of Co_3O_4 samples. The XRD patterns (Fig. 1) of the as-prepared Co_3O_4 nanoparticles (JCPDS 09-0418) and bulky Co_3O_4 (JCPDS 78-1970) indicated high purity of the products with face-centered cubic phase of Co_3O_4 . In addition, all the diffraction peaks of Co_3O_4 nanomaterials were less sharp than those of bulky Co_3O_4 , demonstrating the poorer crystallization degree and lower size of Co_3O_4 nanoparticles.

Fig. 2a and b show the TEM images of Co_3O_4 nanoparticles and bulky Co_3O_4 respectively. It can be found that, the products by the hydrothermal method were uniform nanoparticles with average size about 20 nm, and the products by the pyrogenation method were particles with average size above 200 nm. According to the results of the nitrogen adsorption and desorption isotherms, the BET surface area of Co_3O_4 nanoparticles was

$119.85 \text{ m}^2 \text{ g}^{-1}$, and that of bulky Co_3O_4 was $0.65 \text{ m}^2 \text{ g}^{-1}$. The pH_{pzc} of Co_3O_4 nanoparticles was 6.30, and that of bulky Co_3O_4 was 3.75. The density of surface hydroxyl groups of Co_3O_4 nanoparticles was $3.90 \times 10^{-3} \text{ mol g}^{-1}$, while that of bulky Co_3O_4 was $4.26 \times 10^{-5} \text{ mol g}^{-1}$. Obviously, the two Co_3O_4 samples obtained by different preparation processes had different crystallization degree, particles size and surface properties.

Catalytic degradation efficiency for Ozonation of Phenol.

Fig. 3 (A) shows the degradation of phenol at different ozonation

Figure 1. XRD patterns of Co_3O_4 nanoparticles (a) and bulky Co_3O_4 (b)

Figure 2. TEM images of Co_3O_4 nanoparticles (a) and bulky Co_3O_4 (b)

Figure 3. Time evolution of the concentration of phenol (A), catechol (B), hydroquinone (C) and p-benzoquinone (D) under single ozonation (a), catalytic ozonation of Co₃O₄ nanomaterials (b) and catalytic ozonation of bulky Co₃O₄ (c). Catalyst dose: 0.50 g, volume of simulated wastewater: 200 mL, initial concentration of phenol: 100 mg L⁻¹, flow rate of ozone: 0.40 mg min⁻¹, reaction temperature: 298 K

time in single ozonation and catalytic ozonation with Co₃O₄ nanoparticles or bulky Co₃O₄. It can be clearly seen that Co₃O₄ nanoparticles demonstrated remarkably high catalysis efficiency on the ozonation degradation of phenol, while bulky Co₃O₄ hardly showed any catalysis effect. For example, the residual concentration of phenol was 34.7 mg L⁻¹ after single ozonation of 60 min, while it was merely 10.0 mg L⁻¹ in presence of Co₃O₄ nanomaterials. Compared with single ozonation, the degradation efficiency of phenol increased about 37.8% in presence of the nano-catalyst.

Before being degraded to small organic acids, phenol is easily oxidized to more toxic intermediates such as catechol, hydroquinone and p-benzoquinone.¹⁷⁻²² The time dependent concentrations of these intermediates in the single ozonation and the catalytic ozonation were investigated. The results are shown in Fig. 3B, C and D. It can be found that, the concentrations of these intermediates in the catalytic ozonation by nano-catalyst were lower than that in single ozonation at the same ozonation time. At the ozonation of 60 min, the concentrations of catechol, hydroquinone and p-benzoquinone in catalytic ozonation by Co₃O₄ nanoparticles were 0.3, 1.7 and 0.1 mg L⁻¹, respectively, while those in single ozonation were 7.5, 4.5 and 5.6 mg L⁻¹. That is, the total residual concentration of the three intermediates

in the presence of the nano-catalyst was only 11.9% of that without catalyst. The results indicated that, besides the removal of phenol, the Co₃O₄ nano-catalyst was also helpful for the degradation of these toxic intermediates. As for the ozonation in the presence of bulky Co₃O₄, the residual concentrations of catechol, hydroquinone and p-benzoquinone were 6.5, 5.6 and 0.4 mg L⁻¹ at 60 min. Compared with single ozonation, the concentration of p-benzoquinone was decreased obviously, while the concentrations of catechol and hydroquinone were hardly affected by bulky Co₃O₄.

Influence of temperature. Operation temperature usually influences the ozonation degradation of organic pollutants. Besides 298 K (Fig. 3), the catalytic ozonation experiments using Co₃O₄ nano particles were also carried out at 283 and 313 K (Fig. 4). Compared with the results at 298 K (Fig. 3A), the degradation rates of phenol at 283 and 313 K were lower.

Ozone is very unstable in water. 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;^{23,24} (3) diffusion rate of the reacting substances is enhanced. Therefore the efficiency in the

Figure 4. Time evolution of the concentration of phenol at 283 K (A) and 313 K (B) under single ozonation (a) and catalytic ozonation of Co_3O_4 nanomaterials (b). Catalyst dose: 0.50 g, volume of simulated wastewater: 200 mL, initial concentration of phenol: 100 mg L^{-1} , flow rate of ozone: 0.40 mg min^{-1} .

catalytic degradation of phenol increased from 283 K to 298 K may be due to that (2) and (3) played a predominant role. When the temperature increased from 298 K to 313 K, (1) was the main factor, and the degradation rate of phenol decreased.

After the single ozonation of 60 min at 283, 298 and 313 K, the removal of phenol were 60.5, 65.3 and 57.3 mg L^{-1} , respectively. While after the catalytic ozonation of 60 min at 283, 298 and 313 K, the removal of phenol were 82.6, 90.0 and 56.1 mg L^{-1} . That is, the degradation efficiencies of phenol were increased by about 36.5%, 37.8% and -2.0% at 283, 298 and 313 K due to the presence of Co_3O_4 nano-catalyst. We can see that the Co_3O_4 exhibited evident catalytic activity at 283 and 298K, while there was not any catalytic activity at 313 K.

Influence of hydroxyl radicals scavenger. According to traditional catalytic ozonation theory, molecular ozone can oxidize organic substances *via* a direct route or can undergo decomposition *via* a chain reaction mechanism to produce free hydroxyl radicals.³ As is known, *tert*-butanol can easily react with hydroxyl radicals ($k = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and hardly react with molecular ozone ($k = 3.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$), it has been widely used as a probe to determine the role of hydroxyl radicals in ozonation.^{3,17,25,26} In our experiment, 1.0 g of *tert*-butanol was introduced to 200 mL of the above reaction system with other reaction conditions kept constant to investigate the influence of hydroxyl radical scavenger on the degradation of phenol.

As can be seen from Fig. 5, *tert*-butanol demonstrated obviously negative effect on the single ozonation of phenol, while it showed much less negative effect on catalytic ozonation by Co_3O_4 nano-catalyst. The results indicated that the transformation from ozone molecules to hydroxyl radicals in catalytic ozonation decreased compared with that in single ozonation. The results also suggested that hydroxyl radicals were not the main oxidant in catalytic ozonation.

Analysis of catalysis ozonation mechanism. Based on the ozonation theory and our experimental results, the catalytic ozonation of phenol in presence of Co_3O_4 nanoparticles may be concluded as an oxidation process by ozone molecules: both ozone molecules and pollutants molecules were adsorbed on

Figure 5. Influence of hydroxyl radicals scavenger (*tert*-butanol) on the ozonation degradation of phenol. (a) single ozonation, (b) single ozonation + *tert*-butanol, (c) catalytic ozonation, (d) catalytic ozonation + *tert*-butanol. Addition of *tert*-butanol: 1.0 g, Co_3O_4 nano-catalyst dose: 0.50 g, volume of simulated wastewater: 200 mL, initial concentration of phenol: 100 mg L^{-1} , flow rate of ozone: 0.40 mg min^{-1} , reaction temperature: 298 K.

the surface of Co_3O_4 nano-catalyst, and then pollutants molecules were oxidized by ozone molecules. The adsorption process enhanced the contact probability of ozone molecules and pollutants molecules, and the degradation of pollutants was accelerated. Based on this mechanism, the experimental results shown in Fig. 5 and Fig. 4B could be reasonably explained. Strictly speaking, the ozonation at the surface of nano-catalyst and the aqueous solution can take place simultaneously. In catalytic ozonation, some ozone molecules directly reacted with pollutants on the surface of nano-catalyst. Therefore, as shown in Fig. 5, the transformation from molecular ozone to hydroxyl radicals in aqueous solution decreased. Usually, adsorption is an exothermic equilibrium process. At higher temperature such as 313 K, due to the low concentration of molecular ozone in aqueous solution and thermal effect, the adsorption of ozone

molecules on solid-liquid interface was restrained. At the same time, the generation of hydroxyl radicals from ozone molecules in aqueous solution was accelerated. Then, the total result was that the degradation rates of phenol were similar in single ozonation and catalytic ozonation at 313 K (Fig. 4B).

As for the different catalysis properties of Co_3O_4 nanoparticles and bulky Co_3O_4 , the surface state may be an important factor. The crystalline degree of Co_3O_4 , which was determined by the preparation conditions, influenced the attractive power of surface oxygen atoms for protons. Consequently, the pH_{pzc} of two samples were different (the pH_{pzc} of Co_3O_4 nanoparticles was 6.30, while that of bulky Co_3O_4 was 3.75). In aqueous solution, the pH_{pzc} of Co_3O_4 and the pH of the solution determined the surface charge states of the catalyst.²⁷ The oxide surface becomes protonated or deprotonated when the pH of the aqueous solution is below or above the pH_{pzc} , as shown in equation (1) and (2).

In our ozonation experiments, the pH of the solution changed from 6.30 to 3.80 gradually. For Co_3O_4 nanoparticles (with pH_{pzc} of 6.30), the surface- OH_2^+ should be the predominant surface group. Molecular ozone, which possesses a strong electrophilic and nucleophilic reactivity due to its dipole structure, could interact with the surface- OH_2^+ through two simultaneous attractive forces: electrostatic forces and hydrogen bonding. Obviously, the surface properties of Co_3O_4 nanoparticles were advantageous for adsorption of ozone molecules. For bulky Co_3O_4 , the pH of the solution was above its pH_{pzc} , and the surface- O^- should be the predominant surface group. Compared with that of Co_3O_4 nanoparticles, the surface of bulky Co_3O_4 was absent of attraction forces for molecular ozone. The fewer molecular ozone was adsorbed, the lower catalysis efficiency was obtained by the catalyst. In addition, the surface area, the density of surface hydroxyl groups and the dispersibility of Co_3O_4 nanoparticles were greatly higher than those of bulky Co_3O_4 , which were also important and favorable for the higher catalysis efficiency of Co_3O_4 nanoparticles than that of bulky Co_3O_4 . Of course, the surface area, the density of surface hydroxyl groups and the dispersibility correlate closely with the size of particles.

Conclusion

The Co_3O_4 nano-catalyst exhibited remarkable higher catalysis efficiency on ozonation degradation of phenol and its ozonation intermediates compared with bulky Co_3O_4 and ozonation alone. The removal rate of phenol for catalytic ozonation was higher at 298 K than that of 283 K and 313 K. The presence of *tert*-butyl alcohol had little negative effect on catalytic ozonation. These experimental results confirmed the proposition that degradation of phenol by Co_3O_4 nanoparticles was through a reaction process between ozone molecules and pollutants on the interface of solid-liquid. The surface state, the higher surface area, the density of surface hydroxyl groups and the well dis-

persibility of Co_3O_4 nanoparticles were favorable for its higher catalysis efficiency than bulky Co_3O_4 .

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

References

- Liotta, L. F.; Gruttadauria, M.; DiCarlo, G.; Perrini, G.; Librando, V. *J. Hazard. Mater.* **2009**, *162*, 588.
- Faria, P. C. C.; Orfao, J. J. M.; Pereira, M. F. R. *Catal. Lett.* **2009**, *127*, 195.
- Kasprzyk-Hordern, B.; Ziółek, M.; Nawrocki, J. *Appl. Catal. B: Environ.* **2003**, *46*, 639.
- Dong, Y.; He, K.; Zhao, B.; Yin, Y.; Yin, L.; Zhang, A. *Catal. Commun.* **2007**, *8*, 1599.
- Jung, H.; Choi, H. *Appl. Catal. B: Environ.* **2006**, *66*, 288.
- Jung, H.; Park, H.; Kim, J.; Lee, J. H.; Hur, H. G.; Myung, N. V.; Choi, H. *Environ. Sci. Technol.* **2007**, *41*, 4741.
- Jung, H.; Kim, J. W.; Choi, H.; Lee, J. H.; Hur, H. G. *Appl. Catal. B: Environ.* **2008**, *83*, 208.
- Yang, Y.; Ma, J.; Qin, Q.; Zhai, X. *J. Mol. Catal. A: Chem.* **2007**, *267*, 41.
- Rosal, H.; Rodríguez, A.; Gonzalo, M. S.; García-Calvo, E. *Appl. Catal. B: Environ.* **2008**, *84*, 48.
- Dong, Y.; Yang, H.; He, K.; Song, S.; Zhang, A. *Appl. Catal. B: Environ.* **2009**, *85*, 155.
- Dong, Y.; He, K.; Yin, L.; Zhang, A. *Nanotechnology* **2007**, *18*, 435602.
- Zhang, T.; Li, C.; Ma, J.; Tian, H.; Qiang, Z. *Appl. Catal. B: Environ.* **2008**, *82*, 131.
- Laiti, E.; Öhman, L. O.; Nordin, J.; Sjöberg, S. J. *Colloid Interface Sci.* **1995**, *175*, 230.
- Tamura, H.; Tanaka, A.; Mita, K.; Furuichi, R. *J. Colloid Interface Sci.* **1999**, *209*, 225.
- Stumm, W. *Chemistry of the Soil-Water Interface*; John Wiley & Sons: New York, 1992; p 15.
- Newcombe, G.; Hayes, R.; Drikas, M. *Colloid Surface. A* **1993**, *78*, 65.
- Dong, Y.; Yang, H.; He, K.; Wu, X.; Zhang, A. *Appl. Catal. B: Environ.* **2008**, *82*, 163.
- Bremner, D. H.; Burgess, A. E.; Houlemare, D.; Namkung, K. C. *Appl. Catal. B: Environ.* **2006**, *63*, 15.
- Lesko, T.; Colussi, A. J.; Hoffmann, M. R. *Environ. Sci. Technol.* **2006**, *40*, 6818.
- Wu, C.; Liu, X.; Wei, D.; Fan, J.; Wang, L. *Water Res.* **2001**, *35*, 3927.
- Santos, A.; Yustos, P.; Quintanilla, A.; Ruiz, G.; García-Ochoa, F. *Appl. Catal. B: Environ.* **2005**, *61*, 323.
- Santos, A.; Yustos, P.; Quintanilla, A.; Rodríguez, S.; García-Ochoa, F. *Appl. Catal. B: Environ.* **2002**, *39*, 97.
- Field, R. J.; Raghavan, N. V.; Brummer, J. G. *J. Phys. Chem.* **1982**, *86*, 2443.
- Hoigné, J.; Bader, H. *Water Res.* **1983**, *17*, 173.
- Carbajo, M.; Beltrán, F. J.; Medina, F.; Gimeno, O.; Rivas, F. J. *Appl. Catal. B: Environ.* **2006**, *67*, 177.
- Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, W. P. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Zhao, L.; Sun, Z.; Ma, J. *Environ. Sci. Technol.* **2009**, *43*, 4157.