

Synergistic Effect of Copper and Cobalt in Cu-Co-O Composite Nanocatalyst for Catalytic Ozonation

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A novel Cu-Co-O composite nanocatalyst was designed and prepared for the ozonation of phenol. A synergistic effect of copper and cobalt was observed over the Cu-Co-O composite nanocatalyst, which showed higher activity than either copper or cobalt oxide alone. In addition, the Cu-Co-O composite revealed good activity in a wide initial pH range (4.11-8.05) of water. The fine dispersion of cobalt on the surface of copper oxide boosted the interaction between catalyst and ozone, and the surface Lewis acid sites on the Cu-Co-O composite were determined as the active sites. The Raman spectroscopy also proved that the Cu-Co-O composite was quite sensitive to the ozone. The trivalent cobalt in the Cu-Co-O composite was proposed as the valid state.

Key Words : Catalytic ozonation, Synergistic effect, Water treatment, Nanomaterials

Introduction

Heterogeneous catalytic ozonation, which can be carried out under natural conditions and may be easily applied in real water treatment without any auxiliary light or thermal systems, has received increasing research interests in recent years especially for the removal of refractory organic pollutants in water.¹ Phenolic compounds are particularly important among organic pollutants.² The most widely used catalysts in heterogeneous catalytic ozonation are metal oxides (MnO₂,³ TiO₂,^{4,5} Al₂O₃,⁶ FeOOH⁷ and CeO₂⁸), metals on supports (Ru/Al₂O₃,⁹ TiO₂/AC¹⁰) and porous materials (ceramic honeycomb,¹¹ zeolites¹²).

In recent years, composite catalysts have gained much attention from the researchers. Due to the component interaction, doped catalyst might display better catalytic activity. According to Li *et al.*,¹³ the synergistic interaction between the MnO₂ and CeO₂ through the formation of solid solution enhanced the mobility of oxygen species in the mixed oxide. Jiang *et al.*¹⁴ studied the SO_x oxidation and adsorption by CeO₂/MgO, and observed the synergistic effect between the CeO₂ and MgO. They reported that the CeO₂ acted as the oxidation promoter and MgO was the active phase for SO_x adsorption. Feng *et al.* reported the chemical interactions of Cu-Co-O species as catalyst for higher alcohols synthesis from syngas through a supported Cu_xCo_{3-x}O₄.¹⁵ Up to now, little attention has been focused on the synergistic effect of ozonation catalyst between nano-sized single-component. Furthermore, the catalytic ozonation processes in aqueous solutions are very complex in nature, and minor achievements are made in this domain because of the lack of highly efficient catalysts as well as the difficulty in identifying active sites.¹⁶

In this work, a Cu-Co-O composite was proposed as

catalyst for the ozonation of phenol. A synergistic effect of copper and cobalt was observed over the Cu-Co-O composite nanocatalyst, which showed higher activity than either copper or cobalt oxide alone. The fine dispersion of cobalt on the surface of copper oxide boosted the interaction between catalyst and ozone, and the trivalent cobalt in the Cu-Co-O composite was proposed as the valid state.

Experimental

Preparation of Catalysts. The precursors of Cu-Co-O composite were prepared *via* a co-precipitation method. Typically, 8 mmol CuSO₄·5H₂O and 2 mmol Co(CH₃COO)₂·4H₂O were dissolved in 30 mL ethylene glycol. The mixture was heated to 80 °C to form a homogeneous solution. Then, 100 mL of 0.2 M Na₂CO₃ aqueous solution was added dropwise under vigorous stirring. The precipitation was further aged at 80 °C for 1 h in the mother liquid. After being washed with distilled water and absolute ethanol in turn, the solid was dried at 100 °C overnight and calcined at 400 °C for 2 h. For comparison, pure Co₃O₄ and CuO were prepared under the same procedure.

Experimental Procedure. Phenol ozonation experiments were carried out in a glass flask (250 mL) equipped with a gas inlet. Ozone was produced from pure oxygen (20 mL/min) with an ozone generator (3S-A5, Tonglin Technology, Beijing) and bubbled into the flask with a rate of 0.75 mg/min. The initial concentration of phenol aqueous solution was 300 mg/L. 0.20 g catalyst was added into the reactor containing phenol aqueous solution (200 mL). Then, the catalytic ozonation experiments were initiated under continuous magnetic stirring. The reaction temperature was controlled with thermostatic water bath. Samples withdrawn at certain time interval (15 min) were subsided for a whole

night before analysis. The experiments of ozonation alone (without catalyst) were operated under the same conditions.

Static ozone depletion experiments were implemented in water. Firstly, the water was continuously bubbled with gaseous ozone for 30 min. Then, the ozone flow was stopped and 1.0 g/L of catalyst was added into the ozone-containing aqueous solution immediately. Samples withdrawn at definite time interval (2 min) were filtered at once for determination. In dynamic ozone depletion experiments, the gaseous ozone was continuously bubbled into the aqueous suspension of 1.0 g/L catalyst all the time. The collected samples were filtered successively every 10 min. Blank experiments (without catalyst) for both static and dynamic ozone depletion were conducted under the same conditions.

The influence of phosphate on static ozone depletion was carried out in phosphate buffer solution. The pH of phosphate solution was kept at 7 by adjusting the addition ratio of Na_2HPO_4 and NaH_2PO_4 . Detailed operations were as same as the static ozone depletion experiments in water as mentioned above.

Characterization. The compositions and phases of the products were identified by powder X-ray diffraction (XRD) on an D8 X-ray diffractometer (Bruker AXS, German) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The morphologies and sizes of the products were examined by transmission electron microscopy (TEM) with a JEM-2100 (JEOL, Japan) transmission electron microscope at an accelerating voltage of 200 kV. The specific surface area of the catalyst samples was measured according to the Brunauer-Emmett-Teller (BET) method with nitrogen adsorption at 77.4 K on a ASAP 2020 instrument (Micromeritics, USA), and the degas conditions was 110 °C for 3 h. The specific surface area was calculated by multipoint Braunauer Emmett Teller (BET) analysis of the nitrogen adsorption isotherm. A TAS-990NFG atomic absorption spectrometer (Beijing), equipped with copper and cobalt hollow cathode lamps, was used to determine the trace amounts of metal ions. All measurements were carried out in air/acetylene flame and the samples were nitrified with dilute nitric acid previously. The pH at the point of zero charge (pH_{pzc}) was measured with a powder addition method.¹⁷ A Mirco-Raman Spectroscopy/invia-reflex (Renishaw) with a 785 nm laser light irradiation was used to characterize the interaction between catalyst and ozone. The catalyst (0.02 g) was placed in ozone atmosphere (25 °C) for 1 h. Then, the samples were spread on a microscope slide with a double-sided tape and scanned at a duration time of 10 s.

The concentration of phenol was determined by high-performance liquid chromatography (HPLC, WATERS, USA) with a UV absorbance detector (UV 2487). Absorbance detection system for phenol was set at 270 nm. Elution was carried out by pumping methanol (HPLC/Spectro)-water (3:1 v/v) at a ow rate of 1.0 mL/min. The absorbance of the ozone in aqueous solution was measured directly by a UV-vis spectrometer at 258 nm with the TU-1900 spectrophotometer (Beijing).

Results and Discussion

Characterization of Products. In this work, three samples were prepared by controlling the molar ratio of Cu:Co in raw materials, *i.e.* cobalt element only, copper element only, and mixture of copper and cobalt. According to atomic absorption analysis results, the molar ratio of Cu:Co in composite sample was 7.61.

The XRD patterns of these samples were shown in Figure 1. For the sample with Cu:Co = 0:10, the strong diffraction peaks was assigned to the cubic phase of Co_3O_4 (74-1657). When there was not any cobalt in raw material, the diffraction peaks attributed to monoclinic CuO were detected (74-1021). The Cu-Co-O composite showed diffraction peaks of monoclinic CuO and orthorhombic Cu_6O (77-1898/80-0076). No diffraction peaks of cobalt element was found, which may be interpreted by high dispersion of cobalt element. Figure 2 showed the TEM images of the prepared samples. For CuO in c, obvious aggregation of nano-sized sheet-like products was observed. For pure Co_3O_4 in b, the products were nanoparticles with mean size of approximate 10 nm. Due to the introduction of cobalt, the aggregation of composite samples (in a) was lighter than that of CuO. The S_{BET} were found to be 31.33, 98.66 and 42.82 m^2/g for CuO, Co_3O_4 and Cu-Co-O composite, respectively. Compared with CuO and Cu-Co-O composite, Co_3O_4 revealed obvious larger BET surface area due to better dispersion. The introduction of cobalt did not significantly change the BET surface areas

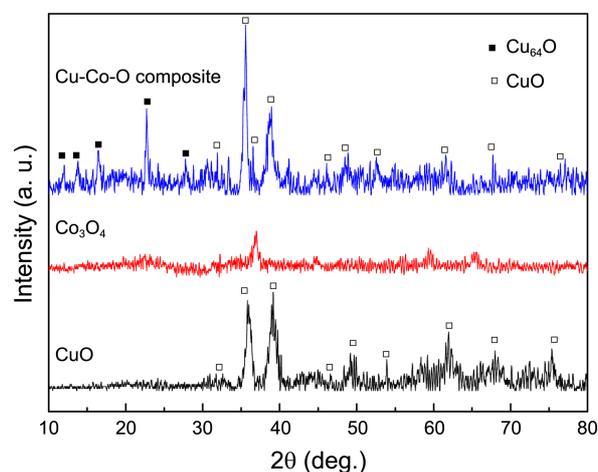


Figure 1. XRD patterns of samples: Co_3O_4 , CuO, and Cu-Co-O composite.

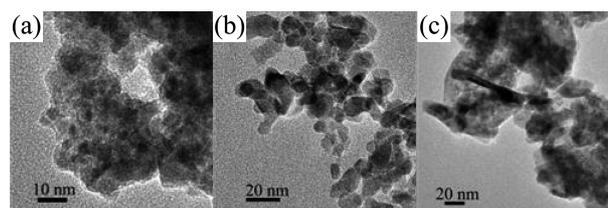


Figure 2. TEM images of samples: Cu-Co-O composite (a), Co_3O_4 (b), and CuO (c).

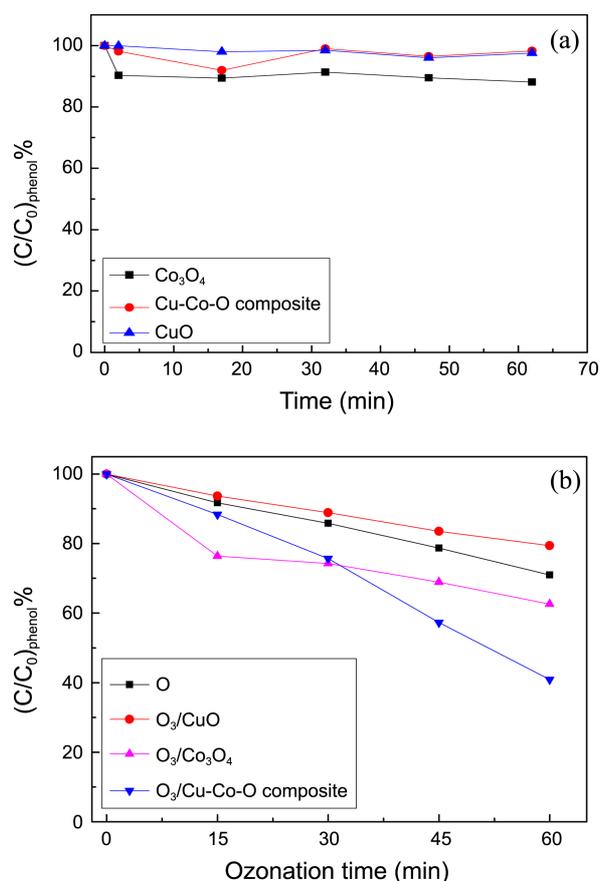


Figure 3. Adsorption (a) and catalytic ozonation (b) of phenol with CuO, Co_3O_4 , and Cu-Co-O composite (200 mL of 300 mg/L phenol solution, 25 °C, 0.75 mg/min ozone, catalyst dose 1.0 g/L).

of CuO. The results indicated that cobalt element dispersed well on CuO, which was consistent with the XRD patterns.

Catalytic Activity. Firstly, a series of experiments were conducted to investigate the adsorption of phenol on catalyst samples. 0.2 g catalyst was added into the phenol-containing solution (200 mL), and ozone did not take part in this process. Figure 3(a) showed the adsorbed amounts of phenol on Co_3O_4 , CuO and Cu-Co-O composite in a neutral environment. There was hardly adsorption on the surface of the CuO. For Co_3O_4 , the adsorbed amount of phenol was about 12%. Slight adsorption could be observed for Cu-Co-O composite.

Then the catalytic activity was evaluated by testing the degradation efficiency of phenol in ozonation process in presence of catalyst. Ozonation alone (without any catalyst) was also carried out to comparison. As illustrated in Figure 3(b), both Co_3O_4 and Cu-Co-O composite facilitated the degradation of phenol, while there was no catalytic activity for CuO. If the adsorption is considered, the Cu-Co-O composite displayed the highest activity. The degradation efficiency increased 103.44% for Cu-Co-O composite after the catalytic ozonation of 60 min. The data indicated that trace of cobalt was beneficial to the degradation of phenol and a synergic effect existed between copper and cobalt. In addition, the cobalt was the active component in the Cu-Co-O

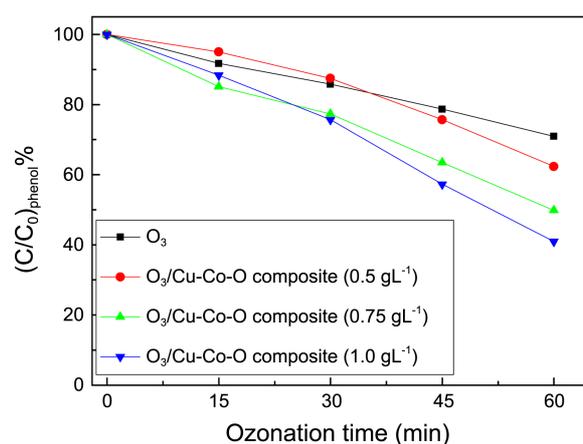


Figure 4. Catalytic ozonation of phenol with different catalyst doses: 0.5 g L⁻¹, 0.75 g L⁻¹, and 1.0 g L⁻¹ (200 mL of 300 mg/L phenol solution, 25 °C, 0.75 mg/min ozone).

composite.

Effect of Catalyst Dose. Catalytic ozonation of phenol in aqueous solution was a three-phase reaction system of gas-liquid-solid, in which the solid catalyst was a crucial factor affecting the degradation efficiency. Figure 4 showed that the increase of Cu-Co-O composite catalyst dose (0.5-1.0 g L⁻¹) was favorable for the removal of phenol. And the degradation efficiency of phenol increased about 29.71% (0.5 g L⁻¹), 72.73% (0.75 g L⁻¹), and 103.44% (1.0 g L⁻¹), respectively. Considering that surface active sites were one of the most important factors, more catalysts may provide more surface active sites which favored such catalytic reaction and hence promoted the catalytic reaction efficiency. Therefore, catalyst dose exerted a positive influence on phenol degradation in catalytic ozonation process.

Effect of the Initial pH. Since pH was a key parameter for both ozone stability and catalyst surface properties in aqueous solution, it was important to examine the influence of pH on catalytic ozonation. In this experiment, we studied the effect of initial pH of the phenol solution on the catalytic activity.

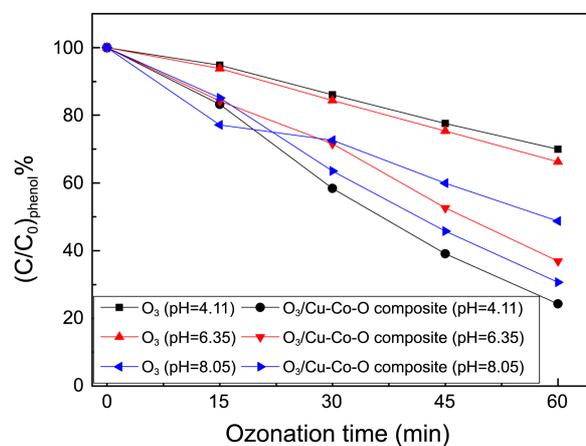


Figure 5. The ozonation of phenol under different initial pH (200 mL of 300 mg/L phenol solution, 25 °C, 0.75 mg/min ozone, catalyst dose 1.0 g/L).

As shown in Figure 5, the degradation efficiency of phenol in ozone alone was reduced with the decrease of initial pH. And significant ascension can be observed in the ozonation process at initial pH of 8.05. It may be explained as the alkaline environment was favorable to the decomposition of ozone. However, the degradative phenol in the catalytic ozonation process boosted 2.52, 1.87, and 1.35 times with the increase of initial pH. This meant that the Cu-Co-O composite nanocatalyst was effective in catalytic ozonation phenol in a wide initial pH range (4.11-8.05).

In addition, it was well known that the acid/base properties of the hydroxyl groups on the metal oxide catalysts surface could be changed with the conversion of pH_{pzc} and pH (as shown in Eqs. (1) and (2)). When the solution pH was near the pH_{pzc} , most of surface hydroxyls existed in neutral state. Otherwise, the oxide surface became protonated or deprotonated when solution pH was below or above its pH_{pzc} . The pH_{pzc} of the Cu-Co-O composite was 6.20. Hence, the catalyst surface was positively charged at initial pH 4.11. With the increase of initial pH, the number of the positively charged site decreased and the catalyst surface would become negatively charged when the initial pH was higher than the pH_{pzc} of the catalyst. Due to the nucleophilicity of ozone molecule, the positive and zero charged surface might be more easily attacked by ozone molecule than the negative charged surface. Therefore, the catalytic efficiency of phenol degradation at initial pH 4.11 was higher than that at initial pH 6.35 and 8.05.



Ozone Depletion. The interaction between the ozone and catalyst was studied in this work. Figure 6(a) showed the evolution of aqueous ozone concentration (without phenol) in the presence of Cu-Co-O composite, CuO and Co_3O_4 . In this experiment, ozone was in a certain concentration (static) at the early stage. Compared with that of ozone natural decomposition process, the Cu-Co-O composite significantly reduced aqueous ozone concentration (over 99% in the first 4 min). However, the CuO and Co_3O_4 were much less efficient. For instance, the aqueous ozone concentration decreased 63.26% in presence of CuO and 69.5% in presence of Co_3O_4 at the same time. Hence, a synergistic effect of copper and cobalt existed, and it positively affected the depletion of ozone.

In order to further confirm the ozone depletion without phenol, ozone was bubbled constantly (dynamic, Figure 6(b)). The aqueous ozone concentration increased gradually and achieved equilibrium after 30 min in the blank experiment. Obviously, the addition of catalysts resulted in the decrease of the equilibrium value. Especially, the aqueous ozone concentration of $\text{O}_3/\text{Cu-Co-O}$ process kept a lower balance than the processes of O_3/CuO and $\text{O}_3/\text{Co}_3\text{O}_4$. These results showed that the CuO, Co_3O_4 , and Cu-Co-O composite could affirmatively promote the depletion of ozone, and Cu-Co-O composite was more effective. Meanwhile, a synergistic effect

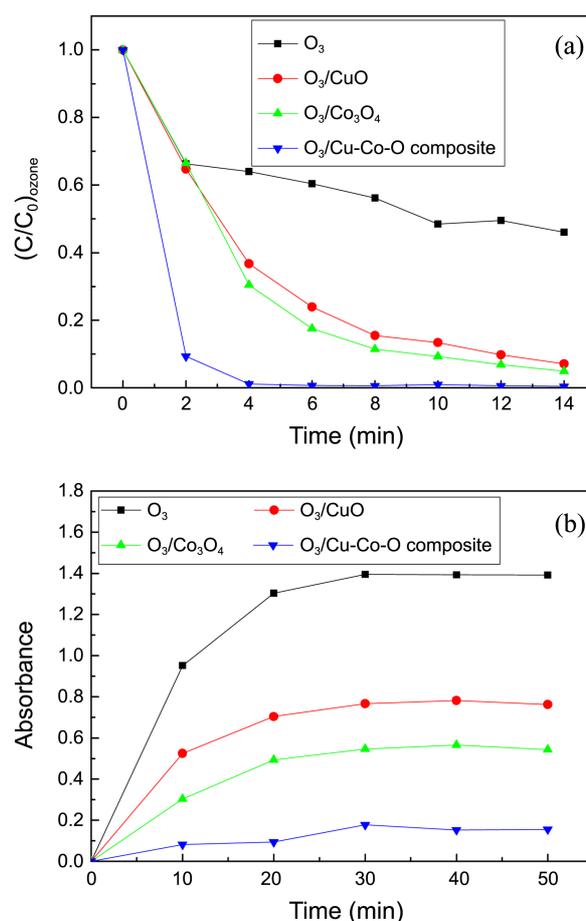


Figure 6. Influence of catalysts on aqueous ozone concentration (without phenol) in ozone saturated water (a) and ozone continuously bubbling water (b) (150 mL of water, 25 °C, 0.75 mg/min ozone, catalyst dose 1.0 g/L).

of copper and cobalt also existed in the $\text{O}_3/\text{Cu-Co-O}$ composite process in continuous ozone.

The difference of catalytic performance could be explained by the interaction with phenol and ozone. Due to the scarce adsorption of phenol on CuO, the ozone which was depleted on the surface of CuO might be useless for degradation of phenol. Then, CuO revealed negative influence on the ozonation of phenol. Co_3O_4 revealed obvious catalysis owing to the slight adsorption of phenol and the promoted decomposition of ozone. The Cu-Co-O composite could not only adsorb phenol, but also enhance the ozone decomposition intensively. Therefore higher activity was observed in the catalytic ozonation process.

Active Site. Phosphate was introduced here to detect the active site on the surface of Cu-Co-O composite. Since phosphate was a harder Lewis base than water, it should hold the surface Lewis acid sites on the catalyst. If the Lewis acid sites are effective for catalytic ozonation, the presence of phosphate may lead to lower activity. In order to express this, the influence of phosphate on the decomposition of ozone was examined (without phenol). In this experiment, the pH of phosphate solution was kept at 7 by adjusting the addition ratio of Na_2HPO_4 and NaH_2PO_4 . As can be seen

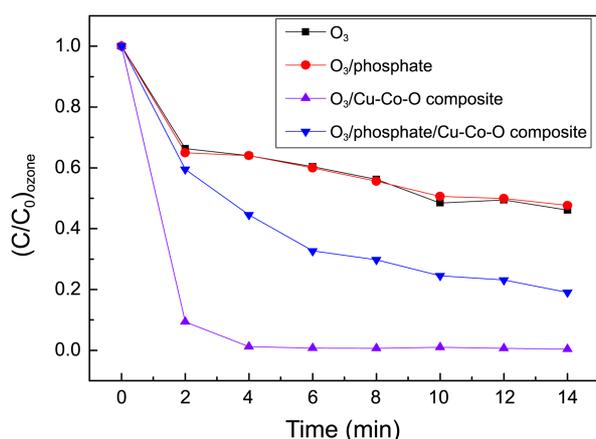


Figure 7. The effect of phosphate on performance of Cu-Co-O composite for ozone decomposition (150 mL of phosphate buffer solution, 25 °C, 0.75 mg/min ozone, catalyst dose 1.0 g/L).

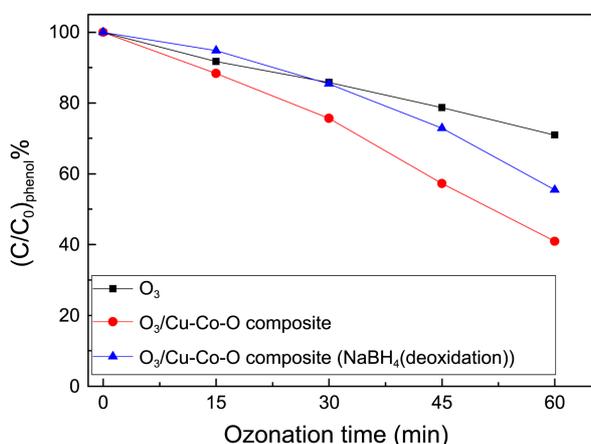


Figure 8. Catalytic ozonation of phenol with the Cu-Co-O composite deoxidized by NaBH₄ (200 mL of 300 mg/L phenol solution, 25 °C, 0.75 mg/min ozone, catalyst dose 1.0 g/L).

from Figure 7, phosphate did not largely affect the ozone natural decomposition process. The Cu-Co-O composite significantly resulted in the decrease of aqueous ozone concentration (over 90% in the first 2 min). At the same time, the ozone concentration was reduced only 40.47% in the phosphate/Cu-Co-O process. The results showed that the catalytic decomposition of ozone was nearly depressed in the presence of phosphate at the early stage, indicating that the surface Lewis acid sites on the Cu-Co-O composite were the active sites.

Considering that both the trivalent cobalt and bivalent cobalt were in the Cu-Co-O composite, reduction methods were adopted to investigate the valid state. Specifically, the contents of the trivalent cobalt would decrease relatively after the reduction. And this might result in the change of the catalytic activity. The reduction experiment was operated in the alkaline environment and 0.1 M NaBH₄ solution was chosen as the reductant. Firstly, an alkaline solution (pH = 7.65, 50 mL) was added into the flask containing 0.25 g Cu-Co-O composite. Then, 0.1 M NaBH₄ solution (1.60 mL) was added to the mixture at the room temperature. After

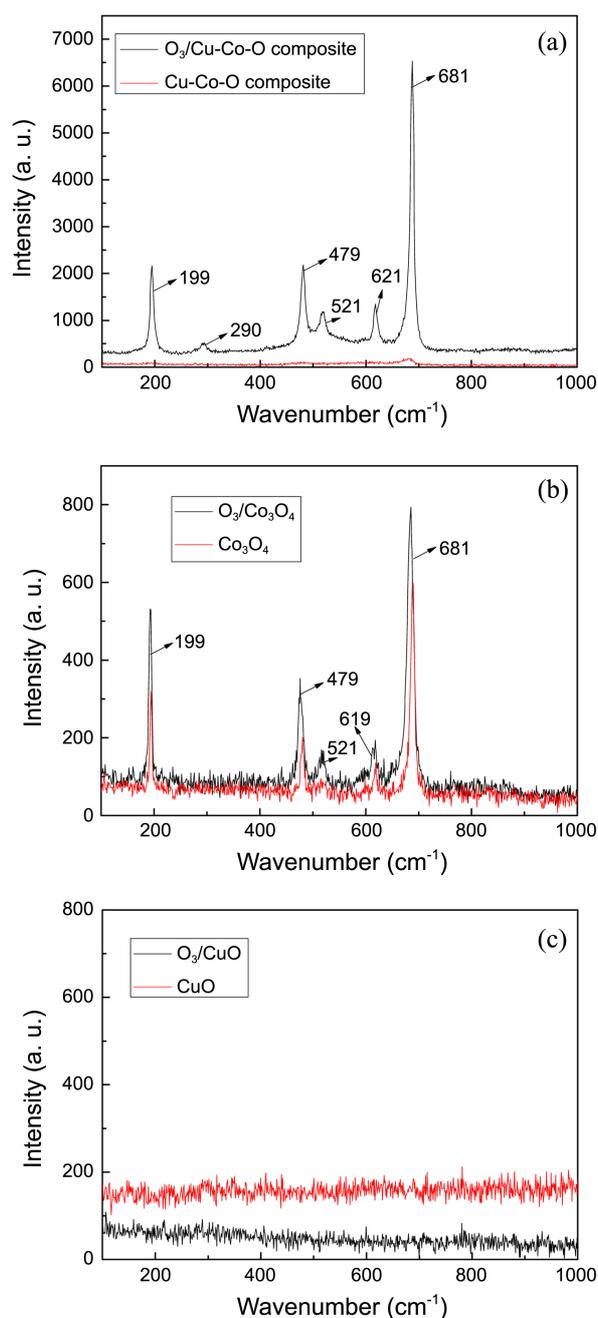


Figure 9. Raman spectra of Cu-Co-O composite (a), Co₃O₄ (b), and CuO (c) in the absence and presence of ozone.

repeated washing with distilled water, the products were dried at 60 °C for 12 h in a vacuum drying oven. From Figure 8, the residual phenol increased from 40.92% to 55.46% after the reduction reaction. In other words, the Cu-Co-O composite deoxidized by NaBH₄ solution became obviously less effective. These results showed the more existence of the trivalent cobalt, the more elimination of phenol. That was to say, the trivalent cobalt in the Cu-Co-O composite was the valid state.

Raman spectroscopy had been used to characterize the PdO/CeO₂ in contact with gaseous ozone.¹⁶ It was applied here to get insights on the interaction between ozone and the

catalyst. Figure 9(a) showed the Raman spectra of Cu-Co-O composite in the presence of ozone. Ozone itself had no Raman signal in this spectrum range. The peaks of 199, 477, 525, 619, and 681 cm^{-1} corresponded to the Co_3O_4 .^{18,19} The peak of 290 cm^{-1} was ascribed to the CuO.^{20,21} The intensities of the peaks at 199, 290, 479, 521, 619, and 681 cm^{-1} increased significantly for Cu-Co-O composite in presence of ozone. The reason may be the stronger effects of chemical bonding on the Raman scattering from the catalyst contacted with ozone.²² Due to the strong effect with ozone, the polarizability of metal-oxygen bonds became stronger and the electrons cloud was easier to change, resulting in the increase of Raman peaks. Slight increase of intensities at 199, 479, 521, 619, and 681 cm^{-1} were also observed for Co_3O_4 in contact with ozone (Figure 9(b)). Ozone did not reveal any influence on the Raman spectra of CuO (Figure 9(c)). These results indicated that the Cu-Co-O composite was more sensitive to the ozone and there was a strong interaction between them.

Conclusion

The Cu-Co-O composite nanocatalyst significantly improved the degradation of phenol compared with the ozonation alone. A synergistic effect of copper and cobalt was observed on the catalytic ozonation of phenol and aqueous ozone depletion. The fine dispersion of cobalt promoted the interaction between Cu-Co-O composite nanocatalyst and ozone. And the trivalent cobalt in the Cu-Co-O composite was the valid state in catalytic ozonation. In addition, the Cu-Co-O composite nanocatalyst was effective in catalytic ozonation phenol in a wide initial pH range (4.11-8.05). Hence, it may be prospective in catalytic ozonation of organic pollutants.

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