Efficient Treatment of Phenol Wastewater by Catalytic Ozonation over Micron-Sized Hollow MgO Rods

Shanshan Zhang,† Lilong Zhou,*⊥ Zhengjie Li, Ali Asghar Esmailpour, Kunjie Li, Shuhuan Wang, Runjing Liu, Xiaoyan Li, and Jimmy Yun*

ABSTRACT: Phenol is a nocuous water pollutant that threatens human health and the ecological environment. CoOx-doped micron-sized hollow MgO rods were prepared for the treatment of phenol wastewater by catalytic ozonation. Magnesium sources, precipitants, initial precursor concentration, Co/Mg molar ratio, and catalyst calcination temperature were optimized to obtain the best catalysts. Prepared catalysts were also well characterized by various methods to analyze their structure and physical and chemical properties. In this process, CoOx/MgO with the largest large surface area (151.3 m²/g) showed the best catalytic performance (100 and 79.8% of phenol and chemical oxygen demand (COD) removal ratio, respectively). The hydrolysis of CoOx/MgO plays a positive role in the degradation of phenol. The catalytic mechanism of the degradation of O₃ to free radicals over catalysts has been investigated by in situ electronic paramagnetic resonance (EPR). The catalyst can be reused at least five times without any activity decline. The prepared CoOx/MgO catalyst also showed excellent catalytic performance for removal and degradation of ciprofloxacin, norfloxacin, and salicylic acid.

1. INTRODUCTION

Phenol, an important chemical, is widely used in the production of preservatives, fungicides, and drugs and is also an important product of coking industry. However, low concentrations of phenol have often been detected in industrial and surface water, which caused serious threats to the ecological environment and human health. Due to high toxicity and inertia, traditional treatment methods, such as biological and physical methods, are difficult to treat phenol and its derivatives effectively.1−6

Ozone is widely used in wastewater treatment, which can be decomposed into hydroxyl radicals and destroy various unsaturated carbon bonds. However, intermediates produced in the reaction can hinder ozone decomposition, so single ozone oxidation cannot completely degrade the organic matter and its intermediates efficiently.7 To overcome these drawbacks, catalysts have been applied to improve production of the hydroxyl radical in the reaction process. The hydroxyl radical has strong oxidizability and plays an important role in the degradation of organics. As known, the catalytic ozonation process can enhance mineralization efficiency by transforming ozone into more reactive hydroxyl radicals. The current catalysts studied for catalytic ozonation treatment of wastewater include Fe₃O₄@SiO₂@CeO₂, (MnO₂-Co₃O₄)/AC, MgMnO₃, Mn/γ-Al₂O₃, etc.8−11 However, these catalysts have various disadvantages in the reaction, such as tedious synthesis, difficult recovery, ecumenic effect, and an unknown mechanism.12 Therefore, it is pivotal to find an efficient catalyst for the improvement of phenol wastewater treatment efficiency.

MgO has been used in catalytic ozonation due to its high activity, strong alkalinity, good stability, and environmental friendliness. Moussavi et al. have reported that MgO has good

Received: July 5, 2021
Accepted: September 6, 2021
Published: September 24, 2021

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https://doi.org/10.1021/acsomega.1c03497
ACS Omega 2021, 6, 25506−25517
activity in the treatment of Red 198 azo dye. However, the removal rate of chemical oxygen demand (COD) only reached about 60% with an initial Red 198 azo dye concentration of 200 mg/L, an initial pH of 8, and a MgO dosage of 5 g/L.\textsuperscript{13} Zhu et al. used MgO to decompose quinoline. The TOC removal rate can reach about 45% over MgO (0.2g/L) with an initial pH of 6.8 and initial quinoline concentration of 20 mg/L.\textsuperscript{14} The catalytic performance of mono-MgO can hardly meet the requirements of industrial applications due to the large proportion of lattice oxygen and relatively few active sites. One effective way to overcome this drawback is doping a heteroatom into MgO to improve its catalytic activity. MgO modified by S showed impressive activity for the degradation of antibiotic tetracycline (TTC), in which the degradation rate of TTC increased from 20 to 90%. MgO modified by C showed good performance for the removal of humic acid due to the increase of defects and improvement of electron transfer.\textsuperscript{15} MgO has weak oxidizability. Doping of certain metal oxides may change their surface electrical and catalytic properties.\textsuperscript{15} CoOx is an oxide with various valence states, which can provide oxygen vacancy for catalytic oxidation. MgO doped by CoOx showed excellent activity for the oxidation of ammonia to nitrogen with an ammonia nitrogen removal rate of 85.2% and gaseous nitrogen selectivity of 44.8%\textsuperscript{16} However, its low surface area (28.55 m²/g) hindered the further improvement of catalytic activity. To improve the catalytic performance of MgO, its surface area and oxidizability need to be further improved. CoOx exhibits high catalytic activities for Co oxidation.\textsuperscript{17,18} CoOx may enhance the activity of MgO for catalytic ozonation.

In this work, the CoOx-doped hollow micron-sized MgO rod with the highest surface area and efficient activity has been prepared for treatment of high content phenol wastewater by catalytic ozonation. A series of influence factors have been investigated to verify the efficiency of catalytic ozonation. It is interesting that the hydrolysis of CoOx/MgO devoted a great contribution to catalytic ozonation. Various characterization methods have been applied to verify the catalytic mechanism. Finally, the stability and wide applicability of the catalyst were investigated.

2. RESULTS AND DISCUSSION

2.1. Characterization of Catalysts. 2.1.1. Crystalline Structures of Catalysts. Figure 1 shows the diffractions of CoO\textsubscript{x}, MgO, 2\% CoO\textsubscript{x}/MgO, and used 2\% CoO\textsubscript{x}/MgO. Several pronounced peaks at about 19.2, 38.2, 42.5, 62.2, and 78.5° can be ascribed to the 001, 111, 200, 220, and 222 crystallographic facets of MgO. For the diffractions of CoO\textsubscript{x}, peaks corresponding to CoO\textsubscript{x}, Co(OH)\textsubscript{2}, or Co\textsubscript{3}O\textsubscript{4} can be observed (shown in Figure 1). However, peaks of Co and Mg species overlap in CoO\textsubscript{x}/MgO. It suggests that CoO\textsubscript{x} and MgO formed an oxide solid solution due to their similar oxide crystal structure, cation size, and coordination, which can form a solid solution over the entire range of compositions.\textsuperscript{21} The peak strength of MgO(200) and MgO(220) decreased after loading the CoO\textsubscript{x} it may due to the coverage of CoO\textsubscript{x}. For patterns of used 2\% CoO\textsubscript{x}/MgO, peaks belonging to Co(OH)\textsubscript{2}, Mg(OH)\textsubscript{2}, MgO, or CoO can be found. It indicates that Mg(OH)\textsubscript{2} was generated from the hydration of MgO. As seen in the overall view of Figure 1, doping CoO\textsubscript{x} has little influence on the size of MgO. The regenerated catalyst is shown in Figure S2; it can be seen that the catalyst was regressed to MgO after regeneration.

2.1.2. Morphologies and Crystalline Structures of Catalysts. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of CoO\textsubscript{x}/MgO, and used and regenerated CoO\textsubscript{x}/MgO are shown in Figure 2. Figure 2a shows that the catalyst presented a hollow rod structure with a length of 5–20 μm and a width of 0.5–5 μm. Some porous particles can be found on the hollow rod, which can correspond to CoO\textsubscript{x}. It indicates that some CoO\textsubscript{x} was loaded on the surface of MgO. However, it is hard to determine whether Co atoms entered the crystal structure of MgO by TEM, so TEM was performed. As can be seen in Figure 2b, the crystals with lattice distances of 0.472 and 0.248 nm can correspond to CoO\textsubscript{x}(111) and MgO(111), respectively.\textsuperscript{22,23} Two stripes with different lattice distances also indicate the crystal including two different metal atoms; Co binds to MgO by atom substitution. The results demonstrate that CoO\textsubscript{x} and MgO formed a solid solution, which is also proved by XRD. After the reaction, the catalyst was washed and dried and became rod constituted by sheet solid (as shown in Figure 2b). It suggests some MgO was hydrated to form Mg(OH)\textsubscript{2}, which is in accordance with XRD results. Figure 2c suggests that the recovered catalyst was regenerated after calcination and form a rodlike structure again. It indicates that the catalysts can be recovered by calcination. Figure 2e shows that the rodlike structure is mainly the crystal for the graph of electron diffraction of electron diffraction, suggesting the completion of particle crystallization (Figure 2e). The change of surface morphology in CoO\textsubscript{x}/MgO plays a positive role in the degradation of organic matter during ozonation, which will be discussed in this work.\textsuperscript{5} 2.1.3. Surface Areas and Pore Structures of Catalysts. Surface areas and pore structures of MgO, CoO\textsubscript{x}/MgO, and used and regenerated CoO\textsubscript{x}/MgO were characterized by nitrogen physical adsorption/desorption measurements. As illustrated in Figures S3 and S4, the samples show typical IV isotherms with hysteresis loops, which can be attributed to the mesoporous structure of catalysts.\textsuperscript{24} The surface areas of MgO and 2\% CoO\textsubscript{x}/MgO (Table 1) were about 144 and 151 m²/g, respectively. The results suggest that the addition of CoO\textsubscript{x} into MgO can increase the surface area of catalysts. The introduction of Co species combined with Mg species may
result in pore enlargement, which leads to an increase of the specific surface area. It is well known that a higher specific surface area means more active sites. More phenol and intermediates can be absorbed on the catalyst, which can accelerate the degradation rate of phenol and intermediates. More ozone can be converted to free radicals over the catalyst, further increasing the catalytic reaction rate.11 The catalysts were prepared by NaOH (strong alkaline) and NH₃·H₂O (weak alkaline) as precipitators. The specific surface areas of CoOₓ/MgO prepared with NaOH and NH₃·H₂O as precipitators are 45 and 67 m²/g, respectively (shown in Figure S4 and Table 1), which were much lower than that of the one prepared by Na₂CO₃. It suggests that alkalinity has a great influence on the structures and properties of catalysts. The catalytic activities of catalysts prepared by different precipitators are also different,

| samples                  | BET surface area (m²/g) |
|--------------------------|-------------------------|
| MgO (NH₃·H₂O)            | 67                      |
| MgO (NaOH)               | 45                      |
| MgO (Na₂CO₃)             | 144                     |
| 2% CoOₓ/MgO (Na₂CO₃)     | 151                     |
| used 2% CoOₓ/MgO         | 60                      |
| regenerated 2% CoOₓ/MgO  | 122                     |

Figure 2. (a) SEM image of the prepared 2% CoOₓ/MgO. (b) SEM image of the used 2% CoOₓ/MgO. (c) SEM image of regenerated 2% CoOₓ/MgO. (d), (e) TEM images of the prepared 2% CoOₓ/MgO.
which will be discussed in Section 2.2. There are some factors that affect the decrease of the surface area of used CoOx/MgO, such as conversion of MgO, adsorption of other organics, and so on. The recovered catalysts were alternately washed with ethanol and water, then dried, and calcined; the surface area of regenerated catalysts was almost recovered.

2.1.4. Surface Chemical States of Catalysts. To further investigate the surface chemistry of catalysts, X-ray photo-

Figure 3. XPS spectra of Mg 1s, Co 2p, and O 1s.
electron spectroscopy (XPS) was performed to study the surface Mg, Co, and O species on MgO, 2% CoOx/MgO, and used 2% CoOx/MgO (Figure 3). The binding energy (BE) values of 1303.6 and 1303.7 eV can be attributed to Mg$^{2+}$ in Mg(OH)$_2$ and Mg salts, respectively. The peaks appearing at 1302.5, 1302.7, and 1303.1 eV can correspond to Mg species in the three catalysts. As seen in Table S1 that after CoO$_x$ loading, the intensity of the Mg(OH)$_2$ peak increased. It suggests that the addition of CoO$_x$ can increase the amount of OH$^-$ on the surface of catalysts, which is in good agreement with the results of Fourier transform infrared (FTIR) spectroscopy. The increase of OH$^-$ on the surface is beneficial for catalytic ozonation, which provides active sites for the decomposition of ozone to radicals. Peak’s area of Mg species changed little after the reaction.

The Co 2p profile was achieved with the assumption of four species. The peaks emerging at 792.6, 792.7, 792.9, 793.1, 794.1, 794.4, 794.6, and 794.8 eV correspond to Co$^{2+}$ (sat), Co$^{3+}$ (sat), Co$^{3+}$ (sat), Co$^{2+}$, and Co$^{3+}$, respectively. The results also show that Co was successfully loaded on MgO. The binding energies of these Co species were all increased, and the area ratios of Co$^{3+}$ and its satellite peak became larger. It suggests that some Co$^{2+}$ has been oxidized to Co$^{3+}$ during the reaction. To maintain an electrostatic charger balance on the catalyst surface, the transition occurring in different valence states of Co may activate the lattice oxygen and enhance the catalytic activity.

The Co 2p profile was achieved with the assumption of four species. The peaks emerging at 802.6, 799.5, 796.3, 785.4, 786.1, 780.2, and 780.6 eV can correspond to Co$^{2+}$ (sat), Co$^{3+}$, Co$^{3+}$, Co$^{3+}$ (sat), Co$^{3+}$ (sat), Co$^{3+}$, and Co$^{3+}$, respectively. The binding energies of these Co species were all increased, and the area ratios of Co$^{3+}$ and its satellite peak became larger. It suggests that some Co$^{2+}$ has been oxidized to Co$^{3+}$ during the reaction. To maintain an electrostatic charger balance on the catalyst surface, the transition occurring in different valence states of Co may activate the lattice oxygen and enhance the catalytic activity.

In the case of O 1s spectra shown in Figure 3, the peaks at 531.3, 531.3, and 531.5 eV can be attributed to chemisorbed oxygen species, such as O$_2^-$, O$_2^-$, and O$^2-$. It should be noted that the electrophilic chemisorbed oxygen species play a vital role in deep oxidation of organics. It can be seen from the spectrum of O 1s in MgO and CoO$_x$/MgO and Table S3 that when Co was doped with MgO, the ratio of adsorbed oxygen to lattice oxygen increased obviously, which was one of the main reasons for the improvement of catalytic activity. However, for the used CoO$_x$/MgO, the ratio of lattice oxygen species to adsorbed oxygen is 1.40 to 1; this may be because the surface of adsorbed oxygen was converted to lattice oxygen in a saturated ozone atmosphere. The synergistic effect of uniform distribution of Co and Mg active sites in the nanocages and the optimum molar ratio of Co/Mg also can cause this phenomenon, so CoO$_x$/MgO exhibits better catalytic performance than pure MgO catalysts.

2.1.5. Surface Alkalinity of Catalysts. The alkaline properties of MgO, 2% CoO$_x$/MgO, and used 2% CoO$_x$/MgO were analyzed by temperature-programmed desorption of CO$_2$ (CO$_2$-TPD), which are shown in Figure 4. The peaks shown at around 105°C in MgO can correspond to the weak alkalenescent site. The peaks at higher temperatures than 200°C correspond to the strong alkalenescent sites, such as oxygen in the Mg$^{2+}$ and O$^{2-}$ pairs and isolated O. With the addition of CoO$_x$, the CO$_2$ desorption temperature of these two peaks increased obviously. This indicates that the addition of CoO$_x$ can improve the surface alkalenescent of catalysts. The surface alkalenescent of catalysts was further enhanced after the reaction. The reason was that some MgO was transformed to Mg(OH)$_2$ due to the hydration reaction between MgO and H$_2$O. The number of strong alkalenescent sites is much more than that of weak ones in these three catalysts, and the strong alkalenescent sites can promote the active sites on the surface of the catalyst.

FTIR has also been performed to detected –OH on these catalysts (Figure 5). Species of surface functional groups on CoO$_x$/MgO have not changed much before and after the reaction except the strength. The vibrations at 1445 and 3700 cm$^{-1}$ can correspond to the stretching vibrations of Mg–O and O–H vibrations in Mg(OH)$_2$ or hydroxyl groups formed from water molecules absorbed on catalysts, respectively. The existence of hydroxyl groups on the surface of MgO can change the pH of the solution to about 11, thereby promoting the generation of free radicals and improving the catalytic activity.

2.2. Catalytic Ozonation. 2.2.1. Catalytic Ozonation over Different Catalysts. Figure 6 shows that the removal rate of COD can reach 24.3, 37, 59.1, 76.2, and 79.8% without catalysts over CoO$_x$, market MgO, MgO, and 2% CoO$_x$/MgO in 120 min, respectively. It suggests that 2% CoO$_x$/MgO and MgO showed much better activity than other catalysts. The addition of CoO$_x$ further enhanced the activity of MgO. The removal rate of COD is relatively fast with MgO and 2% CoO$_x$/MgO as catalysts in the first 30 min due to high
concentrations of organic substances at the beginning of reactions. The originally acidic solution becomes alkalescent after the addition of catalysts (pH is about 11) at the same time. Some research studies show that ozone is more soluble in alkalescent conditions and results in generation of more hydroxyl radicals for the degradation of phenol and its intermediates than in acidic or neutral conditions. However, if NaOH was added to tune the solution to alkalescent (pH 11) and as a catalyst, the COD removal rate was very low (about 25% in 2 h). After 30 min, the reaction rate was relatively slow. The reason may be that the increase of OH\(^{-}\) concentration led to the quenching reactions, which can hinder the further increase of \(\cdot\)OH concentration.\(^{35}\) On the other hand, more CO\(_2\) was generated by the increase of solution pH from the decomposition of phenol and its intermediates. This generated CO\(_2\) can react with OH\(^{-}\) to produce CO\(_3^{2-}\) and HCO\(_3^{-}\). \(\cdot\)OH can also be consumed by CO\(_3^{2-}\) and HCO\(_3^{-}\), which can decrease the \(\cdot\)OH concentration and then decrease the reaction rate.\(^{36}\) The decrease of phenol and its intermediates' concentration also led to a decrease of reaction rate. It also can be seen from Figure 5 that the COD removal rate over CoO\(_x\)/MgO is 3.6% higher than that over MgO. The results have been confirmed by three parallel experiments to make sure it is not an error. XRD, TEM, XPS, and CO\(_2\)-TPD proved that the surface morphology, surface activity, and surface alkalinity of the catalyst had been changed after CoO\(_x\) loading. The details of the reaction mechanism will be discussed in the following sections.

2.2.2. Synergistic Effect of CoO\(_x\)/MgO and O\(_3\). The major role of catalytic ozonation rather than adsorption in the removal rate of COD was only 25% without O\(_3\) by CoO\(_x\)/MgO alone. This indicates that the amount of COD removed by adsorption is very small. The COD removal rate was only 25% in the system with O\(_3\) but without catalysts in 120 min. This demonstrates that catalysts are essential for the efficient removal of COD. Although the specific surface area, pore size, pore volume, and surface morphology of CoO\(_x\)/MgO catalyst changed after modification, the changes of these physical parameters did not have a favorable effect on the removal rate of COD in the adsorption process. To demonstrate the role of the catalyst in catalytic ozonation, the synergistic effect of CoO\(_x\)/MgO and ozone is calculated.\(^{33-35}\) It can be seen from Figure 7 that the synergistic effect can reach 57.3% after 30 min. This verifies the high activity of CoO\(_x\)/MgO for the degradation of phenol by the ozone reaction.

2.2.3. Effect of Catalysts’ Calcination Temperature and Molar Ratio of Co to Mg. The calcination temperature of catalysts and the molar ratio of Co to Mg have been optimized to get the best catalytic results (Figures S6 and S7). As can be seen in Figure S6, with an increase of calcination temperature, the removal rate of COD first increased from 75.1 to 79.8% (500 °C) and then decreased to 75.8% with the calcination temperature increased from 400 to 600 °C. The reason may be that the precursor cannot be completely decomposed at low calcination temperatures, while catalysts will be sintered at too high temperatures. Too high or too low temperatures all lead to fewer active sites. The lattice defects produced on the catalyst prepared at 500 °C can increase the charge density of O atoms and increase the number of active sites.\(^ {38}\) About 90% phenol has been removed in 50 min and 100% phenol has been removed in 2 h (Figure S8).

The removal rate of COD increased from 76.9 to 79.8% (50:1) and then decreased with the Co molar ratio increasing from 10:1 to 110:1 (Figure S7). The pH of the reaction mixture increased from 9.5 to 11.3 (50:1) and then decreased with the Co molar ratio increasing from 10:1 to 110:1. This indicated that too much Co may cause a decrease of catalyst alkalinity, and the active sites were reduced. However, too little Co will reduce the oxygen defects on the catalyst and lead to a decrease of active sites, and the catalytic performance is reduced. Indeed, the appropriate molar ratio of Mg to Co was 50:1.

2.2.4. Effect of Phenol Concentration. The COD removal rates over CoO\(_x\)/MgO for different initial concentrations of the phenol solution have been tested. With the increase of initial concentration of phenol from 50 to 400 mg/L, the removal rate of COD decreased from 96.1 to 66.1% (Figure 8). With the increase of initial concentration of phenol, the treatment capacity increased, which resulted in the decrease of

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**Figure 6.** COD removal of phenol in ozonation and catalytic ozonation with time. Reaction conditions: temperature = 25 °C; [phenol]\(_0\) = 210 mg/L; [O\(_3\)]\(_0\) = 43 mg/L; gas flow rate = 1.5 L/min; solution pH = 5.51; catalyst loading = 500 mg; CoO\(_x\) loading amount = 2%.

**Figure 7.** Effect of CoO\(_x\)/MgO adsorption alone on the COD removal rate.
COD removal rate. The high initial concentration of phenol will produce more intermediates, and the complex substance species in the solution will result in the decrease of COD removal efficiency, so this catalyst is suitable to treat phenol wastewater with concentrations lower than 210 mg/L, which is more common in the industrial situation.

To further analyze the catalytic ozonation process, the pseudo-second-order dynamical models were fitted. It can be seen from Table 2, the correlation coefficients were 0.9709, 0.9533, 0.9612, 0.9515, and 0.9588 corresponding to the initial phenol concentrations of 50, 100, 210, 300, and 400 mg/L, respectively. It indicated that the phenol degraded by catalytic ozonation over CoOx/MgO tallied with pseudo-second-order kinetic laws. The reaction rate $K_1$ decreased with the initial concentration increasing due to the decrease of the amount of phenol treated per unit and the increase of intermediate products accumulate amount at the same time, so the initial concentration of phenol is negatively correlated with the reaction rate constant.

2.2.5. Effect of pH. The effect of pH of the initial phenol solution has little influence on catalytic performance. When the pH is 2.48, 4.45, 6.30, 8.34, and 10.23, the COD removal rate can reach 79.0, 79.7, 79.8, 79.8, and 82.1% (Figure S8), respectively. It indicated that the phenol degraded by catalytic ozonation over CoOx/MgO tallied with pseudo-second-order kinetic laws. The reaction rate $K_1$ decreased with the initial concentration increasing due to the decrease of the amount of phenol treated per unit and the increase of intermediate products accumulate amount at the same time, so the initial concentration of phenol is negatively correlated with the reaction rate constant.

2.3. Reaction Mechanism. 2.3.1. Effect of Hydroxyl Radicals and Surface Lewis Acid Sites. Hydroxyl radical is the strongest oxidable species in this system and plays a key role in the treatment of organic wastewater by catalytic ozonation.

TBA (Tianjin Damao Chemical Reagent Factory, China) was added to the reaction system to verify the role of hydroxyl radical in the reactions. It is well known that TBA can be used as a radical scavenger to suppress the generated hydroxyl radicals, which can react with $^*$OH at a high reaction rate constant of $6 \times 10^8$ M$^{-1}$·s$^{-1}$, while it reacts with O$_3$ only at a reaction rate constant of $3 \times 10^{-3}$ M$^{-1}$·s$^{-1}$.$^{37,38}$ As can be seen from Figure 9, the COD removal rate was only about 1% with the addition of TBA in 2 h, while the removal rate of COD can
reach 79.8% in the experiment without TBA in 2 h. Therefore, the hydroxyl radical plays a dominant role in the experiment. These results also indicated that 2% CoOₓ/MgO can effectively promote the conversion of ozone molecules to hydroxyl radicals, which results in nonselective reactions with intermediates and leads to a high COD removal rate.

According to the previous report, Lewis acidic sites may act as active sites for the generation of hydroxyl radicals from ozone, so NaH₂PO₄ (Tianjin Damao Chemical Reagent Factory, China) was added to the reaction system to verify the effect of Lewis acid position on the catalyst surface. It is a strong Lewis base, which can easily cover the Lewis acid site on the surface of the catalyst. It can be seen from Figure 8 that the COD removal rate was 53.6% after the addition of NaH₂PO₄, which was much lower than the one without NaH₂PO₄. It indicates that Lewis acidic sites act as parts of active sites for this process, while other kinds of active sites also exist, which will be discussed in the next section. It can be seen from Figure S5 that the regenerated catalyst from the system which was added some NaH₂PO₄ has only a few petal-like changes on the surface of the catalyst, and the shape is almost unchanged compared with the catalyst before the reaction. It demonstrates that it suppressed the hydration of MgO to Mg(OH)₂, which is important for this process. NaH₂PO₄ also leads to the passivation of the catalyst, inhibits the electron transfer on the surface of CoOₓ/MgO, and reduces the number of active sites, which leads to the decrease of catalytic activity. The results show the change of Lewis acid position on the catalyst surface. The surface morphology of the catalyst is closely related to the catalytic activity.

2.3.2. Mechanism of Catalytic Ozonation over CoOₓ/MgO.

To detect the radicals generated from O₃ degradation, in situ EPR has been performed. In situ EPR experiments have been carried out by the following steps. First, 50 mL of phenol solution of 210 mg/L and catalysts (or without catalysts) were added into a three-necked flask. Second, O₃-containing air flow was blown into the solution. The mixture was stirred for 10 min, and then, 0.1 g of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was added to the mixture and reacted for 5 min. Solution samples were taken by injectors and characterized by EPR. As can be seen in Figure 10, three main peaks emerged in these four spectra marked by a four-pointed star, which can correspond to singlet oxygen combined by DMPO. The intensity of these peaks remained constant after the addition of Mg(OH)₂, while it decreased obviously after the addition of MgO and CoOₓ/MgO. Four peaks with the relative intensity ratio of 1:2:2:1, which were marked by cycles, can correspond to *OH combined with DMPO (DMPO-OH). These four peaks appeared in all of these four systems, which indicates the generation of *OH in these systems. *OH is the main oxidant for the degradation of phenol, so some phenol molecules can be decomposed by O₃ even without any catalysts. After the addition of MgO and CoOₓ/MgO, the intensity of DMPO-OH peaks increased by about 4.2 and 4.3 times, respectively. This
demonstrates that the addition of MgO and CoOx/MgO can accelerate the generation of *OH, which led to the great increase of the COD removal rate and ratio. The addition of CoOx in MgO can enhance the catalytic activity of MgO. The addition of Mg(OH)2 seemed to have a little influence on the generation of *OH because there was no obvious increase of DMPO-OH peaks’ intensity, and the COD removal rate and ratio were also much lower than the ones with the addition of MgO and CoOx/MgO. This indicates that the catalytic activity of Mg(OH)2 is much weaker than that of MgO and CoOx/MgO. The COD removal ratio of systems with Mg(OH)2 (38.2% in 120 min) is higher than the one without any catalysts (22.5% in 120 min, Figure S9). This demonstrates that Mg(OH)2 may not accelerate phenol degradation by the way of acceleration of *OH generation. It may increase the solubility of O3 due to its strong alkalinity.

MgO hydration may play the main role in the degradation of phenol because when the Lewis acidic sites have been blocked, there was still 53.6% COD removal ratio, while when Mg(OH)2 was used as catalysts, only 38.2% COD removal rate was obtained in 120 min (Figure S9). It was also proved by the results of SEM and XRD that the hydration of MgO did occur during the experiment. It can be seen from the SEM images shown in Figure S2 that the surface morphology of CoOx/MgO changed little after the addition of phosphate. The COD removal rate decreased significantly after the addition of phosphate (Figure S8). This suggests that the hydration of MgO has a certain effect on the catalytic oxidation reaction.

Combined with the hydration mechanism of MgO, the possible degradation mechanism of phenol by CoOx/MgO was summarized. MgO reacts with water to form surface hydroxyl and free hydrogen and oxygen radicals. MgO−OH− reacts with ozone molecules to form oxygen free radicals on the surface of MgO. The ozone and water molecules are adsorbed in an environment where CO2 is constantly produced. Finally, MgO2− and *OH react with phenol to form CO2, H2O, and intermediates. Intermediates further react with MgOO− and *OH to generate CO2 and H2O.\(^{13}\)

2.4. Stability of Catalysts. The stability of a catalyst is an important factor for its application. A series of experiments were carried out to explore the stability of the catalyst. It can be seen from Figure 11 that the removal rate of COD is about 79% after each cycle (120 min). The result indicates that prepared catalysts have good reusability for the catalytic ozonation reaction. The reason for the long catalytic life is the regeneration of oxygen vacancies on the catalyst surface and the increase of surface hydroxyl groups during calcination.

2.5. Removal of COD from Wastewater with Different Contaminants. The universality of a catalyst is also very important for its applications. Salicylic acid, ciprofloxacin, and norfloxacin solutions (initial concentration is 210 mg/L) were used for the catalytic ozonation over CoOx/MgO to test the universality of the catalyst under the same conditions as other experiments. It can be seen from Figure 12 that the COD removal rate can reach 97.6, 95.6, and 75.2% for the ciprofloxacin solution, norfloxacin solution, and salicylic acid solution, respectively. These results show that CoOx/MgO also has a significant removal effect on other pollutants.

3. CONCLUSIONS

CoOx/MgO was successfully prepared by coprecipitation, and it showed good activity in catalytic ozonation. The COD removal rate can reach 79.8% for phenol wastewater with initial concentrations of catalysts of 210 mg/L and 1.67 g/L. The various characterizations showed that high catalytic activity was due to the high specific surface area (151.3 m²/g) and strong alkalinity of CoOx/MgO. The addition of CoOx in MgO can increase the ability of catalysts for conversion of O3 to free radicals, which degrades phenol more effectively. At the same time, hydration of MgO in the process can improve the ratio of COD. The experimental results showed that CoOx/MgO also had high COD removal rates for norfloxacin, ciprofloxacin, and salicylic acid at the same initial concentration. Moreover, the prepared catalyst could be recycled five times without reducing its activity. This work provided a method for the subsequent design of catalysts with higher catalytic performance. It also provided an effective catalyst for phenol removal in wastewater.

4. MATERIALS AND METHODS

4.1. Preparation and Characterization of Catalysts. CoOx/MgO was prepared by a coprecipitation method. First,
Mg(NO₃)₂·6H₂O (23.59 g, AR, Tianjin Yongda Chemical Reagent Co., China) and 9.75 g of Na₂CO₃ (AR, Tianjin Yongda Chemical Reagent Co., China) were dissolved in 100 mL of deionized water. Second, 0.9769 g/L Co(NO₃)₂ (AR, Tianjin Yongda Chemical Reagent Co., China) solution was poured into the Mg(NO₃)₂ solution and stirred with a magnet in a beaker at room temperature for 15 min; then, the Na₂CO₃ solution was quickly poured into the mixed solution of Co(NO₃)₂ and Mg(NO₃)₂ and stirred for 45 min. The obtained suspension was aged for 4 h. Mg²⁺ and Co²⁺ combined with CO₃²⁻ form precipitation. The ratio of Mg²⁺ to Co²⁺, the combining rate of Mg²⁺ or Co²⁺ with CO₃²⁻, and the numbers of Mg²⁺ or Co²⁺-coordination complexes are different; these factors may cause the catalysts to form a microrod structure. The suspension was filtered and washed with deionized water three times. The solid was dried at 90 °C for 6 h, calcined in a muffle furnace at 500 °C (heating rate is 5 °C/min) for 4 h, and naturally cooled down to room temperature. The catalysts were prepared. CoOx/MgO was also prepared by different precipitants, NaOH and NH₃·H₂O, by the same process.

The crystallinity and crystal species of catalyst were analyzed by a D/MAX-2500 X-ray diffractometer (XRD) (Japan, Cu Kα radiation, 60 kV, 300 mA). Catalyst morphologies were observed by an S-4800-I scanning electron microscopy (SEM) unit with 3 kV voltage and 10 mA beam current. Transmission electron microscopy (TEM) was utilized to observe the internal structure of the catalyst using a lanthanum hexaboride filament as an electron emission source (Japan, JEOL, JEM-2100, 80−200 kV). The specific surface area and pore size distribution of the catalysts were analyzed by Brunauer−Emmett−Teller (BET) and Barret−Joyner−Halenda (BJH) methods on a Quantachrome NOVA2000 analyzer, respectively. Fourier transform infrared (FTIR) spectra were recorded by a Nicolet iS5, Thermal Fisher infrared spectrometer. The chemical states of the catalyst were determined by X-ray photoelectron spectroscopy (XPS) with a Kratos Axis Ultra DLD spectrometer and monochromated Al Kα radiation. The surface alkalinity of the catalyst was measured by temperature-programmed desorption of CO₂ (CO₂-TPD) on an AutoChemIIChemisorption Analyzer (Micromeritics). EPR was performed on a Bruker EMXplus-9.5/12 electronic paramagnetic resonance (EPR) spectrometer with the following settings: resonance frequency of 9.85 GHz, microwave power of 10.02 mW, modulation frequency of 100 kHz, modulation amplitude of 2.0 G, sweep width of 1000 G, time constant of 0 ms, sweep time of 40.96 s, and receiver gain of 2.0 × 10⁴.

4.2. Catalytic Ozonation. Wastewater treatment by catalytic ozonation is a semi-intermittent process. The experiment was carried out in a three-necked round-bottom flask at 25 °C and atmospheric pressure. Ozone is produced by an ozone generator (MTS-CFG-50A, Qingdao Meites, mixed gas flow is 50 g/h). The concentration of ozone in the gas phase was measured by the iodine method according to the CJ/T3028.2-1994 standard, which was about 43 mg/L. The flow rate of mixed gas was 1.5 L/min (Figure S1). The excess ozone was also measured by KI (Tianjin Yongda Chemical Reagent Co., China) solution prior.¹⁹

Phenol solution (300 mL) with a concentration of 210 mg/L (in which COD was 520 mg/L) was added to the reactor. CoOx/MgO (0.5 g) was added into the reactor. Then, O₃ was inlet into the suspension with magnetic stirring. Samples of water were taken every 10 min and filtered with a 0.22 μm filter membrane; chromic acid was added immediately for digestion and analyzed immediately. After the experiments, the catalyst was filtered, washed alternately with water and anhydrous ethanol (Tianjin Yongda Chemical Reagent Co., China), and dried. The catalyst was roasted at 500 °C for 4 h for recycling.

4.3. COD Analytical Method. Chemical oxygen demand (COD) is an index to test the mineralization rate of organic compounds in water. Therefore, digestion and determination of samples were carried out according to the standard method by COD digestion instrument and a COD analyzer (Leici COD-571) (K₂Cr₂O₇, AR, Tianjin Damao Chemical Reagent Factory, China).³⁰ The samples were taken at different times and filtered with 0.22 μm filter membrane after the beginning of the experiment; then, 2 mL of samples and 3 mL of chromic acid solutions were added to the sample tube immediately. The mixture was put into the digestion instrument for digestion. At the end of digestion, the digestion tube was removed and cooled to room temperature. The COD-571 tester was preheated for 30 min. After calibration, the digested sample was carefully poured into the colorimetric dish and put into the instrument. After the display is stable, the COD concentration of the current sample was obtained.

The degree of phenol mineralization in the selected process was measured based on the initial COD (COD₀) and the COD of the solution after the reaction (CODₜ)

\[
\text{COD removal rate} (\%) = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100
\]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03497.

(1) Ozone solubility; (2) catalyst characterization: XRD details of CoOx/MgO, N₂ physical adsorption and desorption isotherms of MgO, 2% CoOx/MgO, and used 2% CoOx/MgO composites; N₂ physical adsorption and desorption isotherms of MgO(NH₄)NO₃ and MgO(NaOH); SEM image of used 2% CoOx/MgO (added Na₃PO₄); XPS data of Mg, Co, and O in different catalysts; and FTIR spectra of MgO, 2% CoOx/MgO, and used and regenerated 2% CoOx/MgO; (3) catalytic ozonation: effect of CoOx/MgO adsorption alone on the COD removal rate; effect of different calcination temperatures on the COD removal rate; effect of different molar ratios of Co to Mg on the COD removal rate; effect of different initial concentrations of phenol on the COD removal rate; and effect of Mg(OH)₂ catalytic ozonation on the COD of phenol wastewater; and (4) summary

AUTHOR INFORMATION

Corresponding Authors

Lilong Zhou − College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China; orcid.org/0000-0003-3745-501X; Email: lanruohe@126.com

Jimmy Yun − College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China; School of
Complete contact information is available at:

Shanshan Zhang — College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China; Email: jimmy.yun@unsw.edu.au

Zhengjie Li — College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China

Ali Asghar Esmailpour — School of Chemical Engineering, The University of New South Wales, Australia, Sydney, NSW 2052, Australia

Kunjie Li — College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China

Shuhuan Wang — College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China

Runjing Liu — College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China

Xiaoyan Li — College of Textile and Garments, Hebei University of Science and Technology, Shijiazhuang, Hebei 050018, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03497

Author Contributions
S.Z. and L.Z. contributed equally to this work.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors gratefully acknowledge financial support from the Youth Found of Education Department of Hebei Province (No. QN2019230), the Natural Science Foundation of Hebei Province Youth Project (No. B2019208333), and the Youth Projects of the National Natural Science Foundation of China (22005083).

REFERENCES
(1) Zhao, P.; Qi, Y.; Yang, Y. L. Treatment Technologies of Non-degradable Organic Wastewater. Sichuan Environ. 2006, 4, 98–103.
(2) Pi, Y.; Wang, J. Mechanism and reaction pathway of ozonation of 4-chlorophenol in water. Sci. China, Ser. B 2006, 36, 87–92.
(3) Pratam, W.; Pornsiri, T.; Thanit, S. Adsorption and ozonation kinetic model for phenolic wastewater treatment. Chin. J. Chem. Eng. 2011, 19, 76–82.
(4) Chen, B.; Hu, Y.; Tao, W. Formation and Treatment Technology of Volatile Phenolic in Refinery Purifying Water. Technol. Dev. Chem. Ind. 2013, 4, 48–50.
(5) Turhan, K.; Uzman, S. Removal of phenol from water using ozone. Desalination 2008, 229, 257–263.
(6) Lishman, L.; Shirley, A. S.; Kurtis, S. Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario. Sci. Total Environ. 2006, 367, 544–558.
(7) Xie, Y. B.; Chen, Y. Y.; Yang, J. Distinct synergistic effects in the ozone enhanced photocatalytic degradation of phenol and oxalic acid with Fe3+/TiO2 catalyst. Chin. J. Chem. Eng. 2018, 26, 1528–1535.
(8) Dai, Q.; Wang, J.; Yu, J. Catalytic ozonation for the degradation of acetylsalicylic acid in aqueous solution by magnetic CeO2 nanometer catalyst particles. Appl. Catal., B 2014, 144, 686–693.
(9) Li, C.; Jiang, F.; Sun, D. Catalytic ozonation for advanced treatment of incineration leachate using (MnO2-Co3O4)/AC as a catalyst. Chem. Eng. J. 2017, 325, 624–631.
(10) Lu, J.; Sun, J. X.; Chen, X. X. Efficient mineralization of aqueous antibiotics by simultaneous catalytic ozonation and photo-catalysis using MgMnO4 as a bifunctional catalyst. Chem. Eng. J. 2019, 358, 48–57.
(11) Wang, Y.; Yang, W. Z.; Yin, X. S. The role of Mn-doping for catalytic ozonation of phenol using Mn/r-Al2O3 nanocatalyst: Performance and mechanism. J. Environ. Chem. Eng. 2016, 4, 3415–3425.
(12) Esmailpour, A. A.; Moradi, S.; Yunb, J. Promoting Surface Oxygen Vacancies on Ceria via Light Pretreatment to Enhance Catalytic Ozonation. Catal. Sci. Technol. 2019, 9, 5797–5800.
(13) Moussavi, G.; Mahmoudi, M. Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles. J. Hazard Mater. 2009, 168, 806–812.
(14) Zhu, H.; Ma, W. H.; Han, H. J. Catalytic ozonation of quinoline using nano-MgO: Efficacy, pathways, mechanisms and its application to real biologically pretreated coal gasification wastewater. Chem. Eng. J. 2017, 327, 91–99.
(15) Moussavi, G.; Mashayekh-Salehi, A.; Yaghmaeian, K. The catalytic destruction of antibiotic tetracycline by sulfur-doped manganese oxide (S-MgO) nanoparticles. J. Environ. Manage. 2018, 210, 131–138.
(16) Asgari, G.; Salari, M. Optimized synthesis of carbon-doped nano-MgO and its performance study in catalyzed ozonation of humic acid in aqueous solutions: Modeling based on response surface methodology. J. Environ. Manage. 2019, 239, 198–210.
(17) Chen, Y.; Wu, Y.; Liu, C. Low-temperature conversion of ammonia to nitrogen in water with ozone over composite metal oxide catalyst. J. Environ. Sci. 2018, 66, 265–273.
(18) Moussavi, G.; Rashidi, R.; Khavanin, A. The efficacy of GAC/MgO composite for destructive adsorption of benzene from waste air stream. Chem. Eng. J. 2013, 228, 741–747.
(19) Scorza, E.; Birkenheuer, U.; Pisani, C. The oxygen vacancy at the surface and in bulk MgO: an embedded cluster study. J. Chem. Phys. 1997, 107, 9645–9658.
(20) Rezaei, F.; Moussavi, G.; Bakhtiari, A. R. Toluene removal from waste air stream by the catalytic ozonation process with MgO/GAC composite as catalyst. J. Hazard. Mater. 2016, 306, 348–358.
(21) Moussavi, G.; Aghapour, A. A.; Yaghmaeian, K. The degradation and mineralization of catechol using ozonation catalyzed with MgO/GAC composite in a fluidized bed reactor. Chem. Eng. J. 2014, 249, 302–310.
(22) Chen, J.; Tian, S. H.; Lu, J. Catalytic performance of MgO with different exposed crystal facets towards the ozonation of 4-chlorophenol. Appl. Catal., A 2015, 506, 118–125.
(23) Jia, Y. C.; Wang, S. Y.; Lu, J. Q. Effect of Structural Properties of Mesoporous Co3O4 Catalysts on Methane Combustion. Chem. Res. Chin. Univ. 2016, 32, 808–811.
(24) Turhan, K.; Uzman, S. Removal of phenol from water using ozone. Desalination 2008, 229, 257–263.
(25) Karim, A. M.; Su, Y.; Engelhard, M. H.; King, D. L.; Wang, Y. Catalytic Roles of Co0 and Co2+ during Steam Reforming of Ethanol on Co/MgO Catalysts. Desalination 2011, 279, 286–295.
(26) Yan, F. G.; Huang, J. C.; Ling, G. S. Study on the Effect of Acetic Acid on the Light Burned Magnesia Hydration. J. Salt Sci. Chem. Ind. 2019, 1, 10–15.
(27) Brunauer, S.; Deming, L.; Teller, W. On a theory of the van der waals adsorption of gases. J. Am. Chem. Sci. 1940, 62, 1723–1732.
(28) Zhang, X. F.; Shen, T. D.; Ding, Y. L. Graphite Felt Supported MgO Catalytic Ozonation of Bisphenol A. Ozone: Sci. Eng. 2019, 41, 541–550.
(29) Shen, T. D.; Wang, Q. W.; Tong, S. P. Solid Base MgO/Ceramic Honeycomb Catalytic Ozonation of Acetic Acid in Water. *Ind. Eng. Chem. Res.* 2017, 1–30.

(30) Afzal, S.; Quan, X.; Lu, S. Catalytic performance and an insight into the mechanism of CeO$_2$ nanocrystals with different Characterization Methods. *Appl. Catal., B* 2019, 248, 526–537.

(31) Dubecký, F.; Kindl, D.; Hubík, P. A comparative study of Mg and Pt contacts on semi-insulating GaAs: Electrical and XPS characterization. *Appl. Surf. Sci.* 2017, 395, 131–135.

(32) Li, C. H.; Jiang, F.; Sun, D. Z. Catalytic ozonation for advanced treatment of incineration leachate using (MnO$_2$-Co$_3$O$_4$)/AC as a catalyst. *Chem. Eng. J.* 2017, 325, 624–631.

(33) Luo, Y. J.; Zheng, Y. B.; Zuo, J. C. Insights into the high performance of Mn-Co oxides derived from metalorganic frameworks for total toluene oxidation. *J. Hazard. Mater.* 2018, 349, 119–127.

(34) Feng, Y. J.; Li, L.; Niu, S. F. Controlled synthesis of highly active mesoporous Co$_3$O$_4$ polycrystals for low temperature CO oxidation. *Appl. Catal., B* 2012, 111–112, 461–464.

(35) Li, B.; Li, L. W.; Dong, Y. N. Glucose Isomerization into Fructose Catalyzed by MgO/NaY Catalyst. *Chin. J. Chem. Phys.* 2018, 31, 203–210.

(36) Chen, J.; He, X.; Zhao, H. Research on treatment properties of azo dye wastewater with catalytic ozonation by iron magnesium composite oxide. *J. Bengbu Univ.* 2018, 2, 28–32.

(37) Huang, Y. X.; Cui, C. C.; Zhang, D. F. Heterogeneous catalytic ozonation of dibutyl phthalate in aqueous solution in the presence of iron-loaded activated carbon. *Chemosphere* 2015, 119, 295–301.

(38) Moussavi, G.; Khavanin, A.; Alizadeh, R. The integration of ozonation catalyzed with MgO nanocrystals and the biodegradation for the removal of phenol from saline wastewater. *Appl. Catal., B* 2010, 97, 160–167.

(39) Zhu, J. B.; Zhuang, X. Y.; Tong, D. S. *Preparation of Magnesium Oxide and Its Application in Catalysis*; Zhejiang Chemical Industry, 2017; Vol. 48.