# Degradation of Chlorophenols by Supported Co−Mg−Al Layered Double Hydrotalcite with Bicarbonate Activated Hydrogen Peroxide

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S *Supporting Information*

ABSTRACT: Toxic and bioresistant compounds have attracted researchers to develop more efficient and cost-effective technologies for degradation of organic compounds in wastewater. This work demonstrates the degradation of 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and phenol as model compounds using bicarbonate-activated H_2O_2 oxidation system in the presence of supported catalysts. The catalytic activity of the catalyst was investigated in term of degradation of target compounds, chemical oxygen demand (COD), and total organic carbon (TOC) removals both for batch mode and in fixed bed reactor using CoMgAl-HTs and CoMgAl-SHTs, respectively. The leaching of cobalt ion was efficiently prohibited because of the presence of a weakly basic medium provided by bicarbonate, and the CoMgAl-SHTs catalyst was found to retain its stability and good catalytic activity in fixed bed reactor for over 300 h. Extensive chemical probing, fluorescence, and electron paired resonance (EPR) studies were conducted to identify the actual reactive species in the degradation pathway, which revealed that the reaction proceeds through generation of superoxide, hydroxyl radical along with carbonate radical.
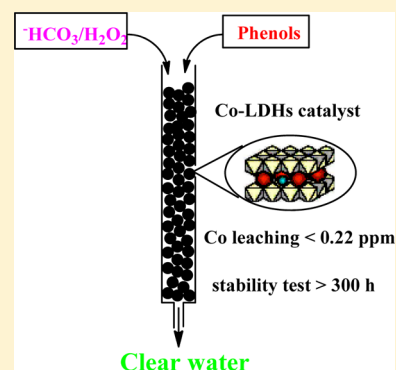
INTRODUCTION

The availability of clean and safe water is the biggest demand of all functional societies, and its supply seems challenging because of excessive growth in population. The recycling and disposal of industrial wastewater is another concern that requires a highly efficient as well as a clean and safe technology. So far the available techniques such as conventional biological, thermal, chemical, and even advanced oxidation technologies have certain limitations such as long treatment time, energy consumption, sever operational conditions, high cost, and leaching of toxic heavy metals.[1−6] Hydrogen peroxide (H_2O_2) is a high active oxygen content, environment friendly slow oxidant in the absence of activator,[7] and different methods have been used to activate H_2O_2 for its application in organic synthesis and pollutant treatments.[8−10] In common advanced oxidation technologies, for example, Fenton and Fenton-like technologies, H_2O_2 is popularly employed under acidic conditions or neutral conditions but with proceeding degradations, and the medium turns acidic because of the formation of acids, which always causes the leaching of toxic metal ions from catalyst and apparently causes short lifetime of catalyst, thus increasing the catalyst cost. Alternatively, bicarbonate activated H_2O_2 generates a weakly basic pH condition that can efficiently prohibit the leaching of metal ions from supported metal oxide catalyst.[11] Traditionally, bicarbonate and carbonate are considered as ·OH radical scavenger;[12] however, recent studies have also revealed that the presence of bicarbonate or carbonate can enhance the degradation of various organic compounds, and the combined

applications of bicarbonate activated H_2O_2 with aqueous redox metals ion further accelerates pollutant degradation, even if this practice is associated with the problem of heavy metals pollution.[13−17] Clearly, the use of recyclable heterogeneous catalyst with bicarbonate activated H_2O_2 seems a promising alternative to avoid metal ion leaching in H_2O_2 based wastewater treatment. Indeed, our previous studies using diatomite supported catalyst with bicarbonate activated H_2O_2 has significantly eliminated metal ion leaching in dye degradation, and in fixed bed test, the lifetime of catalyst was extended to 180 h without significant activity loss.[11] However, the lifetime of catalyst is still not satisfactory for its practical application, and more robust catalysts need to be explored in bicarbonate activated H_2O_2 system. Meanwhile, such a combined technology also needs to be extended to other pollutant treatments.

Compared with simple adsorption of metal salts on diatomite by impregnation, layered double hydrotalcites (LDHs) with tunable properties can be considered as important precursors to meet the demand of multiple environmental problems in catalyst preparation. The chemical composition of LDHs or hydrotalcite-like compounds can be expressed by a general formula $[M^{2+}_{1−x} M^{3+}_x (OH)_2]^{x+}A^{n−}_{x/n}·mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cations, $A^{n−}$ is an interlayer anion with valency n, and x is the proportion of trivalent metal

cations. The wide application of hydrotalcites is associated with its special features like the replacement of divalent cations (Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ru^{2+}, Rh^{2+}, and Zn^{2+}) by some trivalent cations (Al^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Cr^{3+}, Ga^{3+}), which creates positive holes balanced by the presence of counteranions such as OH^-, CO_3^{2-}, Cl^-, NO_3^- located in the interlamellar region. The chemistry of LDH has been extensively studied as CO_2 adsorbent, ion exchange host, and catalyst for pollutant degradations.[18−22] In this work, LDHs supported cobalt catalysts were prepared and tested for chlorophenol degradation with bicarbonate activated H_2O_2. Compared with diatomite clay which provides simple physical adsorption, the LDH catalysts demonstrate a more promising merit for prohibiting the leaching of catalyst, thus extending the lifetime of catalyst.

■ EXPERIMENTAL SECTION

Chemicals and Reagents. $Co(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, $NaHCO_3$, phenol, chlorophenols (purity, >99%), H_2O_2 (30%), and other chemicals were purchased from local Sinopharm Chemical Reagent Co. Ltd. and were used as received without further purification. For EPR analysis, 5,5-dimethyle-1-pyrolene *N*-oxide (DMPO) (98%, Adamas Reagent Co. Ltd.) and *N-tert*-butyl-α-phenyl-nitrone (BPN) (98%, Alfa Aesar) were used.

Preparation of Powdered Catalyst for Bench Experiments (CoMgAl-HTs and MgAl-HTs). The catalysts used in bench experiments were prepared by the coprecipitation method. In a typical procedure, a salt solution A (100 mL) containing 15.00×10^{-2} M $Mg(NO_3)_2 \cdot 6H_2O$, 5.00×10^{-2} M $Al(NO_3)_3 \cdot 9H_2O$, and 7.5×10^{-4} M $Co(NO_3)_2 \cdot 6H_2O$ was added dropwise to a basic solution B (100 mL), which consists of 3.0×10^{-1} M Na_2CO_3, with continuous stirring at 60 °C. For MgAl-HTs, the same procedure as mentioned above was adopted with changing of the composition of solution A (Mg(II) and Al(III) salts only). The pH of solution B was kept constant (10 ± 0.02) using 1 M NaOH during the addition of solution A. The mixture was further stirred for about 1 h at 60 °C and then aged at room temperature for 24 h without stirring. The precipitate was collected by filtration and thoroughly washed with deionized water until neutral pH was obtained. The precipitate was then dried in an oven at 80 °C for 12 h and calcined in a muffle furnace for 16 h at 500 °C. The synthesized catalysts were characterized by X-ray diffraction (XRD, X'Pert PRO), Fourier transform infrared (FT-IR, Bruker Equinox 55), and BET surface area analysis (Micromeritics ASAP 2020).

Preparation of Supported Catalyst for Fixed Bed Experiments (CoMgAl-SHTs). Diatomite support was prepared by dissolving a mixture of 3 g of pullulan, 2 g of $(NH_4)_2CO_3$, and 0.50 g of K_3PO_4 in 25 mL of water and then adding 20 g of diatomite clay under continuous agitation. The resulting paste was shaped into strips and calcined in a muffle furnace at different temperatures and times, i.e., at 60 °C for 2 h, at 100 °C for 2 h, at 250 °C for 1 h, and at 1000 °C for 3 h. For synthesis of supported catalyst, the metal nitrates were impregnated on the calcined diatomite supports. In a typical procedure, 20 g of diatomite support (strips) was contacted with 25 mL of aqueous solution containing 0.09 M $Co(NO_3)_2 \cdot 6H_2O$, 3 M $Mg(NO_3)_2 \cdot 6H_2O$, and 0.99 M $Al(NO_3)_3 \cdot 9H_2O$ for 6 h. The contents were dried in a muffle furnace at 200 °C for 2 h. The support was again impregnated in the corresponding solution for 24 h. The impregnated support was transferred into 25 mL of aqueous solution of 1.5 M Na_2CO_3 and 0.1 M NaOH in a Teflon holder and placed in an autoclave and then heated in the furnace for 6 h at 90 °C. The material was washed with flushing deionized water to remove easily the surface bound catalyst and further dried in oven for 24 h at 80 °C. The supported catalyst was further calcined to 500 °C for 16 h.

Pollutants Degradation in Bench Test Experiments. A total of six samples with volume 20 mL (aqueous solution of 100 mg/L chlorophenols (CPs), 30 mM $NaHCO_3$, and H_2O_2) were added to 25 mL flasks containing 0.03 g of catalyst. The resulting solution was stirred in a water bath equipped with a magnetic stirrer at 40 °C. Periodically one sample was taken out at time interval of 10 min and analyzed for removal of CPs, TOC, and COD.

Pollutants Degradation in Fixed Bed Experiments. Fixed bed experiments for the degradation of model compound 4-chlorophenol (4-CP) were conducted in a double jacketed glass reactor, with dimension of height 60 cm and inner diameter 1 cm. A total of 15 g of catalyst (0.37% cobalt) in the form of cylindrical blocks of 5 mm × 4 mm (length × diameter) size was loaded in the reactor. The model solutions consisted of 50 mg/L 4-CP and oxidant solution containing H_2O_2 and $NaHCO_3$ (30 mM each). Both solutions were pumped from the top of the reactor simultaneously in the ratio of 1:1 (v/v) at a flow rate of 47 mL/h at 40 °C, and the retention time of the reaction mixture was 24 min in the reactor. Samples were collected after flushing the reactant solution for 12 h through the reactor and analyzed for concentrations of CP, COD, TOC, and cobalt leached. In fixed bed experiments, the supported CoMgAl-SHTs catalyst was retained in the reactor for 300 h without replacing or adjusting the cobalt content.

Analyses. Quantitative analysis of 4-CP was performed using high performance liquid chromatography (HPLC FL-2200) equipped with UV detector and C_{18} column (250 mm × 4.6 mm). The eluent composition was 70% methanol with water (70:30 v/v). The quantification of COD and TOC was performed with portable HACH-1010 [23] and TOC analyzer (Analytikjena Multi N/C-3100), respectively. EPR signals for DMPO and PBN were recorded at ambient temperature using Bruker A200. Fluorescence study was conducted with Hitachi F-4500 fluorescence spectrophotometer. The concentration of metals leached into solution was determined by using an atomic absorption spectrophotometer (AAnalyst 300 PerkinElmer).

■ RESULTS AND DISCUSSION

Characterization of Powdered Catalysts. The characterization of powdered catalyst was conducted using BET, XRD, and FT-IR. The surface area of CoMgAl-HTs catalyst calcined at different temperatures (300, 400, 500, 600, 700, and 800 °C) changed from 82.08, 81.78, 124.31, 71.44, 79.72 to 100.28 m^2 g^{-1}, respectively. The surface area of CoMgAl-BHTs calcined at 500 °C was 15.59 m^2 g^{-1}. The AAS analysis shows that the cobalt loading in CoMgAl-HTs and CoMgAl-SHTs are 0.57% and 0.37%, respectively. The XRD patterns of CoMgAl-HTs calcined at different temperatures are displayed in Figure 1. All the samples indicate the characteristic crystalline planes of the hydrotalcite in good agreement with standard planes (41-1428 JCPDS); the prominent peaks can be observed for 006, 018, 024, 021, and 0216 planes.[24,25] This shows that in all samples Co has successfully been introduced into the brucite layers without distorting the crystallite lattice. A peak at a 2θ value of 43, which is less pronounced in samples calcined at lower
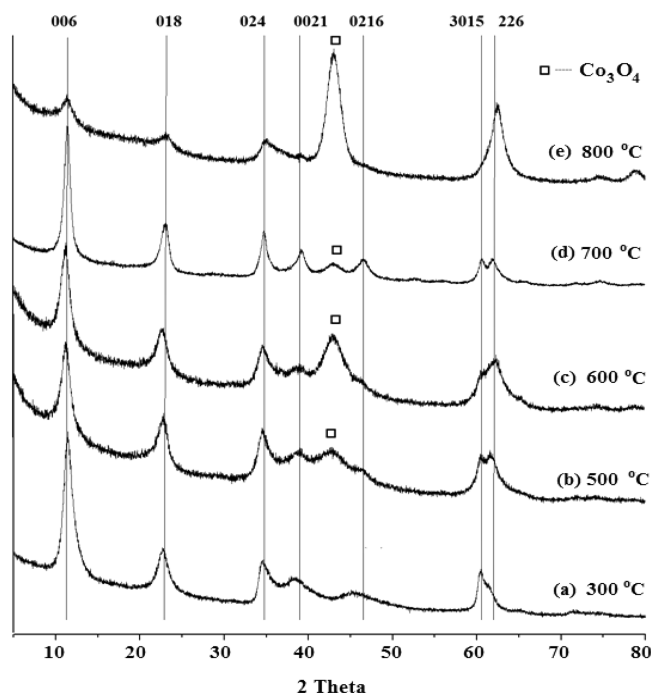
Figure 1. XRD patterns of CoMgAl-HTs precursor after calcinations at different temperatures.

Figure 2. Influence of $NaHCO_3$ on the degradation of 4-CP. Conditions: (a) 4-CP 100 ppm, H_2O_2 20 mM, 15−40 mM $NaHCO_3$, temperature 40 °C, catalyst 0.03 g, reaction time 1 h; (b) 15−40 mM $NaHCO_3$ with no H_2O_2 under condition a; (c) condition a + 1 M NaOH, no $NaHCO_3$; (d) condition a + 15−40 mM $NaHCO_3$ without catalyst; (e) removal of COD at condition a; (f) condition a + 0.03 g of MgHTs as catalyst.

temperature but is prominent in samples calcined at high temperature, may be attributed to Co_3O_4.[26] The crystallite nature is predominantly influenced by calcination temperature. The sample calcined at 300 °C shows less sharp peaks at high 2θ values, and with an increase in temperature to 500, 600, and 700 °C the crystalline planes are more prominent, giving sharp peaks. At further high temperature the peak intensities predominantly decrease and some peaks diminish, indicating the variation in the crystal lattices possibly due to thermal decomposition of the hydrotalcite phase.[26] FT-IR analysis (not shown) also shows a characteristic hydrotalcite broad band at 3456 cm^{-1}, and a small one centered at 1619 cm^{-1} can be assigned to hydroxyl groups and physically adsorbed water. A small narrow band near 1383 cm^{-1} can be attributed to carbonate anion, and bands below 800 cm^{-1} are associated with M−O−M and M−OH type bonding.

Activity of Catalyst/HCO_3^-/H_2O_2 System on Bench Level. To evaluate the efficiency of CoMgAl-HTs in bicarbonate activated H_2O_2 system, 4-CP was taken as model compound on bench scale in aqueous medium and the removal efficiency was monitored by HPLC. As demonstrated in Figure 2, the role of bicarbonate addition was studied extensively in a series of control experiments under different conditions. In all control experiments (Figure 2b−d,f), the degradation of 4-CP was negligible. The degradation of 4-CP increased with bicarbonate concentration up to 30 mM. Above 30 mM the degradation of 4-CP followed a suppressing trend which strongly demonstrates its scavenging properties for the ·OH radical. Interestingly in control experiment in Figure 2f with MgAl-HTs catalyst, the degradation of 4-CP was substantially very small, suggesting that Mg and Al just provide support in CoMgAl-HTs catalyst while cobalt is the active part. At optimized conditions, the degradation of 4-CP increases to 86% with 81% COD removal (see Supporting Information Figure S1). In the control experiments, the same trend of negligible
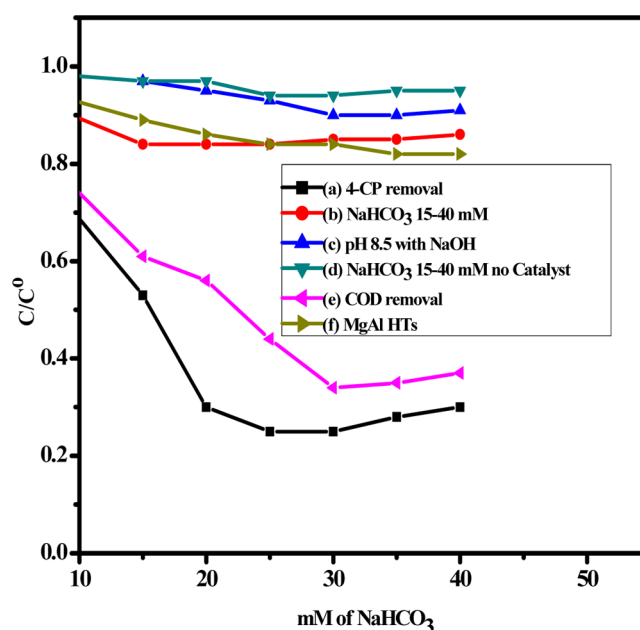
degradation was repeated that reinforces the role of every component in HCO_3^-/catalyst/H_2O_2 system.

The degradation of 4-CP was further investigated while varying the reaction time (5, 10, 20, 30, 40, 50, and 60 min) and catalyst calcination temperature (see Supporting Information Figure S2 and S3). At a time span of 5 min we observed 84% and 78% removal for 4-CP and COD, respectively. After the reaction time was increased to 1 h, the removals increased to 87% and 81%, respectively. This small change in removal of 4-CP after 1 h indicates that the maximum removal takes less than 5 min. As a result of variation in catalyst calcination temperature, it was found that the highest catalytic reactivity is obtained at 500 °C. It was also observed that increasing or decreasing the temperature around 500 °C leads to reduced efficiency. As evident from the data in Table 1, the maximum

Table 1. Leaching of Co from Powdered Catalyst Prepared under Different Calcination Temperatures in Bench Test[a]

	calcination temperature					
	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
Co leaching (ppm)	0.10	0.10	0.14	0.12	0.11	0.10

[a]Conditions: 4-CP solution 100 ppm, $NaHCO_3$ and H_2O_2 30 mM, 0.03 g of catalyst, time 1 h, and 40 °C.

amount of Co leached is still very low (0.14 ppm) and possibly the dissolved Co ion may play a role in the degradation of 4-CP. In the control experiment using $Co(NO_3)_2 \cdot 6H_2O_2$ as catalyst (0.20 ppm), TOC removal of 20% was attained which is much smaller than 78% with supported Co catalyst. The supported catalyst gives the maximum of its efficiency in less than 5 min while leached cobalt (0.14 ppm) accumulated in 1 h of reaction time. Hence, this will be strong evidence for the

negligible role of leached Co in 4-CP degradation. In particular, the Co leaching in this catalyst series is substantially lower than those reported in our previous work,[11] supporting that LDHs based catalyst preparations are more efficient in prohibiting leaching than diatomite by simple impregnation. The oxidative degradation was also investigated for other phenolic compounds such as phenol, 2-CP, 2,4-DCP, and 2,4,6-TCP using the same oxidation system; the results are displayed in Table 2.

Table 2. Activity of the Powdered Catalyst for Different Phenolic Compounds[a]

| targeted compound	% removal	% COD removal	% TOC removal
4-CP	86	80	78
2-CP	68	56	53
2,4-DCP	70	61	57
2,4,6-TCP	76	63	60
phenol	52	39	35

[a]Conditions: targeted compounds 100 ppm, H_2O_2 and $NaHCO_3$ 30 mM, 0.03 g of catalyst, reaction time 1 h, temperature 40 °C.

The data show that a significant removal of COD and TOC was attained in all of tested compounds in 1 h reaction time. The degradation order follows 4-CP > 2,4,6-TCP > 2,4-DCP > 2-CP and phenol. Literature reports show different reactivity patterns among various compounds, but in general the rate of reactivity declines with the increased number of chlorine atoms on the aromatic ring.[27−30]

Mechanistic Discussions. To explain the degradation of organic pollutants using H_2O_2, two mechanistic approaches have been forwarded so far in the literature, including the classical free radical mechanism and the high valent metal oxo species or associative metal ion formation, and occasionally both pathways are regarded to be compatible.[31] In the present study leaching of Co from supported catalyst was carefully monitored, which was found to be very low, and the control experiments were also conducted under similar conditions to elaborate the role of Co ions as stated above, which revealed that the significance of metal oxo or associative metal ions in degradation is also small.
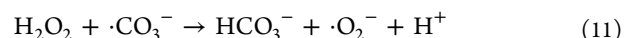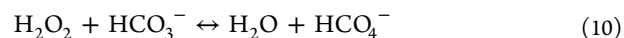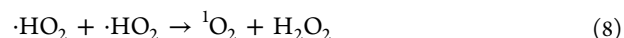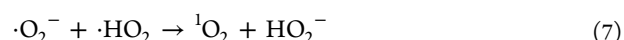
$$\cdot OH + HCO_3^- \rightarrow H_2O + \cdot CO_3^-;$$
$$k_{OH} = 8.5 \times 10^6 \ M^{-1} \ s^{-1} \tag{1}$$
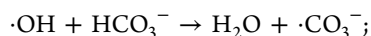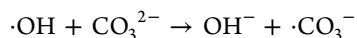
$$\cdot OH + CO_3^{2-} \rightarrow OH^- + \cdot CO_3^-$$
$$k_{OH} = 3.9 \times 10^8 \ M^{-1} \ s^{-1} \tag{2}$$

Carbonate and bicarbonate are considered as scavengers for $\cdot OH$ (eqs 1 and 2).[12] At neutral pH the inorganic carbon mostly exists in the form of bicarbonate which is able to activate H_2O_2, producing peroxymonocarbonate.[32,33] In fact, the radical−radical interaction of bicarbonate ($1.2 \times 10^6 \ M^{-1} \ s^{-1}$) is much slower than hydroxyl radical ($5.5 \times 10^9 \ M^{-1} \ s^{-1}$); hence, they are more available for degradation of pollutants.[34] The carbonate radical anion, which is produced generally by eq 1 or 2, exists for a long time with better oxidizing efficiency and generates various reactive oxygen species (ROS) such as perhydroxyl radical, singlet oxygen, and superoxide in a series of reactions which are potential oxidants that degrade pollutants under different conditions.[35−37]

$$H_2O_2 + \cdot CO_3^- \rightarrow HCO_3^- + \cdot HO_2 \tag{3}$$

$$\cdot CO_3^- + HO_2^- \rightarrow \cdot O_2^- + HCO_3^- \tag{4}$$

$$\cdot HO_2 \rightarrow H^+ + \cdot O_2^- \tag{5}$$

$$\cdot O_2^- + \cdot OH \rightarrow {}^1O_2 + OH^- \tag{6}$$

$$\cdot O_2^- + \cdot HO_2 \rightarrow {}^1O_2 + HO_2^- \tag{7}$$

$$\cdot HO_2 + \cdot HO_2 \rightarrow {}^1O_2 + H_2O_2 \tag{8}$$

$$\cdot CO_3^- + \cdot O_2^- \rightarrow CO_5^{2-} \tag{9}$$

$$H_2O_2 + HCO_3^- \leftrightarrow H_2O + HCO_4^- \tag{10}$$

$$H_2O_2 + \cdot CO_3^- \rightarrow HCO_3^- + \cdot O_2^- + H^+ \tag{11}$$
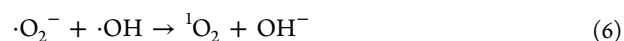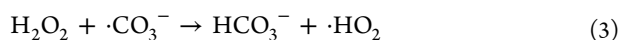
In order to identify the dominant ROS in catalyst/HCO_3^-/H_2O_2 system, extensive studies were conducted using radical scavengers, EPR, and fluorescence probing techniques. The ascorbic acid, which is a well-known probe for free radicals,[38,39] was found to markedly influence the degradation of CP, indicating that the current oxidative degradation system consists of free radical environment (see Figure S4 in Supporting Information). The inhibition of aqueous phase reaction by *tert*-butanol is indicating of hydroxyl radical prevailing in the medium (see Figure S5 in Supporting Information), and it is more powerful scavenger than bicarbonate ($k_{t\text{-BuOH}} = 6 \times 10^8 \ M^{-1} \ s^{-1}$ vs $k_{HCO3-} = 8.5 \times 10^6 \ M^{-1} \ s^{-1}$). A prominent inhibition of reaction was also observed with the addition of *tert*-butanol, and its influence was enhanced with increasing in its concentration. The hydroxyl radical can be generated by the decomposition of H_2O_2 or by peroxymonocarbonate (HCO_4^-) which is produced through equilibrium reaction (eq 10) and is considered as effective activator for hydrogen peroxide.[8−10] In literature, the commonly used ${}^1O_2$ probe like sodium azide (NaN_3) is also an efficient $\cdot OH$ scavenger, as their rate constants are nearly close to each other ($2 \times 10^9 \ M^{-1} \ s^{-1}$ vs $1 \times 10^{10} \ M^{-1} \ s^{-1}$).[40,41] In our previous work, it was demonstrated that NaN_3 strongly inhibits the degradation of methylene blue which was accounted for by singlet oxygen.[11] A similar experiment was conducted with NaN_3 in this study, and the results are presented in Figure 3. In contrast to the previous study, the degradation of 4-CP increased upon addition of NaN_3 and completely disappeared with 10 mM or at higher concentration. In control experiments nearly no degradation was observed that ruled out the possibility of catalytic role for NaN_3. It has been reported that NaN_3 can react with ${}^1O_2$ and $\cdot OH$ radical to produce azidyl radical and superoxide (through eq 12 and 13), which is a strong oxidant and has the ability to oxidize thiols, phenols, and other compounds.[42−45] In the current study, as in the presence of azide the reaction rate increases; hence, it might be concluded that azide competes with CP for singlet oxygen producing two reactive species (azidyl radical and superoxide) that may in turn enhance the degradation of CP. In another scavenger test, the degradation of CP was strongly inhibited by benzoquinone that may be accounted for by superoxide (Figure 4 e).[46−48]

$$N_3^- + {}^1O_2 \rightarrow \cdot N_3 + \cdot O_2^- \tag{12}$$

$$N_3^- + \cdot OH \rightarrow \cdot N_3 + OH^- \tag{13}$$

The results of experiments conducted with different scavengers clearly demonstrate that these reactions may
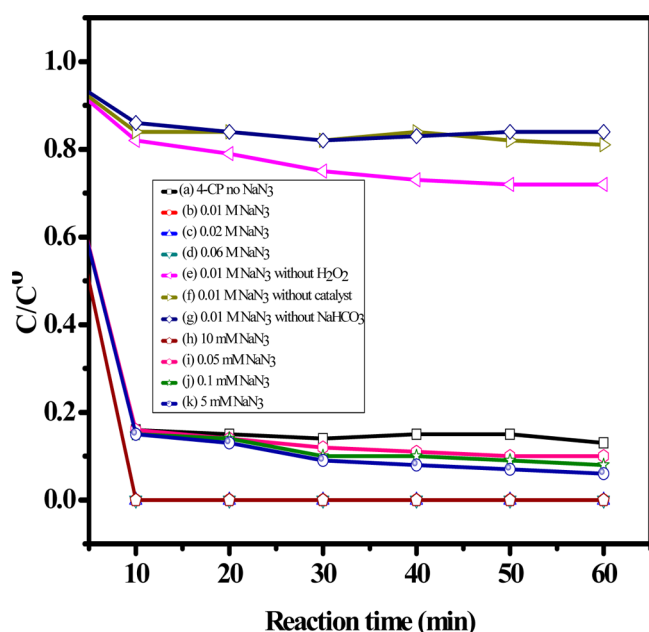
Figure 3. Influence of sodium azide on the degradation of 4-CP. Conditions: (a) 4-CP solution 100 ppm, H_2O_2 and $NaHCO_3$ 30 mM, temperature 40 °C, 0.03 g of catalyst, time 5−60 min; (b) condition a + 0.01 M NaN_3; (c) condition a + 0.02 M NaN_3; (d) condition a + 0.06 M NaN_3; (e) condition a + 0.01 M NaN_3 without H_2O_2; (f) condition a + 0.01 M NaN_3 without catalyst; (g) condition a + 0.01 M NaN_3 without $NaHCO_3$; (h) condition a + 10 mM NaN_3; (i) condition a + 0.05 mM NaN_3; (j) condition a + 0.1 mM NaN_3; (k) condition a + 5 mM NaN_3.
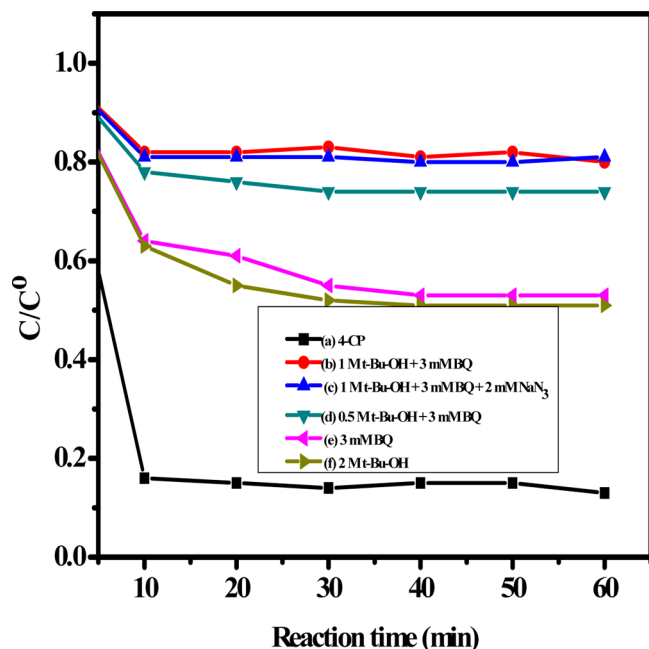

Figure 4. Influence of t-BuOH, benzoquinone, and sodium azide on the degradation of CP. Condition: (a) 4-CP solution 100 ppm, H_2O_2 and $NaHCO_3$ 30 mM, temperature 40 °C, 0.03 g of catalyst, time 1 h; (b) condition a + 1 M t-BuOH + 3 mM BQ; (c) condition a + 1 M t-BuOH + 3 mM BQ + 2 mM NaN_3; (d) 0.5 M t-BuOH + 3 mM BQ; (e) condition a + 3 mM BQ; (f) condition a + 2 M t-BuOH.

proceed through formation of hydroxyl radical, singlet oxygen, and superoxide, but none can quench it completely. Actually

the half-lives for ROS are extremely short (e.g., 4×10^{-9} and 40×10^{-9} s for $^1O_2$ and ·OH, respectively).[49] Their detection or quantification with available scavengers in aqueous solution is a challenging job, as its addition will potentially disturb the chemistry and nature of the system. In fact, these ROS undergo self-reactions, decays through vibronic coupling with water or catalytic decay with metals. A comprehensive study using combination of different scavengers for trapping either two or all radicals was conducted, and the results are demonstrated in Figure 4. The quenching of reaction with tert-butanol is concentration dependent and its maximum sink equal to benzoquinone alone (nearly 50%). Furthermore, using a combination of different scavengers reveals that the inhibition effects of tert-butanol and benzoquinone are more significant than that of azide which is relatively less pronounced. From these observations it can be concluded that hydroxyl radical and superoxide might be participating directly in the degradation of 4-CP, while for $^1O_2$ no evidence was found. For superoxide, which is involved in producing different transient species as demonstrated in eqs 3−9, it might be suggested that the radical−radical interactions are slower than its participation in degradation or its trapping with benzoquinone. However, none of the scavengers can quench the reaction completely, implicating some other active species involved in degradation of 4-CP. As in the control experiments, the degradation of CP with H_2O_2 and bicarbonate is negligible, which indicates that neither H_2O_2 nor peroxymonocarbonate anion (HCO_4^-) directly degrades CP; consequently, the carbonate anion radical may serve as an alternative key ROS. The carbonate radical serves as a source of many ROS, as evident from eqs 3−8. Also its radical−radical interaction (1.2×10^7 M^{-1} s^{-1}) is much slower than ·OH radical (5.5×10^9 M^{-1} s^{-1}), and therefore, its concentration will be much higher than ·OH radical in the reaction medium.[50−53] Furthermore, it is more selective than ·OH in organic reactions and consequently reacts quickly with phenols, aniline, and some amino acids. It has also been reported that carbonate radical can also degrade adaptable pesticides, dyes, and even tert-butyl ether.[34,54,55]

EPR is a useful tool for monitoring the paramagnetic species. This technique was carefully applied to confirm the generation of superoxide and hydroxyl radicals, and the results are shown in Figure 5. It has been reported that the DMPOH−OH adduct can be produced not only by ·OH but also by the decomposition of the DMPO−OOH/O_2^- adduct due to its half-life of less than 1 min.[56] In order to detect superoxide, BPN was applied as an EPR spin trap in aqueous medium. A characteristic triplet BPN−O_2^- signal with g = 2.007 was observed under all experimental conditions that confirmed the existence of superoxide as exhibited in Figure 5A (curves a−e). The formation of quartet DMPO−OH adduct signal with intensities of 1:2:2:1 is considered for ·OH with DMPO. In a series of experiments as demonstrated in Figure 5B (curves a−i), prominent quartet DMPO−OH adduct peaks with characteristic intensities of 1:2:2:1 and g = 2.0067 were observed which decrease markedly with addition of tert-butanol and 4-CP. This change in peak intensities may be attributed to the scavenging of ·OH (Figure 5B (curves d−g,i)). Apart from the DMPO−OH adduct signal, some additional peaks were constantly produced that were more pronounced in Figure 5B (curve f). A very clear DMPO−OH signal was found in control experiment Figure 5B (curve d), and a similar observation in aqueous medium was also reported for only the bicarbonate solution.[57] One possibility may be the existence of minor
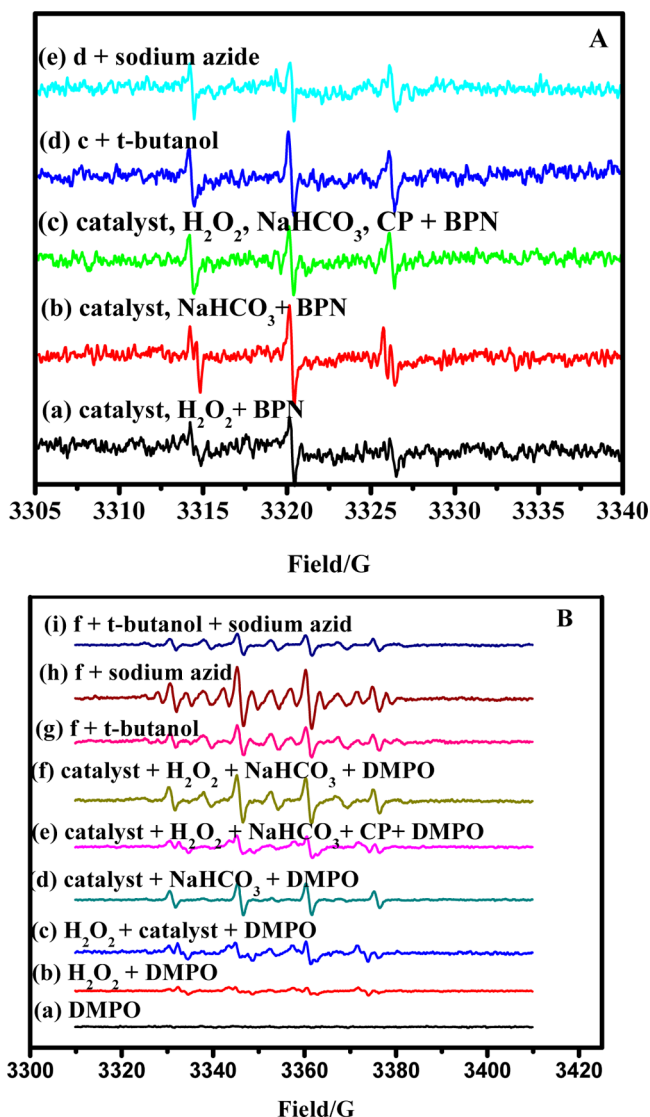
Figure 5. (A, B) Generation of superoxide and hydroxyl radical with BPN and DMPO in bicarbonate activated H_2O_2 system. Condition A: BPN 20 mM, H_2O_2 10 mM, $NaHCO_3$ 15 mM, catalyst 0.03 g, *tert*-butanol 0.5 M, NaN_3 10 mM, reaction time 5 min, reaction temperature 25 °C. Condition B: DMPO 80 mM, H_2O_2 10 mM, $NaHCO_3$ 15 mM, catalyst 0.03 g, *tert*-butanol 0.5 M, NaN_3 10 mM, reaction time 5 min, reaction temperature 25 °C.

dissolved O_2 in reaction medium that may interact with the transition metal catalyst producing ·OH or other active ROS. To ensure the presence of hydroxyl radical as predicted in both scavenger and EPR techniques, fluorescence study was conducted with coumarin as fluorescence agent that has strongly supported the existence of ·OH radical (see Supporting Information Figure S6).

Application of Catalyst in Fixed Bed Reactor. The supported catalyst (CoMgAl-BHTs) was applied in fixed bed in order to evaluate its efficiency in real practical environment in term of 4-CP degradation along with depletion of TOC and COD as the main indicators. The supported catalyst was evaluated in glass reactor for 300 h with continuous flow of reactant solution, and its efficiency was evaluated by withdrawing samples periodically after sufficient flushing of reactant solution. Results indicated that in the initial 168 h, almost complete removal of CP was observed with an average of 80%

removal in COD and about 75% removal in TOC. The efficiency of fixed bed catalyst gradually dropped to 72% and 68% for COD and TOC removals, respectively, while CP degradation still remained higher than 90% even after 300 h (Figure 6). During the experiments, leaching of Co was also
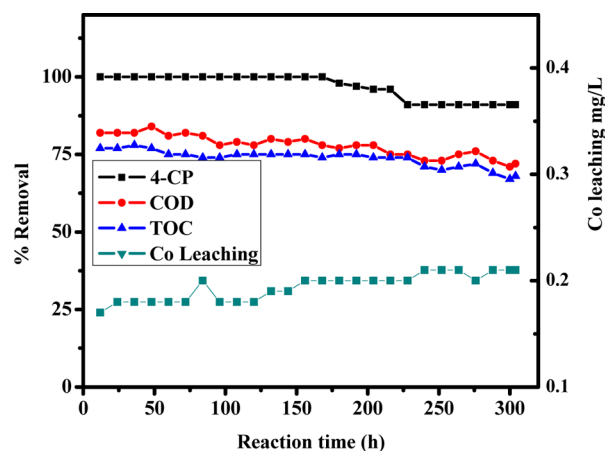

Figure 6. 4-Chlorophenol degradation and COD and TOC removal in fix bed down flow reactor. Conditions: reactor (height of 60 cm and inner diameter 1 cm), 15 g of supported catalyst (cylindrical blocks, length of 5 mm, diameter of 4 mm), 50 ppm 4-CP solution, 30 mM H_2O_2 and $NaHCO_3$ oxidant solution, 47 mL/h (1:1 (v/v) chlorophenol/oxidant), 24 min retention time, reaction temperature 40 °C.

monitored. Results show that during the entire catalytic run, the leaching of Co was ranging from 0.17 to 0.21 ppm, which is greatly lower than the permissible limit for Co (1 ppm) according to Chinese standards GB 25467-2010. It is important that for real practical applications, any measurable release of metal ions into the solution after treatment will be considered as a potential limitation for a process. However, most advanced oxidation technologies are associated with formation of various acidic intermediates that considerably decreases the pH of the medium and hence leads to leaching of metals ions from their oxide catalysts. In the present oxidation system, the pH of the solution ranges between 8.84 and 8.98 because of the presence of bicarbonates, which prohibits the leaching of metals ion into the solution. On the other hand, the oxidation state of Co regularly changes between +2 and +3 during pollutant treatments, which causes a loose coordination environment and thereby encourages the leaching of cobalt. Accordingly, with leaching of Co, the catalytic activity gradually drops for any catalytic process. It is worth mentioning that the content of Co in this fixed bed catalyst was only 0.37%, which is much lower than the common oxide catalysts used in related studies. One may expect that with the increase of Co content on the catalyst, its lifetime would also extend remarkably. Here, the long life and stability of the fix bed test are quite encouraging for practical applications and a minor change in its efficiency may be attributed to Co leaching as the treatment proceeded for a longer duration.

■ **CONCLUSIONS**

In the present study, the catalysts CoMgAl-HTs and CoMgAl-SHTs showed good catalytic activity at ambient conditions. For both catalysts nearly 80% COD and TOC removal was achieved on bench level as well as in fixed bed reactor,

respectively. The leaching of active cobalt metals was controlled by using sodium bicarbonate that provides weak alkaline buffer conditions. The leaching of cobalt metals ions in fixed bed catalyst falls in the range of 0.17−0.21 ppm for the entire 300 h running time. The catalyst on bench level showed the maximum of its activity in less than 5 min, while the catalyst in fixed bed reactor showed 100% CP removal for the first 168 h and then it remained constant at 90% even after 300 h. The activity of the catalyst markedly increased with addition of bicarbonate producing superoxide, hydroxyl and carbonate radical. The generation of these possible reactive oxygen species involved in the degradation process was confirmed by using radical scavengers, photoluminescence probing, and electron paired resonance (EPR) measurements. This bicarbonate activated hydrogen peroxide technology may provide an alternative choice for the common advanced oxidation technologies in wastewater treatments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Influence of H_2O_2 on the degradation of 4-chlorophenol (Figure S1), influence of reaction time on the degradation of 4-chlorophenol (Figure S2), influence of calcination temperature on degradation of 4-chlorophenol (Figure S3), influence of ascorbic acid on the degradation of 4-chlorophenol (Figure S4), influence of tert-butanol on the degradation of 4- chlorophenol (Figure S5), and fluorescence study as indication of generation hydroxyl radical (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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