

Catalytic Efficiency and Stability of Cobalt Hydroxide for Decomposition of Ozone and *p*-Chloronitrobenzene in Water

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Abstract:

Cobalt hydroxide, a stable and efficient catalyst prepared in the laboratory, has been successfully used in the decomposition of ozone and trace quantities of *p*-chloronitrobenzene (*p*CNB) in water. The cobalt hydroxide was characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and the Brunauer-Emmet-Teller (BET) method. The decomposition rate of aqueous ozone was increased by 1.527 times in the presence of cobalt hydroxide. Increasing the catalyst loading from 0 to 500 mg/L increased the removal efficiency of *p*CNB from 59% to 99%. The catalyst morphology and its composition were found to be unaltered after the catalytic reaction. After five successive recycles, the catalyst remained stable in the catalytic ozonation of *p*CNB.

Keywords: Cobalt hydroxide; Catalytic ozonation; Ozone decomposition; *p*-chloronitrobenzene; Catalytic stability

1. Introduction

Ozone has recently received much attention in water treatment technology, due to its high capacity for oxidation and disinfection. The ozonation process is a proven technology for

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removing various types of environmental pollutants, such as dyes, herbicides and other pesticides in aqueous solution [1-3]. It is well known that the reaction of ozone with organic substrates follows two reaction mechanisms [4]: (1) molecular ozone oxidation (direct reaction), and (2) free radical oxidation (indirect reaction). Recent studies on ozonation focus on the enhancement of ozone gas-liquid mass transfer and the production of OH radicals ($\cdot\text{OH}$). For lower cost and simpler operation, catalytic ozonation has been considered to be an efficient method in studies reported in the last few years [5]. Promising results have been obtained using metal oxides, supported metals or carbon catalysts as the catalyst for ozonation [6].

Hydroxides are well known as the simplest compounds formed by highly charged cations, not only in neutral and basic, but also in acidic, water solutions. Hydroxides of many metals are widely used as, for example, sorbents, ion exchangers and collectors of admixtures. Despite some properties of hydroxides being highly attractive for catalysis in general, and for catalytic oxidation processes in water solutions in particular [7], hydroxides have not yet found extensive application as catalysts and have not yet been practically studied as catalysts in catalytic ozonation processes. Some hydroxides, such as FeOOH , have received some attention [8-10], but, to date, studies of cobalt hydroxide as a catalyst for ozonation have not been reported.

As a typical chemical raw material, halogenated nitroaromatic compounds are widely used in fields such as agricultural chemicals, medicines, dyes, lumber preservation and materials synthesis. The nitro group and the halogen atom are both electron-withdrawing groups, resulting in the density of the electron cloud of the benzene ring being decreased compared to benzene itself. Halogenated nitroaromatic compounds are therefore less susceptible to electrophilic attack, e.g. from oxidase in biological systems. As a result, halogenated nitroaromatic compounds undergo

limited biodegradation and are likely to be found as contaminants in environmental systems. For example, *p*-chloronitrobenzene (*p*CNB), a typical and ordinary halogenated nitroaromatic compound, has already been detected in many lakes and rivers [11,12]. Methods for removal of these halogenated nitroaromatic compounds from aqueous environmental systems must therefore be developed. One possible method for their removal is catalytic ozonation.

The objectives of this study were (1) to identify the characteristics of cobalt hydroxide catalyst, (2) to investigate the catalytic efficiency of cobalt hydroxide for the decomposition of ozone and *p*CNB in water, and (3) to explore the stability of the catalyst cobalt hydroxide.

2. Materials and Methods

2.1 Materials

Milli-Q ultrapure water (specific resistance ≥ 18 M Ω -cm) was used throughout these experiments. A stock solution of *p*CNB (99.5% purity, Chem Service, USA) was prepared with a concentration of 100 mg/L and stored in an amber flask. All other chemicals were reagent grade, or HPLC grade when available, and used without further purification.

The catalyst, cobalt hydroxide, was prepared in the laboratory by the alkali precipitation method. The precipitate was obtained by slowly mixing aqueous solutions of 1 mol/L NaOH and 0.5 mol/L cobalt nitrate with magnetic stirring. The suspension was aged at 60 °C and pH 12 for over 72 h. The precipitate was then collected and repeatedly rinsed with water until the pH and conductivity of the rinse water remained constant in three consecutive rinses. The precipitate was dried at 70 °C for 16 h and then ground. Particles with diameter less than 0.35 mm were used as catalyst for the decomposition of ozone and trace *p*CNB in water. The characteristics of the catalyst were investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM) and

the Brunauer-Emmet-Teller (BET) method, and the results are listed in [Table 1](#).

Table 1 Major characteristics of cobalt hydroxide

Parameter	Before use	After use
BET surface area (m ² /g)	23.9	29.3
Pore volume (single point, cm ³ /g)	0.088	0.132
BET pore size (Å)	147.54	132.82
Particle size (nm)	hexagonal platelets <200	hexagonal platelets <200
pH _{pzc} (point of zero charge)	7.34	7.25
pH _{iep} (isoelectric point)	10.5	10.3
Amount of surface hydroxyl groups (mmol/g)	3.21	3.22

2.2 Experimental procedure

Catalytic activity experiments were carried out in a [1200 mL](#) flat-bottomed flask as the reactor vessel. Ozone was generated from pure oxygen by an ozone generator (DHX-SS-1G, Harbin Jiu Jiu Electrochemistry Engineering Ltd., China). Ultrapure water (1 L), with pH pre-adjusted by addition of aqueous solutions of NaOH or HClO₄, was transferred into the reactor. Using a silicon dispenser, ozone was bubbled into the reactor to the desired concentration, which was tested by the indigo method. Then, the catalyst (100 mg) and stock *p*CNB solution (1 mL) were immediately dosed into the reactor to achieve concentrations of 100 mg/L and 100 µg/L, respectively. A magnetic stirrer was used to achieve sufficient mixing of ozone solution with the catalyst and stock *p*CNB solution, so that a favorable mass transfer rate was expected. The reaction temperature was maintained at 20±1 °C by a thermostatted water bath. Samples (50mL) were taken at specific time intervals (0, 3, 5, 10 and 20 min), and the residual ozone was instantly

quenched by 0.1 mL of aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (0.1 mol/L). The quenched samples were then analyzed by gas chromatography (GC) for *p*CNB quantification.

2.3 Analytical methods

XRD powder patterns were recorded on a diffractometer (D/max-rB, Japan) using Cu $K\alpha$ radiation ($\lambda=0.15418$ nm, 40 kV voltage, 150 mA electric current, 0.02° of step, and $10-90^\circ$ of scanning range). Scanning electron microscopy (SEM, Hitachi S-4700, Japan) was used in imaging. Prior to SEM measurements, the samples were mounted on a platform using PVC glue and were then gold-coated by a sputter. The plate containing the sample was placed in the electron microscope for analysis with magnification of 10,000. The textural properties such as Brunauer-Emmet-Teller (BET) specific surface area, pore volume and pore size were determined by nitrogen adsorption. Nitrogen adsorption-desorption isotherms were recorded on a commercial gas adsorption system (ASAP 2020M, Micromeritics, USA). The density of surface hydroxyl groups, expressed in mmol per unit gram, was measured according to a method described by Tamara and Tanaka [13]. The pH_{pzc} (pH of point-of-zero charge) of the catalyst was measured with a powder addition method [14]. The isoelectric point was determined by a Zeta-Meter System (Zetasizer Nano, Malvern, British).

The concentration of aqueous ozone was determined by the indigo method at 612 nm with a UV-visible spectrophotometer (T6, Beijing, China) [15]. *p*CNB was extracted from water samples using hexane and the hexane extracts were analyzed using a GC equipped with an electron capture detector (6890D, Agilent, USA) and a capillary column (Hewlett Packard HP-5, $15\text{ m}\times 0.53\text{ mm}\times 1.5\text{ }\mu\text{m}$, USA) [12]. Metals leaching from the catalyst into the solution were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima5300DV, Perkin

Elmer, USA).

3. Results and Discussion

3.1 Characterization of the catalyst

The crystal structure of cobalt hydroxide (unused catalyst) was examined by XRD as shown in Fig. 1. From the peak intensity of the diffractograms, this pink powder has XRD patterns which correspond to β -Co(OH)₂ in the JCPDS databank. The surface configuration with thin hexagonal platelets was clearly observed in the SEM micrograph (Fig. 2a), which showed the typical appearance of the cobalt hydroxide β . The average size of the hexagonal platelets was in the range of 50~200 nm.

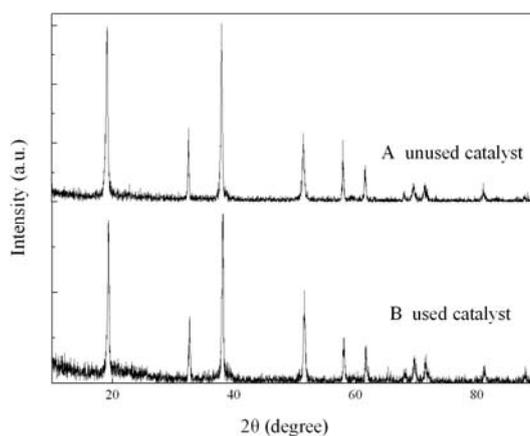


Fig. 1. XRD pattern of cobalt hydroxide catalyst, A: before use, and B: after use, in catalytic ozonation experiments

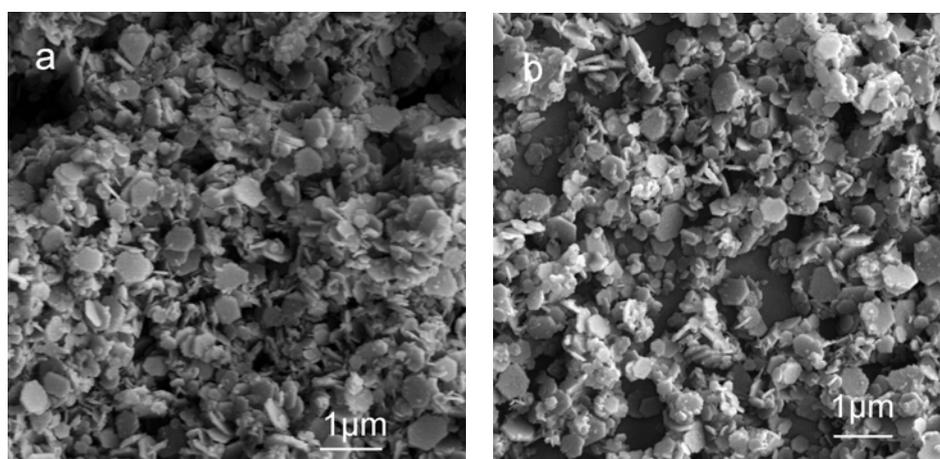


Fig. 2. SEM micrographs of cobalt hydroxide catalyst, a: before use, and b: after use, in catalytic ozonation experiments

3.2 Catalytic efficiency of the catalyst

The decomposition of ozone in water at $\text{pH}=7.5\pm 0.1$, both with and without cobalt hydroxide, was studied in order to determine the role of cobalt hydroxide on the decomposition of dissolved ozone. From Fig. 3A, the decomposition of ozone followed first-order kinetics both with and without cobalt hydroxide. The first-order decomposition of aqueous ozone was obviously enhanced in the presence of cobalt hydroxide, with its decomposition rate increasing by 1.527 times.

Ozonation of *p*CNB both with and without cobalt hydroxide was then studied and the normalized concentration of *p*CNB versus time is shown in Fig. 3B. Compared to 60% removal efficiency of *p*CNB with ozonation alone, *p*CNB was more effectively degraded (98%) at the reaction time of 30 min in the catalyzed ozonation process. It is proposed that cobalt hydroxide induced and promoted the chain decomposition of ozone, which leads to the generation of hydroxyl radicals. In this way, the dominant oxidant in the process was not ozone but rather hydroxyl radicals. Hence, cobalt hydroxide showed a great effect on the catalytic decomposition of ozone and *p*CNB. Fig. 3B also shows the solution cobalt ion concentration during the course of the ozonation experiment. During the catalytic ozonation of *p*CNB, the plateau concentration (0.017 ± 0.002 mg/L) of cobalt cation in water was observed after the reaction time of 10 min. Ozonation of *p*CNB in the presence of 0.05 mg/L dissolved Co^{2+} (added in the form of CoCl_2) was also investigated under the same experimental conditions, but the increase in removal of *p*CNB was less than 2%, so it is the cobalt hydroxide solid which is providing the catalytic effect on the

decomposition rather than the Co^{2+} in solution.

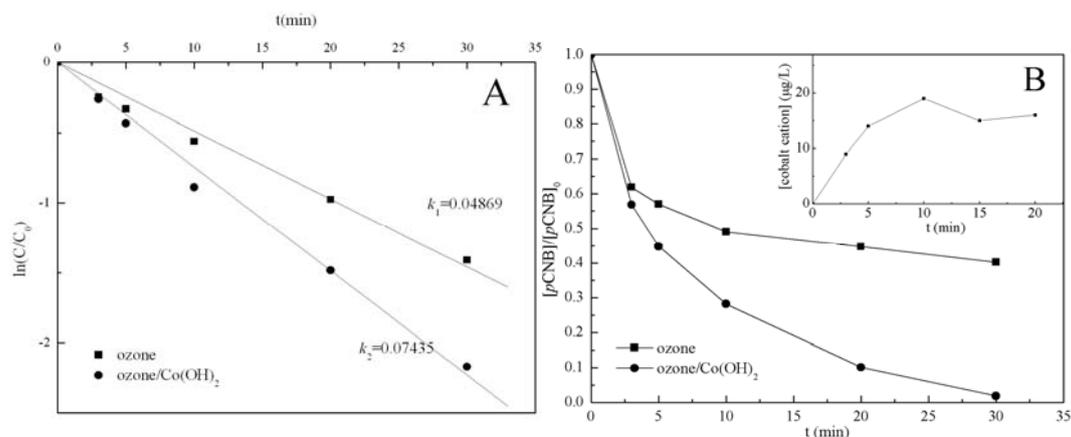


Fig. 3. Cobalt hydroxide catalyzed decomposition of (A) ozone and (B) *p*CNB ($[\text{O}_3]=1 \text{ mg/L}$, $[\beta\text{-Co(OH)}_2]=100 \text{ mg/L}$, $\text{pH}=7.5\pm 0.1$, $t=20\pm 1 \text{ }^\circ\text{C}$, $[\textit{p}\text{CNB}]=100 \text{ }\mu\text{g/L}$)

3.3 Catalyst dose

Catalyzed ozonation of *p*CNB using various concentrations of cobalt hydroxide (50 to 500 mg/L) was then studied. As demonstrated in Fig. 4, increasing the cobalt hydroxide dose significantly increased the decomposition of *p*CNB when the concentration of ozone was constant, indicating that the dominant oxidant in the reaction increased when the catalyst dose was increased. Increasing the catalyst loading from 0 mg/L to 50mg/L, 100mg/L, 200mg/L and 500 mg/L increased the *p*CNB removal efficiency from 59% to 80%, 94%, 98% and 99%, respectively, at reaction time 30 min. These results provide further evidence for the generation of some other, more effective oxidant (such as hydroxyl radical) when cobalt hydroxide is used as a catalyst in the process and illustrate the effectiveness of cobalt hydroxide as a catalyst in catalyzed ozonation. The removal efficiency of *p*CNB at the different catalyst concentrations was found to be directly related to the ozone decomposition rate, presumably because the increased amount of catalyst provided more active sites for adsorption and further decomposition of ozone and *p*CNB. However, when the catalyst loading was more than 100 mg/L, increasing the cobalt hydroxide

concentrations resulted in only low increases in the removal efficiency of *p*CNB. This was possibly due to more combination of the hydroxyl radicals with each other when more hydroxyl radicals were produced at the higher catalyst concentrations. The formation of dissolved cobalt ion during the catalytic ozonation process was determined, with concentrations of cobalt ion after 30 min reaction time being found to be 0.009 mg/L, 0.015 mg/L, 0.039 mg/L and 0.057 mg/L when 50 mg/L, 100 mg/L, 200 mg/L and 500 mg/L of catalyst was used, respectively. These results suggest that increasing the catalyst loading is likely to bring proportional increases in cobalt dissolution, although the overall amount of this dissolution is minimal.

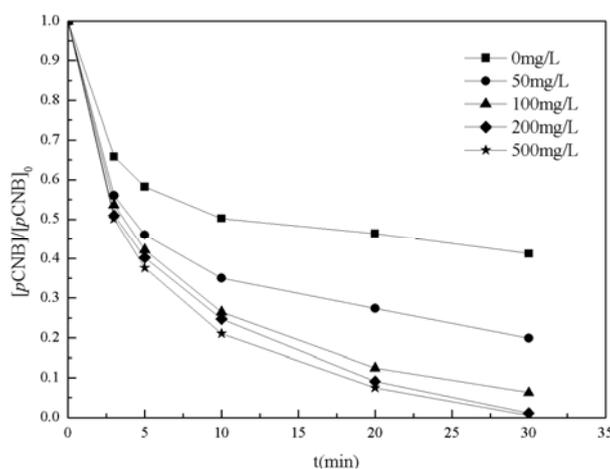


Fig. 4. Effect of catalyst dosage on the ozonation of *p*CNB ($[O_3]=1$ mg/L, $pH=7.5\pm 0.1$, $t=20\pm 1$ °C, $[pCNB]=100$ $\mu\text{g/L}$)

3.4 Catalyst stability

Since the stability and reusability of the catalyst are important factors in catalyzed reactions, especially for practical industrial applications, the stability of the cobalt hydroxide catalyst was investigated by reuse of one sample of catalyst in five successive ozonation experiments. All of the catalyst reuse experiments were carried out under identical reaction conditions. At the end of each catalytic ozonation process, the insoluble catalyst was isolated and then rinsed gently with

boiled Milli-Q ultrapure water. The washed catalyst was dried under atmospheric conditions, ready for use in the next ozonation experiment. Results of the catalyzed ozonation of *p*CNB with the recycled sample of catalyst are shown in Fig. 5. In the five catalytic ozonation experiments, 99%, 97%, 93%, 88% and 86% of decomposition of *p*CNB was observed at reaction time 30 min. The ozonation efficiencies of the first and second use of the catalyst were very similar. However, slight decreases in *p*CNB removal efficiencies were observed with further reuse of the catalyst sample, although the efficiencies still remained very high. Similar results were reported by Rivas and coworkers using cobalt-alumina catalysts in aqueous ozone decomposition reactions [16]. ICP analysis showed that, after 30 min of reaction time, 0.027 mg/L, 0.034 mg/L, 0.041 mg/L, 0.043 mg/L and 0.062 mg/L of cobalt cation was detected in the reaction solution in the five successive reuses of the catalyst, respectively. Less than 0.1 mg/L of cobalt cation was observed in all recycles; the percentage of cobalt leached from the catalyst was less than 0.03% for all reuses of the catalyst. These results indicate that the catalyst has excellent long-term stability.

The excellent consistency of the catalytic activity is likely to be attributable to the stable structure of the catalyst, which is indicated by the XRD, SEM and BET measurements. Fig. 1 shows the XRD patterns of the used and unused catalysts. There is no distinct difference between the two patterns, indicating that no obvious change in cobalt hydroxide crystal structure occurred during the catalytic reaction. From the morphology in the SEM micrograph, the used catalyst (Fig. 2b) seems to be identical to the fresh catalyst (Fig. 2a), with both existing as thin hexagonal platelets in the configuration. As can be seen in Table 1, no significant changes were observed in the BET surface area, pore volume (single point), BET pore size or particle size after use of the catalyst. The XRD, SEM and BET results confirmed that the cobalt hydroxide catalyst was stable

during the decomposition of ozone and *p*CNB and that the catalyst is suitable to reuse in repeated decomposition experiments.

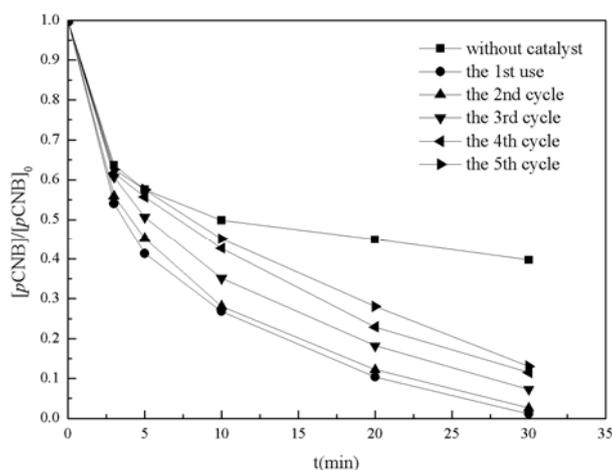


Fig. 5. Effect of catalyst recycle on the ozonation of *p*CNB ($[O_3]=1$ mg/L, $[\beta-Co(OH)_2]=200$ mg/L, $pH=7.5\pm 0.1$, $t=20\pm 1$ °C, $[pCNB]=100$ μ g/L)

4. Conclusions

Synthesised cobalt hydroxide was observed to have the typical appearance of cobalt hydroxide β , with thin hexagonal platelets. This cobalt hydroxide was found to be a useful catalyst for the decomposition of aqueous ozone and heterogeneous ozonation of trace concentrations of *p*CNB in water. The addition of cobalt hydroxide increased the decomposition efficiency of ozone and *p*CNB as compared to ozone alone. Increasing cobalt hydroxide doses resulted in significantly increased decomposition efficiencies of *p*CNB. It is proposed that cobalt hydroxide induces and promotes the chain decomposition of ozone, which leads to the generation of hydroxyl radicals. The catalyst was found to be stable and to retain its catalytic activity for up to at least five successive recycles. Studies of fresh and used catalysts by XRD, SEM and BET confirmed the stability of the catalyst. Cobalt dissolution was found to be less than 0.1 mg/L in all experiments. Overall, cobalt hydroxide catalyst was found to be an efficient and potential catalyst in the

industrial application of the decomposition of ozone and *p*CNB in water.

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