Co-Mn-Al 层状双氢氧化物催化臭氧氧化水中有机污染物的活性

隋铭皓*, 段标标, 盛 力, 黄书杭, 余 磊

同济大学环境科学与工程学院污染控制与资源化国家重点实验室, 上海 200092

摘要: 采用共沉淀法制备了 Co-Mn-Al 层状双氢氧化物, 并将其用于以硝基苯为目标污染物的催化臭氧降解反应中。结果表明, Co-Mn-Al 层状双氢氧化物存在时, 硝基苯的降解和矿化效率较单独臭氧氧化系统显著提高。采用加入羟基自由基捕获剂 (叔丁醇) 和电子顺磁共振检测 (5,5-二甲基-1-吡咯啉-*N*-氧化物为捕获剂) 的间接、直接方法, 探讨了 Co-Mn-Al 层状双氢氧化物是否强化了羟基自由基的生成。结果表明, 加入叔丁醇降低了硝基苯的降解效率; 电子顺磁共振检出了更强的羟基自由基加成物生成信号。Co-Mn-Al 层状双氢氧化物的存在促进了羟基自由基的生成。

关键词: 层状双氢氧化物; 催化臭氧; 硝基苯; 叔丁醇; 电子顺磁共振; 羟基自由基

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*通讯联系人. 电话: (021)65982691; 传真: (021)65986313; 电子信箱: suiminghao.sui@gmail.com

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Catalytic Performance of Layered Double Hydroxides Co-Mn-Al for Ozonation of Organic Pollutants in Water

SUI Minghao*, DUAN Biaobiao, SHENG Li, HUANG Shuhang, SHE Lei

State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

Abstract: The catalytic activity of layered double hydroxides containing Co, Mn, and Al for the ozonation of organic pollutants in water was investigated. The Co-Mn-Al layered double hydroxides were prepared by coprecipitation. Nitrobenzene was used as a model compound, and it was shown that the degradation and mineralization of nitrobenzene was increased by the presence of Co-Mn-Al layered double hydroxides as compared to ozonation alone. Both an indirect method of adding a scavenger (*tert*-butanol) of the hydroxyl radical chain reaction and direct electron spin resonance using 5,5-dimethyl-1-pyrroline-*N*-oxide as a spin trapping agent were used to investigate the generation of hydroxyl radicals in the ozonation by the Co-Mn-Al layered double hydroxides. The inhibiting effect of *tert*-butanol on the degradation of nitrobenzene and the detection of the stronger 5,5-dimethyl-1-pyrroline-*N*-oxide/hydroxyl radical adduct showed that the Co-Mn-Al layered double hydroxides catalyzed the generation of hydroxyl radicals.

Key words: layered double hydroxide; catalytic ozonation; nitrobenzene; *tert*-butanol; electron spin resonance; hydroxyl radical

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*Corresponding author. Tel: +86-21-65982691; Fax: +86-21-65986313; E-mail: suiminghao.sui@gmail.com

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Heterogeneous catalytic ozonation is an efficient technology to remove organic pollutants in aqueous solutions [1,2]. The key to high degradation effectiveness is to have

highly active catalysts. Transition metals are commonly applied as catalysts in ozonation because they have variable oxidation states [3–5]. The effectiveness of the heterogene-

ous catalytic ozonation process is often ascribed to the generation of hydroxyl radicals ($\cdot\text{OH}$), which are strong oxidative species that react non-selectively with compounds [6].

Layered double hydroxides (LDHs) have received increasing attention in recent years. They have been used in environmental remediation as adsorbents, catalysts, and catalyst supports [7–9]. The general formula of the LDHs is $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}] \cdot \text{H}_2\text{O}$, where M^{II} represents a divalent metal, M^{III} a trivalent metal, and A^{n-} an anion. The many choices for M^{II} and M^{III} , especially from the transition metals, and the hydroxyl groups in the layer structure give the LDH materials high catalytic activity towards ozone [1]. Furthermore, the OH^- groups behave as a weak base that can also activate ozone to decompose into hydroxyl radicals [10]. However, there has been no investigation of the catalytic activity of LDHs in ozonation.

In the present study, the catalytic activity of LDHs containing cobalt and manganese cations on ozonation was investigated using nitrobenzene (NB) as a model organic pollutant. NB is resistant to oxidation by ozone alone because of the strong electron-withdrawing property of the nitro group [11]. Both cobalt and manganese have shown catalytic activity with ozone for the removal of organic pollutants in aqueous solution [12–14]. Thus a catalyst that combines cobalt and manganese in a composite material is also expected to have good catalytic activity with ozone.

1 Experimental

1.1 Catalyst preparation and characterization

The catalysts were prepared by the coprecipitation method [15]. The samples are denoted by their elemental compositions and molar ratios of the constituents. The following samples were prepared: Co4Al2, Co4MnAl, and Co4Mn2. For example, Co4MnAl is a sample containing Co, Mn, and Al in the molar ratio of 4:1:1. The detailed preparation procedure is as follows. Nitrate solution (250 ml) comprising $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the $\text{Co}/(\text{Mn} + \text{Al})$ molar ratio equal to 2 and a total metal ion concentration of 1.0 mol/L was added with a flow rate of 5.0 ml/min into a mixed flow reactor. Simultaneously, alkaline solutions of 0.5 mol/L Na_2CO_3 and 3.0 mol/L NaOH were added at a variable flow rate to keep the reaction pH at 10.0 ± 0.1 . The coprecipitation was carried out at 25 °C under vigorous stirring for 2 h. The resulting suspension was centrifuged and the product was filtered off and repeatedly washed, and then dried at 60 °C in air.

The chemical composition of the samples was determined by a S4 Explorer X-ray spectrometer (Germany). XRD patterns were recorded by a D8 Advance Bruker AXS. The

specific surface area and porosity were measured using a QuadraSorb SI instrument from Quantachrome (America). A JEM2011 transmission electron microscope (JEOL, Japan) was used to record the TEM images of the samples.

1.2 Ozonation procedure

The ozonation experiments were performed in semi-batch mode in a glass column reactor. Ozone was generated by a corona discharge ozone generator using air as feed gas (DHX-I, Harbin Jiujiu Electrochemistry Technology Co. Ltd., China). In a typical catalytic ozonation, catalyst and NB solution (500 ml) were first added into the reactor, which was followed by the continuous feeding of ozone. In the adsorption test, air but not ozone was fed into the reactor with the other reaction conditions being the same as with the catalytic process. Ozone decomposition test was performed in batch mode. Ozone was first continuously bubbled into 250 ml water for 5 min. Then the catalyst was added accompanied with stirring. Samples were withdrawn at intervals to determine the residual ozone concentration. Each ozone decomposition test was conducted in triplicate and the results were expressed as mean $\pm$ standard deviation. An analysis of variance (ANOVA) was used to test the significance of results.

1.3 Analytical methods

The concentration of NB was determined by a high performance liquid chromatograph (HPLC, Waters UV/Visible 2489, Waters e2695 Separation Module, Welch Materials, Inc.). The mineralization of NB was measured by a total organic carbon (TOC) 3201 analyzer (Shimadzu Co., Japan). Ozone concentrations in the gas and aqueous solution were determined using the iodometric titration and indigo methods, respectively [16,17]. Electron spin resonance (ESR) spectra were recorded on a Bruker EMX-8/2.7 spectrometer (ER 4119HS cavity) at 18 °C. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO, 97%) was pre-purified with activated carbon powder under N_2 atmosphere. The instrument parameters used were: microwave frequency, 9.875 GHz; microwave power, 20.0 mW; modulation frequency, 0.1 GHz; modulation amplitude, 1 Gs; and the spectral width, 100 G.

2 Results and discussion

2.1 Characterization of LDHs

The physicochemical properties of the catalysts are listed in Table 1. The molar ratios of cations in the samples corresponded approximately to those in the nitrate solutions used

Table 1 Physicochemical properties of the LDHs samples

Sample	Elemental composition (wt%)			Co:Mn:Al molar ratio	<i>a</i> /nm	<i>c</i> /nm	Surface area (m ² /g)	Pore volume (ml/g)	Average pore diameter (nm)
	Co	Mn	Al						
Co4Al2	35.50	—	8.23	4.00:0:2.03	0.30666	2.25972	59.60	0.442	29.64
Co4MnAl	34.10	8.38	4.65	4.00:1.05:1.19	0.30902	2.27472	66.65	0.487	29.23
Co4Mn2	32.70	16.20	—	4.00:2.13:0	0.31172	2.27478	104.10	0.524	20.11

for coprecipitation. Of the three samples, Co4Mn2 possessed the highest specific surface area, highest pore volume, and smallest pore diameter.

As illustrated in Fig. 1, all the samples showed diffraction

Fig. 1. XRD patterns of Co-Mn-Al LDH.

patterns typical of layered double hydroxides, in which the features included a high intensity peak (003) at low degree ($2\theta = 11.72^\circ$) followed by two weaker peaks at $2\theta = 23.5^\circ$ (006) and 34.7° (009), and two small peaks (110) and (113) corresponding to the characteristic peaks of transition metal oxides at $2\theta = 60^\circ$ – 63° [18,19]. Poorer crystallinity was observed with the intercalating of manganese ions. The lattice parameters are summarized in Table 1, in which “*a*” was obtained from the position of the (110) peak as $a = 2d(110)$, and “*c*” was calculated from the position of the first basal (003) peak as $c = 3d(003)$ [20].

The TEM images of the Co4Al2, Co4MnAl, and Co4Mn2 LDHs are also shown in Fig. 2. The average size of the particles was 50 nm. Relatively homogeneous layers consisting of thin curved platelets were formed as shown for Co4Al2, Co4MnAl, and Co4Mn2, which showed that the samples all exhibited the typical structure of a LDH. Further, the Co4MnAl and Co4Mn2 showed poorer crystallinity in comparison to Co4Al2.

Fig. 2. TEM images of Co-Mn-Al LDHs. (a, d) Co4Al2; (b, e) Co4MnAl; (c, f) Co4Mn2.

2.2 Catalytic activity of Co-Mn-Al LDHs on ozonation of NB

All the samples gave good catalytic activity in the ozonation of NB. This is shown in Fig. 3. The degradation of NB was increased in the presence of Co₄Al₂, Co₄MnAl, and Co₄Mn₂ compared to the case of ozonation alone. The most degradation of NB (59.5%) was observed with ozone and 0.5 g/L of Co₄Mn₂. The adsorption of NB on the surface of Co-Mn-Al LDHs was investigated under the same experimental conditions as used in the catalytic ozonation but with air and no ozone feed into the reactor. Only 3.5%, 2.8%, and 3.9% NB were observed to be adsorbed on Co₄Al₂, Co₄MnAl, and Co₄Mn₂, respectively. Thus, it was deduced that the adsorption of NB was not important to the catalytic effectiveness of the Co-Mn-Al LDH in the ozonation of NB. Since the conversion of organic pollutants in aqueous solution into carbon dioxide and water is the final goal of water treatment, evolution of TOC during ozonation and catalytic ozonation was monitored. As shown in Fig. 3, only 2.5% mineralization efficiency (including NB and its degradation intermediates) was obtained with ozonation alone together with 13.2% NB degradation efficiency. However, the mineralization efficiency reached 11.3%, 15.7%, and 20.8% in the presence of Co₄Al₂, Co₄MnAl, and Co₄Mn₂, respectively. On comparing the degradation and mineralization of NB in the heterogeneous catalytic ozonation process with what was obtained with the ozonation alone and the adsorption of NB on the catalysts, it was obvious that the Co-Mn-Al LDHs had catalytic effects with ozone for the degradation and further mineralization of NB.

Fig. 3. Catalytic activity of Co-Mn-Al LDHs on ozonation of NB in aqueous solution. Solid lines: degradation; Dotted lines: mineralization. Ozone gas flow rate 400 ml/min, ozone gas concentration 0.41 mg/min, initial concentration of NB 10 μ mol/L, dose of Co-Mn-Al LDHs 0.5 g/L, initial pH 6.99, temperature 19 $^{\circ}$ C.

2.3 Reaction mechanism

In heterogeneous catalytic ozonation, it is now widely accepted that the increased oxidizing capacity is due to hydroxyl radical generation by ozone decomposition. To identify the reaction mechanism in Co-Mn-Al LDH catalytic ozonation, experiments on ozone decomposition in the presence of Co-Mn-Al LDHs and in their absence were carried out. Furthermore, to confirm that the generation of hydroxyl radicals was catalyzed by the Co-Mn-Al LDHs by the decomposition of ozone, an indirect method using *tert*-butanol as an inhibitor and direct ESR determination of the radical were both employed. *tert*-Butanol is a common scavenger of hydroxyl radicals. It has a relatively fast reaction rate with hydroxyl radicals ($k = 6 \times 10^8$ mol/(L·s) [21]) to generate inert intermediates, which consequently terminates the radical chain reaction. By converting the short-lived hydroxyl radicals into the relatively stable spin-adduct DMPO-OH that can be easily detected by ESR, the ESR spin trapping technique also gives direct confirmation of a hydroxyl radical reaction mechanism [22–24].

As illustrated in Fig. 4, ozone decomposition in the presence and absence of Co-Mn-Al LDHs all followed first order reaction kinetics. The decomposition rate constants of ozone with the presence of Co-Mn-Al LDHs and with ozone alone were statistically significant ($p < 0.05$). The presence of Co-Mn-Al LDHs notably accelerated ozone decomposition, and the fastest decomposition of ozone occurred in the presence of Co₄Mn₂. The decomposition rate constants were 1.2, 1.6, and 2.7 times of those in the presence of Co₄MnAl, Co₄Al₂, and ozone alone, respectively.

Fig. 4. Ozone decomposition in the presence of Co-Mn-Al LDHs. Initial concentration of ozone 2.55–2.67 mg/L, dose of Co-Mn-Al LDHs 0.5 g/L, initial pH 6.99, temperature 19 $^{\circ}$ C. Error bars represent standard deviations in triplicate tests.

The effect of *tert*-butanol on the ozonation of NB in the absence and presence of Co-Mn-Al LDHs is shown in Fig. 5. For the case of ozonation alone, the presence of *tert*-butanol impaired the degradation of NB. In the current study, all the experiments were carried out under neutral pH conditions (initial pH = 6.99), thus, it was easy to understand the effect of *tert*-butanol on NB degradation in ozonation alone. This was explained by that hydroxyl radicals were generated by ozone decomposition by hydroxide ion initiation [10]. The inhibition effect of *tert*-butanol on the Co-Mn-Al LDH catalytic ozonation processes was also observed. The presence of *tert*-butanol has a negative effect on NB degradation in the Co-Mn-Al LDH catalytic ozonation processes. The degradation of NB decreased 15.6%, 18.8%, and 27.9% when 350 $\mu\text{mol/L}$ of *tert*-butanol was added to the Co4Al2, Co4MnAl, and Co4Mn2 catalytic ozonation processes, respectively. An increase of the concentration of *tert*-butanol (700 $\mu\text{mol/L}$) further resulted in the decrease of the degradation of NB. The experimental results indicated that the Co-Mn-Al LDHs catalytic ozonation followed the hydroxyl radical reaction mechanism, and the presence of Co-Mn-Al LDHs promoted ozone decomposition into hydroxyl radicals.

Fig. 5. Effect of *tert*-butanol on ozonation of NB in the presence and absence of Co-Mn-Al LDHs. Ozone gas flow rate 400 ml/min, ozone gas concentration 0.41 mg/min, initial concentration of NB 10 $\mu\text{mol/L}$, dose of Co-Mn-Al LDHs 0.5 g/L, initial pH 6.99, temperature 19 °C. Error bars represent standard deviations in triplicate tests.

The generation of hydroxyl radicals as determined by the ESR technique is shown in Fig. 6. Its typical four line signal with the quartet signal with an intensity ratio of 1:2:2:1 and hyperfine coupling with $\alpha_N = \alpha_H = 15.0$ G were observed for the ozonation processes with and without the presence of the LDHs, which proved the generation of hydroxyl radicals. The signal intensity of the DMPO-OH adduct in the presence of the LDHs was stronger than that with ozonation

Fig. 6. Relative intensity of the DMPO-OH adduct signal in the ozonation catalyzed by Co-Mn-Al LDHs. Recording time 4.0 min, ozone dose 2.32 mg/L, LDH dose 0.50 g/L, initial pH 6.99, initial DMPO concentration 100 mmol/L, temperature 18 °C.

alone, and was in the order $\text{Co4Mn2/O}_3 > \text{Co4MnAl/O}_3 > \text{Co4Al2/O}_3 > \text{O}_3$. This confirmed that the LDHs promoted ozone decomposition which generated hydroxyl radicals.

3 Conclusions

Layered double hydroxides containing cobalt and manganese cations, designated as Co4Al2, Co4MnAl, and Co4Mn2, were used to catalyze ozonation degradation of NB in water. All the Co-Mn-Al LDHs displayed high catalytic activity for ozonation by the generation of hydroxyl radicals. Further investigation of the role of the transition metals on the generation of hydroxyl radicals will be performed to better understand LDH catalytic ozonation.

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