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Catalytic activity of CuO_n–La_2O_3/γ-Al_2O_3 for microwave assisted ClO_2 catalytic oxidation of phenol wastewater

Xiaoyi Bi, Peng Wang *, Hong Jiang

Research Center for Green Chemistry and Technology, School of Municipal and Environmental Engineering,
Harbin Institute of Technology, Harbin 150090, China

Abstract

In order to develop a catalyst with high activity and stability for microwave assisted ClO_2 catalytic oxidation, we prepared CuO_n–La_2O_3/γ-Al_2O_3 by impregnation–deposition method, and determined its properties using BET, XRF, XPS and chemical analysis techniques. The test results show that, better thermal ability of γ-Al_2O_3 and high loading of Cu in the catalyst can be achieved by adding La_2O_3. The microwave assisted ClO_2 catalytic oxidation process with CuO_n–La_2O_3/γ-Al_2O_3 used as catalyst was also investigated, and the results show that the catalyst has an excellent catalytic activity in treating synthetic wastewater containing 100 mg/L phenol, and 91.66% of phenol and 50.35% of total organic carbon (TOC) can be removed under the optimum process conditions. Compared with no catalyst process, CuO_n–La_2O_3/γ-Al_2O_3 can effectively degrade contaminants in short reaction time and with low oxidant dosage, extensive pH range. The comparison of phenol removal efficiency in the different process indicates that microwave irradiation and catalyst work together to oxidize phenol effectively. It can therefore be concluded from results and discussion that CuO_n–La_2O_3/γ-Al_2O_3 is a suitable catalyst in microwave assisted ClO_2 catalytic oxidation process.
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Keywords: Microwave; ClO_2; Catalyst; Phenol

1. Introduction

Phenol and phenolic compounds are a group of organic pollutants that often appear in wastewaters from many heavy chemical, petrochemical, and oil refining industries. Because of their toxicity and poor biodegradability [1], phenolic wastewaters must be specially treated before disposing off. Various treatment techniques have been applied to remove or eliminate phenolic compounds from wastewaters, including chemical oxidation [2], catalytic ozonation process [3], solvent extraction [4], membrane techniques [5], adsorption [6], photodegradation [7], coagulation flocculation [8], biological process [9], and so on. However, such technologies usually involve complicated procedures and are not economically viable.

Chlorine dioxide (ClO_2) catalytic oxidation process is a well-established technique to decompose toxic and/or non-biodegradable organic compounds in wastewater [10], which is able to oxidize organic pollutants into carbon dioxide or into products that can be eliminated by biological treatment. However, the traditional ClO_2 catalytic oxidation process has not been largely implemented for wastewater treatment because of the severe experimental conditions such as the limited range of pH, longer reaction time resulting in higher economical costs. Microwave assisted catalytic process offers a potential solution to these problems. In recent years, some research progresses in microwave chemistry have presented the feasibility to apply microwave in pollution control [11]. The use of microwave irradiation in catalytic reactions, including decomposition of volatile organic compounds (VOC) [12] and non-biodegradable organics in wastewater [13–15], has given some remarkable results.

Many investigators have been trying to improve the catalytic activity and stability of heterogeneous oxidation catalysts to enhance the efficiency of microwave assisted catalytic oxidation process [14–16], and lanthanum oxide or La_2O_3-containing materials have been studied as catalysts, structural and electronic promoters used for heterogeneous catalysis over past years. It has been shown that lanthanum oxide can reinforce the thermal ability of the support and improve the loading of transitional metal oxides in the catalyst [17,18].

* Corresponding author. Tel.: +86 451 86283801; fax: +86 451 86283801.
E-mail address: pwang73@hit.edu.cn (P. Wang).

In this paper, CuO/γ-Al$_2$O$_3$ and CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalysts are prepared by impregnation-deposition and characterized by BET nitrogen adsorption method, X-ray fluorescence (XRF), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques, and their catalytic activities were investigated by microwave assisted ClO$_2$ catalytic oxidation process to treat phenol, so that the catalytic activity is correlated with catalyst characteristics and the effect of La$_2$O$_3$ on the properties of CuO/γ-Al$_2$O$_3$ can be further understood.

2. Experimental

2.1. Materials

All of reagents used for these experiments were analytical grade and were used as supplied. Deionized water was used in all experiments. The stock ClO$_2$ solution was prepared by mixing a vitriol solution and a sodium chlorite solution. The stock ClO$_2$ solution was stored in dark at 4 °C and was standardized daily.

2.2. Preparation of catalysts

The catalysts were prepared by impregnation-deposition method, and γ-Al$_2$O$_3$ ($\varphi = 2$–3 mm) as carrier. The CuO/γ-Al$_2$O$_3$ was prepared by impregnation of 10 g γ-Al$_2$O$_3$ with 100 mL aqueous solution containing 0.3 mol/L CuCl$_2$ for 24 h under room condition, deposited of Cu^{2+} with the help of precipitator [19] for 24 h, dried the samples at 80 °C for 12 h and then dried at 110 °C for 2 h. The dried samples were calcined at 450 °C in an oven for 4 h to obtain CuO/γ-Al$_2$O$_3$ catalyst. The CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$, was prepared in such a sequence that La was first loaded on γ-Al$_2$O$_3$, carrier by dipping of 10 g γ-Al$_2$O$_3$, in 100 mL aqueous solution containing 0.03 mol/L for 12 h under room condition, and the samples were dried at 80 °C for 12 h and then dried at 110 °C for 2 h. The dried samples were calcined at 550 °C in an oven for 4 h, so that the intermediate La$_2$O$_3$/γ-Al$_2$O$_3$ was obtained, and Cu was then loaded on La$_2$O$_3$/γ-Al$_2$O$_3$ by impregnation, too, and following the same calcination procedure for the preparation of CuO/γ-Al$_2$O$_3$ catalyst.

2.3. Characterization of catalysts

The surface area, total pore volume and average pore size of samples were analyzed using the BET nitrogen adsorption method in an automated volumetric adsorption analyzer (model Quantachrome Autosorb-1).

The elementary compositions of samples were determined using an AXIOS pw4400 XRF analyzer operating at 4 kW with Rh Kα used as X-ray source.

XRD was employed to identify mineral phases and estimate crystallinity. Measurements were made on a D-MAX-RB diffractometer with Cu Kα radiation (λ = 1.54050 Å) at 30 mA and 35 kV in the Bragg Brentano θ–θ geometry. Samples used for XRD analysis were air-dried, crushed, and mounted on a glass sample holder. The XRD patterns were obtained using a graphite monochromator, divergence and scattering slits of 1°, detector slit of 0.15 mm, and a step scanning rate of 0.02° 2θ/s.

X-ray photoelectron spectroscopy (XPS) was used to confirm the chemical speciation of CuO, La$_2$O$_3$ on the surface of γ-Al$_2$O$_3$. XPS measurements were performed with a physical electronic 5700 spectrometer equipped with a hemispherical electron analyzer and Mg Kα X-ray source (1486.60 eV, 12.5 kV, 250 W). The pressure in the analysis chamber ranged typically from 10^{-8} to 10^{-9} mbar during spectra acquisition. Survey scan spectra (kinetic energy range: 0–1500 eV, Constant Retarding Ratio mode, retarding ratio = 3) and detailed spectra (kinetic energy range: 50 eV, Constant Analyser Energy mode, pass energy = 50 eV) were recorded for each sample. All XPS spectra were acquired at a 90° takeoff angle. Binding energies (BE) were calculated using the C 1s peak at 284.9 eV. The resolving power of the BE values was ±0.2 eV. Curve fitting was carried out using a Physical Electronics PC-ACCESS ESCA-V6.0E program with a Gaussian–Lorentzian sum function.

2.4. Analysis of catalytic activity

At the beginning of each test run, 100 mL of synthetic wastewater containing 100 mg/L phenol was placed in a sealed reactor, 50 g/L catalysts and amounts of the stock ClO$_2$ solution were added. The reactor was loaded in the microwave oven operating at 2450 MHz with 50 W and the run time was 5 min. Upon the arrival of the reaction time, the sealed reactor was taken out and refrigerated rapidly with cooling water, then added the reagent of sodium thiosulfate (Na$_2$S$_2$O$_3$) to dechlorinate ClO$_2$ residuals.

The temperatures of the wastewater were measured using a thermocouple inserted into the wastewater. The pH values were determined by a pH–3C pH meter. The concentrations of ClO$_2$, ClO$_2^-$, ClO$_3^-$ and Cl$^-$ in the 'stabilized chlorine dioxide' solution were measured by the method of continuous iodimetry and precipitation titration, respectively [20]. The suspensions were analyzed for their phenol concentrations using a 721-type ultraviolet-visible spectrophotometer by means of 4-AAP spectrophotometric method. For all tests, blank experiments were carried out with the same experimental procedures to check the extent of phenol sorption by the glass flasks, which must be deducted. In order to check the reproducibility of the results, random tests were done for different experimental conditions. TOC measurement was carried out with a TOC-VCPN Shimadzu TOC analyzer.

For evaluating the catalytic activity of catalysts, both phenol removal efficiency and TOC removal efficiency were calculated as shown below:

$$X\ (\%) = \frac{C_0 \times V_{\text{wastewater}} - C_t \times (V_{\text{wastewater}} + V_{\text{ClO}_2} + V_{\text{Na}_2\text{S}_2\text{O}_3})}{C_0} \times 100 \qquad (1)$$

Table 1
Results of BET tests

	BET surface area (m^2/g)	Total pore volume (mL/g)	Average pore size (nm)
γ-Al$_2$O$_3$	459.43	0.8131	7.078
CuO/γ-Al$_2$O$_3$	155.42	0.4270	10.988
CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$	163.72	0.4255	10.396

where C_0 and C_t are the initial and final concentration of phenol, or the initial and final TOC, respectively; $V_{wastewater}$, V_{ClO_2} and $V_{Na_2S_2O_3}$ are the volume of wastewater and adding ClO$_2$, Na$_2$S$_2$O$_3$, respectively.

3. Results and discussion

3.1. Catalysts characterization and analysis

3.1.1. BET tests of catalysts

The BET surface area, total pore volume and average pore size of the investigated catalysts are listed in Table 1. CuO/γ-Al$_2$O$_3$ catalyst and CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst reduced the surface area from 459.43 to 155.42 m^2/g and 163.72 m^2/g, respectively. Because of the introduction of Cu and La, the total pore volume and average pore size of the catalysts is largely reduced compared with the carrier. But, the BET surface area of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ is much higher than CuO/γ-Al$_2$O$_3$, the effect of La$_2$O$_3$ doping on the pore structure of CuO/γ-Al$_2$O$_3$ catalyst is obvious.

The results of BET comparison between CuO/γ-Al$_2$O$_3$ catalyst and CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst under different calcinations temperature were shown in the Fig. 1. It indicated the BET of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst was higher than the BET of CuO/γ-Al$_2$O$_3$ when calcinations temperature were 450 °C and 600 °C, respectively. But the predominance was not obvious, when calcinations temperature was 750 °C. It proved the surface modification of the carrier γ-Al$_2$O$_3$ by La$_2$O$_3$ could reinforce the thermal ability of the support within a certain extent.
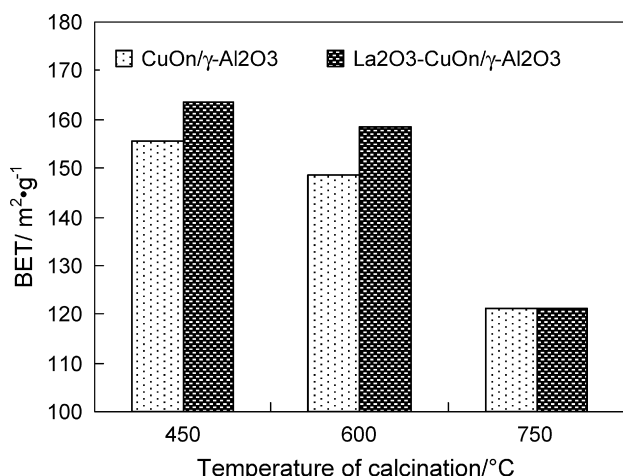
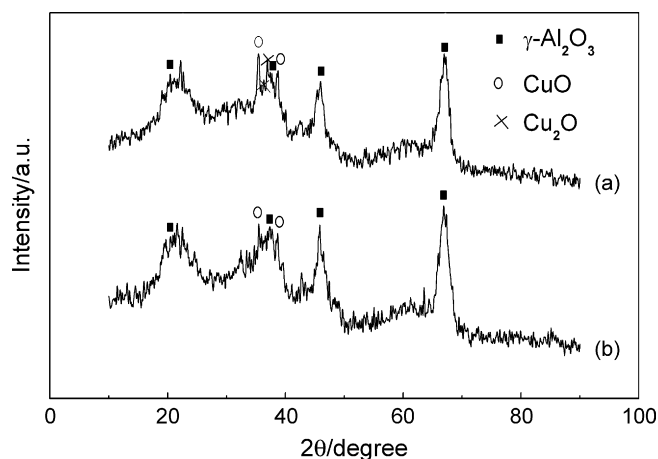Fig. 1. BET of catalyst under different calcinations temperature.

Fig. 2. XRD patterns of catalysts: (a) CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$; (b) CuO/γ-Al$_2$O$_3$.

3.1.2. XRD patterns of catalyst

Fig. 2 shows the XRD patterns of CuO/γ-Al$_2$O$_3$ catalyst and CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst. γ-Al$_2$O$_3$ phase can easily be seen in its pattern. The peaks characterizing CuO crystal can be seen in the pattern of CuO/γ-Al$_2$O$_3$ catalyst and CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst, but in the pattern of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst, the peaks characterizing Cu$_2$O crystal also appear, which verifies the addition of La$_2$O$_3$ promotes copper existing with two oxidation states. The peaks characterizing La$_2$O$_3$ crystals cannot be seen in the XRD pattern of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst, because the content of La doped in CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst is too low.

3.1.3. XPS and XRF of catalysts

The component contents of the two investigated catalysts analyzed by XRF are shown in Table 2. The content of Cu in CuO/γ-Al$_2$O$_3$ catalyst clearly increases from 0.56% to 8.12% by introduction of La, although the content of La is only 1.14% in CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst. This shows that La$_2$O$_3$ can promote the structure of supports and intensify the interaction between active component and support, so that the loading of Cu in the catalyst is improved.

Fig. 3 shows the survey XPS patterns of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst and CuO/γ-Al$_2$O$_3$ catalyst, Cu, O, Al exists on the surface of both catalysts and La is tested on the surface of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst, it is in accord with the catalyst preparation process. The Cu 2p characteristic peaks of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst is much stronger and the peaks of Cu KLL is also appeared in the survey XPS patterns of CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$ catalyst, these all prove La$_2$O$_3$ can intensify the interaction between active component and support and improve the loading of Cu in the catalyst.

Table 2
Results of XRF analysis

Catalyst	Al (%)	O (%)	Cu (%)	La (%)
CuO/γ-Al$_2$O$_3$	25.23	74.21	0.56	0
CuO$_n$–La$_2$O$_3$/γ-Al$_2$O$_3$	30.84	59.90	8.12	1.14
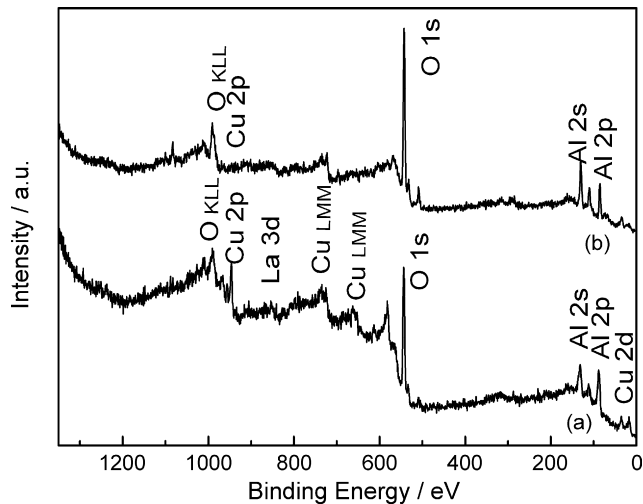
Fig. 3. Survey XPS patterns of catalyst: (a) CuO_n–La_2O_3/γ-Al_2O_3; (b) CuO/γ-Al_2O_3.

The characteristic peaks of La is not obvious in the survey XPS pattern of CuO_n–La_2O_3/γ-Al_2O_3 catalyst possibly because the loaded content of La is much lower than Cu, and CuO_n–La_2O_3/γ-Al_2O_3 catalyst is prepared by successive impregnation-sedimentation so that most of La is covered by CuO_n. It is well known that XPS can be used to analyze the surface and a limited (5–10 nm) depth of catalysts only, and so the characteristic peaks of La on the surface of CuO_n–La_2O_3/γ-Al_2O_3 catalyst is not obvious.

It can be seen from Fig. 4 that the Cu $2p_{3/2}$ peak of CuO/γ-Al_2O_3 catalyst appears at 933.5 eV, while that of CuO_n–La_2O_3/γ-Al_2O_3 catalyst appears at 933.2 eV, which is ascribable to CuO. There is no great change in Cu $2p_{3/2}$ peak before and after La_2O_3 doping, and this indicates that La_2O_3 has only a slight effect on the chemical state of CuO.

According to the results of XRD, there is Cu^+ in the CuO_n–La_2O_3/γ-Al_2O_3 catalyst, but the characteristic peaks of Cu^+ cannot be observed in the survey XPS pattern of CuO_n–La_2O_3/γ-Al_2O_3 catalyst. The reason probably is the load-

Fig. 5. Cu 2p curves fitting of CuO_n–La_2O_3/γ-Al_2O_3 catalyst (curve fitting was carried out using a Physical Electronics PC-ACCESS ESCA-V6.0E program with a Gaussian–Lorentzian sum function.).

ing of Cu^+ is too low, the characteristic peaks are covered by the characteristic peaks of Cu^{2+}. To evaluate how much Cu^+ was loaded on the CuO_n–La_2O_3/γ-Al_2O_3 catalyst, the Cu 2p spectra was fitted roughly as shown in Fig. 5. The Cu 2p peaks can be fitted into three peaks: one peak can attribute to the Cu^{2+}, one peak is due to the Cu^{2+} that cause the shake-up peak, the last one is assigned to Cu^+. The cover area ratio of Cu^+ to total area of Cu 2p is the content of Cu^+ and it perhaps is 19.11% of Cu 2p.

Fig. 6 shows La 3d XPS pattern of CuO_n–La_2O_3/γ-Al_2O_3, and La $3d_{5/2}$ peak can be observed at the binding energy of 835.8 eV, which is ascribable to La_2O_3.

It can be seen from Fig. 7 that O 1s XPS peaks of CuO_n–La_2O_3/γ-Al_2O_3 catalyst and CuO/γ-Al_2O_3 catalyst are both 530.87 ev, this indicates adding La_2O_3 cannot affect the existence of oxygen.

3.2. Demonstration of catalytic activity

Fig. 8 demonstrates the effect of ClO_2 concentration on phenol removal efficiency in microwave assisted ClO_2 oxidation
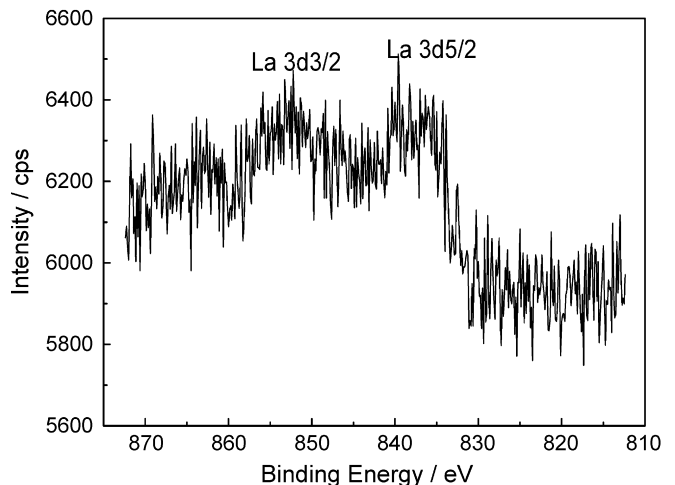

Fig. 4. Cu 2p XPS patterns of catalyst: (a) CuO_n–La_2O_3/γ-Al_2O_3; (b) CuO/γ-Al_2O_3.

Fig. 6. La 3d XPS pattern of CuO_n–La_2O_3/γ-Al_2O_3 catalyst.
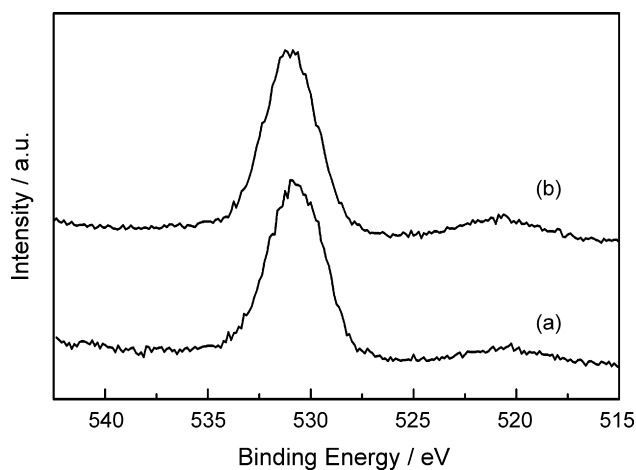
Fig. 7. O 1s XPS patterns of catalyst: (a) $CuO_n–La_2O_3/\gamma-Al_2O_3$; (b) $CuO/\gamma-Al_2O_3$.

Fig. 9. Effect of the pH value on phenol removal percentage (conditions: phenol concentration 99.7 mg/L, solution volume 100 mL, microwave power 50 W, reaction time 6 min, 80 mg/L ClO_2, 50 g/L catalyst and pH adjusted by HCl and NaOH.).

process with and no $CuO_n–La_2O_3/\gamma-Al_2O_3$ as catalyst. The results clearly show that, with catalyst, the removal percentage of phenol is much higher than that without catalyst. In the microwave assisted catalytic oxidation process, when the concentration of the ClO_2 solution was 100 mg/L, the removal rate of phenol was 91.66%. If the process without catalyst reached the same efficiency, the expense of the ClO_2 solution would be more than twice. It indicates as catalyst in microwave assisted ClO_2 oxidation process, $CuO_n–La_2O_3/\gamma-Al_2O_3$ can highly improve the removal efficiency of phenol and reduce the dosage of ClO_2 used in wastewater treatment.

In the microwave assisted ClO_2 catalytic oxidation process, wastewater will be heated by microwave irradiation, so the temperature of treated water will have a rise. In our test, the temperature of treated water would reach 47 °C under the operation conditions, so the volatility of phenol in this process should be investigated. It can be seen in Fig. 8, when the concentra-
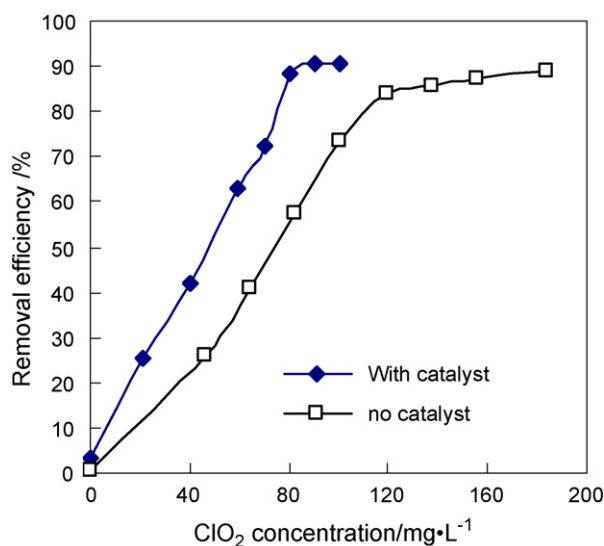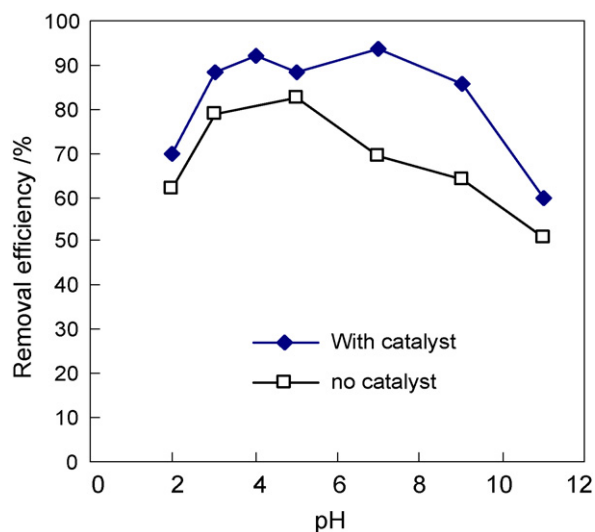

Fig. 8. Effect of ClO_2 concentration on phenol removal efficiency (conditions: phenol concentration 99.7 mg/L, solution volume 100 mL, microwave power 50 W, reaction time 6 min, 50 g/L dosage of catalyst and pH 5.6.).

tion of the ClO_2 solution was 0 mg/L in the microwave assisted ClO_2 oxidation process without catalyst, the phenol removal efficiency is only 0.78% even though the temperature of treated wastewater is 47 °C, it indicates the volatilization of phenol in our test maybe can be ignored. The corresponding point of 0 mg/L ClO_2 in the microwave assisted ClO_2 catalytic oxidation with $CuO_n–La_2O_3/\gamma-Al_2O_3$ also verified that as a carrier of catalyst, $\gamma-Al_2O_3$ could absorb phenol, but the ability was very weak, the absorption of phenol was 2.57%. Therefore, the phenol removal efficiency we got from tests is very referential.

Fig. 9 summarizes the pH value dependence of phenol removal efficiencies in the microwave assisted catalytic oxidation process with or no $CuO_n–La_2O_3/\gamma-Al_2O_3$ as catalyst, respectively. The results show that the efficiency of the phenol removal depends strongly on the pH. With the catalyst, the optimum system pH value ranged from 3 to 9, it was much wider than without catalyst, which indicated that the catalyst could obviously improve not only the removal percentage of phenol but also the ability of ClO_2 to adapt the change of system pH value.

The appropriate pH range of traditional ClO_2 catalytic oxidation process reported in other literature was lower than 7 [21], but in the microwave assisted catalytic oxidation process, the optimum pH range was lower than 9. Under pH 9, the removal efficiency in the literature decreased to 70% while that of microwave assisted catalytic oxidation process was more than 85%. It indicated that catalyst associated with microwave could improve the system adaptability of pH of wastewater, suggesting this process had advantages for the engineering application.

Treat synthetic wastewater containing 100 mg/L phenol in the different process to study the effect of microwave irradiation and catalyst, the results shown in Fig. 10 indicate that microwave irradiation or catalyst could not oxidize phenol effectively with-
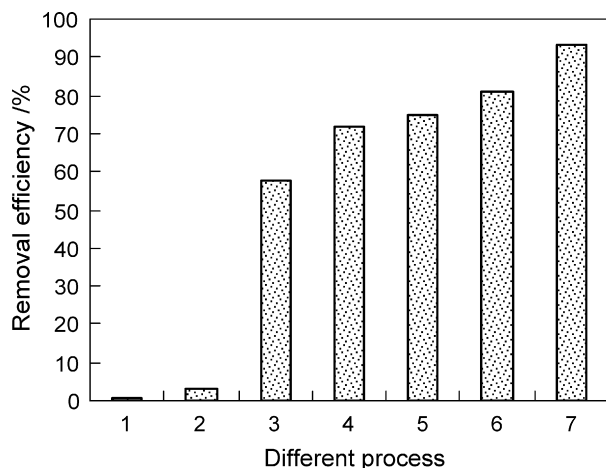
Fig. 10. Comparison of phenol removal efficiency by different treatment processes. (1) Microwave irradiation; (2) microwave irradiation + catalyst; (3) water bath + ClO_2; (4) microwave irradiation + ClO_2; (5) water bath + ClO_2 + catalyst; (6) microwave irradiation + ClO_2 + γ-Al_2O_3; (7) microwave irradiation + ClO_2 + catalyst (conditions: phenol concentration 99.7 mg/L, solution volume 100 mL, microwave power 50 W, reaction time 6 min, 80 mg/L ClO_2, 50 g/L catalyst, pH 5.6, temperature of treated wastewater under microwave irradiation 47 °C and temperature of water bath 47 °C).

out ClO_2. Under the same operation conditions, the phenol removal efficiency in microwave assisted system is much higher than traditional water bath, it can be concluded that microwave irradiation can enhance the oxidation process obviously. The effect of catalyst in process is so clear that the phenol removal efficiency is increase more than 10% compared with no catalyst. Therefore, in the microwave assisted ClO_2 catalytic oxidation process, microwave irradiation and catalyst work together to improve the phenol removal efficiency.

To investigate the oxidation degree of phenol, test the TOC of treated wastewater that the removal efficiency of phenol got by 4-AAP spectrophotometric method is 91.66%. The results show that the removal efficiency of TOC is only 50.35%. It suggests that phenol in this treatment process is not entirely oxidized into carbon dioxide. So, much effort should be given to detect new products which phenol is oxidized into and improve the TOC removal efficiency in the next study.

4. Conclusions

CuO_n–La_2O_3/γ-Al_2O_3 exhibits an excellent catalytic activity in the microwave assisted ClO_2 catalytic oxidation process so that 91.66% removal efficiency of 100 mg/L of phenol wastewater can be achieved through treatment for 5 min by keeping the power of microwave always be 50 W, adding 50 g/L and 80 mg/L of CuO_n–La_2O_3/γ-Al_2O_3 and ClO_2, respectively.

The characterization results of CuO_n–La_2O_3/γ-Al_2O_3 catalyst show that the metal oxides are dispersed equally on the surface of catalyst, and the loading amount of Cu and La in the catalyst is 8.12%, 1.14%, respectively, and La exists in the form of La_2O_3, Cu exists on the surface of catalyst in the form of CuO and Cu_2O, the ratio of Cu^+ in Cu 2p is 19.11%. Compared CuO_n–La_2O_3/γ-Al_2O_3 catalyst with CuO/γ-Al_2O_3 catalyst, we

could conclude that the surface modification of the carrier γ-Al_2O_3 by La_2O_3 could reinforce the thermal ability of the support within a certain extent and improve the loading of Cu in the catalyst. Better dispersion and smaller size of CuO_n crystal can also be achieved by adding La_2O_3.

With the existence of CuO_n–La_2O_3/γ-Al_2O_3, microwave-assisted ClO_2 catalytic oxidation process can degrade contaminants in short reaction time and with low oxidant dosage, extensive pH range. The comparison of phenol removal efficiency in the different process indicates that microwave irradiation and catalyst work together to oxidize phenol effectively. It can therefore be concluded that CuO_n–La_2O_3/γ-Al_2O_3 is a suitable catalyst in microwave assisted ClO_2 catalytic oxidation process.

Acknowledgement

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