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Effect of Rare Earth Doping on the Catalytic Activity of Copper-Containing Hydrotalcites in Phenol Hydroxylation

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Abstract: The copper-containing hydrotalcites (Cu-HTLcs) are synthesized under microwave irradiation, the effect of rare earth elements (RE) on the synthesis of Cu-HTLcs, wherein RE stands for rare earth elements, e.g., La, Y, Sm and Ce, is also investigated in the present work. The hydrotalcite structure of the synthesized samples is verified by XRD and FT-IR. The results of their catalytic performances in phenol hydroxylation show that the doped rare earth elements can promote the catalytic activity of Cu-HTLcs, exhibiting a good trend as follows: La > Y > Sm > Ce. XPS results show that the Cu^+ species are produced after the interaction of La-Cu-HTLcs with H_2O_2. Combining with the catalytic test results, we propose a new mechanism about the generation of $HO^{\bullet}$ radicals in phenol hydroxylation, it is assumed that HO-Cu^+-OH species are first formed by the reduction of HO-Cu^{2+}-OH located in hydrotalcites in the presence of H_2O_2, and then react with H_2O_2 to give rise to $HO^{\bullet}$ radicals.

Keywords: copper-containing hydrotalcites; microwave irradiation; phenol hydroxylation; rare earth elements

Introduction

Phenol hydroxylation is an industrially important reaction, its main products include catechol and hydroquinone, which are involved in diverse applications.[1] The processes using H_2O_2 as oxidant are considered to be the best foreground technique for environmentally benign chemistry due to their final by-product being water. Hydrotalcite-like compounds (HTLcs), especially copper-containing HTLcs as catalysts, have attracted increasing attention in recent years for this reaction owing to their peculiar configuration and properties.[2,3] The chemical structure of HTLcs is

$$[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[X^{m-}_{x/m}\cdot nH_2O]$$

wherein M^{II} represents divalent metal ions and M^{III} trivalent metal ions, X^{m-} stands for the negative ions such as SO_4^{2-} and CO_3^{2-} and so on, n is the amount of water in the crystal, and x is the molar ratio of trivalent metal ions to all metal ions.[4] Recent researches have shown that copper-containing HTLcs (Cu-HTLcs) exhibit good catalytic performances in the phenol hydroxylation with hydrogen peroxide as hydroxylating agent.[5] As far as the synthesis of HTLcs is concerned, the classical method is hydrothermal crystallization under the conventional heating, however, it needs a long crystallization time of over 15 hours.[6,7] In recent developments, microwave-assisted synthesis has become popular in the crystallization of the solid catalyst materials,[8,9] because it can give rise to high yields, represents a clean synthetic method and has short crystallization times in comparison with the conventional method. However, until now, there are only few reports about the application of microwaves on the synthesis of HTLcs. Therefore, in the present work, we have synthesized the copper-containing hydrotalcite samples (Cu-HTLcs) and modified them through the doping of rare earth elements under microwave irradiation. At the same time, the thus synthesized samples were applied in the catalytic hydroxylation of phenol with aqueous H_2O_2 solution as hydroxylating agent. The present work also investigated the effects of reaction medium and reaction time on phenol hydroxylation in detail. Based on the catalytic hydroxylation of phenol and the XPS characterization of catalysts, a new mechanism for phenol hydroxylation has been proposed.

Results and Discussion

Synthesis and Characterization

Copper as an active metal component was widely applied in selective oxidation reactions,[10–12] the previous studies[1,5] showed that Cu-HTLcs could give rise to good catalytic performances in phenol hydroxylation. Therefore, in the present work we synthesized Cu-HTLcs under microwave irradiation and, in order to investigate the effect of rare earth elements on the catalytic activities of Cu-HTLcs, we also synthesized La-Cu-HTLcs, Sm-Cu-HTLcs, Y-Cu-HTLcs and Ce-Cu-HTLcs under the same conditions through the doping of the corresponding rare earth elements. The RE-doped amount was 4 mol % of the total metal elements in HTLcs. The formulae of the various HTLcs is calculated to be $Cu_{7.68}RE_{0.40}Al_{1.92}(OH)_{20}(CO_3)_{1.16}\cdot 7.77\ H_2O$, which is almost coincident with the results obtained by the ICP-AES techniques.

The structures of Cu-HTLcs and RE-Cu-HTLcs were characterized by XRD and IR techniques. The spectra are shown in Figures 1 and 2, respectively. It can be observed that the XRD patterns of all samples give some typical reflections at $2\theta = 12.8, 25.7, 33.5, 60.9°$, which are almost identical to the typical pattern characteristic of the hydrotalcite-like phase as previously reported.[4,13–15] These reflection peaks are ascribed to the diffraction by basal planes (003), (006), (009), (110), respectively. At the same time, the IR spectra of all samples give two main absorption bands centered at 3445 cm^{-1} and 1388 cm^{-1}, respectively, and as well as a group of other small bands below 1200 cm^{-1}. These further prove that all the synthesized copper-containing samples exhibit the structure of hydrotalcite-like compounds. The band centered at around 3445 cm^{-1} is attributed to the ν_{OH} stretching mode of hydroxy groups from water molecules in the layers and interlayer of hydrotalcites[16–18] and the O–H vibrations of M–(OH). The sharp band at 1388 cm^{-1} is due to the antisymmetric mode of interlayer carbonate anions. The group of peaks in the region below 1200 cm^{-1} are from the *M*–OH stretching and *M*–*O*–*M′* bending modes[16] wherein *M* and *M′* represent the metal elements such as Cu, Al and RE so on. From the XRD and IR spectra of samples, it can be concluded that microwave irradiation results in the formation of the copper-containing hydrotalcite-type materials (Cu-HTLcs) in a short crystallization time, and the doping of rare earth elements has no obvious influence on the formation of the hydrotalcite structure.

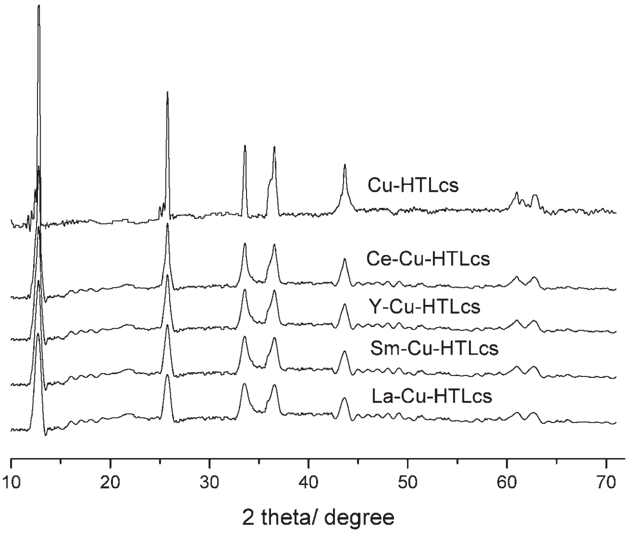


Figure 1. X-ray diffraction pattern of the copper-containing hydrotalcites.

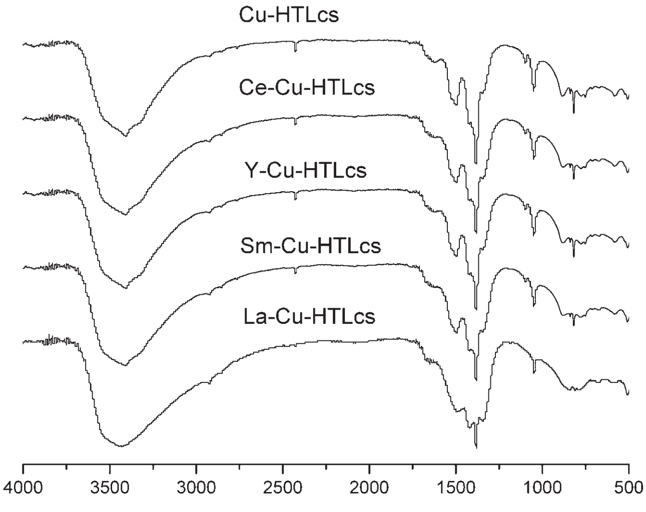


Figure 2. FT-IR spectra of the copper-containing hydrotalcites.

In Figure 3 are illustrated the XPS spectra of all copper-containing hydrotalcites samples. It can be observed that all samples give a peak near 934.5 eV, which is assigned to Cu $2P_{3/2}$ of Cu^{2+} ions according to the literature.[19–21]. At the same time, the Cu $2P_{1/2}$ peak near 954.5 eV can also be clearly seen in all samples. However, the peaks for both Cu $2P_{3/2}$ and Cu $2P_{1/2}$ exhibit a positive shift as the order of Cu-HTLcs < Ce-Cu-HTLcs < Y-Cu-HTLcs < Sm-Cu-HTLcs < La-Cu-HTLcs. This indicates that the Cu^{2+} species in the RE-doped copper-containing hydrotalcites will have an increasing electron-withdrawing capacity with the order of Ce < Y < Sm < La.

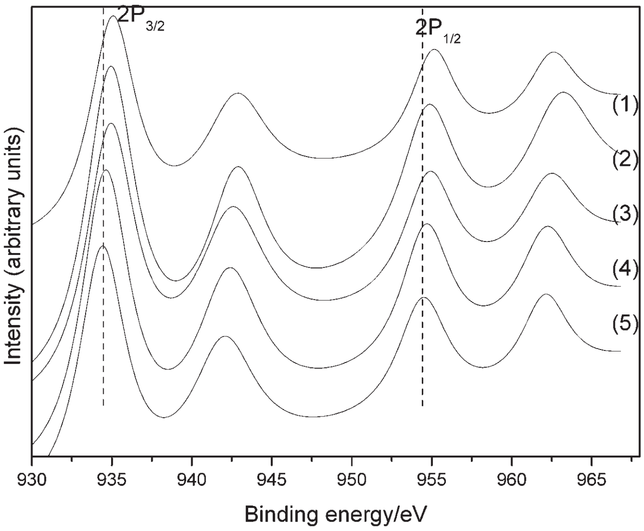


Figure 3. Cu 2p XPS region in the corresponding XPS spectra of (**1**) La-Cu-HTLcs, (**2**) Sm-Cu-HTLcs, (**3**) Y-Cu-HTLcs, (**4**) Ce-Cu-HTLcs and (**5**) Cu-HTLcs.

Phenol Hydroxylation

Effect of Catalyst Types

Copper-containing hydrotalcites are efficient catalysts for phenol hydroxylation, as has been reported previously.[1,5,17] However, there are still only few reports about phenol hydroxylation catalyzed by the RE-doped Cu-HTLcs, wherein RE stands for the rare earth elements, e.g., La, Sm, Y and Ce. In the present work, the catalytic performances of RE-Cu-HTLcs with the RE/(RE+Al+Cu) ratio of 4 mol % are investigated and compared with those of Cu-HTLcs in the phenol hydroxylation, the results are summarized in Table 1. From Table 1, it can be observed that the two main products are catechol and hydroquinone, and the main by-product is benzoquinone, and that the distribution of products is almost similar for all catalysts in phenol hydroxylation.

In the case of RE-Cu-HTLcs samples as catalysts, phenol conversions are always higher than those of Cu-HTLcs. At the same time, from Table 1 it can be also clearly observed that the La-HTLcs free from copper has no catalytic activity in phenol hydroxylation. This shows that the rare earth elements in hydrotalcites cannot act as the catalytically active centers. However, the doping of rare earth elements does lead to an improvement in the catalytic activity of the copper-containing hydrotalcites. The increase in the catalytic activities of RE-Cu-HTLcs probably comes from the synergistic effect of rare earth element on the Cu^{2+} species in hydrotalcites, is also probably due to an improvement of the H_2O_2 efficiency. Moreover, from Table 1, the different rare earth elements are observed to exert different degrees of improvement in the catalytic activity of RE-Cu-HTLcs. The catalytic activity of RE-Cu-HTLcs is increased in the order of Ce $<$Y$<$Sm$<$La, which is probably due to the increase of electron-withdrawing capacities of Cu^{2+} species in hydrotalcites. It can be deduced that the catalytic active centers of Cu^{2+} species probably absorb electrons to form the transition state Cu^{+} species in the phenol hydroxylation.

Additionally, from the above-obtained results in Table 1, it can be observed that the La-doped Cu-HTLcs (La-Cu-HTLcs) exhibits the highest phenol conversion, indicating that La-Cu-HTLcs is the best catalyst among all the synthesized copper-containing hydrotalcites in phenol hydroxylation. Therefore, the present work further investigates the catalytic performance of La-Cu-HTLcs in phenol hydroxylation with various reaction parameters in details.

Effect of Reaction Medium

In order to investigate the effect of the reaction medium on the phenol hydroxylation catalyzed by La-Cu-

Table 1. Catalytic properties of copper-containing HTLcs in phenol hydroxylation.*

Catalysts	Phenol conversion [mol %]	Products distribution [mol %]			CAT/HQ
		CAT[a]	HQ[b]	BQ[c]	
La-Cu-HTLcs	53.2	54.7	42.4	3.0	1.3
Sm-Cu-HTLcs	50.2	55.0	41.7	3.3	1.3
Y-Cu-HTLcs	47.9	61.3	35.1	3.6	1.3
Ce-Cu-HTLcs	46.8	63.4	33.5	3.1	1.9
Cu-HTLcs	44.8	62.9	33.2	4.0	1.9
La-HTLcs[d]	0.0	–	–	–	–

* Reaction conditions: 0.5 g phenol, 0.025 g catalyst, 1 mL 30 wt % H_2O_2 solution, 10 mL distilled water, temperature 70 °C, time 120 min.

[a] CAT = catechol.

[b] HQ = hydroquinone.

[c] BQ = benzoquinone.

[d] La content being 4 mol %.

Table 2. Effect of reaction medium on phenol hydroxylation catalyzed by La-Cu-HTLcs.*

Solvent	Phenol conversion [mol %]	Product distribution [mol %]			CAT/HQ
		CAT	HQ	BQ	
Water	53.2	54.7	42.4	3.0	1.3
Water + acetone (1:1)	16.1	61.5	36.9	1.5	1.7
Acetone	0.0	–	–	–	–
Acetonitrile	0.0	–	–	–	–

* Reaction conditions: 0.5 g phenol, 0.025 g La-Cu-HTLcs, 1 mL 30 wt % H_2O_2 solution, temperature 70 °C, time 120 min.

Table 3. Effect of phenol/H_2O_2 molar ratio on the phenol hydroxylation.*

Phenol/H_2O_2 (mole ratio)	Phenol conversion [mol %]	Product distribution [mol%]			CAT/HQ	H_2O_2 utilization ratio [mol%]
		CAT	HQ	BQ		
3:1	18.2	58.9	37.0	4.1	1.6	52.3
2:1	26.4	53.1	42.6	4.3	1.3	50.5
1:1	34.7	54.1	41.4	4.5	1.3	33.1
1:2	53.2	54.5	42.3	3.3	1.3	25.8
1:3	56.7	53.2	43.4	3.5	1.2	18.2

* Reaction conditions: 0.5 g phenol, 0.025 g La-Cu-HTLcs, 10 mL distilled water as solvent, temperature 70 °C, time 120 min.

HTLcs, the reaction was performed in various solvents such as water, acetone, mixtures thereof, and acetonitrile. The results are summarized in Table 2. From Table 2, it can be clearly seen that the La-Cu-HTLcs-catalyzed phenol hydroxylation gives the highest phenol conversion in water as solvent, however, and almost has no catalytic activity in acetone and acetonitrile. This is perhaps due to the following reasons: (1) acetone and acetonitrile simply trap the hydroxyl radicals in contrast to water, thereby preventing the hydroxylation of phenol; (2) water is a kind of perfect solvent for the easy and simultaneous dissolution for both phenol and H_2O_2, leading to the rapid approach on the catalytically active centers; (3) water is beneficial to the generation of $HO^\bullet$ radicals being the active species involved in phenol hydroxylation with H_2O_2; and (4) the $HO^\bullet$ radicals are easier stabilized in water than in other organic solvents.[17] On the other hand, water is also beneficial to both industrial production and the elimination of environmental pollution. Hence, water is indicated to be the best choice as solvent for the phenol hydroxylation.

Effect of the Ratio of Phenol to H_2O_2

The present work investigates the effect of the molar ratio of phenol to H_2O_2 on the phenol hydroxylation, the results are listed in Table 3. The phenol conversion can be observed to increase with the decreasing molar ratio of phenol to H_2O_2, indicating that it is possible to improve the per pass conversion of phenol and the production of dihydroxylbenzenes through reducing the molar ratio of phenol to H_2O_2. However, the H_2O_2 utilization ratio decreases with the decreasing molar ratio of phenol to H_2O_2, this is because most of the H_2O_2 is probably decomposed to O_2 on the catalytically active sites.[5] That is to say, the higher the added amount of H_2O_2 is, the lower is the H_2O_2 utilization ratio obtained. Therefore, for the purpose of keeping both a high phenol conversion and a high H_2O_2 utilization ratio, it is very important for the phenol hydroxylation to select a proper molar ratio of phenol to H_2O_2.

Effect of Reaction Time

The present work investigates the phenol conversion and the distribution of products in different hydroxylation times using La-Cu-HTLcs as catalyst, the results are shown in the Figure 4. From Figure 4, it can be seen that phenol conversion increases drastically with an increasing reaction time at the beginning and then levels off at 53 mol % after 120 min, because of the reaction fulfillment. However, the selectivities of the three products, such as catechol, hydroquinone and even benzoquinone, remain unchanged during the whole hydroxylation process, indicating that the production of three products may be carried out through three parallel reactions.

Investigation of the Mechanism of Phenol Hydroxylation

In the case of copper-containing hydrotalcites as catalyst, the HO-Cu^{2+}-OH species, located in the layer of

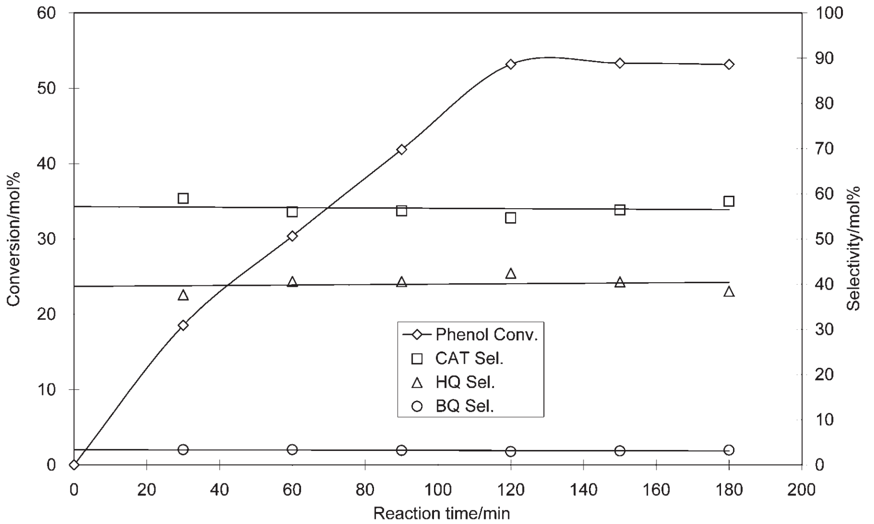


Figure 4. Effect of reaction time on phenol hydroxylation. *Reaction conditions:* 0.5 g phenol, 0.025 g La-Cu-HTLcs, 1 mL 30 wt % H_2O_2 solution, 10 mL distilled water, temperature 70 °C.

the hydrotalcites, have been considered as the catalytically active centers for phenol hydroxylation with H_2O_2 as hydroxylating agent, and it has also been considered that the hydroxylation reaction is carried out through the produced $HO^{\bullet}$ radicals on the HO-Cu^{2+}-OH species.[5,18] Therefore, the generation of $HO^{\bullet}$ radicals is an important factor for the phenol hydroxylation with H_2O_2 aqueous solution. Zhu et al.[5] assumed that the $HO^{\bullet}$ radicals were produced by the reduction of H_2O_2 on HO-Cu^{2+}-OH species, leading to the fact that HO-Cu^{2+}-OH species were oxidized to HO-Cu^{3+}-OH.

From the results in the present work, RE-Cu-HTLcs samples exhibit higher catalytic activities than Cu-HTLcs in phenol hydroxylation. It has also been testified that the increase in the catalytic activity of RE-Cu-HTLcs is not from the simple summation between the activities of Cu-HTLcs and RE-HTLcs. Moreover, the different rare earth elements exert a different effect on the catalytic activity of copper-containing hydrotalcites, the catalytic activity of the RE-doped Cu-HTLcs decreases in the order of La-Cu-HTLcs > Sm-Cu-HTLcs > Y-Cu-HTLcs > Ce-Cu-HTLcs > Cu-HTLcs. If the HO-Cu^{2+}-OH species are oxidized to HO-Cu^{3+}-OH during the generation of $HO^{\bullet}$radicals as reported in previous references,[5,18] the HO-Cu^{2+}-OH species in the layer of hydrotalcites should be a kind of electron-donor. Thus, for RE-Cu-HTLcs samples, the order of electron-donating capability should also decreases in the order of La-Cu-HTLcs > Sm-Cu-HTLcs > Y-Cu-HTLcs > Ce-Cu-HTLcs > Cu-HTLcs, and their Cu 2p electron binding energies should exhibit a reverse order. However, this is contrary to the detected results about the Cu 2p electron binding energy of the RE-doped Cu-HTLcs by XPS described above.

For the purpose of the further investigation on the generation mechanism of $HO^{\bullet}$ free radicals on the catalysts, we surveyed the valence change of copper in the HO-Cu^{2+}-OH species of La-Cu-HTLcs mixed with aqueous H_2O_2 solution by the XPS technique, the results are depicted in Figure 5. It can be clearly observed that the fresh La-Cu-HTLcs sample only exhibits four signals, which are attributed to the Cu 2p electron binding energies of Cu^{2+} ions. However, the La-Cu-HTLcs/H_2O_2 system, resulting from the solid-liquid interaction between La-Cu-HTLcs and H_2O_2, gives two additional strong signals located at the binding energies of 932.1 and 953.9 eV, attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu^+, respectively.[22] The same results are also found in the Cu-HTLcs/H_2O_2 system. Associated with the effect of RE-doping on Cu 2p binding energies and catalytic activities of RE-Cu-HTLcs, it can be concluded that

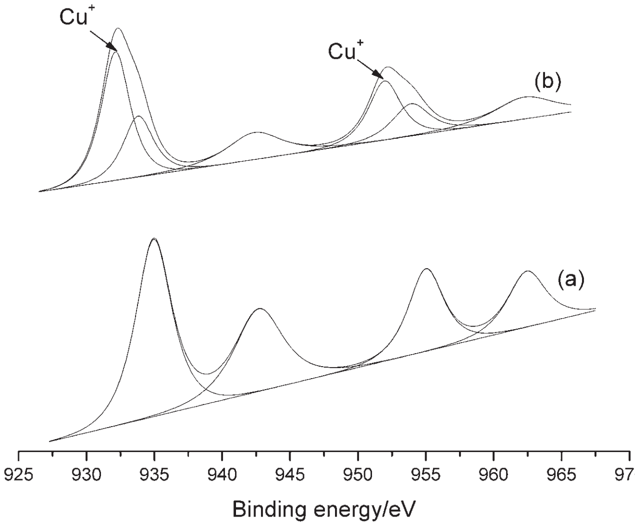
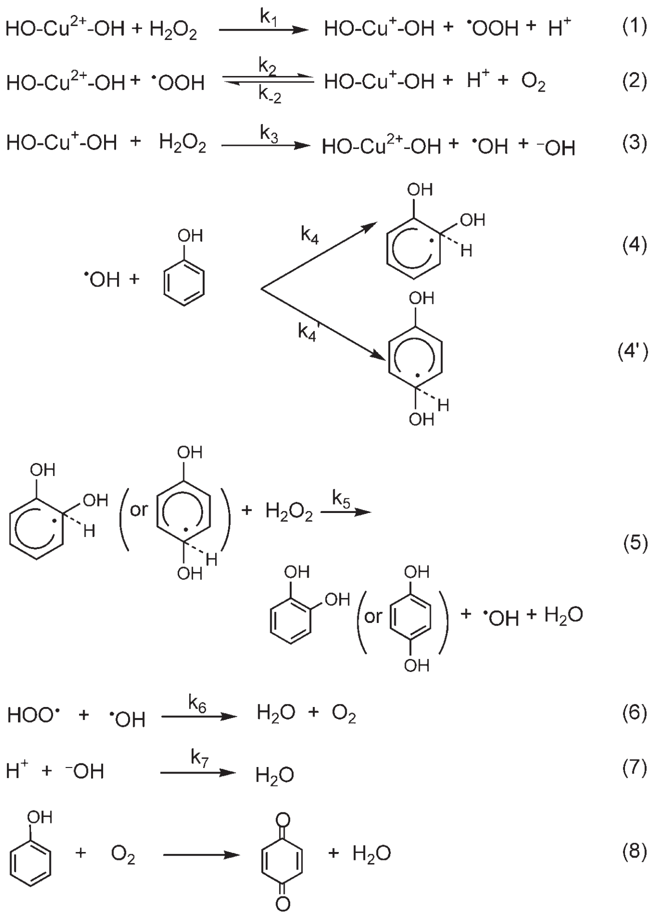


Figure 5. Comparison of Cu 2p XPS spectra of La-Cu-HTLcs before (**a**) and after (**b**) H_2O_2 treatment.



Scheme 1. Reaction mechanism for phenol hydroxylation.

the transition state HO-Cu^{+}-OH species will be produced in the phenol hydroxylation with H_2O_2 catalyzed by copper-containing hydrotalcites. Therefore, the generation of HO$^{\bullet}$ radicals is deduced to be carried out not through the oxidation of HO-Cu^{2+}-OH to HO-Cu^{3+}-OH as previously reported,[5,18] but through the reduction of HO-Cu^{2+}-OH to HO-Cu^{+}-OH as shown in the following reactions (see Scheme 1):

The HO$^{\bullet}$ radicals are generated through the redox reaction of H_2O_2 with HO-Cu^{2+}-OH species. HO-Cu^{2+}-OH species in hydrotalcites are firstly reduced by H_2O_2 to HO-Cu^{+}-OH according to Equations (1) and (2), and then HO-Cu^{+}-OH species react with H_2O_2 to produce HO$^{\bullet}$ radicals. This path for the generation of HO$^{\bullet}$ radicals can also be supported by the previous reports.[23–27] According to the proposed mechanism, Equation (1) is a chain-initiation step, the produced HO$^{\bullet}$ radicals attack phenol to form two kinds of transition complexes [see Equations (4) and (4′)], and then the transition complexes continue to react with H_2O_2 to yield catechol and hydroquinone, respectively, and also give rise to the HO$^{\bullet}$ radicals, simultaneously. Thus, Equations (2) to (5) can be considered as the chain-propagation steps. Of course, the produced HO$^{\bullet}$ radicals can also contact with HOO$^{\bullet}$ radicals to form O_2, which is regarded as the chain-termination step. If a proper solvent, such as water, is used in the reaction system, the mutual collisions of HOO$^{\bullet}$ with HO$^{\bullet}$ radicals can be avoided, resulting in the increase of the probability for phenol hydroxylation, which has been proved by the effect of solvent types on phenol hydroxylation in the present work. On the other hand, Equations (2) and (6) are main processes for the side reactions, namely decomposition of H_2O_2.

Conclusion

Under microwave irradiation, the copper-containing hydrotalcites with a good crystalline structure can be synthesized in a short time of 10 min. Moreover, doping with rare earth elements improves the catalytic activity of Cu-HTLcs. And the catalytic activity of RE-Cu-HTLcs increases in the order of Ce < Y < Sm < La. The binding energy of Cu 2p in copper-containing hydrotalcites increases in the order of Cu-HTLcs < Ce-Cu-HTLcs < Y-Cu-HTLcs < Sm-Cu-HTLcs < La-Cu-HTLcs, which is identical to the increased order of their catalytic activities in phenol hydroxylation. Combining with the XPS results of the La-Cu-HTLcs/H_2O_2 system, we propose that HO-Cu^{2+}-OH species in hydrotalcites are first reduced by H_2O_2 to HO-Cu^{+}-OH, and then HO-Cu^{+}-OH species react with H_2O_2 to produce HO$^{\bullet}$ radicals.

Experimental Section

Synthesis and Doping of Copper-Containing HTLcs

The copper-containing HTLcs (Cu-HTLcs) were synthesized in a three-necked, round-bottom flask. A mixed aqueous solution containing metal nitrates [such as $Cu(NO_3)_2$ and $Al(NO_3)_3$, respectively, the ratio of Cu^{2+} to Al^{3+} being 4] formed solution A, another mixed solution containing 0.6 mol/L NaOH and 0.45 mol/L Na_2CO_3 was solution B. The solutions A and B were synchronously titrated into the three-necked, round-bottom flask under vigorous stirring at 70 °C, the titration rates of solutions A and B were controlled in order to maintain the pH value of mixture solution at about 9. After the titration, the stirring was continued for another one hour, a heavy precursor gel was obtained and then crystallized at 70 °C for 10 min under microwave irradiation in a domestic microwave oven (LG, the maximum power of 700 W and a frequency of 2.45 GHz), the temperature was controlled by the temperature feedback monitoring system with dual IR sensors. Finally, the precipitates were filtered, washed with double-distilled water to pH 7. The synthesized samples were dried for 30 min under microwave irradiation, thus the obtained copper-containing sample was denoted as Cu-HTLcs.

The doping of rare earth elements in Cu-HTLcs was carried out in the preparation of solution A. Rare earth (RE) nitrate with the amount of RE/(RE + Cu + Al) being 4 mol % was added to solution A, the other processes were the same, the obtained samples were denoted as RE-Cu-HTLcs, whereby RE stood for rare earth elements, e.g., La, Sm, Y, and Ce.

Characterization Methods

X-ray powder diffraction (XRD) patterns of the samples were obtained on a Philips analytical X-Ray diffractometer in the range of $10^\circ \leq 2\theta \leq 70^\circ$, using CuKα radiation combined with a nickel filter. Fourier transform infrared spectra (FT-IR) of samples were recorded on the Nicolet MX-1E FT-IR in the range of 500–4000 cm^{-1} using the KBr pellet technique. The X-ray photoelectron spectra (XPS) were collected using a Kratos Model XSAM 800 surface science instrument equipped with an Al-Kα anode (1486.6 eV) operating at 180 W, 12 kV and 15 mA. All binding energy values [BE (eV)] were determined with respect to the scale calibrated versus the Au_{4f} line at 84.0 eV and Ag_{3d} line at 386.3 eV.

Phenol Hydroxylation

Phenol hydroxylation was carried out in a two-necked, round-bottom flask (50 mL) fitted with a condenser, magnetic stirrer and thermostat. Copper-containing HTLcs as catalyst, phenol and solvent were added successively into the reactor. Then a requisite amount of hydrogen peroxide (30 wt %) aqueous solution was added through dropping wisely to the reaction mixture under stirring at a desired reaction temperature. The products were analyzed by gas chromatography (GC) on the SC-1001 gas chromatograph (China) fitted with flame ionization detector (FID), PTE^{TM}-5 QTM capillary column (15 m × 0.53 mm × 0.5 μm film thickness, Supelco, USA).

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