

# Deactivation and reactivation of copper-containing pentatomic hydrotalcite in catalytic hydroxylation of phenol

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## Abstract

The phenol hydroxylation catalyzed over copper-containing pentatomic hydrotalcite (Cu-PHTL) is investigated during the catalyst cycle lifetime. The results show the fresh catalyst exhibits very high initial activity for the reaction. However, the rapid deactivation of catalyst is observed after the fifth operation. The cause of catalyst deactivation is discussed according to the characterizations of ICP-AES, XRD, FT-IR, TEM and XPS, which is mainly attributed to carbon deposit on the surface of the catalyst. Moreover, the deactivated catalyst is easily reactivated by burning deposited carbon in air and then washing with acetone, and the reactivated catalyst shows catalytic activity as almost high as the fresh sample. However, a small difference in catalytic activities between reactivated and fresh catalysts is possibly owing to the slight Cu leaching.

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**Keywords:** Deactivation; Pentatomic hydrotalcite; Reactivation; Phenol hydroxylation

## 1. Introduction

Hydroxylation of phenol with hydrogen peroxide is a very useful reaction for synthesis of catechol and hydroquinone, which are important intermediates for perfumes, drugs, antioxidants, and pharmaceuticals [1,2]. Hydrotalcite-like compounds (HTLcs) have attracted an increasing attention in recent years, which act as heterogeneous catalysts to give a high activity, selectivity and stability; moreover, the hydrotalcites can be easily removed from the reaction mixture and are further usable for the reaction [3]. The recent researches have shown that copper-containing HTLcs (Cu-HTLcs) is a good catalyst in phenol hydroxylation with hydrogen peroxide as a hydroxylating agent [2,4]. Cycle lifetime is one of the important focal points of catalysts; however, that of HTLcs has not still been reported in phenol hydroxylation. Therefore, the present work investigated the effect of duty-cycle operation on the Cu-PHTL-catalyzed phenol hydroxylation. At the same time, the Cu content leached into the reaction solution was examined by ICP-AES, and the fresh and deactivated catalysts were thoroughly characterized

by XRD, IR, XPS and TEM. Furthermore, the catalyst could be reactivated by calcination at low temperature and then washing with acetone. Based on the characterizations of fresh and deactivated catalysts, the causes of catalyst deactivation in phenol hydroxylation have been analyzed in detail.

## 2. Experimental

### 2.1. Synthesis of Cu-PHTL

The copper-containing pentatomic hydrotalcite with the  $M^{II}/M^{III}$  (molar ratio of 3;  $M^{II}$  standing for  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ;  $M^{III}$  standing for  $Al^{3+}$ ,  $Fe^{3+}$ ) was prepared by co-precipitation from aqueous solutions. The mixture of metal nitrates and the other solution containing NaOH and  $Na_2CO_3$  were simultaneously added dropwise, while the pH was maintained around 9–10 under vigorous stirring at 70 °C. After the titration and the stirring continued for 1 h, a heavy precursor gel was obtained and then crystallized at 70 °C for 10 min under the 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. Lastly, the precipitate was filtered, and washed by the double-distilled water to pH 7. The synthesized sample was

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dried for 30 min under the microwave irradiation. Thus, obtained copper-containing sample was designated as Cu-PHTL.

## 2.2. Characterization

The Cu content leached into the reaction solution was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-ray powder diffraction (XRD) pattern was carried out on a Philips analytical X-ray diffractometer in the range of  $10^\circ \leq 2\theta \leq 70^\circ$ , using Cu K $\alpha$  radiation combined with a nickel filter. Fourier transform infrared spectra (FT-IR) was recorded on the Nicolet MX-1E FT-IR in the range of 500–4000  $\text{cm}^{-1}$  using the KBr pellet techniques. The X-ray photoelectron spectra (XPS) was collected using a Kratos Model XSAM 800 surface science instrument equipped with an Al K $\alpha$  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. Transmission electron microscopy (TEM) was performed on a JEM-1000CX electron microscope (JEOL) with the acceleration voltage of 80 kV and amplifying multiple of 100,000.

## 2.3. Phenol hydroxylation

Phenol hydroxylation was carried out in a glass reactor (50 ml) fitted with a condenser, magnetic stirrer and thermostat. Cu-PHTL as catalyst, phenol and solvent were added successively into the reactor. Then a requisite amount of hydrogen peroxide (30 wt.%) aqueous solution was added to the reaction mixture under the stirring at a desired reaction temperature. The products were analyzed by gas chromatography (GC) on an SC-1001 gas chromatograph (China) fitted with a flame ionization detector (FID) and a PTE<sup>TM</sup>-5QTM capillary column (15 m  $\times$  0.53 mm  $\times$  0.5  $\mu\text{m}$  film thickness, Supelco, USA).

## 3. Results and discussion

### 3.1. Cycle lifetime of Cu-PHTL

The cycle lifetime of Cu-PHTL in phenol hydroxylation was investigated under the following conditions: phenol/catalyst mass ratio of 10, H $_2$ O $_2$ /phenol mole ratio of 2, distilled water as solvent, temperature 70  $^\circ\text{C}$ , time 120 min. Fig. 1 shows that phenol conversion in phenol hydroxylation catalyzed over Cu-PHTL is mutative from 63 to 52% during duty-cycle operation. Obviously, initial changes are smooth; however, activity of the catalyst abruptly decreases after the operation of the fifth cycle. The products catechol (CAT), hydroquinone (HQ), and benzoquinone (BQ) exhibit a similar distribution for the whole cyclic process.

The activity of Cu-PHTL gradually decreases during duty-cycle operation of catalytic hydroxylation of phenol, indicating the occurrence of catalyst deactivation. Catalyst deactivation is a problem of great and continuing concern in the practice of industrially catalytic processes.

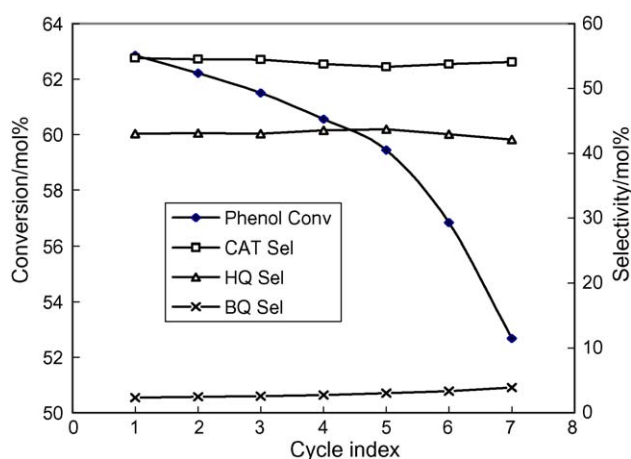


Fig. 1. Cycle lifetime of Cu-PHTL in phenol hydroxylation.

### 3.2. Causes of the catalyst deactivation

Three most possible causes of catalyst deactivation are fouling, poisoning or leaching of active species into reaction solution. Fouling involves the deposition of material on catalyst surface to block active sites; coke deposition is the most common phenomenon. Poisoning involves strong chemical interaction of a component in the feed or products with active sites on the catalyst surface [5,6]. With the first two causes, the catalyst might be reactivated in some ways [7]. In order to investigate whether Cu active species leach into the reaction solution, we examined the extracted reaction solution by an ICP-AES technique. The result shows that there is only 0.04% Cu being spent, indicating Cu leaching into the reaction solution is not the main reason for the catalyst deactivation in phenol hydroxylation.

#### 3.2.1. XRD and IR of the fresh and deactivated catalysts

The structures of fresh and deactivated Cu-PHTL were characterized by XRD and IR techniques. The XRD and FT-IR spectra are shown in Figs. 2 and 3, respectively. The XRD patterns of both samples give typical reflection peaks at  $2\theta = 11.7, 24.1, 35.6$  and  $61.9^\circ$ , which are almost identical to the pat-

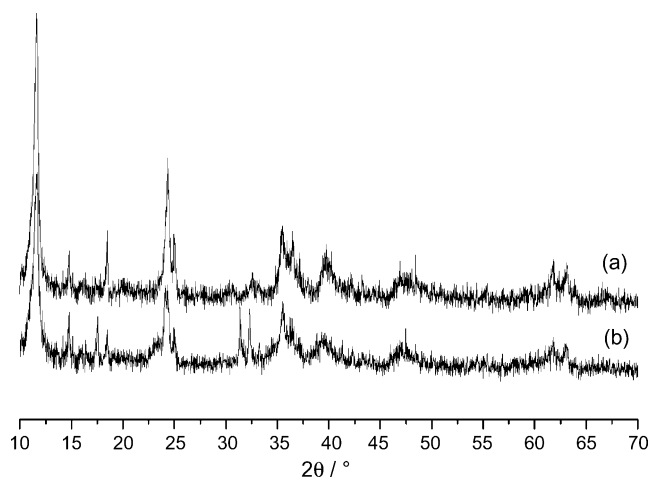


Fig. 2. XRD spectra of the fresh (a) and deactivated (b) catalysts.

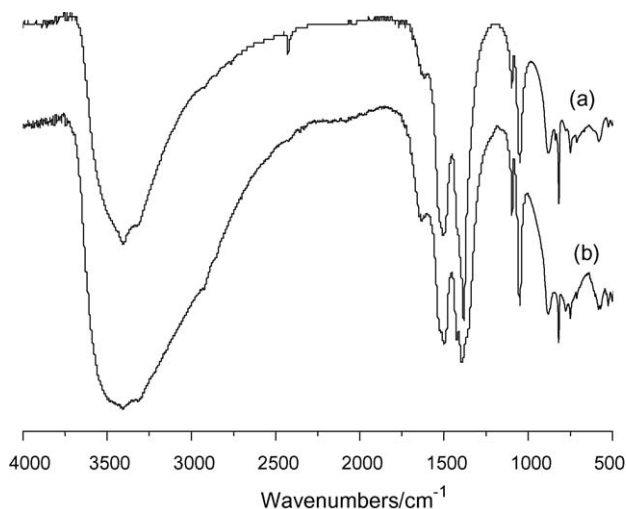


Fig. 3. FT-IR spectra of the fresh (a) and deactivated (b) catalysts.

tern characteristic of hydrotalcite phase as previously reported [8–11]. These reflection peaks are ascribed to the diffraction by basal planes (003), (006), (009) and (110), respectively.

The IR spectra of both samples gives two main absorption bands centered at  $3407$  and  $1370\text{ cm}^{-1}$  as well as a group of other small bands below  $1200\text{ cm}^{-1}$ . The band centered at around  $3407\text{ cm}^{-1}$  is attributed to the  $\nu_{\text{OH}}$ -stretching mode of hydroxyl groups from water molecules in the layers and interlayer of hydrotalcites [12–14]. The sharp band at  $1370\text{ cm}^{-1}$  is due to the antisymmetric mode of interlayer carbonate anions. The group peaks in the region of below  $1200\text{ cm}^{-1}$  are from the M–OH stretching and M–O–M' bending modes [12], wherein M and M' represent the metal elements such as Cu, Al, Fe and so on.

From the XRD pattern and IR spectra of the samples, we can conclude that the deactivated Cu-PHTL still has a weak hydrotalcite structure. However, XRD of the deactivated catalyst has some impurity peaks around  $2\theta = 17.5$  and  $32.5^\circ$ . At the same time, there are typical reflection peaks at  $2\theta = 11.7$ ,  $24.1$ ,  $35.6$  and  $61.9^\circ$ , however, the peak intensities in the whole angle region significantly decrease, suggesting that the regularity of Cu-PHTL hydrotalcite structure is weakened after the reaction. From the IR spectra, both the  $\nu_{\text{OH}}$ -stretching band centered at around  $3407\text{ cm}^{-1}$  and the carbonate band at  $1370\text{ cm}^{-1}$  widen,

indicating the deactivated catalyst has overmuch carbonate and hydroxy.

### 3.2.2. TEM of the fresh and deactivated catalysts

The TEM technique was employed to further characterize the fresh and deactivated catalysts (see Fig. 4). From the TEM image, it is obvious that the dispersion of the deactivated catalyst is much worse than that of the fresh catalyst, indicating that Cu-PHTL is fouled in the catalytic phenol hydroxylation, resulting in the collapse or the weakening of the long-range regularity of hexagon or quadrilateral hydrotalcite figure. In most of the catalytic processes, fouling with the deposition of carbon or coke plays a major role. Depending on the feed, the reaction can lead to coke or carbon material left on the catalyst surface, which makes the active sites inaccessible [7]. Furthermore, carbonaceous residues left on the catalyst surface limits dispersion of the catalyst. The agglomeration of species on the catalyst surface makes the catalytic activity centre blocked, which reduces the diffusivities, resulting in the decline in the catalytic activity.

### 3.2.3. XPS of the fresh and deactivated catalysts

Carbonaceous deposits reduce the activity of the catalyst because they block the active sites and distort the catalyst structure, thus reducing the diffusivities of the reactants [15]. In order to investigate causes of the catalyst deactivation, we have measured C 1s and Cu 2p XPS spectra, which are shown in Figs. 5 and 6. Fig. 5 shows four components at binding energies 279.5, 281.8, 284.9 and 289.2 eV, where the peaks at 279.5 and 281.8 eV are unambiguously due to carbon of the C–M bond in Cu-PHTL. The C 1s peak at 284.9 eV is interpreted as interstitial carbon present in a defect C–C structure, whereas the last broad peak at 289.2 eV originates from the C–O bond. It is clear that the deactivated Cu-PHTL has higher C–C bound peak, indicating that the deactivated catalyst has an increased C–C content up to 48.2%, while the fresh catalyst has a C–C content of 36.1%. The fractions of individual C wt.% derived from the XPS data (Table 1) indicate the total carbon concentration reaching 31.1% in the fouled Cu-PHTL and 28.0% in the fresh catalyst.

Fig. 6 illustrates the active centre Cu 2p XPS spectra of the fresh and deactivated samples. It can be observed that both samples give a peak near 935 eV along with a satellite peak at 942 eV,

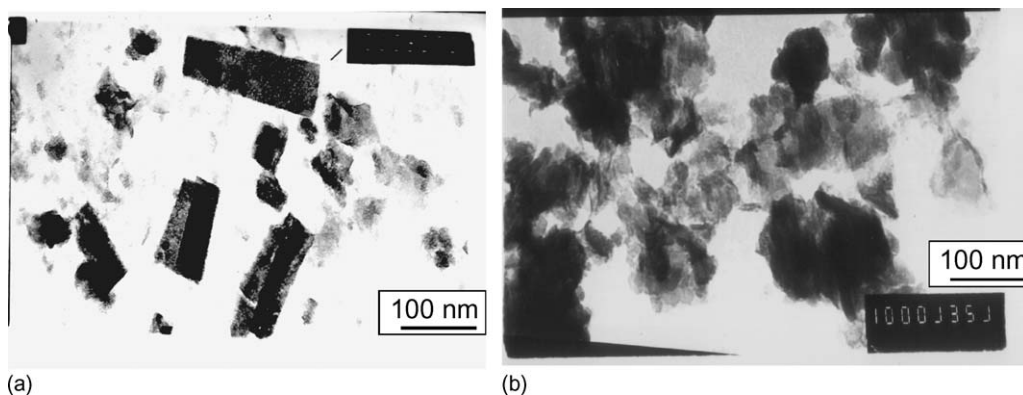


Fig. 4. TEM of the fresh (a) and deactivated (b) catalysts.

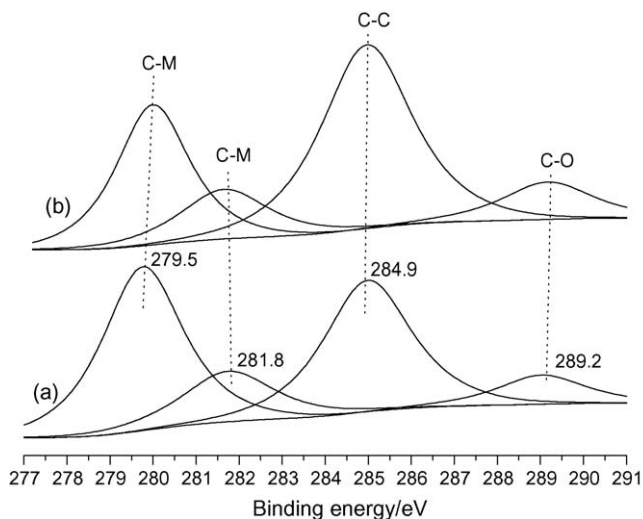


Fig. 5. C 1s XPS spectrum of the fresh (a) and deactivated (b) Cu-PHTL.

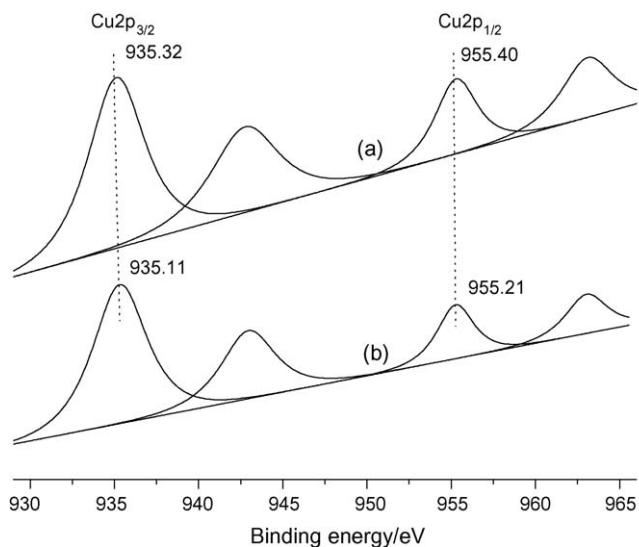


Fig. 6. Cu 2p XPS spectrum of the fresh (a) and deactivated (b) Cu-PHTL.

which are assigned to Cu  $2p_{3/2}$  of  $\text{Cu}^{2+}$  ions according to the literatures [16–18]. At the same time, the Cu  $2p_{1/2}$  peak near 955 eV and its satellite peak at about 963 eV can also be clearly seen in both samples. However, the peaks for both Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  exhibit a positive shift in the order of the deactivated Cu-PHTL < the fresh Cu-PHTL, indicating that the HO– $\text{Cu}^{2+}$ –OH species in the deactivated Cu-PHTL is less electron-deficient than that in the fresh catalyst. Therefore, the activity of the catalyst decreases, which is consistent with the results reported in

Table 1  
XPS of the fresh and deactivated Cu-PHTL about different carbon and copper content

Catalyst	C (wt.%)	Cu (wt.%)	C–M (wt.%)	C–C (wt.%)	C–O (wt.%)
Fresh	28.0	72.0	55.9	36.1	8.0
Deactivated	31.1	68.9	42.0	48.2	9.8

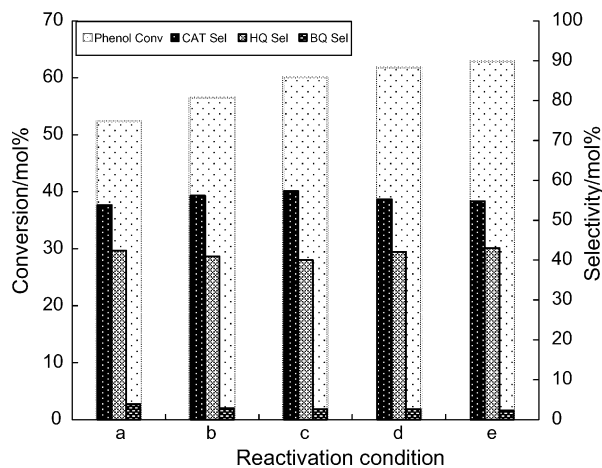


Fig. 7. Reactivation of the deactivated catalyst. (a) The deactivated catalyst without treatment, (b) calcination under low temperature, (c) washing with acetone, (d) burning deposited carbon in air and washing with acetone and (e) the fresh catalyst.

the previous refs. [19,20]. From XPS spectra of the fresh and fouled catalysts, we can conclude that the main cause of the catalyst deactivation is coke or carbon deposition.

### 3.3. Reactivation of the deactivated catalyst

Here, the reactivation of the deactivated catalyst have been attempted by three methods. Firstly, the calcination at low temperature is often the preferred route with the temperature being carefully controlled [5]. The appropriate conditions depend on characters of the catalyst, due to memory effect of the HTLcs [21]. So we calcine the deactivated catalyst at low temperature in air, which does not change the structure of the catalyst. However, it may not always be necessary by burning deposited carbon in air. Washing foulants from catalyst is a possibility that can be effective. Here, we remove residual of coke or carbon by washing with organic solvent, such as acetone, acetonitrile and so on. This is our second measure. Finally, we combine the two measures by burning deposited carbon in air and then washing

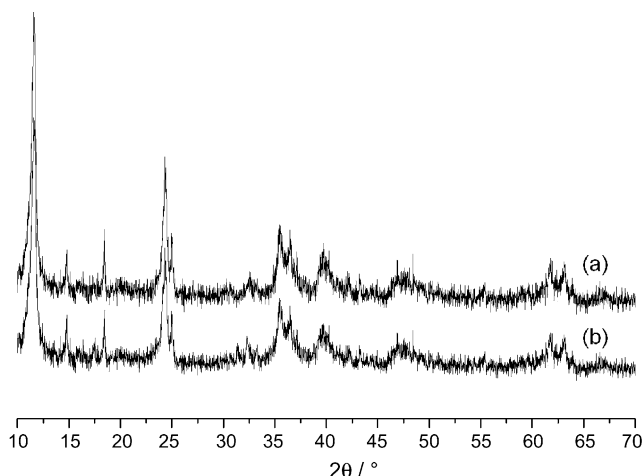


Fig. 8. XRD spectra of the fresh (a) and reactivated (b) catalysts.



with acetone to reactivate the deactivated catalyst. The comparison of the three reactivation measures is summarized in Fig. 7. Both phenol conversion and main-product selectivity return to the almost original values by the third measure. After the treatment with the first measure, the phenol conversion only reaches 57%; the third measure has a more favourable effect on the fouled catalyst, which reaches 62% close to that of the fresh catalyst. Moreover, XRD pattern of the reactivated catalyst is almost coincident with that of the fresh sample (see Fig. 8), indicating the hydrotalcite structure of reactivated catalyst has been recovered.

#### 4. Conclusion

Cu-PHTL catalyst prepared by microwave radiation synthesis shows high activity in the phenol hydroxylation with hydrogen peroxide as a hydroxylating agent, resulting in the production of diphenol with the phenol conversion of 63% and the selectivity above 95%. However, after duty-cycle operation of Cu-PHTL in the catalytic phenol hydroxylation, the deactivation occurs, mainly due to the carbon deposition on the catalyst surface. The deactivated catalyst can be easily reactivated by burning deposited carbon in air and washing with acetone; moreover the reactivated catalyst shows almost the same catalytic performances and hydrotalcite structure as the fresh one.

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