

# Characteristics of titania supported copper oxide catalysts for wet air oxidation of phenol

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## Abstract

Various techniques have been used to characterize the  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading. Surface area, pore volume and pore size distribution of the prepared catalysts were estimated from nitrogen adsorption isotherm. Temperature programmed reduction (TPR), X-ray diffraction (XRD), electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) experiments were performed to investigate the chemical state of the copper species. The chemical state of copper in the  $\text{CuO}_x/\text{TiO}_2$  catalysts varied with copper loading (1–25 wt.%): highly dispersed  $\text{Cu}^{2+}$  cluster for 1 and 5 wt.%, and bulk CuO for 7–25 wt.%. The activity and mineralization selectivity of the  $\text{CuO}_x/\text{TiO}_2$  catalysts increased with copper loading up to 20 wt.%, and remained almost constant for higher copper loading. The optimum copper loading was 20 wt.% for the wet air oxidation of phenol over the  $\text{CuO}_x/\text{TiO}_2$  catalysts in this work. The stability of the  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading was also studied with respect to carbonaceous deposits and copper leaching.  
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**Keywords:** Wet air oxidation; Copper oxide; Titania; Phenol; Leaching

## 1. Introduction

Wastewater from industries such as pulp, dyeing, chemical, petrochemical, etc., contains refractory organic pollutants too difficult to be treated through conventional processes. Wet air oxidation is suitable for the treatment of the wastewater which is too dilute to incinerate and too concentrated and/or toxic to be treated with biological approach since any organic compound could be ideally mineralized to the desired end product by wet air oxidation. The main drawback of the wet air oxidation treatment comes from the high cost of materials, which must be selected to bear the operating conditions. The heterogeneous catalytic oxidation allows a significant reduction of the temperature and pressure employed by the non-catalytic oxidation processes.

Various solid catalysts including noble metals and metal oxides have been studied for the wet air oxidation of the model pollutant solution or the real wastewater [1–3]. Among them, the catalysts based on copper oxides exhibit considerable efficiencies in the oxidation process and are one of the most typically used to examine the catalytic wet air oxidation of wastewater

containing refractory pollutants [4–7]. In many of these studies, phenol and phenolic compounds have been employed as model pollutants because they are widely used in industries and phenol is considered to be an intermediate product in the oxidation pathway of higher molecular weight aromatic hydrocarbons [8–10].

In this study, the nature of active copper species in the  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading was examined with various techniques and the effect of copper loading on the activity and selectivity was also investigated for the wet air oxidation of phenol. Surface area, pore volume and pore size distribution of the prepared catalysts were estimated from nitrogen adsorption isotherm. TPR, XRD, ESR, XPS and XANES experiments were performed to investigate the chemical state of the copper species. Also, the stability of the  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading was studied with respect to carbonaceous deposits and copper leaching.

## 2. Experimental

### 2.1. Preparation of catalysts

$\text{TiO}_2$  used in this study as support was P25 (Degussa). Copper oxide was supported on  $\text{TiO}_2$  by incipient wetness impregnation

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method using an aqueous copper(II) nitrate solution, followed by drying at 100 °C for 24 h, finally by calcination in air at 500 °C for 10 h. Copper loading was determined by the concentration of the copper(II) nitrate solution used in the impregnation. For simplicity, each catalyst will be designated according to the copper loading; for example, Cu5 represents the copper oxide catalyst supported on TiO<sub>2</sub> with 5 wt.% of Cu.

## 2.2. Wet air oxidation of phenol

Phenol (+99% purity) was purchased from Aldrich and was used without further purification. A stirred reactor (1 L; Autoclave Co.) with suspended catalysts was used batchwise for the wet oxidation of phenol. It was equipped with a Teflon liner, magnetically driven impeller (Hastelloy), sampling line (Hastelloy), control units of temperature and agitation speed, and a liquid-injection vessel (SS316; 100 mL capacity) mounted on the top of the autoclave. To conduct a reaction experiment, 225 mL of distilled water, 0.75 g of catalyst, which corresponds to 3 g/L, and air of 2.02 MPa at ambient temperature were charged into the autoclave. It was stirred with a 1000 rpm blade rotating speed and heated to the desired temperature, 150 °C. In the meantime, 25 mL of 10000 mg/L phenol solution and air of 2.02 MPa was charged in the injection vessel and preheated to about 100 °C. When the temperature of reaction vessel reached to a desired point, preheated reactant solution was injected with 5.05 MPa air to obtain 250 mL of a 1000 mg/L phenol solution. The experimental runs were performed at initial pH value of 7. As soon as the phenol was injected, a sample was taken, and it was referred to as the sample at time zero. The phenol concentration and total organic carbon (TOC) concentration of each sample were determined using HPLC system (Young-Lin 930) and TOC analyzer (Shimadzu TOC-V). After 3 h reaction, the used catalysts were filtered, washed with distilled water several times, and dried at 100 °C.

## 2.3. Characterization of the catalysts

Surface area, pore volume and pore size distribution of the prepared catalysts were measured through nitrogen adsorption method at liquid nitrogen temperature using an ASAP 2000 (Micromeritics) surface area analyzer.

Temperature programmed reduction (TPR) experiments of the prepared catalysts were carried out using 5% H<sub>2</sub>/Ar gas mixture. The samples were pretreated with O<sub>2</sub> at 400 °C for 2 h. The hydrogen consumption was recorded with TCD cell while the sample was linearly heated from 50 to 600 °C at 10 °C/min.

Powder X-ray diffraction (XRD) patterns of the catalysts were obtained with D/MAX-III (Rigaku) diffractometer using monochromic Cu K $\alpha$  ( $\lambda = 0.1506$  nm) radiation as the radiation source. The data were scanned from 20° to 80° ( $2\theta$ ) in steps of 0.01° and the scanning rate was 6° min<sup>-1</sup>.

Electron spin resonance (ESR) measurements were carried out with ESP-300S (Bruker) spectrometer operating in X-band (ca. 9.7 GHz). The magnetic field was modulated at (100 kHz). The  $g$  values were obtained in comparison with a diphenylpicrylhydrazyl (DPPH) standard ( $g = 2.0036$ ). Before

each ESR measurement, the catalyst was dried at 110 °C for 12 h. All the ESR measurements were performed at 77 K.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with ESCALAB MK-II (VG Scientific) equipped with a magnesium anode (1253.6 eV). The binding energy was adjusted to the C 1s peak at 284.6 eV which existed in all measurements.

X-ray absorption near edge structure (XANES) experiments were performed for Cu K-edges at room temperature by using Beamline 7C1 at Pohang Light Source. The energy was calibrated by the distinct peak at the Cu K-edge of a Cu foil as 8980.3 eV. Copper(II) oxide powder and copper(I) oxide powder from Aldrich, and copper foil were used as the Cu<sup>2+</sup>, Cu<sup>1+</sup> and Cu<sup>0</sup> standard, respectively.

The carbonaceous deposits on the used catalysts were quantified by elemental analysis using Flash EA 1112 series of CE Instruments.

The pH values of the samples were measured with pH meter (ORION, model 290A) and the extent of Cu leached out from the catalyst to the liquid phase was determined with X-ray fluorescence analyzer (Panalytical, Minipal 2) and ICP/AES spectrometer (Thermo Jarrell Ash, POLYSCAN 60E).

## 3. Results and discussion

The surface area, pore volume and average pore diameter of the CuO<sub>x</sub>/TiO<sub>2</sub> catalysts are summarized in Table 1. The surface area of the prepared catalysts decreased with copper loading mainly due to pore blocking.

### 3.1. Reducibility of CuO<sub>x</sub>/TiO<sub>2</sub> catalysts

TPR profiles of CuO<sub>x</sub>/TiO<sub>2</sub> catalysts with different copper loading are shown in Fig. 1. The shape and temperature of the reduction peaks were changed as the copper loading increased, indicating that the state of copper species varied significantly with copper loading. Cu1 and Cu5 give only one reduction peak at 146 and 140 °C, respectively. Dow et al. [11] reported that at low copper loading, copper is present as highly dispersed clusters or as isolated copper ions which could interact strongly with the support. Both Cu1 and Cu5 might have highly dispersed clusters and the cluster size for Cu5 seemed larger. As the copper loading increased from 5 to 7 wt.%, a second reduction peak appears at higher temperature. In case of Cu7–Cu25,

Table 1  
Surface area, pore volume and average pore diameter

Catalyst	Surface area (m <sup>2</sup> /g-cat.)	Pore volume (mL/g-cat.)	Average pore diameter (Å)
TiO <sub>2</sub>	54	0.14	107
Cu1	37	0.19	250
Cu5	35	0.22	245
Cu7	33	0.22	222
Cu10	32	0.22	241
Cu15	31	0.19	222
Cu20	28	0.17	222
Cu25	25	0.16	217

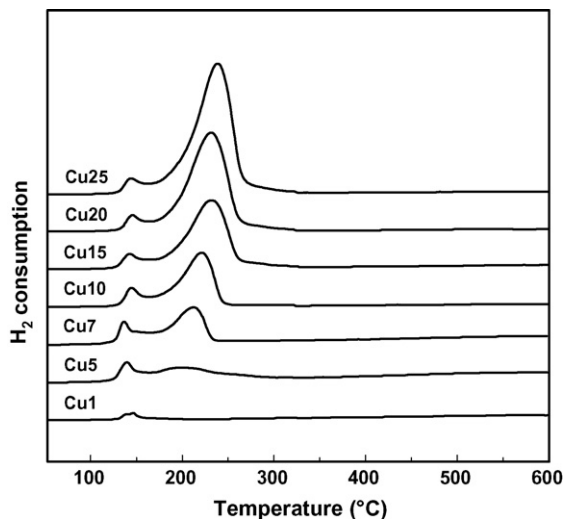


Fig. 1. TPR profiles of the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading.

each has a large reduction peak, together with a small reduction peak located at lower temperature region than the main peak. These large reduction peaks shifted to the high temperatures as copper loading increased, while the small peaks remained at the almost same temperature, 145 °C. At high copper loading, copper is mainly present as large particles [11–14]. The small reduction peak should be due to the reduction of the surface copper, which is reduced more easily than the bulk copper oxide.

### 3.2. Chemical state of copper species in the $\text{CuO}_x/\text{TiO}_2$ catalysts

Fig. 2 shows XRD patterns of the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts. For copper loading lower than 5 wt.%, the catalysts do not show any characteristic peaks of either metallic copper or copper oxide. This indicates that copper is finely dispersed in these catalysts or not detected due to too low a loading. At higher copper loading, the characteristic peaks of CuO crystal (▼ in Fig. 2)

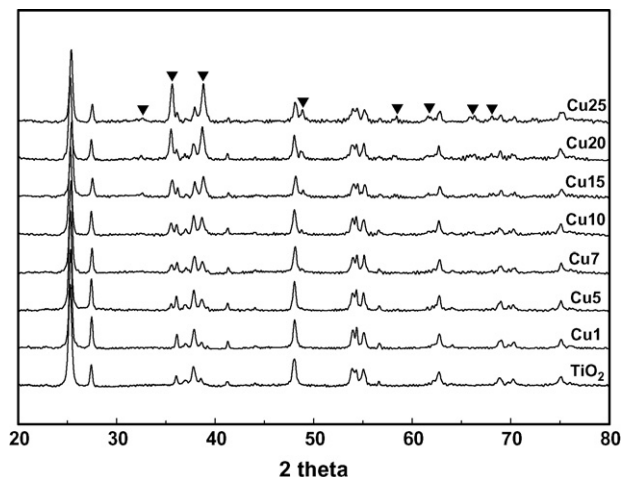


Fig. 2. XRD patterns of the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading. (▼) Characteristic peaks of CuO crystal.

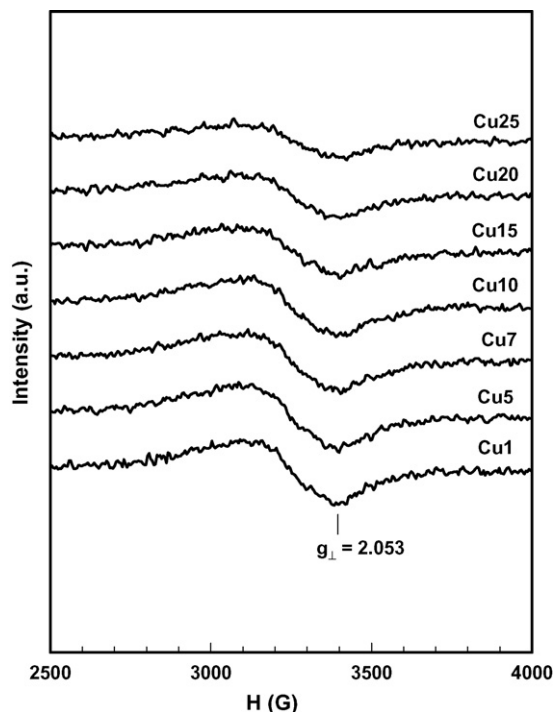


Fig. 3. ESR spectra of the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading.

were observed, indicating that the copper of high loading catalyst (higher than 7 wt.%) existed as CuO crystals [14].

To investigate the chemical state of copper for the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts, ESR spectra were obtained (Fig. 3). ESR measurement can detect only paramagnetic species which, by definition, contain one or more unpaired electrons [15]. A strong axially symmetric signal ( $g_{\perp} = 2.053$ ), which is generally attributed to highly dispersed  $\text{Cu}^{2+}$  ions on the  $\text{TiO}_2$  surface, exists for the prepared catalysts. As the Cu loading increased, the signal intensities of the ESR spectra decreased. This indicates that the isolated copper species were transformed into the interacting-copper phase with the increase of copper loading [11,14,16]. From the ESR data, it can be known that all the prepared catalysts have  $\text{Cu}^{2+}$ , because only  $\text{Cu}^{2+}$  revealed the ESR peak among  $\text{Cu}^0$ ,  $\text{Cu}^{1+}$  and  $\text{Cu}^{2+}$ .

To investigate the oxidation state of the catalysts surface, XPS spectra were obtained (Fig. 4). The shake-up peak and the higher Cu  $2p_{3/2}$  binding energy are two major XPS characteristics of CuO, while the absence of the shake-up peak and the lower Cu  $2p_{3/2}$  binding energy are the characteristics of the reduced copper species [17]. It was reported that the Cu 2p binding energies of  $\text{Cu}_2\text{O}$  and CuO are 932.8 and 933.8 eV, respectively [18]. The catalysts with more than 5 wt.% of copper loading showed the shake-up peak and the Cu 2p binding energy of these catalysts increased with copper loading, indicating that CuO existed on the surface of these catalysts and its amount increased with copper loading. At copper loading higher than 7 wt.%, the surface oxidation state of the copper was mainly CuO. In case of Cu1, there was no shake-up and the binding energy was much lower than that of CuO, indicating nearly no bulk CuO on the surface of Cu1 catalyst. This XPS result conflicts with the ESR result

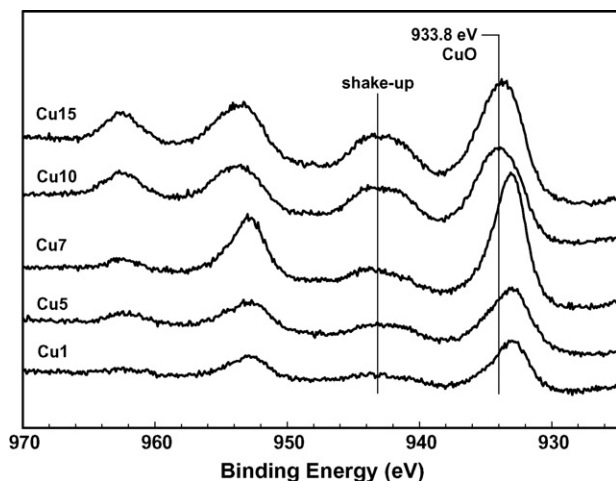


Fig. 4. XPS spectra of the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading.

which confirmed the existence of  $\text{Cu}^{2+}$  in the Cu1 catalyst. Even very small amount of  $\text{Cu}^{2+}$  could be detected by ESR because of its good sensitivity. It is known, however, that supported copper oxide can be reduced by the X-ray beams during XPS analysis. It is assumed that the reduction of  $\text{Cu}^{2+}$  in Cu1 by X-ray beams and/or the interaction between copper and support could explain the inconsistency between XPS result and ESR result.

Fig. 5 shows the Cu XANES spectra of the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading. The XANES of  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Cu}$  standards were also measured for the comparison with other samples. A pre-edge was clearly observed for  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$  and  $\text{Cu}$  standards. For  $\text{CuO}$  standard, the absorption

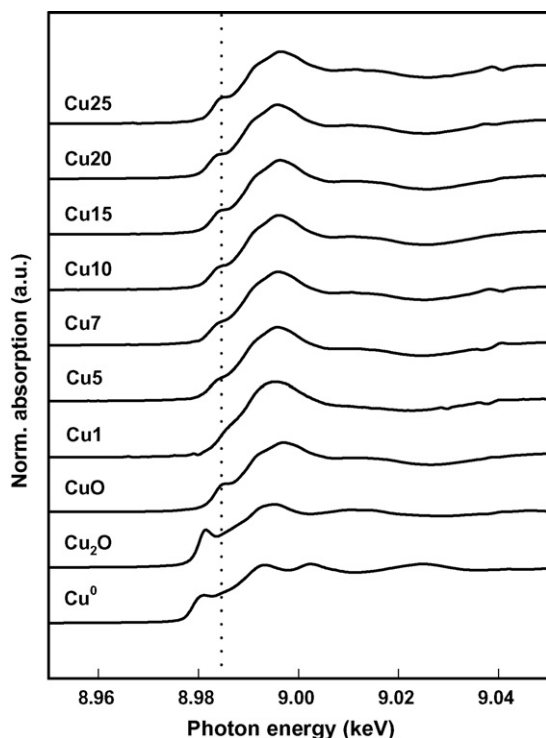


Fig. 5. XANES spectra of the prepared  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading.

edge was slightly shifted to higher photon energy from  $\text{Cu}_2\text{O}$  and  $\text{Cu}$  standard. Comparing the pre-edge peaks of the standards, the oxidation states of the prepared catalysts were closer to  $\text{CuO}$  and not to  $\text{Cu}_2\text{O}$ , or  $\text{Cu}$ ; the  $\text{CuO}$  pre-edge peaks of the prepared catalysts developed more as the copper loading increased.

From the above characterization results, the chemical state of copper in the  $\text{CuO}_x/\text{TiO}_2$  catalysts could be summarized as follows: highly dispersed  $\text{Cu}^{2+}$  cluster for Cu1 and Cu5 and bulk  $\text{CuO}$  for Cu7–Cu25.

### 3.3. Effect of copper loading on the wet air oxidation activity and selectivity

Fig. 6 shows phenol and TOC conversion profiles over the  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading, 1–25 wt.%. As can be seen, the phenol and TOC conversion for  $\text{TiO}_2$  was even lower than those for blank test. Zhang and Chuang [19]

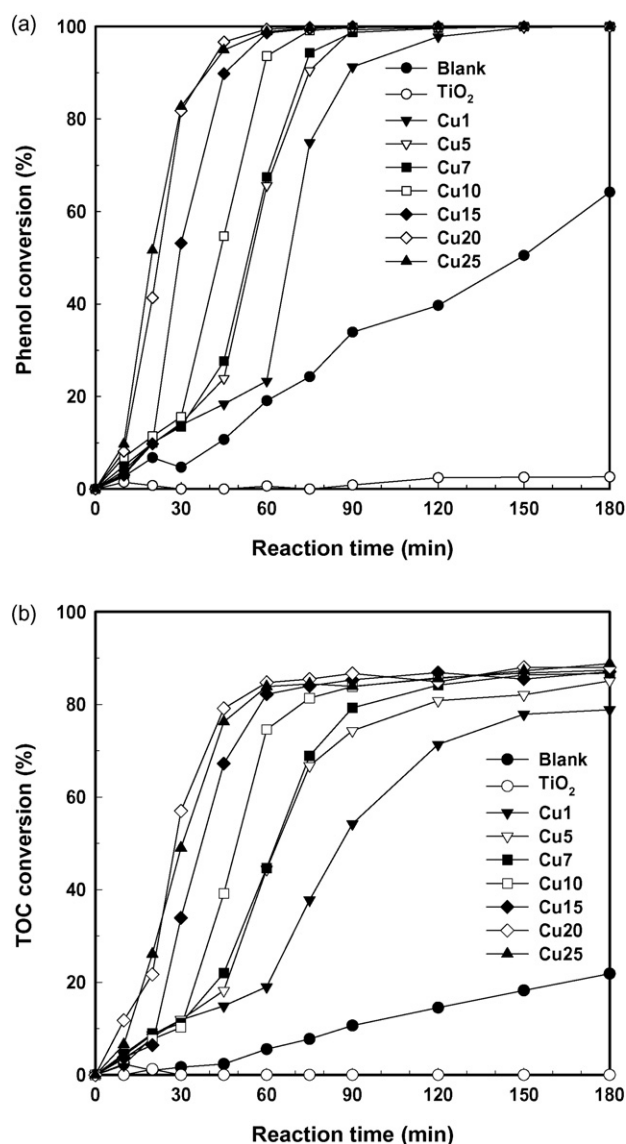


Fig. 6. Conversion of phenol (a) and TOC (b) over the  $\text{CuO}_x/\text{TiO}_2$  catalysts with different copper loading.

reported that catalysts inhibit the wet oxidation process through a free-radical mechanism. This low conversion for TiO<sub>2</sub>, nearly zero, can be explained that TiO<sub>2</sub> terminates the generated radicals through interaction with them. There were induction periods especially when using the CuO<sub>x</sub>/TiO<sub>2</sub> catalyst with low copper loading and the induction periods time decreased with copper loading. The activity of the CuO<sub>x</sub>/TiO<sub>2</sub> catalysts for wet air oxidation of phenol increased as the copper loading increased up to 20 wt.%; the activity seemed constant for the catalysts of which the copper loading is higher than 20 wt.%.

In the wet oxidation process, phenol is converted mainly to one of the following three items: CO<sub>2</sub> in the gas phase; aqueous intermediates or products in the liquid phase and carbonaceous deposits on the catalyst. The phenol conversion, fraction of deposited carbon, intermediate selectivity, and mineralization selectivity for 45 min reaction are summarized in Table 2. The carbon content for the catalysts used for 3 h was measured by elemental analysis and the amount of carbonaceous deposits on the catalysts for 45 min reaction was calculated on the assumption that carbonaceous deposits increased with reaction time linearly. The intermediate selectivity and mineralization selectivity represent the fraction of organic compounds in the aqueous phase and CO<sub>2</sub> to the converted phenol, respectively. Details on them are available elsewhere [20]. As can be seen in Table 2, phenol was hardly decomposed after 45 min reaction without catalyst. The phenol conversion over the CuO<sub>x</sub>/TiO<sub>2</sub> catalysts increased with copper loading up to 20 wt.% although it remained constant for the catalysts with higher copper loading. Similarly, intermediate selectivity decreased and mineralization selectivity increased with copper loading up to 20 wt.%. The 19% of converted phenol over Cu20 was converted to the aqueous intermediates and 79% of that was transformed to CO<sub>2</sub>.

Considering the activity and selectivity of the CuO<sub>x</sub>/TiO<sub>2</sub> catalysts, the optimum loading of copper was 20 wt.% in this work.

### 3.4. Carbonaceous deposits on the used catalysts

The third column of Table 2 shows the fraction of the amount of deposited carbon on a catalyst to the amount of carbon initially injected into the batch reactor. As can be seen, the carbonaceous deposits on the used catalysts decreased with copper loading. In spite of the carbonaceous deposits on the used catalyst, the

XRD patterns of the used catalysts (data not shown) were found similar to those of fresh catalyst, although the peak intensities of characteristic peaks decreased slightly, indicating that copper remains as CuO.

### 3.5. Copper leaching

The leaching out of active metal component is one of the main factor of deactivation in catalysts and modifies the reaction mechanism for wet oxidation. The metal component is leached out from the catalyst when it is in contact with hot acidic compounds. This is difficult to avoid because the final intermediates in the wet oxidation of phenol are short chain acids [6,10,21–23].

The trends of phenol and TOC conversion over Cu10 are compared with pH and copper leaching in Fig. 7. The extent of copper leaching increased from 3.1 mg/L after 30 min to 48.5 mg/L after 45 min of reaction time, while the pH value decreased from 6.8 to 4.8. After 60 min reaction, the extent of copper leaching was 83.1 mg/L with the pH value of 3.7. These copper leaching content and pH value remained almost constant over further phenol

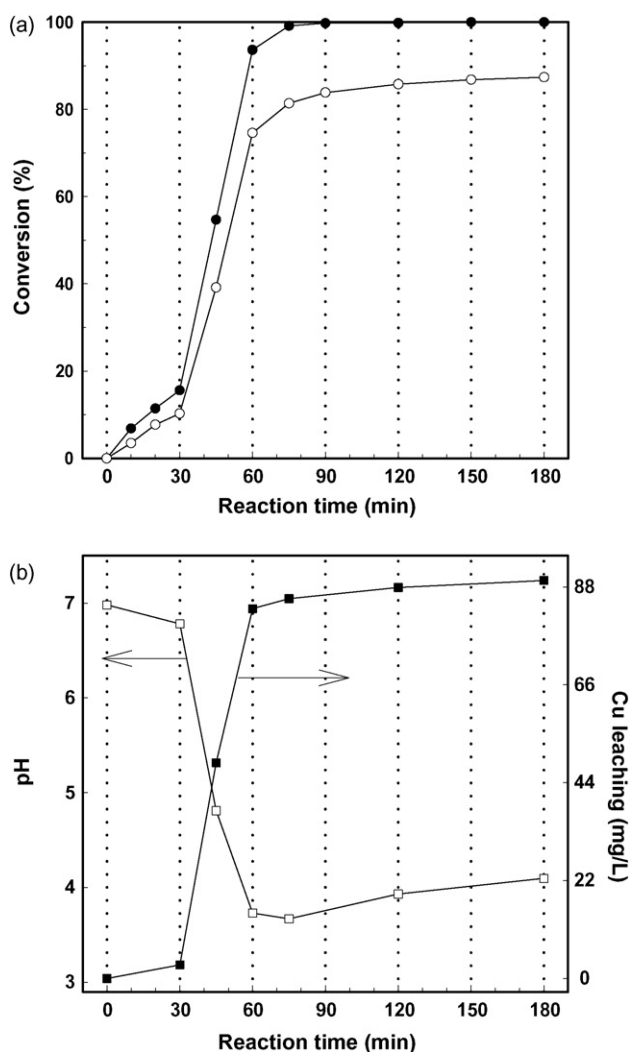


Fig. 7. Wet oxidation of phenol over the 10 wt.% CuO<sub>x</sub>/TiO<sub>2</sub> catalyst. (a) Phenol (●) and TOC (○) conversion and (b) pH (□) and extent of Cu leaching (■).

Table 2  
Intermediate selectivity and mineralization selectivity for 45 min reaction

Catalyst	Conversion	Deposited carbon/initial carbon	Intermediate selectivity	Mineralization selectivity
Blank	0.11	–	0.28	0.72
Cu1	0.18	0.054	0.41	0.29
Cu5	0.24	0.049	0.40	0.39
Cu7	0.28	0.047	0.39	0.44
Cu10	0.55	0.034	0.34	0.59
Cu15	0.90	0.027	0.25	0.71
Cu20	0.97	0.026	0.19	0.79
Cu25	0.95	0.030	0.20	0.77

Table 3  
Extent of copper leaching after 3 h reaction

Catalyst	Reactant	Leached Cu (mg/L)	Leached Cu/total Cu (%)
Cu5	Phenol	49.3	32.9
Cu10	Phenol	89.4	29.8
Cu15	Phenol	120.9	26.9
Cu20	Phenol	139.2	23.2
Cu20	Water	0.6	0.1

oxidation reaction. The leached copper ions may be responsible for additional homogeneously catalyzed reactions in the heterogeneous reaction and a homogeneous–heterogeneous reaction system should be considered rather than a purely heterogeneous reaction [6,10,21–23]. Pintar and Levec [23] reported that catalytic phenol oxidation exhibits an induction period and involves a heterogeneous–homogeneous free radical mechanism. The induction period is observed from the conversion profiles in Fig. 7(a). During this time, the conversion and extent of copper leaching remained very low levels, while pH value hardly changed. After induction period, the extent of copper leaching rapidly increased corresponding to the drop in the pH value caused by the acidic intermediates, which are formed during the wet oxidation of phenol. The phenol and TOC conversion also increased with copper leaching.

Table 3 shows the extent of copper leaching for Cu5, 10, 15 and 20 after 3 h of wet oxidation. As presented, the extent of copper leaching for Cu20 is about 139 mg/L when the phenol was used as a reactant. When the water was used as a reactant, on the other hand, leached copper content is only 0.6 mg/L under the same operating conditions. The presence of phenol or its oxidation intermediates must contribute to the copper leaching. The pH value decreased from 7 to about 3.7, which signals the formation of intermediate acidic compounds such as short chain carboxylic acids which are refractory to further oxidation during the wet oxidation of phenol. The extent of copper leaching decreased with copper loading, i.e., 33% for Cu5 and 23% for Cu20.

#### 4. Conclusion

The chemical state of copper in the  $\text{CuO}_x/\text{TiO}_2$  catalysts could be summarized as follows: highly dispersed  $\text{Cu}^{2+}$  cluster for Cu1 and Cu5, and bulk CuO for Cu7–Cu25. The activity of the catalysts increased with copper loading up to 20 wt.%, and remained almost constant for higher copper loading. Similarly, the mineralization selectivity of Cu20 was the highest although it seemed constant for the catalysts with higher copper loading. The optimum copper loading was 20 wt.% for the wet air oxidation of phenol over the  $\text{CuO}_x/\text{TiO}_2$  catalysts in this work.

Carbonaceous deposits on the used catalysts decreased with copper loading. In spite of the carbonaceous deposits on the used catalyst, the XRD patterns of the used catalysts were found similar to those of fresh catalyst, although the peak intensities of characteristic peaks decreased slightly, indicating that copper remains as CuO.

The conversion and extent of copper leaching remained very low levels, while pH value hardly changed during the induction period. Thereafter, the extent of copper leaching rapidly increased corresponding to the drop in the pH value caused by the acidic intermediates. The phenol and TOC conversion also increased with copper leaching. The extent of copper leaching decreased with copper loading, i.e., 33% for Cu5 and 23% for Cu20.

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